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Structure of methyl 3-(trimethylammonium)benzoate iodide studied by X-ray diffraction, DFT calculations, NMR and FTIR spectra

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1. Introduction

Zwitterions are compounds with oppositely charged centers and are often referred to as betaines, dipolar ions, salt-bridgedcontaining molecules, and inner salts. This diverse nomenclature reflects the extraordinary importance of these species in biological transformations, organic synthesis, the preparation of novel materials, and as chromatographic supports [1–3].

An interesting group of compounds of this type are ortho- metaand para-N,N,N-trimethylammoniumbenzoates (benz-betaines), $(CH_3)_3N^+-C_6H_4-COO^-$, their salts and esters [4–6].

In the pyrolysis electron impact (EI) mass spectrometry experiment on N,N,N-trimethylammoniumalkanocarboxylates $(Me_3N^+-(CH_2)_nCOO^-)$ and their hydrochlorides, Wood and Collacott [7] have observed the methyl transfer to more volatile methyl esters $(Me_2N-(CH_2)_nCOOMe)$. Quaternization of N,N-dimethylaminobenzoic acids by an excess of methyl iodide in methyl alcohol depends on temperature and time of refluxing [6]. In N,N,N-trimethylammoniumbenzoic acid hydroiodide, heating triggers methyl transfer and methyl N,N-dimethylaminobenzoate hydroiodide is formed $(Me_2N-C_6H_4-COOMe\cdotHI)$.

Recently, we have described the structures of methyl 4-(trimethylammonium)benzoate iodide [8], 4-(trimethylammonium)benzoic acid chloride [9] and 4-(trimethylammonium)benzoate [10]. In this paper, we report the crystal structure and spectroscopic properties of methyl 3-(trimethylammonium)benzoate iodide (m-carboxymethoxyphenyltrimethylammonium iodide) (1a).

ABSTRACT

The structure of methyl 3-(trimethylammonium)benzoate iodide, $3-(Me)_3N^+C_6H_4CO_2Mel^-$, (**1a**) has been determined by X-ray diffraction, DFT calculations and characterized by FTIR and NMR spectroscopy. The crystals are orthorhombic, space group *Pnma* and the structure is stabilized by interaction of I anion with the N, O(1) and O(2) atoms. The N···I distances vary between 4.541(3) and 7.752(3) Å. The correlation between the atomic distances and the Mulliken atomic charges is linear. Charge on the quaternary nitrogen atom depends on options used for generating electrostatic potential-derived charges. The interpretation of ¹H and ¹³C NMR spectra in DMSO-d₆ has been based on 2D experiments and calculated GIAO/B3LYP/6-311G(d,p) magnetic isotropic shielding constants. The FTIR spectrum of the solid compound is consistent with the X-ray results. The probable assignments of the anharmonic requencies are proposed. © 2012 Elsevier B.V. All rights reserved.

2. Experimental and calculations

2.1. Synthesis

A solution of 3-(dimethylamino)benzoic acid (15 g) in methanol (70 cm³) and methyl iodide (30 g) was heated at 70 °C in a sealed tube for 40 h. Yellow crystals were filtered off and washed with small amount of acetone. The filtrate was evaporated to dryness under reduced pressure and the solid residue was washed with acetone. Both fractions of the crystals were combined and recrystallized from methanol, total yield 65 %, m.p. 210 °C, 220–221 °C Ref. [6].

2.2. Measurements

The X-ray diffraction measurements were carried out on a KUMA KM4-CCD diffractometer [11,12]. The structure of **1a** was solved by direct methods with the SHELXS-97 and refined on F^2 full-matrix least-squares with SHELXL-97 [13]. All hydrogen atoms were calculated from the molecular geometry and their isotropic displacement parameters were based on U_{eq} of their carriers. The crystal data, together with the details concerning data collection and structure refinement are given in Table 1 and the atomic coordinates in Table A in Supplementary material. The experimental and the calculated bond lengths, bond angles, and selected torsion angles are summarized in Table 2. The crystal data and atomic parameters in the CIF form are available as Electronic Supplementary Information from the Cambridge Crystallographic Database Center (CCDC 859169). Molecular illustrations were prepared using ORTEPII [14] and XP [15] programs.





