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Synthesis, spectral analysis and quantum chemical studies on molecular geometry, chemical reactivity of 7-chloro-9-(2′-chlorophenyl)-2,3-dihydroacridin-4(*1H*)-one and 7-chloro-9-(2′-fluorophenyl)-2,3-dihydroacridin-4(*1H*)-one

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Spectral analysis
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ABSTRACT

7-Chloro-9-(2'-chlorophenyl)-2,3-dihydroacridin-4(*1H*)-one (**3a**) and 7-chloro-9-(2'-fluorophenyl)-2,3-dihydroacridin-4-(*1H*)-one (**3b**) were synthesized from 2-amino-2′,5-dichlorobenzophenone (**1a**) and 2-amino-5-chloro-2'-fluorobenzophenone (**1b**) respectively with 1,2-cyclohexanedione (**2**) in the presence of 1-butyl-3-methylimidazolium tetrafluoroborate and $InCl_3$ condition. The synthesized compounds have been recorded of FT-IR, NMR spectra and the structure was further confirmed by using single crystal X-ray diffraction. The synthesized compounds have been further checked the photo physical properties like UV, emission and fluorescent quantum yields were calculated. FT-NMR spectra and ^{1}H and ^{13}C NMR chemical shifts have been measured and computational calculations of compounds **3** are done by using B3LYP method with 6-311G basis set in gas phase. Similarly calculated vibrational frequencies were found in good agreement with experimental findings. The optimized geometry of molecules **3** was compared with experimental XRD values. DFT calculations of the molecular electrostatic potential (MEP) and HOMO - LUMO frontier orbitals identified chemically active sites of compounds **3** responsible for its chemical reactivity.

1. Introduction

Acridones in particular are naturally occurring alkaloids which can be considered as aza-analogs of xanthones [1]. A number of acridine derivatives serve as chemotherapeutic agents, especially in the field of antitumor DNA-binding agents [2]. Promising biological and pharmacological activity shown by some acridine derivatives emphasizes the importance for developing new acridine-based poly cyclic heterocycle syntheses, as there are many known naturally occurring acridone derivatives with significant biological activity such as anti-bacterial, anti-HIV, antimalarial and anticancer agents [3–6]. Most of the conventional metal salts utilized as Lewis acid catalysis has attracted much attention in organic synthesis [7]. Among the Lewis acids, indium chloride have emerged mild and water tolerant Lewis acid catalyst can effective for various chemical transformations because of the relatively low toxicity indium (III) compounds, their stability in air and water, and their recyclability. These features encouraged our interest in exploring the synthetic utility of indium (III)chloride as a catalyst for the synthesis of acridones, and herein, we report a simple, high-yielding, convenient, and elegant procedure for the synthesis of quinolines. In particular, we recently reported the $InCl_3$-catalyzed synthesis of important heterocycles, such as Pyranocarbazoles, pyranoquinolines and pyridocarbazoles [8–10].

The most interesting method for the development of organic synthesis is constantly reporting new methodologies and catalytic reactions. Syntheses of acridones in green environment based methods on the human body has more attention of organic chemists due to the cost effectiveness, safe, easy and waste

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minimization for solvent free methods [11]. A wide range of applications are envisaged using solvents and recently the ionic liquids are much attention for alternative for green solvents and having more specificity, reaction rate and yield [12]. Room temperature ionic liquids based on the 1,3- dialkylimidazolium cation are attracting increasing interest as alternative reaction media. The same reaction was synthesized by using room temperature ionic liquids are used to reaction condition [13]. Another method for efficient procedure for the preparation of quinolines through a Friedländer reaction catalyzed by $FeCl_3 \cdot 6H_2O$ in an ionic liquid [14]. In previously, the Friedländer syntheses were synthesized many methods, catalysis and solvents to give 3-substituted quinolines and poly heterocycles [15]. Our group would like to report first time by using Ionic liquids in Lewis acid for synthesis of polycyclic quinolines in Friedländer synthesis. This way, polycyclic quinoline derivatives have been prepared by condensation of 2-aminoarylketones with carbonyl compounds possessing a reactive methylene group, followed by cyclodehydration. To this day it is still considered the most useful method for preparing such compounds; we recently [16] reported the synthesis of hetero annulated quinoline and carbazole derivatives.

