



# On the roles of close shell interactions in the structure of acyl-substituted hydrazones: An experimental and theoretical approach



Aamer Saeed <sup>a,\*</sup>, M. Ifzan Arshad <sup>a</sup>, Michael Bolte <sup>b</sup>, Adolfo C. Fantoni <sup>c</sup>, Zuly Y. Delgado Espinoza <sup>d</sup>, Mauricio F. Erben <sup>d,\*</sup>

<sup>a</sup> Department of Chemistry, Quaid-I-Azam University, Islamabad 45320, Pakistan

<sup>b</sup> Institut für Anorganische Chemie, J.W.-Goethe-Universität, Max-von-Laue-Str. 7, D-60438 Frankfurt/Main, Germany

<sup>c</sup> Instituto de Física La Plata (UNLP-CONICET), Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 49 y 115, La Plata, Buenos Aires, Argentina

<sup>d</sup> CEQUINOR (UNLP, CONICET-CCT La Plata), Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C.C. 962 (1900) La Plata, Buenos Aires, Argentina

## ARTICLE INFO

### Article history:

Received 21 September 2015

Received in revised form 2 December 2015

Accepted 20 December 2015

Available online 24 December 2015

### Keywords:

Hydrazone

Crystal structure

FTIR spectroscopy

Raman spectroscopy

Hydrogen bond

NBO

AIM topological analysis

## ABSTRACT

The 2-(phenyl-hydrazono)-succinic acid dimethyl ester compound was synthesized by reacting phenylhydrazine with dimethylacetylene dicarboxylate at room temperature and characterized by elemental analysis, infrared, Raman, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies and mass spectrometry. Its solid state structure was determined by X-ray diffraction methods. The X-ray structure determination corroborates that the molecule is present in the crystal as the hydrazone tautomer, probably favored by a strong intramolecular N–H···O=C hydrogen bond occurring between the carbonyl (–C=O) and the hydrazone –C=N–NH– groups. A substantial fragment of the molecular skeleton is planar due to an extended π-bonding delocalization. The topological analysis of the electron densities (Atom in Molecule, AIM) allows characterization of intramolecular N–H···O interaction, that can be classified as a resonant assisted hydrogen bond (RAHB). Moreover, the Natural Bond Orbital population analysis confirms that a strong hyperconjugative lpO1 → σ\*(N2–H) remote interaction between the C2=O1 and N2–H groups takes place. Periodic system electron density and topological analysis have been applied to characterize the intermolecular interactions in the crystal. Weak intermolecular interactions determine the crystal packing, and the prevalence of non-directional dispersive contributions are inferred on topological grounds. The IR spectrum of the crystalline compound was investigated by means of density functional theory calculations carried out with periodic boundary conditions on the crystal, showing excellent agreement between theory and the experiments. The vibrational assignment is complemented with the analysis of the Raman spectrum.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Hydrazone compounds having the general formula R<sup>1</sup>R<sup>2</sup>C=N–NHR<sup>3</sup> (R = alkyl or aryl groups), are substances formally derived from aldehydes or ketones by reaction with hydrazine or a hydrazine derivative. The hydrazones are well-known compounds for which methods of preparation and structural properties [1] as well as biological aspects [2] were reviewed recently. In particular, these molecular organic compounds have received considerable attention as nonlinear optical materials due to their potentially high nonlinear effects and rapid response in electro-optic devices [3,4]. For example, the second harmonic generation (SHG) efficiency of benzaldehyde phenylhydrazone was evaluated to be higher than that of urea [5]. It was postulated that the large value of second order hyperpolarizability displayed by this kind of molecules is associated with an Internal Charge Transfer (ICT) process between electron-donor and electron-acceptor groups, facilitated by an extended

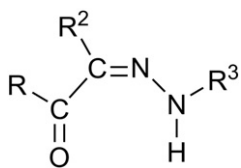
conjugated π system. In this direction, a family of phenylhydrazone compounds containing the curcumin group was prepared and its structural and electronic properties were determined, showing that the frontier orbital energies are dependent on the electron-donor or electron-withdrawing nature of the substituent groups [6].