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Crystal data and structure refinement for methyl 3-(trimethylammonium)benzoate iodide (1a).

| Empirical formula | $C_{11}H_{16}INO_2$ |
|---|------------------------------------|
| Formula weight | 290.07 |
| Temperature | 293(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Orthorhombic |
| Space group | Pnma |
| Unit cell dimensions | a = 12.2502(5) Å |
| | b = 7.0998(4) Å |
| | c = 14.8763(7) Å |
| Volume | 1293.85(11) Å ³ |
| Ζ | 4 |
| Calculated density | 1.489 g/cm ³ |
| Absorption coefficient | 2.450 mm^{-1} |
| F(000) | 556 |
| Crystal size | $0.09\times0.06\times0.05~mm$ |
| θ range for data collection (°) | 2.15-26.51 |
| Max/min. indices h, k, l | -11/15, -8/8, -18/18 |
| Reflections collected/unique | 8260/1440 [R(int) = 0.0989] |
| $\theta_{Max}(^{\circ})/Completeness$ (%) | 26.51/99.1 |
| Absorption correction | None |
| Refinement method | Full-matrix least-squares on F^2 |
| Data/restraints/parameters | 1440/0/85 |
| Goodness-of-fit on F ² | 1.085 |
| Final <i>R</i> indices $[I > 2\sigma_I]$ | R1 = 0.0376, wR2 = 0.0836 |
| R1/R2 indices (all data) | 0.0490/0.0902 |
| Largest diff. peak and hole | 3.804 and -1.210 e Å ⁻³ |

FTIR spectra were recorded in Nujol and Fluorolube mulls on a Bruker IFS 66v/S spectrometer, evacuated to avoid water and CO_2 absorptions, at 2 cm⁻¹ resolution. Each FTIR spectrum was measured by acquisition of 64 scans.

NMR spectra were recorded on a Bruker Avance DRX spectrometer operating at 599.93 and 150.85 MHz for ¹H and ¹³C, respectively. The spectra were measured in DMSO-d₆ solution relative to TMS. The 2D ¹H–¹H (COSY), ¹H–¹³C (HETCOR) and Heteronuclear Multiple-Bond Connectivity (HMBC) spectra were obtained with the standard Bruker software.

2.3. Calculations

The optimization of geometrical parameters was performed using the Gaussian 03 program package [16]. The X-ray geometry of **1a** was used as a starting point of calculations. The calculations employed the hybrid B3LYP exchange–correlation functional, which combined the exchange functional of Becke [17,18] with the gradient–correlation functional of Lee et al. [19] approach in conjunction with the 6-311G(d,p) basis set [20]. The basis set for iodine is not available in the standard set of basis functions offered by the Gaussian 03 program. Therefore it has been fetched from the EMSL Basis Set Library [21,22], where the 6-311G(d,p) basis set created by Glukhovtsev et al. [23] is provided.

The conductor like-screening solvation model, COSMO [24–26] was applied to calculate the structure of $3-(Me)_3N^+C_6H_4CO_2MeI^-$ of isolated molecule and in DMSO. The magnetic isotropic shielding constants were calculated using the standard GIAO/B3LYP/6-311G(d,p) (Gauge-Independent Atomic Orbital) approach with the Gaussian 03 program package using COSMO model [24–26].

3. Results and discussion

3.1. Molecular parameters

The molecular structure and atom numbering of $3-(Me)_3N^+C_6H_4CO_2MeI^-$ are shown in Fig. 1, while a projection of the crystal structure viewed in perpendicular to the layers formed of the ions is in Fig. 2. A view of the structure along the sheets of ions is presented in Fig. 3. The crystal structure of **1a** can be

Table 2

Experimental (X-ray) and calculated by the B3LYP/6-311G(d,p) method bond lengths (Å), bond and torsion angles (deg.) for methyl 3-(trimethylammonium)benzoate iodide.

