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# Evans hole and non linear optical activity in Bis(melaminium) sulphate dihydrate: A vibrational spectral study



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# HIGHLIGHTS

- Spectral analysis of BMSD has been performed by FT IR and FT Raman techniques.
- Molecular geometry and vibrational spectra have been computed by B3LYP method.
- Evans hole analysis has been used to explain the band profile of IR spectrum.
- NBO analysis has been carried out to assess the strength of hydrogen bonding.
- The HOMO LUMO and MEP plots have been generated to explain NLO activity.

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The crystalline network and the optimized geometry of Bis(melaminium) sulphate dihydrate.



# ABSTRACT

Bis(melaminium) sulphate dihydrate (BMSD), an interesting melaminium derivative for nonlinear optical activity, has been subjected to vibrational spectral analysis using FT IR and FT Raman spectra. The analysis has been aided by the Potential Energy Distribution (PED) of vibrational spectral bands, derived using density functional theory (DFT) at B3LYP/6-31G(d) level. The geometry is found to correlate well with the XRD structure and the band profiles for certain vibrations in the finger print region have been theoretically explained using Evans hole. The detailed Natural Bond Orbital (NBO) analysis of the hydrogen bonding in BMSD has also been carried out to understand the correlation between the stabilization energy of hyperconjugation of the lone pair of donor with the  $\sigma^*$  orbital of hydrogen-acceptor bond and the strength of hydrogen bond. The theoretical calculation shows that BMSD has NLO efficiency, 2.66 times that of urea. The frontier molecular orbital analysis points to a charge transfer, which contributes to NLO activity, through N–H…O intermolecular hydrogen bonding between the melaminium ring and the sulphate. The molecular electrostatic potential (MEP) mapping has also been performed for the detailed analysis of the mutual interactions between melaminium ring and sulphate ion.

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#### 1. Introduction

Melaminium derivatives are the object of extensive chemical research for their role in living organism [1], self-assembly process in supra molecular architectures [2] and nonlinear optics [3]. A few hydrogen bonded complexes of melaminium, possessing second

\* Corresponding author. E-mail address: vsjkumar@gmail.com (V.S. Jayakumar). harmonic generation (SHG) activity, have been reported [4]. The recent toxicological and pharmacological investigations explore nephrotoxicity, crystal formation in kidney and renal toxicity induced by melamine or its derivatives [5,6]. Polyamide 6, one of the principal thermoplastics, used in the plastic engineering and in textile industries is prepared from Melaminium derivative [7]. The colour change induced by triple hydrogen-bonding enables on-site and real-time detection of melamine in raw milk and in infant formula, even at a concentration of 2.5 ppb without the aid of any advanced instruments [8]. The diverse applications of melamine and its derivatives offer tremendous scope for exploring structural and bonding features of BMSD and their role in its NLO activity, with the aid of Fourier Transform Infrared and Raman spectroscopy.

The present study focuses on geometry optimization and vibrational spectral analysis of Bis(melaminium) sulphate dehydrate (BMSD), a compound that potentially exhibits non-linear optical properties, using FT IR and FT Raman spectra aided by density functional theoretical computations at B3LYP/6-31G(d) level, along with the analysis of Evans hole and MEP mapping. NLO activity has been theoretically investigated using the computed hyperpolarizability tensor, supported by NBO and frontier molecular orbital analysis.

# 2. Experimental

# 2.1. Preparation

The starting compound Melamine (99%, Aldrich) and sulphuric acid (Merck) has been used for the present preparation. Melamine was dissolved in a 20% solution of  $H_2SO_4$  at molar ratio 2:1, and the resulting solution was evaporated slowly. After several days, colourless crystals of the title salt appeared [9].

### 2.2. Spectroscopic measurements

The vibrational measurements were carried out at room temperature. The polycrystalline powders of BMSD were achieved by grinding in agate mortar with pestle. Samples, as suspensions in Nujol, were put between KBr windows. Infrared spectrum has been recorded with a Bruker IFS-88 spectrometer in the region 4000– 80 cm<sup>-1</sup> with a resolution of 2 cm<sup>-1</sup>. The Fourier Transform Raman (FT Raman) spectrum of powder sample of BMSD was taken with FRA-106 attachment to the Bruker IFS-88 spectrometer equipped with Ge detector cooled to liquid nitrogen temperature. The signal to noise ratio was established by 32 scans, weak apodisation. Nd<sup>3+</sup>:YAG air-cooled diode pumped laser, 1064 nm of power 200 mW was used as an exciting source. The scattered light



**Fig. 2.** (a) XRD showing formula unit with intermolecular hydrogen bonding. (b) The molecular arrangement in the unit cell showing the hydrogen bonding interactions.

was collected at the angle of  $180^{\circ}$  in the region 3600-80 cm<sup>-1</sup>, resolution 2 cm<sup>-1</sup>, 256 scans.

#### 3. Computational

The computed results reported in this paper are obtained with the Gaussian '03 program package [9]. The geometry optimization was carried out by employing hybrid Becke's three-parameter Lee-Yang-Parr correlation functional (B3LYP), at 6-31G(d) level of theory, which can provide reliable results for energy data. The IR and Raman spectra were simulated from the optimized geometry of



Fig. 1. Optimized geometry of BMSD at B3LYP 6-31 G(d) level.

BMSD, and the computed wavenumbers are scaled using 0.9613 for the correlation with experimental band positions [10]. The vibrational Potential Energy Distribution (PED) has been calculated from the simulated vibrational spectra using the software VEDA [11]. PED can provide the contribution of stretching, bending and deformation motions of the functional groups to each vibrational mode, in terms of (3N-6) linearly independent, internal coordinates, which allows unambiguous vibrational assignment. The HOMO– LUMO analysis has been carried out in BMSD to explain the charge transfer within the molecule. In order to elucidate the intermolecular hydrogen bonding, intermolecular charge transfer, rehybridization and delocalization of electron density, NBO analysis has been carried out on BMSD at B3LYP/6-31G(d) level. Also the Molecular Electrostatic Potential surfaces (MEPs) were calculated using the same basic set.

