Arkivoc
Archive for
Organic Chemistry

The Free Internet Journal
for Organic Chemistry

Review

Arkivoc 2018, part vi, 0-0

Naturally occurring taiwaniaquinoids: biosynthetic relationships and synthetic approaches

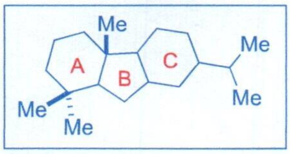
Vishnumaya Bisai,*[a] Aditi Gupta,[b] and Alakesh Bisai*[c]

[a]Department of Chemistry, Indian Institute of Science Education and Research Berhampur, Government ITI, Engineering School Junction, Berhampur, Odisha 760 010, India; [b]*Department of Chemistry, St. Stephen's College, Delhi University, India;* [c]*Department of Chemistry, Indian Institute of Science Education and Research Bhopal, Bhauri, Bhopal – 462066, Madhya Pradesh, India*
Email: vishnumayabisai@gmail.com; alakesh@iiserb.ac.in

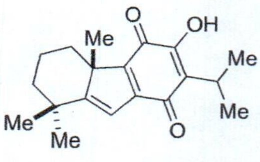
Received 05-20-2018 **Accepted** 07-11-2018 **Published on line** 09-01-2018

Abstract

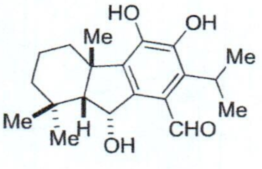
The diterpenoids possessing a fused 6,5,6-*abeo*-abietane skeleton (**1**, Figure 1) have gained interest from synthetic community owing to their significant biological properties in addition to interesting complex architecture. These are a family of carbotricyclic diterpenoids bearing an unusual 4a-methyltetra- (and hexa-) hydrofluorene skeleton with an all-carbon quaternary stereocenter. A number of *abeo*-abietanes isolated from different East Asian conifers viz. Taiwanese pine tree *Taiwania cryptomerioides* and hence they are popularly named as the taiwaniaquinoids. In this review article, we discuss on the biosynthetic proposal as well as recent efforts on the total syntheses of naturally occurring complex taiwaniaquinoids.



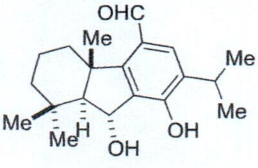
abeo-abietane skeleton (**1**)



dichroanone (**1a**)



dichroanal A (**1b**)



standishinal (**1c**)

Keywords: Taiwaniaquinoids, *abeo*-abietane diterpenoids, natural products, total synthesis, biological activities

PRINCIPAL
ST. STEPHEN'S COLLEGE
DELHI-110007

DOI: https://doi.org/10.24820/ark.5550190.p010.631

Journal of Inclusion Phenomena and Macrocyclic Chemistry
https://doi.org/10.1007/s10847-018-0801-5

ORIGINAL ARTICLE

Influence of polyether chain on the non-covalent interactions and stability of the conformers of calix[4]crown ethers

Satish Kumar[1] · **Jaspreet Kaur**[1] · **Anjai Verma**[2] · **Mukesh**[3] · **Arun Kumar**[1] · **Sojkumar Dominic**[1]

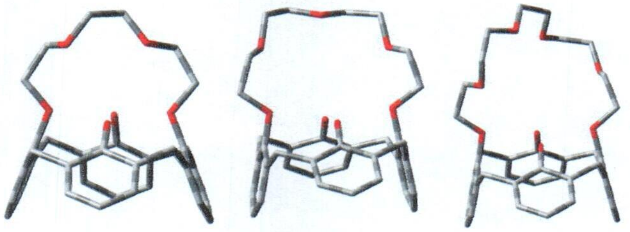
Received: 8 November 2017 / Accepted: 24 March 2018

Abstract

Conformational preferences of the calix[4]crown-(4,5,6,7)-ethers were studied utilizing HF/6-31G(d), B3LYP/6-31G(d), B3LYP/6-311G(d), MPWB95/6-31G(d), MPWIPW91/6-31G(d) and M062X/6-31G(d) methods. DFT-D3 (Becke–Johnson) dispersion correction method was also employed. The results acquired from the analysis of the computational data indicated that the stability of conformers of calix[4]crown-(4,5,6,7)-ethers follows the order; cone conformer > partial cone conformer > 1,3-alternate conformer. It was initially assessed, in general, that both hydrogen bond and OH···π interactions play a crucial role in determining the stability of the different conformers. It was further observed that the strength of both H-bond and OH···π interactions, are dependent on the length of the polyether bridge. Hence, in order to comprehend them better, the effect of these interactions was studied systematically on the conformational stability of different isomers. It is found that both intramolecular hydrogen bonds and O–H···π interactions are mainly responsible for relative stabilities of these conformers, which in turn is also dependent on the length of the polyether bridges.

Graphical Abstract

The computational study reported here demonstrate that the size of the polyether bridge along with non-covalent interactions such as hydrogen bond and OH···π interactions play an important role in determining the stability of the conformers of calix[4]crown ethers.



Keywords Calix[4]crown ether · Calixarenes · Computational methods · Calix[4]crown ether conformers · Crown ether

Introduction

Development of synthetic molecular receptors, for selective recognition of important guest molecules, is an area of intense research [1–3]. The recognition of guest species by the synthetic receptor is largely controlled by forces resulting from non-bonding or non-covalent electrostatic and dispersion (intermolecular and intramolecular) interactions. A variety of supramolecular receptors based on calix[n]arene, cyclodextrin, cyclotriveratrylene and crown ethers are available for trapping ionic and molecular species [1–3]. Among a variety of

---

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10847-018-0801-5) contains supplementary material, which is available to authorized users.

✉ Satish Kumar
satish@ststephens.edu

[1] Department of Chemistry, St. Stephen's College, University Enclave, Delhi 110007, India

[2] Department of Chemistry, Atma Ram Sanatan Dharma College (University of Delhi), Delhi 110021, India

[3] Department of Chemistry, Keshav Mahavidyalaya (University of Delhi), Delhi 110034, India

