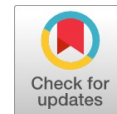


Xrd, Quantum Chemical, Vibrational, Thermal and Antifungal Activity Analysis on 3-Nitroanilinium Hydrogen Oxalate

S. Thangarasu, V. Siva, S. Athimoolam, S. Asath Bahadur



Abstract: 3-nitroanilinium hydrogen oxalate has been crystallized successfully by solvent evaporation method. Optimized molecular geometrical parameters and the vibrational assignments of 3NAOX has been calculated by using Hartree-Fock (HF) and density functional method (B3LYP) with 6-311++G (d, p) basis set. The computational analysis showed good agreement with the experimental data. The energy and various parameters were obtained by HOMO–LUMO plot. The apparent pharmaceutical/biological activity of the salt confirmed by lower band gap value obtain from the Frontier Molecular Orbital (FMO) analysis. Thermal properties of 3NAOX were analyzed by TGA/DTA. The grown crystals were involved in an antimicrobial activity against certain potentially threatening microbes which shows that grown crystal screened the bacteria.

Keywords: 3-Nitroaniline, Quantum chemical analysis, HOMO–LUMO, Antifungal activity.

I. INTRODUCTION

The intramolecular charge transfer from the $-NH_2$ (electron-donor group) to $-NO_2$ (electron-acceptor group) through the phenyl ring in nitroaniline, called as push-pull molecules. Optical nonlinearity by using experimental and computational method on 3-Nitroaniline and 4-nitroaniline as reference compounds [1–3]. Biologically important compounds, such as 3-Nitroaniline and its derivatives are owing to produced significant antihyperglycemic as well as hypoglycemic effects in alloxan-induced and normal diabetic rabbits [4]. Also 3-Nitroaniline plays an essential role in several biological processes and has considerable chemical

and pharmacological importance

A new family of organic-inorganic crystals is proposed with the background such as: biological importance, with physical, chemical and thermal properties through inorganic sub networks. Based on the above specifics, 3-nitroaniline was reacted with oxalic acid and 3-nitroanilinium hydrogen oxalate (3NAOX) crystals were grown. In this paper, the synthesis, crystal growth, structural, spectroscopic, thermal and antifungal analyses of 3NAOX is reported.

II. EXPERIMENTAL SECTION

3-nitroanilinium hydrogen oxalate (3NAOX) is synthesized from the AR grade 3-nitroaniline and oxalic acid obtained from Himedia fine Chemicals taken in 1:1 ratio in acetone. This solution stirred well about 1 hour to get clear solution. The title crystal was synthesized according to the scheme as shown in Fig. 1. After many attempts, the compound 3-nitroanilinium hydrogen oxalate (3NAOX) has not yielded good quality single crystal; which is not suitable for single crystal X-ray diffraction. Hence, the powder XRD study of 3NAOX was carried out to confirm the new phase of the complex.

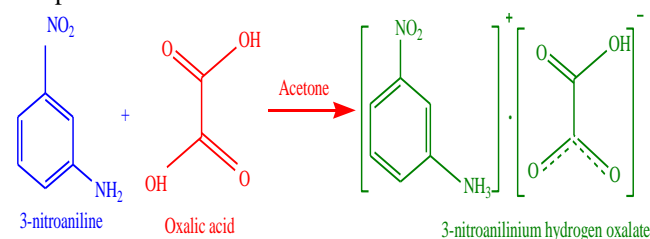


Fig. 1. Chemical Scheme of 3NAOX

A. Powder XRD analysis

Powder XRD studies of grown crystal of 3NANO was carried out by Bruker X-ray diffractometer of D8 advanced ECO XRD system with SSD160 1D Detector. The range of 2θ was 0° to 50° . The preliminary data of the powdered sample was calculated by indexing in the first 2θ strong intensity peaks using DASH 3.3.2 program [5].

B. Computational analysis

The molecular structure of 3NAOX are computed by performing both HF and B3LYP with basis set 6-311+G(d,p) in the ground state. Computational calculations for 3NAOX are performed using GAUSSIAN 09W [6] program package on i5 processor/3.20 GHz personal computer without any constraint on the geometry [7]. The first job was optimized geometry of title compound determined by computational work.

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The HF and B3LYP method [8,9] combined with gradient-corrected correlational functional of Lee, Yang and Parr (LYP) [10]. Using principle of statistical mechanics, thermodynamic properties of 3NAOX have been calculated from normal mode of vibrational frequencies which provide the details about title compound in gas phase. GAUSSVIEW program [11] with symmetry considerations were used to assign vibrational frequencies. The electronic properties and energy value from FMOs analysis were calculated by the HF and B3LYP method.

