NJC

ROYAL SOCIETY OF CHEMISTRY

PAPER

Cite this: *New J. Chem.*, 2023, **47**, 2495

Unveiling the Mg(II) promoted [3+2] cycloaddition reaction of mesitonitrile oxide to Baylis–Hilman adduct from the molecular electron density theory perspective†

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The Grignard reagent promoted [3+2] cycloaddition (32CA) reaction of mesitonitrile oxide (MNO) with Baylis–Hilman adduct (BHA) has been studied within the Molecular Electron Density Theory (MEDT) at the ωB97X-D/6-311G(d,p) computational level. Topological analysis of the Electron Localization Function (ELF) allows classifying MNO as a zwitterionic three-atom-component (TAC), participating in *zw-type* 32CA reactions. In spite of the strong nucleophilic character of MNO, the low electrophilic character of BHA and the BHA:Mg(II) complex make the corresponding 32CA reactions to have a very low polar character, respectively. The reaction presents total *ortho* regioselectivity to afford 2-isoxazolines, while the diastereoselectivity is reversed in the Mg(II)-promoted 32CA reaction relative to that in the absence of the Mg(II) cation, in complete agreement with the experiments. The preferred transition state structure (TS) associated with the Mg(II)-promoted process shows complexation of the magnesium atom with the oxygens of MNO and BHA (hydroxyl oxygen), with the corresponding critical points (CPs) showing non-covalent interactions (NCIs) in the AIM-RDG isosurfaces. This MEDT study provides a complete comprehension of the role of the Grignard reagent in the *zw-type* 32CA reactions of nitrile oxides with Baylis–Hilman adduct; although formation of the BHA:Mg(II) complex slightly accelerates the 32CA reaction to decrease the activation Gibbs free energy by 3.1 kcal mol^{-1}, the more remarkable role of the Mg(II) cation is the change of the diastereoselectivity of these 32CA reactions involving a chiral ethylene.

Received 4th November 2022,
Accepted 29th December 2022

DOI: 10.1039/d2nj05424h

rsc.li/njc

1. Introduction

The [3+2] cycloaddition (32CA) reactions[1,2] of nitrile oxides offer broad synthetic potential to afford 2-isoxazoline adducts that can be transformed to β-hydroxyketones or γ-amino alcohols by reductive cleavage.[3] Terminal alkenes generally add to nitrile oxides with total regiocontrol leading to 5-substituted isoxazolines, while a regioisomeric mixture is obtained with the 1,2-substituted internal alkenes.[2] 32CA reactions of nitrile oxides with the terminal alkenes bearing a chiral centre show poor stereocontrol. Kanemasha and coworkers[4] performed 32CA reaction of benzonitrile oxide (BNO) **1** with the α,β unsaturated ketone **2** in presence of Lewis acid (LA) catalysts, while the reaction presented no improvement in stereoselectivity relative to the non-catalysed version owing to the deactivation caused by the formation of unreactive nitrile oxide–LA complex (Scheme 1).

In 1994, Kanemasha *et al.*[4] reported the first successful metal catalyzed nitrile oxide 32CA reactions with appreciable regio- and stereochemical control, and acceleration in the reaction rate relative to the non-catalyzed version (Scheme 2). In these 32CA reactions, Grignard reagent (EtMgBr) in dichloromethane (DCM) was used to form the BNO:EtMgBr complex **3**, which was then subjected to addition with the electron rich alkene 1-penten-3-ol **6** and afforded *syn* isomer **7** [5-(1-hydroxypropyl)-3-phenyl-2-isoxazoline] with 95% stereoselectivity.

Subsequently, in 1999, Krygowski and coworkers[5] reported the reversal of stereoselectivity in MeMgBr catalyzed 32CA reaction of mesitonitrile oxide (MNO) **9** with Baylis–Hilman

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† Electronic supplementary information (ESI) available: Figure with the ωB97X-D/6-311G(d,p) optimized geometries of **MC-Mg**. Table with the ωB97X-D/6-311G(d,p) total electronic energies, in the gas phase and toluene, of the stationary points involved in the *zw-type* 32CA reaction of MNO **9** with BHA **10**. Table with the ωB97X-D/6-311G(d,p) enthalpies, entropies, and Gibbs free energies of the stationary points involved in the *zw-type* 32CA reaction of MNO **9** with BHA **10**. Table with the ωB97X-D/6-311G(d,p) total electronic energies, in the gas phase and DCM, of the stationary points involved in the Mg(II)-promoted *zw-type* 32CA reaction of MNO **9** with BHA **10**. Table with the ωB97X-D/6-311G(d,p) enthalpies, entropies, and Gibbs free energies of the stationary points involved in the Mg(II)-promoted *zw-type* 32CA reaction of MNO **9** with BHA **10**. See DOI: **https://doi.org/10.1039/d2nj05424h**

Computational and Theoretical Chemistry 1230 (2023) 114393

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

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

Unveiling the mechanism, regiochemistry and substituent effects of the [3 + 2] cycloaddition reactions of *C*, *N*-diaryl nitrile imine to ethylene derivatives from the molecular electron density theory perspective

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ARTICLE INFO

Keywords:
Nitrile imines
[3+2] cycloaddition reactions
Molecular Electron Density Theory
Conceptual DFT
Electron localization function

ABSTRACT

The [3 + 2] cycloaddition (32CA) reactions of C-(4-methoxyphenyl)-*N*-phenyl nitrile imine (NI) with a series of ethylene derivatives of increased electrophilic character have been studied within the framework of Molecular Electron Density Theory (MEDT). These 32CA reactions are kinetically controlled with activation Gibbs free energies between 14.8 and 24.0 kcal mol^{-1}, and with the preferred regioselectivity involving the nucleophilic attack of the carbenoid carbon of NI on the non-substituted carbon of the electrophilic ethylenes in agreement with the experimental outcomes. The presence of electron-withdrawing substituents in the ethylene makes the 32CA reaction of forward electron density flux (FEDF) more quickly, relative to that with nucleophilic propene, showing the highest activation parameters and non-polar character. Electron localization function (ELF) and atom-in-molecules (AIM) topological analysis of the electron density at the transition state structures characterize the non-concerted nature of these one-step *cb-type* 32CA reactions.

1. Introduction

Pyrazolines and pyrazoles represent one of the significant class of heterocycles to exhibit wide range of biological activities, namely anticancer, antibacterial, anti-inflammatory, antidepressant, analgesic etc[1–3]. The [3 + 2] cycloaddition (32CA) reactions of *in situ* generated nitrile imines (NIs) to ethylene derivatives proposed by Huisgen[4] have emerged as a well documented convenient approach to pyrazoline derivatives[5]. For instance, 2-methyl-5-phenyltetrazole **1** undergoes elimination of nitrogen on heating to generate *C*-phenyl-*N*-methyl nitrile imine **2** which upon 32CA reaction with *trans* stilbene **3** affords the pyrazoline derivative **4** (Scheme 1).

The reactivity of NIs is influenced by electronic effects and consequently change in the substitution of the ethylene counterpart is expected to induce appreciable differences in the corresponding 32CA reactions and the theoretical implications are worth investigating in terms of density functional theory (DFT) calculations. Within the Molecular Electron Density Theory (MEDT) proposed by Domingo in 2016, [6,7] a reasonable correlation between the electronic structure and the molecular reactivity of three-atom-components (TACs) participating in 32CA reactions has been established.[8] Depending on its electronic structure, the TACs have been classified in *pseudodiradical*[9] *(pdr)*, *pseudo(mono)radical*[10] *(pmr)*, *carbenoid*[11] *(cb)* and zwitterionic[12] *(zw)*, with the reactivity order *pdr type* > *pmr type* ≈ *cb type* > *zw type*. For the simplest NI, Ríos-Gutiérrez et al.[11] proposed two dissimilar electronic structures, namely the ground state (GS) allenic structure **5a** with *cb*-type reactivity, and the propargylic structure **5p**, which is a transition state structure (TS) between two stereoisomeric allenic structures (Scheme 2).

The reactivity of simplest NI in the 32CA reactions towards ethylene and electrophilic dicyanoethylene was studied by Ríos-Gutiérrez and Domingo in 2019[11], while in the same year, Domingo et al studied the reaction mechanism of the 32CA reaction between diphenyl nitrile imine and methyl 1-methyl-allenoate[13]. The difference in chemical reactivity of diphenyl nitrile imine and phenyl nitrile oxide in the 32CA reactions with (R)-carvone has also been recently investigated[14].

In 2007, Wang and coworkers reported experimental findings for the mild photoactivated 32CA reactions of 2,5-disubstituted tetrazole **6** with ethylene derivatives to generate highly functionalized pyrazolines[15]. These 32CA reactions involved *in situ* generation of non-symmetric *C*-(4-

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https://doi.org/10.1016/j.comptc.2023.114393
Received 1 August 2023; Received in revised form 16 October 2023; Accepted 8 November 2023
Available online 10 November 2023

Journal of Molecular Structure 1274 (2023) 134418

Contents lists available at ScienceDirect

Journal of Molecular Structure

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

Spectroscopic, reactivity analysis and docking studies of 3-(adamantan-1-yl)-4-(4-fluorophenyl)-1-[(4-phenylpiperazin-1-yl)methyl]-4,5-dihdyro-1H-1,2,4-triazole—5-thione: DFT and MD simulations

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ARTICLE INFO

Article history:
Received 28 August 2022
Revised 16 September 2022
Accepted 23 October 2022
Available online 25 October 2022

Keywords:
DFT
Solvent effects
MD simulations
Adamantane

ABSTRACT

An adamantane-thione derivative, 3-(adamantan-1-yl)-4-(4-fluorophenyl)-1-[(4-phenylpiperazin-1-yl)methyl]-4,5-dihdyro-1H-1,2,4-triazole—5-thione (ATT) is investigated experimentally and theoretically to predict its various chemical and electronic properties. The solvation energies are predicted in acetone, DMSO, ethanol and water and acetone is a better solvent due to high value of solvation energy. When compared to the gas phase, the chemical descriptors of ATT decreased in the solution phase. The adamantane cage breathing mode is assigned at 785 (theoretical) and 784 cm^{-1} (IR). Topological study of the atom in molecules (AIM) shows the ring critical points corresponding to the phenyl, pyrazine, triazole and 4-fluorophenyl rings.From molecular dynamics (MD) simulations, solvent accessible surface area (SASA) values are from 656 to 736 and 289 to 294 ($Å^2$) for unbound and bound structures.

1. Introduction

Adamantane is symmetrical polycyclic cage molecule with exceptional properties, similar to diamondoids-hydrogen-terminated hydrocarbons [1]. The adamantane is commonly incorporated into active medicines to boost the pharmacological effects. The stiff adamantane cage helps neighboring groups from metabolic cleavage, thus improved the drug's stability [2]. Furthermore, the adamantly moiety can function as a suitable fit for various host molecules or operate as a blocking agent for ion channels because to its size and bulkiness [3]. The stability and solubility of cage-type adamantanes are all outstanding [4]. Hydrogen on adamantane's carbons had high activity and can make bonds with atoms of strong electronegative charge [5]. Adamantane-substituted acridine are used in organic light emitting diodes [6]. Many drugs with piperazine skeleton have important pharmacological properties [7]. Synthesis and antinociceptive properties of certain thiazole-piperazine compounds are reported [8]. Amoxapine, trazodone, hydroxyzine, buspirone, clozapine, aripiprazole and vortioexetine are all CNS-related medications that have the piperazine molecule [9,10]. Prine linked piperazines are inhibitors of tuberculosis. [11]. Multi target piperazines has been synthesized and biologically evaluated as possible antipsychotics [12]. Triazoles are a class of heterocycles with different biological activities [13,14]. As therapeutic candidates, a growing number of triazole based molecules are being developed [15]. Al-Alshaikh et al. reported crystal structure of ATT [16] and due to the various biological activities of ATT, we reported the spectroscopic, reactivity analysis and MD simulations in detail.

