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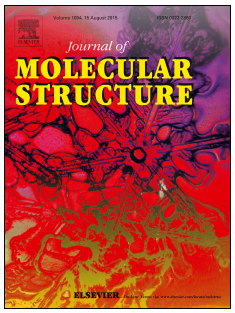

Synthesis, crystal and DFT studies of *N*-(carboxyethyl)-2-methylbenzothiazolium bromide

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Synthesis, Crystal and DFT Studies of *N*-(carboxyethyl)-2-methylbenzothiazolium Bromide

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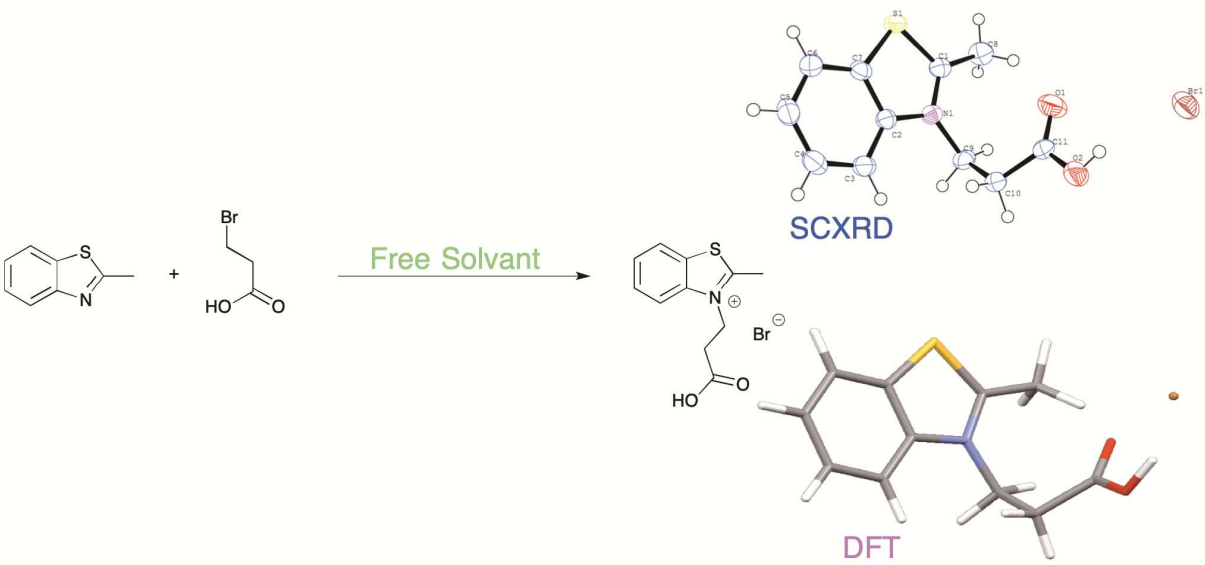
Abstract

The synthesis of benzothiazolium salt, *N*-(carboxyethyl)-2-methylbenzothiazolium bromide has been carried out by condensation of 2-methylbenzothiazole and 3-bromopropionic acid in solvent free conditions. The desired compound was obtained in excellent yield and its structural characterization was performed by FTIR, ^{1}H-NMR, ^{13}C-NMR techniques and XRD-analysis. Further the structural properties of the suitable crystal was obtained and analyzed by single crystal X-ray diffraction analysis indicates that the compound crystallizes in the triclinic space group P-1, with Z = 2 and cell parameters a = 8.6554(3) Å, b = 8.9811(3) Å, c = 9.3168(3) Å, α= 61.237(1)°, β = 71.240(1)°, γ= 72.675(1)°. The molecular structure of the corresponding salt was optimized by Density Functional Theory (DFT) method using B3LYP/6-311G++(d,p) level. The molecular geometrical parameters (bond length. bond angle and dihedral angle) were obtained from the optimized structure. In addition, the IR frequencies were calculated using the same level of theory. The comparisons between the experimental and theoretical values of geometrical parameters and FT-IR vibrational spectra have also been discussed.

Keywords: Benzothiazole, Solvent free, Crystal structure, DFT calculation, FT-IR and NMR.

Graphical Abstract



Highlights

- A novel benzothiazolium salt, *N*-(carboxyethyl)-2-methylbenzothiazolium bromide has been synthetized under solvent free conditions.
- The structure was characterized by both spectroscopic and crystallographic methods
- The optimized structure was compared with X-ray diffraction data.
- Spectral data were compared with computational ones.

1. Introduction

The heterocyclic compounds are versatile products existing in almost all natural and synthetic organic compounds [1]. Owing to their diverse physical and chemical properties, aromatic heterocycles have been the subject of great interest to scientists making it a promising candidate for various applications including biological and pharmaceutical activities. A considerable attention has been given to the development of novel heteroaromatic compounds, and several synthetic approaches have been proposed. From chemical point of view, a heterocyclic compound or ring structure is a cyclic with at least two different kinds of heteroatoms in the ring. The most common heterocycles are those having five- or six-membered rings and containing heteroatoms of nitrogen (N), oxygen (O) or sulfur (S). Among various heterocycles. 1,3-benzothiazole derivatives are an interesting heterocycles class being studied by many researchers and are reported to possess a wide spectrum of biological properties [2].

