Online ISSN: 2249-4626
Print ISSN: 0975-5896

Global Journal

of Science Frontier Research: B

Chemistry

Synthesis of Bridgehead

Infrared Studies on Samarium

Highlights

Biological Activity Studies

Synthesis of New Pyrazolinic

Discovering Thoughts, Inventing Future

VOLUME 15 ISSUE 3 VERSION 1.0

Global Journal of Science Frontier Research: B
Chemistry

Global Journal of Science Frontier Research: B
Chemistry
Volume 15 Issue 3 (Ver. 1.0)

Open Association of Research Society

Incorporation No.: 0423089
License No.: 42125/022010/1186
Registration No.: 430374
Import-Export Code: 1109007027
Employer Identification Number (EIN):
USA Tax ID: 98-0673427

Global Journals Inc.

*(A Delaware USA Incorporation with "Good Standing"; **Reg. Number: 0423089**)*

Sponsors: Open Association of Research Society
Open Scientific Standards

Publisher's Headquarters office

Global Journals Headquarters
301st Edgewater Place Suite, 100 Edgewater Dr.-Pl,
Wakefield MASSACHUSETTS, Pin: 01880,
United States of America
USA Toll Free: +001-888-839-7392
USA Toll Free Fax: +001-888-839-7392

Offset Typesetting

Global Journals Incorporated
2nd, Lansdowne, Lansdowne Rd., Croydon-Surrey,
Pin: CR9 2ER, United Kingdom

Packaging & Continental Dispatching

Global Journals
E-3130 Sudama Nagar, Near Gopur Square,
Indore, M.P., Pin:452009, India

Find a correspondence nodal officer near you

To find nodal officer of your country, please email us at *local@globaljournals.org*

eContacts

Press Inquiries: *press@globaljournals.org*
Investor Inquiries: *investors@globaljournals.org*
Technical Support: *technology@globaljournals.org*
Media & Releases: *media@globaljournals.org*

Pricing (Including by Air Parcel Charges):

For Authors:
22 USD (B/W) & 50 USD (Color)
Yearly Subscription (Personal & Institutional):
200 USD (B/W) & 250 USD (Color)

Integrated Editorial Board
(Computer Science, Engineering, Medical, Management, Natural Science, Social Science)

Dr. Bart Lambrecht
Director of Research in Accounting and FinanceProfessor of Finance
Lancaster University Management School
BA (Antwerp); MPhil, MA, PhD (Cambridge)

Dr. Carlos García Pont
Associate Professor of Marketing
IESE Business School, University of Navarra
Doctor of Philosophy (Management), Massachusetts Institute of Technology (MIT)
Master in Business Administration, IESE, University of Navarra
Degree in Industrial Engineering, Universitat Politècnica de Catalunya

Dr. Fotini Labropulu
Mathematics - Luther College
University of ReginaPh.D., M.Sc. in Mathematics
B.A. (Honors) in Mathematics
University of Windso

Dr. Lynn Lim
Reader in Business and Marketing
Roehampton University, London
BCom, PGDip, MBA (Distinction), PhD, FHEA

Dr. Mihaly Mezei
ASSOCIATE PROFESSOR
Department of Structural and Chemical Biology, Mount Sinai School of Medical Center
Ph.D., Etvs Lornd University
Postdoctoral Training,
New York University

Dr. Söhnke M. Bartram
Department of Accounting and FinanceLancaster University Management SchoolPh.D. (WHU Koblenz)
MBA/BBA (University of Saarbrücken)

Dr. Miguel Angel Ariño
Professor of Decision Sciences
IESE Business School
Barcelona, Spain (Universidad de Navarra)
CEIBS (China Europe International Business School).
Beijing, Shanghai and Shenzhen
Ph.D. in Mathematics
University of Barcelona
BA in Mathematics (Licenciatura)
University of Barcelona

Philip G. Moscoso
Technology and Operations Management
IESE Business School, University of Navarra
Ph.D in Industrial Engineering and Management, ETH Zurich
M.Sc. in Chemical Engineering, ETH Zurich

Dr. Sanjay Dixit, M.D.
Director, EP Laboratories, Philadelphia VA Medical Center
Cardiovascular Medicine - Cardiac Arrhythmia
Univ of Penn School of Medicine

Dr. Han-Xiang Deng
MD., Ph.D
Associate Professor and Research
Department Division of Neuromuscular Medicine
Davee Department of Neurology and Clinical NeuroscienceNorthwestern University
Feinberg School of Medicine

Dr. Pina C. Sanelli
Associate Professor of Public Health
Weill Cornell Medical College
Associate Attending Radiologist
NewYork-Presbyterian Hospital
MRI, MRA, CT, and CTA
Neuroradiology and Diagnostic Radiology
M.D., State University of New York at Buffalo,School of Medicine and Biomedical Sciences

Dr. Roberto Sanchez
Associate Professor
Department of Structural and Chemical Biology
Mount Sinai School of Medicine
Ph.D., The Rockefeller University

Dr. Wen-Yih Sun
Professor of Earth and Atmospheric SciencesPurdue University Director
National Center for Typhoon and Flooding Research, Taiwan
University Chair Professor
Department of Atmospheric Sciences, National Central University, Chung-Li, TaiwanUniversity Chair Professor
Institute of Environmental Engineering, National Chiao Tung University, Hsin-chu, Taiwan.Ph.D., MS The University of Chicago, Geophysical Sciences
BS National Taiwan University, Atmospheric Sciences
Associate Professor of Radiology

Dr. Michael R. Rudnick
M.D., FACP
Associate Professor of Medicine
Chief, Renal Electrolyte and Hypertension Division (PMC)
Penn Medicine, University of Pennsylvania
Presbyterian Medical Center, Philadelphia
Nephrology and Internal Medicine
Certified by the American Board of Internal Medicine

Dr. Bassey Benjamin Esu
B.Sc. Marketing; MBA Marketing; Ph.D Marketing
Lecturer, Department of Marketing, University of Calabar
Tourism Consultant, Cross River State Tourism Development Department
Co-ordinator , Sustainable Tourism Initiative, Calabar, Nigeria

Dr. Aziz M. Barbar, Ph.D.
IEEE Senior Member
Chairperson, Department of Computer Science
AUST - American University of Science & Technology
Alfred Naccash Avenue – Ashrafieh

President Editor (HON.)

Chief Author (HON.)

Dr. R.K. Dixit
M.Sc., Ph.D., FICCT
Chief Author, India
Email: authorind@computerresearch.org

Dean & Editor-in-Chief (HON.)

Contents of the Issue

Global Journal of Science Frontier Research: B
Chemistry
Volume 15 Issue 3 Version 1.0 Year 2015
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

Thermogravimetric, X-Ray Diffraction and Infrared Studies on Samarium and Praseodymium Hexadecanoate in Solid State

By Darshana Rodric, Kirti Vishwakarma & S. K. Upadhyaya
S. S. L. Jain P. G. College, INDIA

Abstract- The kinetics of thermal decomposition of samarium and praseodymium hexadecanoate (palmitate) was found to be of zero order and the energy of activation for the decomposition reaction for samarium and praseodymium hexadecanoate was in the range of 30-35 KJ mol-1 .The X-ray analysis showed that samarium and praseodymium hexadecanoate soaps have double layer structure with molecular axis slightly inclined to the basal plane. The IR results confirmed that the fatty acids exists with dimeric structure through hydrogen bonding between the carboxyl groups of two acid molecules, whereas the metal soaps have an ionic character.

Keywords: *samarium hexadecanoate, praseodymium hexadecanoate, ir spectra, x-ray diffraction, thermogravimetry.*

GJSFR-B Classification : *FOR Code: 039999*

Strictly as per the compliance and regulations of :

Thermogravimetric, X-Ray Diffraction and Infrared Studies on Samarium and Praseodymium Hexadecanoate in Solid State

Darshana Rodric [α], Kirti Vishwakarma [σ] & S. K. Upadhyaya [ρ]

Abstract- **The kinetics of thermal decomposition of samarium and praseodymium hexadecanoate (palmitate) was found to be of zero order and the energy of activation for the decomposition reaction for samarium and praseodymium hexadecanoate was in the range of 30-35 KJ mol^{-1}. The X-ray analysis showed that samarium and praseodymium hexadecanoate soaps have double layer structure with molecular axis slightly inclined to the basal plane. The IR results confirmed that the fatty acids exists with dimeric structure through hydrogen bonding between the carboxyl groups of two acid molecules, whereas the metal soaps have an ionic character.**

Keywords: samarium hexadecanoate, praseodymium hexadecanoate, IR spectra, x-ray diffraction, thermogravimetry.

I. Introduction

A metallic soap is a chemical combination of a metallic element with a fatty acid organic group. Because of the presence of both lyophillic and lyophobic moieties in the same molecule and their increased solubility in non polar solvents lend to them unique characteristics. Due to their unique characteristics, metal soaps found to be very important class of complexes in technological and academic fields. The alkaline, alkaline earth and transition metal soaps have been thoroughly investigated but the lanthanide and actinide soaps have remained overlooked class of complexes. These compounds have several interesting application based on the metal ion radius, hardness, softness, valency and alkyl chain structure. They find extensive applications in protective coating agents, paints, ink driers, polymer stabilizers, catalysts, waterproofing agents, lubricants, fuel additives and fungicides[1-2]. They are also used in photo thermogravimetry[3] and in manufacturing of pharmaceuticals.

Metal soap with elements of lanthanide series were synthesized for the first time by Mishra et al[4].Mehrotra et al[7-8] investigated acoustical and thermodynamic properties of lanthanide soaps and concluded that these soaps behave as weak electrolyte in dilute solutions. Koga and matuura[9] studied the X-ray diffraction pattern and IR spectra of alkaline earth metal soaps. The present paper deals with the studies of the structure of samarium and praseodymium hexadecanoate in solid state using X-ray, IR and TGA. The results have been used to evaluate various kinetic parameters.

II. Experimental

a) Materials

i. Fatty Acids

The fatty acids used in this studies were supplied from from Indian Rare Earth Limited, Kerala) were used for the present investigation. The purities of fatty acids were confirmed to be over 98.5%.

ii. Metal salts

The inorganic chemicals used in the preparation of metal soaps were analr.grade: samarium nitrate and praseodymium nitrate.

iii. Preparation of metal soap

The samarium and Praseodymium hexadecanoate were prepared by the direct metathesis of corresponding potassium soaps by pouring a slight stochiometric excess of aqueous metal salt solution into the clear dispersion at raised temperature with vigorous stirring. After initial drying in an air oven 50-60°C, final drying was carried out under reduced pressure. The precipitates was filtered off and washed with hot distilled water and acetone.

iv. Apparatus

Infrared absorption spectra of hexadecanoic acid corresponding to potassium, samarium hexadecanoate and praseodymium hexadecanoate were recorded with Fourier transform infrared spectrometer, Tensor 27, Bruker in the region 4000-400 cm-1 using potassium bromide disc method.

The X-Ray diffraction patterns of samarium hexadecanoate and praseodymium hexadecanoate were obtained with a Bruker AXS D8 Advance x-ray diffractometer using Cu-Kα radiations filtered by a nickel foil. The instruments yield an automatically recorded curve of intensity of diffracted x-rays vs. diffraction angle 2θ.

Author α σ ρ: P. G. Department of Chemistry, S. S. L. Jain P. G. College, Vidisha (M.P.) India. e-mails: darshanarodric@gmail.com, kirtiv.2009@gmail.com, Upadhyaya_20kumar@Yahoo.co.in

The thermo gravimetric analysis of samarium metal soaps was undertaken at constant rate of heating (20°c/min) under nitrogen atmosphere in a thermo balance. The results of TGA of samarium metal soaps were obtained from Sophisticated Instrumentation Centre (S.I.C), IIT, Indore.

III. Result and Discussion

The infrared spectral bands (Figures 1 & 2) and their tentative assignments for samarium hexadecanoate and praseodymium hexadecanoate are assigned and compared with potassium hexadecanoate, as well as with corresponding fatty acid (hexadecanoic acid) Tables I& II.

The characteristic frequencies in the spectra of fatty acid at 2640 (O-H stretching vibrations), 1700 (C=O stretching vibrations), 1450 (O-H in plane bending and C-O stretching) and at 950 cm-1 (out of plane bending of O-H group) indicates the presence of carboxyl group in the form of dimeric12 structure and confirms the existence of intermolecular hydrogen bonding between two molecules of fatty acid.

The infrared spectra of potassium, samarium & praseodymium hexadecanoate illustrate marked difference with the spectra of corresponding fatty acids in some spectral region. Some characteristic vibrations of free fatty acids were found completely absent in their respective regions in the spectra of potassium, samarium & praseodymium hexadecanoate. The disappearance of carboxyl frequency (1700cm-1) in the spectra of these soaps indicate that there may be a complete resonance in the two C-O bonds of the carboxyl groups of the soap molecule.

Table 1 : Frequencies (cm^{-1}) of Absorption maxima with their Assignments of hexadecanoic acid, Potassium decanoate, Samarium hexadecanoate.

s.no	Assignment	Palmitic Acid	Potassium palmitate	Samarium palmitate
1	CH3, C-H asym. Stretching	2960ms	2960ms	2956.59vs
2	CH_2, C-H asym stretching	2920vs	2910vs	2918.80vs
3	CH_2, C-H sym stretching	2850s	2850s	2850.61s
4	O-H stretching	2654w	2650w	_
5	C=O stretching	1700vs	_	_
6	COO-, C-O asym stretching	1550vs	_	1529s
7	CH_2 deformation	1460ms	1460m	1466s
8	C-O stretch + O-H in plane deformation	1450ms	_	_
9	COO-, C-O sym stretching	1430ms	_	1423w
10	CH_2 (adjacent to COOH group),deformation	_	1410ms	_
11	CH_3 sym deformation	1380ms	1350w	1302w
12	Progressive bands(CH_2,Twist and wag)	1325-1190m	1340-1100vw	1191m
13	CH_3 rocking	1100w	1110vw	1110s
14	OH out of plane deformation	_	930vw	_
15	CH_2 rocking	720ms	720w	721s
16	COOH bending mode	690w	680w	686m
17	COOH wagging mode	550s	550ms	_

The appearance of the two absorption bands of the carboxyl group corresponding to the symmetric and asymmetric vibrations of two carboxylate ions lies in the vicinity of 1410-1438cm-1 and 1524-1600 cm-1, respectively in the spectra of potassium, samarium & praseodymium hexadecanoate confirms the formation of soaps and indicates that these soaps have an ionic character.

Table 2 : Frequencies (cm^{-1}) of Absorption maxima with their Assignments of hexadecanoic acid, Potassium decanoate, Praseodymium hexadecanoate

S.N	ASSIGNMENT	Palmitic acid	potassium palmitate	praseodymium Palmitate
1	CH_3,C-H asymmetric-streching	2960 ms	2960 ms	2959 (m)
2	CH_2,C-H asymmetric-streching	2920 vs	2910 vs	2919.69 (Vs)
3	CH_2,C-H symmetric-streching	2850 s	2850 s	2850.55 (s)
4	OH,streching	2654 w	2650 w	-
5	C=O,streching	1700 vs	-	1713.07 (w)
6	COO^-,C-O asymmetric stretching	1550 vs	-	1536.79 (Vs)
7	CH_2, deformation	1460 ms	1460 m	1458.62 (
8	COO^-,C-O symmetric stretching	1430 ms	-	
9	C-O streching,O-H in plane deformation	1450 ms	-	
10	CH_2 (adjacent to COOH group),deformation	-	1410 ms	
11	CH_3,symmetric deformation	1380 ms	1350 w	
12	Prograsive bands (CH_2 twisting and wagging)	1325-1190 m	1300-1100 vw	
13	CH_3,rocking	1100 w	1110 vw	
14	OH ,out of plane deformation	-	930 vw	
15	CH_2 ,rocking	720 ms	720 w	
16	COOH,bending mode	690 w	680 w	
17	COOH, wagging mode	550 s	550 ms	

In the spectra of hexadecanoic acids, no bands corresponding to symmetric and asymmetric of carboxylate ions are observed. Naturally the OH stretching band near 2650-2550 cm-1 and OH deformation band at 940cm-1 observed in the spectra of fatty acids disappeared in the spectra of samarium & praseodymium soaps. The progressive bands of the medium and weak intensity observed in the region of 1360-1110cm-1 for samarium & praseodymium soaps are assigned to the wagging and twisting vibrations of the chains of successive methylene groups of the molecule of the soap and fatty acids.

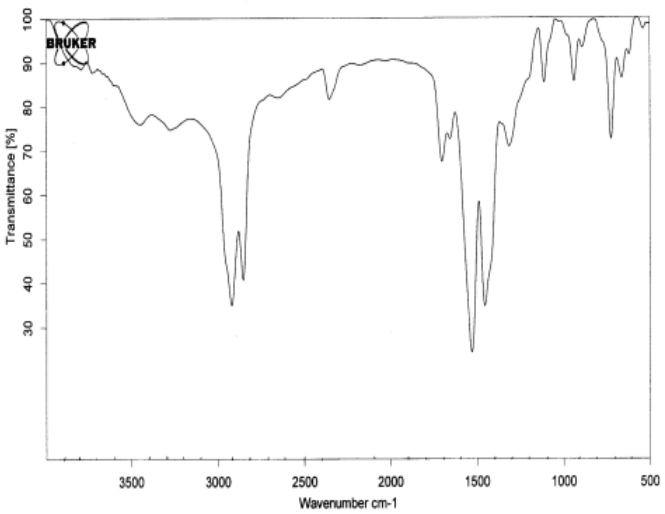


Fig. 1: IR of Samarium hexadecanoate

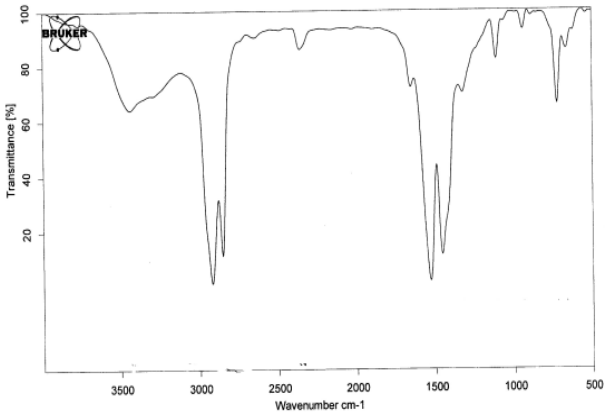


Fig. 2 : IR of Praseodymium hexadecanoate

These results confirm that the fatty acid (hexadecanoic acids) in the solid state exists with dimeric structure through hydrogen bonding whereas metal to oxygen bond in samarium & praseodymium soaps are ionic in nature. It is also proved that the soap molecules retain the resonance character of the carboxylic group. The infrared spectra of samarium soaps do not indicate any maxima in the region of 3500-3300 cm-1 which confirms the absence of any coordinated water molecules in the soaps. The assigned frequencies are in agreement with the results of other worker[5-6].

a) X-Ray Diffraction Analysis

The x-ray diffraction studies of samarium & praseodymium hexadecanoate has been done to characterize the structure in the solid state (table 3& 4). The intensities of diffracted x-ray as a function of diffraction angle,2(twice the Bragg angle) for samarium & praseodymium soaps were recorded with the help of x ray diffractometer and the recorded curves are reproduced over the range of 2-80°C corresponding to successive order of single long spacing [9-10].

Table 3 : X-Ray analysis of samarium hexadecanoate

S.no	2θ	θ	sin θ	λ/2 Sin θ	d (Å)	n
1	2.127	1.0635	0.0185	0.037	41.512	1
2	4.12	2.06	0.0359	0.0718	41.654	2
3	6.10	3.05	0.0532	0.1064	41.225	3
4	8.073	4.0365	0.0703	0.1406	41.385	4
5	10.085	5.0425	0.0878	0.1756	41.474	5
6	12.08	6.04	0.1052	0.2104	41.579	6
7	12.73	6.365	0.1108	0.2216	41.734	7
8	14.054	7.027	0.1223	0.2446	41.856	8
9	15.08	7.54	0.1312	0.2624	41.942	10
10	22.29	11.145	0.1932	0.3864	41.88	11
11	25.54	12.77	0.221	0.442	41.982	12

Average value of d = 41.656

Table 4 : X-Ray analysis of praseodymium hexadecanoate

S.no	2 θ	θ	Sin θ	λ/2 Sin θ	d (Å)	n
1	2.381	1.19	0.0207	37.212	46.92	1
2	3.887	1.943	0.0339	22.7227	47.43	2
3	7.11	3.555	0.062	12.4241	47.67	4
4	7.814	3.907	0.0681	11.3113	47.79	4
5	9.804	4.902	0.0854	9.0199	47.85	5

6	12.677	6.338	0.1103	6.9836	47.39	7
7	13.76	6.88	0.1197	6.435	47.54	7
8	15.77	7.885	0.1371	5.6185	47.82	9
9	17.78	8.89	0.1545	4.9857	47.71	10
10	19.779	9.889	0.1717	4.4863	47.65	11
11	21.81	10.905	0.1891	4.0735	47.69	12

Average value of d = 47.580

On the basis of long and short spacing, it is proposed that the metal ions in transition and rare earth metal soaps are arranged in a parallel plane, i.e. a basal plane equally spaced in the soap crystal with fully extended zig zag chains of fatty acid radicals on both directions of each basal plane and these soaps possesses double layer structure. The double layer structure of some heavy metal soaps was also suggested by Vold et al[11]. The molecular axes of transition metal soaps were found to be more inclined to the basal plane than rare earth metal soaps [12-13].

b) Thermogravimetric studies

The thermal decomposition of samarium and praseodymium hexadecanoate was studied by thermogravimetric analysis. The heating rate 20°c/min and nitrogen atmosphere were used. The final decomposition product or residues left on heating these soaps were the samarium & praseodymium oxide as the weights of the residues were almost in agreement with the theoretically and calculated weights of samarium & praseodymium soaps and samarium & praseodymium oxide from the molecular formula of the corresponding soap. The thermal decomposition of samarium& praseodymium soaps may be expressed as:-

$$(RCOO)_3Sm \rightarrow Sm^{3+} + 3RCOO^-$$

$$2(RCOO)_3Sm \rightarrow 3RCOR + Sm_2O_3 + 3CO_2$$

$$(RCOO)_3Pr \rightarrow Pr^{3+} + 3RCOO^-$$

$$2(RCOO)_3Pr \rightarrow 3RCOR + Pr_2O_3 + 3CO_2$$

Where R = C11H23 and C13H27

The results of thermal decomposition of samarium & praseodymium soaps were explained in the light of some well known equations, the Freeman-Carroll's[14]and Coats Redfern's [15] equations expressed as follows

$$\frac{\Delta[\log (dw/dt)]}{\Delta(\log W_r)} = -\frac{E}{2.303R} \cdot \frac{\Delta(1/T)}{\Delta \log (W_r)} + n$$

The plots of the loss in weight of the soaps, w, against time, t are shown in fig 3 & 4 and values of (dw/dt) are obtained from the curves by drawing tangents at appropriate times. The plots of Δ [log(dw/dt)] / Δ(log w_r) versus Δ(1/T)/Δ(log w_r) provide linear relationship. Slope of this enables us to calculate activation energy for the decomposition process and intercept provides n. The order of the reaction which was found zero and the values of the activation energy for the decomposition were found to be lie between 30-35 KJ mol-1.

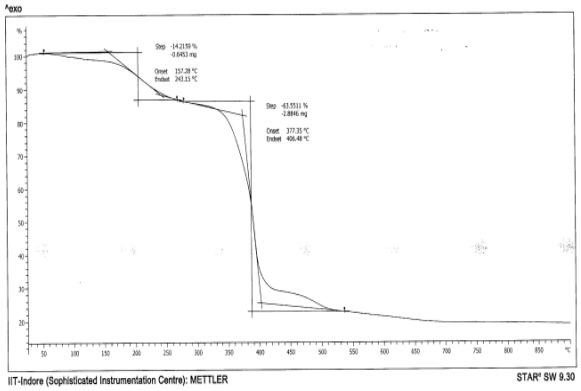


Fig. 3 : Thermal decomposition of samarium hexadecanoate

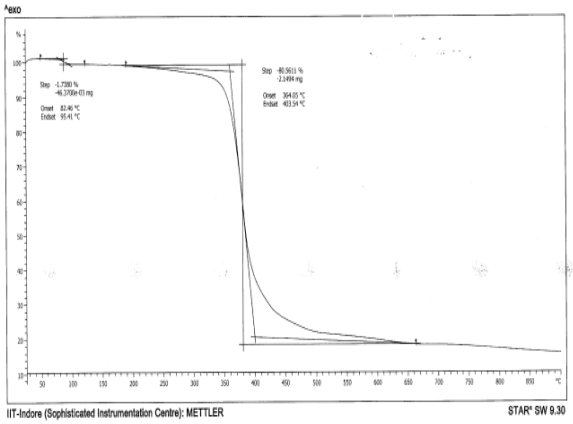


Fig. 4 : Thermal decomposition of praseodymium hexadecanoate

IV. Conclusion

The IR results showed that fatty acid exists in a dimeric structure as a result of hydrogen bonding between the carboxyl groups of two fatty acid molecules, whereas samarium& praseodymium soaps possess ionic character. The X-ray analysis showed that samarium & praseodymium soaps have double layer structure with molecular axes slightly inclined to the basal plane. The thermal decomposition of these soaps was found to be zero order and the energy of activation for the decomposition process was in the range 30-35 KJ mol-1.

