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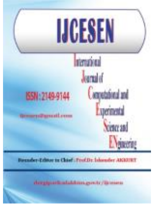

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Research Article

The Investigation of the Structural Properties of 3-nitrophthalonitrile Using Spectroscopic and Quantum Chemical Computational Methods#

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Abstract: In this study, we reported structural properties of the 3-nitrophthalonitrile compound using spectral techniques such as FT-IR, ^{1}H-NMR, ^{13}C-NMR, X-ray single crystal diffraction. The quantum chemical computational calculations were realized with DFT/B3LYP method and 6-311G(d,p) basis set. Results of the spectral analysis were compared with theoretical molecular geometry parameters, vibrational frequencies, and chemical shift values. Some global reactivity structure parameters of the 3-nitrophthalonitrile were examined using the same method and basis set.

1. Introduction

Phthalonitriles are essential building blocks for the synthesis of phthalocyanines and can be used as starting materials [1]. Phthalocyanines have a wide range of applications, such as a catalysis, chemical sensors, dyes, pigments and colors, gas sensors, electrochromism, batteries, semiconductive materials, liquid crystals, non-linear optics and photodynamic therapy [2].

In this paper, our aim is to determine structural features of 3-nitrophthalonitrile by using experimental and theoretical approaches. For this purpose, the compound has been characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR, X-ray single crystal analyses and theoretical calculations have been compared with the results obtained from experimental values. To better understand molecular structure properties of that compound, some global reactivity descriptors were examined using computational methods.

2. Experimental Details

The single-crystal X-ray data were collected on a Bruker D8 QUEST diffractometer. IR spectra were recorded on a Perkin Elmer Frontier FT-IR Spectrometer as KBR pellets. ^{1}H-NMR and ^{13}C-NMR studies were done on an Agilent 400/54 (400 MHz) spectrometer. 3-nitrophthalonitrile was synthesized according to the reported procedure [3]. All other reagents and solvents were of reagent-grade quality and were obtained from commercial suppliers. DMF was dried and purified as described by Perrin and Armarego [4].

3. Computational Details

All the computational analysis of the 3-nitrophthalonitrile were realized at DFT (Density Functional Theory)/B3LYP (Becke’s Three-Parameter Hybrid Functional using the Lee, Yang and Parr Correlation Functional) method with 6-311G(d,p) basis set using Gaussian 09W [5] electronic structure program and GaussView 5.0 interface program [6]. The geometrical optimization of 3-nitrophthalonitrile was made over the geometry formed with crystallographic data and other theoretical analyses were carried out based on this constitution. The molecular geometry of the compound was optimized by DFT/B3LYP with 6-311G(d,p) basis set in the ground state. To determine characteristic functional groups of the 3-nitrophthalonitrile, theoretical harmonic vibrational frequencies were obtained and scaled by 0.9682 for B3LYP/6-311G(d,p) basis set so as to eliminate systematic deviation in computed values [7]. The theoretical ^{1}H-NMR and ^{13}C-NMR and TMS, which is the internal standard for calibrating NMR spectroscopy, chemical shifts were calculated using the Gauge-Independent Atomic Orbital (GIAO) method with DMSO as the solvent. The GIAO method provides an effective prediction of the theoretical chemical shift values [8]. Also, some structure parameters for the compound were examined using the same method and basis set.

