

Tetrabutylammonium Hydrogen Bisbenzoate: Crystal Structure and Study of Short Hydrogen Bonds in Hydrogen Bisbenzoate Anion System†

Vedavati G. Puranik,^a Sudam S. Tavale,^a Venkat S. Iyer,^b Jagdish C. Sehra^b and Swaminathan Sivaram^{b,*}

^a Physical Chemistry Division, National Chemical Laboratory, Pune 411008, India

^b Polymer Chemistry Division, National Chemical Laboratory, Pune 411008, India

Tetrabutylammonium hydrogen bisbenzoate (bioxyanion) is a useful nucleophile, soluble in organic solvents and capable of catalysing the silylketene acetal initiated group transfer polymerisation of alkylacrylate monomers, as well as a carbonate interchange reaction of aromatic biphenols with diphenyl carbonate. Tetrabutylammonium hydrogen bisbenzoate has been characterised by ¹H and ¹³C NMR as well as FTIR spectroscopy and compared with its acid and corresponding salts. The structure of [N(Bu)₄]⁺[(PhCOO)₂H]⁻ was determined by single crystal X-ray diffraction. Crystals of C₃₀H₄₇NO₄ are orthorhombic, space group *P*_{ccn} with *a* = 13.038(1), *b* = 13.589(1), *c* = 17.124(3) Å and *Z* = 4. Half of each cation and anion is related to the other half by a two fold axis parallel to the *c* axis and nitrogen atoms as well as hydrogen atoms of the O...H...O group being placed on the two-fold axis. Two benzoate residues in the anion are linked through a short crystallographically symmetrical O...H...O hydrogen bond with O...O distance of 2.459(3) Å. Bifurcated C-H...O hydrogen bonds from oxygen of the carbonyls connect the cations and anions to form infinite chain networks in the crystal.

Quaternary alkylammonium hydrogen biscarboxylates (bioxyanions) have assumed significance in recent years on account of their ability to catalyse the group transfer polymerisation of alkylacrylate monomers in the presence of silylketene acetal as initiators.¹ The role of bioxyanion is to promote the facile nucleophilic desilylation of the ketene silyl acetal in a solvent such as tetrahydrofuran. We also observed that bioxyanions show significant catalytic activity for the melt phase carbonate interchange reaction of diphenylcarbonate with 4,4'-isopropylidenediphenol (bisphenol-A)² and as a general transesterification catalyst.³

Quaternary alkylammonium hydrogen biscarboxylates result from a reaction of equimolar proportions of a quaternary alkylammonium carboxylate with the corresponding carboxylic acid. They are generally crystalline solids, freely soluble in organic solvents and reasonably stable to moisture and handling.

Hydrogen biscarboxylate anions form very short hydrogen bonds, either symmetrical or unsymmetrical. In the former case, the anions have a crystallographic symmetry either $\bar{1}$ or 2. However, the question as to whether the hydrogen atom is situated at the symmetry point or at a disordered position has not been unequivocally answered.⁴

A number of hydrogen biscarboxylates have been examined crystallographically in the literature (Table 1).⁵⁻¹¹ In all ammonium hydrogen bisbenzoates studied, the hydrogen attached to the cation takes part in N-H...O hydrogen bonding. However, in the case of quaternary ammonium hydrogen bisbenzoates, where the nitrogen is completely substituted, there is no possibility for N-H...O hydrogen bonding. Therefore, a single crystal X-ray diffraction study of tetrabutylammonium hydrogen bisbenzoate was undertaken to delineate the nature of hydrogen bonding in the molecule and other geometrical features.

Experimental

Tetrahydrofuran, diethyl ether, benzene, light petroleum (b.p. 63°C), and benzoic acid were purified by reported procedures.¹² Tetrabutylammonium hydroxide in water (40%) and

methanol-toluene (20%) was used as received. Tetrabutylammonium benzoate¹³ and tetrabutylammonium hydrogen bisbenzoate¹ were synthesised by the procedures reported. Tetrabutylammonium benzoate was prepared by neutralising benzoic acid (1 g, 8.19 mmol) with 10.6 cm³ tetrabutylammonium hydroxide (20% in methanol-toluene). After stirring for 15 min at room temperature, the solvent was evaporated to dryness, and the viscous liquid was crystallised from dry benzene and light petroleum, yield 2.5 g (84%); $\delta_{\text{H}}(\text{CDCl}_3)$ 8.0 (2 H, m, Ar-H), 7.22 (3 H, m, Ar-H), 3.18 (2 H, t, NCH₂), 1.42 (4 H, m, CH₂-CH₂), 0.93 (3 H, t, CH₃) and 4.5 (broad OH, variable).