کلامِ اقبال میں تارے کی معنوی جہات

ڈاکٹر شمیم احمد

سینٹ اسٹیفنز کالج، دہلی یونیورسٹی، دہلی

علامہ اقبال نے اپنے پیغام کی ترسیل کے لیے اظہار کے مختلف اسالیب کو اس طرح برتا کہ ان کا کلام فکر وفن کے اعتبار سے خصوصی انفرادیت کا حامل ہو گیا۔ اس میں اعلیٰ ادبی شان پیدا ہو گئی، معنی کی ایک دنیا آباد ہو گئی جو قاری کو نئے نئے جہانوں کی سیر کراتی ہے، نئے نئے اشخاص سے روشناس کراتی ہے، نئے نئے موضوعات پر سیر حاصل تبصرے کرتی ہے، شاعری کی نئی سے نئی تحسین کا موقع فراہم کرتی ہے اور لطافت وخطابت سے آمیز مخصوص اندازِ بیان سے اردو ادب کو عالمی معیار عطا کرتی ہے۔ فطرت کے مشاہدات کا بیان اردو شاعری میں نیا نہیں، ہر عہد میں ہر شاعر نے اپنی اپنی صلاحیتوں کے مطابق فطرت یا قدرتی مظاہر کے بیان سے اپنے کلام کو زینت بخشی ہے۔ تاہم فطرت کے مشاہدات کی جو افراط علامہ اقبال کے کلام میں نظر آتی ہے وہ ہمارے دوسرے شعرا کے یہاں ناپید ہے۔ بات صرف افراط کی نہیں، اقبال نے فطری مظاہر کے بیان سے جو کام لیا ہے۔ جس طرح انھیں زبان عطا کی ہے اور ان کے ذریعے اپنے پیغام میں زور اور تاکید پیدا کی ہے وہ اپنی مثال آپ ہے۔ اولین مجموعۂ کلام کا تو آغاز ہی فطرت کے ایک بہت بڑے مظہر 'ہمالہ' سے ہوتا ہے اور اسی نظم سے بانگِ درا کا مزاج اور آہنگ طے ہو جاتا ہے کہ یہ کلام ہمالہ ہی کی طرح بلند، گردشِ ایام کے اثرات سے پاک اور آفاقی نوعیت کا حامل ہے۔ اقبال نے اس نظم میں ہمالہ کی چوٹیوں کو ثریا سے سرگرمِ سخن قرار دیا ہے جب کہ ان کے کلام کا مطالعہ اس بات کا بیّن ثبوت ہے کہ وہ بہ نفسِ نفیس ثریا سے سرگرمِ سخن ہیں۔ بلکہ وہ تو ثریا کو بھی خاطر میں نہیں لاتے۔ ان کی نظر تو اس مقام پر رہتی ہے جہاں تک رسائی انجم کو سہادیتی ہے، اندیشوں میں مبتلا کر دیتی ہے کہ یہ ٹوٹا ہوا تارہ مہِ کامل کی معراج پر نہ پہنچ جائے۔

فطرت کے دیگر مظاہر کے مقابلے اقبال نے اپنے کلام میں جس کثرت سے تاروں کا ذکر کیا ہے اس سے ظاہر ہوتا ہے کہ انہیں اس مظہر سے خصوصی شغف ہے۔ تمام کلام میں جا بجا بکھرے تاروں اور ستاروں کے حوالوں سے قطعِ نظر صرف بانگِ درا میں ہی 7 نظمیں ایسی ہیں جو براہِ راست ستاروں کے عنوان پر ہیں۔ 'صبح کا ستارہ، اخترِ صبح، چاند اور تارے، ستارہ، دو ستارے، بزمِ انجم اور 'شبنم اور ستارہ' میں اقبال نے ان تاروں کے ذریعے اپنے پیغام کو روشن وتابناک بنایا ہے۔ کسی نظم میں ان تاروں کو اپنے ڈوبنے کا خوف ستاتا ہے۔ کسی نظم میں یہ تارے اپنی تھکن کا اظہار کرتے ہیں اور چاند ان مزرعِ شب کے خوشہ چینوں کو مشورہ دیتا ہے کہ جنبش سے ہے زندگی جہاں کی۔ کسی نظم میں دو ستارے آپس میں ملنے کی خواہش کا اظہار کرتے ہیں، لیکن جانتے ہیں کہ وصال کی یہ تمنا سراپا فراق کا حکم رکھتی ہے۔ کہیں انھیں تاروں کو شرابِ تقدیر میں مست قرار دے کر اور انھیں زندانِ فلک میں پابہ زنجیر بتا کر قدرت کی اس ستم ظریفی کا شکوہ کیا ہے:

کوئی نہیں غم گسارِ انساں
کیا تلخ ہے روزگارِ انساں

نظم بزمِ انجم میں انہی تاروں کی زبانی اقبال نئے اصولوں اور نئے قوانین کو پرکھنے اور اختیار کرنے کا وہ پیغام سناتے ہیں جو ضرب المثل کے طور پر موقع بہ موقع دہرایا جاتا ہے:

آئینِ نو سے ڈرنا، طرزِ کہن پہ اڑنا
منزل یہی کٹھن ہے، قوموں کی زندگی میں

تاروں کی زبانی اقبال کا پیام نظم کے آخری دو اشعار میں اپنے نقطۂ عروج کو پہنچتا ہے اور تارے فرماتے ہیں:

اک عمر میں نہ سمجھے اس کو زمین والے
جو بات پا گئے ہم تھوڑی سی زندگی میں
ہیں جذبِ باہمی سے قائم نظام سارے
پوشیدہ ہے یہ نکتہ تاروں کی زندگی میں

اتحاد ویگانگت کا یہ پیغام اقبال کے اس شعر کی یاد دلاتا ہے جس

اختر الایمان کی نظم گوئی

ڈاکٹر شمیم احمد

سینٹ اسٹیفنز کالج، دہلی یونی ورسٹی، دہلی

اختر الایمان کی شاعری قدامت سے جدت، پابندی سے آزادی اور وسعت سے بے کرانی کی طرف سفر ہے۔ ان کی نظموں میں نئی زندگی اور نئے ماحول کی ترجمانی نظر آتی ہے وہ ان موضوعات کی طرف توجہ کرتے ہیں جن کا بیان اُن سے پہلے نہیں ہوا ہے۔ انسان کی ذہنی اور جذباتی کیفیات، اس کی داخلی اور خارجی دنیا، انفرادی اور اجتماعی زندگی کے مختلف معاملات و مسائل ان کی نظموں کے نمائندہ موضوعات ہیں۔ وہ روایتی قسم کے رومانی موضوعات پر توجہ نہیں کرتے اس کے برعکس ان کی نظموں میں اپنے عہد کی سماجی زندگی سے مایوسی کا اظہار نظر آتا ہے۔ اپنے عہد کے انسان کی خود غرضی، تشدد اور جارحیت پسندی سے انھیں خاص کد ہے۔ ان کی شاعری کا متکلم ایسا شخص ہے جس نے دنیا میں امن و سکون اور محبت و عافیت کی خواہش کی تھی، جو اپنے خوابوں کی دنیا کا شیش محل سجانا چاہتا تھا، جس کی آرزو تھی کہ یہ دنیا گلوں کا مسکن ہو، زمین کے سینے سے شگوفے پھوٹیں، نئی بہاریں قائم ہوں، فرازِ کوہ سے تیز اور تند آبشاریں بہیں۔ کوئی ایسا ہو جس کی آغوش میں اسے سکون مل سکے۔ لیکن جب اختر الایمان نے اپنے خوابوں کی اس دنیا کو ٹوٹتے پایا تو خدا سے شکوہ کیا:

مگر مجھے کیا دیا یہ تو نے
شباب اک زہر میں بجھا کر
خراب آنکھیں لہو رُلا کر
خدائے عالم، بلند و برتر
نہ ایک مونس بھی ایسا بخشا
کہ جس کی آغوش میں تڑپ کر
سکون کے ساتھ مر سکوں میں