2. Methods

ATT is synthesized as reported [16,17] and spectra (Figs.S1 and S2) were recorded on a DR/Jasco FT-IR and Bruker RFS spectrometers. Frontier molecular orbitals (FMOs), molecular electrostatic potential (MEP) and solvation free energies of ATT (Fig. 1) were evaluated using Gaussian 09 and Gaussview 5 via wB97XD/6-311+G* [18,19]. There are no imaginary frequencies that correlate to lo-

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https://doi.org/10.1016/j.molstruc.2022.134418
0022-2860/

Journal of Molecular Structure 1285 (2023) 135541

Contents lists available at ScienceDirect

Journal of Molecular Structure

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

Insights on adsorption properties of a DNA base, guanine on nano metal cages ($Ag_{24}/Au_{24}/Cu_{24}$): DFT, SERS, NCI and solvent effects

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ARTICLE INFO

Article history:
Received 25 February 2023
Revised 28 March 2023
Accepted 9 April 2023
Available online 10 April 2023

Keywords:
DFT
SERS
Metal nanocages
Reactivity analysis
Solvent effects

ABSTRACT

A detailed theoretical study was implemented on 2-amino-1,7-dihydropurin-6-one's (ADO). Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) simulations were accomplished to explain the adsorption performance of the ADO drug molecule on metal nanocages. Adsorption energy og ADO was calculated to be -53.90, -50.67 and -63.56 kcal/mol for Ag, Au and Cu cages, respectively. ADO interacts with Ag/Cu through the N_5, N_4 and N_6 atoms with a perpendicular orientation and Au-ADO, the interaction is through O, N_3-H_{13} and NH_2 groups with a perpendicular orientation. Reactivity computations were used to find the electron density in NMC-containing ADO complexes. The intermolecular interaction forces were found by the establishment of numerous bond critical point, monitored by ring critical points at the midpoint of interaction state. The ADO molecule will also be examined as part of the computational study to ascertain its bioactivity and docking studies. We can get accurate estimates of the atomic contact energies for drug delivery using the docking process.

1. Introduction

Researchers have focused on developing cancer treatments and boosting the bioactivity of currently available anticancer drugs in response to the rapidly rising incidence of cancers worldwide. In order to produce better and more efficient treatments, more research is required in the subject of cancer. The three most common methods for treating or slowing the spread of cancer are surgery, chemotherapy and radiotherapy [1]. The goal of recent research is to kill cancer cells without harming healthy cells. Through the use of nanoparticles, a variety of drugs are delivered to the body using biocompatible polymers, liposomes and gold nanocages [2,3]. Cancer especially breast cancer, which is the most common type in women and causes thousands of women to die each year, is one of the major health problems facing the world. Studies on clinical characteristics, phases and age distribution of this tumor are lacking, but many analytical techniques have been developed to track the effectiveness of the cancer drug [4]. The wide-ranging scientific and technological ramifications of the interaction between metals and nucleobases have made it a subject of great interest. We thoroughly investigated the ground-state electrical characteristics of the guanine nucleobase interacting with metal clusters using a combination of DFT simulations. The investigation of how biological systems, and in particular nucleic acids, interact with metals had to wait until more thorough basis sets were created that could accurately anticipate the well-established experimental data [5]. The structural levels of DNA polymer structure range from primary to quaternary. The alignment and attachment order of nucleobases are re-described at the fundamental level [6]. If a molecule with superior qualities to DNA existed, evolution most likely would have chosen it for the critical job of storing and encoding information of earth's living organisms. Despite the society's and the researcher's best efforts, there are still unanswered questions regarding, among other things, self-recognition and assembly, hybridization, reproduction and interaction. Since the discovery of the structure of these molecules, the adsorption of metal-DNA has been a subject of utmost concern [7]. The inclusion of metals is crucial for the stability of long strands in solution because the phosphodiester backbone is charged [8,9]. It has been demonstrated experimentally that the DNA duplex is more stable at high salt concentrations

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https://doi.org/10.1016/j.molstruc.2023.135541
0022-2860/

POLYCYCLIC AROMATIC COMPOUNDS
https://doi.org/10.1080/10406638.2023.2172052

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Taylor & Francis Group

Structural, Spectral, Molecular Docking, and Molecular Dynamics Simulations of Phenylthiophene-2-Carboxylate Compounds as Potential Anticancer Agents

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ABSTRACT

Important biological compounds, namely, methyl 3-amino-4-(4-bromophenyl)thiophene-2-carboxylate (BPTC) and methyl 3-amino-4-(4-chlorophenyl)thiophene-2-carboxylate (CPTC), were characterized using complementary techniques of Fourier transform infrared (FT-IR), Raman spectroscopy. Nuclear magnetic resonance spectroscopy (NMR) confirmed the structural features, while Ultra Violet–Visible Spectroscopy was used to investigate the electronic properties of both compounds. The quantum chemical calculations for both compounds were performed using the DFT/B3LYP functional with the 6-311++G(d,p) basis set. This study computes electrostatic potential observation, electron localization function (ELF) assessment, and atoms-in-molecules (AIM) analysis. In the present investigation, the global hardness, chemical softness, electrophilicity, nucleophilicity indices, and dipole moment of both compounds were calculated. In addition, a molecular docking analysis was conducted to determine the binding potential of target molecules with protein tyrosine phosphatase. A 200-ns molecular dynamics (MDs) simulation had been performed to assess the compound's binding stability.

ARTICLE HISTORY
Received 22 August 2022
Accepted 14 January 2023

KEYWORDS
Vibrational spectroscopy; DFT calculations; ELF; chemical reactivity; molecular docking; molecular dynamics simulations

1. Introduction

Sulfur is a chemical element that is present in practically all natural products, pharmaceuticals, precious products, and living things, making it strongly connected with many areas of human life.[1–3] Owing to the accessibility of non-bonding pairs of electrons and the disparity in electronegativity, sulfur heterocycles have received attention for their crucial roles in the creation of medications. One of the most significant categories of heterocyclic compounds that are frequently used in the analysis of cyclic molecular structures is those that include sulfur.[3–5] There are several sulfur-containing scaffolds in diverse natural substances and pharmaceuticals that act as physiologically active molecules in a variety of pathophysiological circumstances. It's also been observed to have a mild cytotoxic activity and a high therapeutic property when compared to sulfur and nitrogen heterocycles, which dominated pharmaceutical research studies.[6–8] Biologically active substances and natural products are the main sources of thiophene, a simple five-membered

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Supplemental data for this article can be accessed online at https://doi.org/10.1080/10406638.2023.2172052

Computational and Theoretical Chemistry 1227 (2023) 114243

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

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

Unveiling the atropoisomerism induced facial selectivity and regioselectivity in the [3 + 2] cycloaddition reaction of benzonitrile oxide with 5-methylenehydantoin from the molecular electron density theory perspective

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ARTICLE INFO

Keywords:
Molecular Electron Density Theory
Electron Localization Function
Benzonitrile Oxide
Methylene hydantoins

ABSTRACT

The [3 + 2] cycloaddition (32CA) reaction of benzonitrile oxide BNO with 5-methylenehydantoin (MH) has been studied with the MEDT perspective at the DFT/B3LYP/6–31 + g(d,p) level of theory. Topological analysis of the ELF shows zwitterionic character of this 32CA reaction and the non-polar character is revealed form the global electron density transfer (GEDT) calculations at the TSs, consistent with the calculated high relative free energies between 27.6 and 39.1 kcal mol^{-1}. The energetically predicted regioselectivity and atropisomerism induced facial selectivity towards *anti* isomer is in complete agreement with the experimental outcome. The activation energy in this 32CA reaction is associated with the creation of non-bonding electron density at N2 nitrogen and *pseudoradical* center at C3 and the formation of new C—C and C—O covalent bonds were not observed at the TSs which was in conformity with the calculated total electron density and the positive Laplacian of electron density at the bond critical points observed at the interatomic bonding regions of the TSs.

1. Introduction

Atropisomerism represents a type of axial chirality representing restricted bond rotation due to the presence of sterically hindered substituents around a single sigma bond. Several interesting applications of atropisomerism have been reported in medicinal chemistry especially for drug discovery [1]. The C—N stereogenic axis induced atropisomerism shares a unique place in pharmaceuticals and in asymmetric catalysis [2–5], and the stereoselective construction of C—N atropisomers are well documented in literature [6]. Atropisomerism induced facial selectivity serves as a versatile strategy to introduce three dimensional arrangement in small molecules through spiro linkages. The [3 + 2] cycloaddition (32CA) reaction of nitrile oxides with exocyclic methylene compounds can be performed for the construction of such spiroheterocycles [7–11]. In 2012, Harding and Savage reported the 32CA reactions of benzonitrile oxide BNO **1** with 4-methylene-2-oxazolidinones **2**, to generate 5-spiro isoxazoline adducts **3** in which the facial selectivity was induced by *N*-aryl atropisomerism leading to the *anti* isomer as the major product [12] (Scheme 1). The atropisomerism induced facial selectivity in 32CA reactions of BNO **1** with exocyclic methylene benzosultams have also been reported [13].

In 2011, Said and Savage reported the atropisomerism induced facial selectivity in 32CA reactions of BNO **1** with 5-methylenehydantoin MH **4** [14] affording the anti isomer **5** as the major product (Scheme 2). These reactions serve as the synthetic pathway to access spirohydantoin derivatives which have wide spectrum of applications in pharmaceutical industries [15,16].

With the advent of advance software applications, the theoretical implications of chemical reactions can be analyzed precisely in terms of the density functional theory [17] (DFT) calculations. The molecular electron density theory (MEDT) [18] proposed by Domingo in 2016 analyzes the electron density changes along the reaction path and

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https://doi.org/10.1016/j.comptc.2023.114243
Received 8 May 2023; Received in revised form 27 June 2023; Accepted 13 July 2023
Available online 21 July 2023

Theoretical Chemistry Accounts (2023) 142:33
https://doi.org/10.1007/s00214-023-02972-3

RESEARCH

Unveiling the mechanism, selectivity, solvent and temperature effects on the [3 + 2] cycloaddition reaction of *N*-methyl-C-(2-furyl) nitrone with maleimide derivatives from the molecular electron density theory perspective

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Received: 14 October 2022 / Accepted: 12 March 2023

Abstract
The [3 + 2] cycloaddition (32CA) reactions of *N*-methyl-C-(2-furyl) nitrone with maleimide derivatives have been studied in gas phase, ethanol and acetonitrile within the Molecular Electron Density Theory (MEDT) framework at the B3LYP-D3/6-31G(d) level. Topological analysis allows classifying the nitrone as a zwitterionic (*zw-)* three-atom component (TAC) associated with high energy barrier. Interestingly, the global electron density transfer (GEDT) between 0.10 and 0.13 e predicts low polar character of forward electron density transfer (FEDF) type with the electronic flux from the nitrone to the maleimides, resulting in decreased activation parameters relative to that of the nitrone cycloadditions with simple alkenes. These 32CA reactions follow a one-step mechanism under kinetic control with highly asynchronous bond formation, and no new covalent bonds are formed at the TSs. The predicted *exo*-selectivity agrees well with the experimental findings. Inclusion of solvent effects increases the activation energy, in particular along the *endo* pathway. The activation enthalpies are between 5.58 and 7.68 kcal/mol in gas phase and between 6.61 and 11.10 kcal/mol in ethanol and acetonitrile. Also, the influence of temperature was investigated at 289.15 K, 298.15 K and 393.15 K. Non-covalent interactions (NCIs) were identified at the interactions regions of the TSs from the topological analysis of the AIM (atoms-in-molecules) and characterized using Independent Gradient Model (IGM) analysis.

Keywords *N*-methyl-C-(2-furyl) nitrone · Maleimides · DFT · B3LYP-D3 · Cycloaddition reaction · MEDT · ELF

1 Introduction

The [3 + 2] cycloaddition (32CA) reactions of nitrones have received significant attention owing to their wide range of applications in chemical synthesis and medicinal chemistry [1]. A vast array of five membered heterocycles can be produced from nitrone cycloadditions such as the isoxazolidines [2], from nitrone olefin 32CA reactions. Isoxazolidines serve as valuable synthetic intermediates owing to the presence of a labile N–O bond [3]. Besides, isoxazolidine derivatives exhibit diverse pharmacological activities, namely antibacterial, anticonvulsant, antifungal, antiviral, antitumor [2] etc. Consequently, numerous synthetic strategies [4] have been employed to optimize the selectivity, solvent, catalytic, temperature and substituent effects and consequently reach at reasonable yields of the targeted isoxazolidine compounds. Within such 32CA reactions, the choice of the olefin

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Published online: 30 March 2023

Structural Chemistry
https://doi.org/10.1007/s11224-023-02175-3

RESEARCH

Revealing the cyclization selectivity in intramolecular [3 + 2] cycloaddition reactions of allenic nitrones from the molecular electron density theory perspective

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Received: 7 April 2023 / Accepted: 18 April 2023

Abstract
The intramolecular [3 + 2] cycloaddition (32CA) reactions of allenic nitrones have been studied within the molecular electron density theory (MEDT) at the MPWB1K/6-311G(d,p) computational level. These zwitter-ionic type 32CA reactions show high activation free energies between 22.2 and 34.9 kcal mol^{-1} in ethanol consistent with their predicted non-polar character and follow one-step mechanism with highly asynchronous transition states. Interestingly, when the nitrone and the allene moieties are separated by two methylene units, the [3 + 2] addition is energetically feasible along the C5-C6 terminal double bond of the allene, while the presence of four methylene units change the cyclization selectivity towards the internal C4-C5 double bond of the allene. This is in complete agreement with the experimental outcomes. The molecular mechanism study in terms of bonding evolution theory (BET) shows varied electron density changes along these two reaction paths. Finally, the topological analysis of AIM (atoms-in-molecules) reveals the presence of non-covalent interactions at the interatomic bonding regions of the transition states, which agrees well with the electron localization function analysis and the forming C–C and C-O bond distances.