References Références Referencias

1. Licata, F. J. (1957) "some metallic soaps used in the protective coating industry", *Official Digest* (388), 485-491.
2. Rinse J. (1967) Metal soaps, *American Paint Journal*, 22-28.
3. Salager, J. (2002) Surfactants: Types & Uses, FIRT; http/www.nanoparticles.org.
4. Zang, Q., Ming, H. and Zhai, Y.,(1996) *Polymer Int.*,41: 413.
5. Zang, Q., Ming, H. and Zhai, Y.,(1996)J.Appl.Polymer.sci.,62:887.
6. Nene, P.N.(2008) Adv.in.Nat.Appl.Sci.2(2): 73.
7. Upadyaya, S.K., Sharma, P.S. (1993) *J. Indian Chem.soc*, 70, 735-739.
8. Doletti, L., Esposito, P., Bottri, L., (1994) *Eur J.Pharm.*40, 161-167.
9. Mehrotra, K.N., Chauhan, M., Shukla, R.K.(1997) *Tenside surf. Det*., 34, 124-127.
10. Marques, E.F., Burrows, H.D., Miguel Graca, Da.M., (1998) Faraday Trans, *J. Chem. Soc*, 94, 1729-1739.
11. Binnemans, K., Heinrich, B., Gullion, D., Bruce, W.D., (1999) *Liq. Cryst*., 26, 1717-1721.
12. Robinet, L. and Corbeil, M.C.(2003) *Studies in conservation,* 48(1): 23.
13. Nakanishi, K.(1977) "Infrared absorption spectroscopy", *Holden-Day, (San Francisco)*, p. 39.
14. Vold, R.D. and Hattiangdi, G.S. (1949) *Ind. Eng. Chem.* 41, 2311.
15. Freeman, E.S. and Caroll, B.S.(1958) *Ohys. Chem.,* 62, 394.
16. Coats, A.W. & Redfern, J.P.(1964) *Nature*, 201, 68.
17. Suleman Verghese, S. P., Prasad, F. M.(2008) J. *Indian Chem. Soc.,* 85: 856.
18. Upadhyaya, S.K. and Chaturvedi, P.K.(2007) *J. Ind. Coun. Chem.,* 24(4): 74.
19. Kishore.K and Upadhyaya, S.K.(2010) *Portugaliae Electrochimica Acta*, 28, 13-19.
20. Upadhyaya.S.K., Chaturvedi. P.K.(2007) *J Ind Coun Chem.*, 24:74.
21. Rawat, M.K., Sharma, Y., Kumari, S.(2008) *Asian J Chem.,* 20:1464.
22. Kishore.K, Upadhyaya, S.K.(2011) *Tenside Surf Det.,* 47:189.

Global Journal of Science Frontier Research: B
Chemistry
Volume 15 Issue 3 Version 1.0 Year 2015
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

Synthesis, Spectroscopic, Thermodynamic and Biological Activity Studies of Schiff Base and Metal Complexes Derived from 2-[1H-Pyrrol-2-Ylimino Methyl]- 5-Phenyl-1,3,4-Oxadiazole

By Nazk Mohammed Aziz, Naser Dhiya Shaalan & Dr. Sahar Sabeeh Hassan
University of Sulaimani, Iraq

Abstract- New metal complexes of the ligand (HL) 2-[1H-Pyrrol-2-ylimino methyl]- 5-phenyl-1, 3,4-oxadiazol with the metal ions Co(II), Ni(II) and Cu(II), were prepared in alcoholic medium. The Schiff bases were condensed by using [Pyrrolcarboxaldehyde] with[2-amino-5-(phenyl-1, 3,4-oxadiazole] in alcoholice medium. As the Schiff baseprepared was tridentate ligand, it was used for forming complexes with Co+2, Ni+2, Cu +2 and Zn+2 ions of type M (HL)2. All the synthesized Schiff base and their metal complexes were characterized by FTIR Spectroscopy, Electronic Spectroscopy, Elemental Analysis, Magnetic Susceptibility Measurements, Thermal Analysis , 1H-NMRSpectra, and Mass Spectra.

Keywords: *schiff base, microwave synthesis, thermodynamic parameters, biological activity.*

GJSFR-B Classification : *FOR Code: 030306p*

Strictly as per the compliance and regulations of :

Synthesis, Spectroscopic, Thermodynamic and Biological Activity Studies of Schiff Base and Metal Complexes Derived from 2-[1H-Pyrrol-2-Ylimino Methyl]- 5-Phenyl-1,3,4- Oxadiazole

Nazk Mohammed Aziz [α], Naser Dhiya Shaalan [σ] & Dr. Sahar Sabeeh Hassan [ρ]

Abstract- New metal complexes of the ligand (HL) 2-[1H-Pyrrol-2-ylimino methyl]- 5-phenyl-1, 3,4-oxadiazol with the metal ions Co(II), Ni(II) and Cu(II), were prepared in alcoholic medium. The Schiff bases were condensed by using [Pyrrolcarboxaldehyde] with[2-amino-5-(phenyl-1, 3,4-oxadiazole] in alcoholice medium. As the Schiff base prepared was tridentate ligand, it was used for forming complexes with Co^{+2}, Ni^{+2}, Cu^{+2} and Zn^{+2} ions of type M $(HL)_2$. All the synthesized Schiff base and their metal complexes were characterized by FTIR Spectroscopy, Electronic Spectroscopy, Elemental Analysis, Magnetic Susceptibility Measurements, Thermal Analysis , 1H-NMR Spectra, and Mass Spectra. The Activation Thermodynamic Parameters, such as ΔE*, ΔH*, ΔS* and ΔG*were calculated from the TGA curve using Coats-Red fern method. From the spectral measurements, structures for the complexes were proposed. Preliminary in vitro tests for antimicrobial activity showed that all prepared compounds displayed good significant activity to *Staphylococcusaureus, Escherishia coli, Pseudononasaeroginosa and Cndidaalbicans.*

Keywords: schiff base, microwave synthesis, thermodynamic parameters, biological activity.

I. Introduction

Increasing physiological importance of donor organic compounds including nitrogen and oxygen have active roles played by certain coordinated metal ions. These compounds have magnificent characteristics in synthesizing and studying structural aspects of metal complexes with some oxygen and nitrogen donor ligands.

Literature survey reveals that out of various isomers particularly 1,3,4-oxadiazole derivatives exhibit wide range of biological activities. Various methods for the synthesis of 1,3,4-oxadiazole have also been reported[1-4]. These biological activities are probably due to the presence of the –N=C–O group [5]. Pyrrole, oxadiazol and its derivatives form an important class of organic compounds due to their chemical structure and biological activities as analgesic, antipyretics and anti-inflammatory [6]. Even the simplest Pyrrole derivatives are widely used for analgesic medicines. Pyrroles are efficient extractants of metal ions and they have potential to form different types of coordination compounds. In addition, a pyrrolecan form a variety of Schiff bases and are reported to be superior reagents in biological, clinical and analytical applications [8,7]. The present study confines itself to study the metal complexes of Schiff bases encompassing some new metal ions such as Co(II), Ni (II) , Cu (II) and Zn (II), derived from Pyrrole and 2-amino-5-(2-hydroxy-phenyl-1,3,4-oxadiazole. Preparation, characterization and antibacterial activity of above metal complexes with this Schiff bases are reported here. Where, HL is a Schiff base of 2-amino-5-(2-hydroxy-phenyl-1,3,4-oxadiazolre acting with Pyrrole along with complexes with some oxygen and nitrogen donor ligands [9]. From the TGA curves recorded for the successive steps in the decomposition process of these ligands and complexes, it was possible to determine the following characteristic of the thermal parameters for each reaction step: initial point temperature of decomposition (T_i) stands for initial temperature point at which TG curve starts deviating from its base line. Final point temperature of decomposition (T_f) at which TG curve returns to its base line. Peak temperature, i.e. temperature of maximum rate of weight loss: the point obtained from the intersection of tangents to the peak of TG curve, whereas (DM) stands for the mass loss at the decomposition step which is the amount of mass that extends from the point T_i up to the reaction end point T_f on the TG curve, i.e. the magnitude of the ordinate of a TG curve. The material released at each step of the decomposition is identified by attributing the mass loss (Dm) at a given step to the component of similar weight calculated from the molecular formula of the investigated complexes, comparing with literatures of relevant compounds considering their temperature. This may assist identifying the mechanism of reaction in the decomposition steps taking place in the complexes under question. Activation energy (E) of the composition

Author α: Department of Chemistry, School of Science, Faculty of Science and Science Education, University of Sulaimani, Kurdistan, Iraq. e-mail: nazek64@.yahoo.com
Author σ: Department of Chemistry, College of Science for Women, University of Baghdad, Baghdad, Iraq.
e-mail: ndsh1972@gmail.com
Author ρ: Department of Chemistry, College of Science for Women, University of Baghdad, Baghdad, Iraq.

step: the integral method used is the Coats-Redfern equation [10]. For reaction order n≠1or n= 2, which when linearised for a correctly chosen n yields the activation energy from the slop:

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log\frac{ZR}{qE}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.303RT} \quad \ldots\ldots n\neq 1$$

$$\log.\left[\frac{-\log.(1-\alpha).}{T^2}\right] = \log.\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{2.303RT} \quad \ldots\ldots n=1$$

$\Delta S^* = 2.303R\ [\text{Log}\ (Ah/K\ T_{max})]$, $\Delta H^* = E - RT_{max}$, $\Delta G^* = \Delta H^* - T_{max}\ \Delta S^*$where: α = fraction of weight loss, T = temperature (°K), n = order of reaction, A or Z = pre-exponential factor, R = molar gas constant, E = activation energy and q = heating rate. Order of reaction (n) is the one for which a plot of the Coats-Redfern expression gives the best straight line among various trial values of n that are examined relative to that estimated by the Horovitz-Metzger method [11].

II. Experimental

All chemicals used were of reagent grade (supplied by either sigma Aldrich or fluka) and used as supplied. The FTIR spectra in the range (4000-400) cm^{-1} cut were recorded as KBr disc on FTIR.4200 Jasco Spectrophotometer. The UV-Visible spectra were measured in ethanol using Shimadzu UV-Vis. 160 A-Ultra-violet Spectrophotometer in the range (200-1000) nm. Magnetic Susceptibility measurements for complexes were obtained at room temperature using (Magnetic Susceptibility Balance) Jhonson Mattey Catalytic Systems Division. Gall encamp M.F.B600.010 F melting point apparatus were used to measure the melting point of all the prepared compounds. Elemental microanalysis was carried out using CHNO Elemental Analyzer Model 5500 Carlo-Elba Instruments (Italy).

a) Synthesis of [2-amino-5-(2-hydroxy-phenyl-1,3,4-oxiadiazole][12] [L]

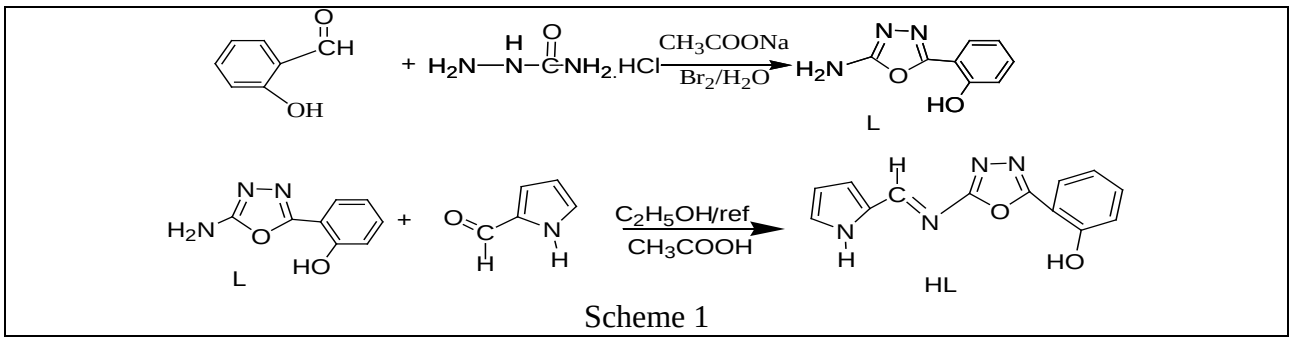
A. Synthesis Semicarbazone: Semicarbazide Hydrochloride (0.1M) and sodium acetate (0.2M) were added and dissolved in 15-20mL of distilled water placed in flat-bottomed flask. In a separate beaker containing required Salicylaldehyde (0.1M) was dissolved in free alcohol. This ethanolic aromatic aldehyde solution was added slowly to the solution of semicarbazide hydrochloride. The precipitate, which was separated, was filtered, dried and recrystallized from 95% hot ethanol.

B. Semicarbazone (0.1M) and sodium acetate (0.2M) were dissolved in 300-400 mL of glacial acetic acid with continuous stirring. Bromine (7 mL in 50 mL of GAA) was added slowly to it. The solution was stirred for an hour and then poured on crushed ice the resulting solid was separated, dried and recrystallizedfrom hot ethanol (95%). Thetable (1)showsC.H.N.S analysis of the yielded.

b) -2-[1H-Pyrrol-2-ylimino methyl]- 5-phenyl-1,3,4-oxadiazol[13][HL]

Method (1): A mixture of equal molar amounts (0.05 mol.) of both appropriate [Pyrrolcarboxaldehyde] and the [2-amino-5-(2-hydroxy-phenyl-1,3,4-oxiadiazole], in absolute ethanol (25 ml) with (3) drops of glacial acetic acid was refluxed (4)hours. The reacted mixture was then allowed to cool at room temperature, and the precipitate was filtered, dried, and recrystallized from mixture (methanol and ethanol) (1:1) to give yellow powder.

Method(2): A mixture of equal molar amounts (0.05 mol.) of appropriate [Pyrrole-2-carbaldehyde] and the (2-amino-5-(2-hydroxy-phenyl-1,3,4-oxadiazole), were ground with a mortar, mixed, dried and subjected to microwave irradiation 280W for (10) minutes, after completion the reacted mixture was cooled to room temperature, then the solid obtained was recrystallized twice from mixture (methanol and ethanol) (1:1) to get yellow powderyield. The table (1) shows C.H.N.S analysis of the yielded.



Scheme 1

III. Preparation of Complexes

Method(1) : An ethanol solution of the metal salts of Co(II), Ni (II), Cu (II) and Zn (II) was added to an ethanolic solution of (HL) in 1:1 (metal : ligand) molar ratios. After stirring for 2 hours with heating 70 °C, crystalline colored precipitates formed cooling at room temperature, the resulting solids were filtered off, washed with distilled water, dried and recrystallized from ethanol and dried at 50 °C.

Method(2) : An ethanol solution of the metal salts of Co(II), Ni (II), Cu (II) and Zn (II)were added to an ethanolic solution of (HL) in 1:1 (metal : ligand) molar ratios. Then it was put in ultrasonic bath heated to 65^{0}C After 50 minutes crystalline colored precipitates formed, cooling at room temperature, the resulting solids were filtered off, washed with distilled water, dried and recrystallized by using ethanol and dried at 50 ^{0}C. Thetable (1) shows C.H.N.S analysis of the yielded.

IV. Result and Discussion

The synthetic procedure of Schiff base ligand is presented in Scheme 1. Then, the divalent transition metal ions *viz.*, Co (II), Ni (II), Cu(II) and Zn(II) reacted with the ligand. The composition of the complexes formed in solution has been established by mole ratio and job methods. In both cases, the results reveal (2:2) metal to ligand ratio yielded the corresponding metal chelates. Shows the decomposition point, color and electronic absorption bands for ligand and complexes are shown in Table (1, 2). The bands are classified into three distinct groups: The intermolecular transitions appeared in the UV region, charge transfer from ligand to metal, and d-d transitions appeared in the UV-Visible region.

a) [2-amino-5-(2-hydroxy-phenyl-1, 3,4-oxiadiazole] [L]

The reaction of Semi-carbazide Hydrochloride with Salicylic aldehyde in presence of sodium acetate/Br_2 afforded 2-amino-5-phenyl-1, 3,4-oxiadiazole [11]. The structural assignment of the product was based on its melting point and spectral (FT-IR and UV/Vis.) data as shown in table (1). The FT-IR spectrum of compound (L) exhibited significant two bandshaving the range (3402–3213)cm^{-1} which could be attributed to asymmetric and symmetric stretching vibrations of the NH_2 group. Stretching vibration band of (OH) occurs in the (3428) cm^{-1}. Besides this, band ranges at about (1475-1423 cm^{-1}) due to cyclic (C = N) stretching is also observed. Other bands occurring at (1518 cm^{-1}) and (1484 cm^{-1}) are due to the (N-H) bending and (C-N) stretching vibrations, respectively [14].

b) [2-[(1H-Pyrrol-2-ylimino methyl)]- 5-(2-hydoxy-phenyl)-[1,3,4-oxiadiazol] [HL]

The FT-IR spectra shows the disappearance of the two absorption bands due to (-NH2) stretching of amino oxadiazole [HL] showed all the suggested bonds for olefin (C-H), (C=C) aromatic, endocyclic (C=N) and exocyclicimine group. All the prepared compounds (Schiff bases) exhibited the stretching band near the region (1475-1423) cm^{-1}, this is due to the (=N-N=C-) cyclic group; 3426 cm^{-1} (υ OH Stretching), a band at 3155 cm^{-1} attributed to NH stretching (pyrrole ring), 1595cm^{-1} (υ C=N Stretching of amine), 1229 cm^{-1}, 1468 cm^{-1} (Characteristic bands of oxazole ring).All the spectral data for other compounds are listed in table (2).

^{1}H-NMR spectrum of compounds [HL], shows the following characteristic chemical shift, (CDCL3-d_6) ppm. The four aromatic ring protons of phenyl (δ 6.95 - 7.55) (s, 4H, Ar), and three pyrrole ring appeared at (δ 6.00 – 7.45) ppm, the signal at (δ 8.78)was attributed to (N=C-H) proton (azomethine). Beside the signal at (δ 9.56) ppm, was attributed to (N-H) proton, δ=11.95(s, 1H, OH),δ 1.584(organic solvent).

The positive ion mass spectral analysis of (HL) observed at m/z 255. (M+1) (Figure5), confirms the theoretical molecular weight i.e. 254.1.

Table 1 : The characterization data of the prepared compounds

Compound Formula,	Yield %	C	H	N	O	Cl	M
L $C_8H_7N_3O_2$	70	54.60 (54.24)	3.82 (3.98)	23.39 (23.72)	18.19 (18.06)	---	--
HL C13H10N4O_2	81	61.74 (61.41)	3.91 (3.96)	22.15 (22.04)	12.65 (12.59)	---	--
$[Co_2 (HL)_2.4(H_2O)]Cl_2$	72	40.94 (40.81)	3.22 (3.16)	14.85 (14.64)	16.91 (16.73)	9.13 (9.27)	14.95 (15.40)
$[Ni_2 (HL)_2.4(H_2O)] Cl_2$	67	40.96 (40.83)	3.12 (3.16)	14.99 (14.65)	16.57 (16.74)	9.20 (9.27)	15.16 (15.35)
$[Cu_2 (HL)_2.4(H_2O)]Cl_2$	65	40.49 (40.32)	3.11 (3.12)	14.31 (14.47)	16.69 (16.53)	9.03 (9.15)	16.37 (16.41)
$[Zn_2 (HL)_2.4(H_2O)]Cl_2$	55	40.32 (40.13)	3.17 (3.11)	14.25 (14.40)	16.22 (16.45)	9.23 (9.11)	16.94 (16.81)

Table 2 : some physical data electronic spectra for ligands and complexes in DMF

Symbol	Dec. Point ^0C	Conductivity $ohm^{-1}cm^2mol^{-1}$	MagneticMoment (B(B.M)	Color	Absorption Bands (nm)	AssignedTransition
L	244	-	-	White-yellow	209	$\pi\rightarrow\pi^*$
					285	$n\rightarrow\pi^*$
HL	285	--	-	yellow	215	$\pi\rightarrow\pi^*$
					390	$n\rightarrow\pi^*$
Co(II)	295d	146	4.78	Pale -Red	775	$^4T_1g\rightarrow{}^4A_2g$
					545	$^4T_1g^{(F)}\rightarrow{}^4t_1g^{(p)}$
					350	Charge Transfer
Ni(II)	300d	136	3.22	Pale green	230	$\pi\rightarrow\pi^*$
					290	$n\rightarrow\pi^*$
					375	Charge Transfer
					650	$^3A_2g\rightarrow{}^3t_1g^{(p)}$
					940	$^3A_2g\rightarrow{}^3t_1g^{(F)}$
Cu(II)	300d	139	1.92	Light Brawn	225	$\pi\rightarrow\pi^*$
					290	$n\rightarrow\pi^*$
					370	Charge Transfer
					425, 610,640	$^2B_1g\rightarrow{}^2B_2g$
Zn(II)	300d	161	Dia	Purple White	315	Charge Transfer

V. Infrared Spectral Analysis of Metal Complexes

The infrared spectra of the ligands show (υO-H) (weakly H-bonded) at 3429cm^{-1} and (υN-H) at 3151 cm^{-1}. The absence of this band in all the metal complexes indicates the removal of a proton of hydroxyl group of benzene ring and a proton of NH group of pyrrole ring during the chelation. The sharp intense band at 1593 cm-1 in the ligands can be assigned to υC=N (azomethine). A shift ∆ υ = 7-15 cm^{-1}) in υC=N (azomethine) is observed upon the coordination indicating that the nitrogen of azomethine group is involved in coordination. All the complexes show broad band in the region(3285-3378) cm^{-1} which may be assigned to (υ O-H) of coordinated water [15]. To account for the octahedral stereochemistry of the metal complexes, the coordination of two water molecules is expected.

The bands at 561cm^{-1}in Co(II) complexes, 579 cm^{-1} in Ni(II) complex , 588 cm^{-1} in Zn(II) complex and 587cm^{-1} in Cu(II) complex may be due to metal-nitrogen stretching vibration[16,17]. In the free ligand, the band at 1606 cm^{-1} is assigned to the stretching of C=N(oxazole ring). On complexes, this band was shifted to a lower frequency region. This shift is probably due to the lowering of bond order of the carbon-nitrogen bond resulted in forming complexes of the metal ion to the ligand through nitrogen in (υC=N) compared to its respective ligands. This suggests that the nitrogen atom of the ring has not participated in the chelation. However, in water containing chelates, this band is observed as a broad band. This may be due to coupling of the bending mode of coordinated [18].

Table 3 : Infrared data of Ligand and its metal complexes (cm^{-1})

Symbol	ν(C=N)	ν(N-H) pyrrol	ν(C-N=N-C)	ν(M-O)	ν(H2O)	ν(O-H)	ν(M-N)
HL	1594(s)	3155	1475-1423	-	-	3426	-
Co(II)	1610(s)	-----	1490-1429	477(s)	3275	-	561(s)
Ni(II)	1617(s)	-----	1485-1430	444(s)	3281	-	579(s)
Cu(II)	1603(s)	-----	1484-1427	437(s)	3241	-	588(s)
Zn(II)	1611(s)	-----	1460-1430	447(s)	3255	-	587(s)

VI. Thermal Analysis

To understand thermal decomposition process, the Schiff base and its metal complexes were examined by thermo gravimetric analysis in the temperature range of 35–700 ^{o}C. The obtained thermo analytical results from TGA curves for all these compounds which are given in table (4). The decomposition was completed at 693 ^{o}C for all the complexes. The data from the thermo gravimetric analyses indicated that the decomposition of the complexes (three steps) and the ligand proceeds in (two) steps. The final decomposition products were metal oxide mixture formed above 598 ^{o}C for the metal[19].

Table 4 : Thermodynamic parameters of the ligands and metal complexes

Sample (step)	T.range ^{o}C	N	R^2	T_{max} ^{o}K	Ea K.J mol^{-1}	ΔH^* KJ mol^{-1}	ZSec^{-1} x10^5	ΔS^* J mol^{-1}K^{-1}	ΔG^* KJ mol^{-1}
HL(1)	37-300	1	0.99	512.79	170.4906	166.2344	1.7762	-34.0617	183.700
HL(2)	300-700	0.9	0.99	780.77	-7.87418	-14.3548	4.82	-354.698	262.5828
Co(1)	37-368	0.9	0.99	476.4	31.57044	27.61632	7.25	-289.758	165.6572
Co(2)	368-467	0.9	1	643.09	-6.84804	-12.1857	5.6	-351.864	214.094
Co(3)	368-700	0.9	0.99	766.6	-6,58243	-13.0282	6.35	-352.37	260.6221
Ni(1)	37-150	0.9	0.99	384	19.3764	16.1892	0.00381	-312.457	136.1727
Ni(2)	150-390	0.9	0.99	507	36.5	32.2919	0.017	-283.109	175.828
Ni(3)	390-700	0.9	0.99	775.12	-11.19	-17.6235	35.4	-257.205	259.2532
Cu(1)	37-180	0.9	0.99	423	125.9	46.49	7.68	-222.79	135.39
Cu(2)	180-395	0.9	0.99	554	54.214	121.04	0.5357	-100.31	169.81
Cu(3)	395-700	0.9	1	726.35	12.696	-5.734	4.91	-359.81	306.7
Zn(1)	37-190	0.9	0.99	480.8	23.71	19.72	1.5x10^{-4}	-321.9	174.52
Zn (2)	190-450	0.9	0.99	550	98.17	92.77	258.69	-205.2	226.16
Zn (3)	450-700	0.9	0.99	819	-10.14	-17.78	3.7x10^{-6}	-358.3	311.69

VII. Biological Activity

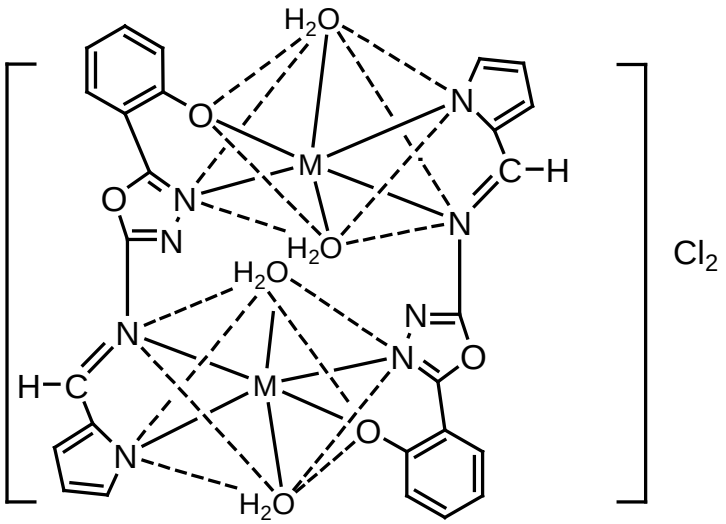
With a view to explore the possibility of obtaining biologically useful complexes that contain 1,3,4- oxadizole and pyrrole ring system, such a biological activity encourages us to prepare some new series of compunds containing the above mentioned unit. The antimicrobial activity of these compounds was determined by the agar diffusion method[20]. These types of bacteria Staphylococcus aureus, Escherishia coli, Pseudononasaeroginosa and Cndidaalbicans were used to show the biological activities of the ligand and its complexes. In this method, a standard 5mm diameter sterilized filter paper disc impregnated with the compound. Then, (1 mg per 1 ml of acetone) was placed on an agar plate seeded with the test organism. The plates were incubated for 24 hours at 37 ^{0}C. The zone of inhibition formed was measured in mm and are represented by (+), (+ +) and (+ + +) depending upon the diameter and clarity, as presented in table (5).The preliminary screening results reveal that the compound contained thiadizole and pyrrolecomplexes exhibits highest antibacterial activity against Escherishia coli.

