Instrumental Achievements

Crystal Structure of 2-Benzoyl-3,4,5,6-tetrachlorobenzoic Acid

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2-Benzoylbenzoic acid derivatives are widely used as reaction intermediates in the synthesis of a variety of phthaleins and fluorans. Besides their importance in synthetic chemistry, this class of compounds also furnishes interesting research topics in structural chemistry. Lalancette *et al*.[1] studied the X-ray structure of the simplest acid, 2-benzoylbenzoic acid (BBA). They demonstrated that BBA crystallizes in dimorphic (anhydrous and hydrated) forms, where BBA molecules take the open conformation as shown in Fig. 1(a), and form centrosymmetric dimers through intermolecular hydrogen bonds between carboxylic acid groups. This type of intermolecular hydrogen bonding is normally seen in carboxylic acids. Recently we have analyzed the X-ray structure of *o*-(*p*-*N*,*N*-dimethylaminobenzoyl)benzoic acid (DMABBA) and pointed out that intermolecular hydrogen bonds are formed between the carboxyl OH and the ketone oxygen of adjacent DMABBA molecules to form catemeric chains.[2] In solution, 2-benzoylbenzoic acids also exist as the lactone form (Fig. 1(b)) as well as the open form. Bhatt *et al*. investigated the effect of the benzene ring substitution on the tautomeric equilibrium between the open and the lactone form.[3] Interestingly, he suggested that 2-benzoyl-3,4,5,6-tetrachlorobenzoic acid (TCBBA) takes the lactone form in the crystalline state. In this work, we have undertaken the X-ray analysis of TCBBA in order to clarify the crystal and molecular characteristics of 2-benzoylbenzoic acids having a typical lactone form.

The title compound was prepared as follows. Anhydrous aluminum(III) chloride (2.320 g:8.1 mmol) was added portionwise to tetrachlorophthalic anhydride (2.160 g:16.2 mmol) in benzene (20 ml). The mixture was refluxed for 20 h. The reaction was stopped by adding 1 M HCl (10 ml) and the raw product was extracted with ethyl acetate. After evaporation of the extract *in vacuo*, the residue was purified by column chromatography (hexane/ethyl acetate = 1/3). Colorless crystals suitable for X-ray diffraction analysis were obtained by crystallization from aqueous acetone solution at room temperature (m.p. 196.0˚C).

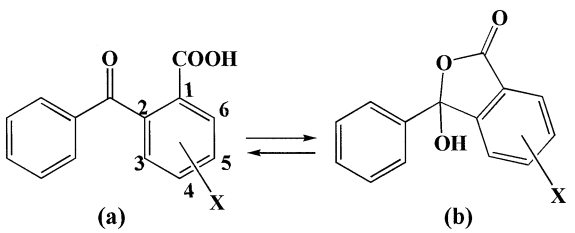

Fig. 1 Tautomerism of 2-benzoylbenzoic acid derivatives: (a) the open and (b) the lactone form.

All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by a difference Fourier synthesis and a geometrical calculation, with the parameters of H atom bonded to O3 also being refined. The crystal and experimental data are listed in Table 1. The final fractional atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are given in Table 2. Selected bond

Table 1 Crystal and experimental data

TCBBA	
Formula: $C_{14}H_6O_3Cl_4$	
Formula weight = 364.01	
Crystal color, habit: colorless, plates	
Crystal size: 0.05 × 0.11 × 0.35 mm	
Crystal system: triclinicic	
Space group: $P\bar{1}$	$Z = 2$
Radiation: Mo K_α (0.71069 Å)	
T = 296 K	
$2\theta_{max}$ = 54.25˚	
Scan type: ω–2θ	
F(0 0 0) = 364.00	
a = 8.474(3)Å	α = 87.19(1)˚
b = 8.928(1)Å	β = 82.33(1)˚
c = 10.363(3)Å	γ = 115.520(2)˚
V = 696.1(3)Å^3	
D_{calc} = 1.736 g/cm^3	
R, Rw = 0.067, 0.080	
μ = 8.53 cm^{-1}	
No. of observations = 1548 ($I > 2.00\sigma(I)$)	
No. of variables = 194	
Goodness-of-fit = 1.08	
$(\Delta/\sigma)_{max}$ = 0.001	
$(\Delta\rho)_{max}$ = 0.32 eÅ^{-3}	
$(\Delta\rho)_{min}$ = –0.25 eÅ^{-3}	
Measurement: Quantum CCD/Rigaku AFC-7	
Program system: teXsan	
Structure determination: direct method (SIR92)	
Refinement: full-matrix least-squares	