C. Spectral analysis

FTIR and FT-Raman spectra of 3NAOX crystal were recorded in the range of 400 to 4000 cm^{-1} using Nexus 670 FTIR spectrometer and BRUKER RFS 27 FT-Raman Spectrometer, respectively. Nd:YAG laser at 1064 nm was used as source.

D. Thermal analysis

TG/DTA analyses of all the 3NAOX crystals were carried out by SII (SEIKO), Japan Analytical Instrument, and Model No: TG/DTA-6200 with N_2 Atmosphere of range 20°C/Min. The samples used for this analysis were prepared by crushing the grown crystals.

III. RESULTS AND DISCUSSION

A. Powder XRD Study

The possible unit cell parameters for 3NAOX given in the Table 1. By comparing the powder XRD spectra and the predicted unit cell values in the salt formation is confirmed.

Table I: Unit cell parameters of 3NAOX

Unit cell Parameters	3NAOX
a (Å)	21.929 (2)
b (Å)	9.083 (9)
c (Å)	13.943 (1)
α (°)	90
β (°)	104.9
γ (°)	90
Volume	2682.7

Powder XRD pattern of grown crystal 3NAOX compared with stimulated XRD pattern of 3-nitroaniline and oxalic acid was shown in Fig. 2. Some of the new intensity peaks appear in 3NAOX crystals and some of the peaks are disappear were compared to 3-nitroaniline pattern. The possible unit cell parameters were identified and 3NAOX crystal belongs to monoclinic system was notable using DASH 3.3.2 program.

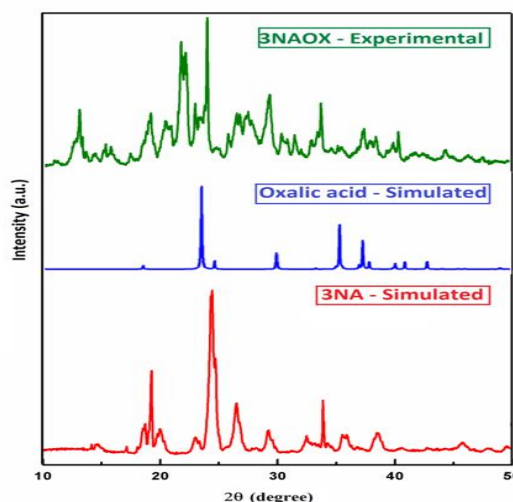


Fig. 2. Powder XRD pattern of 3NAOX

B. Molecular geometry

In 3NAOX, asymmetric part of unit cell contains 3-nitroaniline (cation) charge is neutralized with Hydrogen oxalate (anion). The optimized structure of 3-nitroanilinium hydrogen oxalate diagram and atom numbering scheme are shown in the Fig. 3.

In phenyl ring, optimized bond length of C-C is calculated as 1.389–1.401 Å in B3LYP level and 1.379–1.391 Å in HF level, which illustrates a good agreement with the experimental results. The values are obtained in the expected range with acceptable deviation which shows the effective optimization of the molecular structures. The C–O bond lengths were calculated as 1.197–1.329 Å in B3LYP level and 1.184–1.306 Å in HF level in oxalate anion. These results are closed to the experimental values.

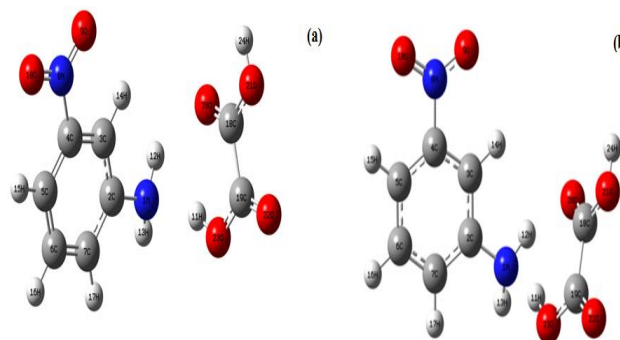


Fig.3. Optimized geometry of 3NAOX by (a) HF & (b) DFT

C. Mulliken atomic charge Analysis

The histogram of atomic charges for 3NAOX is shown in Fig. 4. The hydrogen atom (H11) in oxalic acid group of 3NAOX is more electropositive (0.471e in HF and 0.461e in B3LYP). Because, it attached with electronegative oxygen atom(O23). Also, carbon atom has more electro negativity (C7) (-0.680e in HF and -0.434e in B3LYP). Because, it surrounded by two carbon atoms (C2 and C6) (electronegative) and one hydrogen atom (H17).