Tautomeric equilibria of azo-hydrazone compounds were reported very recently, the azo-enamine tautomer being the predominant form in the solid state, whereas the hydrazone-imine form is the preferred form in solution [7]. Structural properties of salicylhydrazone and aroylhydrazones derived from nicotinic acid hydrazide have been studied [8], the co-existence of two tautomeric forms was determined for the solid substance, as well as for highly concentrated solutions, whereas only the hydrazone tautomer is present in diluted solutions [9,10]. It is anticipated that the formation of inter- and intra-molecular hydrogen bonds strongly influences these equilibria [11].

It is an interesting observation that hydrazone species bearing a carbonyl group, i.e. R<sup>1</sup> = acyl radical (RC=O, see Scheme 1), are scarcely studied, mostly because the general method for the synthesis of hydrazones failed when the hydrazine is in the presence of an electrophilic substituent such as the C=O group. Examples include a

\* Corresponding authors.

E-mail addresses: [aamersaeed@yahoo.com](mailto:aamersaeed@yahoo.com) (A. Saeed), [erben@quimica.unlp.edu.ar](mailto:erben@quimica.unlp.edu.ar) (M.F. Erben).



**Scheme 1.** Representation of acyl substituted hydrazones.

series of *N*-acylhydrazone compounds with antinociceptive and anti-inflammatory activities synthesized by Barreiro et al. [12], for which the conformational properties in solution were also determined by using NMR data [13]. Regarding structural aspects, the configurational and conformational landscape of 3-oxo-2-(phenylhydrazono) derivatives is influenced by the environment, and a complex interplay between inter- and intra-molecular hydrogen bond interactions was observed in the crystalline structures [14]. Acyl hydrazone compounds bearing also the tetrahydrocabazole group were recently synthesized by Sarigöl and coworkers [15] and the conformation adopted by the C=O double bond and the hydrazone group was investigated by using quantum chemical calculations. More recently, the tautomeric equilibria of azo-hydrazones dye compounds and their Ni(II) and Cu(II) metal complexes were reported [16–18].

Prompted by this versatile tautomeric and conformational equilibria displayed by hydrazone-carbonyl compounds, we became interested in the study of 2-(phenyl-hydrazono)-succinic acid dimethyl ester (R = CH<sub>3</sub>O-, R<sup>2</sup> = CH<sub>3</sub>OC(O)CH<sub>2</sub>-, R<sup>3</sup> = C<sub>6</sub>H<sub>5</sub>-, see Scheme 1). Quite recently, this species was postulated as an intermediate in the synthesis of 3,5-di-functionalized pyrazoles [19]. The aim of this work is to provide a comprehensive structural study for this molecule, including the detailed description of the intramolecular and intermolecular interactions in the solid phase, and to determine how these properties influence the vibrational properties. Thus, the preparation, isolation and full characterization are presented, along with the study and analysis of its molecular structure in the crystalline state as determined by single-crystal X-ray diffraction analysis and vibrational spectroscopic techniques (FTIR and FT-Raman). The most salient conformational, tautomeric and configurational properties for the isolated molecule have been studied by using quantum chemical calculations at the B3LYP/6-311++G(d,p) level of approximation. Vibrational frequencies and modes were also calculated at the B3LYP/6-31G\*\* level at the  $\Gamma$  point of the periodic system, after optimization of all atom positions with cell parameters kept at the experimental values. Furthermore, Natural Bond Orbital (NBO) [20] population analysis has been performed in order to evaluate the donor  $\rightarrow$  acceptor intramolecular interactions. Since the large number of sites potentially able to establish C–H...O intermolecular interactions makes the system particularly suitable for studying the directional characteristics of this kind of weak interactions and their contribution to crystal packing, we decided to perform an AIM topological analysis of the crystal electron density.

## 2. Experimental

### 2.1. General

Melting points were recorded using a digital Gallenkamp (SANYO) model MPD.BM 3.5 apparatus and are uncorrected. <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were determined in CDCl<sub>3</sub> at 300 MHz and 75.4 MHz respectively using a Bruker spectrometer. Mass Spectra (EI, 70 eV) on a gas chromatography–mass spectrometry (GC–MS) instrument Agilent technologies, and elemental analyses were conducted using a LECO-183 CHNS analyzer. Solid-phase (in KBr pellets) infrared spectra were recorded with a resolution of 2 cm<sup>-1</sup> in the 4000–400 cm<sup>-1</sup> range on a Bruker EQUINOX 55 FTIR spectrometer. The FT-Raman spectra of the powdered solid sample were recorded in the region 4000–100 cm<sup>-1</sup> using a Bruker IFS 66v spectrometer

equipped with Nd:YAG laser source operating at 1.064  $\mu$ m line with 200 mW power of spectral width 2 cm<sup>-1</sup>.