4. Results and Discussion

4.1. The Single-Crystal Structure and Optimized Structure Analysis

The 3-nitrophthalonitrile compound crystallizes in the orthorhombic crystal system and $P2_12_12_1$ space group with a=6.2575(5) Å, b=8.8306(8) Å, c=28.326(2) Å and Z=8 unit cell parameters, the asymmetric unit contains two independent molecules (CCDC Number:1440852). The ORTEP-3 view of the compound has shown in Figure 1. It can be said that the crystal structure parameters are in agreement with the theoretical ones. C7-N1, C8-N2 bond lengths are 1.149, 1.091 Å accordingly X-ray analysis data, 1.153, 1.154 Å for DFT/B3LYP/6-311G(d,p) method and these values are in agreement with a typical carbon-nitrogen triple bond (about 1.16 Å). These lengths were stated 1.138 Å as experimental, 1.146 Å for 6-31G(d,p) basis set [9] and 1.154 Å for 6-311++G(d,p) in other DFT study containing nitrile group [10]. For the nitro groups, the bond lengths of N3-O1, N3-O2 are 1.213, 1.216 Å experimentally, 1.219, 1.220 Å theoretically.

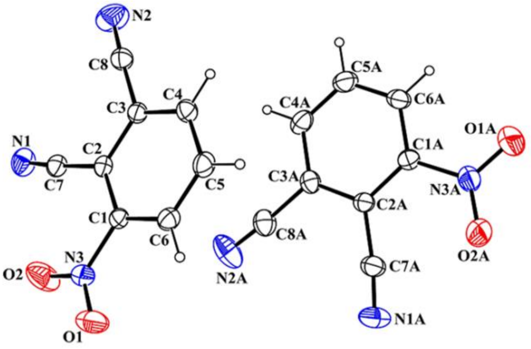


Figure 1. *An ORTEP-3 view of 3-nitrophthalonitrile showing the atom-numbering scheme*

Also, N1-C7-C2, N2-C8-C3 bond angles are 174.6, 175.9° and 172.1, 178.5° experimental and theoretical, respectively, while these values are recorded 178.3, 178.6° for 6-311++G(d,p) basis set in a similar paper [11].

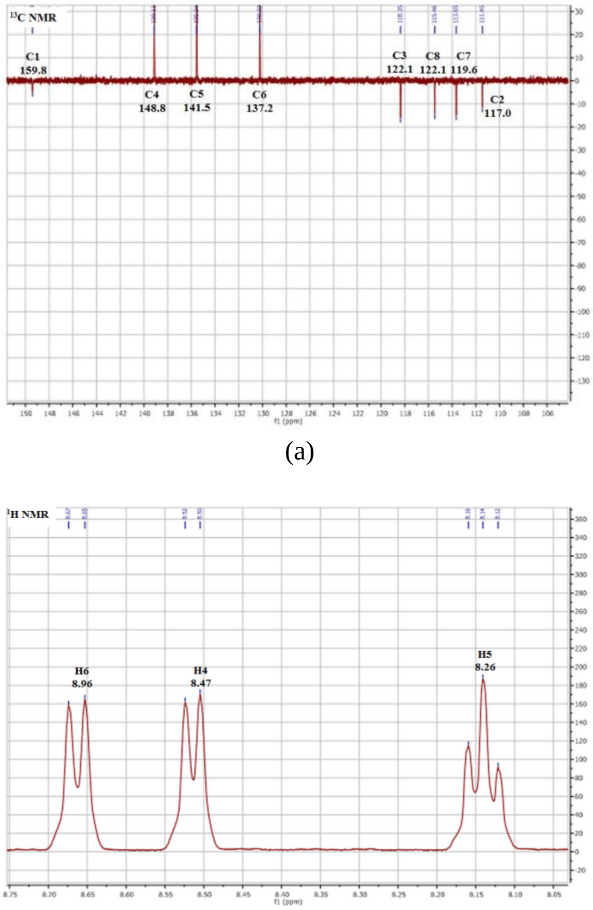
4.2. Assignments of the Vibrational Modes