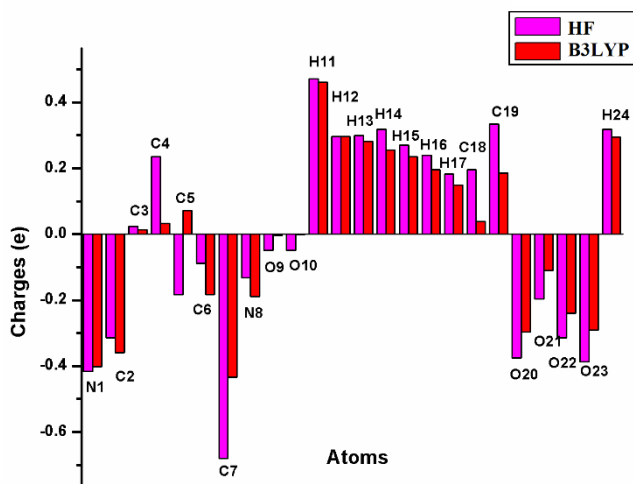


Fig.4. Histogram of atomic charges on 3NAOX by HF & B3LYP methods

D. Vibrational Analysis

The 3NAOX consists of 24 atoms and undergoes 66 modes of vibrations. The experimental and computed IR and Raman spectra of 3NAOX are given in Fig. 5.

Vibrations of $-NH_2$ group

The NH_2 group vibrations are assigned as the asymmetric & symmetric stretching, wagging, twisting, scissoring and rocking vibrations are spread over a region. In 3NAOX, the calculated wavenumber at 3894 cm^{-1} in HF and 3616 cm^{-1} in DFT(B3LYP) are assigned to NH_2 antisymmetric stretching. NH_2 symmetric stretching wavenumber are observed at 3852 and 3525 cm^{-1} in HF and DFT respectively. NH_2 scissoring vibrations in addition with out-plane bending C–H vibrations scaled at 1835 in HF and 1666 cm^{-1} in DFT(B3LYP) level. Those vibrations peaks are absent in experimental spectra. NH_2 twisting vibrations identified as a weak peak at 921 cm^{-1} in IR spectrum and scaled by HF and DFT(B3LYP) levels at 894 and 817 cm^{-1} , respectively. The NH_2 rocking vibrations are observed as a weak peak at 1347 in IR and 1359 cm^{-1} in Raman.

Vibrations of $-NO_2$ group

The symmetric and asymmetric stretching vibrations of NO_2 group are observed in the region around $1300\text{--}1370\text{ cm}^{-1}$ and $1500\text{--}1570\text{ cm}^{-1}$ for nitrobenzene and its substituted compounds. The NO_2 asymmetric stretching vibrations are theoretically computed by HF and DFT(B3LYP) at 1770 and 1589 cm^{-1} , respectively. The NO_2 symmetric stretching vibrations are theoretically scaled at 1574 in HF and 1371 cm^{-1} in DFT(B3LYP).

C–N and C–C vibrations

The C–N and C–C stretching vibrations occurs in region around $1300\text{--}1600\text{ cm}^{-1}$ due to literature. The weak intensity peak at 1542 in IR spectrum is assigned to C–N stretching vibrations and it is computed at 1574 in HF and 1371 cm^{-1} in DFT(B3LYP) level. C–C stretching vibration scaled at 1835 and 1666 cm^{-1} in HF and DFT(B3LYP) level, respectively.

C–H vibrations

These vibrations represent aromatic structure in 3NAOX and these vibrations are at around 3100 cm^{-1} . Hence a shoulder peak at $3441, 3338\text{ cm}^{-1}$ and a broad at 2901 cm^{-1} are obtained in IR spectrum is identified for C–H stretching. The same stretching vibrations are theoretically by HF and DFT level at

mode 62, mode 61, mode 60 and mode 59 in the range of $3402\text{--}3169\text{ cm}^{-1}$. The aromatic C–H out-plane bending and in-plane bending vibrations are representing the band around of $900\text{--}1100\text{ cm}^{-1}$ and $1100\text{--}1300\text{ cm}^{-1}$, respectively. For the title compound C–H in-plane bending vibration observed as a weak peak at 1623 cm^{-1} in IR spectrum and calculated at 1626 cm^{-1} in HF and 1490 cm^{-1} in DFT(B3LYP) level, respectively. A weak peak presented at 1093 cm^{-1} in IR spectrum for C–H out-plane bending vibration and its calculated at 1082 cm^{-1} in HF and 995 cm^{-1} in DFT(B3LYP) level.