Table 5 : Antibacterial activity of the prepared compounds

Symbol	*Staphylococcus aureus*	*Escherishia coli*	*Pseudononas aeroginosa*	*Cndidaalbicans*
HL	+	+ + +	+	+
Co(II)	+	+ + ++	++	++
Ni(II)	+	+ + +	++	+
Cu(II)	++	+ ++	+++	++
Cu(II)	++	+ +	+++	++

Note (-) = no inhibition, (+) = (5-10) mm, (+ +)=(11-20) mm, (+ + +) = more than (20)mm

From the FTIR Spectroscopy, electronic susceptibility measurements, thermal analysis suggest spectroscopy, Elemental analysis, magnetic the structure.

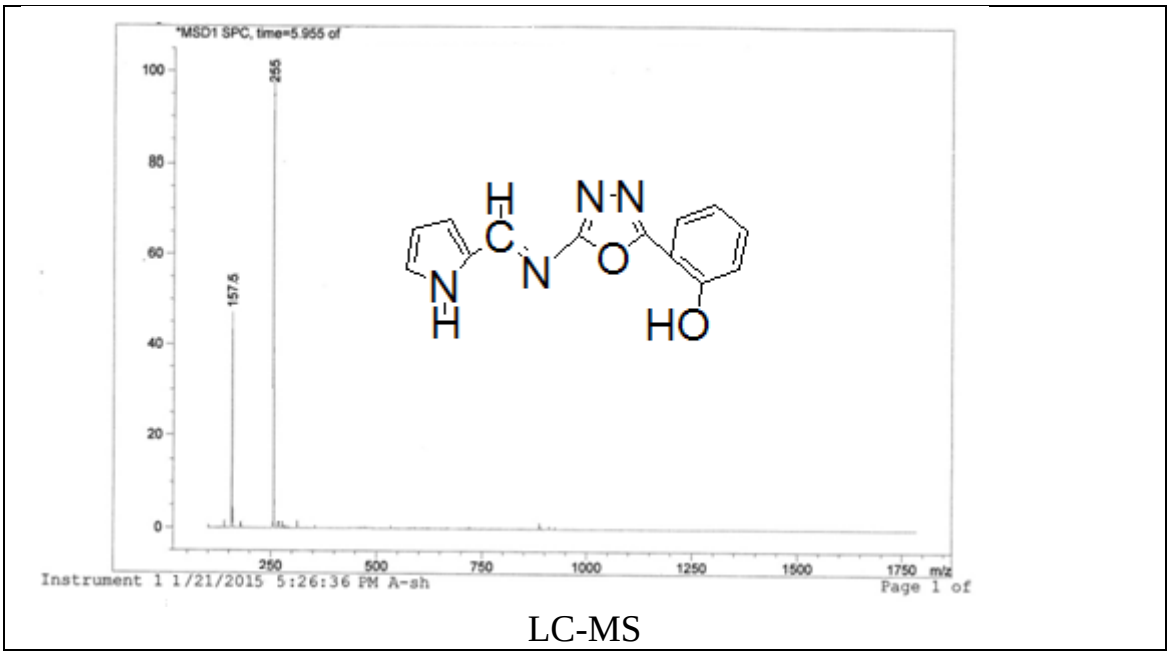


[M2L2.4H2O]Cl2 ,M= Co (II), Cu (II), Zn (II)

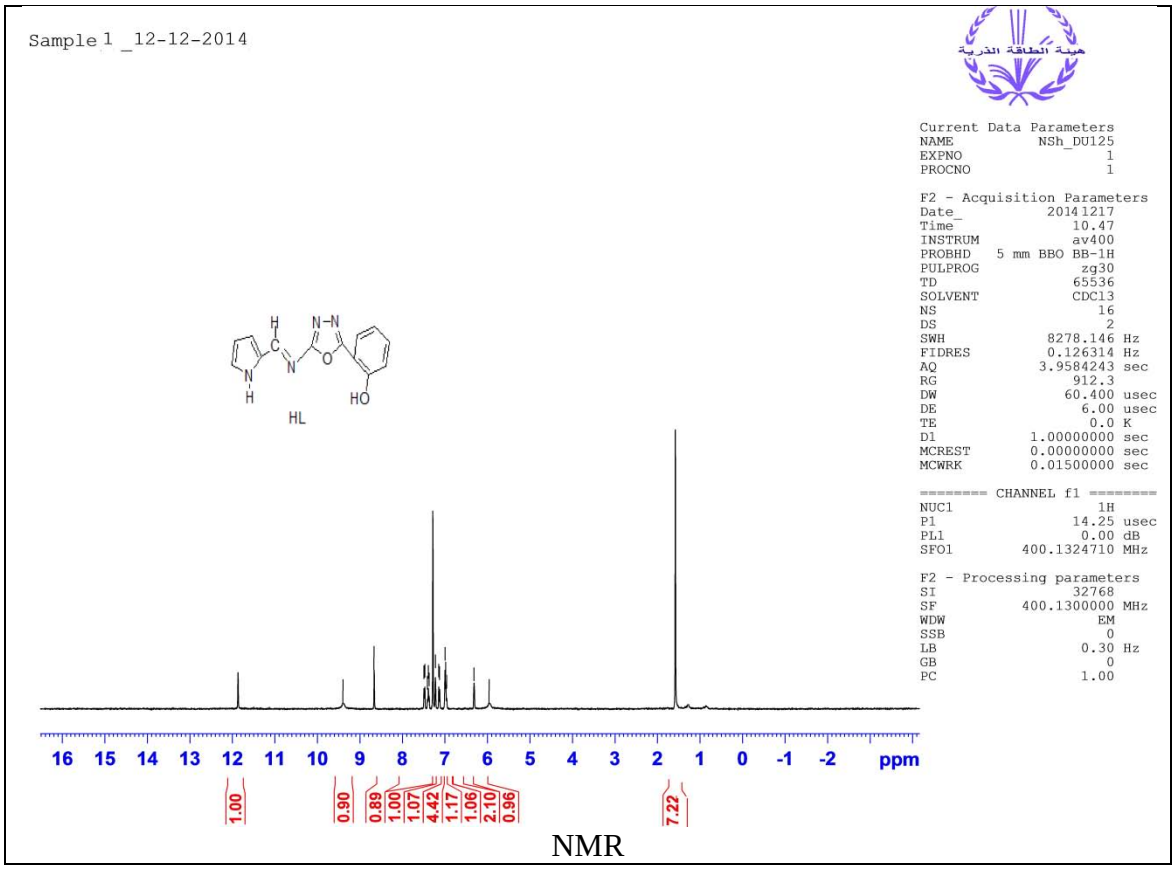
References Références Referencias

1. Farah M., Pilotti A., *Drug Discovery Today*, 11(3-4), 165-174 (2006).
2. Waston B., Tierney J. and Lidstrom P., *Drug Discovery Today*, 6, 373–380 (2002).
3. Kidwai M., Kumar P. and Goel Y., *Ind. J. Chem.,* 36B, 175-179 (1997).
4. Khan K.M., Rani M. and Haider S.M., *Lett. Org. Chem.*, 1, 151 (2004).
5. Yousif E. Ameer A.A and Sabbah A.M," Complexes of 2-Amino-5- (*p*-propoxyphenyl)-1, 3, 4-oxadiazole With Some Metal Ions". Journal of Al-Nahrain University, 2: pp.65-69.(2004).
6. Abbiati G, Arcadi A, Attanasi O A, De Crescentini L and Rossi E," Synthesis of functiona lisedpyrazolones and imidazolines /imidazoles through divergent cyclisation reactions " Tetrahedron, 57: pp. 2031-2038,(2001).
7. Yang Z. Y, Yang R D, Li F S and Yu K B." (Z)-4-{1-[(2-Hy¬droxy¬ethyl) ¬amino]¬ethyl¬idene}-3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one" Polyhedron, 19: pp. 2599,(2001).
8. Joshi K.T., Dabhi H.R., Pancholi A.M. And Rana A.K., "Ligand field parameters of Cu (II), Ni (II) and Co (II) chelates with some 4-substituted-1-phenyl-3-methyl-2-pyrazolin-5-ones", Orient. J.Chem., 12 (3), 287-290 ,(1996).
9. Emad, Y., Hadeel A., Farah M. Synthesis and characterization of some metal ions with 2-amino acetate benzothiazol. Journal of applied sciences research, 6(7): PP. 879-882, (2010).
10. Coats, A.W. and Redfern,J. P., "Kinetic parameters from thermogravimetric". Nature, 201:pp. 68,(1964).
11. Horovitz, H. H. and . Metzger, G., "Analysis of thermogravimetric traces as an approach to determine the mechanism of dissociation of copper (II)-α-aryl azoacetoacetylaminopyridine chelates". ThermochimicaActa, 159: pp.43-54,(1963).

12. Johnsoa, A and Wilcox; (1969) *Lab. Exp. Org. Chem. (The Macmillan Company, Collier Macmillan Limited, London)* p.219.
13. Chudgar,N.K; Shan,S.N and Vorat, R.A; "Mesogenic Semicarbazones and Amino Oxadiazoles "; *Mol. Cryst. Liq. Cryst*; 172, pp.51-56,(1989).
14. Sliverstien R.; Bassler G.; Morrill T.Spectrometric Identification of Organic Compounds. 7th addition, John-Wiley, New York, (2005).
15. NakamotoK,Infrared spectra of Inorganic and coordination Compounds, JohnWilley, New York,(1963).
16. Adans D M. "Metal-Ligand and related Vibration", Edward Arnold, London, 33:pp.310, (1967).
17. Rahman S M F, Ahmad J and Haq M. M, "Tris-(salicylaldehyde)-complexes"JInorgNuclChem, Journal of scientific Research, 4(4): pp. 229-234,(2009).
18. Sahoo, K. K. Das, P. K. and Nayak, S.C. "Synthesis and Characterization of Some Cobalt (III) 35: pp. 1011, (1973).
19. Sarika, R. Y. Amit, R. Y. Gaurav, B. P. and Anand, S. A." Synthesis and characterization of transition metal complexes with N, O-chelating Hydrazone Schiff base ligand", American-Eurasian Complexes Containing Heterocyclic Nitrogen Donor Ligands", Chem Pap., 57, (2): pp 91-96, (2003).
20. Manish srivastava, Deepak Singh, Aashishsinghkushwah and P.D.Gokulan Journal of Current Pharmaceutical Research 04,pp 20-24,(2010).



LC-MS



NMR

Global Journal of Science Frontier Research: B
Chemistry
Volume 15 Issue 3 Version 1.0 Year 2015
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

Dipolar 1, 3-Cycloaddition: Synthesis of New Pyrazolinic Compounds Derived from Eugenol

By Fatima Rouda, Imane Lakhtib, Abdelmejid Bahloul, Abdelmajid Abourriche, Abdelfettah Sebban & Said Kitane

Hassan II Mohammedia, Morocco

Abstract- It is now well known that pyrazolic and pyrazolinic derivatives are a class of heterocyclic compounds with high biological activity.

In our laboratory, many studies have been made on the synthesis, stereochemistry, the complexing power and biological properties of various pyrazolic and pyrazolinic structures.

The new pyrazolines presented in this work were prepared by cycloaddition of 1,3-dipole (the diarylnitrilimine) on eugenol and acetyleugenol which are two natural extracted dipolarophiles from cloves.

The structures of the obtained cycloadducts have been studied and confirmed on the basis of IR spectroscopic parameters, NMR-1H and 13C.

Keywords: *dipolar 1,3-cycloaddition; synthesis; eugenol; pyrazolinic compounds.*

GJSFR-B Classification : *FOR Code: 030399p*

Strictly as per the compliance and regulations of :

Dipolar 1, 3-Cycloaddition: Synthesis of New Pyrazolinic Compounds Derived from Eugenol

Fatima Rouda [α], Imane Lakhtib [σ], Abdelmejid Bahloul [ρ], Abdelmajid Abourriche [ω], Abdelfettah Sebban [¥] & Said Kitane [§]

Abstract- It is now well known that pyrazolic and pyrazolinic derivatives are a class of heterocyclic compounds with high biological activity.

In our laboratory, many studies have been made on the synthesis, stereochemistry, the complexing power and biological properties of various pyrazolic and pyrazolinic structures.

The new pyrazolines presented in this work were prepared by cycloaddition of 1,3-dipole (the diarylnitrilimine) on eugenol and acetyleugenol which are two natural extracted dipolarophiles from cloves.

The structures of the obtained cycloadducts have been studied and confirmed on the basis of IR spectroscopic parameters, NMR-1H and 13C.

Biological tests, Complexity trials and synthesis using the rest of the series diarylnitrilimines are in progress.

Keywords: dipolar 1,3-cycloaddition; synthesis; eugenol; pyrazolinic compounds.

I. Introduction

Since its development by Huisgen and al. Dipolar cycloaddition reaction appears among the most applied reactions for the synthesis of heterocyclic compounds not readily accessible by other synthetic methods [1-8].

In our laboratory, the synthesis of new pyrazolinic and pyrazolic heterocycles via such cycloaddition with diary lnitrilimines (DANI) as a dipole has been the subject of several theoretical and experimental studies [9-13].

Furthermore several cycloadducts, or derivatives thereof, synthesized showed very interesting biological activities.

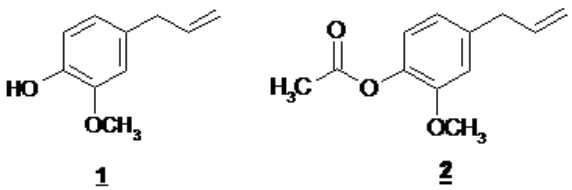
These compounds have in fact antimicrobial, antifungal and antileishmanial [14-16]. In order to continue this work and to broaden the scope of investigation of our research team, we diversify the nature of used dipolarophiles (natural instead of synthetic), we have opposed DANI to two dipolarophiles eugenol and acetyleugenol which are extracted from a natural substance "nails chanterelle."

II. Bibliographic Details

Cloves are the dried buds, unhatched, the clove and are among the oldest spices and drugs described in the story. They have antiseptic, analgesic and are widely used in dentistry against toothache. They are also antibacterial, antifungal and prevent infectious diseases and helps to eliminate intestinal parasites.

Eugenol 1 and acetyleugenol 2 are natural compounds that can be extracted from natural oil of cloves.

They belong to a class of compounds called vanilloid. They are known for their antioxidant properties and may reduce the risk of diseases such as cancer, cardiovascular disorders and also malaria, AIDS and the effects of aging [17-20].



1 2

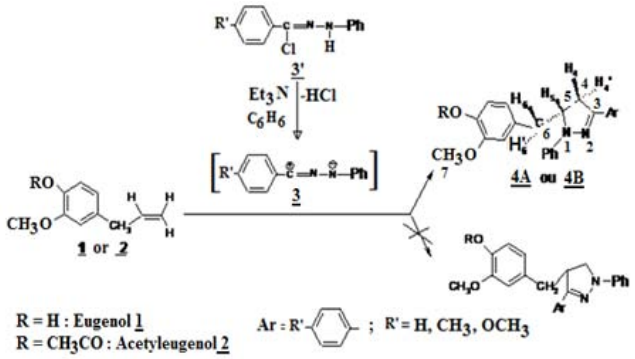
Cycloaddition Reaction

To develop essential oils and compounds 1 and 2 whose structures have activated ethylenic dipolarophiliques sites similar to the 7-allyl-8-hydroxyquinoline studied in our laboratory [13], we have opposed them to 1,3-dipole : the diarylnitrilimine (DANI) 3.

In fact, heating at reflux in dry benzene for 48 hours, eugenol 1 or acetyleugenol 2 with DANI 3, generated "in situ" by means of triethylamine after reaction with the precursor 3' gives in regiospecific manner both single cycloadducts with a good yield varying from 50 to 67%.

The structure of the compounds obtained was established on the basis of spectroscopic data of IR, 1H NMR (300 MHz), 13C NMR (50 MHz) and DEPT (Distortionless Enhanced Polarization Transfer).

Author α σ ρ ω ¥: Biomolecular and Organic Synthesis Laboratory (BIOSYNTHO), Faculty of Sciences Ben M'sik, University Hassan II Mohammedia-Casablanca. e-mail: a-rouda@hotmail.fr
Author §: Mines, Environment and Durable Developpement Laboratory, Superior National School of Mine of Rabat (ENSMR), Morocco.



Eugenol and Acetyleugenol structures

III. Results and Discussion

On the IR spectrum of cycloadducts 4A (we note the absorption bands, which are characteristics bands due to C = N vibration around 1600 cm^{-1} and OH vibration at about 3475 cm^{-1} (Table 1).

The ^1H NMR spectrum of all compounds 4A in $CDCl_3$ at 300 MHz (Table 1) has four split doublets. We discuss the cycloadduct A1 for example. Indeed, we assigned the two split doublets centered at 2.63 and 3.20 ppm respectively protons H_4 and H'_4, and the two split doublets centered at 3.07 and 3.28 ppm respectively in two protons H_6 and H'_6. The transitions 12 which degenerates multiplet centered at 4.69 ppm characteristic of a proton bound to a carbon adjacent to a heteroatom which cannot be that the H_5 proton bound to a heteroatom. Protons H_4, H'_4, H_5, H_6 and H'_6 thus form a ABMXY system. As the most intense peak at 3.87 ppm; we attributed to the methoxy protons 3. It should also be noted that another intense peak at 3.22 ppm result of a union between two transitions, the H'_4 and H'_6.

We can also note that the protons H_6 and H_4 are respectively more armored than H'_6 and H'_4.

On the other hand the four values of the coupling constants characterizing H_4 and H_6 protons show that H_6 and H_4 are in cis position relative to the H_5 proton while H'_4 and H'_6 are in transposition compared to the same proton. Indeed, protons H6 and H4 have values larger coupling constant respectively, found $^3J_{H6-H5}$ = 10.8 Hz; $^3J_{H4-H5}$ = 9.6 Hz, H'_6 and H'_4 give respectively $^3J_{H'6-H5}$ = 4,5 Hz and $^3J_{H'4-H5}$ = 3,3 Hz (Table 2).

The structure 4A was also confirmed after examining the parameters 13C NMR (50 MHz) (Table 3). In case of cycloadduct 4A (R'=H), the signals corresponding to the pyrazolinic carbon C^4, C^5 and méthylenic C^6 are 37.36; 60.91 and 37.06 ppm, with respect to the carbon of methoxy function, it resonates at 56 ppm. DEPT spectrum further confirms the proposed structure since we observe reversal of carbons C^4 and C^6.

Regarding the adducts 4B, its IR spectrum (Table 1) shows in addition to the C = N band, another characteristic band at 1700 cm-1 corresponding to the vibration of C=O.

The ^1H NMR spectrum at 300 MHz of cycloadducts 4B (Table 1) were substantially identical to that of cycloadducts 4A, only one difference in that a single corresponding to the methyl group of acetyl is observed.

Furthermore the 13C NMR spectrum at 50 MHz cycloadducts 4B (Table 3) shows, in addition to signals attributable to carbons pyrazoliniques C^4, C^5 and C^6 methylenic carbon two significant signals to 20.69 ppm and 168 ppm respectively corresponding to the carbon of the methyl group acetyl and of carbonyl carbon C=O.

Table 1 : IR & ^1H NMR Characteristics of cycloadducts 4A and 4B

		NMR ^1H (δ in ppm)							Infra Red (ν in cm^{-1})	
		R'	H_4	H'_4	H_5	H_6	H'_6	H_7	$\nu_{C=N}$	ν_{O-H}
4A	4A1 (R'=H)	----	2,63	3,20	4,69	3,07	3,28	3,87	1597	3476
	4A2 $(R'=OCH)_3$	3,78	2,65	3,32	4,70	3,11	3,36	3,92	1596	3475
		R'	H_4	H'_4	H_5	H_6	H'_6	H_7	$\nu_{C=N}$	$\nu_{C=O}$
4B	4B1 (R'=H)	----	2,6	3,15	4,70	3,03	3,24	3,96	1596	1700
	4B2	2,34	2,58	3,10	4,76	3,00	3,20	3,82	1600	1700
	$(R'=CH_3)$									

Table 2 : Values of the coupling constants

	J (Hz)					
	H_4-H'_4	H_4-H_5	H'_4-H_5	H_6-H'_6	H_6-H_5	H'_6-H_5
4A1 (R'=H)	14,6	9,6	3,3	17,1	10,8	4,5
4B1 (R'=H)	13,98	9,1	2,89	17,28	10,92	4,62

Table 3 : ^{13}C NMR Characteristics of cycloadducts 4A and 4B

		NMR^{13}C (δ in ppm)					
	R'	C_4	C_5	C_6	C_7	R = O<u>C</u>H$_3$ R = <u>C</u>H$_3$-<u>C</u>=O	R' = CH_3
4A1	H	29,75	60,9	37,06	59,99	56,12 --------	--------
4A2	OCH_3	29, 79	61,02	37,17	58,79	55,86 -------	--------
4B1	H	37 ,1	60,45	29,7	58,96	56,15 20, 76; 168,65	--------
4B2	CH_3	37 ,0	60,5	30,0	58,86	56,10 20, 96; 170,0	21,5

IV. Experimental

a) Extraction of eugenol A and acetyleugenol B

We place in a 250 ml three ground cloves mixed with water and we proceed to a steam distillation. The distillated essential oil being transferred to a separator funnel and extracted three times with dichloromethane, and will be finally collected.

The collected organic layer contains the mixture of the two main constituents eugenol A and acetyleugenol B.

To separate the mixture, the organic phase is treated in a separator funnel, two times with a solution of 5 % sodium hydroxide.

The thus obtained organic phase, containing the acetyleugenol B, dried over anhydrous magnesium. Acetyleugenol B is recovered after evaporation of dichloromethane in a rotary evaporator.

Furthermore, the aqueous phase containing eugenol A as eugenolate sodium, is treated with concentrated hydrochloric acid until about pH = 3.

We Dry over magnesium sulphate or anhydrous sodium. The removal of solvent on a rotary evaporator recovers the Eugenol A.

V. Cycloaddition : General Procedure

In a 100 ml flask equipped with a condenser and a CaCl2 guard are successively introduced 6,6 mmol of eugenol A or acetyleugenol B and 6 mmol of hydrazonoyle chloride in 40 ml of anhydrous benzene. 4 ml of triethylamine was added through a dropping funnel.

Magnetic stirring this mixture was heated to reflux for 48 hours after complete addition of triethylamine. The triethylamine hydrochloride formed is filtered hot and the benzene and excess triethylamine are removed in a rotary evaporator. The oil obtained crystallized from ethanol in a refrigerator. The crystal of cycloadducts obtained are filtered and washed with cold ethanol (Table 4).

Table 4 : Yield and physical caracteristics

	F° C	yield%	Aspect
4A1	150	67	Pale yellow crystals
4A2	162	63	Pale yellow crystals
4B1	158	58	Beige Crystals
4B2	160	50	Beige Crystals

VI. Conclusion

Cycloaddition of arylnitrilimine with eugenol or acetyleugenol is a regiospecific reaction whose sense of direction resulting steric effects theoretically expected. The structure of obtained adducts and the regiochemistry of the reaction was confirmed on the basis of spectroscopic parameters IR, 1H NMR (300 MHz) and 13C NMR (50 MHz) are in perfect agreement with literature data. Biological tests and tests of complexation are in progress as well as the synthesis using the rest of the series diary Initrilimines (DANI).

References Références Referencias

1. R. Huisgen, Angewandte Chemie International Edition, vol. 2, no 10, p. 565–598 (DOI

10.1002/anie.196305651, lire en ligne [archive] [abstract]), October 1963.
2. Huisgen, R., The Journal of Organic Chemistry, vol. 41, no 3, p. 403–419 (DOI 10.1021/jo00865a001), 1976.
3. J Vebrel,Tetrahedron; 39(24):4163-4174, 01/1983.
4. Journal of Heterocyclic Chemistry (Impact Factor: 1.22). 28(1):73 – 76, 03/2009.
5. Karin Monnier, Gérard Schmitt, Bernard Laude, Marie-France Mercier, Marek M. Kubicki, Michel Jannin, Canadian Journal of Chemistry (Impact Factor: 0.96),73(2):181-190. DOI:10.1139/v95-027,02/2011.
6. Tahar Lakhlifi, Ahmed Sedqui, Toufik Fathi, Bernard Laude, Jean-François Robert, Canadian Journal of Chemistry (Impact Factor: 0.96). 72(6):1417-1423, 02/2011.
7. Karin Monnier, Gérard Schmitt, Bernard Laude, Marie-France Mercier, Marek M. Kubicki, Michel Jannin, Canadian Journal of Chemistry (Impact Factor: 0.96), 73(2):181-190, 02/2011.
8. Saoussen Haddad, Imen Jalloul, Sarra Boudriga, Moheddine Askri, Michael Knorr, Yoann Rousselin, Marek M. Kubicki , J. Soc. Chim. Tunisie; 15:1-8, 01/2013.
9. S. kitane, A. Sebban, J. Vebrel et B. Laude, Bull. Soc. Chim. Belg.. 98 (2), 105, 1989.
10. Bahloul, S. Kitane, A. Sebban et M. Berrada, J. Soc. Alg. Chim., 10 (1), 131-134, 2000.
11. S. Kitane, A. Taimi, A. Bahloul, A. Sebban, M. Berrada and J. P. Joly, J. Heterocyclic Chem., 37, 1641, 2000.
12. Sebban, A. Bahloul, M. Berrada, S. Kitane, K. Bougrin & M. Soufiaoui, Journal de la Société Chimique de Tunisie, 4, N° 11, 1403, 2002.
13. A. Bahloul, A. Sebban, Z. Dardari, M. Boudouma, S. Kitane, T. Belghiti & J.P. Joly, J. Heterocyclic Chem., 40, 243-248, Avril - Mai 2003.
14. Z. Dardari, M. Lemrani, A. Bahloul, A. Sebban, M. Hassar, S. Kitane, M. Berrada and M.Boudouma,. Il Farmaco (Societa Chimica Italiana), 59, issue 3, 195-199, Mars 2004.
15. Z. Dardari, M. Boudouma, A. Sebban, A. Bahloul, S. Kitane, M. Berrada, Il Farmaco (Societa Chimica Italiana), 59, issue 9, 673-678, Septembre 2004.
16. Z. Dardari, M. Lemrani, A. Sebban, A. Bahloul, M. Hassar, S. Kitane, M. Berrada et M.Boudouma, Arch. Pharm. Chem. Life Sci., 339, Janvier 2006.
17. S. Fujisawa, T. Atsumi, Y. Kadoma, H. Sakagami, Toxicology 177, 39, 2002.
18. K. Satoh, H. Sakagami, T. Tanaka, S. Fujisawa, Anticancer Res., 18, 1549, 1998.
19. C.E.N. Damiani, L.Venturini Rossoni, D.V. Vassallo,Vascular Pharmacol.,40, 59, 2003.
20. L.W. Wadell, H.N. Crooks, P.L. Carmichael, Toxicol. Sci., 79, 38, 2004.

