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Análisis de la estructura y propiedad de óptica no lineal de 1,2 difenil-2-(3-toluidina)-1-etanona tiosemicarbazona mediante cálculos *ab initio*

Structure and non linear optical property analysis of 1,2-diphenyl -2-(3-toluidino)-1-ethanone thiosemicarbazone by ab initio *calculations*

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Resumen

Se examinó teóricamente la geometría molecular, carga atómica neta, densidad electrónica del átomo, las energías de los orbitales de frontera HOMO y LUMO y las frecuencias vibracionales de la 1,2 difenil-2-(3-toluidina)-1-etanona tiosemicarbazona mediante cálculos ab initio, utilizando el nivel de teoría HF/6-31G(d,p). Se reportan los coeficientes de correlación para las distancias de enlace, ángulos de enlace y frecuencias vibracionales. La distribución de carga, teniendo en cuenta los métodos de Mulliken y de orbitales naturales de enlace muestra posibles sitios de coordinación del compuesto cuando el mismo se coordine con iones de metales de transición. El compuesto exhibe actividad de óptica no lineal.

Palabras clave: 1,2 difenil-2-(3-toluidina)-1-etanona tiosemicarbazona, Hartree-Fock, análisis vibracional, HOMO-HUMO, óptica no lineal.

Abstract

The molecular geometry, net atomic charge and atom electron densities, HOMO-LUMO energy and vibrational frequencies of 1,2-diphenyl-2-(3-toluidino)-1-ethanone thiosemicarbazone were examined theoretically using ab-initio method at the HF/6-31G(d,p) level. The correlation coefficients are reported for bond lengths, bond angles and vibrational frequencies. The Mulliken and natural atomic charges of title molecule reveal the coordination sites when it undergoes complexation with transition metal ions. The title compound exhibit good nonlinear optical activity.

Keywords: 1,2-diphenyl-2-(3-toluidino)-1-ethanone thiosemicarbazone, Hartree-Fock, vibrational, HOMO-HUMO, nonlinear optical activity.

Introduction

Thiosemicarbazones are a class of compounds obtained by condensing thiosemicarbazide with suitable aldehydes or ketones and are well known to possess biological and carcinostatic activities [1, 2]. These biological activities include antitumor, antifungal, antibacterial antiviral, anticancer and antimalarial activities. These properties are often related to metal ion coordination. Lipophilicity, which controls the rate of entry into the cell, is modified by coordination. Also, the metal complex can be more active than the free ligand. In addition, the complex can exhibit bioactivities which are not shown by the free ligand.

Due to its critical role in DNA synthesis and proliferation, iron is a potential target for the treatment of cancer. To this end, the cellular antiproliferative effects of a number of iron specific chelators and their complexes have been examined. A class of chelators with pronounced and selective activity against tumour cells are the thiosemicarbazones. The antitumor properties of heterocyclic thiosemicarbazones are partly related to their ability to inhibit the ribonucleoside diphosphate reductase enzyme, which is essential in DNA synthesis [3].

In almost all cases, the ligands are bidentate and bind to the metal through the S and hydrazinic N atoms. It has been postulated that extensive electron delocalization in the thiosemicarbazone moiety helps the free thiosemicarbazone ligands and their metal complexes to exhibit second-harmonic generation (SHG) efficiency [4]. Therefore, studies on structure and reactivity of thiosemicarbazones are important from the point of view of organic, biological chemistry and structure activity relationships. The present work deals with NLO effects, vibrational spectral analysis, Mulliken´s net charges and atomic natural charges, HOMO LUMO analysis of 1,2-diphenyl-2-(3-toluidino)-1-ethanone thiosemicarbazone (abbreviated as DTET). To the best of our knowledge this is the first report on the preparation and computational study of DTET.

Experimental

Elemental analyses were carried out on a Thermo Finnigan EA1112 Elementary Analyser Flasch EA 1112. FT-IR spectrum was recorded on a Midac M2000 by using KBr discs

Preparation of 1,2-diphenyl-2-(3-toluidino)-1-ethanone thiosemicarbazone [5].

In a 250 mL round bottom flask appropriate 1,2-diphenyl-2-(3-toluidino)-1-ethanone (5 mmol) and thiosemicarbazide (5 mmoL) were taken. To reaction content 1 mL of pure chorhidric acid was added and dissolved. The mixture was refluxed for 6 hour and then cooled, filtered, washed and recrystallized from absolute ethanol. Yield 89 %; yellow powder; Elemental Analysis calculated for $C_{22}H_{22}N_4S$: C, 70,56; H, 5,92; N, 14,96; S, 8,56 %. Found: C, 70,96; H, 5,87; N, 14,94; S, 8,52 %.