Vibrations of carboxylic anion

The carboxylic ($COOH$) group and COO^- group usually expected in 1755 cm^{-1} . In 3NAOX crystal, it is computed in the range $2063\text{--}1789\text{ cm}^{-1}$ in the HF and DFT(B3LYP) level. The OH stretching mode of the carboxylic group is computed in range $3263\text{--}4103\text{ cm}^{-1}$ in the HF and DFT level. But corresponding peak are absent in experimental spectra. The scissoring vibrations of carboxylic group is found as a weak peak at 1013 cm^{-1} in Raman spectrum, it is calculated at 1029 and 941 cm^{-1} in the HF and DFT(B3LYP) level, respectively. The rocking vibrations of carboxylic group is computed at 263 and 246 cm^{-1} in the HF and DFT(B3LYP) level, respectively.

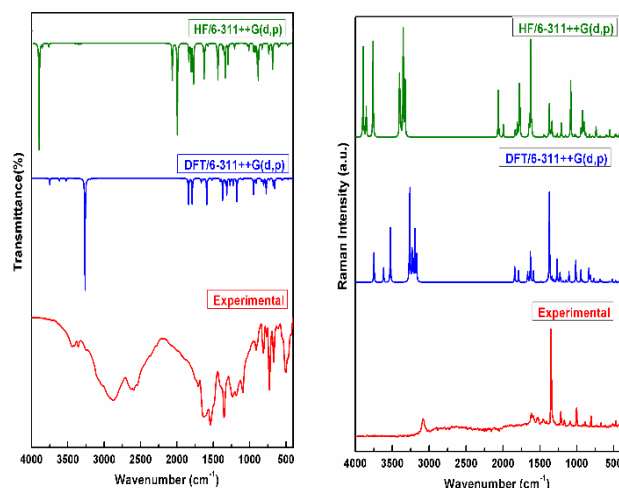


Fig. 5. Experimental and computed IR & Raman spectra of 3NAOX

E. Frontier Molecular Orbital Analysis

In the organic molecules, optical and electric properties proposed by using frontier molecular orbital analysis [12]. In molecular orbital have two important interactions; such as HOMO represents the ability to donate an electron and another one is LUMO describe electron acceptor. Also, these orbitals are named as frontier orbitals. FMO analysis [13] is used to identify the highly reactive position in π -electron systems and it also explains several types of reaction in conjugated system. Also, FMO plays an essential part in abiding chemical stability of the compound [14–16].

The calculated HOMO and LUMO energies and some important parameters of the 3NAOX were calculated by HF and DFT/B3LYP method as shown in the Table 2.

The corresponding energy level diagrams of the present molecules are shown in Fig. 6. A huge amount of charge transfer occurred in 3NAOX is indicated by small energy gap, which is connected with a high chemical reactivity. The small value of energy gap and high value of charge transfer leads the molecules to biologically active. For 3NAOX, 407 energy values are obtained in the range of -20.649 – +51.775 au and -19.215– +50.032 au in HF and DFT(B3LYP) method, respectively. The computed HOMO and LUMO energy values are -0.344/0.028 au in HF and -0.264/-0.111 au DFT(B3LYP) method and energy gap was 0.372 a.u in HF and 0.153 a.u in DFT(B3LYP) method.

Table II: Molecular orbital values of 3NAOX

Parameters (a.u.)	HF/ 6-311++G(d,p)	B3LYP/ 6-311++G(d,p)
E _{LUMO}	0.028	-0.111
E _{HOMO}	-0.344	-0.264
Δ(E _{LUMO} - E _{HOMO})	0.372	0.153
Electrophilicity index	0.067	0.230
Ionization potential (I)	0.344	0.264
Chemical hardness (η)	0.186	0.077
Electronegativity (χ)	0.158	0.188
Electron affinity (A)	-0.028	0.111
Chemical potential (μ)	-0.158	-0.188