Optimized structures of 7-chloro-9-(2'-chlorophenyl)-2,3-dihydroacridin-4(*1H*)-one **(3a)** and 7-chloro-9-(2'-fluorophenyl)-2,3-dihydroacridin-4(*1H*)-one **(3b)** are done at B3LYP/6-311G level in vacuum. IR spectra of these compounds are calculated at same level of theory. Some peaks which are related with experimental results are selected and the agreements between experimental and calculated frequencies are examined in detail. Nuclear magnetic resonance (NMR) spectra of these compounds are calculated by using gauge-including-atomic-orbital (GIAO) method. Molecular orbitals (MOs) energy diagrams, molecular electrostatic potential (MEP) maps, MEP contours and chemical reactivity of synthesized compounds are examined. Additionally, UV-VIS spectra of mentioned compounds were calculated at same level of theory in gas phase (vacuum), ethanol and methanol. Conductor-like polarizable continuum model was selected to examine the interactions of solute–solvent.

7-Chloro-9-(2'-chlorophenyl)-2,3-dihydroacridin-4(*1H*)-one **(3a)** and 7-chloro-9-(2'-fluorophenyl)-2,3-dihydroacridin-4(*1H*)-one **(3b)** were synthesized from 2-aminoaryl ketones (**1**) and 1,2-cyclohexanedione (**2**) in the presence of 1-butyl-3-methylimidazolium tetrafluoroborate and $InCl_3$ condition. The synthesized compounds were subjected to absorption, emission with fluorescent quantum yields.

2. Experimental details

2.1. General procedure for synthesis of 3

Appropriate 2-amino-arylketone (**1,** 1 mmol) was reacted with 1,2-cyclohexanedione (**2,** 1.2 mmol) with $InCl_3$ (1.5 mmol) and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4) (1.0 mmol) at 100 °C for 2 h. The completion of the reaction was monitored by TLC. The obtained product was extracted from the ionic liquid phases using ethylacetate as solvent. The ethylacetate solution was distilled under reduced pressure to isolate the product and the ionic liquid medium was used again for subsequent reaction cycles. Evaporation of the solvent was followed by purification via column chromatography over silica gel using petroleum ether: ethyl acetate (97:3) as eluent to yield the corresponding products (**3**).

*7-Chloro-9-(2'-chlorophenyl)-2,3-dihydroacridin-4(1H)-one (**3a**)*

Yellow solid; M.p. 188–190 °C. Yield 96%, FT-IR (KBr, cm^{-1}) ν_{max}: 1700.62 (-C=O), 1599.66 (-C=N), 759.816 & 700.998 (-C-Cl). ^{1}H NMR (**$CDCl_3$** 400 MHz) (ppm) δ: 2.151–2.218 (m, 2H, C_{10}-CH_2), 2.748–2.837 (m, 2H, C_{11}-CH_2), 2.851–2.953 (m, 2H, C_9-CH_2), 7.227–7.497 (m, 2H, C_3, C_5-H), 7.508–7.635 (m, 2H, C_{16}, C_{18}-H), 7.650–7.685 (m, 2H, C_{17}, C_{19}-H), 8.348 (d, 1H, J = 8.80 Hz, C_2-H); ^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) δ: 22.190 (C_{10}), 27.372 (C_9), 40.125 (C_{11}), 123.909 (C_6), 127.507 (C_8), 128.881 (C_5), 130.251 (C_{18}), 130.622 (C_{16}), 130.430 (C_{19}), 133.276 (C_3), 133.221 (C_{15}), 130.883 (C_{17}), 134.273 (C_2), 135.028 (C_4), 135.363 (C_{14}), 144.470 (C_1), 145.541 (C_7), 148.616 (C_{13}), 196.946 (C_{12}); Anal. Calcd. for: $C_{19}H_{13}Cl_2NO$: C, 66.68; H, 3.83; N, 4.09; found C, 66.61; H, 3.89; N, 4.12%.