1,2-diphenyl-2-(3-toluidino)-1-ethanone was obtained as previously reported [6].

Computacional details

The quantum chemical calculations have been performed at Hartree-Fock (HF) method with 6-31G(d,p) as basis set calculations using the Gaussian 03 software package [7], utilizing gradient geometry optimization on a Intel Dual Core 2,8 GHz personal computer. Vibrational frequencies were calculated to make sure no imaginary frequency existing for these structures. The assignments of the calculated wavenumbers is aided by the animation option of Gauss View 3.0 graphical interface for Gaussian programs which gives a visual presentation of the shape of the vibrational modes. Due to the neglect of anharmonicity effect at the beginning of calculation, initially the predicted vibrational wavenumbers by HF/6-31G(d,p) are found to be disagreement with experimental wave numbers. In order to improve the calculated values in agreement with the experimental values it is necessary to scale down the calculated harmonic frequencies. Hence, the vibrational frequencies calculated using HF/6-31G (d,p) level are scaled by 0,899 2 [8].

The electronic properties HOMO-LUMO energies were calculated basing on the optimized structure in solvent DMSO. Furthermore, in order to show nonlinear optical (NLO) activity of 1,2-diphenyl-2-(3-toluidino)-1-ethanone thiosemicarbazone molecule, the dipole moment, linear polarizability and first hyperpolarizability were obtained from molecular polarizabilities based on theoretical calculations.

Results and discussion

Geometric structure

The molecular structure along with numbering of atoms is obtained from Gaussian 03 program (figure 1). At the optimized geometry for the title molecule no imaginary frequency modes were obtained, therefore a true minimum on the potential energy surface was found.

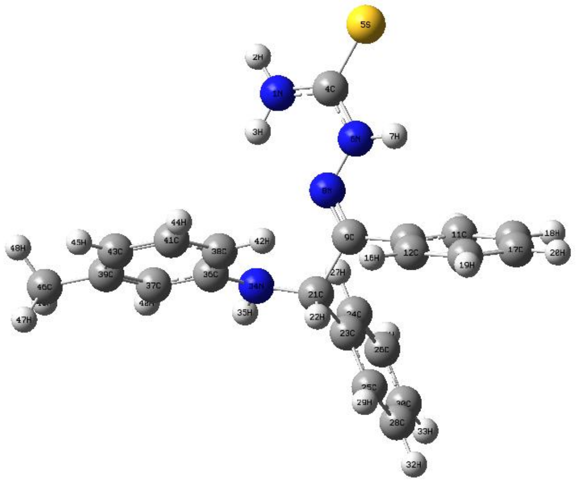

Figure 1. Molecular structure and atomic numbering scheme of 1,2-diphenyl-2-(3-toluidino)-1-ethanone thiosemicarbazone in DMSO

The N8-C9-C21-N34 dihedral angle is a relevant coordinate for conformation flexibility for DTET molecule. Conformation of this molecule is feasible depending on the orientation around C9-C21 bond. The internal rotation potential profile of the C9-C21 bond was obtained by the torsional coordinate N8-C9-C21-N34 to vary in steps of 30°, in gas phase and in solvent DMSO. As it can be seen (figure 2), the internal rotation of C9-C21 bond yielded four minima in approximately 0°, 120°, 210° and 300° in gas phase an two minima in approximately 30° and 270° in DMSO.

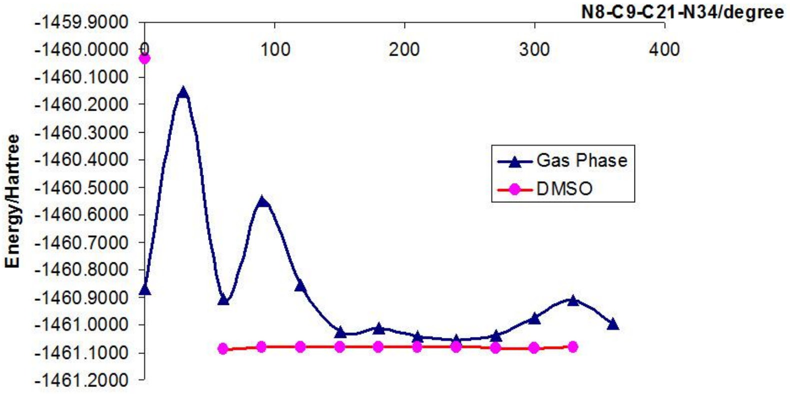

Figure 2. Rotational energy curve for the 1,2-diphenyl-2-(3-toluidino) -1-ethanone thiosemicarbazone compound along N8-C9-C21-N34 dihedral angle