Global Journal of Science Frontier Research: B
Chemistry
Volume 15 Issue 3 Version 1.0 Year 2015
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

Synthesis of Bridgehead-Fused 1, 2, 3-Triazolo [1, 5-C]-1, 2, 4-Triazines: Novel Anti-Inflammatory and Analgesic Therapeutic Systems

By Odin, E.M. & Onoja, P.K
Kogi State University, Nigeria

Abstract- An efficient method has been developed for the preparation of three novel heterocyclic compounds: Bridgehead-fused-5-methyl-6-methylketone-1,2,3-triazolo[5,1-c]-1,2,4-triazine(12), Bridgehead-fused-5-methoxyl -6- methylester-1,2,3-triazolo-[5,1-c]-1,2,4-triazine (14) and Bridgehead - fused - 5-methyl- 6-methylester-1,2,3-triazolo-[5,1-c] -1,2,4-triazine (16). The new heterocyclic systems were obtained utilizing 1H -1,2,3 – triazolo -5- diazonium salt (10) which was produced via thiourea sulphanilic acid(7). A mixture of this compound(7) with hydrazine in anhydrous acetonitrile, followed by continuous stirring afforded a solid compound: hydrazine carboximidamide (8). Addition of this hydrazine derivative to trimethyl orthoformate in a sealed vessel gave 5- amino – 1H- 1, 2,3 – triazole (9). Diazotization of this aminotriazole compound while maintaining the pH at 2, yielded the 1H – 1,2,3 – triazole -5- diazonium salt (10) in excellent yield.

Keywords: *bridgehead-fused1,2,3-trizolo[1,5-c]1,2,4-triazines, novel therapeutic systems, anti-inflammatory, egg-albumin, oedema.*

GJSFR-B Classification : *FOR Code: 250599*

Strictly as per the compliance and regulations of :

Synthesis of Bridgehead-Fused 1,2,3-Triazolo [1,5-c]-1,2,4-Triazines: Novel Anti-Inflammatory and Analgesic Therapeutic Systems

Odin, E. M. [α] & Onoja, P. K. [σ]

Abstract- An efficient method has been developed for the preparation of three novel heterocyclic compounds: Bridgehead-fused-5-methyl-6-methylketone-1, 2, 3 triazolo [1,5- c]-1, 2, 4-triazine(12),Bridgehead-fused-5-methoxyl -6-methylester-1, 2, 3-triazolo-[1,5-c]-1,2,4-triazine (14) and Bridgehead - fused - 5-methyl- 6-methylester-1,2,3-triazolo-[1,5-c] -1,2,4-triazine (16). The new heterocyclic systems were obtained utilizing 1H -1,2,3 – triazolo -5- diazonium salt (10) which was produced via thiourea sulphanilic acid(7). A mixture of this compound(7) with hydrazine in anhydrous acetonitrile, followed by continuous stirring afforded a solid compound: hydrazine carboximidamide (8). Addition of this hydrazine derivative to trimethyl orthoformate in a sealed vessel gave 5-amino – 1H- 1, 2,3 – triazole (9). Diazotization of this aminotriazole compound while maintaining the pH at 2, yielded the 1H – 1,2,3 – triazole -5- diazonium salt (10) in excellent yield.

The three fused heterocyclic systems were produced by coupling compound (10) with active methylene compounds: β-diketone, β-diester (dimethyl malonate) and β-keto ester respectively and heated under reflux in acetic anhydride. Recrystallization of the products in DMF – water, afforded pure colourless compound 12, light yellow system 14 and colourless fused compound 16 respectively. Structures were established by analytical and spectral data. The results of the anti-inflammatory and analgesic screening data revealed the potential analgesic values residing in the novel compounds which placed them as very strong drug candidate. The dose and time dependant effects of these compounds in the egg-albumin induced paw oedema showed the effect was real. The average inflammation was below 0.20 mm in the first 20min. At time 120min, there was a complete inhibition of oedema by 91.38%, 84.48% and 63.79% from the compounds(16,14 & 12) respectively, while the standard drug acetyl salicylic acid showed inhibition by 41.38%.The effect of substituent on inhibition was also recorded. The suppression of oedema by the compounds was correlated with anti-inflammatory potential.

Keywords: bridgehead-fused1,2,3-trizolo[1,5-c]1,2,4-triazines, novel therapeutic systems, anti-inflammatory, egg-albumin, oedema.

I. Introduction

Triazolo-Triazines are well known class of aza-bridgehead fused heterocyclic compounds which have miscellaneous pharmaceutical applications (Akpanisi, 2004, Katrizky *et al*, 2004; Mohammed, 2009). Their structural pattern is well established in pharmaceutical agents, particularly psychotropic agents such as risperidone and paliperidone (Khan. 1997; Jeste *et al* 2000).

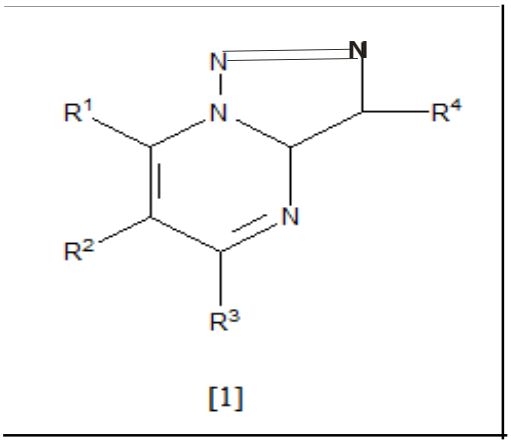
Triazolo heterocycles occupy a central position in modern heterocyclic chemistry, because they form an important recognition element in biologically active molecules (Romain *et al*.,2010).

Bridgehead-fused triazolo triazines contain three nitrogen atoms in both a five membered ring and a six membered ring fused together to form a bridgehead-fused ring system (Akpanisi, 2004).The triazolotriazine is capable of exhibiting diazoakyllideneamine-triazole ring chain tautomerism. This isomerism is also known as the Dimroth rearrangement (Akpanisi, 2004). These heterocyclic fused systems have attracted much interest since the last decades.

The global effort to eradicate cancer has motivated us to search for new products with analgesic and anti-inflammatory activities that could join the list of non steroidal anti-inflammatory drugs (NSAIDs) that could provide better therapeutic activity. Research into inflammation has shown that it is a complex process involving many biochemical pathways and a variety of agents and mediators (Davies et al, 1989). Inflammation is a tissue reaction by the body to injury which is classically characterized by swelling (tumor), pain (dolor), redness (rubor) as well as loss of function (Macpheson, 1992). The anti-inflammatory activities of bridgehead-fused heterocycles have been attributed to their ability to irreversibly inhibit prostaglandin G/H synthase by acting on the active site of the enzyme (Laurence, *et al*,1997).

The chemistry of bridgehead fused 1,2,3-triazolo [1,5-a] pyrimidine **(1)** is well documented (Akpanisi, 2004 and Odin & Akpanisi, 2007).

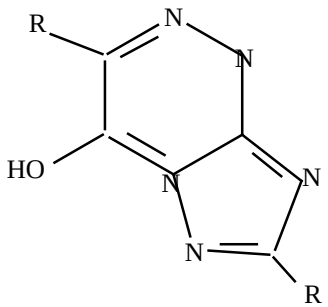
Author α σ: Department of Pure and Industrial Chemistry, Kogi State University, Anyingba, Nigeria. e-mail:odinem2005@yahoo.com



[1]

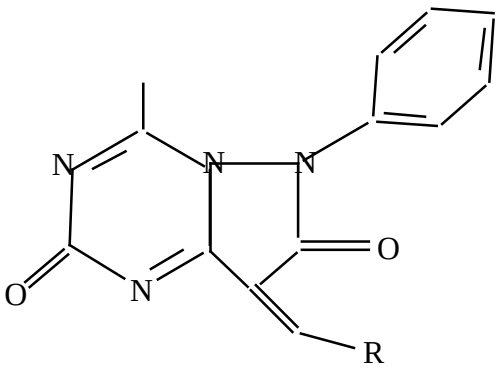
The bridgehead-fused triazolo triazines systems of types (2) : 1,2,4-triazolo[3,4-c]-1,2,4-triazine (Reda *et al*, 2010 and Duanis *et al*,1975; (3):2,4-diarylpyrazolo[1,5-a]-1,3,5-triazine (Sun, 2013); (4): 2-amino-4-thioxo-3-aryl-pyrazolo[1,5-a]-triazine (Sun, 2013); (5): 1,2,4-triazolo[1,5-a]-1,3,5-trizine (Federica *et al*, 2011) and their known pharmacological applications have previously been prepared.

In continuation of our research programme directed towards the preparation of heterocycles with pharmaceutical importance (Odin, *et al*, 2013), Bridgehead-fused-1,2,3,triazolo[1,5-c]-1,2,4-triazines of types 12,14 and 16 to the best of our knowledge have not been reported . In this paper we report the total synthesis of these novel fused heterocyclic systems (12, 14 and 16) and their analgesic/anti-inflammatory properties.

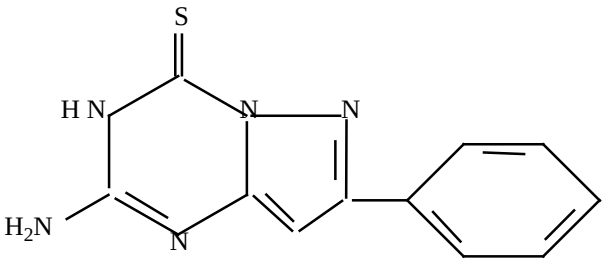


R = Me

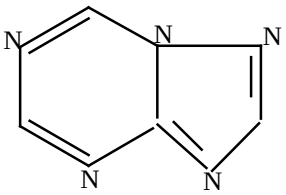
[2]



[3]



[4]



[5]

II. Materials and Methods

All chemicals were obtained from different sources and were used without further purification. The melting points were determined on a SMP3 melting apparatus and are reported in °C uncorrected. Column chromatography was performed in Scharian silica gel 60 (70-230 mesh). HPLC separations were performed in a Bulk scientific 500 apparatus using a reverce phase lichrosper 100RP-18 (5μm) column at room temperature (eluent: methanol :water 8:2 v/v).

a) Spectra analysis

The methods of Predrag et al, 2000; Hujo et al, 1957 and Sigites et al, 2005 were adopted and modified.

The identity of the compounds was confirmed by IR and MS methods as reported by Predrag et al,

2000, Mohammed et al, 2009 and were recorded in Cm^{-1} on a Bulk Scientific 500 Spectrophotometer and Schimadzu GCMS-QP-1000E mass spectrophotometer at 700eV respectively. Elemental analysis was on a Perkin-Elmer analyzer 2400. Proton Spectra (^1H NMR) and ^{13}C NMR were recorded on a Varian Gemini 2000 spectrophotometer operating at 200 and 50 MHz respectively.

b) Animals

In this study we followed the" principle of laboratory animal care" (NIH publication No 85-23, revised 1985). We employed Swiss Albino mice (16-40g) for the toxicity and analgesic studies, while the anti-inflammatory studies employed adult Wister rats (16-300g). All the animals were maintained at the Animal Facility Centre of Kogi State University at standard conditions and temperature (25°C) and fed with standard diet (Pfizer feed, PLC, Lagos) and water *adlibitum.*

c) Synthesis

The synthetic routes for all the compounds are outlined in scheme 1. The details are given below:

d) Thioureasulphanilic acid(7)

This compound was produced according to the methods of Maryanoff *et al*, 1986 and Romain *et al*, 2010. Thiourea (4 g, 0.08 mol) and sodium molybdate (5.2 g, 0.057 mol) were dissolved in a 1:1 mixture of chloroform/methanol (16 ml). This solution was added to H_2O_2 (0.5 ml, 12 mmol). The reaction mixture was stirred at 25°C for 1h and was separated by preparative silica gel thin layer chromatography (eluent: 40-60 petroleum ether/ethyl acetate (2:3 v/v) to give thioureasulphanilic acid. Yield :15.72 g (82.4%). m.p. 163-164°C. IR: 3290 (NH_2), 2990 (C-N), 3600 ($O\text{-}H_{aliphatny}$). ^1H NMR: 2.4 (s, NH_2), 5.26 (s, C-H). ^{13}C NMR: 90 (C). Anal. Cal. For $C_1H_6N_2O_3S$: C, 8,20, H, 4.14, N,32.86, O, 48.0, S, 21.94%. Found: C, 8.18, H,4.12, N, 32.84, O, 47,1, S, 21.93%.

e) Hydrazine carboximidamide (8)

The The method of Romain *et al*, 2010 was adopted and modified. 300 mg, 1.5 mmol of thioureasulphanilic acid (7) was mixed with hydrazine (110 mg, 1.1 mmol) in anhydrous acetonitrile (1.2 mL). The mixture was stirred at 35°C for 2 h. The reaction mixture was concentrated to a faint blue crystals. Yield: 7.8 g (76.3%). m. p 159-161°C. 1R: 3292 (NH_2), 3351 (NH), 1650 (C=N)

^1H NMR : 4.62(s.NH_2), 4.65(s.NH).

^{13}C NMR :163 (C-NH) .

Calculated for $C_1H_6N_4$: C, 16.21,H, 8.07, N,75. 63%. Found : C, 16.19, H, 8.05, N,75.60%

f) 5-amino-1H-1,2,3-triazole (9)

The method of Romain *et al*, 2010 was employed. Trimethylortho formate (1.5 ml) was added to 420 mg, 2.8 mol compound **(8)** and heated for 24 h at 145°C in a sealed vessel. The resulting mixture was cooled to room temperature and filtered. The filterate was washed with 30% ethanol in CH_2Cl_2, concentrated and purified using column chromatography (eluent : n-hexene/ethyl acetate 5:2 v/v). The result was yellow solid. Yield 180 mg, 70%. m.p 143-147°C. IR: 3293 (NH_2), 3311 (NH), 3021 (C-N). ^1H NMR: 3.9 (d 4H), 4.0 (m, NH protons), 4.20 (m, NH_2 protons), 5.8 (m. C-H). ^{13}C NMR: 79.9 (CH), 80.2 (CNH).

Calculated for $C_2H_6N_4$: C,27.90, H,7.03, N,65.08%. Found: C,27.70, H,7.02, N,65.06%.

g) 1H-1,2,3-triazolo-5-diazonium salt (10)

This was prepared according to Draganov and Naicheva, 1981 and Odin *et al*, 2004. 200 ml of 8% aqueous HCl was added to 0.10 mol 5-amino-1H-1,2,3-triazole **(9)** in a reaction vessel while stirring. The mixture was cooled to 5-10°C for a period of 1 h. At this temperature, a solution of sodium nitrite (3.5 g dissolved in 20 ml H_2O) was added while the pH was held at 2.

h) Reaction of 1H-1,2,3-triazolo-5-diazonium salt(10) with active methylene compounds

i. *General Procedure*

The methods adopted were that of Akpanisi, 2004, Ahmad et al, 2004 Nataliya et al, 2010, Kin and Yoon, 2004, Brehme et al, 2007, Parmeter, 1959 and Patentent US 7122548, 2006. A solution of compound **10** (0.88 g, 0.006 mol) in aqueous ethanolic solution (20.0 ml) was added to cooled solutions of β-diketone (0.2 mol), β-diester (0.2 mol) and β-keto ester (0.2 mol) respectively. The diazonium salt was added proportion-wise while stirring over a period of 35 min at temperature 0-5°C. The pH of the reaction medium was lowered by adding sodium acetate. At the end, the reaction mixtures were intermittently stirred for another 2.5 h. The crude products were filtered, washed with cooled water and recrystallized from dimethylformamide-water to afford the corresponding hydrazones **(11)**, **(13)** and **(15)** respectively.

i) 1H-1,2,3-triazolo-2-methyl-2-hydrazonoketone (11)

Yield: 2.1 g (63%), m.p. :283-285°C. IR: 3020 (C-N arom), 1670 (C=O), 3252 (CH arom), 2929-2861 (C-H stretch), 2385(CH_3 groups), 3140-3138 (2NH), 3022 (C-N), 1645 (C=N). ^1H NMR: 9.11 (s, NH), 7.21-7.19 (d, Ar-H), 10.12 (s, CHOO), 2.16 (s, CH_3). ^{13}C NMR: 169.4 (-$COCH_3$), 138 (C=N), 88.6 (CH_3). Anal. Calculated for $C_6H_{10}N_5O$: C, 42.84, H, 6.0, N, 41.65, O, 9.51%. Found: C,42.82, H, 5.9, N,41.63, O,9.49%.

j) 1H-1,2,3-triazolo-2-methoxy-2-hydrazonoester (13)

Yield: 3.2 g (71%), m.p. 289-290°C. IR: 3159, 3143 (2NH), 1623 (C=O), 3024 (C-N), 1644 (C=N), 2928-2918 (C-H stretch). ^1H NMR: 9.14 (s, NH), 2.14 (s, CH3), 720-756 (Ar-H). ^{13}C NMR: 69.5 (C=O), 149 ($COCH_3$), 139 (C=N). Anal. Calculated for $C_6H_{10}N_5O_3$: C,

36.00, H, 5.04, N, 35.03, O,23.98%. Found: C,35.98, H,5.02, N, 35.01, O, 23.96%.

k) 1H-1,2,3-triazolo-2-methyl-2 hydrazonomethylester (15)

Yield: 2.9 g (77%), m.p. 294-298°C. IR: 3154, 3148 (2NH), 1620 (C=O), 3023 (C-N), 1644 (C=N), 2927-2867 (C-H stretch). ^{1}H NMR: 9.16 (s, NH), 2.16 (s, CH_3), 721-725 (Ar-H). ^{13}C NMR: 69.8 (C=O), 148 ($COCH_3$), 138 (C=N). Anal. Calculated for $C_6H_{10}N_5O_2$: C, 39.12, H, 5.47, N, 38.03, O, 17.37%. Found: C, 39.10, H, 5.45, N, 38.01, O, 17.35%.

l) Synthesis of Bridgehead-fused heterocyclic compounds 12, 14 and 16

i. *General Procedure*

We employed the general procedures of Akpanisi, 2004; Ahmad, *et al*, 2004 and Nataliya, *et al*, 2010. A solution of the hydrazones **11**, **13** and **15** (2 mmol) respectively in acetic anhydride was refluxed for 4 h. The mixture was allowed to cool to room temperature, the solvent evaporated and the residue left was re-crystalized from dimethyformamide-water to afford the corresponding fused heterocyclic systems **12** (pure colourless), **14** (pure light yellow) and 16 (pure colourless).

m) Bridgehead-fused-5-methyl -6- methylketone 1,2,3-triazolo[1,5-c]-1,2,4-triazine (12):

Yield: 1.8 g (70%).
m.p. 298-300°C. IR: 1500 (C=Carom), 3020 (C-Narom), 1690 (C= 0), 3250 (CH arom),
2929-2861(C-H stretch), 2 671 (C=0 stretch),
2385 (CH3 groups).
^{1}H NMR :7.21-7.59 (d, Ar-H),
4.6 (d,2H), 3.7 (m, 4H),
^{13}C NMR :
111.20 (C=C) , 67.0 (C=0), 88.6 (CH).
Anal. calculated for :$C_7H_7N_5O$
C, 47.45, H, 3.98, N 39.54, O, 9.03%
Found: C, 45.43, H, 3.96, N, 39.52, O.9.01%.

n) Bridgehead-fused -5- methoxy -6- methylester,1,2,3 triazolo[1,5-c]-1,2,4-triazine (14)

Yield: 2.2 g (73%). m.p. 299-301°C. IR: 1500 (C=C arom)
1501 (C=C), 3021 (C-N arom), 1692 (C=0), 3250 (CH arom)
2928-2860 (C-H stretch), 2691, (C=0 stretch)
2385 (CH_3 groups)
^{1}H NMR :
4. 62 (S, 1H), 3.7 (m, 2H), 6.1 (m, CH2), 5. 76 (m, CH3)
^{13} C NMR : 159.0 (C- arom), 111.2 (C=C),
169.4 (-O-C=O), 67.0 (C=O), 64.4 (-CH2), 16.2 , 55. 0 (CH_3), 88. 6 (CH).
Anal calculated for $C_7H_7N_5O_3$
C, 40.19, H, 3.37, N,33.49, O,22.95%
Found: C, 40.17, H,3.35, N,33.45, O, 22.93%

o) Bridgehead-fused-5-methyl-6-methylester-1,2,3-triazolo[5,1-c]-1,2,4-triazine (16)

Yield: 2.45 g (77.3%).
m.p. 297-299°C. 1R : 2911-2818 (Arom, C-H).
714 (C-H out of plane bending). 1096 (C-H in a plane bend).
1504 (C=C arom), 3022 (C-N arom), 1093 (C=0), 2928-2860 (C-H stretch).
^{1}H NMR : 4. 62 (s, 1H), 3.7 (m, 2H)
6. 19 (m, CH2), 5.76 (m. CH3, 9.07, (d.3H), 9.23 (d, 4H),
9.07 (s.5H), 9.23, (s.6H), 9.07, (3.H)
^{13} C NMR : 159.0. (C triazine), 113.4 (C=C), 169.4 (-COO), 67.0 (C=O), 64.4 (-CH2), 16.2 (CH3), 131.2, 127.6, 123.6, 151.4 (CH and C).
Anal. calculated for: $C_7H_7N_5O_2$:C,43.12,
H, 3.65, N, 36.26, O, 16.56%
Found: C,43.10, H, 3.35, N, 33.45, 0.22.93%.

p) Acute toxicity test (LD_{50})

This was determined in Swiss Albino mice by intraperitoneal (i.p) and oral routes according to the methods of Amos et al ,2002, Azuine et al, 1996,Gurad et al, 2011and Lork, 1983 .The animals were divided randomly into seven groups of five mice each. Widely differing doses of 10, 100, 1000, 1500, 2000, 3500 and 5000 mg/kg were administered intraperitoneally and orally. The animals were monitored for 72 h. At the end of the experiment, the animals were sacrificed and then autopsied and examined microscopically for any pathological changes. This was established for the three compounds **12, 14** and **16**.

q) Test for Analgesia

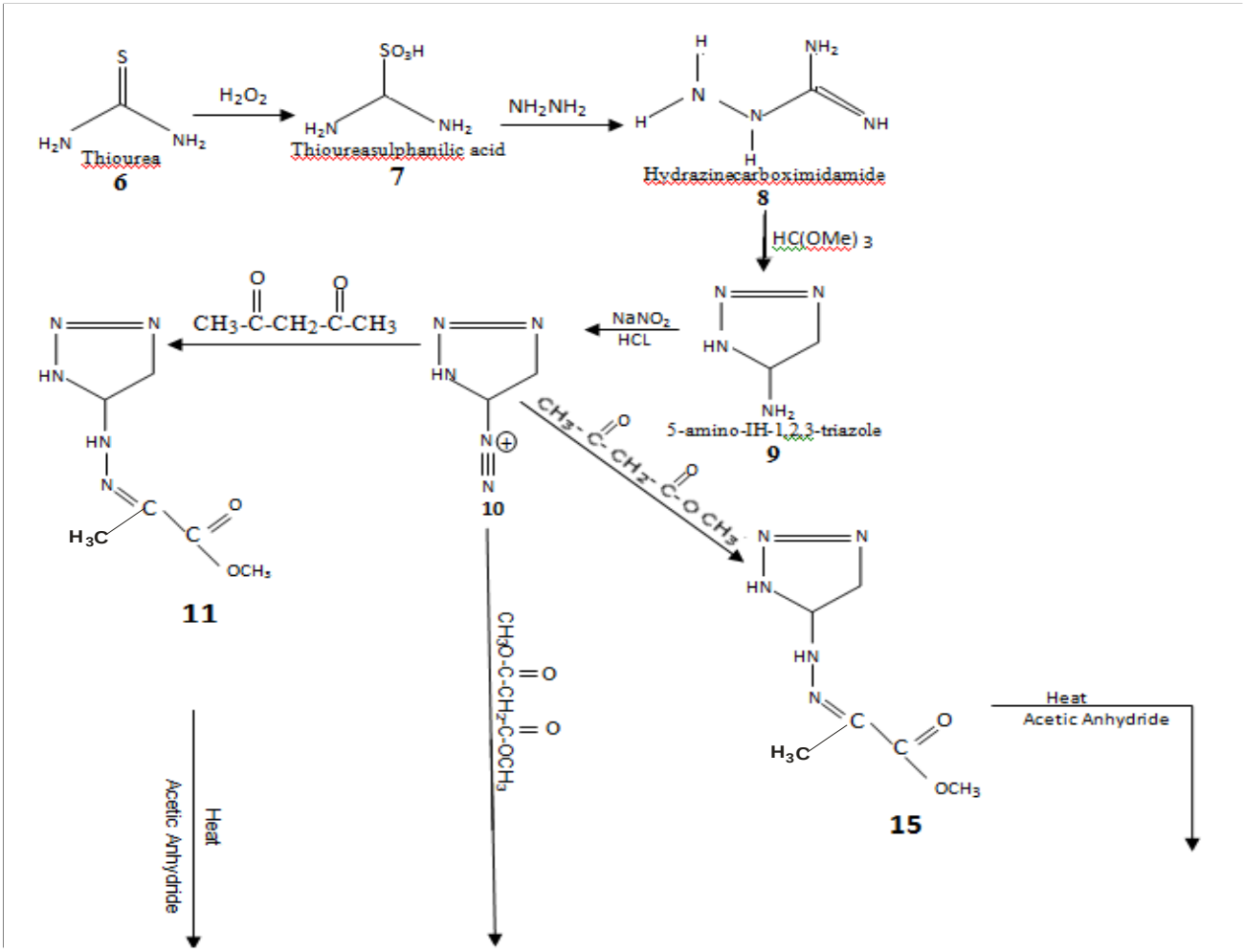
The analgesic property of the compounds was determined on Swiss Albino mice intraperitoneally as described by Koster *et al*, 1959 and Azuine *et al*, 1996. Twenty four (24) mice were treated with compound 12 (100 and 200 mg/kg) intraperitoneally 30 min, 60 min and 90 minutes prior to injection of 0.75% acetic acid (10 ml/kg i.p) (Tables 1and 2). This was to determine the dose and time dependence of the compound. The degree of suppression of writhen episodes were measured and compared to the negative control (10 ml/kg) acetic acid. Indomethacin (10 mg/kg) treated animals were used as the positive control. The test was also repeated for compounds **14** and **16** respectively. This was to establish the effect of substituent on analgesia (Tables 3 and 4).