Keywords Molecular electron density theory · Electron localization function · Activation energy · Allenic nitrones · [3 + 2] cycloaddition reactions

Introduction

Allenes present an intriguing group of reacting counterparts in [3 + 2] cycloaddition (32CA) reactions owing to the presence of two cumulative unsaturations [1]. Although the simplest allene shows limited reactivity in the 32CA reactions with *C*-phenyl-*N*-methyl nitrone **1**, incorporation of electron-deficient substituents (such as cyano (**2**), carbomethoxy (**3**), phenylsulfonyl (**4**), methoxy (**5**), fluoro (**6**)) overcomes the unreactive nature, affording high yield of isoxazolidines under milder reaction conditions with site selectivity towards the generation of $\mathbf{CA_{4\text{-}5}}$ and $\mathbf{CA_{5\text{-}6}}$ addition (Scheme 1) [2–7]. Nitrone-allene 32CA reactions show well-established applications in the total synthesis of alkaloids and natural products [8], and also exhibit interesting selectivity and mechanistic implications. Recently, Lee et al. have reported the mechanism and selectivity of the intermolecular 32CA reactions of nitrones with activated allenes [9].

An interesting alternative to explore the reactivity of unactivated allenes was designed by Lebel and Banucci in 1970 [10] from the intramolecular [3 + 2] cycloaddition (IM32CA) reactions of allenic nitrones, and was also reported by Padwa et al. [11] in 1993 to proceed smoothly affording reasonably good yields. The IM32CA reactions consist of both nitrone and the allenic function suitably placed in the same molecule and exhibit interesting site selectivity for the two allenic double bonds depending on the substrate. For instance, the IM32CA reaction of exocyclic nitrone **7** affords isoxazolidine **8** by addition along the terminal C5-C6 double bond, while the allenic nitrone **9** involves addition along the internal C4-C5 double bond and affords the bridged bicyclic isoxazolidine **10** (Scheme 2).

The IM32CA reaction of the allenic nitrone **11** generated from 5,6-heptadien-2-one and *N*-methylhydroxylamine

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Published online: 28 April 2023

Structural Chemistry
https://doi.org/10.1007/s11224-023-02193-1

RESEARCH

Unveiling [3 + 2] cycloaddition reactions of pyridinium bis(methoxycarbonyl)methylides and pyridinium dicyanomethylides with cyclooctyne for indolizine synthesis from the molecular electron density theory perspective

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Received: 19 April 2023 / Accepted: 17 May 2023

Abstract
The [3 + 2] cycloaddition (32CA) reactions of a series of pyridinium bis(methoxycarbonyl)methylides (PMYs) and pyridinium dicyanomethylides (PCYs) with cyclooctyne to generate indolizines have been studied within the Molecular Electron Density Theory (MEDT). Interestingly, the electronic structure of these azomethine ylides (AYs) revealed from the topological analysis of the electron localization function (ELF) differs considerably from that of the simplest AY and accordingly, the molecular reactivity is changed. Consequently, the corresponding 32CA reactions of PCYs and PMYs require refluxing toluene conditions to overcome the high activation barrier contrary to the unappreciable energy cost demanded by the simplest AY. This is explained by the analysis of conceptual DFT indices characterizing the ambiphilic character of the PMYs and PCYs classified as strong electrophiles and strong nucleophiles within the standard reactivity scales. The 32CA reactions of PCYs are more facile relative to the PMYs in agreement with the experimental outcome. These polar 32CA reactions show the global electron density transfer (GEDT) higher than 0.2 e and proceed through one-step mechanism with highly asynchronous TSs in which the new covalent bond formation has not been started. Herein, we report the first MEDT study to comprehend the reactivity of pyridinium methylides towards 32CA reactions leading to indolizines.

Keywords Molecular electron density theory · Electron localization function · Activation energy · Indolizines · Pyridinium methylides

Introduction

Indolizines [1, 2] consisting of a bridging nitrogen atom between two condensed 5- and 6- membered rings display a wide spectrum of biological and pharmaceutical activities [3–5]. The reactivity of indolizines are well documented [1, 2] and very recently, the indolizine skeleton has been established as the promising framework to develop diverse range of C-H functionalized hybrids [6] (Scheme 1).

The [3 + 2] cycloaddition (32CA) reactions serve as one of the powerful synthetic strategies for stereo- and regioselective construction of five membered heterocycles [7]. The 32CA reactions of pyridinium salt **1** with activated alkenes **2** and alkynes **3** are one of the widely employed processes for the obtainment of functionalized indolizines **4** [8–10] (Scheme 2). In 2023, Xiong et al. have also reported the 32CA reactions of isoquinolium and quinolium salts with 1-bromoethene-1-sulfonyl fluoride for construction of indolizine based heterocyclic sulfonyl fluorides [11].

Matsumoto et al. [12] reported the 32CA reactions of cyclooctyne COY **5** with pyridinium bis(methoxycarbonyl) methylides PMYs **6a-e** and pyridinium dicyanomethylides PCYs **7a-e** under refluxing toluene conditions to generate the indolizines **8a-e** and **9a-e** (Scheme 3). Experimentally, the presence of electron withdrawing 4-cyano substitution of the pyridine ring resulted in increased reactivity and the 32CA reactions of PMYs **6a-e** required longer reaction times relative to the facile addition of PCYs **7a-e** with COY **5**.

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Published online: 06 June 2023

Chemistry of Heterocyclic Compounds **2023**, *59*(3), 145–154

Unveiling the exclusive stereo and site selectivity in [3+2] cycloaddition reactions of a tricyclic strained alkene with nitrile oxides from the molecular electron density theory perspective

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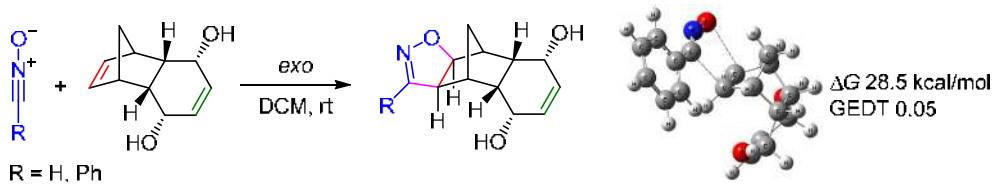
Published in Khimiya Geterotsiklicheskikh Soedinenii, 2023, *59*(3), 145–154

Submitted September 13, 2022
Accepted October 7, 2022



The [3+2] cycloaddition reactions of formonitrile oxide and benzonitrile oxide with a tricyclic strained alkene bearing norbornene and cyclohexene double bonds have been studied from the molecular electron density theory perspective at the MPWB1K/6-311G(d,p) computational level. Electron localization function shows the absence of *pseudoradical* and carbenoid centers, classifying formonitrile and benzonitrile oxides as zwitterionic three-atom components, consistent with the high activation free energies of 26.0 and 28.5 kcal·mol^{-1}, respectively, in their cycloaddition reaction with the strained alkene in CH_2Cl_2. These reactions follow a one-step mechanism under kinetic control and present total site selectivity, as the addition of formonitrile and benzonitrile oxides to the norbornene double bond is energetically preferred by 4.9 and 8.0 kcal·mol^{-1}, respectively, over the cyclohexene double bond in agreement with the experiments, and complete *exo*-stereoselective control is predicted. The minimal global electron density transfer predicts nonpolar character, while the electron localization function topological analysis implies that the activation energy is related only to the formation of non-bonding electron density at N2 nitrogen and *pseudoradical* center at C3 atom of the nitrile oxides. The total electron densities less than 0.1 e and positive Laplacian of electron density at the forming C–C and C–O bond critical points of the early transition states indicate noncovalent interactions which were characterized by visualization of the AIM-RDG isosurfaces.

Keywords: norbornene, strained alkene, [3+2] cycloaddition reactions, molecular electron density theory.

Owing to the presence of the unique angularly strained structural geometry, norbornene (bicyclo[2.2.2]hept-2-ene) serves as a promising synthetic reagent providing efficient entries to stereo- and regiochemically defined organic compounds and consequently finds numerous applications in medicinal, agricultural, polymer, and solar cell industries.[1] The [3+2] cycloaddition (32CA) reactions of norbornene derivatives share the top shelf priority among other synthetic alternatives due to the relatively improved selectivity and yields.[2–4] The addition of norbornene derivatives to *C*,*N*-disubstituted nitrones was first reported by Huisgen et al. in the 1960s,[5] while Fraser and Lin in 1967 established the stereochemical features of the isoxazoline adducts generated from the addition of *N*-methyl-*C*-phenyl nitrone to norbornene.[6] Nitrile oxides have served as important substrates for cycloaddition reactions with interesting mechanistic outcomes since last five decades. Recently, the experimental and theoretical studies on the regioselective 32CA reactions of nitrile *N*-oxides to trichloronitropropene have been reported,[7] and the theoretical implications of the local nucleophile-electrophile interactions in 32CA reactions of benzonitrile oxide and conjugated nitroalkenes have also been analyzed.[8]

Cycloadditions of norbornene (**1**) to nitrile oxides are also well documented in literature. In 1999, Tam et al. reported the intramolecular 32CA reactions of norbornadiene-tethered nitrile oxides,[2] while in 2001, Mayo et al. established the complete stereoselectivity in the 32CA reactions of benzonitrile oxide (**2**) to 1-substituted 2-norbornene derivative **3**[4] leading to regioisomeric *exo* cycloadducts **4** and **5** (Scheme 1). In 2013, Gucma et al. presented NMR studies to establish the selectivity of 4-(trifluoromethyl)-benzonitrile oxides toward norbornene derivatives.[9]

The remarkable stereocontrol in such reactions have prompted chemists to design industrially relevant and biologically active adducts. In 2009, Gutsmiedl et al. reported the facile addition of nitrile oxides to norbornene-modified DNA in a copper-free click reaction,[10] while in 2015, the 32CA reaction of nitrile oxide **6** with norbornene (**1**) leading to *exo* adduct **7** was applied as a bioorthogonal

Journal of Molecular Liquids 392 (2023) 123177

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

An investigation on spectroscopic, wavefunction dependent reactivity, docking and anti-Covid-19 ability of flupentixol dihydrochloride: DFT and MD simulations at different temperatures

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ARTICLE INFO

Keywords:
Flupentixol
DFT
AIM analysis
MD simulations
Docking

ABSTRACT

A detailed vibrational analysis of flupentixol dihydrochloride (FDC) is performed by Density Functional Theory (DFT) calculations. Wavefunction reactivity properties and Atoms In Molecules (AIM) analysis are also performed. There is enormous O_1-H_{1B}…Cl_1, N_1-H_{1A}…Cl_1 and C_9-H_{9A}…F_{3B} intermolecular hydrogen bonding in FDC. Electrons were resonated on the aromatic rings without any interference with aliphatic moiety of both highest occupied molecular orbital (HOMO) and in least unoccupied molecular orbital (LUMO) which is due to participation of fluorine atom intermolecular hydrogen bonding with adjacent C–H. The electron localization function (ELF) shows under populated N-C single bonds of ring A owing to the strong electron withdrawing effect of nitrogen atoms. SARS-CoV-2 main protease with FDC had energy −80 kcal/mol. With the help of molecular dynamics (MD), radial distribution functions (RDF) are calculated to identify the most critical interaction with water molecules.

