RESEARCH ARTICLE

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Growth, Spectroscopic Characterization and DFT-Based Vibrational Analysis of Morpholine Oxalic Acid Single Crystal

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Abstract: Single crystals of morpholine oxalic acid (MO) were grown successfully by the slow evaporation solution growth technique using ethanol as a solvent. The structural and vibrational properties of the grown crystal were investigated using experimental FT-IR and FT-Raman spectroscopy along with density functional theory (DFT) calculations employing the B3LYP/6-311G(d,p) basis set. Optimized molecular geometry confirms the presence of strong intermolecular O–H···O and N–H···O hydrogen bonding interactions. Normal coordinate analysis based on scaled quantum mechanical force field (SQMFF) shows good agreement between experimental and theoretical vibrational frequencies. The observed lowering of carbonyl stretching modes further supports the existence of hydrogen bonding and charge transfer interactions, indicating the potential biological relevance of the MO crystal.

Keywords: Single crystals, Morpholine oxalic acid, FT-IR, SQMFF

1. Introduction

Material Science is the science of solids, a field that encompasses every aspect of modern life. Chemistry plays a vital role in several expanding areas of material science with emphasis on the ways in which new materials are designed, synthesized, evaluated and used [1, 2]. Materials may be broadly defined as any solid component or device that is used to address a current or future societal need, for instance, simple building materials such as nails, wood, coatings etc., that address our need of shelter [3]. The discipline of material chemistry focuses on understanding the relationships between the arrangement of atoms or ions or molecules in a material and overall structural or physical properties of the material [4]. By this designation, common disciplines such as polymer, solid-state and surface chemistry would be placed within the scope of materials chemistry. The field of solid state chemistry involves the study of structure and properties of existing materials and also synthesis and characterization of newer materials [5, 6]. By using advanced computational techniques, structures and properties of materials can be predicted. The study of materials and their properties and applications is an important part of modern science and technology [7, 8]. As may be expected for such a wide-ranging subject, the study of materials is a multidisciplinary effort covering segments of physics, chemistry and essentially all branches of engineering including aerospace, chemical, civil, electrical and mechanical. In addition, it focuses directly on the study of the properties and applications of materials.

Although the use of solid materials dates back to prehistoric period, the systematic study and development of materials have begun much more recently, within the last 100 years. Development of the periodic table of elements in the nineteenth century and the resulting grouping of elements with similar properties played a crucial role in setting the stage for the development of materials with desired properties. The discovery of X-rays and probing the internal structure of solids early in the twentieth century also played a key role in accelerating the study of materials.

2. Materials and Methods

2.1 Materials

Materials purchased from Sigma Aldrich. There is no more further purification. Morpholine acid and oxalic acid are high purity (99.0%) and Ethanol.

2.2 Method of preparation

Commercially available Morpholine and oxalic acid were dissolved in ethanol for crystal formation. To create a saturated 100mL solution of Morpholine and oxalic acid, ethanol was employed as the solvent at room temperature. The fluid was filtered with Whatman filter paper. To ensure slow evaporation [9], the solution beaker was covered with a perforated polythene sheet and kept in a space free of dust. The grown single crystal of Morpholine oxalic acid (MO) is depicted in Figure. 1 after being harvested after 10 days.

3. Results and Discussion

3.1 Synthesis and growth of MO crystal

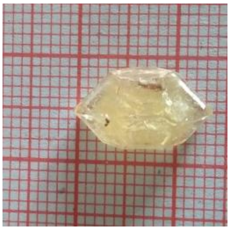

Figure 1. Grown single crystal of Morpholine oxalic acid

3.2 Computational Details

The Gaussian'09 software tool was used to do the quantum chemical computation of MO utilising the B3LYP/6-311 G (d, p) basis set [10, 11, 12]. In order to get a complete interpretation of the fundamental modes, T. Sundius' MOLVIB programme version 7.0 had been used to run the normal coordinate analysis [13].

3.3 Optimized Geometry

The molecular structures of MO was optimized in DFT methods at B3LYP/6-311G(d,p) basis sets. Figure 2 presents the optimized molecular structures of MO and bond length and bond angle are given in Table 1 as well as dihedral angle is given in Table 2. The presence of strong inter molecular hydrogen bond interactions C5-H12...O19 and O17-H23...O1 has been confirmed by the measured distances O1...O17 and C21...H12 bonds which are 2.699 Å and 3.2 Å respectively, for both cases lying wan der Walls for hydrogen interaction [14].