| | X-ray | B3LYP | |
|------------------------------|------------------------|-------------|-----------|
| | 1a | 1b (vacuum) | 1c (DMSO) |
| Bonds | | | |
| O(1) - C(7) | 1.334(16) | 1.3336 | 1.3365 |
| O(1) - C(11) | 1.447(18) | 1.4400 | 1.4448 |
| O(2) - C(7) | 1.197(17) | 1.2128 | 1.2128 |
| C(1) - C(2) | 1.405(17) | 1.4032 | 1.3998 |
| C(1) - C(6) | 1.345(18) | 1.3923 | 1.3941 |
| C(1) - C(7) | 1.490(20) | 1.4959 | 1.4949 |
| C(2) - C(3) | 1.352(18) | 1.3820 | 1.3854 |
| C(3) - C(4) | 1.370(19) | 1.3999 | 1.3963 |
| C(4)-C(5) | 1.410(20) | 1.3872 | 1.3902 |
| C(5)-C(6) | 1.441(19) | 1.3962 | 1.3916 |
| N(1)-C(3) | 1.508(15) | 1.5180 | 1.5080 |
| N(1)-C(8) | 1.508(18) | 1.5049 | 1.5080 |
| N(1)-C(9) | 1.525(14) | 1.5117 | 1.5148 |
| N(1)-C(9A) | 1.525(14) | 1.5117 | 1.5151 |
| Angles | | | |
| O(1) - C(7) - C(1) | 1123(12) | 112 12 | 112.34 |
| O(2) - C(7) - C(1) | 172.3(12) 174.4(13) | 173.42 | 12.54 |
| O(2) = C(7) = O(2) | 123.7(13) | 123.42 | 123.74 |
| C(1) - C(2) - C(3) | 118 8(11) | 118.89 | 119 38 |
| C(1) = C(6) = C(5) | 120 5(13) | 119.00 | 119.50 |
| C(2) - C(3) - C(4) | 120.3(13) 122.8(12) | 121 23 | 120.75 |
| C(2) - C(1) - C(7) | 1177(12) | 116 14 | 116.98 |
| C(2) - C(1) - C(6) | 120 9(13) | 120 50 | 120 35 |
| C(2) - C(3) - N(1) | 120.5(11) | 120.81 | 121.08 |
| C(6) - C(1) - C(7) | 121.4(12) | 123.36 | 122.67 |
| C(3) - C(4) - C(5) | 119.6(13) | 119.31 | 119.41 |
| C(4) - C(3) - N(1) | 116.8(12) | 117.93 | 118.17 |
| C(4) - C(5) - C(6) | 117.3(12) | 120.33 | 120.59 |
| C(3) - N(1) - C(8) | 112.4(10) | 112.62 | 112.80 |
| C(3) - N(1) - C(9) | 109.8(7) | 109.50 | 109.60 |
| C(8)-N(1)-C(9) | 107.4(7) | 107.74 | 107.59 |
| C(9)—N(1)—C(9A) ^a | 109.8(13) | 109.68 | 109.59 |
| C(7) - O(1) - C(11) | 116.8(12) | 102.02 | 116.38 |
| Selected torsion angles | | | |
| C(1)-C(7)-O(1)-C(11) | 180 | -179.99 | 179.77 |
| C(2)-C(1)-C(7)-O(1) | 180 | 180.00 | -179.64 |
| C(6)-C(1)-C(7)-O(1) | 0 | 0.01 | 0.37 |
| C(2) - C(1) - C(7) - O(2) | 0 | 0.00 | 0.11 |
| C(6)-C(1)-C(7)-O(2) | 180 | -179.99 | -179.89 |
| C(2)-C(1)-C(6)-C(5) | 0 | 0.00 | 0.22 |
| C(3) - C(4) - C(5) - C(6) | 0 | -0.004 | -0.15 |
| C(2)-C(3)-N(1)-C(8) | 0 | 0.02 | -1.07 |
| C(4)-C(3)-N(1)-C(8) | 180 | 179.98 | 178.88 |
| C(2)-C(3)-N(1)-C(9) | -119.6(2) | 119.99 | 118.77 |
| C(4)-C(3)-N(1)-C(9) | 60.4(2) | -60.13 | 178.88 |
| C(2)-C(3)-N(1)-C(9A) | 119.6(7) | -119.83 | -120.93 |
| C(4) - C(3) - N(1) - C(9A) | -60.4(7) | 60.16 | 59.02 |
| C(1)-C(2)-C(3)-C(4) | 0 | 0.01 | -0.01 |
| C(1)-C(6)-C(5)-C(4) | 0 | 0.003 | -0.05 |

^a Symmetry code: x, -y + 0.5, z.