Benzothiazole, also called 1-thia-3-azaindene in organic chemistry, is a heterocyclic compound containing a ring complex composed of thiazole ring fused with benzene. It is a weak base and thermally stable molecule [3]. Benzothiazole has electropositive and electronegative regions which allow for functional modifications. In this heterocyclic scaffold. the methine carbon between nitrogen and sulphur atoms in the thiazole ring is the most reactive site for probable substitution [4]. As stated before, benzothiazoles derivatives are of great importance categories of heterocyclic compounds with a wide range of biological activities such as antimicrobial [5], antitumor [6], antidiabetic [7], antitubercular [8], antimalarial [9], anticonvulsant [10], antioxidant [11], anti-inflammatory [12], anti-mycobacterial [13], anti-cancer [14]. Interestingly, benzothiazoles are present in bioluminescent luciferin and are used as fluorophores for two photon excitation as well as absorption processes [15,16]. These compounds have also found application in industry as anti-oxidants [17], vulcanization accelerators. Various benzothiazoles such as 2-aryl benzothiazole received much attention due to unique structure and its uses as radioactive amyloid imagining agents [18]. The importance of benzothiazole derivatives in various fields, and in particular in chemistry, biology [19] and pharmacology [20] has prompted researchers to develop numerous synthesis methods for their preparations and to find new fields of applications. This is confirmed by the presence of benzothiazole nucleus in many traded drugs and dyes such as riluzole, thioflavin, and thioflavin T [21]. In general, the synthesis of

benzothiazole derivatives has long attracted the attention of organic chemists to the extent that these derivatives are found in many biologically active natural products. Numerous methods are available for the synthesis of *N*-benzothiazolium derivatives which involve condensation of benzothiazole with an alkylating agent such as an alkyl iodide, bromide, sulphate or tosylate, among others. These *N*-alkyl quaternary ammonium salts bearing 2-methylbenzothiaole are reported in the literature such as unisolated precursors of cyanine dyes [22] as well as potential for selective targeting towards S. cerevisiae infections which are a major problem in health care [23].

In the recent years, density functional theory (DFT) has been extensively used in theoretical modeling, drug and functional material design [24,25]. Among DFT calculation, Becke's three parameter hybrids functional combined with the Lee–Yang–Parr correlation functional (B3LYP) is the best predicting results for molecular geometry and vibrational wave numbers for moderately larger molecule [26,27]. In the view of above significance, the combination of experimental data with the corresponding DFT/B3LYP calculations has been one of the most effective approaches used to gather insight into the molecular structure. Although similar studies on benzothiazolium derivatives have been reported in the literature [28–30]. As a result, an environmentally benign procedure has been used to synthesize the title compound, the corresponding salt was obtained and its structure was characterized by various spectroscopic methods including IR, ^{1}H-NMR, ^{13}C-NMR spectroscopy, single crystal X-ray diffraction techniques and DFT method at B3LYP/6-311G++(d,p) level. The calculated molecular geometrical parameters and IR frequencies are compared with experimental ones.

2. Experimental

2.1. Materials and measurements

All chemicals used in this work were purchased from Aldrich and were used without further purification. IR spectra were recorded on an ABB Bomem FTLA 2000–102 FTIR instrument, (ATR: SPECAC GOLDEN GATE) in the range 260–4000 cm^{-1}. Melting point was recorded in open capillary on Stuart SMP30 and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 using an Avance 300 (Bruker) instrument.

2.2. Experimental procedure for the Synthesis of salt

The general synthetic procedure was employed to prepare the compound N-(carboxyethyl)-2-methylbenzothiazolium bromide involving the melt reaction of the 3-bromopropionic acid

with 2-methylbenzothiazole in one step procedure. A mixture of 2-methylbenzothiazole (15.75 mmol) and 3-bromopropionic acid (31.50 mmol) was stirred in an oil bath at 150°C for 4h. After the desired time, the reaction mixture was slowly cooled and became a thick semi-solid mass. The solid was recrystallized from methanol to afford the title compound as pale-brown crystals. Yield: 92 %; m.p. 230-233°C; ^{1}HNMR (DMSO-d_6, 300MHz): 2.28(t, ^{3}J = 7.2Hz, CH_2); 3.25(s, CH_3); 4.89(t, ^{3}J = 7.2 Hz, NCH_2); 7.68(dt, ^{3}J =7.2Hz, H_{Ar} 5); 7.85(dt, J = 7.2Hz, H_{Ar} 4); 8.35(dd, J = 8Hz, H_{Ar} 6); 8.47(dd, J = 8.10 Hz, H_{Ar} 3); ^{13}CNMR (DMSO-d_6, 300MHz): 17.7 CH_3 (8); 32.3 CH_2 (10); 45.5 NCH_2 (9); 117.4 CH_{Ar} (3); 125.2 CH_{Ar} (6); 128.5 CH_{Ar} (5); 129.8 CH_{Ar} (4); 129.4 Cq (7); 141.2 Cq (2); 171.9 Cq (1); 178.6 CO_2H (11).

2.3. X-ray data collections, structure solution and refinement

The crystallographic data for CMTB were collected using a Bruker AXS APEX II single crystal X-ray diffractometer equipped with graphite-monochromated MoKα radiation (λ = 0.71073 Å) at room temperature. The solvation of structure determination was carried out by direct methods using ShelXS [31] and the refinemend with the ShelXL [32] using Least Squares minimisation. All non-hydrogen atoms were refined anisotropically. Crystal and data collection parameters are given in Table 1.

Table 1. Crystal data and structure refinement for CMTB

Parameter	Value
Chemical formula	Br. $C_{11}H_{12}NO_2S$
Formula Weight	302.18 g/mol
Temperature	296(2) K
Wavelenght	0.71073 Å
Crystal System, space group	Triclinic, P-1
Unit cell dimensions	a = 8.6554(3) Å α = 61.237(1)°
	b = 8.9811(3) Å β = 71.240(1)°
	c = 9.3168(3) Å γ = 72.675(1)°
Volume	592.16(3) $Å^3$
Z , calculated density	2, 1.695 g/cm^3
F(000)	304
Crystal Size [mm]	0.30x0.25x0.15
Theta range for data collection	2.5° - 30.6°
Limiting indices	$-12 \le h \le 12$; $-12 \le k \le 12$; $-13 \le l \le 13$
Reflections collected	26006
Independent method	3647 [R(int) = 0.073]
Refinement method	Full-matrix, least-square on F^2
Data/restraints/parameters	3647/0/147
R, wR^2, S	0.0297, 0.0687, 0.93
Min. and Max. Resd. Dens.	-0.52 and 0.56 $e/Å^3$