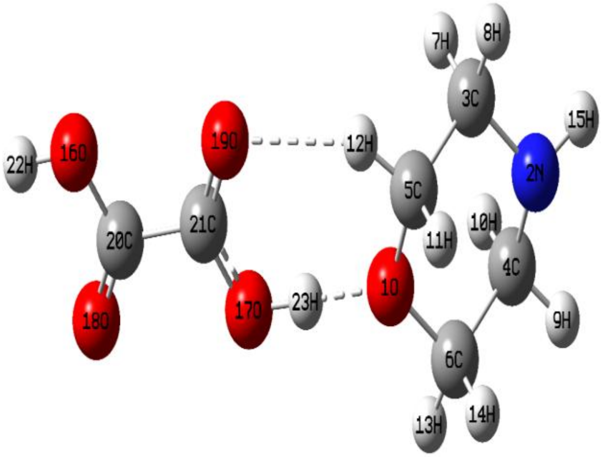

Figure 2. Optimized structure of MO

Table 1. Bond length of MO

Bond length	Theoretical(Å)	Bond length	Theoretical(Å)
O1-C5	1.439	C6-H13	1.091
O1-C6	1.433	C6-H14	1.097
O1-23	1.670	O16-C20	1.342
N2-C3	1.465	O16-H22	0.969

N2-C4	1.463	O17-C21	1.319
N2-H15	1.013	O17-H23	0.995
C3-C5	1.522	O18-C20	1.199
C3-H7	1.103	O19-C21	1.206
C3-H8	1.093	C20-C21	1.544
C4-C6	1.523	C5-H11	1.097
C4-H9	1.093	C5-H12	1.089
C4-H10	1.104		

3.4 Vibrational Analysis

Based on a potential energy distribution (PED) calculation made with MOLVIB -7.0, a detailed vibrational assignment of MO was carried out, and the frequency was compared to the experimental FT-IR and FT Raman spectra as given in Figure 3 and 4. A significant amount of the observed vibrational pattern matches up with theoretically estimated vibrational modes. MO molecule is made up of 31 atoms that vibrate in 87 normal modes [5, 6]. Based on SQMFF (Scaled Quantum Mechanical force field) calculations compares calculated frequencies of molecule structures with the observed frequencies [13]. In Table 4.2 and the measured FT-IR and Raman spectra, the assignments of MO with potential energy distribution (PED) have been presented.

3.5 Carboxylic acid group vibrations

Vibrational analysis of carboxylic acid is made on the basis of carbonyl group and hydroxyl group. The free hydroxyl stretching [7] is observed as a shoulder band in IR at 3412 cm^{-1} and scaled at 3413 cm-1 which are pure and the contributions are scaled as 100% PED. The lowering of O-H stretching vibration is due to the inter- and intramolecular hydrogen bonding effect. The carbonyl group vibration expected to occur in the region 1760–1730 cm^{-1} [6] is observed at 1730 in IR and 1719 cm-1 in Raman with scaled PED value at 1743 and 1707 cm-1 shows that this mode is a stretching mode with 55% contribution. When a carbonyl group participates in hydrogen bonding, resonance can occur, which puts a partial negative charge on the oxygen atom accepting the hydrogen bond and a positive charge on the atom donating the hydrogen, however the partial ‘transfer of allegiance’ of the proton enhances resonance and lowers the C=O stretching wavenumber. The lowering of carbonyl stretching mode is attributed to the fact that the carbonyl group chelate with the other nucleophilic groups, thereby forming both intra and intermolecular hydrogen bonding in the molecule. The C-O stretching mode and

O-H bending modes are not independent vibrational modes because they couple with the vibrations of adjacent groups. The weak band in Raman at 1104cm^{-1} assigned to the in plane bending of the hydroxyl group coupled with C-O stretching mode is in good agreement with scaled value (1232 cm^{-1}) (Socrates, 2001).

