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Molecular structure and computational study of novel NLO single crystal-Metanitroaniline

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ABSTRACT

Quantum mechanical calculations of geometries, vibrational wavenumbers and energies of mNA were carried out by using Density functional theory (DFT) B3LYP method using 6-31G(d,p) basis set. The optimized geometrical parameters obtained by B3LYP method show good agreement with the experimental X-ray data. The best level of theory in order to reproduce the experimental wavenumbers is B3LYP method with the 6-31G(d,p) basis set. A detailed interpretation of the infrared spectra of mNA was also reported.

INTRODUCTION

The search for new advanced materials is an important area of contemporary research in numerous disciplines of science and development of many new technologies [1]. The field NLO organic molecule in dominated by donor acceptor subsitituted asymmetric linear molecules which, however, present important drawbacks such as a high tendency toward unfavorable aggregation, difficult non-centrosymmetric crystallization, and small off-diagonal components. Vibrational crystal studies of the molecules can provide deeper knowledge about the relationships between molecular architecture nonlinear response and hyperpolarizability and support the efforts towards discovery of new efficient material for technological applications. In this present study, conformational stability, analysis, molecular structure and FT-IR crystal investigation of mNA have been performed using density functional theory (DFT). Recently vibrational spectra combined with DFT calculations have been used as an effective tool in the study of NLO active compounds [2-8]. The detailed quantum chemical study will aid in understanding the vibrational mode of the title compound and classifying the experimental data available for this molecule. The research for novel crystal with promising nonlinear optical properties in still a challenge for scientists. The theoretical method of studying the relationship between structure and the nonlinear optical (NLO) susceptibilities may be a better solution

before venturing in to the physical growth of the crystal. The ab initio quantum chemical calculations were extensively applied for the computations of some essential non-linear optical parameters.



Fig.1 Optimized structure of MNA calculated at DFT level

MATERIALS AND METHODS

Material Synthesis:

All the raw materials were of analytical grade MNA was further purified by repeated recrystallization process using acetone as a solvent. The saturated solution of MNA in acetone was prepared at 40°C. The solution was filtered at the same temperature to avoid any insoluble impurities. Then, the solvent was allowed to evaporate, in order to obtain the maximum purification. The yielded material was further recrystallized twice before the growth is initiated. The purified salt was used to grow good optical quality bulk single crystal of m-nitroaniline [9].

Crystal Structure determination:

The experiment was carried out on a parallelepiped single crystals using Enraf- Nonus C4D4 four circle diffractometer with Mo- K α radiation. The crystal structure was solved by direct methods using SHELXS – 97. Full matrix F² least square refinement and subsequent fourier synthesis procedures were performed by SHELXL – 97. The crystal data and Structure solution and refinement details are given in Table 1.

Optical Spectrum:

A Vertex -70 Fourier transform infrared spectrometer was employed to determine the infrared spectrum at room temperature in the range of 4000- 400cm⁻¹. The sample was prepared by pressing the crystal powder with KBr pellet form.

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Computational Details:

Quantum chemical density functional theory calculations were carried out with the 2009 version of the Gaussian program package [10] using B3LYP functions combined with the standard 6- 31+G(d,p) and 6-311++G(d,p) basis sets¹²⁻¹⁴ (referred to as small and large basis sets, respectively). The Cartesian representation of the theoretical force constants has been computed at the optimized geometry by assuming Cs point group symmetry (low symmetry). The optimized geometrical parameters, fundamental vibrational frequencies, IR intensity, dipole moment, Hyperpolarizability and other thermodynamic parameters were calculated. From the intensity theory of Raman scattering [11] the relative Raman intensities (Ii) and Raman activities (Si) were calculated:

$$I_{i} = \frac{f(v_{0} - v_{i})^{4}S_{i}}{v_{i}(1 - \exp(-((hcv_{i})/kT)))}$$

where v_0 is the exciting frequency (in cm-1), v_i is the vibrational wave number of ith normal mode, h, c and k are fundamental constants, and f is a suitably chosen common normalization factor for all peak intensities.