2.4. Computational study

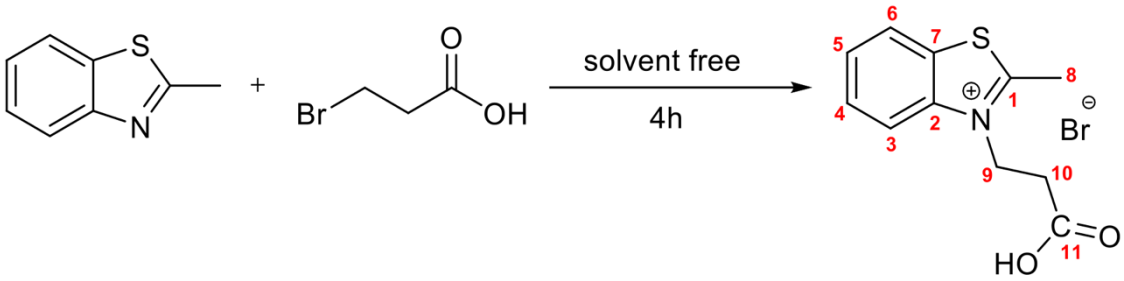
DFT calculations with Becke's three-parameter hybrid exchange functional and the correlation functional of Lee, Yang and Parr (B3LYP) were performed on a personal computer using Gaussian 09 [33]. Geometry optimization of *N*-(carboxyethyl)-2-methylbenzothiazolium bromide (CMTB), was performed by DFT method using B3LYP/6-311G++(d.p) level. Then, in order to access energy and the calculated IR spectra. Frequency calculation was performed at DFT-B3LYP/6-311G++(d,p) level of DFT method. The normal modes assignment of the theoretical IR frequencies is visualized and substantiated with the help of the Gaussview 5.0.9 visualization program. There is no negative frequency in the calculated IR spectrum which confirms that the optimized geometry of the compound is located at the minima on the potential energy state. RMS errors were calculated for bond distance and angle using the following expression.

$$\boldsymbol{RMS} = \sqrt{\frac{\mathbf{1}}{\boldsymbol{n}}\sum_{\boldsymbol{i}}^{\boldsymbol{n}}(\boldsymbol{d}_{\boldsymbol{i}}^{\boldsymbol{calc}} - \boldsymbol{d}_{\boldsymbol{i}}^{\boldsymbol{exp}})^{\mathbf{2}}}$$

Where d_i^{calc} and d_i^{exp} are the theoretical bond distance and experimental bond distance, respectively.

3. Results and Discussion

The title compound, *N*-(carboxyethyl)-2-methylbenzothiazolium bromide (CMBT) was prepared as shown in Scheme 1. The benzothiazolium salt was synthesis using an eco-friendly, one-pot, solvent free reaction, from 2-methylbenzothiazole and the 3-bromopropionic acid. The reactants were mixed thoroughly for a given period of time. It should be noted that, by the eco-friendly method presented herein, better yield has been obtained in comparison to those reported in literature [34,35]. In addition, most of these classical methods suffer from drawbacks, namely high thermal conditions, long reaction times, and the use of organic solvents that result in waste streams. In this work, we decide to move forward and choose the melt reactions that have recently gained popularity because of cleaner conditions and ease of manipulation. These reaction conditions are within the framework of green chemistry or solvent-free synthesis [36].



Numbering scheme for NMR interpretation

Scheme 1. Synthesis of N-(carboxyethyl)-2-methylbenzothiazolium bromide

3.1. NMR spectral analysis

The ^{1}H and ^{13}C NMR spectra were computed to find the nuclear magnetic resonance nature of the salt. The experimental analysis of the title compound was taken using DMSO as solvent (see supporting information). In ^{1}H NMR spectrum, the protons of aromatic ring resonate in the range 7.68-8.47 ppm. In this respect, a doublet of doublet was observed for H3 and H6 by having a coupling constant of 8.10, 8 Hz. respectively. A multiple was observed for the protons H4 and H5 at 7.85 and 7.68 ppm with a coupling constant of J = 7.2 Hz which is always assigned to the aromatic ring protons. Besides, a singlet with three protons integral at 3.25 ppm is conveniently assigned to the CH_3 proton of thiazole ring. The signals at 2.28 ppm and 4.89 correspond to a triplet of CH_2 and NCH_2 protons, respectively. The signal attributed to the OH proton of carboxylic acid group is absent which may be due to the zwitterionic nature of analysed sample. In the ^{13}CNMR spectrum, the appearance of eleven distinct carbon signals in the spectrum explicitly confirms the molecular structure of synthesized salt. In our present investigation, the chemical shifts values of aromatic carbon atoms are observed at 117.4, 125.2, 128.5 and 129.8 ppm. The O atom has more electronegative property polarizes the electron distribution in its bond to adjacent atom and increases the chemical shift value. Consequently, the higher chemical shift for the carboxylic group carbon C11 was observed at 178.6 ppm. Also, the greater deshielding of C1 carbon at 171.9 ppm was caused by the thiazole ring. The CH_3 carbon C8 resonated at 17.7 ppm. While the signals of CH_2 and NCH_2 were observed at 32.3 and 45.5 ppm. The signals appeared at 129.4, 141.2 ppm is attributed to the quaternary carbon (Cq) 2 and 7, respectively.

3.2. Description of the crystal structure

The most widely used method to obtain information about the properties of organic compounds is DFT [37,38] and the most widely used function is B3LYP (Becke's three-

parameter hybrid model using the Lee–Yang–Parr correlation functional. Basis sets are also being used besides these methods and functions for precise calculations [39,40]. In the present study, the *N*-(carboxyethyl)-2-methylbenzothiazolium bromide salt was determined by X-ray analysis and was optimized. The geometry parameters of synthesis compound were examined using DFT calculation by B3LYP method with 6-311++G(d,p) and compared with the data obtained from X-ray crystal structure. The calculated optimized geometrical parameters and the experimental values are depicted in Table 2. The optimized geometric structure of the compound with the atomic numbering scheme is given in figure 1, along with the ORTEP drawing of it with the atom-numbering scheme (figure 2).