Tetrabutylammonium hydrogen bisbenzoate was prepared by dissolving benzoic acid (2 g, 16 mmol) in 15.9 cm³ 40% aqueous tetrabutylammonium hydroxide at 27°C. After 15 min stirring, the solution was extracted with 15 cm³ portions of dichloromethane (five times). Benzoic acid (2 g) was added to the dichloromethane extract. The resulting solution was dried over anhydrous MgSO₄, filtered and stripped free of solvent. Residual solid was dissolved in 15 cm³ dry tetrahydrofuran followed by addition of 50 cm³ of dry diethyl ether down the sides of the flask and was allowed to stand overnight. Long needles of bioxyanion appeared. Yield: 6.9 g (87%), m.p. 103°C (lit.,¹ m.p. 103-105°C) (Obsd. C, 73.8; H, 9.6; N, 2.6. Calc. C, 74.24; H, 9.67; N, 2.89%); $\delta_{\text{H}}(\text{CDCl}_3)$ 8.00 (4 H, m, Ar-H), 7.25 (6 H, m, Ar-H), 3.08 (2 H, t, NCH₂), 1.31 (4 H, m, CH₂CH₂), 0.84 (3 H, t, CH₃) and 8.35 (OH, broad and variable).

FTIR Spectra were recorded in fluolube (and smeared in the case of tetrabutylammonium benzoate) on a Perkin-Elmer model 16PC FTIR spectrophotometer. ¹H NMR spectra were recorded using Bruker WH-90 FT NMR spectrometer, in CDCl₃ at room temperature using trimethylsilane as internal standard. ¹³C NMR measurements were made using a Bruker MSL 300 NMR spectrometer operating at 75.5 MHz using a 5 mm probe. The compounds were dissolved in DMSO and ¹³C spectral data were collected with broad band proton decoupling. A capillary containing D₂O was used for field

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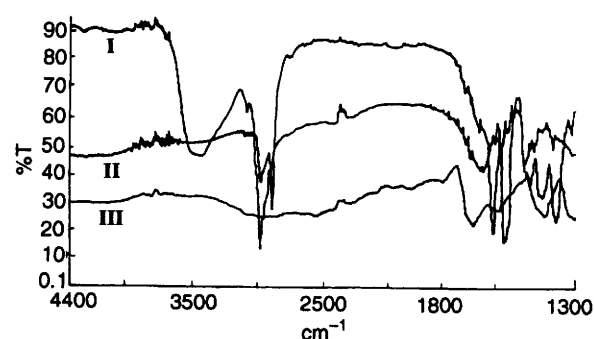
Table 1 O...O and C...O distances for carboxylate anion having symmetric hydrogen bond in hydrogen bisbenzoate system