RESULTS AND DISCUSSION

Empirical Formula	$C_6H_6N_2O_2$	
Formula Weight	138.13	
Temperature	110(2)K	
Wavelength	0.71073A°	
Crystal System	Orthorhombic	
Space Group	P _{ca2}	
	$a = 6.5231 (2) A^{\circ}$	
Unit call Dimensions	b = 18.923 (8) A°	
Unit cell Dimensions	$c = 5.0054(6) A^{\circ}$	
	$\alpha = \beta = \gamma = 90^{\circ}$	
Volume	617.85(12) A ^{°3}	
Ζ	4	
Calculated Density	1.485g/cm ³	
Absorption co- efficient	0.115mm^{-1}	
F(0 0 0)	288	
Crystal size	$1.02 \text{ x } 0.67 \text{ x } 0.18 \text{ mm}^3$	
Theta range of data	$3.30 - 29.57^{\circ}$	
Collection		
Reflections collected	4439	
Independent reflections	1369	
Refinement method	Full matrix least squares on F ²	
Data/restraints/parameters	1369/1/92	
Goodness – of – fit on F^2	1.080	
Final R indices $[1>2\sigma(1)]$	$R_1 = 0.0438 \text{ w} R_2 = 0.1128$	
R indices (all data)	$R_1 = 0.0473 \text{ w} R_2 = 0.1164$	

Table 1 Crystal data and structure refinement of mNA

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Geometric Structure:

The optimized structure parameters of mNA calculated by DFT (B3LYP) level with the 6-31G (d,p) basis set show strong hydrogen bonding, Which listed in the Table 2. From the table it can be seen that there are some deviations in the computed geometrical parameters from those reported in the single crystal XRD data, and these differences are probably due to the intermolecular interactions in the crystalline state. The compound bond length, bond angles and torsional angles are in good agreement with the corresponding experimental values.

From the single crystal XRD data it is observed that the crystal belongs to the orthorhombic system with the following cell dimensions: $a = 6.501A^\circ$, $b = 19.330A^\circ$, $c= 5.082A^\circ$. Comparing bond lengths and bond angles of B3LYP/6-31G (d,p) leads to geometric parameters which are much closer to experimental values.

Bond Length(A°)	Values	
	Experimental	Calculated B3LYP
	Experimental	6-31G(d,P)
$C_1 - C_2$	1.387268	1.3874
$C_1 - C_6$	1.384306	1.385
$C_1 - H_7$	1.083106	0.9500
$C_2 - C_3$	1.384823	1.390
$C_2 - H_8$	1.081943	0.9500
$C_3 - C_4$	1.384372	1.398
$C_3 - N_{14}$	1.509028	1.4665
$C_4 - H_9$	1.082004	0.9500
$C_5 - N_{11}$	1.439758	1.3892
$C_6 - H_{10}$	1.082237	0.9500
$N_{11} - H_{13}$	1.027970	0.8800
$N_{11} - H_{12}$	1.027932	0.8800
$N_{14} - O_{15}$	1.278411	1.2328
$N_{14} - O_{16}$	1.278069	1.2253

Table 2 Comparison between observed and calculated bond length, bond angles of mNA

Bond Angle	Value	
	Experimental	Calculated B3LYP
		6-31G(d,P)
$C_1 - C_2 - H_7$	119.654348	120.9
$C_1 - C_6 - H_7$	119.65435	120.9
$C_2 - C_3 - H_8$	119.83490	120.9
$O_{16} - N_{14} - O_{15}$	124.03906	122.99
$C_3 - C_4 - N_{14}$	118.35620	119.98
$C_4 - C_5 - H_9$	121.53559	121.6
$N_{11}-H_{12}-H_{13}\\$	108.19005`	120.00
$C_5 - C_6 - H_{10}$	119.13976	121.6
$C_2 - C_3 - N_{14}$	118.83757	117.64

Dihedral Angles	Value	
	Experimental	Calculated B3LYP
	-	0-311G(0,P)
$C_1 - C_6 - C_5 - C_4$	0.164	0.2000
$C_2 - C_3 - C_4 - C_5$	0.137038	0.1000
$O_{16} - N_{14} - C_3 - C_4$	-179.14132	-176.83
$O_{15} - N_{14} - C_3 - C_2$	-178.84408	-178.39
$N_{14} - C_3 - C_4 - C_5$	-179.67195	-179.36
$N_{14} - C_3 - C_2 - C_1$	179.77408	179.18
$N_{11} - C_5 - C_6 - C_1$	176.29640	177.23
$N_{11} - C_5 - C_4 - C_3$	-176.33268	-177.33

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Vibrational Spectral Analysis:

The vibrational analysis of mNA was performed on the basis of the characteristic vibrations. Theoretical calculations were performed using density functional theory (B3LYP) with 6-31G(d,p).