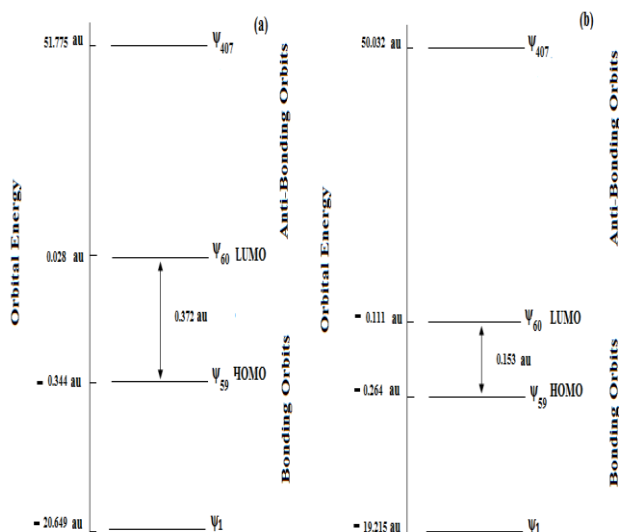


Fig. 6. Molecular orbital energy level diagram of 3NAOX by (a) HF and (b) DFT(B3LYP) method

F. Thermal Analysis

3NAOX thermal behaviour was analyzed by using simultaneous DTA/TGA analysis in the temperature range 40-750°C in air atmosphere. The TGA/DTA curves of 3NAOX were given in the Fig. 7. The TGA/DTA curve represent that the decomposition in the range of 157.5-750°C. The three main stages decomposition of 3NAOX occurred within temperature range as given Fig. 7. In TGA/DTA

curve, weight loss 9.7% noted in temperature range 150-180°C due to the elimination of water group from 3NAOX it indicates first stage of decomposition. The second stage of major weight loss (31%) occurs at 180-220°C temperature range, which is due to the liberation of CO₂. The next decomposition stage is owing to the removal of NO and CO in the temperature range 220-280°C with weight loss of 29%. The loss of water molecule in lattice is identified as two weak endothermic peaks at 81.9°C and 108.7°C and another endothermic peak identified at 157.5°C is may be the melting point of 3NAOX. The decomposition of the organic compound is noted as exothermic peak at 448.1 °C.

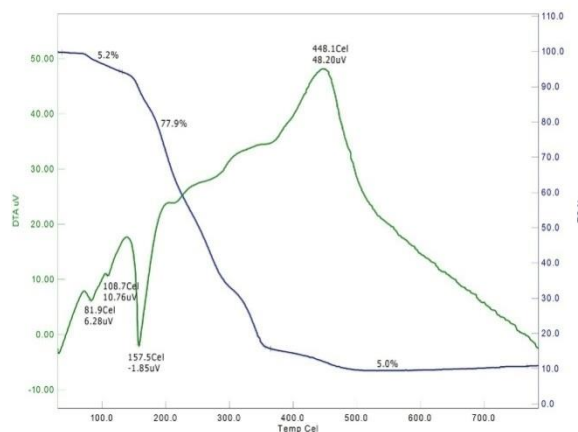
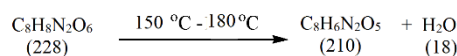
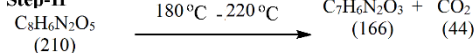


Fig.7. TGA/DTA curve of 3NAOX

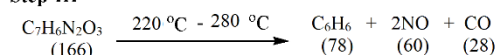
Step-I



Step-II



Step-III



Note: The values given in parenthesis stand for the molecular weights of the respective species.

Fig. 8. Decomposition steps of 3NAOX

G. Antimicrobial Activity Analysis

3NAOX crystal was tested against Candida Albicans (C.albicans) to analyze the antifungal activity by disc diffusion method. The above mentioned bacterial species were prepared at 50 mgmL⁻¹ and 100 mgmL⁻¹ concentrations. The measured diameter zone of inhibition of these microorganisms is shown in Table 3. From the Table III, it was clear that 3-nitroanilinium hydrogen oxalate complex was moderately active against the organisms.

Table III: Antifungal activity of 3NAOX compound against some human pathogens

Sample	Concentration (mg/mL)	Zone Of Inhibition in diameter (mm)
		<i>C. Albicans</i> (Used Micro organisms)
3NANO	50	12
	100	12
SD	50/100	16

SD-Standard drug (Antifungal activity)–Ketokonazole

IV. CONCLUSION

3-nitroanilinium hydrogen oxalate has been synthesized and characterized by various methods. The detailed interpretation of the calculated IR and Raman spectra at HF and B3LYP 6-311G++(d,p) level of theory with the experimental results shows the reliability of 3NAOX molecule. The higher stability of the title molecule is confirmed from the computed HOMO-LUMO energy gap. Thermal stability and antimicrobial activity of the title compound has been calculated.

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