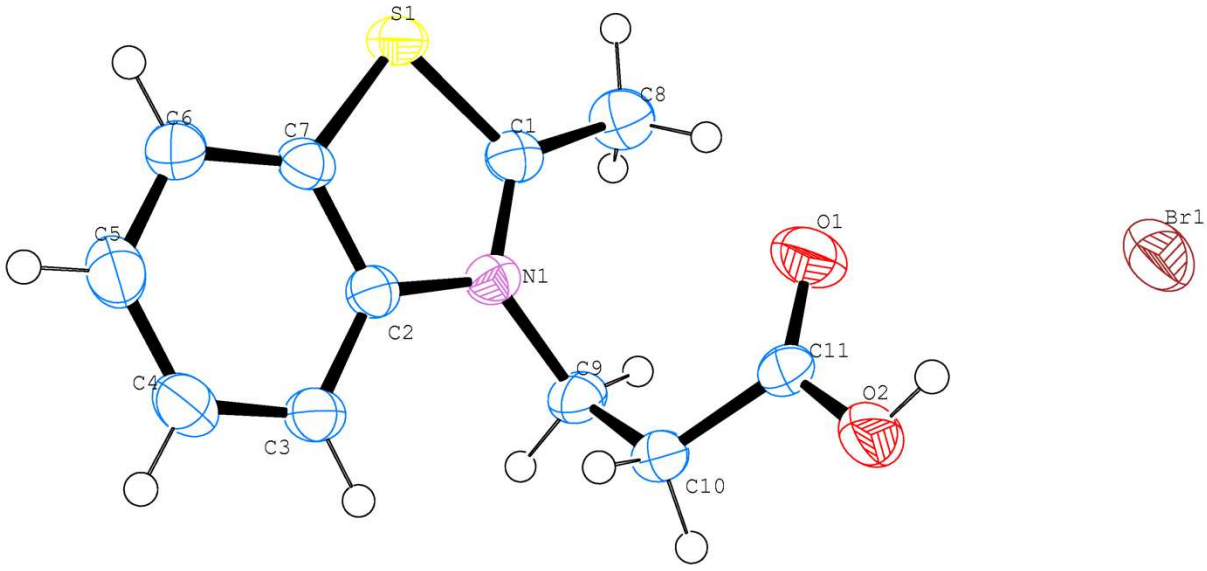


Figure 1. ORTEP plot (30%) for CMTB.

As seen from the given table 2. There are small differences between theoretical and experimental values. This slight deviation may come from the environment of the compound. It is clear that the experimental results belong to solid phase while theoretical calculations belong to gaseous phase [41]. All theoretical computational values of bond lengths are slightly higher than experimental ones except for N1-C9, C2-C7, C1-C8 and C7-C6 bonds. experimental value of C2-C7 (1.396 Å) bond is lower than Calculated value (1.4004 Å). The bond character of C3-C4 is calculated as 1.3874 Å is slightly deviated with experimental (1.379 Å) data. The C-C bonds lengths are in the range 1.368-1.516. The bond lengths of C2-C3 (1.392 Å), C2-C7 (1.396 Å) and C7-C6 (1.394 Å) and these values are greater than that of C3-C4 (1.379 Å) and C5-C6 (1.368 Å) due to adjacent thiazole ring. In the thiazoline moiety,

The S1-C7 bond distance is the longest while the N1-C1 is the shortest. The S1-C7 bond length is calculated to be 1.748 Å, which is close to the typical C-S bond distance for benzothiazoles [42]. While S1-C1 bond (1.709 Å) is shorter than the average distance for C-S single bond (1.811 Å) [43]. The bond length between N1-C1 (1.3208 Å) indicates some double bond character and is conjugated with neighboring bonds. The nitrogen-carbon distance (N1-C2=1.407 Å) is shorter than the distance characteristics of single C-N bond length (1.45 Å) but is comparable with the values reported in the analogous structures [44,45]. The bond lengths C10-C9 (1.516 Å), C11-C10 (1.5037 Å) have shown larger values than the C-C bond lengths which is due to the adjacent C=O and carboxylic groups. Since oxygen is more electronegative than carbon, the bond length O2-C11 (1.315 Å) decrease as compared to C-C bond length.

The calculated bond angles are also closer to the XRD values such as C3-C2-C7=121.24/120.67°, O2-C11-O1=123.35/123.94°, N1-C1-S1=113.37/112.83°, N1-C9-C10=113.27/112.47°. The deviation of bond angle from 120° shows increase in non-planarity of the molecule. Both DFT and experimental angles give shortening of angles C5-C6-C7, C4-C3-C2 involving a common C atom of the two fused rings and increase of angles C6-C7-C2, C7-C2-C3, C3-C4-C5, C4-C5-C6 from 120° at the benzene ring. These asymmetry of angles reveals the conjugation with the thiazole ring. These results are similar to those found in the literature [46]. More distortion in bond parameters is observed in the pentagon ring. The variation in bond angle depends on the electro negativity of the central atom. If the electro negativity of the central atom decreases, the bond angle decreases [47]. Therefore, the large size of the S atom compared with N results in a reduction of the C1—S1—C7 angle (91.11°) compared with the C1—N1—C2 angle (113.71.2°). This reveals that the S atom might be using unhybridized *p*-orbitals for bonding [48]. The presence of higher electronegative group C=O would be the reason for the lesser bond angle of O1-C11-C10 (123.51°). The angle O2-C11-C10 (112.12°) which can be assumed as due to the presence of OH group which is electropositive.