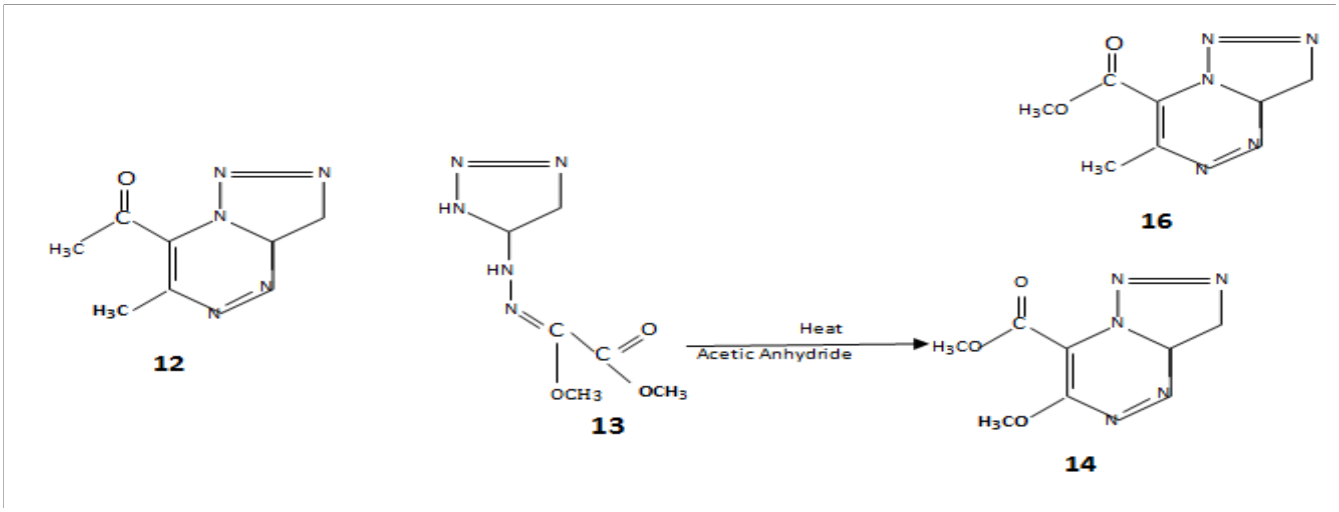
r) Anti-inflammatory Studies

The methods of Winter *et al*,1962 and Azuine *et al*, 1996 and Ratheesh and Helen, 2007 were employed and modified. Wister rats of either sex weighing between 160-275 g were divided into six groups of five rats each. Inflammation of the right hind paw was induced by injecting 0.05 ml of 50% solution of fresh egg albumin into the sub planter surface. Group 1 animals received

normal saline (20 ml/kg) and were designated as negative control. The second and third groups were administered compound **12** doses of 100 mg/kg and 200 mg/kg respectively by intraperitoneal route. Groups four and five animals were administered compounds **14** and **16** doses of 200 mg/kg respectively. While group six animals were given acetyl salicylic acid (200 mg/kg) injected intraperitoneally and served as positive control. All the drugs were administered 30 min before the subplanter injection of the phlogistic agent. The paw volume was measured after every 20 min for a period of 120 min by a volume displacement method (Azuine *et al*, 1996) using a plethysmometer (Table 5). The average inflammation, percentage inflammation and percentage inhibition of oedema were calculated on each dose and recorded (Tables 6,7 and 8). According to the method of Azuine *et al*, 1996, the average inflammation was calculated from the formular: L_t-L_O. Where L_t is the linear circumference at time t and L_O, the linear circumference at zero time (Table 6). The percentage inflammation was calculated as follows:

A/B x100. Where A is the average inflammation of treated group at time t, while B is the average inflammation of control at the same time (Table 7) (Azuine *et al*, 1996). The percentage inhibition of oedema (Table 8) is calculated as follows: 100-Percentage inflammation.





Scheme 1 : Synthesis of bridgehead-fused 1,2,3 triazolo [1,5-c] 1,2,4-triazines

III. Results

Thioureasulphonic acid (2) was produced by reacting thiourea with sodium molybdate dissolved in a mixture of chloroform/methanol. The solution which was added to aqueous H2O2was separated by preparative silica gel thin layer chromatography. Compound (2) when mixed with hydrazine in anhydrous acetonitrile gave a solid hydrazinecarboximidamide **(3)**. Addition of trimethyl orthoformate to compound (3) and heated for 24 h in a sealed vessel afforded 5-amino-1H-1,2,3-triazole **(4)**, which was subsequently added to aqueous HCl and a solution of sodium nitrite. This reaction furnished 1H-1,2,3-triazolo-5-diazonium salt **(5)**. A

solution of compound (5) in aqueous ethanolic solution was separately added to cooled solutions of β-diketone, β- diester and β-keto ester respectively. The crude products were filtered, washed with cold water. Recrystalization from dimethlformamide-water afforeded the corresponding hydrazones **(11), (13)** and **(15)**. Refluxing the hydrazones for several hours and recrystalizing the residue from DMF/H_2O yielded the three novel products: Pure colourless bridgehead-fused-5-methyl-6-methyl ketone-1,2,3-triazolo-[1,5-c]-1,2,4-triazine (12), Light yellow bridgehead-fused-5-methoxy-6-methylester-1,2,3-triazolo-[1,5-c]-1,2,4-triazine (14) and pure colourless bridgehead-fused-5-methyl-6-methylester-1,2,3-triazolo-[1,5--c]-1,2,4-triazine(16). (scheme 1).

The structural assignment of the synthesized compounds is based on the spectral data. In the IR spectrum of compound (7), absorption band at 2990 represents C-N stretching. The NH_2 absorption band appeared at 3290 cm^{-1}, while 3600 cm^{-1} represents OH aliphatic ring indicating complete oxidation.

^1H and ^{13}C NMR studies of this compound confirmed the structure. In ^1H NMR spectra data, compound (7) shows a singlet at δ 2.4 due to NH_2 proton. The –CH protons in the compound showed a singlet at δ5.26.

In compound **(8)**, the hydrogen bonded N–H stretching appeared at 3351 cm^{-1}, while the NH_2 absorption band appeared at 3292 cm^{-1}, and that at 1650 cm^{-1} is characteristics of C=N stretching. In the 1H NMR spectrum, the singlet for HN_2 and NH protons appeared in the region δ4.62 and δ4.65 respectively; while in ^{13}C NMR spectrum, a characteristic signal appeared for (CNH) in the range of δ163.

Addition of trimethyl ortho formate to compound (8) yielded compound (9). The IR spectrum of (9) showed broad bands at 33ll and 3293 cm^{-1} for hydrogen bonded N–H and NH_2 stretching respectively. The band at 3021 cm^{-1} indicating C–N stretching for NH and NH_2 protons were noticed in the regions δ4.0 and δ4.20 respectively. The C–H protons appeared at δ5.8. a characteristic signal for CHN in the ^{13}C NMR appeared at δ80.2, while that of (CH) was at δ79.9.

The three hydrazones: (11), (13) and (15) were produced when compound (10) was coupled with active methylene compounds: β-diketone, β-diester and β-ketoester respectively.

The IR spectrum of (11) showed a broad band at 3140-3138 cm^{-1} for hydrogen bonded 2NH stretching. The band at 3022 cm^{-1} indicated C-N stretching, while the band at 3252 cm^{-1} appeared for aromatic C-H stretching. The bands at 2929-2861 cm^{-1} were for C-H stretching, while that at 2385 cm^{-1} indicated CH_3 groups. The absorption band at 1645 cm^{-1} were located for C=N. The C=O stretching appeared at 1670 cm^{-1}. In the ^1H NMR spectrum of compound **(11)**, the singlet for –NH protons appeared in the region δ 9.11. The –CHOO protons and $–CH_3$ protons of the compound showed a singlet in the region δ 10.12 and δ 2.116 respectively. A characteristic signal appeared for ($-COCH_3$), (-C=N) and (CH_3) in the range of δ 169.4, δ 138 and δ 88.6 respectively in the ^{13}C NMR spectrum.

In compound **13**, 2NH stretching showed at 3159 and 3143 cm^{-1}. The band at 1623 cm^{-1} is assigned to C=O stretching, while the absorption bands at 3024, 1644, and 2928- 2918 cm^{-1} are characteristic of C-N, C=N and C-H stretching vibrations. In the ^1H NMR spectrum, the singlet for NH and CH_3 protons appeared at δ 9.14 and δ 2.14 respectively, while Ar-H protons were noticed at δ 720- 756. The ^{13}C NMR studies of this compound confirmed the structure. A characteristic signal appeared for C=O and $COCH_3$ in the range of δ 69.5 and δ149 respectively, while that of C=N were seen in the range of δ139.

In the IR spectrum of compound **15**, the absorption bands at 3154 and 3148 cm^{-1} represent the hydrogen bonded N-H stretching. There were number of peaks at 1620 cm^{-1}, 3023 cm^{-1},1644 cm^{-1}, and 2927-2867 cm^{-1} representing C=O, C-N, C=N, and CH stretching respectively. In the 1H NMR spectra data, compound 15 showed a singlet at δ 9.16 due to N-H protons. The Ar-H protons appeared in the region of δ 7.21-7.55, while the $–CH_3$ protons in the compound showed a singlet at δ 2.16. In ^{13}C NMR spectrum, a characteristic signal appeared for –C=O, $-COCH_3$, and –C=N in the range of δ 69.8. δ148, and δ 138 respectively.

Compounds **12**, **14** and **16** were synthesized from the general procedure by refluxing the solutions of the hydrazones **11**, **13** and **15** respectively in acetic anhydride.

The IR spectrum of compound (12) showed C = C aromatic at 1500 cm^{-1}, while that of C–N aromatic appeared at 3020 cm^{-1}. The bands at 2929 – 2861 cm^{-1} appeared for C –H stretching while bands at 3250 and 2385 cm^{-1} were for C – H aromatic and CH_2 groups. The bands at 2671 cm^{-1} and 1690 cm^{-1} is characteristic of C=O stretching and C=O groups. In the ^1H NMR spectrum, the duplet for 2H and 4H protons appeared at δ4.6 and δ 3.7 respectively, while in ^{13}C NMR spectrum, a characteristic signal appeared for C=C and C = O in the range of δ111.2 and δ67.0 respectively.

The IR spectrum of compound **(14)**, there were numbers of peaks at 3021cm^{-1} , 1692cm^{-1},3250cm^{-1} and 2691cm^{-1} for C – N aromatic, C = O, CH aromatic and C = O stretching. The absorption band at 2928 – 2860 cm^{-1} were for aromatic C –H stretching.

In the ^1H NMR spectra data, compound (14) showed a multiplet at δ6.19 to 5.76 due to CH_2 and CH_3 protons.

Some characteristic signals appeared for –C – O – O -, -(C=O) in the range of δ 169.4 and δ 67.0 respectively, while in the 13C NMR spectrum, that of CH_2, CH_3 and CH were located at δ 64.4, δ 55.0 and δ 88.6 respectively.

In the IR spectrum of compound (**16**), the absorption band at 2911 -2818cm^{-1} was for aromatic C – H stretching, while 714cm^{-1} represented C – H out of plane bending and 2928 – 2860 cm^{-1} was for C – H stretching. There were other peaks at 1504cm-1, 3022cm^{-1} and 2693cm^{-1} which were for aromatic C=C, aromatic C – N stretching and C = O stretching. In the ^{1}H NMR spectrum, compound (16) showed multiplets for CH_2 and CH_3 at δ6.19 to δ5.76 respectively.

In the ^{13}C NMR spectrum, some signals were noticed at δ113.4, δ169.4 and δ67.0 for C=C, -C-O-O- and C=O respectively. That of –CH_2 and CH_3 were located at δ64.4 and δ16.2 respectively.

The mass spectrophotometric studies performed on the synthesized compounds confirmed the molecular weight values.

The results of the analgesic and anti-inflammatory test are a s presented in figs. 1 and 2, tables 1,2,3,4,5,6,7 &8.

IV. Discussion

The structural assignment of the synthesized compounds was based on spectra data. The IR spectrum of compound **12** showed bands at 2671 cm^{-1} and 1690 cm^{-1} characteristic of C=O stretching and C=O groups, while that of compound **14** was noticed at 2691 cm^{-1} for C=O stretching. Similarly, the IR spectrum of compound **16** was observed for C=O stretching at 2693 cm^{-1}. This confirmed that the three heterocyclic systems have common functional groups.

Differing doses of 10mg/kg to 5000 mg/kg of compound **12**, **14** and **16** were selected so that the entire range of toxicity from high acute toxicity to virtual non-toxicity could be tested.

The weight of the animals after the text showed that they all gained weight. This was taken as a sign of having survived the acute intoxication.

The mice treated intraperitoneally up to 2000 mg/kg did not show signs of toxicity compared with control animals. Similarly, no significant effects were detected in animals treated orally with the compounds up to 5000mg/kg. This high dose only produces intense quietness. This effect was reversed within 3 hours. All the animals survived the test. That is, no death was recorded. This clearly demonstrates that the three synthesized compounds (**12**, **14** & **16**), even at high doses of 5000 mg/kg (5g/kg) were non-toxic to man.

From fig.1, it could be seen that the Bridgehead-fused compounds reduced the acetic acid induced writhing in mice. In control mice treated with 100mg/kg i.p acetic acid, the average writhing movement determined was 31 ± 1 (n = 3) (Table 1).

Pretreatment with 100mg/kg compound 12 30 min, 60 min and 90 min before the administration of the acid reduced the number of writhes to 56.98%, 31.18% and 23.81% of control. This is an indication that the effect of the compound (12) on pain increases with time as shown in fig 1 and table 1.

From fig. 1 and table 2, it shown that, pretreatment with 200mg/kg of the same compound (12) 30 min, 60 min and 90 min before the administration of the acetic acid reduced the number of writhes to 55.56%, 26.67% and 22.22% of control. Similarly, pretreatment with 200mg/kg of compounds **14** and **16**, 30min, 60min and 90min before the administration of acetic acid, reduced the number of writhes to 55.56%, 25.56%, 20.0% and 51.11%, 22.22% and 15.56% of control respectively (Tables 3& 4).

From fig 1, it is seen clearly that the analgesic effect of the Bridgehead-fused compounds (**12**, **14** and **16**) is time and dose dependent. In indomethacin (10mg/kg) treated mice, the number of writhes was reduced to 58.24% of control after 30min (fig. 1).

It is important to draw from here that the potential analgesic values residing in the compounds placed them as very strong drug candidate. This level of potency is highly remarkable.

The effect of the Bridgehead-fused triazolotriazines (compounds **12**, **14** & **16**) on fresh egg albumin-induced oedema in rats are shown in Tables 5, 6, 7 and 8.

From Table 6, it can be seen that in control animals, the sub planter injection of egg-albumin produced a local oedema after 20min.

From fig. 2, it can be said that compound **12** at 100mg/kg and 200mg/kg demonstrated a significant anti-inflammatory effect. The dose dependent effects of this compound in the egg-albumin induced paw oedema showed that the effect was real and not due to counter irritant activity.

In fig.2, it clearly showed that apart from being dose and time dependent, the actions of the Bridgehead-fused compounds on fresh egg albumin induced oedema also depends on substituent effect (compounds **12** **14** & **16**) . The average inflammation was below 0.20mm when the rat was pretreated with compounds **14** and **16** in the first 20min (Table 6), while that of compound **12** was 0.29 mm. At time 120min, there seems to be a complete inhibition of oedema by 84.48% and 91.38% for compounds **14** and **16** respectively, while compound **12** showed inhibition by 63.79%. The standard drug acetyl ssalicylic acid showed inhibition by 41.38% (Table 8) at the same dose of 200 mg/kg. This significant changes was probably due to the nature of the substituent on the triazine ring. Compound **12** contains one moderately activating group and a weakly deactivating group. Compound 14 has two electron withdrawing groups that deactivate the triazine ring which probably enhanced the percentage inhibition

above that of compound **12**. On the other hand, compound **16** showed an ester group that moderately deactivate and one alkyl group that also moderately activate the ring.

The results of this work as indicated in Tables 5, 6, 7 & 8 and fig. 1 and 2 clearly demonstrate the significant anti-inflammatory properties of the Bridgehead-fused compounds (**12**, **14** & **16**). The suppression of oedema by the compounds may be due to the fused triazolo-triazine rings.

The mode of action

The bridge head fused compounds (**12**, **14**, **16**) including Acetyl salicylic acid are among NSAIDs (Non steroidal anti – inflammatory drugs). The mechanisms of action of these systems may be due to their ability to irreversibly inhibit prostaglandin G/H synthesis by acting on the active site of the enzyme. They prevent the formation of products including thromboxane, prostacyclin and other prostaglandins (Laurence, *et al*, 1997).When a tissue is injured or stimulated, prostaglandin synthesis in that tissue increases.

The prostaglandins are mediators of inflammation and they also sensitize nerve endings, lowering their threshold of response to stimuli and the tenderness of inflammation (Laurence, *et al*,1997).

The fact is that a drug that prevents the synthesis of prostaglandins is likely to be effective in relieving pain due to inflammation of any kind. This is how acetyl salicylic acid (aspirin) and other non steroidal anti-inflammatory drugs (NSAIDs) act (Laurence, *et al*, 1997). Meaning that NSAIDs act by inhibiting cyclo-oxygenase (prostaglandin G/H synthase). This shows that the synthesized compounds will relieve pain when there is some tissue injuring with consequent inflammation.

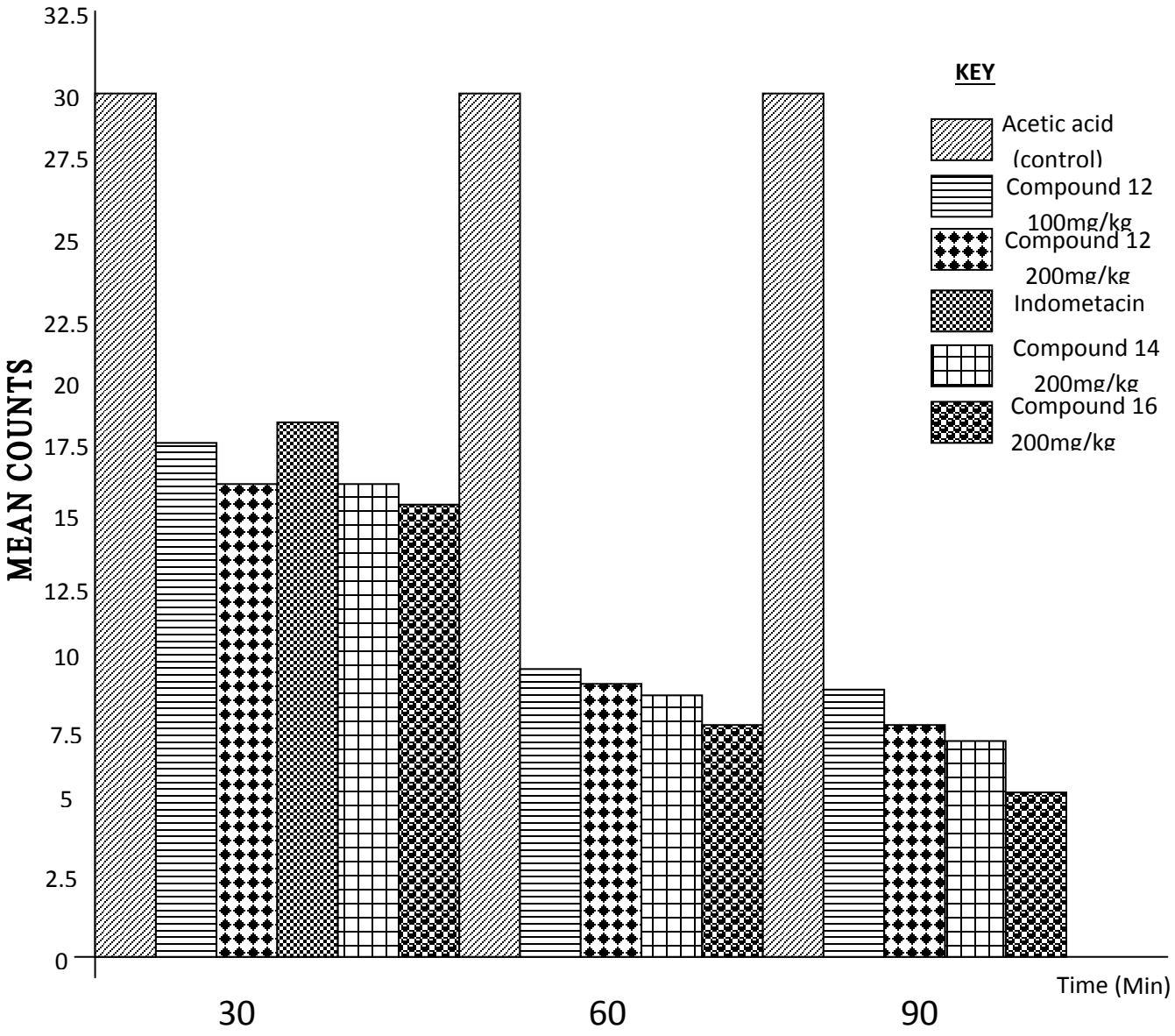


Figure 2 : Mean of Analgesic Writhing of 100 / 200 mg/kg

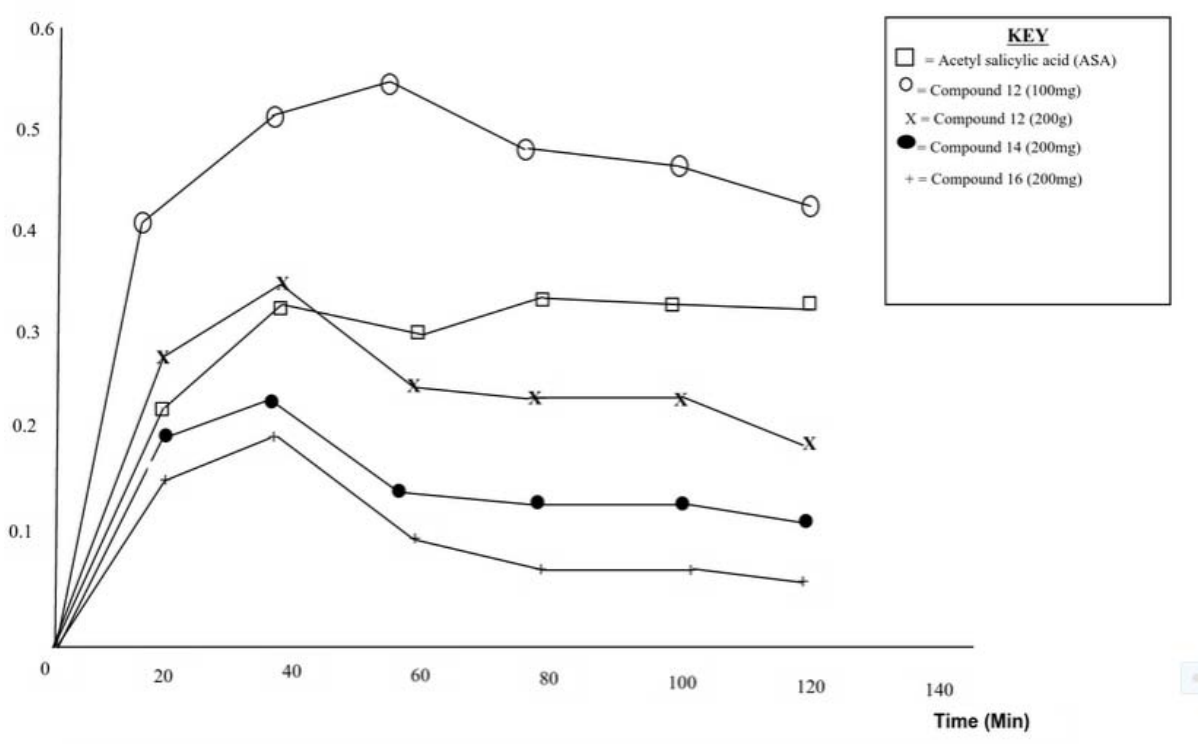


Figure 3 : Comparative test of Bridgehead-fused compounds on egg albumin induced paw oedema in rats. N = 5

Table 1 : Number of Writhing induced by 0.75% acetic acid in mice Pretreated with 100mg/kg Compound 12

Animal	Weight (g)	Dose (ml)	Time (min)	No. of Writhes
NMT	38.3	0.38	0	29 Negative
HDN	31.0	0.31		31 control (Acetic acid)
BKH	39.5	0.20		33
TLN	36.8	0.37		18
TL/BK	39.3	0.39	30	16
RH/TL	31.0	0.31		19
NM	37.7	0.38		10
HDM	31.8	0.32	60	11
BKN	29.1	0.29		8
TLM	30.0	0.30		6
HDT	30.5	0.31	90	9
BK/LE	30.6	0.31		9
RE	30.4	0.30		17
RHM	39.2	0.39	30	17
LHN	29.0	0.29		19
				Positive control (indomethacic)

Table 2 : Number of Writhing induced by 0.75% acetic acid in mice pretreated with 200 mg/kg Compound 12

Animal	Weight (g)	Dose (ml)	Ti me (min)	No. of Writhes
HDN	35.5	0.18	0	28 Negative
BKH	34.6	0.17		30 control
LLT	40.0	0.20		32
RAE	40.1	0.20		17
RL/NT	37.2	0.19	30	15
LA/TL	37.5	0.19		18
TLE	39.8	0.20	8	
REN	40.1	0.21	60	9
LEN	34.1	0.17		7
HD	37.4	0.19		5
RL	36.5	0.18	90	10
BK/N	37.6	0.19	5	

Table 3 : Number of Writhing induced by 0.75% acetic acid in mice pretreated with 200 mg/kg Compound 14

Animal	Weight (g)	Dose (ml)	Time (min)	No. of Writhes
HD	36.5	0.18	0	27 Negative
RAE	35.4	0.17		32 control
LEN	39.5	0.20		31
RL	40.1	0.20		17
HDN	39.2	0.19	30	16
RL/NT	4.5	0.19		17
BK/N	39.8	0.20		7
LLT	40.1	0.21	60	9
TLE	39.1	0.17		7
REN	37.4	0.20		6
BKH	38.5	0.21	90	5
LA/TL	37.6	0.17		7

Table 4 : Number of Writhing induced by 0.75% acetic acid in mice pretreated with 200 mg/kg Compound 16

Animal	Weight (g)	Dose (ml)	Time (min)	No. of Writhes
HDN	35.7	0.19	0	29 Negative
BKH	34.8	0.17		28 control
LLT	42.7	0.21		33
RAE	40.3	0.20		16
RL/NT	37.4	0.19	30	16
LA/TL	37.7	0.19		14
TLE	40.0	0.20		6
REN	40.3	0.20	60	8
LEN	34.3	0.17		6
HD	37.6	0.19		4
RL	36.7	0.18	90	5
BK/N	37.8	0.19		5