Fig. 1. The asymmetric unit of the crystal structure of methyl 3-(trimethylammonium)benzoate iodide (**1a**). Thermal ellipsoids have been drawn at the 50% probability level.

described as built of layers of cations and I anions lying in mirror planes perpendicular to the *y*-axis (Fig. 2). Additionally it is apparent that the cohesion forces in this crystal are controlled in nature by relatively short $N \cdots I$ and $N \cdots O$ distances (Table 3). Within the layers each cation forms three $CH \cdots I$ contacts to three I anions, and two contacts $CH \cdots I$ to the anions in neighboring layers (Table 4). Of these five $CH \cdots I$ contacts, two are formed by the ring hydrogen, C(4)H and C(6)H, and the remaining three by methyl hydrogen atoms, all of methyl $C(8)H_3$. Thus I anion is fivefold coordinated in the form of pseudo-trigonal bipiramid. Another type of short contacts is $C(11)-H(11A)\cdots O(2)$, involving methoxy atoms (Table 4).

The optimized structures (**1b** in vacuum and **1c** in DMSO) are compared to that determined by X-ray analysis in Fig. 4. The calculated bond lengths, bond angles, and selected torsion angles are summarized in Table 2. In the crystals the COOMe group is in plane of the benzene ring $(C(2)-C(1)-C(7)-O(1) = 180^\circ$, $C(2)-C(1)-C(7)-O(2) = 0^\circ$). In the optimized structure the conformation of the cation is also planar (Table 2). In crystal (**1a**) the anion I is engaged in contacts with the nitrogen atoms; the N···I distances are 4.451(3), 4.599(3), 4.795(3) and 7.752(3) Å. The other contacts in **1a** are between I anion and oxygen atoms (Table 3). The relation between N···I and O···I distances and the Mulliken atomic charges is linear (Fig. 5).



Fig. 2. Autostereographic projection [45] of the crystal structure of methyl 3-(trimethylammonium)benzoate iodide (1a) viewed perpendicular to the layers formed of the ions.



Fig. 3. An autostereogram along the sheets of ions (cf. Fig. 2).

Energies (Hartree, a.u.), dipole moments (μ , Debye), the shortest intermolecular contacts and atomic charges for methyl 3-(trimethylammonium)benzoate iodide.

| Compounds | Energy | μ | $N{\cdots}I$ | O(1)· · ·I | O(2)· · ·I | Atomic charge | | | |
|------------------------|----------------|---------|------------------------|-----------------------|-----------------------|---------------|---------|---------|---------|
| | | | | | | Ι | Ν | O(1) | O(2) |
| X-ray | | | | | | | | | |
| 1a | | | 4.541)(3) ^a | 4.794(2) ^d | 4.971(2) ^e | | | | |
| | | | 4.599(3) ^b | 5.038(2) | 6.953(2) | | | | |
| $P2IVD(C_2)(d_n)$ | | | $4.795(3)^{2}$ | | | | | | |
| 1b (vacuum) | -7553 65520995 | 25 8758 | 7.400 | 5 312 | 7 087 | | | | |
| Mulliken atomic charge | 7555.05520555 | 23.0750 | 7.100 | 5.512 | 7.007 | -0.8524 | -0.3892 | -0.3074 | -0.3659 |
| NPA | | | | | | -0.9167 | -0.3069 | -0.5157 | -0.6187 |
| MK | | | | | | -0.8346 | 0.1174 | -0.2225 | -0.5525 |
| CHELPG | | | | | | -0.7810 | 0.1193 | -0.3385 | -0.5393 |
| 1c (DMSO) | -7553.73668195 | 35.4759 | 8.162 | 5.849 | 7.728 | | | | |
| Mulliken atomic charge | | | | | | -0.988 | -0.3948 | -0.3301 | -0.3894 |
| NPA | | | | | | -0.9964 | -0.3134 | -0.5333 | -0.6353 |
| MK | | | | | | -1.0013 | 0.0712 | -0.3048 | -0.5999 |
| CHELPG | | | | | | -0.9418 | 0.0960 | -0.4291 | -0.5793 |