The optimized bond lengths, bond angles and dihedral angles of DTET molecule which were calculated by using ab initio method with 6-31G(d,p) basis set in DMSO as solvent are shown in table 1. To the best of our knowledge, crystal data of the DTET molecule are not available in the literature. Therefore, the optimized structure can only be compared with the crystal structure of the other similar systems.

TABLE 1. SELECTED BOND DISTANTE (Å), BOND ANGLES (°) AND DIHEDRAL ANGLES (°) FOR 1,2-DIPHENYL-2-(3-TOLUIDINO) -1-ETHANONE THIOSEMICARBAZONE

Parameter	**HF/6-31G(d,p)**	**X ray[a]**	**Parameter**	**HF/6-31G(d,p)**	**X ray[a]**
Bond distante (Å)			(continued)		
N1-C4	1,314	1,327	C46-C39-C43	120,152	
C4-S5	1,717	1,685	C46-C39-C37	120,671	
C4-N6	1,335	1,354	CC	-	0,340
N6-N8	1,363	1,377	***Dihedral angle (°)***		
N8-C9	1,258	1,285	N1-C4-N6-N8	-2,594	-7.8
C9-C10	1,500		S5-C4-N6-N8	177,579	174,54
C9-C21	1,531		C4-N6-N8-C9	-179,851	
C21-N34	1,445	1,440 5	N6-N8-C9-C10	-2,360	
N34-C36	1,389	1,381 0	N6-N8-C9-C21	177,971	
C21-C23	1,526		N8-C9-C10-C11	-69,075	
C39-C46	1,512		N8-C9-C10-C12	112,045	
CC	-	0,997 1	N8-C9-C21-N34	-9,863	
Bond angle (^{o})			N8-C9-C21-C23	113,225	
S5-C4-N6	119,585		C9-C10-C11-C13	-178,918	
S5-C4-N1	122,381		C9-C10-C12-C15	179,154	
N1-C4-N6	118,033		C9-C21-C23-C25	117,608	
C4-N6-N8	119,413		C9-C21-C23-C24	-63,258	
N6-N8-C9	119,658		C9-C21-C34-C36	-84,245	
N8-C9-C10	124,976		C11-C10-C9-C21	110,599	
N8-C9-C21	118,509		C12-C10-C9-C21	-68,281	
C9-C10-C11	120,131		C21-C23-C25-C28	179,228	
C9-C10-C12	120,411		C21-C23-C24-C26	-179,043	
C10-C9-C21	116,514		C21-N34-C36-C38	21,012	
C9-C21-N34	113,599	108,31	C21-N34-C36-C37	-159,698	
C9-C21-C23	106,671		N34-C21-C23-C25	-117,005	
C21-C23-C25	120,410		N34-C21-C23-C24	62,129	
C21-C23-C24	120,475		N34-C36-C37-C39	-179,440	
C23-C21-N34	109,652	112,77	N34-C36-C38-C41	179,425	
C21-N34-C36	113,642	122,36	C46-C39-C37-C36	-179,569	
N34-C36-C38	123,510	122,36	C46-C39-C43-C41	179,639	
N34-C36-C37	118,041	119,68			

CC: correlation coefficient [a] Values are taken from Refs [6, 9]

Although the correlations coefficientes (CC) for bond lengths and bond angles for DTET are 0,997 1 and 0,340, respectively, these calculated geometrical parameters represent a good aproximation.

Vibrational spectral analysis

The 1,2-diphenyl-2-(3-toluidino)-1-ethanone thiosemicarbazone molecule consist of 49 atoms. Its optimized structures exhibits Cs symmetry and consequently all the 141 fundamental vibrations of the molecule are IR activ. The assignments of the calculated wavenumbers is aided by the animation option of Gauss View 3.0 graphical interface for Gaussian program, which gives a visual presentation of the shape of the vibrational modes.