# 4. Results and discussion

# 4.1. Geometry

Density Functional Theoretical (DFT) computation shows that the two melaminium ions of BMSD (Fig. 1) are inclined to each other by around 60°. The XRD data [12] reveal that the two melaminium groups are almost in the same plane (Fig. 2), because of the

Table 1

The geometric parameters of BMSD computed at B3LYP/6-31G(d) level.

interconnection through  $SO_4^{2-}$  and  $H_2O$  molecule. The XRD data show that the internal C–N–C angle at protonated nitrogen atom is significantly greater than other internal C–N–C angles of the ring. For the two melaminium rings, the C–N–C angles (Table 1) are 119.8° and 119.7° at protonating position, while the corresponding angles at non-protonated nitrogen are 115.5° and 115.9° for the first ring and 115.9° and 115.7° for the other ring. This ring distortion arises from the steric effect of nitrogen lone pair, consistent with VSEPR theory [12]. This is supported by DFT computation which gives the C–N–C angles at protonating positions equal to 119.5° and 118.7° while the values are 115.5°, 115.4°, 115.7° and 115.9° at non-protonating positions.

The experimental data shows that protonating hydrogen is almost linear with the ring, while for DFT predicted geometry a significant deviation from planarity is observed, which is obvious from the torsion angle of H–N–C–N, whose values are  $-159.8^{\circ}$  and 165.7°. The deviation from planarity is evidently due to the intermolecular N–H…O interactions of the ring with sulphate group. The DFT predicted hydrogen bonding parameters for protonating hydrogen are N–H = 1.06 Å, H…O = 1.59 Å and  $\angle$  N–H…O = 174.8°, while the XRD data shows that this hydrogen bond is weakened, with N–H = 0.873 Å, H…O = 1.9 Å and  $\angle$ N–H…O = 168.5°. Also in the crystalline network, one of the protonating hydrogen engage in intermolecular N–H…O interaction with water molecule whose parameters are N–H = 0.89 Å,