Symmetry codes:

a x = 1, y, z;b 1 = x, -y, 1 = z;c x = 0.5, y, 0.5 = z;d 0.5 = x, -y, z = 0.5;e 1 = x, -y, 1 = z;

| Table 4 | | |
|--|-------------------------------|----------------------|
| The closest $\text{CH}{\cdots}\text{I}$ contacts in methyl | 3-(trimethylammonium)benzoate | iodide (Å and deg.). |

| D—H····A | d(D—H) | $d(H{\cdots}A)$ | $d(D{\cdots}A)$ | <(D—H···A) |
|---------------------------------------|--------|-----------------|-----------------|------------|
| C(4)-H(4)···I(1) ^a | 0.93 | 3.04 | 3.958(12) | 170.9 |
| $C(5) - H(5) \cdots I(1)$ | 0.93 | 3.39 | 3.992(12) | 124.7 |
| $C(6)-H(6)\cdots I(1)$ | 0.93 | 3.25 | 3.932(13) | 132.2 |
| $C(11) - H(11B) \cdot I(1)^{b}$ | 0.96 | 3.29 | 4.090(14) | 142.6 |
| C(8)- $H(8A)$ ··· $I(1)$ ^c | 0.96 | 3.08 | 4.029(14) | 168.8 |
| C(8)-H(8B)···I(1) ^d | 0.96 | 3.02 | 4.029(14) | 170.3 |
| C(11)-H(11A)···O(2) ^e | 0.96 | 2.63 | 3.582(5) | 170.4 |

Symmetry codes:

^b 1.5 - x, 0.5 + y, -z;^c 2 - x, 1 - y, -z;

^d 1 + x, y, z;

```
<sup>e</sup> 0.5 + x, 1.5 – y, z.
```

The Natural Population Analysis (NPA) and Mulliken charges on the nitrogen atom are negative. On the other hand, fitting the electrostatic potential according to MK (MertzKollman) and CHELPG schemes, which are directed to accurately produce molar properties such as dipole moments, shows that the charge of the nitrogen atom is positive (Table 3). A similar charge distribution on the nitrogen atom was observed in betaine [27].



Fig. 4. Comparison of X-ray (1a) and B3LYP (1b-1c) structures of methyl 3-(trimethylammonium)benzoate iodide.

^a 0.5 + x, 0.5 – y, z;



Fig. 5. Correlation between N···I, O(1)···I and O(2)···I distances (Å) with the Mulliken atomic charges; $d(N \cdot I, O(1) \cdot I, O(2) \cdot I) = -4.0291 - 30.1876 \text{ M}(e)$, r = 0.9843 in vacuum and DMSO solution.

Experimental (δ_{exp} in DMSO-d₆) and predicted (δ_{pred} = a + b σ_{calc} , in DMSO) carbon-13 and proton chemical shifts, and calculated GIAO/B3LYP/6-311G(d,p) isotropic magnetic shielding constants (σ_{calc}) for methyl 3-(trimethylammonium)benzoate iodide.

| Atom | δ_{exp} | δ_{pred} | $\sigma_{ m calc}$ |
|-----------------------|----------------|------------------------|--------------------|
| | 1a | 1c | 1c |
| Carbon-13 | | | |
| C(1) | 131.26 | 130.80 | 46.4878 |
| C(2) | 121.06 | 118.53 | 59.2775 |
| C(3) | 147.43 | 145.72 | 30.9508 |
| C(4) | 130.54 | 125.27 | 52.2495 |
| C(5) | 130.77 | 132.70 | 44.5101 |
| C(6) | 125.47 | 132.63 | 44.5866 |
| C(7) | 165.0 | 163.90 | 12.0097 |
| C(8)-C(10) | 56.38 | 55.29 | 125.1609 |
| C(11) | 52.74 | 52.49 | 128.0769 |
| a ^a | | | 175.4223 |
| b^{b} | | | -0.9598 |
| r ^c | | | 0.9960 |
| Av. dif. ^d | | 0.37 | |
| R.m.s ^e | | 3.42 | |
| Proton | | | |
| H(2) | 8.43 | 8.15 | 23.5046 |
| H(4) | 8.31 | 7.99 | 23.6694 |
| H(5) | 7.82 | 8.14 | 23.5114 |
| H(6) | 8.14 | 8.37 | 23.2598 |
| OCH ₃ av | 3.93 | 4.12 | 27.8579 |
| NCH ₃ av | 3.67 | 3.53 | 28.4952 |
| a ^a | | | 29.9009 |
| b ^b | | | -0.9255 |
| r ^c | | | 0.9923 |
| Av. dif. ^d | | 0.04 | |
| R.m.s ^t | | 0.30 | |