Compound	Ref.	Space group	Symmetry	C(7)–O(1) (Å)	C(7)–O(2) (Å)	O(1)...O(1)' (Å)
[K] ⁺ [H(O ₂ CPh) ₂] [–]	4	C2/c	$\bar{1}$	1.24	1.22	2.51
[K] ⁺ [H(O ₂ C–Ar–OMe- <i>p</i>) ₂] [–]	5	<i>P</i> _{bcn}	2	1.32(2)	1.24(2)	2.48(2)
[K] ⁺ [H(O ₂ C–Ar–F- <i>p</i>) ₂] [–]	6	C2/c	$\bar{1}$	1.293(4)	1.231(4)	2.460(4)
[K] ⁺ [H(O ₂ C–Ar–Cl- <i>m</i>) ₂] [–]	8	C2/c	$\bar{1}$	1.290(6)	1.223(6)	2.437(6)
[K] ⁺ [H(O ₂ C–Ar–OH- <i>p</i>) ₂] [–]	7	<i>P</i> 2 ₁ /c	$\bar{1}$	1.284(6)	1.232(5)	2.458(6)
[NH ₄] ⁺ [H(O ₂ CPh) ₂] [–]	9	C2/c	$\bar{1}$	1.27(1)	1.26(1)	2.46(1)
[C ₅ H ₁₀ NH ₂] ⁺ [H(O ₂ C–Ar–Br- <i>p</i>) ₂] [–]	10a	<i>P</i> $\bar{1}$	$\bar{1}$	1.278(6)	1.226(6)	2.451(6)
				1.283(6)	1.242(6)	2.460(8)
[C ₅ H ₁₀ NH ₂] ⁺ [H(O ₂ C–Ar–Me- <i>p</i>) ₂] [–]	11	<i>P</i> _{ccn}	2	1.282(3)	1.232(3)	2.473(4)
[C ₆ H ₁₂ NH ₂] ⁺ [H(O ₂ C–Ar–Cl- <i>p</i>) ₂] [–]	10c	C2/c	$\bar{1}$	1.283(3)	1.226(3)	2.437(4)
[C ₄ H ₈ NH ₂] ⁺ [H(O ₂ C–Ar–Me- <i>p</i>) ₂] [–]	10b	<i>P</i> _{ccn}	2	1.297(3)	1.226(3)	2.445(4)
[NBu ₄] ⁺ [H(O ₂ CPh) ₂] [–]	<i>a</i>	<i>P</i> _{ccn}	2	1.270(4)	1.230(4)	2.459(3)

^a Present study.**Table 2** Crystal data, data collection details and refinement parameters for [N(Bu)₄]⁺[(PhCOO)₂H][–]

Molecular weight <i>M</i>	485.7
Cell dimension (Å):	
<i>a</i>	13.038(1)
<i>b</i>	13.589(1)
<i>c</i>	17.124(3)
Volume of the cell <i>V</i> (Å ³)	3033.92(4)
Space group	<i>P</i> _{ccn}
<i>Z</i>	4
<i>F</i> (000)	1064
<i>T</i> (K)	293
Cell constants from 24 reflections, range 2θ(°)	21–38
<i>D</i> _c (mg m ^{–3})	1.063
Radiation λ (Å) (Mo–Kα)	0.7107
Monochromator	Graphite
Crystal size (mm)	0.3 × 0.48 × length
Linear absorption coefficient μ (cm ^{–1})	0.74
Data collection method	ω/2θ
Average scan speed (°/min ^{–1})	1
2θ limit (°)	47
<i>h</i> , <i>k</i> , <i>l</i> range	<i>h</i> 0 to 14 <i>k</i> 0 to 15 <i>l</i> 0 to 19
Standard reflections for intensity control	(5, 4, 6) (6, 4, 5) and (5, 2, 5)
Intensity variation in standard reflection (%)	< 4
Number of unique reflections collected	2112
Number of unique reflections with <i>I</i> ≥ 3σ(<i>I</i>)	1226
Final <i>R</i> = $\frac{\sum F_o - F_c }{\sum F_o }$	0.055
Final <i>R</i> _w = $\left[\frac{\sum w(F_o - F_c)^2}{\sum w F_o ^2} \right]^{1/2}$	0.051
Final <i>S</i>	1.38
Cruickshank weights $w = [a + b F_o + c F_o ^2]^{-1}$	<i>a</i> = 4.7 <i>b</i> = 1.0 <i>c</i> = 0.009
Final Δρ Excursions (e Å ^{–3})	< 0.2
(Δ/σ) _{max}	0.3
Data collected on	Enraf–Nonius CAD 4F/11M single X-ray diffractometer
Computations on	NEC-1000s computer

frequency lock. The chemical shifts were referenced to dioxane (67.4 ppm from TMS). X-Ray diffraction studies were performed on Enraf–Nonius CAD-4F/11M four circle single crystal X-ray diffractometer. Details of the diffraction experiments, crystal data, data collection and refinement parameters

**Fig. 1** FTIR spectra of benzoic acid 3, its tetrabutylammonium salt 1 and tetrabutylammonium hydrogen bisbenzoate 2

are given in Table 2. The intensities were corrected for Lorentz and polarisation effects but no corrections were made for extinction or absorption.