Bond Bond length (Å)		Á)	Bond angle	Angle (°)		Torsion angle	Angle (°)		
	XRD	DFT		XRD	DFT		XRD	DFT	
$C_1 - N_2$	1.34	1.35	$C_3 - N_2 - C_1$	115.7	114.9	$C_1 - N_2 - C_3 - N_4$	-1.9	0.9	
$N_2 - C_3$	1.32	1.33	$N_4 - C_3 - N_2$	121.4	121.8	N <sub>2</sub> -C <sub>3</sub> -N <sub>4</sub> -C <sub>5</sub>	-1.4	-4.7	
$C_3 - N_4$	1.37	1.37	$C_{5}-N_{4}-C_{3}$	119.7	119.1	$C_3 - N_4 - C_5 - N_6$	3.6	4.6	
$N_4 - C_5$	1.35	1.37	$N_6 - C_5 - N_4$	121.3	121.4	$N_7 - C_1 - N_2 - C_3$	-176.3	-177.5	
$C_5 - N_6$	1.33	1.33	$N_7 - C_1 - N_2$	117.3	116.1	$H_8 - N_7 - C_1 - N_2$	0.1	-2.9	
$C_1 - N_7$	1.32	1.35	$H_8 - N_7 - C_1$	120.3	119.5	$N_2 - C_1 - N_7 - H_9$	176.8	-176.2	
N <sub>7</sub> -H <sub>8</sub>	0.85	1.01	H <sub>9</sub> -N7-C1	120.2	119.4	C3-N4-C5-N10	-178.9	-175.7	
N <sub>7</sub> -H <sub>9</sub>	0.87	1.01	N <sub>10</sub> -C5-N4	118.4	116.9	N <sub>4</sub> -C <sub>5</sub> -N <sub>10</sub> -H <sub>11</sub>	-177.9	178.9	
$C_5 - N_{10}$	1.32	1.33	H <sub>11</sub> -N <sub>10</sub> -C <sub>5</sub>	120.1	120.9	$N_4 - C_5 - N_{10} - H_{12}$	4.5	8.5	
$N_{10}-H_{11}$	0.85	1.01	H <sub>12</sub> -N <sub>10</sub> -C <sub>5</sub>	119.9	122.7	$N_2 - C_3 - N_4 - H_{13}$	175.2	170.0	
$N_{10}-H_{12}$	0.83	1.03	$H_{13}-N_4-C_5$	118.1	120.0	$C_1 - N_2 - C_3 - N_{14}$	177.8	-179.9	
N <sub>4</sub> -H <sub>13</sub>	0.87	1.06	N <sub>14</sub> -C <sub>3</sub> -N <sub>2</sub>	121.7	121.3	$N_4 - C_3 - N_{14} - H_{15}$	2.0	-18.1	
$C_3 - N_{14}$	1.31	1.34	$H_{15}-N_{14}-C_3$	118.0	119.8	$N_4 - C_3 - N_{14} - H_{16}$	179.7	-175.6	
N <sub>14</sub> -H <sub>15</sub>	0.85	1.04	$H_{16} - N_{14} - C_3$	118.5	116.3	O <sub>17</sub> -H <sub>13</sub> -N <sub>4</sub> -C <sub>3</sub>	-115.2	100.9	
N <sub>14</sub> -H <sub>16</sub>	0.86	1.01	O <sub>17</sub> -H <sub>13</sub> -N <sub>4</sub>	168.5	133.7	S <sub>18</sub> -O <sub>17</sub> -H <sub>13</sub> -N <sub>4</sub>	101.5	-139.5	
H <sub>13</sub> -O <sub>17</sub>	1.91	3.15	S <sub>18</sub> -O <sub>17</sub> -H <sub>13</sub>	116.9	54.4	O <sub>19</sub> -S <sub>18</sub> -O <sub>17</sub> -H <sub>13</sub>	164.4	-160.7	
O <sub>17</sub> -S <sub>18</sub>	1.48	1.52	O <sub>19</sub> -S <sub>18</sub> -O <sub>17</sub>	110.3	112.3	O <sub>20</sub> -S <sub>18</sub> -O <sub>17</sub> -H <sub>13</sub>	81.1	80.5	
S <sub>18</sub> -O <sub>19</sub>	1.48	1.49	O20-S18-O17	108.4	106.6	$O_{21} - S_{18} - O_{17} - H_{13}$	-75.8	-35.9	
S <sub>18</sub> -O <sub>20</sub>	1.46	1.54	$O_{21} - S_{18} - O_{17}$	108.9	109.1	$H_{22}-O_{19}-S_{18}-O_{20}$	111.7	14.1	
S <sub>18</sub> -O <sub>21</sub>	1.45	1.52	H <sub>22</sub> -O <sub>19</sub> -S <sub>18</sub>	135.8	117.3	$N_{23}-H_{22}-O_{19}-S_{18}$	-169.5	79.3	
$H_{22}-O_{19}$	1.99	1.91	N23-H22-O19	137.9	154.6	$H_{24} - N_{23} - H_{22} - O_{19}$	19.4	118.	
H <sub>22</sub> -N <sub>23</sub>	0.88	1.03	$H_{24}-N_{23}-H_{22}$	119.5	118.3	$C_{25} - N_{23} - H_{22} - O_{19}$	-149.7	-25.5	
N <sub>23</sub> -H <sub>24</sub>	0.89	1.01	C <sub>25</sub> -N <sub>23</sub> -H <sub>22</sub>	120.6	116.1	$H_{24} - N_{23} - C_{25} - N_{26}$	7.5	6.9	
N <sub>23</sub> -C <sub>25</sub>	1.31	1.34	$N_{26} - C_{25} - N_{23}$	120.7	122.5	$N_{23} - C_{25} - N_{26} - C_{27}$	-179.5	-175.9	
$C_{25} - N_{26}$	1.34	1.33	$C_{27} - N_{26} - C_{25}$	115.5	114.7	$C_{25} - N_{26} - C_{27} - N_{28}$	-1.2	9.1	
$N_{26} - C_{27}$	1.34	1.35	$N_{28} - C_{27} - N_{26}$	126.3	127.0	$N_{26} - C_{27} - N_{28} - C_{29}$	-0.9	-9.2	
$C_{27} - N_{28}$	1.35	1.35	C <sub>29</sub> -N <sub>28</sub> -C <sub>27</sub>	115.9	114.6	$C_{27} - N_{28} - C_{29} - N_{30}$	2.0	-4.5	
N <sub>28</sub> -C <sub>29</sub>	1.33	1.33	$N_{30} - C_{29} - N_{28}$	121.1	121.3	$N_{28} - C_{29} - N_{30} - H_{31}$	-179.6	-168.6	
$C_{29} - N_{30}$	1.36	1.37	$H_{31}-N_{30}-C_{29}$	118.5	120.6	$C_{27} - N_{28} - C_{29} - N_{32}$	-179.1	175.9	
N <sub>30</sub> -H <sub>31</sub>	0.89	1.06	N <sub>32</sub> -C <sub>29</sub> -N <sub>28</sub>	120.2	122.5	N <sub>28</sub> -C <sub>29</sub> -N <sub>32</sub> -H <sub>33</sub>	2.3	-6.8	
C <sub>29</sub> -N <sub>32</sub>	1.31	1.34	$H_{33}-N_{32}-C_{29}$	118.3	115.7	$N_{28} - C_{29} - N_{32} - H_{34}$	-179.1	-152.4	
N <sub>32</sub> -H <sub>33</sub>	0.88	1.01	$H_{34}-N_{32}-C_{29}$	121.5	116.2	$C_{25} - N_{26} - C_{27} - N_{35}$	177.1	-173.5	
N <sub>32</sub> -H <sub>34</sub>	0.85	1.03	N <sub>35</sub> -C <sub>27</sub> -N <sub>26</sub>	116.9	116.5	$N_{26} - C_{27} - N_{35} - H_{36}$	5.4	-6.6	
$C_{27} - N_{35}$	1.33	1.35	$H_{36} - N_{35} - C_{27}$	119.7	119.0	$N_{26} - C_{27} - N_{35} - H_{37}$	179.5	-171.1	
N <sub>35</sub> -H <sub>36</sub>	0.88	1.01	$H_{37} - N_{35} - C_{27}$	118.4	119.0	$H_{38} - O_{17} - S_{18} - O_{20}$	-144.3	133.4	
N <sub>35</sub> -H <sub>37</sub>	0.85	1.01	$H_{38} - O_{17} - S_{18}$	119.3	107.6	$O_{39}-H_{38}-O_{17}-S_{18}$	-148.3	-3.6	
O <sub>17</sub> -H <sub>38</sub>	1.90	1.87	$O_{39} - H_{38} - O_{17}$	174.5	150.3	$H_{40} - O_{39} - H_{38} - O_{17}$	-46.6	16.1	
$H_{38}-O_{39}$	0.84	0.99	$H_{40}-O_{39}-H_{38}$	109.5	98.9	$H_{41} - O_{39} - H_{38} - O_{17}$	51.4	-152.4	
O <sub>39</sub> -H <sub>40</sub>	1.01	0.98	H <sub>41</sub> -O <sub>39</sub> -H <sub>38</sub>	96.3	130.1	O <sub>42</sub> -H <sub>41</sub> -O <sub>39</sub> -H <sub>38</sub>	-60.8	105.9	
O <sub>39</sub> -H <sub>41</sub>	2.02	1.93	$O_{42}-H_{41}-O_{39}$	169.2	158.6	$H_{43} - O_{42} - H_{41} - O_{39}$	-163.7	103.9	
$H_{41}-O_{42}$	0.88	0.98	$H_{43}-O_{42}-H_{41}$	108.6	103.7				
O <sub>42</sub> -H <sub>43</sub>	0.83	0.97							