Regarding the dihedral angles, it is also important to note that the experimental dihedral angles are nearly equal to the calculated values, C9-N1-C1-C8 = 0.66/-0.92, C7-S1-C1-C8 = 178.87/176.9º (deviation 1.97°), C9-N1-C1-S1 = 179.94/177.56 (deviation 2.38°), C3-C2-C7-C6 = 0.92/0.73° (deviation 0.19º) and N1-C2-C3-C4 = -178.77/-179.31°. Planarity of a molecule can be confirmed from their dihedral angle. Generally, dihedral angle values of 0°, 180° or 360° show planarity of the molecule [49]. In the studied molecule, the torsion angles

N1-C2-C3-C4 (-178.77°), S1-C7-C6-C5 (177.44°), C1-S1-C7-C6 (-177.61°) and C1-N1-C2-C3 (175.98°) show that C4, C3, C2, C7, C6, C5, C1, N1, S1 are approximately in the same plane which means that the benzothiazole moiety is somewhat distortion from planarity. Thus, the geometry of the benzothiazole ring is slightly affected by its substituents. The CH_3 group is planar with respect to the benzothiazole ring, this is supported by the torsion angle values, C7-S1-C1-C8 = 178.9° and C2-N1-C1-C8 = -178.0° at C8 position. The CH_2 groups at C9 and C10 are titled from the benzothiazole ring, as is evident from the angles, C3-C2-N1-C9 = -2.82°, C8-C1-N1-C9 = 0.66°, S1-C1-N1-C9 = 179.94°, C9-N1-C2-C7 = 179.7°, C2-N1-C9-C10 = -69.95°, C1-N1-C9-C10 = 111.39°. Likewise, the carboxylic group has the usual cis conformation; the torsion angle of H1-O1-C11-O2 is 11.72°, while the OH group is located in the trans position relatively to the ethyl group (the torsion angle C9-C10-C11-O2 = 173.3°).

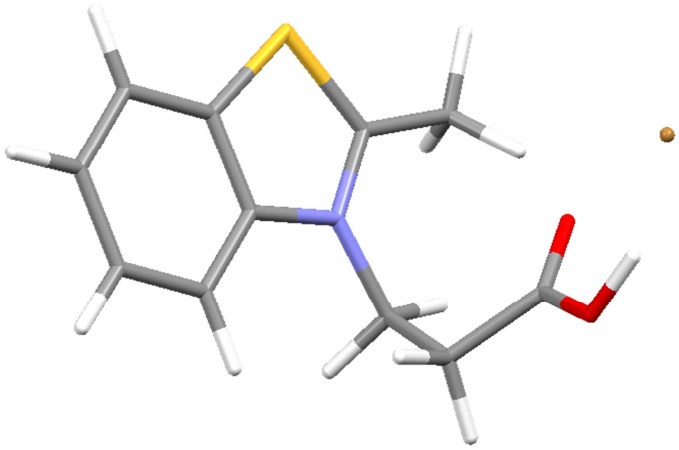


Figure 2. The theoretical optimized geometric structure of the salt of CMTB.

Table 1. Experimental and optimized geometrical parameters of compound CMTB.

Parameter	Experimental	Theoretical	Δ
Bond length (A°)			
N1-C2	1.4073	1.403	0.0043
O2-C11	1.3158	1.3205	0.0047
O1-C11	1.1989	1.212	0.0131
C2-C3	1.3912	1.3977	0.0065
S1-C7	1.7343	1.748	0.0137
C2-C7	1.3952	1.4004	0.0052
S1-C1	1.699	1.7094	0.0104
N1-C1	1.3208	1.3374	0.0166
C3-C4	1.3793	1.3874	0.0081
C11-C10	1.5037	1.5285	0.0248

C4-C5	1.3953	1.4035	0.0082
C7-C6	1.3944	1.3956	0.0012
C5-C6	1.3678	1.3872	0.0194
N1-C9	1.4844	1.483	0.0014
C10-C9	1.516	1.54	0.024
C1-C8	1.482	1.4884	0.0064
RMS	**0.0127**		
Bond Angle (°)			
C7-S1-C1	91.12	91.11	0.01
C2-N1-C1	113.71	114.11	0.4
C2-N1-C9	121.22	121.79	0.57
C1-N1-C9	125.06	124.01	1.05
N1-C2-C3	127.22	127.63	0.41
N1-C2-C7	111.49	111.7	0.21
C3-C2-C7	121.24	120.67	0.57
O2-C11-O1	123.35	123.94	0.59
O2-C11-C10	112.12	111.29	0.83
O1-C11-C10	124.51	124.49	0.02
C2-C3-C4	116.99	117.96	0.97
S1-C7-C2	110.28	110.2	0.08
S1-C7-C6	128.73	128.59	0.14
C2-C7-C6	120.93	121.18	0.25
S1-C1-N1	113.37	112.83	0.54
S1-C1-C8	120.9	121.3	0.4
N1-C1-C8	125.72	125.86	0.14
C3-C4-C5	121.82	121.3	0.52
C4-C5-C6	121.31	120.89	0.42
C7-C6-C5	117.68	118	0.32
N1-C9-C10	113.27	112.47	0.8
RMS	**0.5279**		
Dihedral angle (°)			
C1-N1-C2-C3	175.98	179.88	3.9
C1-N1-C2-C7	-1.5	0.66	2.16
C9-N1-C2-C3	-2.82	3.14	5.96
C9-N1-C2-C7	179.7	176.09	3.61
N1-C2-C3-C4	-178.77	-179.31	0.54
C7-C2-C3-C4	-1.52	-0.14	1.38
C1-S1-C7-C2	-0.41	1.97	2.38
C1-S1-C7-C6	-177.61	-179.93	2.32
N1-C2-C7-S1	1.12	-1.84	2.96
N1-C2-C7-C6	178.57	178.87	0.3
C3-C2-C7-S1	-176.53	-179.98	3.45
C3-C2-C7-C6	0.92	0.73	0.19