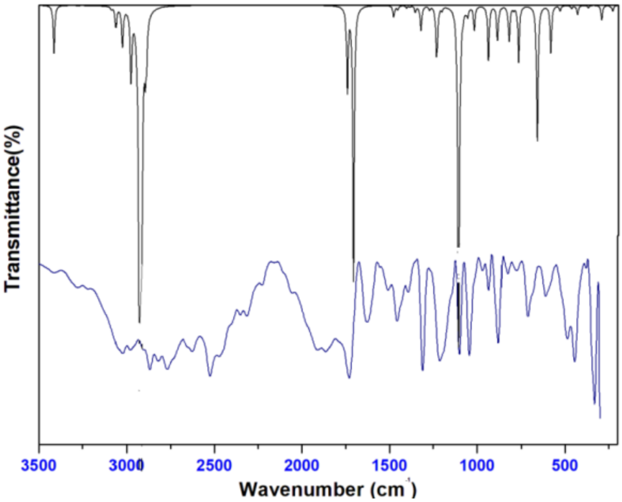

Figure 3. FT IR spectra

3.6 Ring vibrations

Aromatic organic compounds' C-H stretching wavenumbers are frequently found in the 3100–3000 cm^{-1} range (Smith, 2011). Bands in this region aren't greatly altered because to substituent location and nature. The FT-IR spectra of MO have bands at 3022, 2980, 2968 cm^{-1} and 3020, 2988cm^{-1} due to the presence of aromatic C-H bonds. The corresponding scaled values are listed in Table 3 and they are in good agreement with theoretical scaled values of the ring C-H pure stretching mode. The fact that their PED percent are 99 and 98%, respectively, shows how extremely pure C-H modes are. The C-H in plane bending vibration appears in the range of 1000-1350 cm^{-1} [6] and is measured at 1310, 1211 cm^{-1} in the IR spectra, whereas the Raman spectra are 1311 and 1203 cm^{-1} with good agreement with computed values.

υ-stretching; ss- symmetric stretching; AS- asymmetric stretching; β-in-planebending;γ- outofplane bending; W- wagging; TW - twisting; SC- scissoring; T- torsion; ATO-out-of plane asymmetrictorsion; AT-asymmetric torsion; G-gauche; ROCK-rocking; PU -puckering; SD-symmetric deformation; TD- trigonal deformation; AD- asymmetric deformation; ADO - out of plane asymmetric deformation

In heterocyclic compounds, N-H stretching vibration occurs in the region 3500-3000 cm^{-1} [7] and is observed as a very strong band at 3277 cm^{-1} in IR.

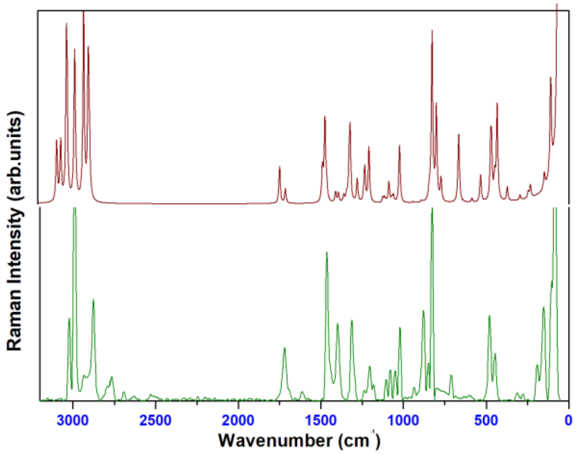

Figure 4. FT Raman spectra

Table 2. Vibrational assignment of MO by Normal Coordinate Analysis based on SQMFF calculations

Observed Fundamentals /cm^{-1}		**Selective Scaled B3LYP with 6-311++G(d,p)force field**	
ν_{IR}	**ν_{Raman}**	**ν_{cal} cm^{-1}**	**Assignment with PED (≥10%)**
3412		3413	υOH (100)
3277		3277	υNH (100)
3219		3085	CHAS (74), CHSS (25)
		3061	CHAS (77), CHSS (23)
		3027	CHAS (63), CHSS (36)
3022	3020	3023	CHAS (63), CHSS (36)
2980	2988	2977	CHSS (69), CHAS (25),
2968		2970	CHSS (75), CHAS (24)
2901		2923	υOH (85), OHB (8)
		2895	CHSS (60), CHAS (37)
	2874	2887	CHSS (61), CHAS (38)
1730		1743	COAS (53), COSS (16), COR (18), CC (17), TOHB(17)
	1719	1707	COAS (55), TOHB (23), COSS (10)
1506		1485	CHSC (86), CSC (6)
1456		1479	CHSC (91)
		1473	CHSC (63), TOHB (22)