H...O = 1.89 Å and  $\angle$  N–H...O = 177°, which is absent in DFT predicted geometry of BMSD formula unit. Hence the deviation from planarity of protonating hydrogen of melaminium ring in the DFT predicted geometry, compared to XRD structure, is justified.

Deviation from normal tetrahedral structure can be observed for sulphate, as predicted by both XRD and DFT, which is evident from the unequal length of S–O bonds and unequal O–S–O angles resulting from the intermolecular interactions with melaminium groups. DFT provides 1.52 Å, 1.49 Å, 1.54 Å and 1.51 Å respectively for bond distances  $S_{18}$ – $O_{17}$ ,  $S_{18}$ – $O_{19}$ ,  $S_{18}$ – $O_{20}$  and  $S_{18}$ – $O_{21}$  and the bond angles are equal to 112.3°, 108.6°, 108.0° and 109.1° for  $O_{17}$ – $S_{18}$ – $O_{19}$ ,  $O_{19}$ – $S_{18}$ – $O_{20}$ ,  $O_{20}$ – $S_{18}$ – $O_{21}$  and  $O_{21}$ – $S_{18}$ – $O_{17}$  respectively. The deviation can be attributed to the intermolecular hydrogen bonding in the network, leading to deviation from resonance structure as well.

#### 4.2. Vibrational analysis

The vibrational analysis (Table 2) is based on the FT IR (Fig. 3a) and FT Raman (Fig. 4a) spectra of BMSD and the PED and eigenvector distribution of the computed vibrational spectra (Figs. 3b and 4b) have been used to assign vibrational bands unambiguously.

#### 4.2.1. Vibrations of amino group

Table 2

The strong broad band in IR at  $3345 \text{ cm}^{-1}$  corresponds to the asymmetric stretching vibration of NH<sub>2</sub>, which is the characteristic

vibration of primary amino group attached to the non-aromatic ring. The band position indicates the extent of aromaticity [13] and here non-aromaticity in the ring is evident from the unequal C-N bond lengths, in addition to the lower wave number of vibrations compared to the vibrations of aromatic primary amines. The medium width and intensity is observed for the band and the broadness can be attributed to the mixing with O-H stretches. The DFT computation predicts primary amino group symmetric stretching at 3483 cm<sup>-1</sup> in both IR and Raman. The absence of symmetric stretching can be regarded as the mixing of possible band within the broad profile in that region, which is the case in Raman also and a weak shoulder is observed in broad profile in Raman. The characteristic NH stretching frequency of the secondary amino group [14] attached to the non-aromatic ring is around 3300 cm<sup>-1</sup> and in BMSD, this vibration produces bands at lower frequencies. The IR wavenumbers at  $3166 \text{ cm}^{-1}$  and 3104 cm<sup>-1</sup> are found in good agreement with the computed wave numbers at 3167 cm<sup>-1</sup> and 3101 cm<sup>-1</sup> respectively where the former band is found to possess a medium intense Raman counterpart at 3149 cm<sup>-1</sup>. The deviation of band positions from the characteristic wavenumbers can be attributed to the N-H...O hydrogen bonding interaction, evident from DFT computed results which correlates with the XRD data. Hence the shift of wave numbers to the lower wave number region in both experimental and computational spectrum is justified.

The shift to higher frequencies for bending motions of NH<sub>2</sub> group in melamine molecules due to intermolecular interactions