The compound, which has 32 atoms and 90 fundamental vibrational frequencies, consists phthalonitrile and nitro groups. The vibrational spectra of the 3-nitrophthalonitrile has some characteristic bands of the stretching vibrations such as C-H, C≡N, N=O. The asymmetric and symmetric C-H stretching vibrations modes in recorded at 3080-2878 cm^{-1} 1 in the FT-IR spectrum and 3109-3096 cm^{-1} in the theoretical IR spectrum of the 3-nitrophthalonitrile as a result of characteristic feature C-H stretching bands are assigned at 3100-3000 cm-1 region in aromatic groups [12,13]. The C≡N stretching band which is characteristic of the phthalonitrile moiety is recorded at 2238 cm^{-1} and 2274 cm^{-1}, as experimental and computed values, respectively. In some other phthalonitrile studies, the band is observed about 2232-2237 cm^{-1} and 2230 cm^{-1} as experimental [14,15]. The NO_2 stretching vibration band, which is a characteristic band of nitro compounds, is assigned at 1539 cm^{-1} in IR spectrum, 1562 cm^{-1} as theoretical and these values are agreement with the literature that recorded about 1505-1565 cm^{-1} [16]. And, C-H in-plane scissoring and rocking, out-of plane bending vibration bands belong to phthalonitrile group were observed at 1447-767 cm^{-1} FT-IR spectrum, appeared at 1425-813 cm^{-1} in theoretical assignments. Also, especially below at these peak values, dominant a ring breathing, deformation in-plane and out of-plane modes were observed in the region 802-431 cm^{-1}, 813-424 cm^{-1} as spectrum and computed values.

4.3. NMR Analysis

The spectral and theoretical ^{13}C-NMR (APT), ^{1}H-NMR chemical shift values of the compound were recorded within the range of 149.40-111.45 ppm, 159.84-117.09 ppm, and 8.66-8.13 ppm, 8.96-8.26 ppm respectively. C1 atom has the highest chemical shift values for both experimental and theoretical values by the reason of the effect electron withdrawing nitro group. The C4, C5, C6 atoms have chemical shift values special to aromatic ring carbon atoms (100-150 ppm) [17] and recorded as 139.13-130.22 ppm experimental, 148.80-137.22 ppm theoretical. The spectral and computed with

GIAO method chemical shift values are belong to aromatic hydrogen atoms H4, H5, H6, in concert with the literature [18] that indicates as 6.0-8.5 ppm for aromatic protons. The theoretical and experimental chemical shift values together with NMR spectrums are shown in Figure 2. (*The values marked in the bold form on the NMR spectrums represent theoretical values*).



(a)

(b)

Figure 2. *(a)The ^{13}C-NMR (APT),(b) ^{1}H-NMR spectrums of the 3-nitrophthalonitrile (Note: The atom numbering according to Fig.1).*

4.4 Global Reactivity Descriptors Analysis

The global reactivity descriptors give knowledge about fundamental properties chemical reactivity and stability of the compounds. The DFT method is an important tool used to calculate these parameters and gives very reliable results [19, 20]. HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy values used in calculation of these parameters such as ionization potential, electron affinity, electronegativity, chemical potential, global hardness and global softness. Also, HOMO-LUMO band gap energy value is the most important determinant of chemical stability [21, 22]. The molecules have the large band gaps, which are usually stable and unreactive. The ionization potential is the minimum energy required to remove an electron from an atom or molecule and can be expressed as, $I=-E_{HOMO}$. According to Koopman's Theory [23], electron affinity (A) is described as the change in energy when is an electron added to a neutral atom in the gas phase and is given as, $A=-E_{LUMO}$. Electronegativity (χ) and chemical hardness (η) [24] help to predict the formation of chemical bonds and the physical, chemical properties of the compound, can be calculated as $\chi=(I+A)/2$ and $\eta=(I-A)/2$. And, chemical softness (S) [25], electronic chemical potential (μ) electrophilicity index (ω) [26] which defined as $S=1/2\eta$, $\mu=-(I+A)/2$, $\omega=\mu^2/2\eta$, respectively. The results are shown in Table 1.