The structure was solved by direct methods using MULTAN78.¹⁴ A full matrix least square refinement¹⁵ of scale factor, positional and anisotropic thermal parameters for non-hydrogen atoms and isotropic refinement for hydrogens was carried out. Hydrogen atoms were located on the basis of stereochemical considerations, and confirmed by difference Fourier except for hydrogen of the carboxylate group which was assumed to lie on a two-fold axis. The final *R* value at convergence was 0.051. Neutral atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography.¹⁶

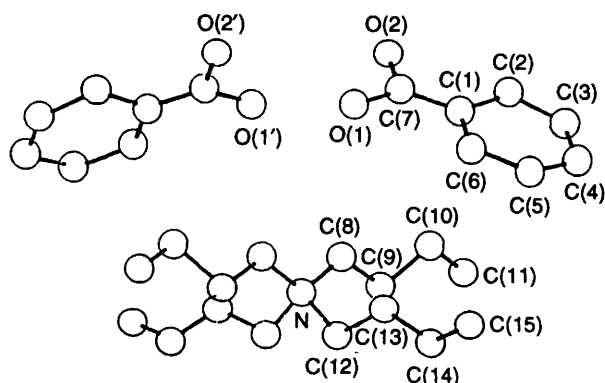
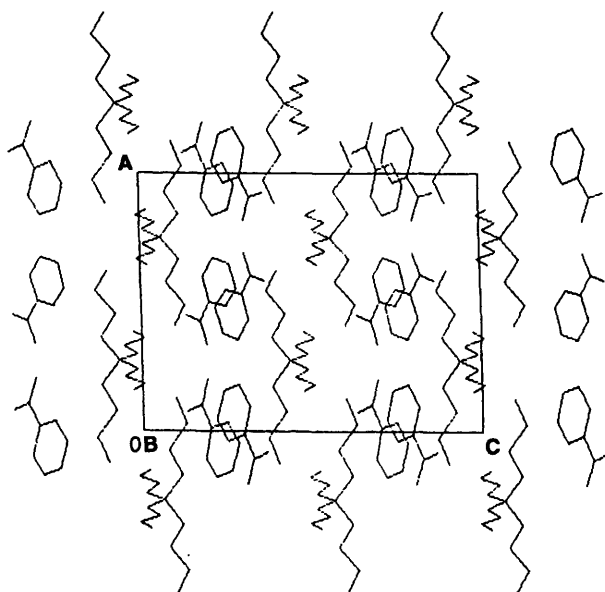
Results and Discussion

The FTIR spectra of benzoic acid, tetrabutylammonium benzoate and tetrabutyl hydrogen bisbenzoate are shown in Fig. 1.

The dimeric nature of benzoic acid in solid state is evident from characteristic absorptions in the region 3000–2500 cm^{–1} containing several submaxima. Tetrabutylammonium benzoate exhibits a strong absorption at 3400 cm^{–1} due to water of hydration. In tetrabutylammonium hydrogen bisbenzoate no O–H stretching band was observed. This observation is similar to that on alkali metal bis benzoates.⁵ In tetrabutylammonium bishydrogen benzoate, the carbonyl absorption peak is observed at 1648 cm^{–1}. On further resolution of this peak, two peaks were observed, one at 1660 cm^{–1} and the other at 1640 cm^{–1}. This could be attributed to two types of C–O bonds which have bond distances lying between a carbonyl and the carboxylate groups.

Table 3 Chemical shifts (ppm) of the carbons of benzoic acid **3**, its tetrabutylammonium salt **1** and the hydrogen bisbenzoate **2** in DMSO (undeuteriated)

SR No.	Compound	Carbonyl carbon	Ipso carbon	Aromatic carbons			Butyl carbons			
				<i>Ortho</i>	<i>Meta</i>	<i>Para</i>	NCH ₂	CH ₂	CH ₂	CH ₃
1	1	169.81	142.52	130.00	128.17	129.49	58.90	24.40	20.50	14.79
2	2	168.67	137.84	130.39	129.01	131.66	58.94	24.45	20.57	14.84
3	3	168.61	132.09	130.57	129.81	134.09	—	—	—	—

**Fig. 2** Perspective view of the molecules showing the crystallographic number of atoms**Fig. 3** Packing of the molecules down *b* axis

¹³C NMR chemical shifts of benzoic acid, tetrabutylammonium benzoate and tetrabutylammonium hydrogen bisbenzoate in undeuteriated DMSO are shown in Table 3.