	1463	1469	CHSC (85), TOHB (7)
		1459	TOHB (74), BCN (7), BOH (6)
		1455	TOHB (71), BCN (8), BOH (6)
		1405	CHW (68), CHT (13), CC (11)
1393	1397	1387	CHW (83), CHT (6)
		1355	CHW (84), CHT (5)
		1338	TOHB (47), BOH (13), COAS (11), COSS (10),
		1324	CHT (43), CHW (38), BCN (6), CN (5)
1310	1311	1317	CHT (67), CHW (18)
		1274	CHT (78), CHR (9)
		1235	TOHB (39), COSS (14), CHT (11), BOH (10),
		1229	TOHB (39), CHT (16), COSS (11), BOH (10),
1211	1203	1203	CHT (84)
		1120	CHR (46), PK (22), CSC (10),
	1104	1109	COSS (46), BOH (17), COAS (17), TOHB (8)
1099		1099	CO (35), CC (23), CN (23)
	1078	1083	CO (34), CN (21), CHR (15), CSC (13),
		1065	CHR (70), CN (13), CSC (8)
1043	1048	1056	CHR (38), CSC (36), CHT (17)
968	1020	1019	TOHB(32), CC (24), CHW (10), CO (10), CN (10),
934		938	TOHB (99)
880		887	CO (43), TOHB (18), CN (14), GCN (9)
	878	879	TOHB (36), CC (24), CN (11), CSC (10),
	847	841	CHR (54), CHT (16), CN (11), CO (10),
826		831	TOHB (66), COW (33)
	825	822	CO (24), CC (21), TOHB(14), GCN (14), CN (10),
		797	TOHB (61), COSS (11), COS (11), CC (10)
775		769	CN (38), GCN (32), CHR (10), CHT (10),
712		664	TOHB (66), TOH (28)
		661	TOHB (45), COS (38)
611		585	CSC (34), CHR (26), TOHB (14), GCN (13),
		532	COR (66), TOHB (7), COAS (7)
486	480	471	CSC (78), CHR (10), CHT (6)
		466	CSC (33), TOHB (26), GCN (12), OHB (10),
444	446	447	TOHB (90), COW (9)
		433	TOHB (26), CSC (22), COS (19), CC (15),
378		371	PK (74), CSC (11), TOHB (7)
332		295	COR (42), TOHB (37), OHB (8)

		245	ATO (33), CSC (31), AT (21)
		232	TOHB (38), ATO (24), AT (20), CSC (8)
	152	148	OHB (54), COR (13), TOHB (9)
		110	TOHB (73), BOHB (16), BOH (6)
	84	70	TOHB (99)
		58	TOHB (68), BOHB (22)
		38	TOHB (71), TCC (23)
		22	TCC (49), TOHB (38), COW (9)
		11	GOHB (41), TOHB (29), PK (8),

Scaled N H stretching vibrations are located at 3277 $cm^{-1}$with pure contribution. These are shifted from the expected region due to red shifting of N-H stretching mode, which provides a strong evidence for the existence of strong N-H...O intermolecular hydrogen bonding and these modes shows good agreement with scaled value.

4. Conclusion

Nowadays, researches on biological active materials are mainly concentrated on the design and the synthesis of new molecules and its spectral, optical and the quantum-mechanical interpretation of their structure-properties relationship. Optimized geometry of the molecule shows the existence of O-H...O hydrogen bonding in the molecule. Spectroscopic methods and the Quantum chemical computation approach were used to conduct an extensive and in-depth investigation of the structural, and vibrational analysis of MO. Assignments of the vibrational bands have been done based on Normal Coordinate Analysis. The vibrational spectral analysis also confirms the existence of strong O-H...O intermolecular interaction by the unusual lowering of carbonyl stretching wavenumber. The probability of intermolecular charge transfer in the molecule makes it a suitable biologically active compound.

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Conflict of interest: The Authors have no conflicts of interest to declare that they are relevant to the content of this article.