Table 1. *Some global reactivity features calculated by B3LYP/6-311G(d,p) in the gas phase of the 3-nitrophthalonitrile.*

Parameters	
E_{HOMO}	-8.37eV
E_{LUMO}	-3.68 eV
I	8.37eV
A	3.68 eV
χ	6.02 eV
η	2.34eV
S	0.21 eV^{-1}
μ	-6.02 eV
ω	7.74V

5. Conclusions

3-nitrophthalonitrile was synthesized and characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR and X-ray crystallographic technique. The theoretical geometric parameters, vibrational frequencies, chemical shift values and chemical activity properties of the compound were examined with DFT/B3LYP/6-311G(d,p) basis set over the ground state and gas phase. When the experimental values compared with theoretical values, the minor discrepancy is observed between them, because the compound is accepted in the gas phase during theoretical calculation process, whereas it is the solid phase in the experimental analysis. We hope that these consequences will be created an infrastructure for researchers carrying out other phthalonitrile derivatives or similar studies and can be used for the further analysis.

Acknowledgments

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References

[1] N.B. McKeown, Phthalocyanine Materials:Synthesis, Structure and Function. Cambridge University Press, UK, 1998. *DOI:10.1080/10426919908907573*.

[2] C.C. Leznoff, A.B.P. Lever, (Eds) Phthalocyanines: Properties and Applications, VCH, New York, Vols. 1-4, 1989-1996.

[3] R. George, A.W. Snow, "Synthesis of 3-nitrophthalonitrile and tetra-α-substituted phthalocyanines". Heterocyclic Chem. 32 (1995) 495-498. *DOI: 10.1002/jhet.5570320219.*

[4] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory chemicals, 2nd Ed., Pergamon, Oxford, 1980.

[5] M.J. Frisch, et al, Gaussian 09, Revision E.01, 2009.

[6] R. Dennington, T. Keith, J. Millam, Gauss View, Version 5, Semichem Inc., Shawnee Mission, KS, 2009.

[7] J.P. Merrick, D. Moran, L. Radom, "An Evaluation of Harmonic Vibrational Frequency Scale Factors". J. Phys. Chem.A.111(2007) 11683-11700. *DOI:10.1021 /jp073974n.*

[8] N.K. Kınaytürk, H. Oturak, "Identification of Structural and Spectral Features of 2-Amino 4-Chlorobenzoic Acid and 4-Amino 2-Chlorobenzoic Acid: A Comparative Experimental and DFT Study". Acta Physica Polonica A 130 (2016) 276-281. *DOI: 10.12693/APhysPolA.130.276*.

[9] H. Tereci, İ. Askeroğlu, N. Akdemir, İ. Uçar, O. Büyükgüngör, "Combined Experimental and Theoretical Approaches to the Molecular Structure of 4-(1-formylnaphthalen-2-yloxy)phthalonitrile". Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 96 (2012), 569–577. *DOI:10.1016/j.saa.2012.07.005*.

[10] P.M. Anbarasan, P. S. Kumar, K. Vasudevan, S. M. Babu, V. Aroulmoji, "DFT and TD-DFT Calculations of Some Metal Free Phthalonitrile Derivatives for Enhancement of the Dye Sensitized Solar Cells". Acta Physica Polonica A, 119 (2011), 395-404. *DOI: 10.12693/APhysPolA.119.395*.

[11] H.T. Akçay, R. Bayrak, E. Şahin, K. Karaoğlu, Ü. Demirbaş, "Experimental and Computational Studies on 4-[(3,5-dimethyl-1H-pyrazol-1-yl)methoxy] phthalonitrile and Synthesis and Spectroscopic Characterization of its Novel Phthalocyanine magnesium(II) and tin(II) Metal Complexes". Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, (2013), 114:531-540. *DOI:10.1016/j.saa.2013.05.042.*

[12] J.R. Ferraro, L.J. Basile, (Editors), Fourier Transform Infrared Spectroscopy: Applications to Chemical Systems (Vol. 1). Academic Press, USA, 1978. 311p. ISBN: 978-0122541018.