Nitro group Vibrations:

The asymmetric stretching of NO₂ compound generally gives a band in the range 1485 -1570 cm⁻¹ and the symmetric one occurs in the region 1320-1370 cm⁻¹. For this compound a strong band observed in the measured IR spectrum at 1535 cm⁻¹ is assigned to NO₂ asymmetric stretching mode. The strongest band observed at 1360cm⁻¹

N- H Vibrations:

The N- H stretching vibrations generally give rise to bands at 3500-3300 cm⁻¹. The NH stretching bands are observed at 3201, 3094, 2923 cm⁻¹ in the spectrum and the calculated value at 3240 cm⁻¹ (DFT) theoretically. Furthermore, the N- H stretching wave numbers are red shifted in the IR spectrum with a strong intensity from the computed wave numbers, which indicates the weakening of the N- H band.

C-C vibrations:

The ring C=C and C- C stretching vibrations, known as semicircle stretching usually occurs in the region 1525-1400 cm⁻¹. In accordance with the above literature data in our present study, the bands for C – C stretching vibrations are observed at 1487 and 1466 in the calculated values [12]. All the bands lie in the expected range except the last band when compared to literature values. These observed frequencies show that, the substitutions in the ring to some extend effect the ring modes of vibrations. The comparison of the theoretically computed values were very good in agreement by B3LYP/6-31G (d,p) [13] method.

C-H Vibrations:

The C- H in plane and out of plane bending vibrations generally lie in the region 1300-1000 cm⁻¹ and 1000-675 cm⁻¹ respectively. In accordance with the above literature data in our present study the weak and very weak bands observed in FT IR spectrum at 1245 and 1200 cm⁻¹ as medium strong band are assigned to C- H in plane bending vibrations.

Fig.2 (a) FT-IR spectra of mNA and (b) simulated IR spectra of mNA



Experimental	Calculated B3LYP/6-31G(d,p)	Assignment
3430	-	NH ₂ asymmetric stretching
3328	-	NH ₂ symmetric stretching
3201	3240	N-H stretching
3094	-	N-H stretching
2923	-	N-H stretching
1623	1610	NH ₂ Stretching
1520	1535	NO ₂ stretching
1487	1466	C-C vibrations
1264	1280	Overtones and combination bands
1348	1360	NO ₂ stretching
1162		C- H stretching
1087	1110	Overtones and combination bands
927	950	C- H stretching
868	857	C- H stretching
669	678	C- H stretching

Table.3 The observed FT-IR and calculated wavenumbers using B3LYP/6-31G(d,p)

Mulliken Charges:

The charge distributions calculated by the Mulliken method for the equilibrium geometry of MNA is given in Table 4. The charge distribution on the molecule has an important influence on the vibrational spectra. The corresponding Mulliken's plot with different B3LYP/6-31G(d,p) basis set. The basis set becomes more negative, while their natural atomic charges show positive values. The above result shows that the natural atomic charges are more sensitive to the charges in the molecular structure than Mulliken's net charges

Other molecular Properties:

The thermodynamic parameters such as zero point irrational energy, rotational constants and dipole moment of mNA are calculated using B3LYP/6-31G (d,p) basis set. The calculated thermodynamical parameters are given in the Table.5

Atoms	Atomic Charges with B3LYP 6-31G(d, p)
C ₁	-0.155737
C ₂	-0.113184
C ₃	0.283663
C_4	-0.112780
C ₅	0.169357
C ₆	-0.090937
H_7	0.145763
H ₈	0.180832
H ₉	0.179744
H ₁₀	0.136143
N ₁₁	-0.695337
H ₁₂	0.294220
N ₁₄	0.066843
O ₁₅	-0.291024
O ₁₆	-0.288258

Table.4 Atomic Charge distribution

Basic set	B3LYP/6-31G(d,p)
Zero point energy(kcalmol ⁻¹)	75.66232
Rotational constants(GHz)	2.66165
	0.96485
	0.70891
Dipole moment (debye)	$\alpha_x = 5.5655$
	$\alpha_{y} = 0.8925$
	$\alpha_{z} = 1.6253$
	$\alpha_{tot} = 5.8663$

Table.5	The calculate	d thermodynamical	parameters of mNA
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SHG study:

The nonlinear optical property of the grown mNA single crystal was tested by passing the output of Nd: YAG Quanta ray laser (model GCR-2 (10)) with pulse energy emitting 1064 nm, generating about 6 mJ / pulse. The SHG efficiency of mNA was determined by Kurtz and Perry powder technique (Kurtz and Perry, 1968). Microcrystalline material of KDP was used as a reference for comparison with mNA for Second Harmonic Generation experiments. For a laser input pulse of 6.2 mJ, the second harmonic signal (532 nm) of 92 mW and 2.6 W, respectively were obtained for KDP and mNA samples. Thus, the SHG efficiency of MNA is twenty eight times higher than KDP [9].