The vibrational spectral analysis has been performed on the basis of the characteristic vibrations of the NH, CH_3, C=S, C-S, C=C and C=N groups [10]. These observed values are in good agreement with the scaled values with a correlation coefficient of 0,996 5 (table 2). Figure 3 shows the FTIR spectrum of DTET molecule.

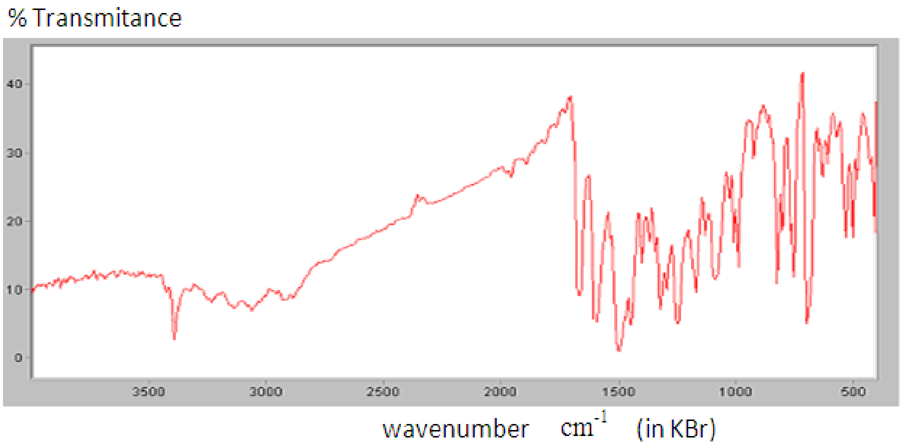

Figure 3. FTIR spectrum of 1,2-diphenyl-2-(3-toluidino)-1-ethanone thiosemicarbazone

TABLE 2. VIBRATIONAL ASSIGNMENT OF SELECTED FUNDAMENTALS OF 1,2-DIPHENYL-2-(3-TOLUIDINO) -1-ETHANONE THIOSEMICARBAZONE

Observed fundamentals/cm^{-1}		**Assignment**
υ_{IR}	υ_{scaled} / cm^{-1}	
3 133,9	3 289,93	υ (N34-H) w
1 500,2	1 588,22	δ (N34-H) s
3 392,8	3 456,33	υ_{as} (N1-H) m
3 232,1	3 307,36	υ_{ss} (N1-H) w
3 321,42	3 419,96	υ (N6-H) w
1 660,1	1 728,85	υ (C = N8) s
502,3	5 06,57	υ (C-S) m
2 924,1	2 889,47	υ_{as} Me, w
-	2 839,47	υ_{ss} Me
-	2 820,59	υ (C21-H)
3 062,5	3 024,07; 2 937,70	υ (C-H) Ph, w
1 602,6	1 609,49; 1 579,56	υ (C = C) Ph s
CC	-	0,996 5

CC: correlation coefficient. υ stretching, δ in plane bending,
υ_{as} asymmetric stretching, υ_{ss} symmetric stretching,
s strong, m medium, w weak.

Mulliken and natural charge distribution

The calculation of atomic charges play a key role in the application of quantum mechanical calculation to describe the electronic characteristic of molecular system [11]. The parameters like dipole moment, polarizability, reactivity depend on the atomic charges of the molecular systems. The charge distributions over the atoms suggest the formation of donor and acceptor pairs involving the charge transfer in the molecule.

Table 3 displays the Mulliken and natural atomic charges of 1,2-diphenyl-2-(3-toluidino)-1-ethanone thiosemicarbazone. The N1 and N34 atoms exhibit a substantial negative charge, which are donor atoms, indicating that the protonation of these locations are possible. At the same time they can present the active centers to coordinate to metal ions.

TABLE 3. CHARGE DISTRIBUTION BY THE MULLIKEN AND NATURAL BOND ORBITAL METHODS OF 1,2-DIPHENYL -2-(3-TOLUIDINO)-1-ETHANONE THIOSEMICARBAZONE

Atoms	**Atomic charges (Mulliken)**	**Natural charges (NBO)**
S5	-0,543	-0,377
N34	-0,744	-0,702
N8	0,303	-0,303
N6	-0,480	-0,512
N1	-0,707	-0,883

NLO properties

Polarizabilities and hyperpolarizabilities characterize the response of a system in an applied electric field. NLO is at in the forefront of current research because of its importance in providing the key functions of frequency shifting, optical modulation, optical switching and optical memory for the emerging technologies in areas such as telecommunications, signal processing, and optical interconnections [12]. NLO techniques are considered as one among the most structure sensitive method to study molecular structures and assemblies. Since the potential of organic materials for NLO devices have been proven NLO properties of many of these compounds have been investigated by both experimental and theoretical methods [13].