ایک مخلص اور ایمان دار شاعر کی طرح اختر الایمان ہر وہ بات بیان کرتے چلے جاتے ہیں جو ان کے دل پر گزرتی ہے۔ کسی تحریک کا کوئی منشور، کسی رجحان کا کوئی ضابطہ ان کے اس شعری خلوص میں مانع نہیں آتا۔ وہ تقلید کے قائل نہیں اپنی راہ الگ بنانا چاہتے ہیں اور انھیں اس بات کا سلیقہ بھی ہے کہ اپنے موضوعات کو کس طرح طاقتِ پرواز دی جائے کہ دل سے نکلی ہوئی بات پر اثر بھی بن جائے۔ اختر الایمان کے ہاں رمزیت بھی ہے اشاریت بھی جن سے معنی و مفہوم کی ایک دنیا آباد ہو گئی ہے جو قاری کو نئے نئے

ACS Chemical Neuroscience
Research Article
Cite This: ACS Chem. Neurosci. 2019, 10, 1462−1477
pubs.acs.org/chemneuro

Amyloid-β Peptide Targeting Peptidomimetics for Prevention of Neurotoxicity

Dmytro Honcharenko,[*,†] Alok Juneja,[†] Firoz Roshan,[‡] Jyotirmoy Maity,[†] Lorena Galán-Acosta,[§] Henrik Biverstål,[§,∥] Erik Hjorth,[§] Jan Johansson,[§] André Fisahn,[‡] Lennart Nilsson,[†] and Roger Strömberg[*,†]

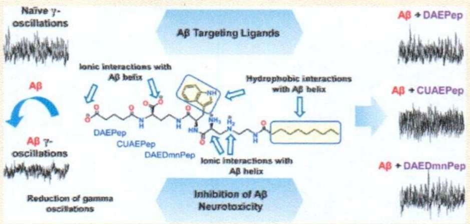
[†]Department of Biosciences and Nutrition, Karolinska Institutet, 14183 Huddinge, Sweden

[‡]Neuronal Oscillations Laboratory, Neurogeriatrics Division, Center for Alzheimer Research, Department of Neurobiology, Care Sciences and Society, Karolinska Institutet, 17164 Solna, Sweden

[§]Division for Neurogeriatrics, Department of Neurobiology, Care Sciences and Society, Karolinska Institutet, 14183 Stockholm, Sweden

[∥]Department of Physical Organic Chemistry, Latvian Institute of Organic Synthesis, Riga LV-1006, Latvia

Supporting Information



ABSTRACT: A new generation of ligands designed to interact with the α-helix/β-strand discordant region of the amyloid-β peptide (Aβ) and to counteract its oligomerization is presented. These ligands are designed to interact with and stabilize the Aβ central helix (residues 13−26) in an α-helical conformation with increased interaction by combining properties of several first-generation ligands. The new peptide-like ligands aim at extended hydrophobic and polar contacts across the central part of the Aβ, that is, "clamping" the target. Molecular dynamics (MD) simulations of the stability of the Aβ central helix in the presence of a set of second-generation ligands were performed and revealed further stabilization of the Aβ α-helical conformation, with larger number of polar and nonpolar contacts between ligand and Aβ, compared to first-generation ligands. The synthesis of selected novel Aβ-targeting ligands was performed in solution via an active ester coupling approach or on solid-phase using an Fmoc chemistry protocol. This included incorporation of aliphatic hydrocarbon moieties, a branched triamino acid with an aliphatic hydrocarbon tail, and an amino acid with a 4′-*N*,*N*-dimethylamino-1,8-naphthalimido group in the side chain. The ability of the ligands to reduce $A\beta_{1-42}$ neurotoxicity was evaluated by gamma oscillation experiments in hippocampal slice preparations. The "clamping" second-generation ligands were found to be effective antineurotoxicity agents and strongly prevented the degradation of gamma oscillations by physiological concentration of monomeric $A\beta_{1-42}$ at a stoichiometric ratio.

KEYWORDS: *Alzheimer's disease, amyloid-β peptide, synthetic ligands, α-helical conformation, molecular dynamics, gamma oscillations*

■ INTRODUCTION

Alzheimer's disease (AD) is a progressive neurodegenerative disorder and the most common cause of dementia, accounting for about 60% of all cases.[1,2] AD belongs to the group of conformational diseases, which arise from protein misfolding and aggregation,[3,4] and is associated with cerebral extracellular deposits, called plaques, which are mainly composed of amyloid fibrils formed from the amyloid-β peptide (Aβ).[5,6] According to the amyloid cascade hypothesis, the aggregation of soluble Aβ and formation of insoluble fibrillar Aβ in plaques is the central pathogenic event in AD.[7−9] However, numerous studies indicate that the prefibrillar soluble oligomers, which are produced early in the aggregation pathway, possess a toxic nature.[10−12]

Currently available treatments of AD are only symptomatic, do not stop the neurodegenerative process, and only delay the development of symptoms.[13] However, substantial efforts are being focused on the development of methods to prevent the occurrence or progression of AD.[14] Several strategies[13,15] have been proposed to achieve inhibition of fibrillization/oligomerization of Aβ, which also include targeting of Aβ in an elongated, β-strand-like conformation with a range of small organic molecules or peptide-based inhibitors.[16] The main problems of these approaches are lack of specificity and potential accumulation of cytotoxic soluble, nonfibrillar Aβ aggregates.[17] Other strategies such as inhibition of the secretase enzymes[18,19] and passive or active immunization[20] may have their limitations through interference with important physiological functions or development of undesirable side effects.[21]

Received: September 12, 2018
Accepted: January 23, 2019
Published: January 23, 2019

DOI: 10.1021/acschemneuro.8b00485
ACS Chem. Neurosci. 2019, 10, 1462−1477

ChemPubSoc Europe
DOI: 10.1002/slct.201900809
ChemistrySELECT Full Papers

Medicinal Chemistry & Drug Discovery

Synthesis of 6′-Methyl-2′-*O*,4′-*C*-methylene-*α*-L-ribofuranosyl-pyrimidine Nucleosides

Priyanka Mangla,[a] Jyotirmoy Maity,[a] Pallavi Rungta,[a] Vineet Verma,[a] Yogesh S. Sanghvi,[b] and Ashok K. Prasad*[a]