1. Introduction

Tricyclic aromatic ketones have been used as starting materials for the production of trycyclic medicines, as well as causing overcrowding in bistricyclic enes [1]. Thioxanthene and numerous of its derivatives have been found to have biologically beneficial properties [2]. However, early clinical trials have revealed that several of the most promising therapeutic candidates derived from this family of chemical have negative hazardous characteristics [3]. In the photo polymerization of ethylene derivatives, various thioxanthone derivatives are utilized as activators or sensitizers [4]. Substituted thioxanthones are employed as radical sources as stabilizers for polyolefins [5]. This family of compounds has been used in a variety of industrial operations. Flupentixol is a thioxanthene derivative with antipsychotic characteristics that is commonly used for diseases with anxiety as a symptom [6]. Flupentixol is a medicine that is commonly administered in India due to the rise in psychiatric disorder. As a result, it is frequently detected in waste water, necessitating a good removal technique [7]. Phenothiazine and similar structures are used to treat psychotic diseases all over the world [8]. Many phenothiazine compounds have powerful antiemetic, antihistaminic or anti-cholinergic properties [9]. Several medications have been observed to interact with phenothiazine antipsychotic medicines [10,11]. They enhance the effect analgesics, anti-histaminics and cold treatments that have been prescribed. Low dose neuroleptics are increasingly being used to treat anxiety and depression [12]. Balasubramani et al., reported removal of flupentixol using graphene oxide [13]. Studies of drug interaction between levocetirizine are reported [14]. El-Zahry and Lendl reported the kinetic study of ofloxacin using SERS [15]. Raghav et al., reported interactions of trifluoperazine with serum albumin using multi spectroscopic methods [16]. Spectroscopic studies of thioxanthens are reported [17,18]. The piperazine ring plays a larger role in drug development, with a higher number of favourable hit

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https://doi.org/10.1016/j.molliq.2023.123177
Received 23 April 2023; Received in revised form 27 July 2023; Accepted 24 September 2023
Available online 27 September 2023

Received: 4 June 2023 | Revised: 13 September 2023 | Accepted: 17 September 2023

DOI: 10.1002/poc.4574

RESEARCH ARTICLE

Journal of Physical Organic Chemistry WILEY

Revealing the influence of tether length on the intramolecular [3 + 2] cycloaddition reactions of nitrones from the molecular electron density theory perspective

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Funding information
University Grants Commission; Ministry of Science and Innovation, Grant/Award Number: PID2019-110776GB-I00

Abstract

The influence of ethylene substitution and the tether length between the two reacting counterparts on the selectivity and reactivity of the intramolecular [3 + 2] cycloaddition (IM32CA) reactions of cyclic nitrones leading to tricyclic isoxazolidines have been studied within the Molecular Electron Density theory at the MPWB1K/6-311G(d,p) computational level. These *zw*-type IM32CA reactions follow one-step mechanism, and the activation barrier decreases with the introduction of electron withdrawing (EW) substituent at the alkene moiety in both the intramolecular and intermolecular versions. The IM32CA reactions involving unsubstituted alkene have non-polar character with minimal electron density flux classified as null electron density flux type, while that involving the EW nitro substituted ethylene is more facile with a strong electron density flux from the nitrone to the ethylene moiety, classified as forward electron density flux type. The increase in the polar character of the IM32CA reaction decreases the activation Gibbs free energies associated with these intramolecular processes, while the highly polar IM32CA reactions are disfavored with respect to the intermolecular ones. Interestingly, the preferred regioselectivity observed in low polar IM32CA reactions having three methylene units between the nitrone and ethylene frameworks is reversed to that in nitrones separated with four methylene units, in conformity with the experimental outcome. Finally, electron localization function and quantum theory of atoms-in-molecules studies reveal that, in general, these IM32CA reactions involve early transition state structures in which the formation of new C-C and C-O single bonds have not yet started.

KEYWORDS

conceptual DFT, electron localization function, intramolecular [3 + 2] cycloaddition reactions, molecular electron density theory, regioselectivity, transition state structures

1 | INTRODUCTION

Spiro heterocyclic derivatives find interesting applications in medicinal chemistry owing to their unique conformational features and structural implications resulting in diversified biological and pharmacological properties.[1] Among the vast array of spiro hereocycles, the spirocyclic amines have received sincere synthetic

Theoretical Chemistry Accounts (2023) 142:129
https://doi.org/10.1007/s00214-023-03068-8

RESEARCH

Diastereoselective green synthesis of pyrrolo[1,2-a]quinolines via [3+2] cycloaddition reaction: insights from molecular electron density theory

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Received: 18 May 2023 / Accepted: 23 October 2023

Abstract
The [3+2] cycloaddition (32CA) reaction between cyclic azomethine ylide (generated from *N*-phenacylquinolinium bromide) and *N*-arylmaleimide, leading to pyrrolo[1,2-a]quinolone, has been investigated using the Molecular Electron Density Theory at the B3LYP/6-311++G(d,p) computational level with D3 correction. This study focuses on the zwitter-ionic type 32CA reaction, highlighting its polar character with the electronic flux from the azomethine ylide to the alkene. The reaction proceeds with complete *endo*-stereoselectivity, and the activation parameters show minimal variations in different solvents, consistent with experimental observations. The activation energy is associated with the depopulation of the N2–C1 and C4–C5 bonding regions, formation of non-bonding electron density at N2 nitrogen and creation of *pseudoradical* centers at C3, C4 and C5. These findings suggest that the formation of new covalent bonds does not occur at the transition states, in line with the presence of non-covalent interactions at the interatomic bonding regions, as revealed by the topological analysis of the Quantum Theory of Atoms-in-Molecules.

Keywords Molecular Electron Density Theory · Pyrrolo [1,2 a] quinoline · Electron localization function · Activation energy

1 Introduction

Pyrrolo[1,2-a] quinoline derivatives are highly interesting tricyclic nitrogen containing heterocycles consisting of a pyrrole ring fused with the quinolone and exhibit a wide range of applications as active pharmaceutical ingredients including anticancer, anti-microbial, antitumor, anti-inflammatory, anti-oxidant and anti-coagulant properties [1–6]. Moreover, they have found utility as organic materials [7, 8]. Consequently, the synthesis of these compounds has received sincere attention and several strategies have been designed such as the copper catalyzed tandem synthetic methodology [9], allene cascade reaction [10] and the visible light mediated one- and twofold annulation of N-arylpyrroles with arylalkynes [11]. An appealing alternative synthesis of pyrrolo[1,2-a] quinolines is through formal [3+2] cycloaddition (32CA) reactions of quinolinium salts [12] (Scheme 1). Quinolinium ylides on cycloaddition with alkenes furnish pyrrolo[1,2-a] quinolines as products and experimental studies on this synthetic strategy using ketones and other carbonyl derivatives are well documented in the literature [12–15]. The experimental studies on the 32CA reactions of *N*-methyl azomethine ylides and alkenes have also been extensively reported and find several applications in the synthesis of catalysts and biologically active compounds [16–18].

Since the last decade, there had been several attempts to replace the conventional synthetic strategies with the environmentally benign approaches, aiming to minimize the use of hazardous chemicals [19]. Notably, Kaur et al. [20] have reported a green synthesis of pyrrolo [1,2-a] quinolines using water as a solvent at room temperature. *N*-phenacylquinolinium bromide was used as the reagent

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Environ Monit Assess (2023) 195:1039
https://doi.org/10.1007/s10661-023-11627-6

RESEARCH

Time series analysis of groundwater quality at selected sites of Purba and Paschim Burdwan, West Bengal, India

Sanghamitra Sanyal · Sanchari Sarkar · Moitreyee Chakrabarty

Received: 21 March 2023 / Accepted: 22 July 2023

Abstract The Water Quality Index (WQI) is used to monitor the health and usability of a water body. In this study, we aimed to construct time series prediction models using groundwater WQI (GW-WQI) at four sites: IISCO-Asansol, Durgapur Town, Burdwan University, and Burdwan Station. While statistical spatio-temporal analysis has been reported earlier, no time series analysis of the data or predictive modelling has been done. Pre-monsoon and post-monsoon physico-chemical data from 2010 to 2022 were obtained from the West Bengal Pollution Control Board website to calculate the GW-WQI. Prediction modelling was performed using R 4.1.3 software. Best fit forecast models were selected to predict future trends of GW-WQI with 80% of the data. Subsequently, the models were validated using *R*-squared, root mean square error (RMSE), mean absolute error (MAE), maximum absolute percentage error (MAPE), and Thiel's *U* for the model using 20% of the data. Our results show that GW-WQI was good in pre-monsoon but unfit for drinking in post-monsoon in IISCO-Asansol, Durgapur Town, Burdwan University, and Burdwan Station. Arsenic, fluoride, and mercury were the major contaminants resulting in poor GW-WQI. Seasonal ARIMA was the best model for Burdwan University and IISCO-Asansol, ETS for Durgapur Station, and BaggedARIMA for Burdwan Station. The forecast model for Durgapur and Burdwan Station predicted a sharp increase until 2027 but was fluctuating for IISCO-Asansol and Burdwan University. Thus, GW-WQI is a major problem in the industrial belt of West Bengal that is likely to remain high or worsen in the future.

Keywords Groundwater · Time series · Water Quality Index · ARIMA · ETS · SNAIVE · BaggedARIMA · Modeling

Introduction

Groundwater is found underground in voids and fissures in rock, sand, and soil. According to the United Nations (UN), about 2 billion people globally rely on groundwater as their primary source of drinking water. In addition, groundwater is heavily used for irrigation, providing water for agriculture in many regions. It is also used for industrial and mining operations and thermoelectric power generation (UN-Water, 2022). Due to over-extraction and pollution, many groundwater resources are under threat globally (Molle et al., 2018). Sustainable management of these

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10661-023-11627-6.

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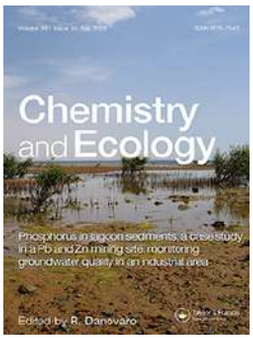
Published online: 12 August 2023



Chemistry and Ecology

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/gche20

Acute and sub-acute toxic effects of cadmium to freshwater tropical oligochaete *Tubifex tubifex* with special reference to oxidative stress and behavioural biomarkers

Neha Majumdar, Nimai Chandra Saha, Priyajit Banerjee, Tapajit Bhattacharya & Shubhajit Saha

To cite this article: Neha Majumdar, Nimai Chandra Saha, Priyajit Banerjee, Tapajit Bhattacharya & Shubhajit Saha (04 Oct 2023): Acute and sub-acute toxic effects of cadmium to freshwater tropical oligochaete *Tubifex tubifex* with special reference to oxidative stress and behavioural biomarkers, Chemistry and Ecology, DOI: 10.1080/02757540.2023.2263439

To link to this article: https://doi.org/10.1080/02757540.2023.2263439

Published online: 04 Oct 2023.

Role of vegetation characteristics on the distribution of three hornbill species in and around Pakke Tiger Reserve, Arunachal Pradesh, India

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The change in physiognomic and floristic characteristics of vegetation composition affects the bird community assemblage and the relative abundance of different species within the community. Hornbills are mutualistic to the forest with their dependency on roosting, nesting and feeding, and helping in the regeneration of different plant species by dispersing the seeds. The relationship between various vegetation characteristics and the relative abundance of three hornbill species (Great Pied Hornbill (GPH, *Buceros bicornis*), Wreathed Hornbill (*Rhyticeros undulatus*) and Oriental Pied Hornbill (OPH, *Anthracoceros albirostris*)) was studied in and around Pakke Tiger Reserve, Arunachal Pradesh, India. We walked transects ($n = 11$; 22 walks) in three study sites to detect hornbills. Vegetation sampling was done using circular plots ($n = 33$; 10 m radius) at every 400 m interval along each transect. Encounter rate (1.5 ± 0.188/km) of GPH was highest in the protected and undisturbed forest area, where food and roosting tree density were also high (114/ha). OPH was common in both the sites in the Reserve, near riverine forests (0.75 ± 0.25/km) and the dense undisturbed forest (0.875 ± 0.226/km). Multivariate analysis revealed that tree density, presence of fruiting trees (utilized by hornbills), canopy cover and tree diversity in a particular area are the major factors responsible for the assemblage of more than one hornbill species. The study shows that protection of forest patches to keep the diversity and density of the tree species intact is crucial for the survival and distribution of hornbills in the landscape.

Keywords: Forest structure, hornbill abundance, mutualism, tiger reserve, vegetation characteristics.

