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Experimental (^{13}C NMR, ^{1}H NMR, FT-IR, single-crystal X-ray diffraction) and DFT studies on 3,4-bis(isoproylamino)cyclobut-3-ene-1,2-dione

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ABSTRACT

In this work, 3,4-bis(isoproylamino)cyclobut-3-ene-1,2-dione $C_{10}H_{16}N_2O_2$ (**I**), was synthesized and characterized by ^{13}C NMR, ^{1}H NMR, FT-IR, UV-vis spectroscopy and single-crystal X-ray diffraction. DFT method with 6-31G(d,p) basis set has been used to calculate the optimized geometrical parameters, atomic charges, vibrational frequencies and chemical shift values. The calculated vibrational frequencies and chemical shift values are compared with experimental FT-IR and NMR spectra. The results of the calculation shows good agreement between experimental and calculated values of the compound **I**. The existence of N–H···O type intermolecular ve C–H···O type intramolecular hydrogen bonds can be deduced from differences between experimental and calculated results of FT-IR and NMR. In addition, the molecular electrostatic potential map and frontier molecular orbitals and electronic absorption spectra were performed at B3LYP/6-31G(d,p) level of theory. HOMO–LUMO electronic transition of 4.90 eV are derived from the contribution of the bands $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ The spectral results obtained from FT-IR, NMR and X-ray of **I** revealed that the compound **I** is in predominantly enamine tautomeric form, which was supported by DFT calculations.

1. Introduction

In recent years, the different derivatives of cyclobutane dione draw attention of the scientists. In these years, to many features of the derivatives in different fields are discovered starting from pharmacology [1], as analgestics for the treatment of pain [2], as fluorescent dye compound used to determine nucleic acids [3] and as inhibitors of transactivation responsive RNA of HIV-1 [4]. Similarly, 3,4-bisamino-3-cyclobutene-1,2-diones (squarbisamides) are known as bioactive agents, and they are the more important structure among the structure of 3-cyclobutene-1,2-dione having biological properties [5,6]. Squarbisamides are used as an organocatalyst [7–9], as a bioisoster group [10,11], as a molecular sensing group [12–16], and in the preparation of bisketenes by using laser flash photolysis [17]. Squarbisamides can be used to synthesize 2,6-disubstituted-2,6-diazabicyclo[5.2.0]non-1(7)-ene-3,5,8,9-tetrones [18] which are coupling components in order to obtain azo dyes (hydrazone from) having valuable biological properties. Squarbisamides are called with various names such as 1,2- and 1,3- bisamides depending on position of amino groups (Scheme 1(a)). They can be converted to each other in various conditions in lower yield [19–23].

The compound obtained in this study was synthesized by Zinner et al. in lower yield as by-products of 3,4-bisalkylamino derivatives instead of 3,4-bishydroxyamine derivates and they recorded that the spectral data of their prepared 3,4-bis(isoproylamino)cyclobut-3-ene-1,2-dione was similar to N-methyl derivative [24], but they did not present spectral data for **I**. In this study, 3,4-bis(isoproylamino)cyclobut-3-ene-1,2-dione (**I**) was synthesized in a good yield and by a similar method described in literature [18,24]. The compound **I** was characterized by using single-crystal X-ray diffraction, FT-IR, NMR, LC-MS (TOF), elemental micro analysis, UV-Vis technique and quantum chemical methods. The compound **I** may exist in three tautomeric forms called as an enamin (A) and two imine forms (B and C) as shown in Scheme 1(b). The properties of structural geometry, molecular electrostatic potential, electronic absorption spectra and frontier orbitals for **I** were studied at DFT/B3LYP/6-31G(d,p) level. The compound **I** is one of starting agents in order to obtain some of coupling components and therefore, this study

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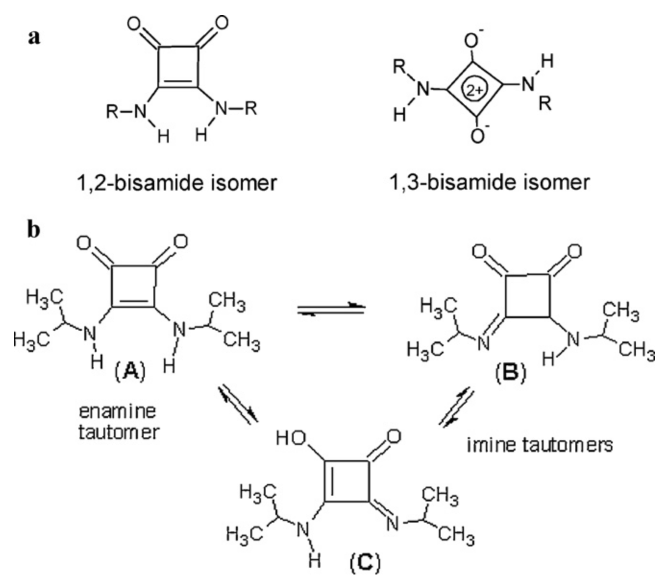

Scheme 1. Isomeric forms of bisamides of 3-cyclobuthene-1,2-dione (a) and structure of tautomeric forms of the compound **I** (b).

can be a guide in characterization of squarbisamides or their derivatives.