^a Intercept.

^b Slope.

^c Correlation coefficient.

 $^{\rm d}$ Average (signed) differences between experimental and predicted chemical shifts.

^f Root-mean-square errors.

3.2. ¹H and ¹³C NMR spectra

The assignments of proton and carbon-13 chemical shifts for 3-(Me)₃N⁺C₆H₄CO₂Mel⁻, listed in Table 5, were based on two dimensional ¹H–¹H, ¹H–¹³C experiments (Figs. 6 and 7). Additionally, the ¹H–¹³C HMBC spectrum (Fig. 7) shows a three bond correlation between the C=O carbon atoms and C(2)H, C(6)H, C(11)H₃ protons in compound **1a** [28]. The relation between the experimental ¹³C and ¹H chemical shifts (δ_{exp}) and the Gauge Including Atomic



Fig. 6. 1 H– 1 H COSY spectrum of methyl 3-(trimethylammonium)benzoate iodide (1a) in DMSO-d₆.

Orbitals (GIAO) magnetic isotropic shielding constants (σ_{calc}), which are widely used [29–32], are usually linear and described by the equation $\delta_{exp} = a + b\sigma_{calc}$. The slope and intercept of the least-square correlation lines are used to scale the GIAO isotropic absolute shielding constants σ , and to predict chemical shifts in DMSO for **1c** (Fig. 8, Table 5). As shown in Table 5, the agreement between the experimental and calculation data is satisfactory, both for 13-carbon and hydrogen atoms.

3.3. FTIR spectra

The solid-state and calculated IR spectra of 3- $(Me)_3N^+C_6H_4CO_2MeI^-$ are shown in Fig. 9. The intense band at 1714 cm^{-1} arises from the vC=O vibration. Table 6 lists the experimental and calculated frequencies, and intensities for normal modes in the optimized molecule 1b. The comparison of calculated and experimental frequencies shows typical differences. Two reasons may be responsible for the differences between the experimental and computed spectra of the molecule investigated. The first is that the experimental spectrum was recorded for complex 1a in the solid state, while the computed spectrum refers to the isolated molecule 1b in the gas phase. The second reason is that the experimental results are anharmonic vibrations, while the calculated values are harmonic ones. Similar discrepancies between the calculated and experimental frequencies have been noted for 4-(trimethylammonium)benzoate iodide [8]. The overestimation of the computed wavenumbers is quite systematic and can be corrected by applying appropriate scaling factors or scaling equations [33–41]. Fig. 10 shows a linear relation between the experimental and calculated frequencies, characterized by a good correlation coefficient. The scaling procedure, recommended by Alcolea Palafox [36] was used. The scaled IR spectrum is shown in Fig. 9b and the predicted frequencies are listed in Table 6 as v_{scaleg} . Scaling of the harmonic vibrational frequencies reproduced the experimental solid-state FTIR frequencies with the r.m.s. error of 57.8 cm⁻¹. The vibrational band assignments of 3-(Me)₃N⁺C₆H₄CO₂Mel⁻ were made using Gauss-View molecular visualization program [42] and data [43,44].



Fig. 7. ¹H-¹³C HMBC spectrum of methyl 3-(trimethylammonium)benzoate iodide (1a) in DMSO-d₆.