VEGETATION is a major determining factor of species assemblages in a bird community and the abundance of certain bird species depends on the vegetation composition of the habitat[1–5]. Both physiognomic and floristic characteristics of vegetation affect the bird species abundance[5,6]. Change in vegetation along the complex environmental and disturbance gradient can change the abundance and distribution of a particular species or species guild[7]. The interplay between vegetation and bird species assemblage is well documented[8–12]. Bird species richness and diversity are directly correlated with physiognomic characteristics such as foliage height, foliage volume, percentage vegetation cover, etc.[10,13–15]. The abundance of some tree species or a group of species can influence the distribution of certain bird species or bird guilds[16,17]. Some species do not have a specialized niche and can thrive under varied environmental conditions; they are named generalists. Whereas, most of the species are specialists, having some definite environmental set-up to survive in[18–20]. Large-bodied bird species such as hornbills are mutualistic in the forest[19]. The Great Pied Hornbill (GPH) found in South and Southeast Asia is predominantly frugivorous[19,20]. The Wreathed Hornbill (WH) is distributed throughout North East India as well as Bhutan, Bangladesh to Southeast Asia. It is largely frugivorous and lives in flocks[19,21]. Oriental Pied Hornbill (OPH) is considered to be the most common hornbill species found in the Indian subcontinent and Southeast Asia. Although frugivorous, it feeds on insects, small birds, reptiles and bats[19,20]. In the tropical rainforest, plant–frugivore interaction is important for the sustenance of the diversity of the plant species. Most tropical species depend on vertebrate frugivores for the dispersal of their seeds[22–24]. Regeneration of forest vegetation depends on the presence of seed dispersers (such as hornbills) in the forest[25]. Seed dispersal in a tropical forest is one of the vital ecosystem services[26–28] and in the absence of dispersers, loss of diversity is well observed throughout the world[29].

Seed dispersers are particularly sensitive to both habitat destruction and hunting[30–32]. A considerable amount of habitat alteration and loss has intensified in the tropical forest of North East India in the Eastern Himalayan region[33,34]. Hunting, loss of habitat due to jhum (shifting cultivation) and developmental activities are severe in the easily accessible foothill forests near the dense human habitation[32]. The remaining forest patches are also under

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MDPI

Article

Wild Felid Diversity, Space Use and Activity Patterns in the Eastern Himalaya, India

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Abstract: Species with similar resource requirements cannot coexist for long. To facilitate co-existence, carnivores adapt different strategies to partition the available resources in space and time. In high-altitude ecosystems with limited resources the operation becomes complex. We assessed species diversity and spatio-temporal resource partitioning among felid species inhabiting the intricate habitats of Khangchendzonga Biosphere Reserve (KBR), Eastern Himalaya. We used systematic camera trap surveys along with abundance and overlap indices to generate information on their space use and activity patterns. We recorded six species of felids belonging to five genera, including four species of global conservation importance. The differential use of space by felids was observed with respect to the habitat types determined by sharp altitudinal gradients with varied levels of spatial and altitudinal overlap. Maximum overlap was observed among Asiatic golden cat *Catopuma temminckii*, jungle cat *Felis chaus* and clouded leopard *Neofelis nebulosa*. The felids had distinct activity profiles from one other, particularly between golden cat and leopard cat *Prionailurus bengalensis*. Pianka's index also provided weak evidence for temporal overlap among species. The overall results indicate that habitat heterogeneity facilitates primary separation at the spatial scale, although species are also segregated temporally. Golden cat was the most adaptive felid in the area, depicting a peculiar pattern of spatio-temporal segregation with other species. We suspect either intense competition or dietary segregation among some species, and propose a further investigation of their diet and the activity patterns of their prey. The study presents an early template of carnivore community organization in resource-scarce high-altitude environments, thus, offering huge ecological and conservation significance.

Keywords: carnivore community; co-existence; Eastern Himalaya; felids; resource partitioning

Citation: Bashir, T.; Bhattacharya, T.; Poudyal, K.; Sathyakumar, S. Wild Felid Diversity, Space Use and Activity Patterns in the Eastern Himalaya, India. *Ecologies* **2023**, *4*, 41–54. https://doi.org/10.3390/ecologies4010005

Academic Editor: José Ramón Arévalo Sierra

Received: 28 November 2022
Revised: 10 January 2023
Accepted: 19 January 2023
Published: 25 January 2023

1. Introduction

Understanding the organization of ecological communities has long been a topic of interest among ecologists [1]. Resource availability is a key factor for shaping the community structure and its functioning, since it is affected by assemblages of species interacting in space and time [2–4]. As all ecosystems have limited resources, species coexist in a range of settings and are, therefore, subjected to various ecological processes at different scales [5–7]. In such an arrangement, even carnivores at the top of the food chain are forced to share their niches, which often results in an overlap in resource use, leading to coexistence or competition [8,9]. To facilitate co-existence and avoid competition, carnivores often adapt different strategies in order to partition the limited available resources [10–13]. These interactions become complex in high-altitude landscapes where resources are even scarcer [14].

According to the competitive exclusion principle, species with similar resource needs cannot coexist for very long [15]. Partitioning by the selection of prey species based on

A STUDY OF AVIAN DIVERSITY IN DURGAPUR GOVERNMENT COLLEGE CAMPUS, WEST BENGAL, INDIA

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Original scientific paper
Received: December 30th, 2021
Accepted: March 15th, 2022
HAE-2195
https://doi.org/10.33765/thate.13.2.2

ABSTRACT

The present study was performed to investigate bird diversity at the Durgapur Government College Campus, West Bengal, India from January 2013 to January 2020. The standard point count method and opportunistic sightings were used to make the checklist of the bird species. A total of 106 different bird species belonging to 47 families were recorded. Sylviidae was recorded as the most diverse family. Out of the 106 bird species, 23 were winter migrants, 4 were summer migrants, 1 was passage migrant, 1 was vagrant and the rest 77 were residents. Winter months supported the highest species richness while maximum bird density was recorded in the month of March. The global population trend chart of the observed bird species showed that most of the species belonged to the stable category (52 %, 55 species). Alexandrine Parakeet (*Psittacula eupatria*) belonged to the Near Threatened category of the IUCN Red List category among the recorded birds. The present study area is now facing various anthropogenic disturbances which are leading to the decline of the bird populations and need special attention. More extensive studies will surely enrich our knowledge of the avifauna of this area.

Keywords: *bird, checklist, diversity indices, migratory birds, urban diversity*

INTRODUCTION

The study of the diversity and distribution patterns of organisms and their function in the ecosystem are important and challenging at the same time. Birds are one of the most important components of any ecosystem [1]. They have been recorded to function as scavengers, pollinators and predators on various organisms, which helps to maintain the balance of the ecosystem [2]. Avifauna exhibit diverse patterns in their habitat selection and studies focusing on their diversity and various habitat conditions are becoming ever more popular [3 - 6]. Moreover, birds have been found to be correlated with an increase in

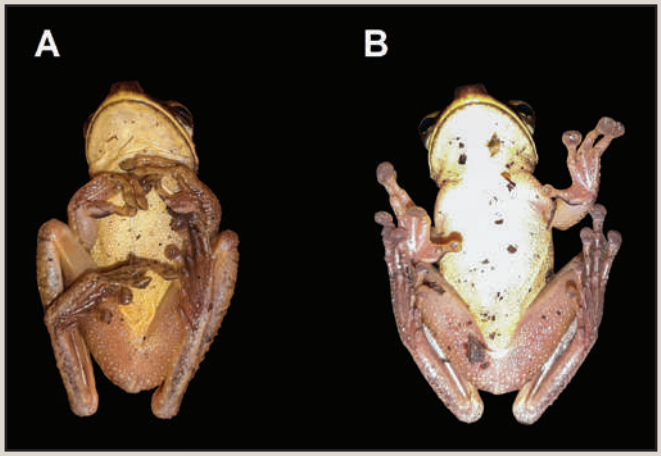

FIG. 1. *Osteocephalus vilarsi* displaying contraction (A) and death feigning (B).

in the Reserva do Desenvolvimento Sustentável Rio Negro, Municipality of Manacapuru, Amazonas, Brazil (3.07003°S, 60.75054°W; WGS 84; 51 m elev.). We simulated predator attacks by using one-finger stimuli and multiple stimuli (see Lourenço-de-Moraes et al. 2016. J. Herpetol. 26:237–244). During these stimuli, *O. vilarsi* displayed contraction, death feigning, and kick aggression (Fig, 1). Death feigning was previously reported by Ferrão et al. (2019, *op. cit.*), however, according to our knowledge and research, this is the first record of contraction and kick aggression for *O. vilarsi*.

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***PHRYNODERMA HEXADACTYLUM* (Indian Pond Frog). PREDATION.** A variety of vertebrates, such as snakes, lizards, mammals, and birds are known to feed on anurans (Toledo et al. 2007. J. Zool. 271:170–177). *Phrynoderma hexadactylum* is an aquatic dicroglossid widely distributed in the coastal plains of India, from Tripura through Bangladesh to Tamil Nadu (Frost 2021. Amphibian Species of the World: an Online Reference. Version 6.1; amphibiansoftheworld.amnh.org, 10 Aug 2022). In West Bengal it is common in the southern regions of the state as well as in the districts of the Gangetic plains. It can be found in ponds, canals, rivers and ditches where there is an abundance of dense floating vegetation (e.g., *Eichhornia*, *Pistia* and *Lemna*). *Phrynoderma hexadactylum* can be easily identified by its smooth skin, large green body, position of eyes and nostrils higher up on the head, presence of full webbing on the toes, and a distinct finger-like inner pedal tubercle on the inner aspect of the sole (Deuti 2021. Amphibians of West Bengal. Nature Books India, New Delhi, India. 152 pp.). *Ardea purpurea* (Purple Heron) is a widespread wading bird (Ardeidae) inhabiting open, shallow freshwater swamps with dense vegetation. Its diet is mainly comprised of fish, frogs, aquatic insects, and crustaceans, but occasionally also feeds upon snakes and lizards. Anuran genera predated by *A. purpurea* include *Pleurodeles*, *Pelobates*, and *Xenopus*, but no study has been done in India documenting anuran prey for *A. purpurea* (Martinez-Vilalta et al. 2020. Purple Heron [*Ardea purpurea*], version 1.0. *In* Birds of the World; del Hoyo et al. [eds.], Cornell Lab of Ornithology, Ithaca, New York. https://doi.org/10.2173/bow.purher1.01). Herein, we report an observation of *P. hexadactylum* being predated by *A. purpurea*.

FIG. 1. Predation of *Phrynoderma hexadactylum* by *Ardea purpurea* in Chupi Kasthashali Pakhiralay, Purbasthali, Purba Bardhaman, West Bengal, India.

The observation took place at 1200 h on 5 January 2020 during a winter waterbird survey conducted by the Faculty and students of PG Department of Conservation Biology, Durgapur Government College at Chupi Kasthashali Pakhiralay, Purbasthali, Purba Bardhaman (23.4531°N, 88.3555°E; WGS 84) in the state of West Bengal, India. The predation event was observed from a distance of ca. 500 m. We first observed the *A. purpurea* standing on dense floating vegetation (*Eichhornia crassipes*) looking downwards. After 1–2 min, it suddenly grabbed an adult *P. hexadactylum* by its head (Fig. 1). It stood there holding the frog for ca. 4–5 min, then slowly started ingesting it headfirst. At first the frog was emitting distress calls and trying to get free, but slowly stopped resisting and became motionless after 4–5 min (Fig. 1). The total time elapsed from initial strike to complete ingestion was ca. 15–18 min.

Not much information is available about the ecology and natural history of *P. hexadactylum*. This report contributes to the knowledge of the trophic ecology and natural history of both *P. hexadactylum* and *A. purpurea*.

The authors acknowledge the help extended by Debnath Palit for his guidance and constant motivation to do this work. We want to thank the PG Department of Conservation Biology, Durgapur Government College and Durgapur WINGS for providing the necessary facilities to do the work. Sincere gratitude to Suvamoy Changder (NIT Durgapur) for accompanying us in the bird survey.

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***PHYSALAEMUS BILIGONIGERUS* (Weeping Frog). PREDATION.** *Physalaemus biligonigerus* is a terrestrial frog inhabitant

Proc Zool Soc
https://doi.org/10.1007/s12595-023-00492-3

RESEARCH ARTICLE

Prediction of Fatty Acid Profile of Fish Skin from the Fish Flesh Fatty Acid Composition: A Regression Modelling Approach

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Received: 15 December 2022 / Revised: 23 April 2023 / Accepted: 6 May 2023

Abstract This study intends to investigate whether the fatty acids of fish flesh could be used to predict the fatty acids of skin using regression analysis. Since it was evident from literature that though the fat content of the skin is larger than the flesh, there has been little effort to measure the same. Fatty acids from flesh and skin of *Labeo rohita, Catla catla, Cirhinus mrigala and Lates calcarifer* were analyzed. Fatty acids in the flesh were correlated ($\alpha = 0.05$) with those of the skin, and significant correlation was found for total fatty acid of the flesh ($r(8) = 0.919$, $p = 0.001$), C16:0 ($r(8) = -0.919$, $p = 0.001$), saturated fatty acids ($r(8) = 0.707$, $p = 0.05$), C16:1 ($r(8) = 0.718$, $p = 0.045$), monounsaturated fatty acids ($r(8) = 0.761$, $p = 0.028$), C18:2c ($r(8) = 0.081$, $p = 0.017$) and polyunsaturated fatty acids ($r(8) = 0.844$, $p = 0.008$). Bivariate correlation test between fatty acids of fish flesh showed no correlation greater than 0.7 ($r > 0.7$). Twelve linear regression models were built and validated. Two among them (models 3 and 8) best explained the experimental and literature data. This study shows that a model can be built to predict fatty acid content of the skin using data from the flesh of fish. However, due to significant difference in the lipid profiles among different fish species, constructing a single model applicable to all fish species can be difficult and needs further exploration.