The carbonyl group in tetrabutylammonium benzoate appears downfield compared to benzoic acid as a result of deshielding owing to anisotropy effects and electric field effects.¹⁷ However, electric field and anisotropy effects are found to produce considerable deshielding (~8–10 ppm) of the carbonyl carbon as a result of deprotonation with alkali metal bases. The smaller shift (~1.2 ppm) in the present case can be ascribed to the use of non-aqueous solvent and a non-metallic counter-cation. The upfield shift of the carbonyl carbon and ipso carbon of the tetrabutylammonium hydrogen bisbenzoate appears as a mean of the chemical shifts of the corresponding

Table 4 Selected bond lengths (Å) and bond angles (°) with esds in paranthesis

Bond lengths		Bond angles	
O(1)–C(7)	1.270(4)	C(2)–C(1)–C(7)	119.7(3)
O(2)–C(7)	1.230(4)	C(6)–C(1)–C(7)	121.7(3)
C(1)–C(7)	1.499(4)	O(1)–C(7)–O(2)	124.7(3)
N–C(8)	1.523(3)	O(1)–C(7)–C(1)	115.7(3)
N–C(12)	1.523(3)	O(2)–C(7)–C(1)	119.6(3)
		C(8)–N–C(12)	111.1(2)
		C(8)–N–C(8')	106.4(2)
		C(12)–N–C(12')	106.1(2)

carbons in benzoic acid and tetrabutylammonium hydrogen bisbenzoate.

Some selected bond lengths and bond angles are listed in Table 4. Tables of atomic co-ordinates, anisotropic thermal parameters, hydrogen positions, and structure factors have been deposited at Cambridge Crystallographic Data Centre (CCDC).*

A perspective view of both cation and anion along with crystallographic numbering of atoms is shown in Fig. 2.

Fig. 3 gives packing of the molecules down the *b* axis. Half of each cation as well as anion is related to other half by a two-fold axis parallel to the *c* axis and nitrogen and hydrogen atoms of O...H...O group, forming an intramolecular hydrogen bond being placed on the two-fold axis. Two benzoate residues in the anion are linked by short, crystallographically symmetrical^{5–11} O...H...O bonds [O...O = 2.459(3), O–H = 1.270(4) Å and O...H...O = 171(3)°]. Bifurcated intermolecular C–H...O hydrogen bonds from the oxygen of the carbonyls connecting the cations and anions form an infinite chain network in the crystal. [O(2)...C(5) (2 – *x*, 1/2 + *y*, 1/2 + *z*) = 3.416(4), C(5)–H = 0.99(4), O(2)...H = 2.53(4) Å, O(2)...H–C(5) = 149(3)°, O(2)...C(12) (*x*, 1/2 – *y*, 1/2 + *z*) = 3.233(4), O(2)...H = 2.30(3), C(12)–H = 0.97(3) Å, and C(12)–H...O(2) = 160(3)°].

The dihedral angle between the two phenyl rings of bisbenzoate group is 72.6° and that between the phenyl ring and carboxylate group is 2.7°. The phenyl ring and the atoms C(7) and O(2) of the carboxylate group form a good plane and atom O(1) is placed at a distance of 0.08 Å from the plane.

Cations and anions are arranged alternately along the *c* axis (Fig. 3). The nitrogen atom of the cation has a distorted tetrahedral geometry (Table 4).

Table 1 provides O...O distances for crystallographically symmetric hydrogen bond distances for the hydrogen bisbenzoate anion compounds examined so far. The hydrogen atom is assumed to lie either on $\bar{1}$ or 2 symmetry and hence H...O¹ distances and O...H...O' angles are omitted. It is seen from this table that for symmetrical compounds, for which

* Details of the deposition scheme are available in 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1993, Issue 1.

the values of distances are quoted up to three places, the intramolecular O...O distances range from 2.437 to 2.473 Å while C(7)–O(1) and C(7)–O(2) distances range from 1.270 to 1.297 Å and 1.223 to 1.242 Å respectively. These values compare well with those given for different symmetrical hydrogen biscalboxylate anions and correspond to the average for ionized and neutral residues for asymmetrical hydrogen biscalboxylate compounds.⁴

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