The efforts on NLO have been largely devoted to prepare first order NLO materials using theoretical methods and exploring the structure- property relationships. Quantum chemical calculations have been shown to be useful in the description of the relationship between the electronic structure of the system and its NLO response. The computational approach allows the determination of molecular NLO properties as an inexpensive way to design molecules by analyzing their potential before synthesis and to determine the higher order hyperpolarizability tensors of molecule [11].

In order to investigate the relationships among photocurrent generation molecular structure and NLO, the polarizabilities and hyperpolarizabilities of the compound MDET were calculated. The complete equations for calculating the magnitude of total static dipole moment μ the mean polarizability α_{tot} total and the mean first hyperpolarizability β_o using the x, y z components from Gaussian 03 output are as follows:

$$\mu = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{1/2} \tag{1}$$

$$\alpha_{tot} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{2}$$

$$\beta_o = \left[(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2\right]^{1/2} \tag{3}$$

The calculated polarizability and first order hyperpolarizability values (in a.u.) have been converted into electrostatic units (esu.) (α, 1 a.u. = 0,148,2 · 10^{-24} esu, β, 1 a.u. = 8,639 3 · 10^{-33} esu). The dipole moment, polarizability and first hyperpolarizability are reported in table 4. According to the present calculations, the dipole moment and mean polarizability of 1,2-diphenyl-2-(3-toluidino)-1-ethanone thiosemicarbazone are found to be 10,74 and 17,670 08 · 10^{-24} esu. The magnitude of the molecular hyperpolarizability β, is one of key factors in NLO system. The calculated first static hyperpolarisability β_o value is equal to 11 309,228 9 · 10^{-33} esu. The calculated total dipole moment of DTET is approximately three times greater than that of urea and first hyperpolarizability is approximately thirty times to that of urea indicating that the title compound is a good candidate of NLO materials (μ and β_o of urea are 3,885 1 Debye and 372,8 · 10^{-33} esu, respectively).

TABLE 4. CALCULATED ELECTRIC DIPOLE MOMENT μ(D), AVERAGE POLARIZABILITY α_{TOT}(X 10^{-24} ESU) AND THE FIRST ORDER HYPERPOLARIZABILITY β_0(X 10^{-33} ESU) OF DTET USING HF/6-31G(D,P)

Parameters	
μ	10,74
α_{xx}	118,261
α_{yy}	66,989
α_{zz}	172,444
α_{tot}	17,670 0
β_{xxx}	43,245
β_{yyy}	-1 150,746
βzzz	-622,504
β_o	11 309,228 9

Frontier molecular orbitals (FMOs)

Highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) are the frontier molecular orbitals (FMOs) which play an important role in the electric and optical properties, as well as in chemical reactions. The HOMO energy characterizes the ability of electron giving. LUMO energy characterizes the ability of electron accepting. The energy gap between HOMO and LUMO characterizes the molecular chemical stability and explain the eventual charge transfer interaction within the molecule, which influences the biological activity of the molecule.

The energy gap represents a critical parameters in determining molecular electrical transport properties because it is a measure of electron conductivity [14]. The increasing value of energy gap in molecule becomes more stable. A molecule with a low energy gap is more polarizable and will exhibit a significant degree of intramolecular charge transfer (ICT) from the electron donor groups to the electron acceptor groups through π conjugated path, indicating a little energy barrier for a possible internal electronic transfer.

The calculated energy value of HOMO of DTET molecule is -7,857 8 eV. LUMO is 2,774 7 eV. The value of energy separation between the HOMO and LUMO is 10,740 eV. This difference in HOMO and LUMO energy supports the charge transfer interaction within the molecule.

Conclusions

In this paper we have calculated the geometrical parameters and vibrational frequencies and some fundamental vibrations of 1,2 difenil-2-(3-toluidina)-1-etanona tiosemicarbazona molecule by using HF method with 6-31G(d,p) basis set. Scaling factor result is in agreement with experimental. The difference in HOMO and LUMO energy supports the charge transfer interaction within the molecule. The first order hyperpolarizability value confirms molecule has NLO property.

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