Vibrational assignm	ent of BMS	SD.					
Computed spectrum			Experimenta	al spectrum	PED (%)		
B3LYP/6-31G(d)		IR		Raman			
$v_{\text{scaled}} (\text{cm}^{-1})$	Relativ	e Intensity	v (cm <sup>-1</sup> )	Relative Intensity	v (cm <sup>-1</sup> )	Relative Intensity	
	IR	Raman					
3514	m	w	3345	vsbr			$v_{as}NH_2(51)v_sOH_2(30)$
3483	m	VS			3318	w brsh	$v_{\rm s} \rm NH_2(100)$
3167	S	VS	3166	vwsh	3149	m	vNH(95)
3091	VS	m	3104	s br	-	-	vNH(91)
			2845	w sh	-	-	vNH (90)
			2685	W	-	-	vNH (89)
1709	S	w	1718	w sh	1711	w	$\delta_{\rm s}$ HOH (77)
1683	m	w	1685	VS	1680	w	$\delta_{s} \text{ OH}_{2} (60) \delta_{s} \text{ NH}_{2} (15) \nu \text{NC} (12)$
1674	s	w	1670	VS			$\delta_{\rm s}  \rm NH_2  (28) \delta_{\rm s}  \rm OH_2  (16)$
1635	w	w			1632	w	$\delta_{\rm s}  \rm NH_2  (61)$
1617	s	w	1613	w sh			Ring mode 3a $(21)\delta_s$ NH <sub>2</sub> (35)
1606	m	w	1566	w	1570	m	$vNC(17)\delta_{s}NH_{2}(59)$
1512	S	w	1513	S	1515	w	Ring mode 3b (64) $\rho$ NH <sub>2</sub> (26)
1504	m	w	1481	w sh	1490	vwsh	Ring mode $3b(43)\delta_s$ NH <sub>2</sub> (14)
1403	m	w	1404	m	1415	vw	δ CNH (28) vNC (31)
1322	vw	vw	1332	w sh	1336	w	Ring mode $5(36)\delta_s$ HNC (11)
1189	w	vw	1182	vwsh	1187	w	Ring mode 6a (29) $\delta$ HNC (28)
1174	vw	vw	1169	vwsh			Ring mode 6b (31)6b HNC (26)
			1146	S	1135	W	
1123	S	w					vSO (65)
1090	m	w	1090	m			Ring mode 8 (23) $\nu$ SO (17) $\rho$ NH <sub>2</sub> (14)
1028	S	w	1035	vwsh			vSO (54)
979	m	w	978	VS	978	S	$v_{\rm s} {\rm SO}_4^{2-}$ (33) $\rho$ NH <sub>2</sub> (12)
911	m	m	910	w sh			vSO (11)3b (25)
782	S	vw	779	VS	775	vw	Ring mode 12 (60)
726	m	m	721	m			Ring mode 12 (66)
685	w	vw	688	w sh	688	VVS	Ring mode 12 (85)
627	S	w	619	S	625	W	lib OH <sub>2</sub> (25)γ NH (28)
580	m	w	572	m	573	S	$\delta_{\rm s}$ OSO (51)
425	w	w	455	w sh	442	w	$\rho$ OSO (60)def SO <sub>4</sub> (14)
409	m	w	408	S	379	m	$\delta_{\rm s}$ OSO (39)def SO <sub>4</sub> (30)
187	w	vw	182	m	185	w sh	v OH (24)
129	m	vw	125	m	120	w sh	$v 0H (27)\omega OH_2 (15)$
							., 2.,

m – medium, s – strong, vs – very strong, wsh – weak shoulder, vw – very weak, vwsh – very weak shoulder, vvs – very very strong, sbr – strong branch, vsbr – very strong, wsh – weak branch, wbrsh – weak branch shoulder, v – stretching,  $v_a$  – asymmetric stretching,  $v_s$  – symmetric stretching,  $\gamma$  – out plane bending,  $\delta$  – inplane bending,  $\delta_s$  – scissoring,  $\rho$  – rocking,  $\omega$  – wagging, lib – libration, def – deformation.

through amino group has been reported in melamine derivatives [15]. The NH<sub>2</sub> bending motion at 1659 cm<sup>-1</sup> observed in the Raman spectrum of melaminium is found to be shifted to 1680 cm<sup>-1</sup> in BMSD, showing a strong hydrogen bonding through NH<sub>2</sub>. Similarly, the intense bands observed at 1683 cm<sup>-1</sup> and 1674 cm<sup>-1</sup> has been respectively shifted to 1685 cm<sup>-1</sup> and 1670 cm<sup>-1</sup>. The DFT computed frequencies at 1596 cm<sup>-1</sup>, 1568 cm<sup>-1</sup> and 1567 cm<sup>-1</sup> for amino group bending in melaminium [16] is found respectively at 1635 cm<sup>-1</sup>, 1617 cm<sup>-1</sup> and 1606 cm<sup>-1</sup> in the computed spectrum of BMSD. The bands at 1635 cm<sup>-1</sup> and 1606 cm<sup>-1</sup> are found to be affected by N–H...O interaction between amino group of melaminium ring and the oxygen atom of sulphate. The mode at 1617 cm<sup>-1</sup> is affected by N–H...O interaction involving the protonating hydrogen, in addition to the above interaction.

The NH out of plane bending vibrations in pure melamine crystals have been reported at 676 cm<sup>-1</sup> and 615 cm<sup>-1</sup> in IR and for the latter mode, there is intense Raman band at same wavenumber owing to NH<sub>2</sub> bend mixed with ring breath [15]. For the present compound, NH out of plane bending mode can be observed in IR as strong band at 619 cm<sup>-1</sup> and a weak band at 625 cm<sup>-1</sup> in Raman.

# 4.2.2. Ring mode

The ring modes arise from the vibrations of central triazine ring and the assignments are based on normal coordinate analysis and the mode numbers suggested by Hannaet et al. [17]. In BMSD crystalline network, spectral changes have been noticed for vibrations of melaminium ring, compared with the vibrational behaviour of the melamine crystal. The analysis indicates that the complexation of melamine is found to lower the frequency for ring modes [18], compared to the corresponding value for melamine alone, owing to the intense ionic and donor–acceptor type interactions within the crystalline environment. This makes the triazine ring more rigid. The ring mode at 1174 cm<sup>-1</sup> reported as the characteristic band in IR spectrum of melaminium derivatives [19] has also been observed in BMSD with wavenumbers 1169 cm<sup>-1</sup> and 1146 cm<sup>-1</sup> corresponding to two melaminium cations in the formula unit of the crystal indicating that two melaminium ions are crystallographically non-equivalent. The most intense band of triazine ring in FT Raman spectrum is observed at 688 cm<sup>-1</sup> which is the characteristic band observed in all melaminium complexes, [15] originating from the symmetric vibration mode 12, (Table 3) of triazine ring.