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Table 2 Positional parameters of non-hydrogen atoms

Atom	*x*	*y*	*z*	B_{eq}/Å^2
Cl(1)	0.6066(2)	0.5779(1)	0.6960(1)	4.13(3)
Cl(2)	0.8171(2)	0.6106(1)	0.4164(1)	4.56(3)
Cl(3)	0.8867(2)	0.3169(2)	0.3237(1)	5.01(3)
Cl(4)	0.7514(2)	-0.0151(1)	0.5134(1)	4.55(3)
O(1)	0.4372(4)	0.0365(3)	0.8850(3)	3.25(6)
O(2)	0.5338(5)	-0.1385(3)	0.7977(3)	3.83(7)
O(3)	0.5801(4)	0.3025(3)	0.9434(3)	3.55(7)
C(1)	0.6090(6)	0.1335(4)	0.6816(4)	2.88(7)
C(2)	0.5712(5)	0.2623(4)	0.7209(4)	2.97(8)
C(3)	0.6394(5)	0.4135(5)	0.6416(4)	3.31(8)
C(4)	0.7329(5)	0.4264(5)	0.5185(4)	3.11(8)
C(5)	0.7681(6)	0.2961(5)	0.4765(5)	3.62(9)
C(6)	0.7059(6)	0.1458(5)	0.5586(4)	3.37(9)
C(7)	0.5261(5)	-0.0071(5)	0.7882(4)	2.86(8)
C(8)	0.4723(6)	0.2137(4)	0.8608(4)	3.07(8)
C(9)	0.2891(5)	0.2126(4)	0.8796(4)	3.11(8)
C(10)	0.2600(6)	0.3280(5)	0.9522(5)	3.85(9)
C(11)	0.0914(8)	0.3257(6)	0.9662(6)	4.8(1)
C(12)	-0.0443(7)	0.2123(7)	0.9106(6)	4.6(1)
C(13)	-0.0140(6)	0.0973(6)	0.8406(5)	4.3(1)
C(14)	0.1502(6)	0.0959(5)	0.8256(4)	3.60(9)

$B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$.

Table 3 Selected bond lengths (Å), bond angles (˚) and torsion angles (˚)

Atom	Atom	Distance	Atom	Atom	Distance
Cl(1)	C(3)	1.714(3)	O(2)	C(7)	1.202(4)
Cl(2)	C(4)	1.718(4)	O(3)	C(8)	1.359(6)
Cl(3)	C(5)	1.714(4)	C(1)	C(2)	1.386(4)
Cl(4)	C(6)	1.711(3)	C(1)	C(7)	1.479(5)
O(1)	C(7)	1.347(4)	C(2)	C(8)	1.515(5)
O(1)	C(8)	1.479(4)	C(8)	C(9)	1.534(5)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
O(1)	C(7)	O(2)	121.9(3)	O(3)	C(8)	C(2)	110.1(3)
O(1)	C(7)	C(1)	107.9(3)	O(3)	C(8)	C(9)	114.7(3)
O(1)	C(8)	O(3)	108.8(3)	C(1)	C(2)	C(8)	108.8(3)
O(1)	C(8)	C(2)	102.1(3)	C(2)	C(1)	C(7)	108.3(3)
O(1)	C(8)	C(9)	105.6(3)	C(2)	C(8)	C(9)	114.6(4)
O(2)	C(7)	C(1)	130.1(3)	C(7)	O(1)	C(8)	111.9(3)