*7-Chloro-9-(2'-fluorophenyl)-2,3-dihydroacridin-4(1H)-one (**3b**)*

Yellow solid; M.p. 198–200 °C. Yield 92%, FT-IR (KBr, cm^{-1}) ν_{max}: 1705.73 (-C=O), 1599.66 (-C=N), 844.699 (-C-F) & 761.744 (-C-Cl). ^{1}H NMR (**$CDCl_3$** 400 MHz) (ppm) δ: 2.122–2.252 (m, 2H, C_{10}-CH_2), 2.804–2.846 (m, 2H, C_{11}-CH_2), 2.862–2.966 (m, 2H, C_9-CH_2), 7.256–7.284 (m, 2H, C_{16}, C_{18}-H), 7.343–7.369 (m, 2H, C_{17}, C_{19}-H), 7.372–7.407 (m, 1H, C_5-H), 7.670 (dd, 1H, J_m = 2.40 Hz, J_o = 8.80 Hz, C_3-H), 8.341 (d, 1H, J = 8.80 Hz, C_2-H); ^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) δ: 22.234 (C_{10}), 27.559 (C_9), 40.088 (C_{11}), 122.744 (C_6), 124.032 (C_8), 124.821 (C_5), 129.236 (C_{16}), 130.826 (C_{18}), 131.157 (C_{19}), 131.240 (C_{17}), 133.234 (C_3), 135.364 (C_2), 135.493 (C_4), 141.233 (C_{14}), 145.500 (C_1), 148.475 (C_7), 158.237 (C_{15}), 160.696 (C_{13}), 196.880 (C_{12}). Anal. Calcd. for: $C_{19}H_{13}ClFNO$: C, 70.05; H, 4.02; N, 4.30; found C, 70.11; H, 3.96; N, 4.26%.

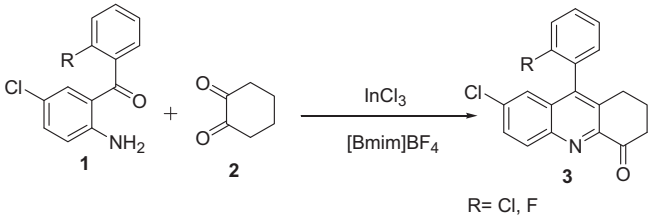
2.2. Computational details

Numerical calculations were performed by using Gauss View 5.0.8 [17] and the Gaussian 09 a.m.64L-G09RevD.01 software package [18]. B3LYP was selected as computational method and 6-311G base sets were selected for all atoms. Selected stretching frequencies from the IR spectra were more closely examined. NMR spectra were calculated at the B3LYP/6-311G level with the GIAO method in vacuum.

3. Results and discussion

3.1. Chemistry

In our initial condition 5-chloro-2-aminobenzophenone was reacted with 1,2-cyclohexanedione in presence of $InCl_3$ and ethanol medium to yielded 89% of 7-chloro-9-phenyl-2,3-dihydroacridin-4(1*H*)-one [19]. To extend the scope of this reaction, to got high yield and time minimization of above reaction. 2-Amino-2′,5-dichlorobenzophenone/2-Amino-5-chloro-2'-fluorobenzophenone, **1a/1b** was reacted with 1,2-cyclohexanedione (**2**) in presence of 1-butyl-3-methylimidazolium tetrafluoroborate and $InCl_3$ solvent free condition to get yellow coloured solid in the moderate to good yield (Scheme. 1). To the best of our knowledge there have been no reports on the utilization of $InCl_3$ in [bmim]BF_4



Scheme 1. Synthesis of 2,3-dihydroacridin-4(*1H*)-one derivatives.