Herein, we report the efficient synthesis of (6′*R*)- and (6′*S*)-6′-methyl-2′-*O*,4′-*C*-methylene-*α*-L-ribofuranosyl-thymine, and (6′*R*)- and (6′*S*)-6′-methyl-2′-*O*,4′-*C*-methylene-*α*-L-ribofuranosyl-uracil starting from diacetone glucofuranose in overall yields of 6.3, 4.7, 5.4 and 4.0%, respectively. The key step in the synthesis of stereochemically defined 6′-Me-bicyclic-nucleosides is the nucleophilic addition of methyl group at methylene carbon of 4-C-CH_2OH moiety of the 4-*C*-*tert*-butyldiphenylsilyloxymethylated sugar precursor. Thus, the methyl group was added on the aldehyde obtained from Dess-Martin periodinane oxidation of the precursor alcohol employing $AlMe_3$ in hexane. Both (6′*R*)- and (6′*S*)-stereoisomers of bicyclic nucleosides T and U were successfully synthesized following Vorbrüggen nucleobase coupling of T and U with triacetylated glycosyl donor obtained from acetolysis of (5*R*)- and (5 *S*)-4-*C*-(*tert*-butyldiphenylsilyloxymethyl)-5-*C*-methyl-1,2-*O*-isopropylidene-3-*O*-(2-naphthylmethyl)-*α*-D-xylofuranoses and further cyclization and deprotection of the resulted nucleoside. One of the nucleosides, (6′*R*)-6′-methyl-2′-*O*,4′-*C*-methylene-*α*-L-ribofuranosyl-uracil has been reported earlier in 1.8% yield, while the present methodology yielded the nucleoside in 5.4% yield. All the synthesized 6′-Me-bicyclic-nucleosides showed no significant anti-viral activity against H1 N1 strain of influenza A virus (A/Puerto Rico/8/1934).

Introduction

The use of modified oligonucleotides to modulate the expression of diseased gene is a promising drug discovery platform.[1,2] However, modified oligonucleotides cannot act as drug entity unless the modification is helpful in improving its affinity towards mRNA and enhancing its metabolic stability towards nucleases.[3] The sugar modifications, such as 2′-F, 2′-OMe and 2′-*O*,4′-*C*-methylene bridge are being widely used to achieve the effectiveness of oligonucleotides.[4] Structurally modified 2′-*O*,4′-*C*-methyleneribofuranosyl-nucleosides (LNA monomers) feature remarkable control over sugar-ring puckering and therefore oligonucleotides derived from them have been extensively used as antisense oligonucleotides (ASOs) to modulate gene expression (Figure 1).[5–8] Some of them have now entered into clinical trials for the treatment of diseases, such as infection of hepatitis C virus,[9,10] spinal muscular atrophy,[11] prostate cancer,[12] etc. Although, ASOs involving 2′-*O*,4′-*C*-methyleneribofuranosyl-nucleosides are known for high affinity recognition, their use is also accompanied with the risk of hepatotoxicity.[13] This has persuaded researchers to explore modifications in their scaffold in pursuit of mitigation of the toxic effect while maintaining the antisense activity.[5,14–25] Among other modifications, methyl substitution at their methylene bridge, *i. e.* 6′-methyl-2′-*O*,4′-*C*-methyleneribofuranosyl-nucleosides have exhibited interesting properties (Figure 1).[16] The methyl group of oligonucleotides derived from (6′*S*)-6′-methyl-2′-*O*,4′-*C*-methyleneribofuranosyl-nucleosides direct inside the minor groove exhibiting similar potency as 2′-*O*,4′-*C*-methyleneribofuranosyl-nucleosides, but with improved safety profiles.[26–28] Seth *et al.*[29] have reported the synthesis of (6′*R*)-6′-methyl-2′-*O*,4′-*C*-methylene-*α*-L-ribofuranosyl-uracil and oligonucleotides involving it, and have studied their duplex stability. The methyl substitution on 2′-*O*,4′-*C* methylene bridge

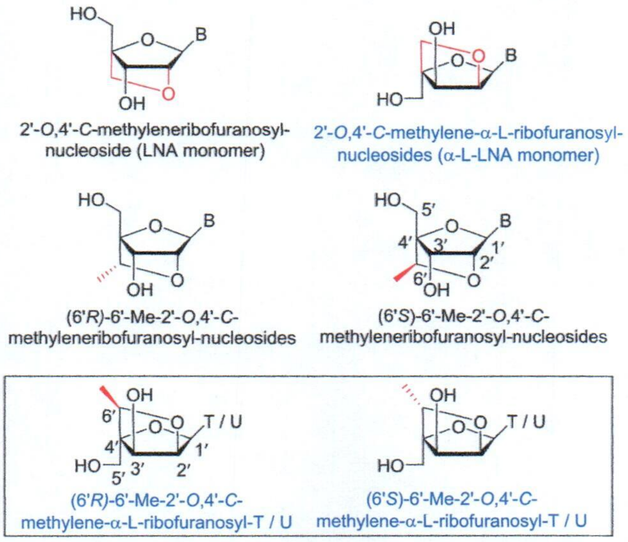


Figure 1. Structures of 2′-*O*,4′-*C*- / 6′-methyl-2′-*O*,4′-*C*-methyleneribofuranosyl-nucleosides.

---

[a] *P. Mangla, Dr. J. Maity, Dr. P. Rungta, V. Verma, Prof. A. K. Prasad*
Bioorganic Laboratory, Department of Chemistry, University of Delhi, Delhi-110 007, India
E-mail: ashokenzyme@gmail.com
[b] *Dr. Y. S. Sanghvi*
Rasayan Inc., 2802 Crystal Ridge Road, Encinitas, CA 92024–6615, U.S.A

Supporting information for this article is available on the WWW under https://doi.org/10.1002/slct.201900809

SYNTHETIC COMMUNICATIONS®
2019, VOL. 49, NO. 15, 1906–1912
https://doi.org/10.1080/00397911.2019.1606921

Taylor & Francis
Taylor & Francis Group

Bamford-Stevens reaction assisted synthesis of styrene *C*-glycosides

Balram Singh, Sandeep Kumar, Jyotirmoy Maity, Indrajit Roy, and Ashok K. Prasad

Bioorganic Laboratory, Department of Chemistry, University of Delhi, Delhi, India

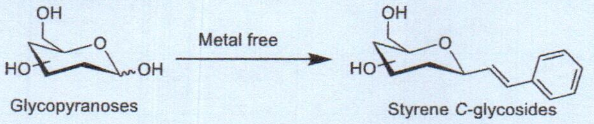
ABSTRACT

Modification of carbohydrates and their analogs is hindered due to multi-step synthetic methodologies involving selective protection and deprotection of multiple hydroxyl groups present in the molecule. A highly efficient route for the synthesis of 1-phenyl-2-(*β*-D-glycopyranosyl)ethenes has been developed from native sugars, which neither requires protection/deprotection of the hydroxyl groups nor use of any metal/metal ions. The key step of the developed methodology is the use of Bamford-Stevens reaction which led to the formation of the desired compounds in moderate to high yields in three steps only.