Atom	Atom	Atom	Atom	Angle	Atom	Atom	Atom	Atom	Angle
O(1)	C(7)	C(1)	C(2)	2.1(5)	O(2)	C(7)	C(1)	C(6)	6.1(9)
O(1)	C(8)	C(2)	C(1)	-8.3(5)	O(3)	C(8)	O(1)	C(7)	-106.4(4)
O(1)	C(8)	C(2)	C(3)	179.6(5)	C(1)	C(2)	C(8)	C(9)	-121.8(4)
O(1)	C(8)	C(9)	C(10)	134.8(4)	C(1)	C(7)	O(1)	C(8)	-7.8(5)
O(2)	C(7)	O(1)	C(8)	170.1(5)	C(2)	C(8)	O(1)	C(7)	9.9(5)
O(2)	C(7)	C(1)	C(2)	-175.6(5)	C(7)	C(1)	C(2)	C(8)	4.2(5)

Estimated standard deviations in the least significant figure are given in parentheses.

distances, bond angles and torsion angles are listed in Table 3.

In the crystal structure, the TCBBA molecule exists as the lactone form. So this is the first report on the X-ray structure of 2-benzoylbenzoic acids having the lactone form. There is a pair of enantiomers, (*R*)- and (*S*)-TCBBA, in the unit cell. Figure 2 presents a view of an (*R*)-TCBBA molecule with the atom-labeling scheme. As shown in Fig. 3, enantiomeric TCBBA molecules are centrosymmetrically connected through the intermolecular hydrogen bond between the OH and the lactone carbonyl groups. This hydrogen bonding forms a twelve-membered ring [O2···O3^{i}] 2.823(4)Å, [O2···H-O3^{i}] 167(7)˚, symmetry operation i) $-x + 1, -y, -z + 2$] with a graph-set motif of $R_2^2(12)$.[4] This type of the hydrogen bonding pattern is quite unique because BBA derivatives in the open form usually form eight-membered rings with a graph-set motif of $R_2^2(8)$. The lactone moiety of TCBBA is well characterized by IR bands at 3300 and 1752 cm^{-1}, which are assigned to the OH stretching and the C=O stretching vibration, respectively.

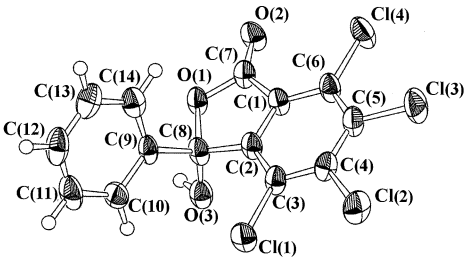

Fig. 2 Moleculer structure of TCBBA with the atom numbering. Thermal ellipsoids of the non-hydrogen atoms are scaled to enclose 50% probability. The spheres of the hydrogen atoms are drawn in an arbitrary scale.

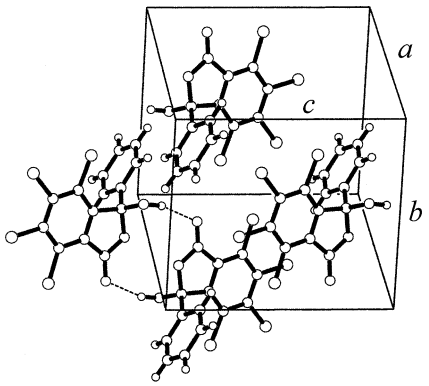

Fig. 3 Molecular packing and intermolecular hydrogen bondings.

The molecular geometries of the lactone moiety are close to those of phenolphthalein (PP).[5] The tetrachlorobenzene ring and the lactone ring are planar within 0.149(7)Å and 0.110(6)Å, respectively. The dihedral angle between the least-squares planes of the tetrachlorobenzene and lactone rings is 1.1(2)˚. Thus the lactone ring is almost coplanar with the tetrachlorobenzene ring.

References

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