# 4.2.3. Sulphate

The bands for sulphate group can be found in two regions of vibrational spectrum, that is  $1100-900 \text{ cm}^{-1}$  and  $600-400 \text{ cm}^{-1}$ , the former arises due to symmetric/asymmetric stretching motion of sulphate group and the latter is due to the sulphate deformation [20]. The medium intense band at  $1090 \text{ cm}^{-1}$  in IR is due to SO stretching motion mixed with the melaminium ring vibration. A highly intense band has been observed at  $978 \text{ cm}^{-1}$  in both IR and Raman and the vibrational PED shows that the band is due to SO<sub>4</sub><sup>2–</sup> symmetric stretching vibration [21]. In Raman, the splitting of this non-degenerate mode into a doublet have been reported [22] for sulphate derivatives and the absence of the removal of degeneracy of the stretching mode, indicates that the angular distortion is greater than the linear distortion [22]. On comparison with other sulphate derivatives, the sulphate



Fig. 3. IR spectra of BMSD (a) experimental. (b) Simulated at B3LYP 6-31G(d) level.

stretching frequency for the above mode is higher and can be attributed to the intermolecular hydrogen bonding of sulphate with neighbouring melaminium units. The deformation modes of sulphate groups, corresponding to OSO scissoring, OSO rocking and  $SO_4^{2-}$  deformation can be observed at 580 cm<sup>-1</sup>, 425 cm<sup>-1</sup> and 409 cm<sup>-1</sup> respectively and their band positions and intensities are found to be correlating with that of computed spectrum.

#### 4.2.4. The vibrations of water molecules

The two water molecules lying in the elementary unit of BMSD crystal has been involved as a donor in hydrogen bond with sulphate ion which simultaneously affects the vibrational spectral behaviour of both sulphate group and water molecule. The stretching band of water molecule is not observed due to mixing with the vibrations of primary amino group, where the broadness and strength of the bands at  $3345 \text{ cm}^{-1}$  in IR and  $3318 \text{ cm}^{-1}$  in Raman might be contributed by OH stretches also. The inplane bending vibrations of water molecule can be found at  $1718 \text{ cm}^{-1}$ ,  $1685 \text{ cm}^{-1}$  and  $1670 \text{ cm}^{-1}$  in IR with appreciable strength and the corresponding Raman bands are dormant or weak. The band positions and intensities are found to be correlating with that of computed spectrum. The librations of water molecule can be found at  $619 \text{ cm}^{-1}$  in IR and as a weak band at  $625 \text{ cm}^{-1}$  in Raman.

# 4.3. Evans hole

A sharp and weak absorption band in IR falling within the energy range of strong and broad band may create a transmission window in its position due to Fermi interaction [23]. Such transmission window/hole, termed Evans hole, is an effective tool in interpreting the shape of hydroxyl stretching profile. In melaminium derivatives the coupling between stretching vibrations of C–N bonds and deformation of N–H...N intermolecular interaction leads to Evans hole [15]. The above interaction is found to create Evans holes at 1613 cm<sup>-1</sup>, 1481 cm<sup>-1</sup>, 741 cm<sup>-1</sup> and 598 cm<sup>-1</sup> in BMSD. The shape of above mentioned bands for both melamine and BMSD can be well explained by theoretically analyzing Evans holes.

Evans holes originate from the interaction between certain vibrational energy levels appreciable in a fraction of the molecules, where one of the energy levels involved is sensitive to intermolecular interaction [26]. Such a restricted perturbation between energy levels  $\epsilon_1^0$  and  $\epsilon_2^0$  having corresponding Eigen functions  $\psi_1^0$  and  $\psi_2^0$  respectively is found to create mixed energy levels given by

$$\epsilon_1 = \frac{(\epsilon_1^0 + \epsilon_2^0) + \Delta}{2} \tag{1}$$

$$\epsilon_2 = \frac{(\epsilon_1^0 + \epsilon_2^0) + \Delta}{2}$$
 (2)

$$y_1 = x\psi_1^0 + y\psi_2^0 \tag{3}$$

$$\psi_2 = x\psi_1^0 - y\psi_2^0 \tag{4}$$

The perturbation energy separation  $\Delta$  is related to unperturbed separation  $\delta$  as



Fig. 4. Raman spectra of BMSD (a) experimental. (b) Theoretical at B3LYP 6-31G (d) level.

Table 3		
The computational vibrational	modes of triazine	at B3LYP/6-31G(d) level.

Sl. no	Mode no	Frequency (cm <sup>-1)</sup>	Eigen vector distribution
1	1	3075	
2	2a	2974	
3	2b	2974	
4	3a	1550	
5	3b	1550	
6	4a	1397	
7	4b	1397	
8	5	1361	
9	6a	1158	
10	6b	1158	
11	7	1150	
12	8	1113	
13	9a	997	
14	9b	997	
15	10	975	
16	11	906	
17	12	730	
18	13a	666	
10	13b	200	
19	10	220	A.
20	14a	339	₩ <b>T</b>

Table 3 (continued)

Sl. no	Mode no	Frequency (cm <sup>-1)</sup>	Eigen vector distribution
21	14b	339	<b>₽</b>

$$\Delta = \sqrt{\delta^2 + 4w_{12}^2} \tag{5}$$

 $W_{12}$  is the perturbation energy. The intensity ratio is given by

$$\frac{I_1}{I_2} = \frac{\Delta - \delta}{\Delta - \delta} \tag{6}$$

The observed band position and the position of the hole are found for BMSD and observed separation has been computed from the intensity ratio (Table 4). The unperturbed separation and interaction energy are calculated and unperturbed  $v_1$  and  $v_2^u + v_2^g$  are deducted from Fermi interaction formula [24] and are tabulated.

It has been reported that the close agreement between unperturbed band position  $v_2^u + v_2^g$  and position of the hole ( $v_h$ ) is the essential criteria for identifying Evans hole [25]. Such a close agreement can be observed for BMSD. The unperturbed position has been computed as 1626 cm<sup>-1</sup>, 1488 cm<sup>-1</sup>, 739 cm<sup>-1</sup> and 603 cm<sup>-1</sup> corresponding to the holes 1613 cm<sup>-1</sup>, 1481 cm<sup>-1</sup>, 741 cm<sup>-1</sup> and 598 cm<sup>-1</sup> respectively, confirming the existence of Evans hole. This explains the presence of shoulder appearing in the bands having peaks 1670 cm<sup>-1</sup>, 1513 cm<sup>-1</sup>, 721 cm<sup>-1</sup> and 619 cm<sup>-1</sup>, in BMSD.