C7-S1-C1-N1	-0.44	-1.65	1.21
C7-S1-C1-C8	178.87	176.9	1.97
C2-N1-C1-S1	1.19	0.89	0.3
C2-N1-C1-C8	-178.08	-177.58	0.5
C9-N1-C1-S1	179.94	177.56	2.38
C9-N1-C1-C8	0.66	-0.92	1.58
C2-C3-C4-C5	0.75	-0.39	1.14
O2-C11-C10-C9	173.34	172.55	0.79
O1-C11-C10-C9	7.86	-1.54	9.4
C3-C4-C5-C6	0.66	0.35	0.31
S1-C7-C6-C5	177.44	178.52	1.08
C2-C7-C6-C5	0.51	-0.77	1.28
C4-C5-C6-C7	-1.28	0.24	1.52
C2-N1-C9-C10	-69.95	-71.42	1.47
C1-N1-C9-C10	111.39	112.16	0.77
C11-C10-C9-N1	-74.56	-72.47	2.09
RMS	**2.7962**		

The crystal structure of the molecule CMTB is consolidated by intra and intermolecular hydrogen bonds involving the bromide anion and carboxylic group. In the crystal structure cations is bridged by Br atoms. Bromide anions, as an acceptor, connect the molecules with O2-H2···Br1 and C5-H5···Br1 hydrogen bonds (table 3).

Table 3. Hydrogen-bond parameters (Å, °).

D-H···A	D-H	H···A	D···A	D-H···A
O2-H2···Br1	0.821(11)	2.361(11)	3.1590(12)	164.3(16)
C6-H6···O1^{i}	0.930(2)	2.449(2)	3.082(2)	125.38(19)
C8-H8···O1	0.960(11)	2.315(10)	3.119(2)	140.9(8)

Symmetry code: (i) *1-x,1-y,1-z*

3.3. FT-IR spectral analysis

In order to give more information on the crystal structure, we have studied the vibrational properties of our compound using infrared absorption. Vibrational spectroscopy is one of the most useful tools for characterization of the chemical compounds in terms of both experimental studies and theoretical calculations. The title molecule under investigation possesses 28 atoms (N = 28), thus 3N = 84 degrees of freedom. It belongs to the C_1 point group symmetry, and it undergoes 78 normal modes of vibrations when the three translational (2A' + 1A") and three rotational (1A' + 2A") degrees are subtracted. All 78 modes of vibration

are distributed as 27 stretching, 26 bending, 21 torsional and 4 out of plan vibration. The bands that are in the plane of the molecule is represented as A' and out-of-plane as A". Of the 78 normal modes of vibrations, 53 modes of vibrations are in-plane and remaining 25 are out-of-plane. Therefore the 78 normal modes of vibrations title molecule are distributed as 53A' + 25A"[50]. In agreement with C_1 symmetry all the 78 fundamental vibrations are active in IR absorption. The vibrational frequency calculations for normal modes have been performed at B3LYP level with 6-311G++(d,p) basis set. The detailed assignments of some specific and important vibrational experimental wavenumbers and their comparisons with theoretically calculated (scaled) wavenumbers for the normal modes along with their %PED are collected in Table 3. The observed FTIR spectra of CMTB along with the simulated infrared spectra in the frequency range 260 to 4000 cm^{-1} are shown graphically in Figure 3.

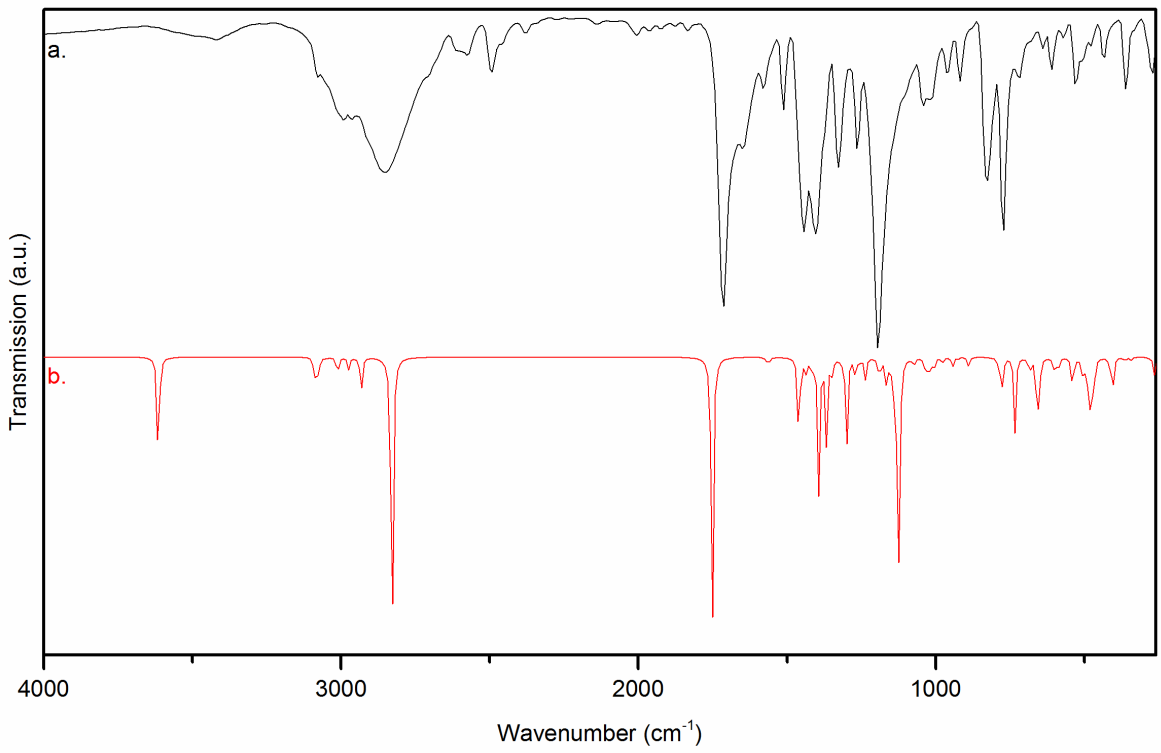


Figure 3. Superposition of (a) the experimental and (b) the DFT computed IR spectra of CMTB