ARTICLE HISTORY
Received 27 February 2019

KEYWORDS
Bamford-Stevens reaction; carbohydrates; Glycopyranosyl ethenes; styrene *C*-glycoside

GRAPHICAL ABSTRACT



Introduction

C-Glycosides are a family of stable carbohydrate derivatives that have drawn the attention of chemists due to their interesting biological properties.[1–3] They are also used as precursors for the synthesis of *C*-glycoside mimics of glycolipids,[4] oligosaccharides,[5] glycoproteins,[6] and other natural and biologically active compounds.[7,8] The conformation of the native sugars and their *C*-glycosides have very little difference[9] but the pharmacological profile of *C*-glycosides vary significantly from its native *O*-glycosides as the glycosidic C–C bond is not cleavable under normal physiological conditions making them ideal surrogates of native *O*-glycosides as therapeutic agents.[10–13] In spite of various utility and natural origin of many *C*-glycosides,[14] their availability is often hedged by the report of complicated synthesis from corresponding native sugars.

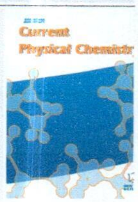
The aim of this study is to develop an efficient metal free synthetic methodology for the preparation of styrene *C*-glycosides, which is a key intermediate molecule en-route to various natural and biologically active carbohydrate derivatives.[15–21] The synthesis of styrene *C*-glycosides reported earlier has been smeared either by inclusion of protection/deprotection steps, use of toxic transition metals or by formation of mixture

CONTACT Ashok K. Prasad ashokenzyme@gmail.com; Indrajit Roy indrajitroy11@gmail.com Bioorganic Laboratory, Department of Chemistry, University of Delhi, Delhi, 110 007, India.

Supplemental data for this article can be accessed the publisher's website.

Current Physical Chemistry, 2018, 8, 232-252

REVIEW ARTICLE



In-silico Molecular Modeling of Low Band Gap Intrinsically Conducting Copolymers

Priyanka Thakral[a], Vimal Rarh[b] and Ashok Kumar Bakhshi[c,*]

[a]Department of Chemistry, St. Stephen's College, University of Delhi, Delhi, India; [b]Department of Chemistry, SGTB Khalsa College, University of Delhi, Delhi, India; [c]Department of Chemistry, PDM University, Bahadurgarh, Haryana, India

Abstract: ***Background***: Over the last four decades, tremendous growth has been witnessed in the field of electrically conducting polymers. A great deal of theoretical and empirical efforts have been made to achieve multifunctional conducting polymeric structures. However, the major challenge in this field is achieving the minimum band gap value which governs various electronic and optoelectronic properties of the structure.

Objective: Artificial optimization *viz*., metaheuristic algorithms have been clubbed with the polymer problem to investigate the electronic properties of copolymers.

Method: Band structures of different homopolymers obtained from *ab-initio* Hartree-Fock crystal orbital method have been used as input to obtain the electronic properties of copolymers using genetic algorithm, ant colony optimization and particle swarm optimization.

Result: Nature-based computing methods employed for tailoring intrinsically conducting copolymers correspond to optimal electronic properties.

Conclusion: This computational cloning approach provides a cost-effective and potent passage for taking forward optimized theoretical solutions to synthetic environment.

ARTICLE HISTORY

Received: July 07, 2018
Revised: October 19, 2018
Accepted: January 29, 2019

DOI:
10.2174/1877946809666190201125603

Keywords: Ant algorithm, artificial intelligence, conducting polymers, copolymerization, electronic properties, genetic algorithm, *in-silico* optimization, particle swarm optimization.

1. INTRODUCTION

1. *In-Silico* Modeling

With a tremendous increase in demand for a variety of low volume high tech components for various applications, it has become important to have exhaustive knowledge of the structure-property relationship for developing smart materials. Almost all the physical and chemical characteristics of importance to an engineer are structure-sensitive, *i.e.*, they can be mutated structurally in significant ways, for instance by changing chemical composition; the arrangement of atoms or molecules; the size, shape and orientation of the units, *etc*. The axiom "*function follows form*" holds true in this regard, *i.e.*, the structure of the molecule - geometric and electronic must contain the attributes responsible for its physical and chemical properties.

The efficient designing of new polymeric structures for various applications requires the predicttion of fundamental properties which can be used to evaluate; screen and help channelize the synthetic route. Today, the need to develop efficient, sustainable, easy to handle, effectively functional and inexpensive polymeric systems for advanced applications has amplified the complexity of the chemical structures of polymers to serve multipurpose applications. Consequently, the development of evaluative methods for predicting the properties of a system under consideration has

---

*Address correspondence to this author at the Department of Chemistry, PDM University, Bahadurgarh, Haryana, India; Tel: +91-8826676577; E-mail: akbakhshi2000@yahoo.com

1877-9476/18 $ 58.00+.00

PRINCIPAL
ST. STEPHEN'S COLLEGE
DELHI-110007

Indian Journal of Chemistry
Vol. 58A, February 2019, pp. 281-287

Notes

Study of Kirkwood-Buff integrals of selected polar and nonpolar amino acids in aqueous-streptomycin sulphate solutions at 298.15 K

Y Bisht[a] & A K Nain[b,*]
[a]Department of Chemistry, Hansraj College
University of Delhi, Delhi 110 007, India
[b]Department of Chemistry, Dyal Singh College
University of Delhi, New Delhi 110 003, India
Email: ak_nain@yahoo.co.in

Received 28 June 2018; revised and accepted 11 January 2019

The Kirkwood-Buff (K-B) integrals play a pivotal role in understanding the physiochemical action of drugs on proteins. The Kirkwood-Buff theory can be used to characterize the intermolecular interactions of amino acids with drug by directly calculating G_{11}, G_{22} and G_{12} parameters which represent solute-solute, solvent-solvent and solute-solvent interactions respectively. The K-B integrals of nonpolar amino acids glycine, L-alanine, L-valine, L-isoleucine and polar amino acids L-histidine and L-arginine in aqueous-streptomycin sulphate solutions (1% and 2% streptomycin sulphate in water, *w/w*) have been calculated from experimental data of ultrasonic speed and density at 298.15 K. All the results obtained by theoretical calculations are in good agreement with those of experimental results.

Keywords: Kirkwood-Buff integrals, Amino acids, Streptomycin sulphate, Apparent molar volumes, Densities, Ultrasonic speeds

The study of thermodynamic stability of the native structure of protein has proved to be quite challenging and still remains a subject of extensive investigation[1]. Owing to the complexities arising from direct thermodynamic study on proteins, investigations of the behaviour of model compound of proteins like amino acids and peptides in aqueous and mixed aqueous solvents make it easy to understand the factor governing their stability[2,3]. To understand the chemistry of biological system, it is important to study properties of amino acids in aqueous-drug solutions[4]. Most of the compounds of medicinal interest undergo a number of complicated interactions of varied nature[5,6]. Drug action has been widely recognized to be the ultimate consequence of physicochemical interactions between the drug and functionally important biomolecules in living organisms. Drugs when administered in the body interact with receptor made up of protein and change their conformation. This makes the body to respond in a particular way. Although various clinical researches are available to optimize the drug dose in human body, the physiochemical study of these drugs with amino acids are still in initial stages[7,8]. Only few reports are available in literature on amino acid-drug interaction[9–18].