#### 4.4. Natural Bond Orbital (NBO) analysis

The NBO analysis has been carried out to investigate hydrogen bonding and delocalization of electron density from occupied Lewis type (donor) NBOs to properly unoccupied non Lewis type (acceptor). NBOs can provide valuable information on charge transfer or conjugative interactions within the molecule [26]. The strength of interaction between electron donors and acceptors can be quantitatively expressed using the stabilization energy  $E^{(2)}$  associated with *i* (donor) - > *j* (acceptor) delocalization [27].

$$E^{(2)} = \frac{-q_i(F_{ij})^2}{E_i - E_i} \tag{7}$$

 $q_i$  is the donor orbital occupancy,  $E_i$ ,  $E_j$  are the diagonal elements, representing the orbital energies and  $F_{ij}$  is the off diagonal element of NBO Fock matrix, computed using second order perturbation theory.

In NBO analysis, intermolecular N–H...O hydrogen bonding has been manifested as the electron transfer from the lone pair of oxygen to antibonding orbital of N–H, with appreciable stabilization energy [28]. In BMSD, the stabilization energy of electron transfer process, Lp (O<sub>21</sub>)  $\rightarrow \sigma^*$  (N<sub>4</sub>–H<sub>13</sub>) is 33.46 kcal/mole and that of electron transfer Lp (O<sub>20</sub>)  $\rightarrow \sigma^*$  (N<sub>14</sub>–H<sub>13</sub>) is 14.03 kcal/mol. Their bonding parameters are H<sub>13</sub>...O<sub>12</sub> = 1.64 Å and H<sub>15</sub>...O<sub>20</sub> = 1.79 Å respectively. A direct correlation is found between the stabilization energy of electron transfer  $E^{(2)}$  and strength of hydrogen bond, which is dependent on bonding parameters (Fig. 5).

Thus NBO analysis is an effective method for investigating intermolecular hydrogen interactions in the molecule/crystalline network. In BMSD, the intermolecular hydrogen bonding of sulphate anion with the melaminium rings, the stabilization energy is found to increase with decrease of H...A distance. For the process, Lp  $(O_{17}) \rightarrow \sigma^* (N_{32}-H_{34})$ , stabilization energy has been computed as 9.95 kcal/mol, while that for Lp  $(O_{20}) \rightarrow \sigma^* (N_{30}-H_{31})$  is 34.92 kcal/mol. These H...A distances are 1.91 Å and 1.61 Å

Table 4
Vibrational data on Evans hole in melamine and Bis(melaminium) sulphate dihydrate.

Details of data	Melamine	BMSD	Melamine	BMSD	Melamine	BMSD	Melamine	BMSD
$v_{\rm h \ (Observed)} \ (\rm cm^{-1})$	1606	1613	1489	1481	742	741	598	598
$v_{1 \text{ (Observed)}} (\text{cm}^{-1})$	1588	1670	1448	1513	776	721	552	619
$v_2^{\rm u} + v_2^{\rm g}$ (Observed) (cm <sup>-1</sup> ) Raman	1572	1570	1520	1415	766	775	558	573
$v_2^{\rm u} + v_2^{\rm g}$ (Calculated) (cm <sup>-1</sup> ) (DFT)	1601	1602	1521	1403	659	777	562	580
$v_1$ (Unperturbed) (cm <sup>-1</sup> )	1598	1657	1648	1506	767	723	562	614
$v_2^{\rm u} + v_2^{\rm g}$ (Unperturbed) (cm <sup>-1</sup> )	1595	1626	1635	1488	751	739	588	603
$\Delta (\mathrm{cm}^{-1})^{-1}$	18	57	41	32	34	20	46	21
$\delta$ (cm <sup>-1</sup> )	15	31	23	19	31	10	36	16
$W_{12} ({\rm cm}^{-1})$	5	24	17	13	7	9	14	7
$\frac{I_1}{I_2}$	0.09	0.290	0.27	0.263	0.048	0.325	0.12	0.143

 $\Delta$  – perturbed separation,  $\delta$  – unperturbed separation,  $I_1$  – observed intensity of weak band,  $I_2$  – observed intensity of strong band.

 $W_{12}$  – perturbation energy,  $v_2^u + v_2^g$  – unperturbed band position,  $v_h$  – position of the hole.



Fig. 5. Variation of stabilization energy with hydrogen-acceptor distance of hydrogen bonding in BMSD.

respectively, showing a direct dependence between strength of hydrogen bonding and extent of hyperconjugation.

For  $SO_4^{2-}$ , the stabilization energies of each four oxygen lone pair with neighbour S–O antibonding orbital, whose values are 12.3, 12.9, 13.7 and 14.5 kcal/mol respectively for the processes Lp  $(O_{17}) \rightarrow \sigma^*$  (S<sub>18</sub>–O<sub>20</sub>), Lp  $(O_{19}) \rightarrow \sigma^*$  (S<sub>18</sub>–O<sub>21</sub>), Lp  $(O_{20}) \rightarrow \sigma^*$ (S<sub>18</sub>–O<sub>21</sub>) and Lp  $(O_{21}) \rightarrow \sigma^*$  (S<sub>18</sub>–O<sub>17</sub>), is found appreciable and are of same range. This shows almost equal strength of four sulphur–oxygen bonds, in the resonance structure of SO<sub>4</sub><sup>2-</sup>. In the melaminium ring, the stabilization energy between adjacent C–N double and single bonds are found larger, responsible for hyperconjugative interaction within the ring. This has been formed to create a resonance structure for the ring, evident from almost equal bond lengths for all C–N bonds of the ring, apart from the distorted ring structure in many melaminium derivatives [16].