Fig. 8. Plots of the experimental chemical shifts (δ_{exp}) in DMSO-d₆ vs. the magnetic isotropic shielding constants (σ_{calc}) from the GIAO/B3LYP/6-311G(d,p) calculated for methyl 3-(trimethylammonium)benzoate iodide in DMSO-d₆; $\delta_{exp} = a + b\sigma_{calc}$; (a) carbon-13, (b) proton.



Fig. 9. Vibrational spectra of methyl 3-(trimethylammonium)benzoate iodide: (a) solid-state FTIR spectrum; (b) calculated and scaled IR spectrum by the B3LYP/6-311G(d,p) approach for 1b.



Calculated frequencies by B3LYP/6-311G(d,p), cm⁻¹

Fig. 10. Correlation between the experimental and calculated wavenumbers (cm⁻¹) for methyl 3-(trimethylammonium)benzoate iodide; $v_{scaled} = 82.5544 + 0.9223$ v_{calc} , r = 0.9976.

Experimental (solid state) and calculated vibrational data for methyl 3-(trimethylammonium)benzoate iodide.

| v _{exp} ^a | v _{cal} | A _{cal} | v_{scaleq}^{b} | Assignments ^c |
|-------------------------------|------------------|------------------|------------------|--|
| 3125vw | 3222 | 5.55 | 3054 | vCH |
| 3093vw | 3192 | 1.51 | 3027 | vCH |
| 3082w | 3187 | 0.18 | 3022 | vCH |
| 3073w | 3182 | 0.40 | 3017 | $vCH + v_{as}CH_3$ |
| 3051w | 3174 | 10.46 | 3010 | $vCH + v_{as}CH_3$ |
| 3025m | 3172 | 28.74 | 3008 | v _{as} CH ₃ |
| | 3171 | 2.18 | 3007 | vasCH3 |
| 2998w | 3170 | 26.20 | 3006 | v _{as} CH ₃ |
| 2951w | 3163 | 2.15 | 3000 | v _{as} OCH ₃ |
| | 3162 | 0.02 | 2999 | v _{as} CH ₃ |
| 2897w | 3124 | 20.48 | 2964 | v _{as} CH ₃ |
| 2844vw | 3089 | 111.43 | 2932 | v _e CH ₃ |
| 2822vw | 3082 | 16.81 | 2925 | v _s OCH ₃ |
| | 3075 | 6.15 | 2919 | $vCH + v_sCH_3$ |
| | 3072 | 2.15 | 2916 | v _e CH ₃ |
| 2696vw | 3052 | 32.89 | 2898 | v _e CH ₃ |
| 1714s | 1767 | 351.39 | 1712 | vC=0 |
| 1674vw | 1636 | 31.22 | 1592 | vCC |
| 1654wv | 1600 | 32.33 | 1558 | vCC |
| 1638wv | 1530 | 58.37 | 1494 | vCC |
| 1611wv | 1510 | 24.98 | 1475 | vCC |
| 1591w | 1509 | 37.78 | 1474 | всн |
| 1517vw | 1501 | 14.23 | 1467 | δCH2 |
| 1487w | 1497 | 4.96 | 1463 | δOCH ₂ |
| 1468w | 1492 | 0.30 | 1459 | δOCH ₂ |
| 1454m | 1491 | 19.30 | 1458 | δCH2 |
| 1440w | 1486 | 0.65 | 1453 | δCH3 |
| 1418w | 1485 | 10.43 | 1452 | $\delta CH_3 + \delta CH$ |
| | 1475 | 0.02 | 1443 | $\delta CH_3 + \delta CH$ |
| 1408vw | 1463 | 24.37 | 1432 | δCH |
| | 1444 | 5.31 | 1414 | δCH |
| 1392vw | 1442 | 8.54 | 1413 | $vCOO + vCN + \delta CH_2$ |
| | 1366 | 6.45 | 1342 | $vCN + \delta CH_2$ |
| 1340vw | 1316 | 64.28 | 1296 | δCH3 |
| 1317w | 1301 | 420.58 | 1283 | ρCH |
| 1291m | 1287 | 47.74 | 1270 | vOCH ₃ |
| 1274m | 1258 | 1.32 | 1243 | γ CH + γ CH ₃ |
| 1238w | 1258 | 35.51 | 1243 | vCH ₃ |
| 1189vw | 1218 | 14.94 | 1206 | νCH |
| 1176wv | 1196 | 62.41 | 1186 | γ OCH ₃ + γ C-O |
| 1139w | 1174 | 0.77 | 1165 | vOCH ₃ |
| 1121vw | 1156 | 33.78 | 1149 | $\delta CH + wag CH_3$ |
| 1111vw | 1138 | 18.13 | 1132 | γCH ₃ |
| | 1137 | 0.61 | 1131 | ßRing |
| 1091vw | 1117 | 3.10 | 1113 | βRing |
| 1049vw | 1098 | 8.59 | 1095 | Ring |
| | 1072 | 0.02 | 1071 | ßRing |
| | 1069 | 0.09 | 1068 | βRing |
| 1003w | 1013 | 36.28 | 1017 | $\gamma CH_3 + \gamma CN$ |
| | | | | |