[13] H. Oturak, N. K. Kınaytürk, G. Şahin, "Structure and Vibrational Studies of ±1-(1H-Benzoimidazol-2-YL) Ethanol, Using DFT Method", Acta Physica Polonica A (2015), 128, B417-B421. *DOI:10.12693 /APhysPolA.128.B-417.*

[14] X-F. Zhang, D. Jia, A. Song, Q. Liu, "3-(2-Nitrophenoxy)phthalonitrile". Acta Cryst. E. (2008) 64 356. *DOI: 10.1107/S1600536807067797.*

[15] M.D. Halls, R. Aroca, D.S. Terekhov, A. D'Ascanio, C.C. Leznoff, "Vibrational spectra of halophthalonitriles". Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy (1998), 54 305. *DOI:10.1016/S1386-1425(97)00236-9.*

[16] A. Raj, K. Raju, H.T. Varghese, C.M. Granadeiro, H. I. S. Nogueira, C. Y. Panicker, "IR, Raman and SERS spectra of 2-(methoxycarbonylmethylsulfanyl)-3,5-dinitrobenzene carboxylic acid". J. Braz. Chem. Soc. vol.20 no.3 São Paulo (2009), *DOI: 10.1590/S0103-50532009000300021.*

[17] H.O. Kalinowski, S. Berger, S. Braun, Carbon-13 NMR Spectroscopy. Chichester, U.K. John Wiley&Sons; 1988. 792 p. ISBN: 978-0-471-91306-1.

[18] M. Balcı, Nükleer Manyetik Rezonans Spektroskopisi. Ankara, Türkiye: ODTÜ Yayıncılık, 2004. 452p. ISBN:975-7064-23-8.

[19] R.P. Gangadharan, S. S. Krishnan, "Natural Bond Orbital (NBO) Population Analysis of 1-Azanapthalene-8-ol". Acta Physica Polonica A (2014), 125, 18-22. *DOI: 10.12693/APhysPolA.125.18.*

[20] R. P. Gangadharan, S. S. Krishnan, "First Order Hyperpolarizabilities, NPA and Fukui Functions of Cyclohexanone by Density Functional Theory Method". Acta Physica Polonica A (2015) 127, 748-752. *DOI: 10.12693/APhysPolA.127.748.*

[21] S. Eryılmaz, M. Gül, E. İnkaya, M. Taş, "Isoxazole derivatives of alpha-pinene isomers: Synthesis, crystal structure, spectroscopic characterization (FT-IR/NMR/GC/MS) and DFT studies". J. Mol. Structure (2016) 1108, 209-222. *DOI:10.1016/j.molstruc. 2015.11.079.*

[22] K. Mesci, S. Eryılmaz, M. Gül, E. İnkaya, "The investigation of spectroscopic and theoretical methods of bisisoxaoline derivative of norbornadien". Anadolu University Journal of Science and Technology A-Applied Sciences and Engineering (2016) 17, 641-659. *DOI:10.18038/aubtda.267054.*

[23] T. Koopmans, "Über die Zuordnung von Wellenfunktionen und Eigenwerten zu den Einzelnen Elektronen Eines Atoms". Physica 1 (1933), 104. *DOI: 10.1016/S0031-8914(34)90011-2.*

[24] R.S. Mulliken, "A New Electroaffinity Scale; Together with Data on Valence States and on Valence Ionization Potentials and Electron Affinities". J. Chem. Phys. (1934), 2, 782., *DOI: 10.1063/1.1749394*.

[25] R.G. Pearson, "Maximum Chemical and Physical Hardness". J. Chem. Educ. (1999), (76), 267. *DOI: 10.1021/ed076p267.*

[26] P.K. Chattaraj, U. Sarkar, D.R. Roy, "Electrophilicity Index". Chem. Rev. (2006), 106, 2065-2091. *DOI:10.1021/cr040109f.*