Keywords Fatty acids · Regression analysis · Fish flesh · Fish skin

Introduction

Fish is a well-known source of nutrients including essential fatty acids which human body cannot synthesize (Memon et al. 2011; Ackman 1994a, b). The beneficial effect of fish oil on human health has been discussed at lengths as it is the ultimate source of poly unsaturated fatty acids (PUFA) such as eicosapentaenoic acid (EPA), docosahexanoic acid (DHA). PUFA are important to human health for prevention of diseases like arthritis, diabetes, hypertension, and cancer (Rincón-Cervera et al. 2020; Łuczyńska et al. 2014; Glick and Fischer 2013; Jabeen and Chaudhry 2011; Sahena et al. 2010). They play a very important role in normal growth and reproduction for all the vertebrates (Memon et al. 2011). PUFA control cholesterol metabolism in the human body and maintain a correlation between neurological disorders, diabetes, obesity and dietary intake of omega 3 long chain poly unsaturated fatty acids (Krueger et al. 2022; Iverson et al. 2018; Yashodhara et al. 2009; Néchet et al. 2007; Kris-Etherton et al. 2003; Connor 2000). Like flesh, fish skin is also a rich source of fatty acids (FA) (Pateiro et al. 2020; Nazeer and Kumar 2012; Njinkoué et al. 2002). Skin being largest organ of the body, prevent water loss and entry of harmful compounds from the environment. Adipose tissue under the skin functions as lipid storage (Kendall et al. 2017). Fish skin being rich source of protein, minerals and vitamins is used as a supplement in animal feed and food

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s12595-023-00492-3.

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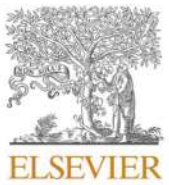
Published online: 19 May 2023

Marine and Petroleum Geology 155 (2023) 106406



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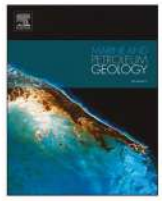

Link between Lesser Himalayan Neoproterozoic Krol succession and the Adelaide rift complex of Australia – evidence from the mudstone deposits of Krol succession, Himachal Pradesh, India

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ARTICLE INFO

Keywords:
Lesser himalaya
Neoproterozoic
Krol succession
Mudstone
Bottom current
Microturbidites
Snowball earth

ABSTRACT

The mudstone deposits, a major constituent of the Lesser Himalayan Krol succession, represents the terminal phase of Marinoan snowball melting, an important part of the most significant events of the Proterozoic time, the Cryogenian Snowball Earth. The Facies analysis suggests that the sediments were supplied to the shelf by meltwater flows, and were later dispersed to the deeper part of the shelf by current/wave-enhanced bottom currents. The upper part of the deposit bears the signature of gradual shallowing of the basin caused due to glacioisostatic rebound. Petrographic study of the samples, randomly collected from different parts of the deposit, reveals that the mud deposit is composed of silt-sized particles of quartz and dolomite, and argillaceous material. Besides the variation in proportion of these constituent components, no other material was found within this deposit. This compositional homogeneity of this huge deposit primarily suggest derivation from some preexisting sediments. Mineralogical similarity and perfect match in trace and Rare Earth elements composition suggest that this mud was derived from the periglacial loess deposits of the Nuccaleena Formation of South Australia. This is in agreement with the provenance of the underlying Krol Sandstone. The mudstones, along with the underlying Krol Sandstone, thus suggest that the Lesser Himalayan Krol succession represent an extended part of the Adelaide rift system of South Australia. The relative position of India and Australia during Neoproterozoic, as per the reconstructed configuration of the Rodinia supercontinent, corroborates this inference.

1. Introduction

Validation of the Cryogenian Snowball Earth hypothesis depends on the reconstruction of the complete history through systematic analysis of stratigraphic record of different stages of Snowball Earth, starting from its prologue to the hothouse aftermath, as conceived by Hoffman and Schrag (2000). The record of the hothouse aftermath, from the onset of thawing to the restoration of the optimum temperature for carbonate deposition, is thus of special importance. The Lesser Himalayan Krol succession of Himachal Pradesh is an important repository of the records of this important chapter of the geological history of Neoproterozoic time (Dey et al., 2022). The initial phase of the hothouse aftermath is represented by the Krol Sandstone-black shale association of this succession (Dey et al., 2022). According to Dey et al. (2022), the black shale is the product of oceanic anoxia developed during the initial thawing phase and as the melting continued, remobilization of some pre-existing aeolian sand sheet deposits, from the upper shelf region, by meltwater led to the deposition of deeper shelf fans, the Krol Sandstone, over the black shale. The Krol Sandstone, in turn, is overlain by a thick (maximum thickness ~428 m), laterally continuous succession of mudstone (*sensu* Lazar et al., 2015), the subject of the present discussion. Previously, this succession was differently described as limestone ("Krol A″ of Auden, 1934; Mahi Formation of Jiang et al., 2002, 2003), a gradation from calcareous shale and argillaceous limestone to dolomitic limestone (Bhattacharya and Niyogi, 1971), perhaps due to its fine-grained nature, low hardness and grey appearance in the outcrop. Recent microscopic investigation reveals that the lithological unit is actually represented by a thick succession of mudstone of uniform

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https://doi.org/10.1016/j.marpetgeo.2023.106406
Received 5 March 2023; Received in revised form 1 July 2023; Accepted 3 July 2023
Available online 5 July 2023

J. Earth Syst. Sci. (2022)131 208
https://doi.org/10.1007/s12040-022-01950-w

Implications of marine Gastropoda *Baylea* DeKoninck, 1883 from the Permian Barren Measures Formation, Lower Gondwana, West Bokaro Basin, eastern India

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MS received 6 February 2022; revised 18 April 2022; accepted 19 April 2022

The consideration of events of marine invasion within the continental Gondwanaland in the Indian subcontinent during the Permian is often doubted due to lack of appropriate fossil record. The Permian Barren Measures Formation within the Lower Gondwana Supergroup in eastern India is considered as deposited in a fluvio-marine estuarine setting, interpreted mostly based on sedimentological signatures in terms of marine tide and wave imprints within the so-called continental fluvial deposits. Fossilized shells of marine Gastropoda genus *Baylea* DeKoninck, 1883, are reported here from the siltstone beds of the prodeltaic sediments of the Barren Measures Formation, West Bokaro Basin. The *in-situ* preservation of the marine invertebrate fossils *Baylea* sp. provides definite proof of marine link of the West Bokaro Basin during the Barren Measures sedimentation. The present fossil record, when combined with sedimentological attributes, clearly signifies a marine inland encroachment event during the Permian time.

Keywords. Lower Gondwana; Barren Measures Formation; Permian fluvio-marine; benthic Gastropoda; *Baylea* sp.; West Bokaro Basin.

1. Introduction

The Gondwana Supergroup (late Carboniferous to early Cretaceous) in peninsular India is extensively studied by workers due to its extensive and thick succession in several intra-continental riftogenic half-graben type basins, characterized by fluvial-lacustrine sedimentations, bituminous to sub-bituminous type coal deposits, and abundant plant fossils (Casshyap 1979; Casshyap and Tewari 1988; Mukhopadhyay *et al.* 2010; Bhattacharya *et al.* 2012, 2018). The earlier model of the continental origin of the Lower Gondwana sedimentary succession (late Carboniferous to Permian) has been challenged in recent years by various workers propounding a mixed, fluvio-marine depositional model, based on sedimentological, ichnological and geochemical evidences (Gupta 1999; Ghosh *et al.* 2004; Mukhopadhayay *et al.* 2010; Bhattacharya *et al.* 2012, 2016a, b, 2018, 2021; Bhattacharya and Banerjee 2015; Bhattacharjee *et al.* 2018; and many others). However, these models are often challenged by traditionalists on the ground of absence of suitable marine invertebrate fossils (hard body part), as well-preserved *in situ* body fossils of hard-shelled

Published online: 24 September 2022

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The Journal of Analysis
https://doi.org/10.1007/s41478-022-00533-8

ORIGINAL RESEARCH PAPER

On best proximity points of cyclic contractions via implicit relations

Pratikshan Mondal[1] · **Hiranmoy Garai**[2] · **Adrian Petruşel**[3] · **Lakshmi Kanta Dey**[4]

Received: 27 October 2022 / Accepted: 30 November 2022

Abstract
Among the existing best proximity point results, in most of the cases, the results are given by using either the completeness or the compactness of the underlying structures. Thus, it becomes legitimate to have some best proximity point results in which we don't need to use the completeness as well as the compactness of the underlying structures. In this context, using some implicit relations for the simulation type functions, we acquire some contraction conditions (such as cyclic $\mathcal{A}_\alpha$-contraction condition and cyclic $\mathcal{A}'_\alpha$-contraction condition) which can serve for our desired purpose. More specifically, we obtain some best proximity point results using the aforementioned contraction conditions in the framework of a metric space.

Keywords Metric space · Best proximity point · Implicit relations · Cyclic $\mathcal{A}_\alpha$-contractions · Cyclic $\mathcal{A}'_\alpha$-contractions

Mathematics Subject Classification 47H10 · 54H25

1 Introduction

Let (M, d) be a metric space and let A, B be two non-empty subsets of M. For a non-self mapping $T : A \to B$, if the fixed point equation $Tx = x$ admits a solution say x^*, then x^* is called a fixed point of the mapping T and the study related to the fixed point of a mapping T is known as fixed point theory. If the fixed point equation does not have a solution, then for any $x \in A$, it is evident that

Communicated by S Ponnusamy.

Extended author information available on the last page of the article

Published online: 06 January 2023


Miskolc Mathematical Notes
Vol. 24 (2023), No. 3, pp. 1337–1350

HU e-ISSN 1787-2413
DOI: 10.18514/MMN.2023.4181

ON COMMON FIXED POINT RESULTS VIA IMPLICIT RELATIONS

HIRANMOY GARAI, PRATIKSHAN MONDAL, AND LAKSHMI KANTA DEY

Received 25 March, 2022

Abstract. There are certain contractive conditions (and contractions) available in the literature that ensure the existence of common fixed points of a couple and a family of mappings. However, to verify the validity of these conditions, each result must be checked separately. Thus, it becomes legitimate to obtain some contraction or contractive conditions that can bypass the computational difficulties of checking contraction and contractive conditions via individual results and ensure the existence of common fixed points simultaneously. In this article, by the virtue of implicit relations, we acquire some contraction and contractive conditions, christened A-contraction and $\mathcal{A}$-contractive conditions, which serve the desired purpose. The utility of the established conditions is exhibited through some typical fixed point results and concrete examples.

2010 *Mathematics Subject Classification:* 47H10; 54H25

Keywords: common fixed point, orbitally continuous mapping, $\mathcal{A}$-contractive mappings, A-contraction

1. Introduction

Throughout the last century, *metric fixed point theory* plays an important role in *nonlinear analysis* due to its simplicity and applicability in different fields. The main aim of this theory is to derive some adequate conditions on a mapping so that we can get the guaranty of existence of a (sometimes unique) fixed point of the mapping. The first one among these adequate conditions is the *contraction* condition which was taken into consideration by Banach [2] in 1922. After this, the contraction condition of Banach have been extended in a variety of ways and as a consequence, a lot of adequate conditions for existence of fixed points of a mapping have been established. Among these adequate conditions, the contraction conditions of Kannan [8], Chatterjea [4], Reich [12], Ćirić [5] are remarkable. In order to verify the validity of these contraction conditions, we need to prove and remember separate results for each contraction conditions. So one may naturally ask whether any contraction condition can

AIMS Mathematics, 8(9): 22067–22080.
DOI: 10.3934/math.20231124
Received: 19 February 2023
Revised: 18 May 2023
Accepted: 05 June 2023
Published: 12 July 2023

http://www.aimspress.com/journal/Math

Research article

On Maia type fixed point results via implicit relation

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Abstract: In order to study Maia type fixed point results for several well-known contractions, we suggest two novel contractions called $\mathcal{A}$-contraction and $\mathcal{A}'$-contraction. The majority of the Maia type fixed point results for various contractions can now be unified through these, which eliminate the need to manage various contractions individually. The advantage of including such contractions in the study of Maia type fixed point results has been demonstrated in suitable examples. We present an application of one of our established results towards the conclusion of the paper.