Table 6 (continued)

| v_{exp}^{a} | v _{cal} | A _{cal} | v_{scaleq}^{b} | Assignments ^c |
|---------------------|------------------|------------------|------------------|------------------------------|
| 985w | 998 | 38.08 | 1003 | γCH_3 |
| 958w | 975 | 0.34 | 982 | βRing |
| 941w | 963 | 14.76 | 971 | γ CH + τ wCOO |
| | 949 | 20.23 | 958 | $\gamma OCH_3 + \gamma CH_3$ |
| 885vw | 912 | 1.71 | 924 | γCH_3 |
| 874m | 873 | 38.72 | 888 | γСН |
| 822w | 829 | 44.11 | 847 | γСН |
| | 826 | 3.75 | 844 | $\gamma CH_3 + \gamma OCH_3$ |
| 755m | 776 | 31.73 | 798 | τRing |
| 742vw | 745 | 9.07 | 770 | $\tau Ring + \gamma CH$ |
| 739vw | 692 | 11.03 | 721 | τ Ring |
| 683w | 668 | 3.51 | 699 | $\tau Ring + \gamma CH$ |
| 635vw | 573 | 12.77 | 611 | βRing |
| 572vw | 563 | 1.16 | 602 | β Ring + γ CH |
| 561vw | 519 | 7.12 | 561 | β Ring + γ CN |
| 518vw | 470 | 1.19 | 516 | τ Ring + γ CN |
| 469vw | 444 | 0.09 | 492 | τ Ring + γ CN |
| 420vw | 424 | 0.10 | 474 | τ Ring + γ CN |
| Av. ^d | -39.11 | | -0.018 | |
| R.m.s. ^e | 91.05 | | 57.81 | |

^a Intensity: s - strong, m - medium, w - weak, vw - very weak.

^b Scaling equation: $v_{scaleq} = 82.5544 + 0.9223v_{cal}$; r = 0.9976.

^c as – asymmetric, s – symmetric, v – stretching, δ – deformation, ρ or β – rocking or in plane bending, γ – out-of-plane bending or wagging, τ w – twisting, β Ring – ring deformation, τ Ring – ring torsion.

^d Average (signed) differences between experimental and computed frequencies.
 ^e Root-mean-square errors.

4. Conclusions

In crystals of methyl 3-(trimethylammonium)benzoate iodide, **1a**, I ion is involved in four short N···I interactions of the average distance 5.422 Å. The cohesion forces are complemented by short CH···I and CH···O contacts. In the isolated molecule **1b** and in DMSO solution **1c**, according to the B3LYP/6-311G(d,p) calculations, the N···I distance is somewhat longer. The correlation between N···I and O···I atomic distances with the Mulliken atomic charges is linear. Charge on the quaternary nitrogen atom depends on options used for generating electrostatic potential-derived charges. The magnetic isotropic shielding constants, σ_{calc} , were calculated by the GIAO/B3LYP/6-311G(d,p) approach and linear correlations with ¹H and ¹³C chemical shifts were obtained. The B3LYP computed wavenumbers, scaled by the scaling equation, reproduced the FTIR solid-state experimental spectrum with r.m.s. of 57.8 cm⁻¹.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2012. 02.051.

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