# 4.5. Molecular electrostatic potential mapping

The reactive sites for the investigated molecule are predicted with the MEP at B3LYP/6-31G(d) level. The electrophilic attack is represented by the negative (red and yellow) region and nucle-ophilic attack is represented by positive (blue) region [29] as shown in (Fig. 6). The most negative V(r) value is associated with oxygen atoms of sulphate ions. Alternatively a maximum value of positive region of V(r) found on the amino group of melaminium, indicates that this site is probably involved in nucleophilic process, which explains the electrostatic interaction between sulphate and melaminium ions responsible for the formation of crystalline network. Uniform negative potential can be observed for all four oxygen atoms of sulphate ion which shows the resonance structure of  $SO_4^{2-}$ .

# 4.6. Frontier molecular orbitals

Frontier molecular orbitals provide insight into structural and physical properties of molecules such as conjugation, aromaticity and lone pairs [30]. Significant degree of intramolecular charge transfer from electron donor group to electron acceptor group is characterized by small HOMO–LUMO separations [31]. HOMO and LUMO are directly related to ionization potential and electron affinity respectively and the energy gap represents the stability of



Fig. 6. Molecular electrostatic potential mapping of BMSD. Colour gradient with most electropositive blue and most electronegative red is shown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 7. HOMO-LUMO analysis of simulated BMSD at B3LYP 6-31 G(d) level.

Table 5
The table showing hyper polarisability tensors of BMSD and calculation of NLO activity at B3LYP 6-31 $G(d)$ level.

$\beta_{\rm xxx}$	$\beta_{xxy}$	$\beta_{xyy}$	$eta_{ m yyy}$	$\beta_{\rm xxz}$	$\beta_{\rm xyz}$	$\beta_{yyz}$	$\beta_{xzz}$	$\beta_{yzz}$	$\beta_{zzz}$	$\beta_{(esu)}$	$\beta(\text{compound})/\beta(\text{urea})$
-157.85	183.71	-27.47	-308.3	185.93	43.6	-9.78	149.59	89.71	-210.18	$\textbf{5.22}\times \textbf{10}^{-31}$	2.66

the molecule. For BMSD, HOMO and LUMO energies has been calculated as, HOMO = -0.221 au, LUMO = 0.032 au, energy gap = 0.253 au (6.88 eV). The calculated energy gap of HOMO-LUMO explains the ultimate charge transfer interaction within the molecule.

The positive and negative phases are represented schematically in red and green colours respectively (Fig. 7). The plots reveal that region of HOMO level spreads over the sulphate ion and LUMO is found to spread over melaminium cation. This reveals that the charge transfer takes place through hydrogen bonds connecting sulphate and melaminium.

#### 4.7. Nonlinear optical activity

The first order hyperpolarizability tensor of BMSD have been computed at B3LYP/6-31G(d) level, represented by  $3 \times 3 \times 3$ matrix (Table 5) and the twenty seven components of the 3D matrix is reduced to 10 components due the Kleinman symmetry [32]. The calculated values of  $\beta_{tot}$  for the title compound is  $3.198 \times 10^{-30}$  esu, 2.66 times that of urea. Thus the title compound can be a potential applicant in the development of NLO materials [33–35]. This phenomenon can be understood with the context of molecular orbital picture. The HOMO-LUMO energy gap of the title compound was calculated as 5.14 eV. As can be seen from the  $\beta_{tot}$  value for this compound, there is an inverse relationship between first hyperpolarizability and HOMO-LUMO gap, allowing the molecular orbitals to overlap to have a proper electronic communication, which is a marker of the intra-molecular charge transfer from the electron donating group system to the electron accepting group [36,37].

# 5. Conclusion

The comparison of geometry optimized using DFT with the XRD data shows that the orientation of melaminium cation in the crystalline network of BMSD is solely determined by the intermolecular interactions through  $SO_4^{2-}$  and  $H_2O$ , which further causes the deviation from planarity of protonating hydrogen with respect to the melaminium ring plane and the disruption of tetrahedral structure and resonance of  $SO_4^{2-}$ . The steric effect of nitrogen lone pair is found to cause distortion of melaminium ring, increasing C–N–C angle of the ring at protonating position, which is supported by both DFT and XRD. Non aromaticity of the melaminium ring is

obvious from the lower wavenumber of NH<sub>2</sub> stretching frequencies, compared to the wavenumbers of asymmetric stretches of aromatic primary amines and also from the unequal C-N bond distances. The intense ionic and donor accepter type of interactions within the crystalline environment is found to make the triazine ring more rigid, raising the frequencies of ring modes in BMSD, compared to those in melamine. The analysis of Evans hole has been identified as an effective method to explain the band profiles of certain modes in the finger print region and here the presence of shoulder appearing in the bands having peaks  $1670 \text{ cm}^{-1}$ ,  $1513 \text{ cm}^{-1}$ ,  $721 \text{ cm}^{-1}$  and  $619 \text{ cm}^{-1}$ , in BMSD has been found to arise due to Evans hole, as explained theoretically. The NBO analysis reveals that there is a direct correlation between the strength of hydrogen bonding or hydrogen-acceptor bond distance and stabilization energy of hyperconjugative interaction between the oxygen lone pair and the antibonding orbital of NH bond. Hence NBO analysis can be effectively used to assess the strength of hydrogen bonding. The HOMO-LUMO analysis has been used to study the charge transfer taking place through hydrogen bonds connecting sulphate and melaminium ion. MEP mapping have been performed to analyze the electrostatic interaction between sulphate and melaminium ions responsible for the formation of crystalline network.

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