The deviations of the calculated frequencies from the experimental ones are obtained due to the harmonic approximation of the calculated frequencies as well as due to neglecting of intermolecular interactions in solid. The calculated vibrational wave numbers are higher than their experimental values for the majority of the normal modes. Theoretically predicted wavenumbers are to be scaled down to cope up with the experimental wavenumbers. Scaling factor used for this title molecule is 0.965 [51,52]. It is also important to note that computed

wavenumbers correspond to gaseous phase of isolated molecular state whereas the observed wavenumbers correspond to the solid-state spectra. In order to investigate the performance and vibrational frequencies for the title compound root mean square value (RMS) and correlation coefficient between calculated and observed vibrational frequencies were calculated. The value of correlation coefficient found to be R^2 = 99.88%, showing good agreement with the calculated wavenumbers with experimental. The correlation graph is shown in figure 4. The root mean square (RMS) difference between calculated and experimental frequencies 32.3 cm^{-1} reveals a better agreement with the experimental data table 4.

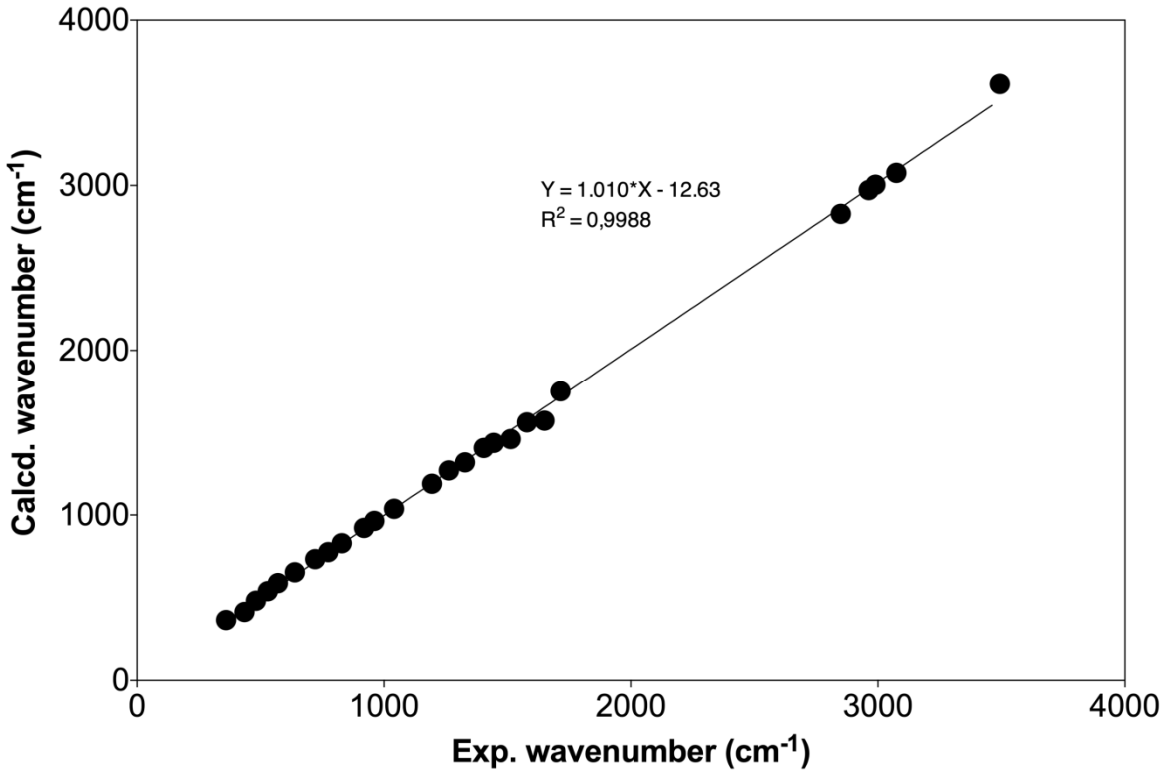


Figure 4. Plots of experimental (exp.) vs. calculated (calcd) IR frequencies

Aromatic compounds commonly exhibit multiple weak bands in the region 3100–3000 cm^{-1} due to aromatic C-H stretching vibrations [53,54] and can be distinguished from aliphatic C–H stretching bands which usually arise below 3000 cm^{-1} region [55]. The experimental spectra show only one very-weak band at 3075 which correspond to C-H stretching of benzene ring. The calculated IR value which corresponds to the observed IR frequency was found as 3076 cm^{-1}. The C–H stretching vibrational modes in the CH_2 and CH_3 groups are defined by the absorption bands in the 3000–2850 cm^{-1} range [56]. For methylene group (CH_2) the observed peak at 2850 cm^{-1} can be assigned to the symmetric C-H stretching mode