Table 5 : Paw Volume (mm)

Treatment Group	0 min	20 min	40 min	60 min	80 min	100 min	120 min
Control Normal Saline 20ml/kg	0.63	1.10±0.12	1.24±0.13	1.27±0.11	1.18±0.06	1.19±0.06	1.21±0.06
Compound 12 100mg/kg	0.64	1.04±0.04	1.18± 0.01	1.20±0.04	1.11±0.03	1.11±0.06	1.08±0.04
Compound 12 200mg/kg	0.65	0.94±0.06	1.03±0.06	0.91±0.06	0.90±0.06	0.90±0.06	0.86±0.05
Acetyl Salicylic Acid 200mg/kg	0.67	0.90±0.03	0.99±0.04	0.97±0.03	1.01±0.05	1. 01±0.05	1.01±0.04
Compd.14 200mg/kg	0.68	0.86±0.13	0.89±0.12	0.80±0.07	0.79±0.08	0.79±0.05	0.77±0.03
Compd.16 200mg/kg	0.68	0.83±0.09	0.86±0.08	0.77±0.04	0.74±0.03	0.74±0.02	0.73±0.02

Table 6 : Average Inflammation (mm) of the Right Hind Paw

Treatment Group	0 min	20 min	40 min	60 min	min	100 min	120 min
Control Normal Saline 20ml/kg		0.57	0.61	0.64	0.55	0.56	0.58
Compound 12 100mg/kg		0.40	0.54	0.56	0.47	0.47	0.44
Compound 12 200mg/kg		0.29	0.38	0.29	0.25	0.25	0.21
Acetyl Salicylic Acid 200mg/kg		0.21	0.32	0.30	0.34	0.34	0.34
Compound 14 200mg/kg		0.18	0.21	0.12	0.11	0.11	0.09
Compound 16 200mg/kg		0.15	0.18	0.09	0.06	0.06	0.05

Table 7 : Percentage inflammation (%) of Right Hind Paw

Treatment Group	0 min	20 min	40 min	60 min	80 min	100 min	120 min
Compound 12 100mg/kg		70.18	83.53	87.50	85.45	83.9	75.9
Compound 12 200mg/kg		50.88	62.23	45.31	45.45	44.6	36.2
Acetyl Salicylic Acid 200mg/kg		36.84	52.46	46.88	61.82	60.7	58.6
Compound 14 200mg/kg		31.58	34.43	18.75	20.00	19.6	15.5
Compound 16 200mg/kg		26.32	29.51	14.06	10.91	10.71	8.62

Table 8 : Percentage inhibition of Oedema (%)

Treatment Group	20 min	40 min	60 min	80 min	100 min	120 min
Compound 12 100mg/kg	9.82	11.47	12.50	14.56	16.07	24.14
Compound 12 200mg/kg	36.12.	37.77	54.09	54.55	55.30	63.79
Acetyl Salicylic Acid 200mg/kg	23.16	27.59	33.12	38.18	39.29	41.38
Compound 14 200mg/kg	64.42	65.57	81.25	80.00	80.36	84.48
Compound 16 200mg/kg	70.49	73.68	85.94	89.09	89.29	91.38

References Références Referencias

1. Ahmad M.F; Kamel M.D and Hatem A.A (2004). Synthesis of a some new pyridazine, 1, 2, 4-triazine and 1, 3, 4 –thiadiazole derivatives. *J Chemical Research*: 808-810.
2. Akpanisi L.E.S (2004). Heterocyclic Chemistry. Louis Printing Enterprises, Nigeria. Pp 56-63
3. Amos S, Binda H.; Vongtau B, Chindo J. Abbah N. Sambo, Odin E.M. and Okwute S.K. Akah P.Wambebe C. and Gamaniel K. (2002). Sedative effect of the metharodic leaf extracted of *Newbouldli laevis* in mice and rats. *Boll. Chin. Farmac* 144 (6) : 471-475.
4. Azuine M.A ; Ibrahim K; Ewerem N.M. and Wammbebe, C (1996). Anti-inflammatory and
5. Duanis J. and, Follet. M (1975). Effect of substiyuents on the orientation of cyclization. *Bull. Soc. Chim , Fr. 857-862; Chem. Abtr.* 83, 335.
6. Koster R; Anderson M. and De Beer E.J. (1959). Acetic acid for analgesic screening. *Federation of proceedings 18, 42*.
7. Machpheson. (1992). Review article on Aloe, vera leaf gel. *J. Ethnopharmacol. 638-737*.
8. Lorke D.A. (1983). A new approach to practical acute toxicity. *Archives of toxicolosy. 54:257*.
9. Odin E.M, Okwute S.K, Aishat A, Gamariel A. and Samson. A. (2004). Anti-inflamatory and Analgestic properties of *Newbouldia laevis leaves (Bigroniaceae). Sav. J. Sci and Agric.* V(i):20-32.
10. Odin E.M. and Akpanisi L.E.S (2007) Variable temperature 1H NMR spectroscopy studies of

bridgehead- fused 1, 2, 3- triazolo [1, 5a] pyrimidines *Continental J. app. Sci 2:38-41*.
11. Odin E.M. Onoja P.K and Saleh J.F (2013): synthesis, characterization and neuropharmacological activity of novel angular pentacyclic phenothaizine. *Int. J . Phy. Sci. 8(26) : 1374-1381.*
12. Gurad A., Anshoo G., Pravin . K. Abadesh K. (2011). Acute toxicity studies of safer and more effective analogous of N,N –diethyl-phenyl acetamide. *J. med Enthomol 48(6):1160-1166*.
13. Romain N., Xinyl S., Rorg J., Micheal J.C, Patrick R.G and Theodure M.K. (2009). Efficient methodology for the synthesis of 3-amimo- 1,2,4 – triazoles . *J. org Chem.* 74(19) :7595-7597.
14. Sam Lingyl (2013). Derivatives of pyrazol [1,5.a] [1,3,5] Triazines as enzyme inhibitors with potential therapeutic value. A thesis submitted for the degree of doctor of philosophy, Department of pharmacy, National University of Singapore.
15. Reda M.A.R, Mohammed S.T. M, Tarick E.S.A and Magdy A.L (2010) .1,2,4-triazine. Chemistry Part 1 : Orientation of cyclization reactions of functionalized 1, 2, 4- triazine derivatives. *European J. Chem.* 1 (3) 236-245.
16. Maryanooff C. A, Stanzione R.C, Plampin J.N., and Mills J.E., (1986). *J.Org. Chem*. *51:1882-1884*.
17. Nataliya P.B., Wim D. and Vasiliy A.B.(2010) Synthensis and properties of hydrozones beering amide, thioamiden and amidine functions. *ARKIVOC (1): 275-332*.
18. Lawrence D.R; Bennett P.N and Brown M.J (1997). Clinical pharmacology. Churchill living Stone. Edinburgh London. 8th edition.
19. Katrizky A.R; Rogers J.W, Witek, R.M and Nair S.K (2004) . Arkriroc 8:52-60.
20. Mohammed A; Mostafa M; Ismail, Wafea R. Abel- Menem and Aisha S.M. (2009): Substituted pyrido pyramidinones.. Synthesis of some novel ether derivatives of 4,4-pyrido –[1,2-a] pyridine -4-one. *J. Mex. Chem. Soc. 53 (2) :48-54*.
21. Khan B.U (1997). *J. Austrian. Dev. Disord 27;479-489*.
22. Jeste D.V Okamoto A. Napolitano J. Kane J.M. and Matinez R.A. (2000) *American .J. Psychiatry. 157:1150-1155.*
23. Patent US7122548. Triazolotriazine compounds and uses there of. Kin, S and Yoon J.Y .(2004). *Sci. Synth.* 27:671.
24. Kin, S and Yoon J.Y.(2004*). Sci. Synth*. 27:671.
25. Brehme R; Enders D. Fernandez R; and Lassaletta, J.M (2007). *Eur. J. Org. Chem. 5629.*
26. Draganov A. and Naicheva T. (1981). Chemistry and Technology of Dyes. Laboratory manuals. Jusautor Press, Sofia.
27. Mohammed A. Mostafa M. Wafaa R. Abdel-Monem and Aishat S.M. (2009). Substituted Pyridopyrimidinones. Part 3. Synthesis of some novel ether derivatives of 4H-Pyrido[1,2-a]pyrimidine-4-one. *J. Mex. Chem. Soc. 531: 48-54*.
28. Sigitas T. Gietrude M. Vladas G. and Povilas V. (2005). Substituent effect on proton chemical shifts of amide and azomethine groups of arylidenehydrazides of 5-substituted 2-pyrimidine-carboxylic acids and their aromatic analogs. *Chemija*. 16(1): 65-68.
29. Hugo E. Vadim K. and Abraham N. (1997). NMR chemical shifts of common laboratory solvents as trace impurities. *J. Org. Chem*. 62: 7512-7515.
30. Predrag N. Danko S. Sanja S. and Drazen V. (200). Sustituent, Temperature and Solvent effects on keto-enol equilibrium in symeeetrical pentane-1,3,5-triones. NMR and Theoretical studies. *Croatica Chemica Acta. 73(4): 1153-1170*.
31. Parmeter, S.M (1959). Inorganic reactions. *John Wiley and sons, inc: New York. 10:3-135*.
32. Winter A. Risley E.A.,Nuss G.W. (1962). Corrageenaa induced oedma in the hind paw of rat as an assey for anti-inflammatory activities. Proc. Soc. Exp. Biol. Ther. 111: 544-547.
33. Ratheesh M and Helen A. (2007). Anti-inflammatory activity of Ruta graveolens linn on carrageena induced paw oedema in wister male rats. Afric, J, Biotech. 6(10): 1209-1211.

This page is intentionally left blank

Global Journal of Science Frontier Research: B
Chemistry
Volume 15 Issue 3 Version 1.0 Year 2015
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

Triarylantimony(V) Dicarboxylates: Synthesis, Characterisation and Reactions

By Ram Nath Prasad Yadav
Tribhuvan University, Nepal

Abstract- A series of new triarylantimony(V) dicarboxylates of the general formula Ar_3SbL_2 (where Ar = $C_6H_5$and L = $C_6H_5CONHCH_2COO^-$, $C_6H_2(OH)_3COO^-$, $C_6H_5COO^-$, $C_6H_5C_2H_2COO^-$, $C_6H_4(OH)COO^-$, $(C_6H_5)_2(OH)C.COO^-$) have been prepared by the reaction of triarylantimony(V) dichloride and a carboxylic acid in the presence of triethylamine as well as the metathesis of sodium or silver salt of the carboxylic acid andtriarylantimony(V) dichloride. The newly synthesized compounds have been characterized by conventional methods. A tentative trigonalbipyramidal structure is suggested in which (OCOR) group occupy axial position and the three organic groups are situated at the equatorial position. The melting points of compounds did not change even after prolong stirring with water at room temperature for several hours indicating their hydrolytic stability.

Keywords: *Triarylantimony, Dicarboxylates, Hydrolytic stability, IR spectra, NMR spectra, Metathesis, Chelate.*

GJSFR-B Classification : *FOR Code: 259999*

Strictly as per the compliance and regulations of :

Triarylantimony(V) Dicarboxylates: Synthesis, Characterisation and Reactions

Ram Nath Prasad Yadav

Abstract- A series of new triarylantimony(V) dicarboxylates of the general formula Ar_3SbL_2 (where Ar = C_6H_5 and L = $C_6H_5CONHCH_2COO^-$, $C_6H_2(OH)_3COO^-$, $C_6H_5COO^-$, $C_6H_5C_2H_2COO^-$, $C_6H_4(OH)COO^-$, $(C_6H_5)_2(OH)C.COO^-$) have been prepared by the reaction of triarylantimony(V) dichloride and a carboxylic acid in the presence of triethylamine as well as the metathesis of sodium or silver salt of the carboxylic acid and triarylantimony(V) dichloride. The newly synthesized compounds have been characterized by conventional methods. A tentative trigonalbipyramidal structure is suggested in which (OCOR) group occupy axial position and the three organic groups are situated at the equatorial position. The melting points of compounds did not change even after prolong stirring with water at room temperature for several hours indicating their hydrolytic stability.

Keywords: triarylantimony, dicarboxylates, hydrolytic stability, ir spectra, nmr spectra, metathesis, chelate.

I. Introduction

Voluminous amount of work done on the chemistry of organic derivatives of antimony(III) and antimony(V) (Yadav 2012[a], Yadav 2013[a], Yadav 2014[a] and Yadav 2014[b]). As a result a variety of carboxylate derivatives, particularly organoantimony(V) were synthesized and characterized by various group of workers. The carboxylate derivatives were obtained by different routes, *e.g.* by oxidation of tertiary antimony(III), the anionic exchange or by salt precipitation reactions (Doak *et al.*1965).

The use of lead tetraacetate as oxidizing agents towards triorganoantimony(III) derivatives resulted in the formation of triorganoantimony(V) dicarboxylates.

$$Ar_3Sb + Pb(OCOR)_4 \rightarrow Pb(OCOR)_2 + Ar_3Sb(OCOR)_2 \ldots\ldots\ldots \quad (1)$$

Where, R= Me, Pr, or Bu

Interaction of triarylantimonydihydroxide with carboxylic acids, *viz*; formic acid could lead to the formation of triarylantimony(V) dicarboxylates (Chang *et al.*1975, Goal & Ridley 1972 and Hevyanek *et al.* 1978).

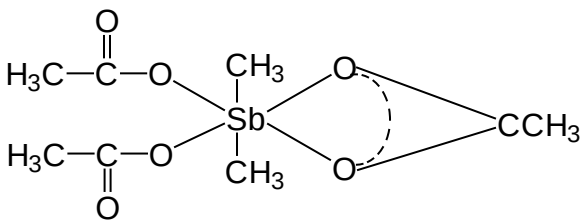
$$Ar_3Sb(OH)_2 + 2HCOOH \rightarrow Ar_3Sb(OCOH)_2 + 2H_2O \ldots\ldots\ldots \quad (2)$$

A series of triorganoantimony(V) dicarboxylates has been obtained by the reaction of triorganoantimony oxides with a number of carboxylic acids. Antimony oxides used in this reaction were preformed by the reaction of triorganoantimonydihalides with silver halides (Chang *et al.* 1975).

$$R_3SbO (\text{or } R_3SbX_2 + Ag_2O) + 2R'OOH \rightarrow R_3Sb(OCOR')_2 + H_2O \ldots\ldots\ldots\ldots \quad (3)$$

The above reaction does not go well with all the acids and it has been reported that the reactions with terphthalic acid, succinic acid and sebacic acids, however, result in the formation of polymeric products (Doak *et al.*1974). Goel and Ridley (Goel & Ridley 1972) were the first to make a systematic and comprehensive study on the physico-chemical parameters of trimethylantimony(V) derivatives of fluoro, chloro, bromo and cyano-acetic acid.

A few organoantimony(V) carboxylates of the type $R_2Sb(OCOR')_3$ and $R_4SbOCOR'$ have also been prepared. Based on the infrared and Raman data, an octahedral structure with two mono dentate and one chelating acetate groups has been proposed for $(CH_3)_2Sb(OCOCH_3)_3$ (Meinema & Noltes 1972).



The synthesis, structure and biological activity of the tertiary substituted arylantimony(V) dicarboxylates

Author: Tribhuvan University, Department of Chemistry, Thakur Ram Multiple Campus, Birganj, Nepal. e-mail: ramnathy@rocketmail.com

has been reported by Kiran *et al.* (Singhal *et al.* 1987). Based on spectroscopic and some solution phase studies a trigonalbipyramidal structure has been suggested for tetraaryl antimony(V) carboxylate derivatives by Raj and co-workers as has been reported in case of tetraphenylformate (Premraj *et al.* 1984).

Kumar Swami (Kumara *et al.* 1999) synthesized mixed halo acetate derivatives of the general formula $R_2SbCl(OAc)_2$. The crystal structure study revealed that both the acetate group act as bidentate ligand leading to hepta coordination around antimony. This is in sharp contrast to $Me_2Sb(OAc)_3$ where coordination number of antimony does not go beyond six and only one carboxylate group act as bidentate moiety (Geol & Ridley1972). It may partly be ascribed due to steric hindrance of three acetate group preventing hepta coordination.

The main objective of this work was to ascertain the mode of bonding of COOH group to antimony atom, to investigate chemical behavior and constitution of triarylantimony(V) carboxylates linear or polymeric and change in the nature of triarylantimony(V) carboxylates on changing the organic group bound to antimony or change of carboxylic group and to investigate the antimicrobial and antiproliferatine activity (Yadav 2012[b] and Yadav 2013[b]) generally associated with organometal carboxylates.

With the above aim in the mind, we have synthesized a few new triarylantimony(V) dicarboxylates. The results of these studies are reported in this paper.

II. Results and Discussion

Under anhydrous oxygen free atmosphere triarylantimony(V) dicarboxylates have been prepared either by the interaction of triarylantimony(V) dichloride with a carboxylic acid in 1:2 molar ratio in presence of triethylamine using benzene as the solvent or by simple metathesis of triarylantimony(V) dichloride with the sodium or silver salt of the corresponding carboxylic acid using methanol as the solvent.

$$Ph_3SbCl_2 + 2HL \xrightarrow{C_6H_6/\,Et_3N} Ph_3SbL_2 + 2Et_3N.HCl. \quad (4)$$

$$Ph_3SbCl_2 + 2ML \xrightarrow{C_6H_6/MeOH} Ph_3SbL_2 + 2MCl. \quad (5)$$

[M= Na or Ag; L = $C_6H_5CONHCH_2COO^-$, $C_6H_2(OH)_3COO^-$, $C_6H_5COO^-$, $C_6H_5C_2H_2COO^-$, $C_6H_4(OH)COO^-$, $(C_6H_5)_2(OH)C.COO^-$]

The reactions were carried out in dried benzene/methanol at room temperature with constant stirring for about 2-3 h. The contents were also refluxed at the reflux temperature of the respective solvent to ensure completion of the reaction. The yields of the products were nearly quantitative except for the losses during the workup process. The complexes are moderately soluble in chloroform and acetonitrile. They are off-white crystalline solids with sharp melting points. The complexes remain unaffected by air and atmospheric moisture. In the representative cases the melting points of compounds did not change even after prolong stirring with water at room temperature for several hours indicating their hydrolytic stability.

The molecular weight measurement in freezing benzene suggests that these carboxylate derivatives have monomeric constitution. The molar conductance of 10^{-3} M solution of all the complexes at room temperature are in the range between 20-30 Ohm^{-1} cm^2 mol^{-1} in acetonitrile which shows the absence of ionic species in solution.

III. Infrared Spectra

As has been discussed above, organoantimony carboxylates display a variety of structures. The coordination number of the central metal atom and the mode of bonding of the ligand are largely affected by the physical state, the numbers of organic groups bound to antimony and nature of ligand. Thus, in Ar_2SbOAc the ligand is bridging giving infinite chain structure in solid state while in chloroform, it assumes a bipyramidal geometry. On the other hand, in $R_3Sb(OAc)_2$ and R_4SbOAc the carboxylate moiety is strictly unidentate imparting pentacoordination around antimony. In $SbO(Ac)_3$. One of the acetate groups is simultaneously chelating and bridging and two of the ligands are chelating. In case of dimethyl triacetate the presence of both monodentate and bidentate has been reported. Carboxylate groups have been observed in tetramethylstibonium acetate, formate, trichloroacetates, propionates bivalate and benzoates, carboxylate group behaving as a monodentate ligand in solution imparting penta coordination around antimony. On the other hand in solid state, carboxylate group behaves as a bidentate ligand in which antimony is hexacoordinated.

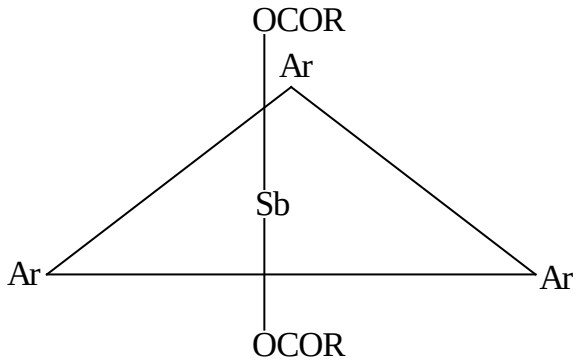
Thus, carboxylate group is capable of behaving as a monodentate as well as bidentate group. It can readily be distinguished with the aid of infrared spectra through a comparison with data previously given for the solid state in similar type compounds as well as for other organoantimony(V) carboxylates for example R_4SbOAc and R_2SbOAc_3 ($R=CH_3C_6H_4$ and C_6F_5) the difference in the position of asymmetric ν(CO) and symmetric ν(CO) is an important key factor in deciding the nature of carboxylate group. The appearance of medium strong band around 1680 cm^{-1} can readily be assigned to the ν(CO) mode of the monodentate 'ester like' carboxylate group. The absence of any band around 1500 cm^{-1} ruled out the possibility of the presence of a bidentate carboxylate group. The

difference between $\nu_{asy}(CO)$ and $\nu_{sym}(CO)$ is more than 200 cm^{-1} ruling out polymeric nature of the carboxylate group. This is also supported by the fact the newly synthesized compound are soluble in chloroform, acetonitrile, methanol etc. Thus the infrared data, molecular weight and molar conductance measurement indicate that the carboxylate derivatives exhibit pentacoordination around antimony. The Sb-C bond corresponding to Y mode was observed between 440-460 cm^{-1}. A medium band appearing in the range 415-422 can tentatively assigned Sb-O bond.

a) ^1H NMR spectra

^1H NMR spectra of a representative compound triphenylantimonydisalicylate or $[(C_6H_5)_3Sb(O_2CC_6H_4OH)_2]$ was recorded in $CDCl_3$ at room temperature on a JEOL FX. 90 Q. spectrometer using TMS as internal indicator. The spectra showed a complex multiplet in the range 8.80 to 6.86 ppm. A singlet at 11.58 ppm is due to hydroxyl proton of the ligand (2H, s -OH).

Thus, on the basis of IR and NMR spectra aided by molecular weight and conductance measurement, the newly synthesized carboxylate derivatives are assigned a trigonalbipyramidal structure in which (OCOR) group occupy axial position and the three organic groups are situated at the equatorial position.



Ar= C_6H_5 and OCOR = $C_6H_5CONHCH_2COO^-$, $C_6H_3(OH)_3COO^-$, $C_6H_5COO^-$, $C_6H_5C_2H_2COO^-$, $C_6H_4(OH)COO^-$, $(C_6H_5)_2(OH).C.COO^-$

Figure : Suggested structure of Ar_3SbL_2.

IV. Experimental

a) Materials and Methods

Triarylantimony(V) dichloride was prepared by slowly passing chlorine for 30 min through a solution of triphenylantimony in pet-ether. Carboxylic acids used in the reactions were purified before use. Sodium/silver salts of the organic moieties were freshly prepared and dried in *vacuo* before use. All solvents were purified, dried and distilled before use as per the literature methods (Vogel 1989) and reactions were carried out under nitrogen atmosphere.

IR spectra were recorded in the range 4000-200 cm^{-1} using KBr/CsI pellets on a Perkin-Elmer 577 spectrophotometer. ^1H NMR spectra were recorded on an EM 360L Varian spectrometer in $CDCl_3$ containing TMS as an external standard at room temperature. The molar conductance of 10^{-3} M solutions was determined at 25°C with a PR-9500 Phillips conductivity assembly. Molecular weights were determined cryoscopically in benzene using a Beckmann thermometer of ±0.01°C accuracy.

b) Preparation of the Antimony(V) Derivatives

Details of the typical experiments are described below. Relevant IR assignments, analytical data and molar conductance values are listed in Table 1-4.