Keywords: metric space; fixed point; $\mathcal{A}$-contractions; $\mathcal{A}'$-contraction; enriched contractions
Mathematics Subject Classification: 47H10, 54H25

1. Introduction

The Banach contraction principle plays the fundamental role in the development of metric fixed point theory since this theory is integrated with the Banach contraction principle due to S. Banach [8] in the year 1922. This principle confirms that a mapping T defined on a metric space (S, d) into itself admits a unique fixed point, i.e., there is a exactly one $s \in S$ such that $Ts = s$ provided that

$$d(Ts, Tt) \leq c\, d(s, t) \tag{1.1}$$

for all $s, t \in S$ with $0 \leq c < 1$, and the metric space (S, d) is complete.

A self-mapping T satisfying (1.1) is known as a Banach contraction mapping. After this fundamental result, metric fixed point theory has become a research field of extensive interest in the literature. Consequently, this theory has encouraged a number of renowned mathematicians to contribute to it. As a result, we have witnessed a large number of fixed point results. Some

Ring Oscillators Under Nonlinear Coupling: Bifurcation and Chaos

Hrishikesh Mondal[1], **Arghya Pathak**[2],
Tanmoy Banerjee[3], and **Mrinal Kanti Mandal**[2†], Non-members

ABSTRACT

The dynamics of two non-linearly coupled ring oscillators are examined in this study. Each ring oscillator consists of three-stage inverters, coupled through a resistor and diode. The system is mathematically modeled by non-linear differential equations. A numerical phase plane, bifurcation, and quantitative measures, like the Lyapunov exponent, confirm the transition from periodic to chaotic oscillation in a broad parameter zone. The system is implemented in a prototype hardware electronic circuit with bifurcation and chaos observed experimentally. This circuit can be used in practical applications such as cryptography and random number generation.

Keywords: Ring Oscillator, Nonlinear Coupling, Bifurcation, Chaos, Electronic Circuit

1. INTRODUCTION

Understanding the dynamics of ring oscillators is an important research topic since they play a crucial role in engineering and biology [1–4]. In electronic engineering, a ring oscillator is a multiphase system which is easy to design by cascading a number of inverters connected in a closed loop chain [5]. A ring oscillator (RO) can be designed by using single-ended or differential inverters. In the case of a single-ended inverter-based RO, the number of inverters in the closed loop chain must always be odd to support Barkhausen's oscillation criteria. However, a differential inverter-based RO can produce oscillation with an even or odd number of inverters in the closed loop chain [6, 7]. Ring oscillators have wide applications in different electronic systems, such as clock signal generation [8], FM demodulation [9], frequency synthesizing [10–12], temperature sensing [13], etc.

The characteristics of ring oscillators [14, 15] and their applications in different fields of electronics are well documented in the literature. However, the dynamic RO model is essentially nonlinear and difficult, if not impossible, to solve exactly. For a complete understanding of the dynamics of a RO one must apply nonlinear bifurcation and chaos tools [16–18]. However, understanding the nonlinear behavior of an RO is very much limited in the literature and the appearance of bifurcation and chaos in RO has not received much attention [1, 19–21].

The motivation for studying the nonlinear behavior of ROs is two-fold. First, apart from man-made electronic circuits, ROs are also found in biological systems. For example, in a synthetic genetic repressilator, three genes in bacteria repress each other and combined behave like a ring oscillator [2]. As with most natural oscillators, genetic oscillators also work in coupled mode, therefore, some studies have explored the collective dynamics of coupled gene-based ring oscillators. In [3, 4], the dynamics of two linearly coupled synthetic genetic ROs were studied in detail. The authors reported the occurrence of multistability, quasiperiodicity, and chaos. However, the effect of nonlinear coupling in genetic ROs has not been explored. Furthermore, experimental observations of the coupled ROs collective dynamics in the biological domain are still lacking.

The second motivation comes from the application potentiality of chaos. In this context the most celebrated chaotic circuit is the Chua, establishing that apart from their academic interests, chaotic circuits can serve in the application of cryptography, random number generation, and chaotic communications [22–26]. In this connection, autonomous Boolean network-based chaos generators open the path to high frequency chaos in a flexible setup [27, 28].

Ring oscillators are also found to be potential chaos generators that can be implemented in IC form. In this endeavor, Hosokawa and Nishio [19] first proposed that when coupled through a combination of cross-coupled diodes, two three-stage ROs are capable of producing a chaotic signal. Since a chaotic signal is aperiodic in nature, it has no regular temporal zero crossings. Thus, it can generate large intrinsic jitter and may be treated as the potential source of entropy for generating a true random number (TRN), an idea implemented by Çiçek

Manuscript received on May 25, 2022; revised on July 1, 2022; accepted on August 24, 2022. This paper was recommended by Associate Editor Kriangkrai Sooksood.

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Digital Object Identifier: 10.37936/ecti-eec.2023211.248668

IETE Technical Review

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/titr20

Sparse Compression-Based Image Encryption using Data Encryption Standards RC5

Arghya Pathak, Hrishikesh Mondal, Jayashree Karmakar, Subhashish Pal, Debasish Nandi & Mrinal Kanti Mandal

To cite this article: Arghya Pathak, Hrishikesh Mondal, Jayashree Karmakar, Subhashish Pal, Debasish Nandi & Mrinal Kanti Mandal (2023): Sparse Compression-Based Image Encryption using Data Encryption Standards RC5, IETE Technical Review, DOI: 10.1080/02564602.2023.2240286

To link to this article: https://doi.org/10.1080/02564602.2023.2240286

Published online: 31 Jul 2023.

IETE TECHNICAL REVIEW
https://doi.org/10.1080/02564602.2023.2240286

Sparse Compression-Based Image Encryption using Data Encryption Standards RC5

Arghya Pathak[1], Hrishikesh Mondal[2], Jayashree Karmakar[3], Subhashish Pal[1], Debasish Nandi[4] and Mrinal Kanti Mandal[1]

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ABSTRACT

In this work, we have used the standard symmetric key block cipher data encryption algorithm RC5(32,16,8) for the encryption of digital greyscale images. For this, we have only considered the nonzero elements of the sparse matrix of the images which have been generated using the sparse representation technique. The security strength of the proposed technique is verified through different quality parameters, *e.g.* information entropy, correlation coefficients, NPCR, UACI, and NIST test. Our proposed algorithm achieved the maximum information entropy value of 7.9977 for the cameraman image and nearly zero correlation coefficient values establish the robustness of the cryptosystem. The highest NPCR and UACI values obtained in our work are 99.6916 and 33.9605, which are closer to the maximum theoretical values. The proposed technique is also compared with some of the contemporary works to validate the credibility of our proposed algorithm.

KEYWORDS

Sparse representation; data compression; dictionary learning; RC5 encryption; symmetric block Cipher

1. INTRODUCTION

Data security is an indispensable part of a secured communication system. Protection of confidential data from stealing by hackers is a challenging task for researchers. So, the necessity of more and more complex and efficient data encryption algorithms to protect the data from unwanted intervention is highly required. In social media platforms, most of the information is communicated in the form of digital images and videos, which demands a secure and fast transmission mechanism. These types of a large amounts of data make the encryption mechanism computationally complex and require high storage memory space. Data compression may be a possible solution to the storage problem [1] but the complexity and unpredictability of the cryptosystem is the major issue for protection.

From the early days to the present, numerous cryptosystems have been developed, but none of them can demand that their system is fully resistive against several third-party attacks. With the improvement of the performance and speed of modern days computers, it becomes easier for the intervention to extract information from the cipher text in a short time. Therefore, it becomes a challenging task for the researchers to design an encryption mechanism that is unpredictable by nature as well as having a high key dependency. The encryption technique should be designed in such a way that it can resist unwanted intervention and provides robust security. Many image encryption algorithms have been reported to date, but all are basically confined within chaos and number theory-based encryption mechanisms [2–12]. A standard data encryption algorithm mainly works through three operations: diffusion, confusion and pixel permutation. DES, AES, RC5, RC6, etc. [13, 14] are some conventional encryption techniques used to encrypt different classes of text data [1, 2, 15, 16]. The well-known cryptographic algorithm like AES, and DES are useful for raw data of small size but in the case of digital images, these algorithms fail to provide the desired result. So, more non-linear science-based encryption techniques have been developed and become popular [3].

One useful and strong encryption technique based on non-linear phenomena is the chaos-based encryption method. The concept of chaos theory introduced by Edward Lorentz has gained the researcher's attention due to its several attractive features like sensitive dependence on initial conditions, randomness, ergodicity, etc. A large number of chaos-based encryption techniques have been reported over the past two decades. We can find a summary of the different chaos-based encryption techniques in [17].

ECTI Transactions on Computer and Information Technology
Journal homepage: https://ph01.tci-thaijo.org/index.php/ecticit/
Published by the ECTI Association, Thailand, ISSN: 2286-9131

A Novel Image Encryption Technique with Four Stage Bit-Interspersing and A 4D-Hyperchaotic System

Subhashish Pal[1], Ansuman Mahanty [2], Arghya Pathak[3], Jayashree Karmakar[4], Hrishikesh Mondal [5] and Mrinal Kanti Mandal[6]

ABSTRACT

This paper introduces a new technique of color image encryption that includes four stages of bit interspersing and a 4D-hyperchaotic system. At first, the pixel values for different RGB channels of a plane color image were represented by an 8-bit binary number. The bit interspersing operation has been implemented on the bit stream generated by considering a particular block size for each color channel and reshaping it to the original size. The cipher image was then constructed by performing a bit XOR operation on the resultant image and the chaotic sequences generated by a 4D hyperchaotic system. The initial state variables of the said chaotic system have been developed from a 32-character secret key. This operation has been repeated three times, considering different block sizes of the newly generated cipher image after each stage. The main strengths of the proposed algorithm are the bit interspersing and image-dependent chaotic key base pixel substitution by bitwise XOR operation. A set of standard security tests are conducted to test the reliability of the suggested encryption method. Comparing the crypto-parameters to other recent works, we find that the proposed algorithm is better than the other methods.

Article information:

Keywords: Bit interspersing, Cryptography, Chaos, Hyperchaotic system, Encryption, Decryption

Article history:
Received: August 29, 2022
Revised: December 9, 2022
Accepted: January 21, 2023
Published: March 4, 2023 (Online)

DOI: 10.37936/ecti-cit.2023171.249733

1. INTRODUCTION

The growth of the internet and communication infrastructure has increased the volume and variety of shared data, making it more difficult for cryptosystem designers to guarantee the privacy of transmitted information. Many researchers have reported essential contributions to data security. Cryptography is a subset of data security systems that encrypts data before sending it across a network so that only the intended recipient can decipher it. In cryptography, keys are essential tools for encrypting and decrypting information. When both the keys are the same, that type of encryption is termed symmetric key cryptography, and if they are different, it is called asymmetric key cryptography [1].