while the peak at 2990 can be attributed the asymmetric C-H stretching mode. The asymmetric C-H stretching vibrational mode in the aliphatic CH_3 group is observed at 2936 cm^{-1}. The PED for these modes suggest that these are pure modes. The aromatic C-H in-plane bending modes of benzene and its derivatives are observed in the region 1300–1000 cm^{-1} [57]. In the case of benzothiazole vibrations involving the C-H in-plane bending are observed at 1513, 1444, 1404 and 1194 cm^{-1}, whereas it was calculated to be found in the range 1461-1190 cm^{-1}. The C-H out-of-plane vibrations are expected below 1000 cm^{-1} [57] and for the title compound the theoretical calculations give bands at 965, 922, 830 and 733 cm^{-1}. Experimentally these bands are observed at 961, 919, 829 and 721cm^{-1} in the IR spectrum. Theoretical values of ring CH, CH_3 and CH_2 stretching and bending vibrations are good coherent in experimental values. Other highly characteristic modes are C=C stretching vibrations for aromatic ring. The spectral assignment was made by Panizzi et al. [58] for benzothiazole. The carbon–carbon stretching modes of the phenyl group are expected in the range from 1650 to 1200 cm^{-1}. In the present case, the carbon-carbon stretching bands of benzene ring are appeared in the infrared spectrum at 1650, 1579, 1444, 1328 cm^{-1} and were matched with the calculated values. The observed vibrational frequencies are generally intense because of the conjugation between benzene and thiazole rings. These assignments were supported by the literature [59,60]. In the other hand, the peak at (Exp. 1041, Cal. 1038 cm^{-1}) can be attributed to the CCC in-plane bending vibrational modes of benzene ring. Similarly, the observed IR peaks at 961 and 919 cm^{-1} can be assigned to the ring torsional vibrational. These are matched well with theoretical bands. The C=N stretching skeletal bands [61,62] are observed in the range 1672–1566 cm^{-1}. Kolts and Collier [63] reported a value of 1517 cm^{-1} for benzoxazole as νC=N stretching mode. For the title compound, the DFT Calculations give νC=N mode at 1513 and experimentally at 1461 cm^{-1}. The C-S bond is highly polarisable and hence produces stronger spectral activity. The stretching vibration assigned to the C-S linkage occurs in the region 700–600 cm^{-1} [63]. The C-S stretching mode recorded in FT-IR spectra at 774, 639 cm^{-1} and calculated at 776, 653 cm^{-1}, respectively. The carbonyl stretching frequency has been most extensively studied by infrared spectroscopy [63]. This multiply bonded group is highly polar and therefore gives rise to an intense infrared absorption band in which the position of C=O stretching band depends on the physical state, electronic and mass effects of neighboring substituents, conjugations and intramolecular and intermolecular hydrogen bonding [63]. Stretching vibration of C=O group is expected to appear at 1715–1680 cm^{-1} [63]. The very strong C=O experimental band observed at 1751 cm^{-1}. The DFT frequency of C=O stretching vibration is in good agreement with the

experimental result. The assignment of the O–H stretching vibrations is pure and apprehensible. The absorption range for the O-H valence-stretching vibration of hydroxyl group is usually quoted as being 3400-3448 cm^{-1} [64] and 3500-3742 cm^{-1} for carboxylic groups [65]. In the title compound the O-H stretching vibration observed at 3420 cm^{-1} experimentally and 3615 cm^{-1} in DFT calculation with a pure mode.

Table 4. Major Experimental and calculated vibrational wavenumbers (cm^{-1}) of salt at B3LYP/6-311++G(d, p) level and their assignments.

Mode No.	Sym.	IR Exp. frequency (cm^{-1})	B3LYP/6-311++G(d,p) calculated wavenumber		Vibrational assignment (PED%)
			Unscaled (cm-1)	Scaled (cm^{-1})	
1	A'	3494 w	3746	3615	νOH (100)
2	A'	3075 vw,sh	3188	3076	νCH (60)
3	A'	2990 vw,	3114	3005	νCH_{2as} (89)
4	A'	2963 vw,	3081	2973	νCH_{3as} (88)
5	A'	2850 m	2932	2829	νCH_{2s} (88)
6	A'	1715 vs	1815	1751	νCO (86)
7	A'	1650 s	1629	1572	νCC (17/28)
8	A'	1579 m	1619	1562	νCC (12/33)
9	A'	1513 m	1514	1461	νNC (17) ; βHCH (29)
10	A'	1444 s	1490	1438	νCC (10); βHCC (12/24)
11	A'	1404 s	1458	1407	βHCH (82)
12	A'	1328 m	1367	1319	νCC (15/18/19/22)
13	A'	1263 m	1316	1270	νCO (10); βHOC (43)
14	A'	1194 vs	1233	1190	βHCC (39); βHCN (11)
15	A'	1041 w	1076	1038	βCCC (11/12)
16	A"	961 vw	1000	965	τHCCC (10/28/41); τCCCC (11)
17	A"	919 vw	956	922	τHCCN (25); τHCCC (26/29); τCCCC (10)
18	A"	829 m	859	830	τHCCN (25); τHCCC (15/32)
19	A'	774 s	804	776	νCC (23); νCO (10) ; νSC (19)
20	A"	721 vw	760	733	τHCCN (23); τHCCC (25/32)
21	A"	639 vw	677	653	τHOCC (32); γOCOC (19); νSC (13)
22	A'	570 vw	621	588	βOCO (40)
23	A"	529 w	559	539	τHOCC (12)
24	A'	481 vw	499	481	βSCN (14)
25	A"	435 vw	428	413	γNCCC (11)
26	A'	360 w	377	364	βOCC (11); βCCN (18); βCNC (29)

ν-stretching; β-in-plane bending; γ-out of plane bending; τ-torsion; vw-very weak; w-weak; m-medium; s-strong; vs-very strong; sh-shoulder; potential energy distribution (PED ≥ 10%) is given in brackets in the assignment column;; s: symmetric; as: asymmetric;

4. Conclusion

In this study, an environmental benign procedure has been proposed to synthesize N-(carboxyethyl)-2-methylbenzothiazolium bromide salt with high yield. The title compound was characterized by elemental analysis, spectroscopic (FT-IR, NMR) and structural (single crystal X-ray diffraction). The structure of the product was studied using the computational method of DFT/B3LYP with the 6-311++G (d, p) basis set. After optimizing the molecular structure, the calculated parameters geometry and vibrational frequencies of the molecule

have been compared with the experimental findings. Therefore, it is found a good coincidence between experimental and computed values.

Supplementary material

The crystallographic information file has been deposited by us in the Cambridge structure database (CCDC 1883515). These data can be obtained free of charge via www.ccdc.cam.ac.uk/datarequest/cif, by e-mailing data-request@ccdc.com.ac.uk or by contacting the Cambridge CB21 EZ, UK; fax: +44 1223 336033.

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