Streptomycin sulphate is one such important drug whose physiochemical interaction with protein is not studied in detail yet. It is an antibiotic used to treat a number of bacterial infections including tuberculosis, plague, endocarditis, rat bite fever, etc. Streptomycin binds with highly conserved structure formed by the 16S rRNA, which interacts with ribosomal protein S12. This may lead to the destabilization of its structure which in turn affects the binding of streptomycin with ribosome. This makes the study of amino acid-aqueous streptomycin even more important. In our earlier investigations we studied solute-solute and solute-solvent interactions of nonpolar amino acids glycine/L-alanine/L-valine/L-isoleucine[19] and polar amino acids L-histidine/L-arginine[20] with water and aqueous-streptomycin sulphate [1% (0.0069 mol kg^{-1}) and 2% (0.0137 mol kg^{-1}) streptomycin sulphate in water] solvents by using physicochemical methods using experimental density (ρ), ultrasonic speed (u) and viscosity (η) data.

But there exists one theory which can directly assess all three interactions, i.e., solute-solute, solute-solvent and solvent-solvent simultaneously, known as Kirkwood-Buff theory (K-B theory)[21]. Although people have done work on the theoretical estimation of thermodynamic properties of liquid mixtures[22–32], there are only few reports on theoretical estimation of thermodynamic properties of amino acids[33,34]. In the present study, we have applied K-B theory to evaluate the solute-solute, solute-solvent and solvent-solvent interaction parameters of four nonpolar amino acids: glycine/L-alanine/L-valine/L-isoleucine and two polar amino acids: L-histidine/L-arginine and have studied their interaction with aqueous-streptomycin sulphate (1% and 2% streptomycin sulphate in water, *w/w*). The experimental density and ultrasonic speed data at 298.15 K required for the calculations have been taken from our previous studies[19,20].

BRILL

Worlds of Advice

Going Places with Nazir Ahmad

In: Journal of World Literature

Author: Soofia Siddique[1]

Download Citation

Get Permissions

Get Access

Abstract

This article situates the nineteenth-century Urdu writer Nazir Ahmad's *Chand Pand* as a piece of advice literature on an Arabic-Persian continuum, and equally a text of its time and place. Linguistic features of its discourse show that, as a self-conscious performance of the possibilities of Urdu, it imparts culturally resonant ways of inhabiting a multifarious world, and inscribes an expansive and inclusive view of culture. In particular, the narrative organization of the focal section "A Brief Account of the World" is strongly evocative of a conceptual organization of the world by concentric circles that is comparable to the view of human sociality invoked by the tenth-eleventh century Persian ethicist Miskawayh and illuminates the location of Nazir Ahmad's text in the continuum of ethics (*akhlaq*) literature. At the same time, beside these signs of literary cosmopolitanism, I argue that Nazir Ahmad's account of the world stakes a claim for the irreducible particularity of places and their associated textures of life, and offers a view of the world that supports "place-based thinking or imagination" (Dirlik) as opposed to the potentially obfuscating abstraction of globalized "space."

UGC Approved Journal No – 40957
(IIJIF) Impact Factor- 4.172
Regd. No. : 1687-2006-2007 ISSN 0974 - 7648

JIGYASA

AN INTERDISCIPLINARY PEER REVIEWED REFEREED RESEARCH JOURNAL

Chief Editor : *Indukant Dixit*

Executive Editor : *Shashi Bhushan Poddar*

Editor
Reeta Yadav

Volume 12 May 2019 No. IV

Published by
PODDAR FOUNDATION
Taranagar Colony
Chhittupur, BHU, Varanasi
www.jigyasabhu.blogspot.com
www.jigyasabhu.com
E-mail : jigyasabhu@gmail.com
Mob. 9415390515, 0542 2366370

आशुतोष शुक्ला

PRINCIPAL
ST. STEPHEN'S COLLEGE
DELHI-110007

आशुतोष शुक्ल

PRINCIPAL
ST. STEPHEN'S COLLEGE
DELHI-110007

भूमण्डलीकरण, हिन्दी और संचार माध्यमों का अन्तःसंबंध

आशुतोष शुक्ल *

भूमण्डलीकरण आज के दौर की वह जमीनी सच्चाई है जिसे नकारा नहीं जा सकता। इसने प्रत्येक देश की राजनैतिक, आर्थिक, सामाजिक एवं सांस्कृतिक परिस्थितियो में आमूल-चूल परिवर्तन ला दिया है।

कहा जाता है कि किसी भी देश के नवयुवक उस देश की 'रीढ़' होते हैं। इन नवयुवकों के मानसिक धरातल को तैयार करने में शिक्षा का पूरा योगदान रहता है। शिक्षा व्यक्ति को गढ़ती है और व्यक्ति राष्ट्र को। ऐसी शिक्षा के बदलते स्वरूप में भूमण्डलीकरण का दबाव स्पष्ट दिखलाई पड़ता है। शिक्षा के साथ-साथ शिक्षा की माध्यम भाषा भी इससे प्रभावित हुई है।

भूमण्डलीकरण ने भौगोलिक दूरियों को कम करके दिलों के बीच की दूरी को बढ़ा दिया है। द्रुतसंचार माध्यम विश्व के किसी भी कोने में बैठे व्यक्ति को कुछ ही पलों में आप से जोड़ देते है। संचार माध्यमों की अधिकता व निरन्तर सम्पर्क ने पहले वाली आत्मीयता भुला दी है।

भूमण्डलीकरण में सम्प्रभुता सैद्धांतिक रह जाती है व्यावहारिक नहीं। इसमें प्रत्येक चीज बाजार से निर्धारित एवं नियन्त्रित होती है। बाजार के अनुच्छेदों पर चलने वाला भूमण्डलीकरण इसीलिए मुक्त-व्यापार को बढ़ावा देता है। इसकी दृष्टि में प्रत्येक वस्तु की सार्थकता इसके उपभोग्य रूप में है इसीलिए आज भाषा का भूमण्डलीकरण किया जा सकता है। वस्तुतः भाषा के भूमण्डलीकरण का तात्पर्य भाषा का बाजारीकरण ही है। भूमण्डलीकरण ने भाषा को भी खपत एवं निवेश की वस्तु बना दिया है। अपने माल को बेचने के लिए, उपभोक्ताओं से सम्पर्क अनिवार्य है और इसीलिए भाषा इनके बीच एक माध्यम का कार्य करती है अतः अत्यधिक महत्वपूर्ण हो जाती है। भूमण्डलीकरण उपभोक्ताओं को आकर्षित करने के लिए भाषा को एक औजार के रूप में प्रयोग करते है जिससे इसका रूप बदलता रहता है।

हिन्दी भाषा पूरे देश में समझी जाती है अतः विभिन्न कम्पनियाँ अपने माल को प्रचारित करने के लिए इसी का प्रयोग करती है। इससे जहाँ एक ओर हिन्दी के प्रसार में सुविधा होती है उसका विस्तार क्षेत्र फैलता है वहां दूसरी ओर इसके रूप में भी परिवर्तन होता है। द्विवेदी युग की हिन्दी, छायावाद युग की हिन्दी और आज की हिन्दी में जमीन-आसमान का फर्क दिखलाई पड़ता है।