Table 1: Preparation and Properties for Triarylantimony (V) Dicarboxylates

S. No.	Complex Ar_3SbL_2	Ligand (g) Solvent (ml)	Ar_3SbCl_2(g) Solvent (ml)	Molar ratio	M.P. (°C)	Colour	Recrystallisation Solvent
	Ar=C_6H_5						
1.	$Ar_3Sb(OCOCH_2.NHCOC_6H_5)_2$	$C_6H_5CONHCH_2COOH$ (0.358) C_6H_6 (30)	0.424 C_6H_6 (30)	1:2	218	White	Hexane
2.	$Ar_3Sb(OCO(OH)_3C_6H_2)_2$	$C_6H_2(OH)_3COOAg$ (0.554) C_6H_6 (30)	0.424 C_6H_6 (30)	1:2	118	Off white	Petroleum ether (40-60°C)

3.	$Ar_3Sb(OCOC_6H_5)_2$	C_6H_5COOH (0.244) C_6H_6 (30)	0.424 C_6H_6 (30)	1:2	160	Light brown	Petroleum ether (40-60°C)
4.	$Ar_3Sb(OCOC_2H_2C_6H_5)_2$	$C_6H_5C_2H_2COOH$ (0.296) C_6H_6 (30)	0.424 C_6H_6 (30)	1;2	197	Light pink	Hexane-petroleum ether (40-60°C)
5.	$Ar_3Sb(OCO(OH)C_6H_4)_2$	$C_6H_4(OH)COONa$ (0.320) C_6H_6 (30)	0.424 C_6H_6 (30)	1:2	142	White	Petroleum ether (40-60°C)
6.	$Ar_3Sb(OCO.C(OH)(C_6H_5)_2)_2$	$(C_6H_5)_2(OH)CCOOH$ (0.456) C_6H_6 (30)	0.424 C_6H_6 (30)	1:2	205	Light brown	Hexane

Table 2 : Elemental Analysis of Triarylantimony (V) Dicarboxylates

S. No.	Complex Ar_3SbL_2	Empirical formula	Found (Calcd.) %		
			C	H	N
	$Ar = C_6H_5$				
1.	$Ar_3Sb(OCOCH_2.NHCOC_6H_5)_2$	$C_{36}H_{31}O_6N_2Sb$	59.92 (60.95)	3.97 (4.37)	3.62 (3.95)
2.	$Ar_3Sb(OCO(OH)_3C_6H_2)_2$	$C_{32}H_{25}O_{10}Sb$	54.99 (55.59)	2.75 (3.62)	-
3.	$Ar_3Sb(OCOC_6H_5)_2$	$C_{32}H_{25}O_4Sb$	63.76 (64.56)	4.00 (4.20)	-
4.	$Ar_3Sb(OCOC_2H_2C_6H_5)_2$	$C_{40}H_{29}O_4Sb$	68.66 (69.09)	3.97 (4.17)	-
5.	$Ar_3Sb(OCO(OH)C_6H_4)_2$	$C_{32}H_{25}O_6Sb$	60.27 (61.27)	3.02 (3.99)	
6.	$Ar_3Sb(OCO.C(OH)(C_6H_5)_2)_2$	$C_{46}H_{37}O_6Sb$	67.92 (68.42)	3.29 (4.59)	-

Table 3 : Molar Conductance and Yield of Triarylantimony (V) Dicarboxylates

C. No.	Molar conductance (Ohm^{-1} cm^2 mol^{-1})	Yield (g)	(%)
1.	19	0.469	66
2.	22	0.477	69
3.	23	0.398	67
4.	26	0.486	70
5.	25	0.426	68
6.	22.2	0.573	71

Table 4 : IR Data for the Triarylantimony (V) Carboxylates (Cm^{-1})

C. No.	ν_{assy} (COO)	ν_{sym}(COO)
1.	1620	1340
2.	1625	1315
3.	1635	1320
4.	1630	1310
5.	1650	1290
6.	1665	1295

i *Reactions of Triarylantimony(V) Dichloride with Hippuric Acid (1)*

A solution of triphenylantimony(V) dichloride (0.424 g, l mmol) in benzene (~40 ml)and silver salt of hippuric acid (0.358 g, 2 mmol) in benzene (~30ml) was stirred together in dark conditions. A white precipitate of AgCl was formed which was filtered off. The filtrate on concentration yielded a white solid of triphenylantimony(V) dihippurate which was recrystallised by hexane. M.P.: 218°C; Yield: 0.468 g, (66%).

ii *Reaction of Triarylantimony(V) Dichloride with Silver Salt of Gallic Acid (2)*

In an oxygen free atmosphere, a solution of triphenylantimony(V) dichloride (0.424 g, 1 mmol) in benzene (~30 ml) and gallic acid (0.554 g, 2 mmol) in the same solvent (~30 ml) were stirred together in the presence of triethylamine at room temperature for 6 h. Et_3N. HCl was formed and filtered off. The filtrate on concentration in *vacuo* yielded a off white crystalline solid which was recrystallized from petroleum ether (40°-

60°C) to a afford triphenylantimony(V) gallate. M.P.: 118°C; Yield: 0.477 g, (69%).

iii *Reaction of Triarylantimony(V) Dichloride with Sodium Salt of Salicylic Acid (5)*

A solution of triphenylantimony(V) dichloride (0.424g, 1mmol) in benzene (~30 ml) and sodium salt of salicylic acid (0.320 g, 2 mmol) in benzene (~30 ml) was refluxed for 6 h. The solution was cooled and after filtration, concentrated *in vacuo* to yield white solid, identified triphenylantimony(V) salicylate and recrystalised from petroleum ether (40°-60°C). M.P.: 142°C; Yield: 0.426 g, (68%).

V. Acknowledgement

The author is thankful to the Head, Department of chemistry, Lucknow University for providing necessary laboratory facilities; the Director, Regional Sophisticated Instrumentation Centre, CDRI, Lucknow for microanalysis and spectral data. Thanks are also due to Dr. Premraj, Professor of Chemistry, Lucknow University, Lucknow India for his valuable suggestions.

References Références Referencias

1. Chang M.M.Y., Su K. and Musher J.I. (1974). Some new organoantimony(V) compounds. *Ishr. J. Chem.*, 12(5), 967-970.
2. Doak G.O., Long G.G. and Freedman L.D. (1965). The Infrared spectra of some phenyl substituted pentavalent antimony compounds. *J. Organomet. Chem.,* 4(1), 82-91.
3. Doak G.O., Long G.G. and Freedman L.D. (1974). Antimony: Annual survey covering the year 1975. *J. Organomet. Chem.*, 130, 365-404.
4. Goel R.G. and Ridley D.R. (1972). Studies on trimethyl and triphenylantimony(V) derivatives of haloacetic acids. *J. Organomet. Chem*, 38, 83-91.
5. Hevyanek J., Mleziva J. and Lycka L. (1978). Triphenylantimonydiester preparation.*J.Organomet. Chem.*, 157(2), 163-166.
6. Meinema H.A. and Noltes J.G. (1972). Investigations on organoantimonycompounds:VI. Preparation and properties of thermally stable dialkylantimony(V) compounds of the types $R_2Sb(OR)_3$, $R_2Sb(OAc)_3$ and $R_2Sb(O)OH$. *J. Organomet. Chem.*, 36, 313-322.
7. Premraj, Ranjan A., Singhal K. and Rastogi R. (1984). Synthesis and characterization of tetraarylstibonium amides, oximates and carboxylates. *Synth. React. Inorg. Met-Org. Chem.*, 14(2), 269-282.
8. Singhal K., Rastogi R. and Premraj. (1987). Synthesis and biological evaluation of some substituted tetriaryarylantimony(V) derivatives. *Ind. J. Chem.*, 26A, 146-150.
9. Swamy K.C. Kumara, Said Musa A. and Netaji M. (1999). A heptacoordinate mononuclear diphenylantimonycarboylate. *J. Chem. Crystallography,* 29(10), 1103-1106.
10. Vogel A.I. (1989). *Practical Organic Chemistry,* 5thedn., Longmans, London.
11. Yadav R.N.P. (2014[a]). Synthesis, characterization and reactions of some pentafluorophenylantimony (III) diamides. *International Journal of Advanced Research in Biological Sciences,*1(2), 108-114.
12. Yadav R.N.P. (2014[b]). Preparation, characterization and reactions of stable adducts of tris(pentaflurophenyl) antimony (V) diisothiocyanates. *Global J. of Science Frontier Research:B. (Chemistry).* 14(3), 5-9.
13. Yadav R.N.P. (2013[a]). Synthesis, characterization and reactions of cationic complexes of arylantimony(III) chlorides Ar_nSbCl_{3-n} with perchlorate and tetrafluoroborate anions. *Int. J. Appl. Sci. Biotechnol.*1(2), 42-48.
14. Yadav R.N.P. (2013[b]). Insecticidal and antimicrobial activity of triarylantimony(V) derivatives. *Academic Voices.* 3(1), 40-45.
15. Yadav R.N.P. (2012[a]). Synthesis and characterization of anionic complexes of pentafluorophenylantimony(III) chloride, $(R_F)_nSbCl_{3-n}$. *Nep. J. of Integrated Sciences*. 2(1),14-19.
16. Yadav R.N.P. (2012[b]). Metals in oncology: An overview. *Academic Voices.* 2(1), 54-58.

Global Journals Inc. (US) Guidelines Handbook 2015

www.GlobalJournals.org

FELLOWS

FELLOW OF ASSOCIATION OF RESEARCH SOCIETY IN SCIENCE (FARSS)

Global Journals Incorporate (USA) is accredited by Open Association of Research Society (OARS), U.S.A and in turn, awards "FARSS" title to individuals. The 'FARSS' title is accorded to a selected professional after the approval of the Editor-in-Chief/Editorial Board Members/Dean.

- The "FARSS" is a dignified title which is accorded to a person's name viz. Dr. John E. Hall, Ph.D., FARSS or William Walldroff, M.S., FARSS.

FARSS accrediting is an honor. It authenticates your research activities. After recognition as FARSB, you can add 'FARSS' title with your name as you use this recognition as additional suffix to your status. This will definitely enhance and add more value and repute to your name. You may use it on your professional Counseling Materials such as CV, Resume, and Visiting Card etc.

The following benefits can be availed by you only for next three years from the date of certification:

FARSS designated members are entitled to avail a 40% discount while publishing their research papers (of a single author) with Global Journals Incorporation (USA), if the same is accepted by Editorial Board/Peer Reviewers. If you are a main author or co-author in case of multiple authors, you will be entitled to avail discount of 10%.

Once FARSB title is accorded, the Fellow is authorized to organize a symposium/seminar/conference on behalf of Global Journal Incorporation (USA). The Fellow can also participate in conference/seminar/symposium organized by another institution as representative of Global Journal. In both the cases, it is mandatory for him to discuss with us and obtain our consent.

You may join as member of the Editorial Board of Global Journals Incorporation (USA) after successful completion of three years as Fellow and as Peer Reviewer. In addition, it is also desirable that you should organize seminar/symposium/conference at least once.

We shall provide you intimation regarding launching of e-version of journal of your stream time to time.This may be utilized in your library for the enrichment of knowledge of your students as well as it can also be helpful for the concerned faculty members.

The FARSS can go through standards of OARS. You can also play vital role if you have any suggestions so that proper amendment can take place to improve the same for the benefit of entire research community.

As FARSS, you will be given a renowned, secure and free professional email address with 100 GB of space e.g. johnhall@globaljournals.org. This will include Webmail, Spam Assassin, Email Forwarders,Auto-Responders, Email Delivery Route tracing, etc.

The FARSS will be eligible for a free application of standardization of their researches. Standardization of research will be subject to acceptability within stipulated norms as the next step after publishing in a journal. We shall depute a team of specialized research professionals who will render their services for elevating your researches to next higher level, which is worldwide open standardization.

The FARSS member can apply for grading and certification of standards of their educational and Institutional Degrees to Open Association of Research, Society U.S.A.
Once you are designated as FARSS, you may send us a scanned copy of all of your credentials. OARS will verify, grade and certify them. This will be based on your academic records, quality of research papers published by you, and some more criteria. After certification of all your credentials by OARS, they will be published on your Fellow Profile link on website https://associationofresearch.org which will be helpful to upgrade the dignity.

The FARSS members can avail the benefits of free research podcasting in Global Research Radio with their research documents. After publishing the work, (including published elsewhere worldwide with proper authorization) you can upload your research paper with your recorded voice or you can utilize chargeable services of our professional RJs to record your paper in their voice on request.

The FARSS member also entitled to get the benefits of free research podcasting of their research documents through video clips. We can also streamline your conference videos and display your slides/ online slides and online research video clips at reasonable charges, on request.

The FARSS is eligible to earn from sales proceeds of his/her researches/reference/review Books or literature, while publishing with Global Journals. The FARSS can decide whether he/she would like to publish his/her research in a closed manner. In this case, whenever readers purchase that individual research paper for reading, maximum 60% of its profit earned as royalty by Global Journals, will be credited to his/her bank account. The entire entitled amount will be credited to his/her bank account exceeding limit of minimum fixed balance. There is no minimum time limit for collection. The FARSS member can decide its price and we can help in making the right decision.

The FARSS member is eligible to join as a paid peer reviewer at Global Journals Incorporation (USA) and can get remuneration of 15% of author fees, taken from the author of a respective paper. After reviewing 5 or more papers you can request to transfer the amount to your bank account.

MEMBER OF ASSOCIATION OF RESEARCH SOCIETY IN SCIENCE (MARSS)

The ' MARSS ' title is accorded to a selected professional after the approval of the Editor-in-Chief / Editorial Board Members/Dean.

The "MARSS" is a dignified ornament which is accorded to a person's name viz. Dr. John E. Hall, Ph.D., MARSS or William Walldroff, M.S., MARSS.

MARSS accrediting is an honor. It authenticates your research activities. After becoming MARSS, you can add 'MARSS' title with your name as you use this recognition as additional suffix to your status. This will definitely enhance and add more value and repute to your name. You may use it on your professional Counseling Materials such as CV, Resume, Visiting Card and Name Plate etc.

The following benefitscan be availed by you only for next three years from the date of certification.

MARSS designated members are entitled to avail a 25% discount while publishing their research papers (of a single author) in Global Journals Inc., if the same is accepted by our Editorial Board and Peer Reviewers. If you are a main author or co-author of a group of authors, you will get discount of 10%.

As MARSS, you will be given a renowned, secure and free professional email address with 30 GB of space e.g. johnhall@globaljournals.org. This will include Webmail, Spam Assassin, Email Forwarders,Auto-Responders, Email Delivery Route tracing, etc.

We shall provide you intimation regarding launching of e-version of journal of your stream time to time.This may be utilized in your library for the enrichment of knowledge of your students as well as it can also be helpful for the concerned faculty members.

The MARSS member can apply for approval, grading and certification of standards of their educational and Institutional Degrees to Open Association of Research, Society U.S.A.

Once you are designated as MARSS, you may send us a scanned copy of all of your credentials. OARS will verify, grade and certify them. This will be based on your academic records, quality of research papers published by you, and some more criteria.

It is mandatory to read all terms and conditions carefully.

AUXILIARY MEMBERSHIPS

Institutional Fellow of Global Journals Incorporation (USA)-OARS (USA)

Global Journals Incorporation (USA) is accredited by Open Association of Research Society, U.S.A (OARS) and in turn, affiliates research institutions as "Institutional Fellow of Open Association of Research Society" (IFOARS).

The "FARSC" is a dignified title which is accorded to a person's name viz. Dr. John E. Hall, Ph.D., FARSC or William Walldroff, M.S., FARSC.

The IFOARS institution is entitled to form a Board comprised of one Chairperson and three to five board members preferably from different streams. The Board will be recognized as "Institutional Board of Open Association of Research Society"-(IBOARS).

The Institute will be entitled to following benefits:

The IBOARS can initially review research papers of their institute and recommend them to publish with respective journal of Global Journals. It can also review the papers of other institutions after obtaining our consent. The second review will be done by peer reviewer of Global Journals Incorporation (USA) The Board is at liberty to appoint a peer reviewer with the approval of chairperson after consulting us.

The author fees of such paper may be waived off up to 40%.

The Global Journals Incorporation (USA) at its discretion can also refer double blind peer reviewed paper at their end to the board for the verification and to get recommendation for final stage of acceptance of publication.

The IBOARS can organize symposium/seminar/conference in their country on behalf of Global Journals Incorporation (USA)-OARS (USA). The terms and conditions can be discussed separately.

The Board can also play vital role by exploring and giving valuable suggestions regarding the Standards of "Open Association of Research Society, U.S.A (OARS)" so that proper amendment can take place for the benefit of entire research community. We shall provide details of particular standard only on receipt of request from the Board.

The board members can also join us as Individual Fellow with 40% discount on total fees applicable to Individual Fellow. They will be entitled to avail all the benefits as declared. Please visit Individual Fellow-sub menu of GlobalJournals.org to have more relevant details.

We shall provide you intimation regarding launching of e-version of journal of your stream time to time. This may be utilized in your library for the enrichment of knowledge of your students as well as it can also be helpful for the concerned faculty members.

After nomination of your institution as "Institutional Fellow" and constantly functioning successfully for one year, we can consider giving recognition to your institute to function as Regional/Zonal office on our behalf.
The board can also take up the additional allied activities for betterment after our consultation.

The following entitlements are applicable to individual Fellows:

Open Association of Research Society, U.S.A (OARS) By-laws states that an individual Fellow may use the designations as applicable, or the corresponding initials. The Credentials of individual Fellow and Associate designations signify that the individual has gained knowledge of the fundamental concepts. One is magnanimous and proficient in an expertise course covering the professional code of conduct, and follows recognized standards of practice.

Open Association of Research Society (US)/ Global Journals Incorporation (USA), as described in Corporate Statements, are educational, research publishing and professional membership organizations. Achieving our individual Fellow or Associate status is based mainly on meeting stated educational research requirements.

Disbursement of 40% Royalty earned through Global Journals : Researcher = 50%, Peer Reviewer = 37.50%, Institution = 12.50% E.g. Out of 40%, the 20% benefit should be passed on to researcher, 15 % benefit towards remuneration should be given to a reviewer and remaining 5% is to be retained by the institution.

We shall provide print version of 12 issues of any three journals [as per your requirement] out of our 38 journals worth $ 2376 USD.

Other:

The individual Fellow and Associate designations accredited by Open Association of Research Society (US) credentials signify guarantees following achievements:

- The professional accredited with Fellow honor, is entitled to various benefits viz. name, fame, honor, regular flow of income, secured bright future, social status etc.

- In addition to above, if one is single author, then entitled to 40% discount on publishing research paper and can get 10%discount if one is co-author or main author among group of authors.
- The Fellow can organize symposium/seminar/conference on behalf of Global Journals Incorporation (USA) and he/she can also attend the same organized by other institutes on behalf of Global Journals.
- The Fellow can become member of Editorial Board Member after completing 3yrs.
- The Fellow can earn 60% of sales proceeds from the sale of reference/review books/literature/publishing of research paper.
- Fellow can also join as paid peer reviewer and earn 15% remuneration of author charges and can also get an opportunity to join as member of the Editorial Board of Global Journals Incorporation (USA)
- • This individual has learned the basic methods of applying those concepts and techniques to common challenging situations. This individual has further demonstrated an in–depth understanding of the application of suitable techniques to a particular area of research practice.

Note :

"

- In future, if the board feels the necessity to change any board member, the same can be done with the consent of the chairperson along with anyone board member without our approval.
- In case, the chairperson needs to be replaced then consent of 2/3rd board members are required and they are also required to jointly pass the resolution copy of which should be sent to us. In such case, it will be compulsory to obtain our approval before replacement.
- In case of "Difference of Opinion [if any]" among the Board members, our decision will be final and binding to everyone.

"

Process of submission of Research Paper

The Area or field of specialization may or may not be of any category as mentioned in 'Scope of Journal' menu of the GlobalJournals.org website. There are 37 Research Journal categorized with Six parental Journals GJCST, GJMR, GJRE, GJMBR, GJSFR, GJHSS. For Authors should prefer the mentioned categories. There are three widely used systems UDC, DDC and LCC. The details are available as 'Knowledge Abstract' at Home page. The major advantage of this coding is that, the research work will be exposed to and shared with all over the world as we are being abstracted and indexed worldwide.

The paper should be in proper format. The format can be downloaded from first page of 'Author Guideline' Menu. The Author is expected to follow the general rules as mentioned in this menu. The paper should be written in MS-Word Format (*.DOC,*.DOCX).

The Author can submit the paper either online or offline. The authors should prefer online submission.Online Submission: There are three ways to submit your paper:

(A) (I) First, register yourself using top right corner of Home page then Login. If you are already registered, then login using your username and password.

(II) Choose corresponding Journal.

(III) Click 'Submit Manuscript'. Fill required information and Upload the paper.

(B) If you are using Internet Explorer, then Direct Submission through Homepage is also available.

(C) If these two are not conveninet , and then email the paper directly to dean@globaljournals.org.

Offline Submission: Author can send the typed form of paper by Post. However, online submission should be preferred.

Preferred Author Guidelines

MANUSCRIPT STYLE INSTRUCTION (Must be strictly followed)

Page Size: 8.27" X 11'"

- Left Margin: 0.65
- Right Margin: 0.65
- Top Margin: 0.75
- Bottom Margin: 0.75
- Font type of all text should be Swis 721 Lt BT.
- Paper Title should be of Font Size 24 with one Column section.
- Author Name in Font Size of 11 with one column as of Title.
- Abstract Font size of 9 Bold, "Abstract" word in Italic Bold.
- Main Text: Font size 10 with justified two columns section
- Two Column with Equal Column with of 3.38 and Gaping of .2
- First Character must be three lines Drop capped.
- Paragraph before Spacing of 1 pt and After of 0 pt.
- Line Spacing of 1 pt
- Large Images must be in One Column
- Numbering of First Main Headings (Heading 1) must be in Roman Letters, Capital Letter, and Font Size of 10.
- Numbering of Second Main Headings (Heading 2) must be in Alphabets, Italic, and Font Size of 10.

You can use your own standard format also.
Author Guidelines:

1. General,

2. Ethical Guidelines,

3. Submission of Manuscripts,

4. Manuscript's Category,

5. Structure and Format of Manuscript,

6. After Acceptance.

1. GENERAL

Before submitting your research paper, one is advised to go through the details as mentioned in following heads. It will be beneficial, while peer reviewer justify your paper for publication.

Scope

The Global Journals Inc. (US) welcome the submission of original paper, review paper, survey article relevant to the all the streams of Philosophy and knowledge. The Global Journals Inc. (US) is parental platform for Global Journal of Computer Science and Technology, Researches in Engineering, Medical Research, Science Frontier Research, Human Social Science, Management, and Business organization. The choice of specific field can be done otherwise as following in Abstracting and Indexing Page on this Website. As the all Global

Journals Inc. (US) are being abstracted and indexed (in process) by most of the reputed organizations. Topics of only narrow interest will not be accepted unless they have wider potential or consequences.

2. ETHICAL GUIDELINES

Authors should follow the ethical guidelines as mentioned below for publication of research paper and research activities.

Papers are accepted on strict understanding that the material in whole or in part has not been, nor is being, considered for publication elsewhere. If the paper once accepted by Global Journals Inc. (US) and Editorial Board, will become the copyright of the Global Journals Inc. (US).

Authorship: The authors and coauthors should have active contribution to conception design, analysis and interpretation of findings. They should critically review the contents and drafting of the paper. All should approve the final version of the paper before submission

The Global Journals Inc. (US) follows the definition of authorship set up by the Global Academy of Research and Development. According to the Global Academy of R&D authorship, criteria must be based on:

1) Substantial contributions to conception and acquisition of data, analysis and interpretation of the findings.

2) Drafting the paper and revising it critically regarding important academic content.

3) Final approval of the version of the paper to be published.

All authors should have been credited according to their appropriate contribution in research activity and preparing paper. Contributors who do not match the criteria as authors may be mentioned under Acknowledgement.

Acknowledgements: Contributors to the research other than authors credited should be mentioned under acknowledgement. The specifications of the source of funding for the research if appropriate can be included. Suppliers of resources may be mentioned along with address.

Appeal of Decision: The Editorial Board's decision on publication of the paper is final and cannot be appealed elsewhere.

Permissions: It is the author's responsibility to have prior permission if all or parts of earlier published illustrations are used in this paper.

Please mention proper reference and appropriate acknowledgements wherever expected.

If all or parts of previously published illustrations are used, permission must be taken from the copyright holder concerned. It is the author's responsibility to take these in writing.

Approval for reproduction/modification of any information (including figures and tables) published elsewhere must be obtained by the authors/copyright holders before submission of the manuscript. Contributors (Authors) are responsible for any copyright fee involved.

3. SUBMISSION OF MANUSCRIPTS

Manuscripts should be uploaded via this online submission page. The online submission is most efficient method for submission of papers, as it enables rapid distribution of manuscripts and consequently speeds up the review procedure. It also enables authors to know the status of their own manuscripts by emailing us. Complete instructions for submitting a paper is available below.

Manuscript submission is a systematic procedure and little preparation is required beyond having all parts of your manuscript in a given format and a computer with an Internet connection and a Web browser. Full help and instructions are provided on-screen. As an author, you will be prompted for login and manuscript details as Field of Paper and then to upload your manuscript file(s) according to the instructions.

To avoid postal delays, all transaction is preferred by e-mail. A finished manuscript submission is confirmed by e-mail immediately and your paper enters the editorial process with no postal delays. When a conclusion is made about the publication of your paper by our Editorial Board, revisions can be submitted online with the same procedure, with an occasion to view and respond to all comments.

Complete support for both authors and co-author is provided.

4. MANUSCRIPT'S CATEGORY

Based on potential and nature, the manuscript can be categorized under the following heads:

Original research paper: Such papers are reports of high-level significant original research work.

Review papers: These are concise, significant but helpful and decisive topics for young researchers.

Research articles: These are handled with small investigation and applications

Research letters: The letters are small and concise comments on previously published matters.

5.STRUCTURE AND FORMAT OF MANUSCRIPT

The recommended size of original research paper is less than seven thousand words, review papers fewer than seven thousands words also.Preparation of research paper or how to write research paper, are major hurdle, while writing manuscript. The research articles and research letters should be fewer than three thousand words, the structure original research paper; sometime review paper should be as follows:

Papers: These are reports of significant research (typically less than 7000 words equivalent, including tables, figures, references), and comprise:

(a)Title should be relevant and commensurate with the theme of the paper.

(b) A brief Summary, "Abstract" (less than 150 words) containing the major results and conclusions.

(c) Up to ten keywords, that precisely identifies the paper's subject, purpose, and focus.

(d) An Introduction, giving necessary background excluding subheadings; objectives must be clearly declared.

(e) Resources and techniques with sufficient complete experimental details (wherever possible by reference) to permit repetition; sources of information must be given and numerical methods must be specified by reference, unless non-standard.

(f) Results should be presented concisely, by well-designed tables and/or figures; the same data may not be used in both; suitable statistical data should be given. All data must be obtained with attention to numerical detail in the planning stage. As reproduced design has been recognized to be important to experiments for a considerable time, the Editor has decided that any paper that appears not to have adequate numerical treatments of the data will be returned un-refereed;

(g) Discussion should cover the implications and consequences, not just recapitulating the results; conclusions should be summarizing.

(h) Brief Acknowledgements.

(i) References in the proper form.

Authors should very cautiously consider the preparation of papers to ensure that they communicate efficiently. Papers are much more likely to be accepted, if they are cautiously designed and laid out, contain few or no errors, are summarizing, and be conventional to the approach and instructions. They will in addition, be published with much less delays than those that require much technical and editorial correction.

The Editorial Board reserves the right to make literary corrections and to make suggestions to improve briefness.

It is vital, that authors take care in submitting a manuscript that is written in simple language and adheres to published guidelines.

Format

Language: The language of publication is UK English. Authors, for whom English is a second language, must have their manuscript efficiently edited by an English-speaking person before submission to make sure that, the English is of high excellence. It is preferable, that manuscripts should be professionally edited.

Standard Usage, Abbreviations, and Units: Spelling and hyphenation should be conventional to The Concise Oxford English Dictionary. Statistics and measurements should at all times be given in figures, e.g. 16 min, except for when the number begins a sentence. When the number does not refer to a unit of measurement it should be spelt in full unless, it is 160 or greater.

Abbreviations supposed to be used carefully. The abbreviated name or expression is supposed to be cited in full at first usage, followed by the conventional abbreviation in parentheses.

Metric SI units are supposed to generally be used excluding where they conflict with current practice or are confusing. For illustration, 1.4 l rather than 1.4 × 10-3 m3, or 4 mm somewhat than 4 × 10-3 m. Chemical formula and solutions must identify the form used, e.g. anhydrous or hydrated, and the concentration must be in clearly defined units. Common species names should be followed by underlines at the first mention. For following use the generic name should be constricted to a single letter, if it is clear.

Structure

All manuscripts submitted to Global Journals Inc. (US), ought to include:

Title: The title page must carry an instructive title that reflects the content, a running title (less than 45 characters together with spaces), names of the authors and co-authors, and the place(s) wherever the work was carried out. The full postal address in addition with the e-mail address of related author must be given. Up to eleven keywords or very brief phrases have to be given to help data retrieval, mining and indexing.