2. Experimental details

2.1. Methods

The melting point of the compound **I** was measured by means of an Electrothermal 9100 melting point apparatus. The FT-IR spectrum of the compound **I** was recorded in the range of 4000–400 cm^{-1} region and for the measurement, a Varian 800 series FT-IR spectrophotometer using KBr pellet was used. The ^1H and ^{13}C NMR spectra were recorded by using a Bruker 400 MHz spectrometer and DMSO-d_6 as solvent, meanwhile chemical shifts (δ) were reported in ppm. Elemental analysis was performed on a LECO CHNS-932 analyzer. The diffraction measurements were carried out by graphite monochromatized Mo K_α radiation with $\lambda = 0.71073$ Å on a STOE IPDS II diffractometer. For the compound **I** data collection and cell refinement: X-AREA [25]; program used to solve structure: SHELXS-97 [26]; program used to refine structure: SHELXL-97 [26]; molecular figures: ORTEP III [27]; publication software: WinGX [28]. The crystal data and details, concerning data collection and parameters of refinement process are given in Table 1. Ultraviolet–visible (UV–vis) absorption spectra were recorded on a Shimadzu UV-1601 spectrophotometer operating between 200 and 800 nm, using solvents in acetic acid, ethanol, DMF in concentrations 10^{-6}–10^{-8} M by using quartz cells.

2.2. Synthesis

All chemicals were provided by Sigma and Aldrich firms, and were used in synthesis further not purified. 1.47 mL (0.01 mole, $d = 1.15$ g/mL) 3,4-diethoxycyclobut-3-ene-1,2-dione was dissolved in 50 mL etanol, 1.72 mL (0.02 mole, $d = 0.688$ g/mL) isopropyl amine were added into the solution, and a white solid formed. The mixture was stirred for further 4 h. Then the solid was filtered and was dried at room temperature. Then, the crude product was recrystallized by using ethanol (yield 85%) to afford the compound **I** [18,24]. m.p: 277–279 °C. Anal. calc. for $C_{10}H_{16}N_2O_2$: C % 61.20; H % 8.22; N% 14.27. Found: C % 61.06; H % 8.21; N % 14.01. LS/MS-TOF: 196.1285 $[M]^+$.

Table 1
Crystallographic data for **I**.

Crystal data	
Chemical formula	$C_{10}H_{16}N_2O_2$
M_r	196.25
Cell setting, space group	Monoclinic, C2/c
Temperature (K)	293
a, b, c (Å)	19.0786 (16), 6.1213 (3), 15.6723 (2)
β (°)	142.848(4)
V (Å^3)	1105.38 (17)
Z	4
D_x	($Mg\,cm^{-3}$) 1.179
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.08
Crystal form, colour	Prism, colourless
Crystal size (mm^3)	0.41 × 0.22 × 0.07
Data collection	
Diffractometer	STOE IPDS 2 diffractometer
Data collection method	Rotation method scans
No. of measured, independent and observed reflections	7573, 1098, 755
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	2.6
θ max	26.0°
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.113, 1.01
No. of reflection	1098 reflections
No. of parameters	65
H-atom treatment	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_0^2) + (0.0652P)^2 + 0.2022P]$ $P = (F_0^2 + 2F_0^2)/3$
$(\Delta/\sigma)_{max}$	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.16, −0.13

2.3. Theoretical methods

The compound **I** was optimized by using DFT method, starting from the experimental structures. DFT calculations with a hybrid functional B3LYP (Becke's three parameter hybrid functional using the LYP correlation functional) at 6-31G(d,p) basis set using the Berny method [29,30] were performed with the Gaussian 03 software package [31], and Gauss-view visualization program [32]. The electronic absorption spectra were calculated using the time-dependent density functional theory (TD-DFT) method [33–35]. Also, it is calculated in ethanol solution using the Polarizable Continuum Model (PCM) [36–39]. The vibrational frequencies for this species were scaled by 0.9627 [40]. After that, the vibrational bands were assigned by using Gauss-View molecular visualization program. The geometry of the compound **I**, together with that of tetramethylsilane (TMS), was fully optimised. ^1H and ^{13}C NMR chemical shifts were calculated. For this calculation, the standard GIAO/B3LYP/6-31G(d,p) (Gauge-Independent Atomic Orbital) approach [41,42] applying B3LYP with 6-31G(d,p) basic set was used. The 1H- and 13C-NMR chemical shifts were converted to the TMS scale by subtracting the calculated absolute chemical shielding of TMS ($\delta = \Sigma_0 - \Sigma_0$, where δ is the chemical shift, Σ is the absolute shielding and Σ_0 is the absolute shielding of TMS), whose values are 31.76 and 191.84 ppm for B3LYP/6-31G(d,p), respectively. To investigate the reactive sites of the compound **I**, the molecular electrostatic potential was calculated using the same method. Additionally, the frontier orbitals and electronic absorption spectra were evaluated using the B3LYP/6-31G(d,p).

3. Results and discussion

3.1. Crystal structure

The compound **I** crystallizes in the monoclinic space group C2/c with unit cell parameters $a = 19.0786$ (16) (Å), $b = 6.1213$ (3) (Å),