आशुतोष शुक्ल

---

* शोधार्थी, हिन्दी विभाग, दिल्ली विश्वविद्यालय, दिल्ली

PRINCIPAL
ST. STEPHEN'S COLLEGE
DELHI-110007

3.3.2 2018-19

Journal of Luminescence 201 (2018) 203–210

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

The experimental and theoretical studies of a merocyanine form based turn off fluorescent sensor for Fe^{3+} ions with nanomolar level sensitivity in aqueous solution

Priya Ranjan Sahoo, Satish Kumar*

Department of Chemistry, St. Stephen's College, University Enclave, University of Delhi, Delhi 110007, India

ABSTRACT

A substituted spirooxazine was synthesized and characterized by ^1H, ^{13}C NMR, and HR-MS spectroscopic techniques. The open form of the spirooxazine derivative was evaluated for the detection of Fe^{3+} ions. The colorimetric evaluation revealed that the receptor **1** is highly selective and sensitive towards Fe^{3+} detection and displayed a turn-off fluorescence response with ferric ions through aggregation induced phenomena. No competitive behavior was observed for detection of Fe^{3+} ions by the receptor in the presence of different metal ions. The paper based strips for **1** displayed an excellent selectivity and sensitivity (38 nm, 2.12 ppb) for Fe^{3+} ions. We believe that the receptor **1** could be used as a Fe^{3+} sensor on field detection tool kit. The B3LYP and B3LYP-D3BJ based methods were used to further investigate the stability of the different stereoisomers of merocyanine in order to find a possible mode of binding, while TD-DFT methods were used to study the UV-Visible and fluorescence spectra observed for the receptor.

1. Introduction

Metal ions in trace concentrations are important to human life to support various functions of the body [1]. Among a variety of metal ions present in the human body, iron represents an important nutrient and abundant heavy metal ion in the body of the humans that support life through control over a variety of biological functions such as O_2 transport and catalysis [1–3]. The deficiency of iron in the body may cause disease such as anemia, and is a sign of gastrointestinal malignancy, while the overload of iron in the body may induce cell damage, β-thalassemia, hereditary hemochromatosis, Alzheimer's disease and other organ dysfunction through the production of reactive oxygen [1,3,4]. The Fe^{3+} is the most common oxidation state of iron found in many important biological roles in living systems [1]. In addition, the continuing and alarming instability in the environment due to heavy metal ion pollution require a variety of samples [1]. Although a number of bulky and expensive instrumental techniques like inductively coupled plasma atomic emission spectrometry [5], voltammetry [6,7] and atomic absorption spectrometry [8] are available for determination, which require masking agent or lead to the destruction of samples [1]. There is a great need to develop receptors for the recognition of metal ions such as ferric ions to provide a promising diagnosis [9–12]. The organic receptors provide flexibleness and are capable of producing an optical response during host-guest interaction [11]. Chemically modified receptors can be attuned for promising applications in the areas of analytics recognition and monitoring through the optical response in the form of color or fluorescence change, which can be easily monitored through the naked eye detection, UV-visible or fluorescence spectroscopic techniques [1]. Therefore, there is always a quick need for selective and sensitive optical sensors for the detection of such heavy metal ions. Although some of the receptors for Fe^{3+} ions are reported in the literature, which mostly include, BODIPY derivative [13], rhodamine analog [14,15], benzimidazole derivatives [16], thiazole derivatives [17], metal organic frameworks [18] and caged compounds [19] more investigation surrounding multiple ion recognition needs critical attention [20]. The optical sensors reported in the literature can also produce either a "turn on" or "turn off" fluorescence response [13,21] that improves the detection limit towards the guest species.

Photochromic molecules are also utilized extensively for the development of optical probes and ionic switches for metal ions due to the production of intense color and fluorescence signal upon binding the guest species [22,23]. The photochromic molecules are known to exist in two structurally interconvertible forms that are known as spiro (colorless) and open (merocyanine) forms. The open colored form of photochromic molecules such as spirooxazine is highly polar, which can attract and coordinate the ionic species after suitable substitution,

---

* Corresponding author.
E-mail address: satish@ststephens.edu (S. Kumar).

https://doi.org/10.1016/j.jlumin.2018.04.048
Received 15 February 2018; Received in revised form 3 April 2018; Accepted 22 April 2018

PRINCIPAL
ST. STEPHEN'S COLLEGE
DELHI-110007

Journal of Photochemistry & Photobiology A: Chemistry 364 (2018) 811–818

Contents lists available at ScienceDirect

Journal of Photochemistry & Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

A highly selective sensor for Cu^{2+} and Fe^{3+} ions in aqueous medium: Spectroscopic, computational and cell imaging studies

Shyam Lal[a], Satish Kumar[b], Sunita Hooda[a,*], Pramod Kumar[c,*]

[a] Department of Chemistry, Acharya Narender Dev College (University of Delhi), Kalkaji, New Delhi 110019, India
[b] Department of Chemistry, St. Stephen's College (University of Delhi), New Delhi 110007, India
[c] Department of Chemistry, University of Delhi, New Delhi 110007, India

ARTICLE INFO

Keywords:
Chemosensor
Colorimetric
Reversibility
Logic gate
Cell imaging
Computations

ABSTRACT

A rationally designed chemosensor L1 (2-(2-amino-4,5-dihydrothiazol-4-yl)-5,5-dimethylcyclohexane-1,3-dione) is capable for the detection of biologically important Cu^{2+} and Fe^{3+} ions. The observable change in absorbance and emission in HEPES buffer solution and binding parameters display notable sensing ability of Cu^{2+} and Fe^{3+} ions. From Job's plot and ESI-MS spectra, 1:1 stoichiometric complexation with Cu^{2+} and Fe^{3+} ions have been established. The chemosensor was also utilized to develop logic gate by reversibility cycles for Fe^{3+} ion by EDTA. In addition, complex formation between the receptor and Cu^{2+}/Fe^{3+} ion was investigated by spectroscopically and computational studies. The cell imaging study indicated that L1 is highly efficient for the detection of Fe^{3+} ion in live cells. The simple synthetic route, multi-stimuli response, regenerative action and solution visualization of the proposed chemosensor potentially make it as excellent sensor for real samples.