### 2.2. Synthesis of 2-(phenyl-hydrazono)-succinic acid dimethyl ester (3)

In a 100 mL two neck round bottom flask, fitted with a reflux condenser, hydrazine (0.22 g, 2 mmol) and dimethyl acetylene dicarboxylate (0.28 g, 2 mmol) were stirred for two hours in 10 mL (1:1) mixture of toluene and dichloromethane. The progress of the reaction was monitored by thin layer chromatography. After the completion of the reaction, the solvent was removed under reduced pressure, the residue was extracted with ethyl acetate and water, the organic layer was dried over anhydrous sodium sulphate and concentrated. The crude product was recrystallized from aqueous ethanol. Yield 73%, mp 81 °C. FT-IR ( $\nu$  cm<sup>-1</sup>): 3268, 3049, 2956, 1739, 1688, 1562, 1437, 1351, 1198, 1164, 1151, 1145, 1000, 791, 691 (see Section 3.4 for details). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  12.2 (br s, 1H, NH), 7.34–6.91 (m, 5H, Ar H), 3.83 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 3.74 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 3.56 (s, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  171.4 (C=O), 163.5 (C=O), 142.9 (C=N), 129.3 (ArC), 122.5 (ArC), 121.8 (ArC), 113.9 (ArC), 52.0 (CO<sub>2</sub>CH<sub>3</sub>), 51.7 (CO<sub>2</sub>CH<sub>3</sub>), 38.9 (CH<sub>2</sub>). The <sup>1</sup>H and <sup>13</sup>C NMR spectra are provided as supplementary material (Figs. S1 and S2, respectively). Anal. Calcd for C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>: C, 57.59; H, 5.64; N, 11.19; %. Found: C, 57.63; H, 5.61; N, 11.23%. EIMS (m/z): 250.1 (53%).

### 2.3. Computational details

Molecular quantum chemical calculations have been performed with the GAUSSIAN 03 program package [21] by using the B3LYP DFT hybrid methods employing Pople-type basis set [22]. The valence triple- $\xi$  basis set augmented with diffuse and polarization functions in both the hydrogen and heavy atoms [6–311++G(d,p)] has been used for geometry optimization and frequency calculations. The calculated vibrational properties corresponded in all cases to potential energy minima for which no imaginary frequency was found. The Potential Energy Distribution PED analysis has been computed using the VEDA4 program [23,24]. Periodic calculations were performed at the B3LYP/6-31G(d,p) level with Crystal98 and Crystal09 codes [25, 26]. The topology of the resulting electron density was then analyzed using the TOPOND98 program [27]. The whole vibrational data are given as supplementary information in Table S1.

### 2.4. Crystal structure determination

Data were collected on a STOE IPDS II two-circle diffractometer with a Genix Microfocus tube with mirror optics using MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) and were scaled using the frame scaling procedure in the X-AREA program system [28]. The structure was solved by direct methods using the program SHELXS [29] and refined against F<sup>2</sup> with full-matrix least-squares techniques using the program SHELXL-97 [29]. H atoms bonded to C were refined using a riding model and the H atom bonded to N was freely refined [28]. Relevant crystallographic data are given as supplementary information in Tables S1–S6. Full crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 896977). Enquiries for data can be directed to: Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, UK, CB2 1EZ or (e-mail) [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or (fax) +44 (0) 1223 336,033.

## 3. Result and discussion

The title compound 2-(phenyl-hydrazono)-succinic acid dimethyl ester was synthesized by slight modification of the literature method [19] using the general Cope-type intermolecular hydroamination of acetylene and hydrazine derivatives reported by Cebrowski et al. [30]. In the present case, equimolar quantities of phenyl hydrazine and dimethylacetylene dicarboxylate (DMAD) in dry toluene and dry

Download English Version:

<https://daneshyari.com/en/article/1229327>

Download Persian Version:

<https://daneshyari.com/article/1229327>

[Daneshyari.com](https://daneshyari.com)