CONCLUSION

Attempts have been made in the present work for the molecular parameters and frequency assignments for the mNA from the FTIR spectrum. The mNA was successfully synthesized and the single crystals have been grown by slow evaporation solution growth technique. From the powder X-ray diffraction analysis, it was confirmed that the grown single crystals belongs to orthorhombic and the lattice parameters were determined. The functional groups have identified from the FTIR analysis. It is found that the SHG efficiency is twenty eight times greater than that of KDP. The title crystal may possesses potential application as nonlinear and electrooptical material as supported by optical absorption studies.

REFERENCES

[1] Madhavan. J, Aruna. S, Anuradha. A, Premanand. D, Vetha Potheher. I, Thamizharasan. K, Sagayaraj. P, *Optical Materials*, **2007**, 29, 1211-1216

[2] Plosker. G. L, Tavish. D, Drugs, 1994, 47, 622-651.

[3] Kaur. I. P., Singh. M, Kanwar. M, Int. J. Pharm. 2000, 199, 119–127.

[4] Famaey. J. P, Inflamm. Res. 1997, 46, 437–446.

[5] Hirayama. N, Taga. J, Oshima. S, Honjo. T, Anal. Chim. Acta, 2002, 466, 295–301.

[6] Moffat. A. C (Ed.), Clarke's Isolation and Identification of Drugs, *The Pharmaceutical Press*, London, **1986**.

[7] Bult. A, Metal Ions in Biological Systems, Dekker. M, NY, 1983, 16.

[8] Chufan. E. E, Pedregosa. J. C, Borras. J, Vib. Spectrosc. 1997, 15, 191–199.

[9] Senthil. S, Pari. S, Sagayaraj. P, Madhavan. J, Physics B 2009, 404, 1655-1660

[10] Frisch. M. J, Trucks. G. W, Schlegel. H. B, Scuseria. G. E, Robb. M. A, Cheeseman. J. R, Montgomery Jr. J. A., Vreven. T, Kudin. K. N, Burant. J. C, Millam. J. M, Iyengar. S. S, Tomasi.

J, Barone. V, Mennucci. B, Cossi. M, Scalmani. G, Rega. N, Petersson. G. A, Nakatsuji. H, Hada. M, Ehara. M, Toyota. K, Fukuda. R, Hasegawa. J, Ishida. M, Nakajima. T, Honda. Y, Kitao. O, Nakai. H, Klene. M, Li. X, Knox. J. E, Hratchian. H. P, Cross. J. B, Adamo. C, Jaramillo. J, Gomperts. R, Stratmann. R. E, Yazyev. O, Austin. A. J, Cammi. R, Pomelli. C, Ochterski. J. W, Ayala. P. Y, Morokuma. Y, Voth. G. A, Salvador. P, Dannenberg. J. J, Zakrzewski. V. G, Dapprich. S, Daniels. A. D, Strain. M. C, Farkas. O, Malick. D. K, Rabuck. A. D, Raghavachari. K, Foresman. J. B, Ortiz. J. V, Cui. Q, Baboul. A. G, Clifford. S, Cioslowski. J, Stefanov. B. B, Liu. G, Liashenko. A, Piskorz. P, Komaromi. I, Martin. R. L, Fox. D. J, Keith. T, Al-Laham. M. A, Peng. C. Y, Nanayakkara. A, Challacombe. M, Gill. P. M. W, Johnson. B, Chen. W, Wong. M. W, Gonzalez. C, Pople. J. A, Gaussian 03, *Gaussian, Inc., Pittsburgh*, PA, **2003**.

[11] Krishanakumar. V, Dheivamalar. S, J. Raman Spectrosc. 2009, 40, 411-415.

[12] Yadav. B. S, Ali. I, Kumar. P, Yadav. P, Indian J. Pure Appl. Phys. 2007, 45, 979.

[13] Musa E. Mohammed, Christina Y. Ishak, Hajir I. Wahbi, Der Chemica Sinica, 2011, 2(4), 133-139