1. Introduction

Copper and iron are the most plentiful elements in human body and play important roles in fundamental physiological processes [1]. Metallic copper and iron naturally occur in soil, rock and water however, the availability of trace amount of these elements are found in many sea-foods, grain products, nuts, meats, seeds, wheat bran cereals etc [2]. In bio-system, copper exists in cupric (Cu^{2+}) ion however; iron exclusively exists in the ferrous (Fe^{2+}) and ferric (Fe^{3+}) states and involve in metabolic processes [3]. The cellular copper and iron are tightly bound to enzymes and play important roles in oxygen transport and several electron transfer processes due to the virtue of their facile redox chemistry and high affinity for O_2 molecule [[4]]. Biologically essential Cu^{2+} and Fe^{3+} ions also can cause serious complications in the body due to their excess as well as deficiency from the normal permissible limit. Overloaded Cu^{2+} ion is potentially toxic and can cause Wilson disease, memory loss and Alzheimer disease, Hashimoto's disease, pelvic inflammatory disease, hypothyroidism and premenstrual syndrome, fibrocystic breast disease, anxiety, diarrhea, depression, bipolar disorder and infertility [4a,5]. On the other hand, copper deficiency is responsible for Menkesdesease, hematological and neurological disorder [6]. In case of iron, cells must carefully control iron levels and its distribution, however, overloaded iron (hyperferremia) is responsible for cell damage, organ dysfunction and cancer through the abnormal production of reactive oxygen species, hepatitis, Alzheimer's disease, hemochromatosis and neurodegenerative diseases [7]. Similarly, iron deficiency (hypoferremia) can be harmful as iron overload [8].

Therefore, it is urgent need for the development of facile and selective methods for detection of biologically important Cu^{2+} and Fe^{3+} ions in environment and in bio-system. The previous techniques for the detection of Cu^{2+} and Fe^{3+} ions such as inductively coupled plasma mass spectroscopy (ICP-MS), ion selective membrane electrode, atomic absorption spectrometry (AAS) and voltammetry [9]. A fluorescent-based method has provided great attention for the detection of metal ions [10]. Synthetic chemical sensors have been developed for the detection of Cu^{2+} ion [11] and Fe^{3+} ion [12] in various solvent systems.

In this article, we describe a simple colorimetric and fluorescent sensor **L1** for the detection of Cu^{2+} and Fe^{3+} ions in HEPES buffer (*p*H = 7.4, 10 mM) (Scheme 1). The visible color changes of **L1** in solution and on paper strips in presence of Cu^{2+} and Fe^{3+} ions can be seen with naked eyes. The chemosensor **L1** have several donor atoms for coordination with Cu^{2+} and Fe^{3+} ions. These complexation were intensively studied by spectroscopically and the computational studies. Moreover, detection of Fe^{3+} ion by fluorescence cell imaging experiments using L929 was also discussed.

---

* Corresponding authors.
E-mail addresses: sunitahooda@andc.du.ac.in (S. Hooda), baliyanpk@gmail.com (P. Kumar).

https://doi.org/10.1016/j.jphotochem.2018.07.021
Received 24 April 2018; Received in revised form 12 July 2018; Accepted 16 July 2018

PRINCIPAL
ST. STEPHEN'S COLLEGE
DELHI-110007

DELHI

Journal of Molecular Structure 1185 (2019) 300–309

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

CuCl/bpy-promoted unusual Z-stereoselective synthesis of trichloroacetic acid phenyl ester for Hirshfeld surface analysis and DFT study

Ram Kumar Tittal [a], [b], [*], Ram Nath Ram [b], Ayushi Nirwan [a], Vikas D. Ghule [a], Satish Kumar [c]

[a] Department of Chemistry, National Institute of Technology Kurukshetra, Haryana, 136119, India
[b] Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas, New Delhi, 110016, India
[c] Department of Chemistry, St. Stephen's College, University Enclave, Delhi, 110007, India

ARTICLE INFO

Article history:
Received 31 December 2018
Received in revised form
2 February 2019
Accepted 5 February 2019
Available online 2 March 2019

Keywords:
CuCl/bpy
Z-Stereoselective
Z-Diphenyl 2,3-dichloromaleate
DFT study
Hirshfeld surface analysis

ABSTRACT

A trichloromethyl ester devoid of suitably substituted C═C bond, any leaving group or a H-atom at the β-position to the radical, which are otherwise known for ATRA/ATRC, 1,2-rearrangement/fragmentation or simple 1,2-H shift respectively, in a reaction of trichloro-acetic acid phenyl ester with 2 mol equiv CuCl/bpy in reflux DCE or benzene under inert N_2 condition resulted to stereoselective synthesis of Z-2,3-dichloro-but-2-enedioic acid diphenyl ester and/or formation of reductive de-chlorination side product. The Z-stereochemistry of the product was confirmed by X-ray diffraction spectroscopy of Z-2,3-dichloro-but-2-enedioic acid dinaphthalen-1-yl ester which crystalizes in monoclinic system of P21/c symmetry elements. Hirshfeld surface analysis of experimentally established structure of Z-2,3-dichloro-but-2-enedioic acid diphenyl ester unrevealed the intermolecular interactions showing both H-bonding and short contacts. The stereochemistry was also interpreted computationally using Density Functional Theory at B3LYP/6-311G(d,p) level of theory. The calculated energies, energy gap and balance between the electrostatic potential on the molecular surface were computed which revealed unusual formation of less stable Z-isomer.

1. Introduction

The trichloromethyl group containing compounds are classically known for the free radical reactions under transition metal salt and their salts complexed with nitrogen containing ligands. The trichloromethyl group containing compounds easily form free radicals by homolysis of an activated C—Cl bond with the help of UV-light, radical initiators, redox active metal salts or its complexes [1]. The study and behaviour of dichloromethyl radical variously substituted at the β-position generated under redox condition of Cu(I) salts and its complexes with nitrogen based ligands were extensively studied by Ram et al. (Scheme 1). The results revealed that generated radicals normally undergo intermolecular addition and/or intramolecular cyclization (Path 1) on to suitably substituted carbon-carbon double bond, which may be free or hindered by bulky groups [2–5]. However, radicals substituted by weak or strong nucleofugal groups at the β-position underwent predominantly rearrangement (Path 2) and/or fragmentation (Path 3) through the intermediate formation of contact ion pair (CIP) which was extensively explored and established by inter or intramolecular tandem nucleophilic attack followed by radical cyclization experiments [6,7]. In two extreme cases the β-position of radical substituted by hydrogen and oxy group underwent 1,2-H shift via intermediate formation of a copper-carbenoid species and Z-stereoselective radical dimerization to ene-1,4-diones (Path 4) [8,9]. Based on these observations it was thought to check the behaviour of trichloromethyl esters under this reaction condition (Path 5).

Stereoselective-alkenes are highly appraised functional groups used in chemical transformations for the development of pharmaceutical products and essential building blocks of biomolecules [10]. The stereo-chemical outcome of any alkene reaction decide the fate of the products. Both Z & E isomers of alkene possesses unique property, hence stereo defined alkene are much demanding. The survey of the literature revealed that Z-alkenes are important

---

[*] Corresponding author. Department of Chemistry, National Institute of Technology, Kurukshetra, Haryana, 136119, India.
E-mail address: rktittaliitd@nitkkr.ac.in (R.K. Tittal).

https://doi.org/10.1016/j.molstruc.2019.02.018
0022-2860/© 2019 Published by Elsevier B.V.

PRINCIPAL
ST. STEPHEN'S COLLEGE
DELHI-110007