In modern cryptography, the encryption algorithm plays a pivotal role in determining the quality of the cryptosystem. The more complex the encryption algorithm leads to a robust cryptosystem against attacks. In the last two decades, chaos-based cryptography [2] has drawn the attention of researchers as the pseudorandom sequences produced by such nonlinear chaotic systems are hard to understand and anticipate because of their structural complexity. Stochasticity, sensitivity to their beginning circumstances, and control parameters contribute to their popularity in such applications. As far back as 1998, Fridrich came up with the concept of chaotic encryption [3]. Permutation and diffusion are the two main components working behind such designs; hence, many cryptography researchers prefer chaotic systems [4]. In the last few years, using hyperchaotic systems in cryptography has become more popular than a standard chaotic system. Hyperchaotic systems are those chaotic systems that have more than one positive

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PHYSICAL REVIEW D
covering particles, fields, gravitation, and cosmology

Superradiant energy extraction from rotating hairy Horndeski black holes

Sohan Kumar Jha, Mohsen Khodadi, Anisur Rahaman, and Ahmad Sheykhi

Phys. Rev. D **107**, 084052 – Published 28 April 2023

ABSTRACT

Adopting the manifestation of low frequency and low mass for the scalar perturbation, we perform a semiclassical analysis of the superradiance phenomenon for a rotating hairy Horndeski black hole (BH). For the spacetime under study enriched by the hairy Horndeski parameter h, in addition to the mass M and spin a, we compute the amplification factor of scalar wave scattering indicating the energy extraction from the BH. We find that due to the addition of the hairy parameter h in the geometry, the superradiance scattering and its frequency range enhance compared to the Kerr BH. This implies that Horndeski's gravity belongs to those alternative theories of gravity that make the amplification factor larger than the Kerr BH so that the energy extraction in its framework is more efficient than general relativity. Calculating the outgoing energy flux measured by an observer at infinity verifies the role of

Issue
Vol. 107, Iss. 8 — 15 April 2023

WATER SCIENCE
2023, VOL. 37, NO. 1, 57–70
https://doi.org/10.1080/23570008.2023.2215573

Ecological assessment of pit lakes in Raniganj, India: Application of different indices and multivariate statistics

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ABSTRACT

Coal mine generated open pit lakes are well distributed in Raniganj coal field area, West Bengal, India. This paper screened out ecological state macrophyte index (ESMI), water quality index (WQI) and multivariate statistical methods to assess the ecological status of four pit lakes, Nagrakonda, Joyalbhanga, Dalurbandh, and Kumardihi. Seven water quality parameters (pH, total dissolved solids, dissolved oxygen, Secchi depth nitrate, chloride, and phosphate) and six sediment quality parameters (pH, organic carbon, bulk density, particle density, available nitrogen and phosphorus) were analyzed for one year on a monthly basis from four pit lakes. The abundance and diversity of aquatic macrophytes were also analyzed. In the studied pit lakes, water and sediment quality variables showed significant spatial variation. WQI showed that the water quality in all pit lakes was good and according to ESMI these lakes were categorized into good ecological status. The results of this study indicated the values of water quality and macrophyte based indices highlighted the ecological condition of the pit lakes of the study sites thus should be considered it as reliable tool for assessing of the ecological status of any wetlands.

ARTICLE HISTORY
Received 4 January 2023
Revised 10 May 2023
Accepted 15 May 2023

KEYWORDS
Macrophytes; Raniganj coalfield; pit lakes; ecological state macrophyte index; water quality index

1. Introduction

Pit lakes are originated after cessation of open mining operation (Castro & Moore, 2000; Ghosh, 2012; Ghosh, Pal, & Mukherjee, 2005; Schultze, Vandenberg, McCullough, & Castendyk, 2022; Tiwary & Dhar, 1994; Vandenberg, Schultze, McCullough, & Castendyk, 2022). There has been a boom in open-pit coal mining, giving up to construct of multiple pit lakes. Because of the vast number of pit lakes that will grow across the world over the next half-century and a large amount of water they have, water quality conditions in these pit lakes will be critical, particularly in locations where water is limited. Weathering of the wall rocks and other exposed rocks in the surrounding drainage releases solutes into the lake water. Pit lakes are distinguished from natural lakes by their much greater relative depths. Pit lakes may be expensive to restore when the mine is closed. However, depending on specific attributes, such as water quality, pit lakes may often provide considerable regional benefit, resolve residual closure concerns associated with both their own and overall project closure, and even offset mining-related environmental costs by establishing new end uses. Water quality, slope stability, and safety considerations all play a role in these prospects (McCullough, Schultze, & Vandenberg, 2020; Schultze, Vandenberg, McCullough, & Castendyk, 2022; Vandenberg, Schultze, McCullough, & Castendyk, 2022). However, some of pit lakes are broadly available and have been utilized by the residents for taking a bath, agribusiness, and fishery. The Raniganj coal field (RCF) has a high proportion of pit lake clusters in West Bengal. Most of them have remained unchanged by anthropogenic activity and preserving their unique character. At present there is no organized strategy for monitoring and management of the pit lakes (Palit & Kar, 2019). As a result, numerous pit lakes have seen water quality degradation and significant water loss. Even though it is strictly illegal, liming, and fertilizing lakes to stock them with fish (mostly Indian major carps) is rather common in these pit lakes. These are some of the major factors that lead to negative and irreversible changes in such ecosystems. Therefore, it is necessary to understand the ecological assessment of these pit lakes to conserve their unique characteristic and biodiversity. Because of their steep slope and the fact that most pit lakes are inaccessible to people, ecological evaluation of pit lakes is a difficult task. Given the study programming aims and objectives, monitoring these systems necessitates balancing sample efforts with available resources. Those macrophytes are commonly utilized for ecosystem monitoring as well as water quality detection. For this reason, indexes have been devised in several countries (Bytyçi et al., 2022; Demars & Harper, 1998; Toso, Marzani, Siligardi, Negri, & Fabris, 2005). Relationship between macrophyte diversity and limnological parameters has been investigated for decades (Bubíková & Richard Hrivnák, 2018; Parray, Koul, & Shah, 2021; Stendera et al., 2012). This knowledge is essential for sustainable freshwater management and protection,

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Indian J. Applied & Pure Bio. Vol. 38(3), 1563-1574 (2023). **ISSN: 0970-2091**
A Web of Science Journal

Water quality of selected Pitlakes of Raniganj coal fields, West Bengal, India

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Abstract

Water is essential for open-pit mining's dust-suppression systems and coal processing units. To meet this requirement, mining companies must buy surface or groundwater supplies from neighbouring domestic or agricultural users. After mining, these water resources are rarely replenished, permanently reducing agricultural production. Whether water is acidic, neutral, or basic depends in large part on the quality of the water. Gunjan Ecological Park Pit Lake's pH value is 7.09 at its lowest, and Joyalvanga 1 Pit Lake has a pH value of 7.88 at its highest. Chora had the lowest level of hardness (180.42 mg/l), while Dalurbandh pit lake had the highest level (334.75mg/l). The lowest DO (Dissolved Oxygen) level was found in Chora pit lake at 3.90 mg/L and the highest DO level was 6.32 mg/ l. Considering the water quality of pitlakes ,it is reflected that water of pitlakes has high mineral and nutrient ccontent which can be used in various aquaculture practices as well as in irrigation for their sustainable use.

Key words : Pitlakes, water quality, sustainable use, Raniganj coalfield area.

When surface mines are shut down, open pits begin to fill with water from a variety of sources, including groundwater recharge, surface water diversion, and active pumping. Water fills open pits left behind after mining operations are finished to create pit lakes. These holes can be filled either through artificial flooding or by letting hydrological processes like precipitation or groundwater infiltration fill them naturally. Pit lake ecosystems are important and environmentally endangered aquatic landscapes as well as a potential source of future biological resources. There might be a wide range of plant and animal species living there, several of which are threatened on a local or global scale. Pit lakes continue to be poorly managed due to a lack of expertise. To provide ecological and environmental benefits in poor countries, wetland and freshwater systems, like Pit Lake,

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WATER SCIENCE
2023, VOL. 37, NO. 1, 98–116
https://doi.org/10.1080/23570008.2023.2221069

Spatial pattern analysis of zooplankton and surface water of pit lakes (Raniganj coal field, India)

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ABSTRACT

Open pit technique is often the simplest and most cost effective mining technology. Coal mining, which began in 1774 in Raniganj, West Bengal, India, led to many abandoned pits, which led to the formation of pit lakes. Mining has a tablvariety of environmental ramifications around the world. On the other hand, the pit lakes of the Raniganj coal field (RCF) are being used for recreational purposes. Knowledge of the spatial pattern in the zooplankton population and surface water quality in pit lakes waters of the Raniganj coal field region is rather limited. Sixteen pit lakes in the RCF in West Bengal, India, were investigated from January 2019 to December 2021. In the present study, we analyzed the spatial pattern and mode of distribution of zooplankton communities based on Coefficient of dispersion methods. To perform a comprehensive analysis of the water quality condition of this study area, we apply water quality index (WQI) methods. A total of 51 taxa were identified and the density was primarily dominated by rotifers. The most dominant species were: *Brachionus forficula*, *Paracyclops* sp. and *Sida* sp. Clumped type of zooplankton distribution pattern was observed in the studied pit lakes. The water quality in most of the studied pit lakes was poor. All the water quality parameters showed significant spatial variations as per Kruskal-Wallis test. The clustering technique produces three groups of pit lakes that are particularly convincing as the pit lakes in these groups showed comparable characteristics.

ARTICLE HISTORY
Received 26 March 2023
Revised 20 May 2023
Accepted 30 May 2023

KEYWORDS
Pit lake; Raniganj coal field; Zooplankton; Water quality index; Rotifers

Introduction

Water resources, both surface and groundwater, will be affected by different stages of coal mining and even after it has ended. This includes the mining operations, mine dewatering, leakages of contaminated leachates and outflows of untreated water (Farhad et al., 2017; Rambabua et al., 2020; Randive & Jawadand, 2020). Due to lack of suitable strategy in India, water is frequently dumped without purification or proper utilization after mining operations. The number of pollutants in mine water can vary significantly. Some sources of mine water are used for industry, agriculture, and even drinking and domestic purposes that can be met with appropriate treatment. In the past several decades, open-cast mining activities have become widespread in India to recover economically viable and valuable ore near the surface (Goswami, 2015). As backfilling is typically tricky or economically unfeasible, an empty pit remains once extraction operations are done. This is known as a mine void (Ghosh, 2012). Later the voids are filled by rainwater, surface and sub-surface water. The once-water-filled mine gap has turned into a pit lake (Palit & Kar, 2019). The water quality in such pit lakes varies greatly depending on the geological catchments. The Raniganj coal field (RCF) has a large concentration of pits lake clusters in West Bengal, India. Mining-induced pit lakes initiated to form in Raniganj in the 20th century. Most pit lakes are formed due to open-cast coal mining, frequently accompanied by clay and sand extraction. The hydro-chemical and hydro-biological characteristics of lakes within the RCF still need to be better understood. The amount of information obtained from the literature from this domain involves either study of a single aspect or just regional-wide studies because the pit lakes are located in inaccessible terrains. As a result, most of them have remained unaltered by anthropogenic activity, retaining their original characteristics. Although some pit lakes are widely accessible and have been utilized for local people for various purposes, including bathing, agriculture, and fish farming, there is currently no systematic monitoring and management strategy for the lakes (Palit & Kar, 2019). For this reason, many pit lakes have faced water quality

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ESSACHESS – Journal for Communication Studies

(Surface) Reading the Interface between the Naga Author Easterine Kire and Select YouTube Channels: A Netnographic Study

ESSACHESS –
Journal for Communication Studies
Volume 16 Issue 2(32), p. 173-194

https://www.essachess.com/
DOI: 10.21409/essachess.1775-352x

Cite: CHATTERJEE, N. (2023). (Surface) Reading the Interface between the Naga Author Easterine Kire and Select YouTube Channels: A Netnographic Study. *ESSACHESS*. 16(32): 173-194. https://doi.org/10.21409/YR9K-ET03

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Abstract: The present study investigates 06 YouTube triads of communications on/by Easterine Kire (the Naga-Norwegian Anglophone author) on YouTube for writing back the Naga indigenous identity. The 06 triads, if examined and analysed, might reveal Kire's performative roles in building trans-local bond with digital participants to shape Naga literary articulations and representations in terms of Naga indigeneity vis-a-vis to build a literary market for Naga Anglophone literature. Applying netnography, the study examines her cultural representations and individualizations as a jazz poet and an interviewee on the YouTube channels. The representations accumulate further significations as critical thinkers, publishers, bookstores, readers, and researchers respond (at various levels) to Kire within the culture groups. The study is unique as it uses netnography as a research tool to 'surface read' the significant but under-noticed interface between a Naga Anglophone novelist from a diasporic subject position, the YouTube owners, and the YouTube audience in the context of Naga indigenous cultural production and reception. Moreover, it might be used as a blueprint for researching on the most obscure under-noticed digital data on the most culturally suppressed problem areas amidst the most uncertain fieldwork plans (for example, during and after the Covid-19 pandemic).

Keywords: netnography, Naga identity, YouTube, communication, Easterine Kire

Article received on July 25, 2023. Article accepted on December 6, 2023.
Conflict of Interest: The author(s) declare(s) no conflict of interest.

Journal of Asian and African Studies

Impact Factor: 1.1 / 5-Year Impact Factor: 1.2 | Journal Homepage | Submit Paper

Restricted access | Research article | First published online March 28, 2023

Disparity in Educational Participation in the Lenses of Educational Returns and Family Background: Evidence from India

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OnlineFirst | https://doi.org/10.1177/00219096231158342

Abstract

The paper attempts to investigate the origin of inequality in educational participation across Indian social groups in terms of inequality in the expected monetary educational returns and other demand-side factors responsible behind educational decision. We employ the binary logit model of regression for the accomplishment of the objective of this study. In addition, we decompose the discrepancy in educational participation into 'response effect' and 'attribute effect' to examine whether there is any discrimination in educational participation against the members of the disadvantaged social groups.

JEL Classification: I21, I24, I26