Abstract, used in Original Papers and Reviews:

Optimizing Abstract for Search Engines

Many researchers searching for information online will use search engines such as Google, Yahoo or similar. By optimizing your paper for search engines, you will amplify the chance of someone finding it. This in turn will make it more likely to be viewed and/or cited in a further work. Global Journals Inc. (US) have compiled these guidelines to facilitate you to maximize the web-friendliness of the most public part of your paper.

Key Words

A major linchpin in research work for the writing research paper is the keyword search, which one will employ to find both library and Internet resources.

One must be persistent and creative in using keywords. An effective keyword search requires a strategy and planning a list of possible keywords and phrases to try.

Search engines for most searches, use Boolean searching, which is somewhat different from Internet searches. The Boolean search uses "operators," words (and, or, not, and near) that enable you to expand or narrow your affords. Tips for research paper while preparing research paper are very helpful guideline of research paper.

Choice of key words is first tool of tips to write research paper. Research paper writing is an art.A few tips for deciding as strategically as possible about keyword search:

- One should start brainstorming lists of possible keywords before even begin searching. Think about the most important concepts related to research work. Ask, "What words would a source have to include to be truly valuable in research paper?" Then consider synonyms for the important words.
- It may take the discovery of only one relevant paper to let steer in the right keyword direction because in most databases, the keywords under which a research paper is abstracted are listed with the paper.
- One should avoid outdated words.

Keywords are the key that opens a door to research work sources. Keyword searching is an art in which researcher's skills are bound to improve with experience and time.

Numerical Methods: Numerical methods used should be clear and, where appropriate, supported by references.

Acknowledgements: Please make these as concise as possible.

References

References follow the Harvard scheme of referencing. References in the text should cite the authors' names followed by the time of their publication, unless there are three or more authors when simply the first author's name is quoted followed by et al. unpublished work has to only be cited where necessary, and only in the text. Copies of references in press in other journals have to be supplied with submitted typescripts. It is necessary that all citations and references be carefully checked before submission, as mistakes or omissions will cause delays.

References to information on the World Wide Web can be given, but only if the information is available without charge to readers on an official site. Wikipedia and Similar websites are not allowed where anyone can change the information. Authors will be asked to make available electronic copies of the cited information for inclusion on the Global Journals Inc. (US) homepage at the judgment of the Editorial Board.

The Editorial Board and Global Journals Inc. (US) recommend that, citation of online-published papers and other material should be done via a DOI (digital object identifier). If an author cites anything, which does not have a DOI, they run the risk of the cited material not being noticeable.

The Editorial Board and Global Journals Inc. (US) recommend the use of a tool such as Reference Manager for reference management and formatting.

Tables, Figures and Figure Legends

Tables: Tables should be few in number, cautiously designed, uncrowned, and include only essential data. Each must have an Arabic number, e.g. Table 4, a self-explanatory caption and be on a separate sheet. Vertical lines should not be used.

Figures: Figures are supposed to be submitted as separate files. Always take in a citation in the text for each figure using Arabic numbers, e.g. Fig. 4. Artwork must be submitted online in electronic form by e-mailing them.

Preparation of Electronic Figures for Publication

Even though low quality images are sufficient for review purposes, print publication requires high quality images to prevent the final product being blurred or fuzzy. Submit (or e-mail) EPS (line art) or TIFF (halftone/photographs) files only. MS PowerPoint and Word Graphics are unsuitable for printed pictures. Do not use pixel-oriented software. Scans (TIFF only) should have a resolution of at least 350 dpi (halftone) or 700 to 1100 dpi (line drawings) in relation to the imitation size. Please give the data for figures in black and white or submit a Color Work Agreement Form. EPS files must be saved with fonts embedded (and with a TIFF preview, if possible).

For scanned images, the scanning resolution (at final image size) ought to be as follows to ensure good reproduction: line art: >650 dpi; halftones (including gel photographs) : >350 dpi; figures containing both halftone and line images: >650 dpi.

Color Charges: It is the rule of the Global Journals Inc. (US) for authors to pay the full cost for the reproduction of their color artwork. Hence, please note that, if there is color artwork in your manuscript when it is accepted for publication, we would require you to complete and return a color work agreement form before your paper can be published.

Figure Legends: Self-explanatory legends of all figures should be incorporated separately under the heading 'Legends to Figures'. In the full-text online edition of the journal, figure legends may possibly be truncated in abbreviated links to the full screen version. Therefore, the first 100 characters of any legend should notify the reader, about the key aspects of the figure.

6. AFTER ACCEPTANCE

Upon approval of a paper for publication, the manuscript will be forwarded to the dean, who is responsible for the publication of the Global Journals Inc. (US).

6.1 Proof Corrections

The corresponding author will receive an e-mail alert containing a link to a website or will be attached. A working e-mail address must therefore be provided for the related author.

Acrobat Reader will be required in order to read this file. This software can be downloaded

(Free of charge) from the following website:

www.adobe.com/products/acrobat/readstep2.html. This will facilitate the file to be opened, read on screen, and printed out in order for any corrections to be added. Further instructions will be sent with the proof.

Proofs must be returned to the dean at dean@globaljournals.org within three days of receipt.

As changes to proofs are costly, we inquire that you only correct typesetting errors. All illustrations are retained by the publisher. Please note that the authors are responsible for all statements made in their work, including changes made by the copy editor.

6.2 Early View of Global Journals Inc. (US) (Publication Prior to Print)

The Global Journals Inc. (US) are enclosed by our publishing's Early View service. Early View articles are complete full-text articles sent in advance of their publication. Early View articles are absolute and final. They have been completely reviewed, revised and edited for publication, and the authors' final corrections have been incorporated. Because they are in final form, no changes can be made after sending them. The nature of Early View articles means that they do not yet have volume, issue or page numbers, so Early View articles cannot be cited in the conventional way.

6.3 Author Services

Online production tracking is available for your article through Author Services. Author Services enables authors to track their article - once it has been accepted - through the production process to publication online and in print. Authors can check the status of their articles online and choose to receive automated e-mails at key stages of production. The authors will receive an e-mail with a unique link that enables them to register and have their article automatically added to the system. Please ensure that a complete e-mail address is provided when submitting the manuscript.

6.4 Author Material Archive Policy

Please note that if not specifically requested, publisher will dispose off hardcopy & electronic information submitted, after the two months of publication. If you require the return of any information submitted, please inform the Editorial Board or dean as soon as possible.

6.5 Offprint and Extra Copies

A PDF offprint of the online-published article will be provided free of charge to the related author, and may be distributed according to the Publisher's terms and conditions. Additional paper offprint may be ordered by emailing us at: editor@globaljournals.org .

Before start writing a good quality Computer Science Research Paper, let us first understand what is Computer Science Research Paper? So, Computer Science Research Paper is the paper which is written by professionals or scientists who are associated to Computer Science and Information Technology, or doing research study in these areas. If you are novel to this field then you can consult about this field from your supervisor or guide.

TECHNIQUES FOR WRITING A GOOD QUALITY RESEARCH PAPER:

1. Choosing the topic: In most cases, the topic is searched by the interest of author but it can be also suggested by the guides. You can have several topics and then you can judge that in which topic or subject you are finding yourself most comfortable. This can be done by asking several questions to yourself, like Will I be able to carry our search in this area? Will I find all necessary recourses to accomplish the search? Will I be able to find all information in this field area? If the answer of these types of questions will be "Yes" then you can choose that topic. In most of the cases, you may have to conduct the surveys and have to visit several places because this field is related to Computer Science and Information Technology. Also, you may have to do a lot of work to find all rise and falls regarding the various data of that subject. Sometimes, detailed information plays a vital role, instead of short information.

2. Evaluators are human: First thing to remember that evaluators are also human being. They are not only meant for rejecting a paper. They are here to evaluate your paper. So, present your Best.

3. Think Like Evaluators: If you are in a confusion or getting demotivated that your paper will be accepted by evaluators or not, then think and try to evaluate your paper like an Evaluator. Try to understand that what an evaluator wants in your research paper and automatically you will have your answer.

4. Make blueprints of paper: The outline is the plan or framework that will help you to arrange your thoughts. It will make your paper logical. But remember that all points of your outline must be related to the topic you have chosen.

5. Ask your Guides: If you are having any difficulty in your research, then do not hesitate to share your difficulty to your guide (if you have any). They will surely help you out and resolve your doubts. If you can't clarify what exactly you require for your work then ask the supervisor to help you with the alternative. He might also provide you the list of essential readings.

6. Use of computer is recommended: As you are doing research in the field of Computer Science, then this point is quite obvious.

7. Use right software: Always use good quality software packages. If you are not capable to judge good software then you can lose quality of your paper unknowingly. There are various software programs available to help you, which you can get through Internet.

8. Use the Internet for help: An excellent start for your paper can be by using the Google. It is an excellent search engine, where you can have your doubts resolved. You may also read some answers for the frequent question how to write my research paper or find model research paper. From the internet library you can download books. If you have all required books make important reading selecting and analyzing the specified information. Then put together research paper sketch out.

9. Use and get big pictures: Always use encyclopedias, Wikipedia to get pictures so that you can go into the depth.

10. Bookmarks are useful: When you read any book or magazine, you generally use bookmarks, right! It is a good habit, which helps to not to lose your continuity. You should always use bookmarks while searching on Internet also, which will make your search easier.

11. Revise what you wrote: When you write anything, always read it, summarize it and then finalize it.

12. Make all efforts: Make all efforts to mention what you are going to write in your paper. That means always have a good start. Try to mention everything in introduction, that what is the need of a particular research paper. Polish your work by good skill of writing and always give an evaluator, what he wants.

13. Have backups: When you are going to do any important thing like making research paper, you should always have backup copies of it either in your computer or in paper. This will help you to not to lose any of your important.

14. Produce good diagrams of your own: Always try to include good charts or diagrams in your paper to improve quality. Using several and unnecessary diagrams will degrade the quality of your paper by creating "hotchpotch." So always, try to make and include those diagrams, which are made by your own to improve readability and understandability of your paper.

15. Use of direct quotes: When you do research relevant to literature, history or current affairs then use of quotes become essential but if study is relevant to science then use of quotes is not preferable.

16. Use proper verb tense: Use proper verb tenses in your paper. Use past tense, to present those events that happened. Use present tense to indicate events that are going on. Use future tense to indicate future happening events. Use of improper and wrong tenses will confuse the evaluator. Avoid the sentences that are incomplete.

17. Never use online paper: If you are getting any paper on Internet, then never use it as your research paper because it might be possible that evaluator has already seen it or maybe it is outdated version.

18. Pick a good study spot: To do your research studies always try to pick a spot, which is quiet. Every spot is not for studies. Spot that suits you choose it and proceed further.

19. Know what you know: Always try to know, what you know by making objectives. Else, you will be confused and cannot achieve your target.

20. Use good quality grammar: Always use a good quality grammar and use words that will throw positive impact on evaluator. Use of good quality grammar does not mean to use tough words, that for each word the evaluator has to go through dictionary. Do not start sentence with a conjunction. Do not fragment sentences. Eliminate one-word sentences. Ignore passive voice. Do not ever use a big word when a diminutive one would suffice. Verbs have to be in agreement with their subjects. Prepositions are not expressions to finish sentences with. It is incorrect to ever divide an infinitive. Avoid clichés like the disease. Also, always shun irritating alliteration. Use language that is simple and straight forward. put together a neat summary.

21. Arrangement of information: Each section of the main body should start with an opening sentence and there should be a changeover at the end of the section. Give only valid and powerful arguments to your topic. You may also maintain your arguments with records.

22. Never start in last minute: Always start at right time and give enough time to research work. Leaving everything to the last minute will degrade your paper and spoil your work.

23. Multitasking in research is not good: Doing several things at the same time proves bad habit in case of research activity. Research is an area, where everything has a particular time slot. Divide your research work in parts and do particular part in particular time slot.

24. Never copy others' work: Never copy others' work and give it your name because if evaluator has seen it anywhere you will be in trouble.

25. Take proper rest and food: No matter how many hours you spend for your research activity, if you are not taking care of your health then all your efforts will be in vain. For a quality research, study is must, and this can be done by taking proper rest and food.

26. Go for seminars: Attend seminars if the topic is relevant to your research area. Utilize all your resources.

27. Refresh your mind after intervals: Try to give rest to your mind by listening to soft music or by sleeping in intervals. This will also improve your memory.

28. Make colleagues: Always try to make colleagues. No matter how sharper or intelligent you are, if you make colleagues you can have several ideas, which will be helpful for your research.

29. Think technically: Always think technically. If anything happens, then search its reasons, its benefits, and demerits.

30. Think and then print: When you will go to print your paper, notice that tables are not be split, headings are not detached from their descriptions, and page sequence is maintained.

31. Adding unnecessary information: Do not add unnecessary information, like, I have used MS Excel to draw graph. Do not add irrelevant and inappropriate material. These all will create superfluous. Foreign terminology and phrases are not apropos. One should NEVER take a broad view. Analogy in script is like feathers on a snake. Not at all use a large word when a very small one would be sufficient. Use words properly, regardless of how others use them. Remove quotations. Puns are for kids, not grunt readers. Amplification is a billion times of inferior quality than sarcasm.

32. Never oversimplify everything: To add material in your research paper, never go for oversimplification. This will definitely irritate the evaluator. Be more or less specific. Also too, by no means, ever use rhythmic redundancies. Contractions aren't essential and shouldn't be there used. Comparisons are as terrible as clichés. Give up ampersands and abbreviations, and so on. Remove commas, that are, not necessary. Parenthetical words however should be together with this in commas. Understatement is all the time the complete best way to put onward earth-shaking thoughts. Give a detailed literary review.

33. Report concluded results: Use concluded results. From raw data, filter the results and then conclude your studies based on measurements and observations taken. Significant figures and appropriate number of decimal places should be used. Parenthetical remarks are prohibitive. Proofread carefully at final stage. In the end give outline to your arguments. Spot out perspectives of further study of this subject. Justify your conclusion by at the bottom of them with sufficient justifications and examples.

34. After conclusion: Once you have concluded your research, the next most important step is to present your findings. Presentation is extremely important as it is the definite medium though which your research is going to be in print to the rest of the crowd. Care should be taken to categorize your thoughts well and present them in a logical and neat manner. A good quality research paper format is essential because it serves to highlight your research paper and bring to light all necessary aspects in your research.

Informal Guidelines of Research Paper Writing

Key points to remember:

- Submit all work in its final form.
- Write your paper in the form, which is presented in the guidelines using the template.
- Please note the criterion for grading the final paper by peer-reviewers.

Final Points:

A purpose of organizing a research paper is to let people to interpret your effort selectively. The journal requires the following sections, submitted in the order listed, each section to start on a new page.

The introduction will be compiled from reference matter and will reflect the design processes or outline of basis that direct you to make study. As you will carry out the process of study, the method and process section will be constructed as like that. The result segment will show related statistics in nearly sequential order and will direct the reviewers next to the similar intellectual paths throughout the data that you took to carry out your study. The discussion section will provide understanding of the data and projections as to the implication of the results. The use of good quality references all through the paper will give the effort trustworthiness by representing an alertness of prior workings.

Writing a research paper is not an easy job no matter how trouble-free the actual research or concept. Practice, excellent preparation, and controlled record keeping are the only means to make straightforward the progression.

General style:

Specific editorial column necessities for compliance of a manuscript will always take over from directions in these general guidelines.

To make a paper clear

· Adhere to recommended page limits

Mistakes to evade

- Insertion a title at the foot of a page with the subsequent text on the next page
- Separating a table/chart or figure - impound each figure/table to a single page
- Submitting a manuscript with pages out of sequence

In every sections of your document

· Use standard writing style including articles ("a", "the," etc.)

· Keep on paying attention on the research topic of the paper

· Use paragraphs to split each significant point (excluding for the abstract)

· Align the primary line of each section

· Present your points in sound order

· Use present tense to report well accepted

· Use past tense to describe specific results

· Shun familiar wording, don't address the reviewer directly, and don't use slang, slang language, or superlatives

· Shun use of extra pictures - include only those figures essential to presenting results

Title Page:

Choose a revealing title. It should be short. It should not have non-standard acronyms or abbreviations. It should not exceed two printed lines. It should include the name(s) and address (es) of all authors.

Abstract:

The summary should be two hundred words or less. It should briefly and clearly explain the key findings reported in the manuscript--must have precise statistics. It should not have abnormal acronyms or abbreviations. It should be logical in itself. Shun citing references at this point.

An abstract is a brief distinct paragraph summary of finished work or work in development. In a minute or less a reviewer can be taught the foundation behind the study, common approach to the problem, relevant results, and significant conclusions or new questions.

Write your summary when your paper is completed because how can you write the summary of anything which is not yet written? Wealth of terminology is very essential in abstract. Yet, use comprehensive sentences and do not let go readability for briefness. You can maintain it succinct by phrasing sentences so that they provide more than lone rationale. The author can at this moment go straight to shortening the outcome. Sum up the study, with the subsequent elements in any summary. Try to maintain the initial two items to no more than one ruling each.

- Reason of the study - theory, overall issue, purpose
- Fundamental goal
- To the point depiction of the research
- Consequences, including definite statistics - if the consequences are quantitative in nature, account quantitative data; results of any numerical analysis should be reported
- Significant conclusions or questions that track from the research(es)

Approach:

- Single section, and succinct
- As a outline of job done, it is always written in past tense
- A conceptual should situate on its own, and not submit to any other part of the paper such as a form or table
- Center on shortening results - bound background information to a verdict or two, if completely necessary
- What you account in an conceptual must be regular with what you reported in the manuscript
- Exact spelling, clearness of sentences and phrases, and appropriate reporting of quantities (proper units, important statistics) are just as significant in an abstract as they are anywhere else

Introduction:

The **Introduction** should "introduce" the manuscript. The reviewer should be presented with sufficient background information to be capable to comprehend and calculate the purpose of your study without having to submit to other works. The basis for the study should be offered. Give most important references but shun difficult to make a comprehensive appraisal of the topic. In the introduction, describe the problem visibly. If the problem is not acknowledged in a logical, reasonable way, the reviewer will have no attention in your result. Speak in common terms about techniques used to explain the problem, if needed, but do not present any particulars about the protocols here. Following approach can create a valuable beginning:

- Explain the value (significance) of the study
- Shield the model - why did you employ this particular system or method? What is its compensation? You strength remark on its appropriateness from a abstract point of vision as well as point out sensible reasons for using it.
- Present a justification. Status your particular theory (es) or aim(s), and describe the logic that led you to choose them.
- Very for a short time explain the tentative propose and how it skilled the declared objectives.

Approach:

- Use past tense except for when referring to recognized facts. After all, the manuscript will be submitted after the entire job is done.
- Sort out your thoughts; manufacture one key point with every section. If you make the four points listed above, you will need a least of four paragraphs.

- Present surroundings information only as desirable in order hold up a situation. The reviewer does not desire to read the whole thing you know about a topic.
- Shape the theory/purpose specifically - do not take a broad view.
- As always, give awareness to spelling, simplicity and correctness of sentences and phrases.

Procedures (Methods and Materials):

This part is supposed to be the easiest to carve if you have good skills. A sound written Procedures segment allows a capable scientist to replacement your results. Present precise information about your supplies. The suppliers and clarity of reagents can be helpful bits of information. Present methods in sequential order but linked methodologies can be grouped as a segment. Be concise when relating the protocols. Attempt for the least amount of information that would permit another capable scientist to spare your outcome but be cautious that vital information is integrated. The use of subheadings is suggested and ought to be synchronized with the results section. When a technique is used that has been well described in another object, mention the specific item describing a way but draw the basic principle while stating the situation. The purpose is to text all particular resources and broad procedures, so that another person may use some or all of the methods in one more study or referee the scientific value of your work. It is not to be a step by step report of the whole thing you did, nor is a methods section a set of orders.

Materials:

- Explain materials individually only if the study is so complex that it saves liberty this way.
- Embrace particular materials, and any tools or provisions that are not frequently found in laboratories.
- Do not take in frequently found.
- If use of a definite type of tools.
- Materials may be reported in a part section or else they may be recognized along with your measures.

Methods:

- Report the method (not particulars of each process that engaged the same methodology)
- Describe the method entirely
- To be succinct, present methods under headings dedicated to specific dealings or groups of measures
- Simplify - details how procedures were completed not how they were exclusively performed on a particular day.
- If well known procedures were used, account the procedure by name, possibly with reference, and that's all.

Approach:

- It is embarrassed or not possible to use vigorous voice when documenting methods with no using first person, which would focus the reviewer's interest on the researcher rather than the job. As a result when script up the methods most authors use third person passive voice.
- Use standard style in this and in every other part of the paper - avoid familiar lists, and use full sentences.

What to keep away from

- Resources and methods are not a set of information.
- Skip all descriptive information and surroundings - save it for the argument.
- Leave out information that is immaterial to a third party.

Results:

The principle of a results segment is to present and demonstrate your conclusion. Create this part a entirely objective details of the outcome, and save all understanding for the discussion.

The page length of this segment is set by the sum and types of data to be reported. Carry on to be to the point, by means of statistics and tables, if suitable, to present consequences most efficiently.You must obviously differentiate material that would usually be incorporated in a study editorial from any unprocessed data or additional appendix matter that would not be available. In fact, such matter should not be submitted at all except requested by the instructor.

Content

- Sum up your conclusion in text and demonstrate them, if suitable, with figures and tables.
- In manuscript, explain each of your consequences, point the reader to remarks that are most appropriate.
- Present a background, such as by describing the question that was addressed by creation an exacting study.
- Explain results of control experiments and comprise remarks that are not accessible in a prescribed figure or table, if appropriate.
- Examine your data, then prepare the analyzed (transformed) data in the form of a figure (graph), table, or in manuscript form.

What to stay away from

- Do not discuss or infer your outcome, report surroundings information, or try to explain anything.
- Not at all, take in raw data or intermediate calculations in a research manuscript.
- Do not present the similar data more than once.
- Manuscript should complement any figures or tables, not duplicate the identical information.
- Never confuse figures with tables - there is a difference.

Approach

- As forever, use past tense when you submit to your results, and put the whole thing in a reasonable order.
- Put figures and tables, appropriately numbered, in order at the end of the report
- If you desire, you may place your figures and tables properly within the text of your results part.

Figures and tables

- If you put figures and tables at the end of the details, make certain that they are visibly distinguished from any attach appendix materials, such as raw facts
- Despite of position, each figure must be numbered one after the other and complete with subtitle
- In spite of position, each table must be titled, numbered one after the other and complete with heading
- All figure and table must be adequately complete that it could situate on its own, divide from text

Discussion:

The Discussion is expected the trickiest segment to write and describe. A lot of papers submitted for journal are discarded based on problems with the Discussion. There is no head of state for how long a argument should be. Position your understanding of the outcome visibly to lead the reviewer through your conclusions, and then finish the paper with a summing up of the implication of the study. The purpose here is to offer an understanding of your results and hold up for all of your conclusions, using facts from your research and generally accepted information, if suitable. The implication of result should be visibly described. Infer your data in the conversation in suitable depth. This means that when you clarify an observable fact you must explain mechanisms that may account for the observation. If your results vary from your prospect, make clear why that may have happened. If your results agree, then explain the theory that the proof supported. It is never suitable to just state that the data approved with prospect, and let it drop at that.

- Make a decision if each premise is supported, discarded, or if you cannot make a conclusion with assurance. Do not just dismiss a study or part of a study as "uncertain."
- Research papers are not acknowledged if the work is imperfect. Draw what conclusions you can based upon the results that you have, and take care of the study as a finished work
- You may propose future guidelines, such as how the experiment might be personalized to accomplish a new idea.
- Give details all of your remarks as much as possible, focus on mechanisms.
- Make a decision if the tentative design sufficiently addressed the theory, and whether or not it was correctly restricted.
- Try to present substitute explanations if sensible alternatives be present.
- One research will not counter an overall question, so maintain the large picture in mind, where do you go next? The best studies unlock new avenues of study. What questions remain?
- Recommendations for detailed papers will offer supplementary suggestions.

Approach:

- When you refer to information, differentiate data generated by your own studies from available information
- Submit to work done by specific persons (including you) in past tense.
- Submit to generally acknowledged facts and main beliefs in present tense.

Please carefully note down following rules and regulation before submitting your Research Paper to Global Journals Inc. (US):

Segment Draft and Final Research Paper: You have to strictly follow the template of research paper. If it is not done your paper may get rejected.

- The **major constraint** is that you must independently make all content, tables, graphs, and facts that are offered in the paper. You must write each part of the paper wholly on your own. The Peer-reviewers need to identify your own perceptive of the concepts in your own terms. NEVER extract straight from any foundation, and never rephrase someone else's analysis.

- Do not give permission to anyone else to "PROOFREAD" your manuscript.

- Methods to avoid Plagiarism is applied by us on every paper, if found guilty, you will be blacklisted by all of our collaborated research groups, your institution will be informed for this and strict legal actions will be taken immediately.)
- To guard yourself and others from possible illegal use please do not permit anyone right to use to your paper and files.

Criterion for Grading a Research Paper (Compilation)
by Global Journals Inc. (US)

Please note that following table is only a Grading of "Paper Compilation" and not on "Performed/Stated Research" whose grading solely depends on Individual Assigned Peer Reviewer and Editorial Board Member. These can be available only on request and after decision of Paper. This report will be the property of Global Journals Inc. (US).

Topics	Grades		
	A-B	**C-D**	**E-F**
Abstract	Clear and concise with appropriate content, Correct format. 200 words or below	Unclear summary and no specific data, Incorrect form Above 200 words	No specific data with ambiguous information Above 250 words
Introduction	Containing all background details with clear goal and appropriate details, flow specification, no grammar and spelling mistake, well organized sentence and paragraph, reference cited	Unclear and confusing data, appropriate format, grammar and spelling errors with unorganized matter	Out of place depth and content, hazy format
Methods and Procedures	Clear and to the point with well arranged paragraph, precision and accuracy of facts and figures, well organized subheads	Difficult to comprehend with embarrassed text, too much explanation but completed	Incorrect and unorganized structure with hazy meaning
Result	Well organized, Clear and specific, Correct units with precision, correct data, well structuring of paragraph, no grammar and spelling mistake	Complete and embarrassed text, difficult to comprehend	Irregular format with wrong facts and figures
Discussion	Well organized, meaningful specification, sound conclusion, logical and concise explanation, highly structured paragraph reference cited	Wordy, unclear conclusion, spurious	Conclusion is not cited, unorganized, difficult to comprehend
References	Complete and correct format, well organized	Beside the point, Incomplete	Wrong format and structuring

INDEX

Global Journal of Science Frontier Research

Visit us on the Web at www.GlobalJournals.org | www.JournalofScience.org
or email us at helpdesk@globaljournals.org

ISSN 9755896