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The Crystal and Molecular Structure of *p*-Bromobenzoic Acid

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In the course of X-ray crystallographic study of the 1:1 addition compound of *p*-bromobenzoic acid and piperidine,[1] it became desirable to determine the molecular structure of the parent acid itself. The unit cell dimensions and space group of *p*-bromobenzoic acid have already been determined by Toussaint,[2] who has also shown that the (*hk*0) Patterson projection closely resembles that of *p*-chlorobenzoic acid.[2] However, no further refinement of the structure has yet been undertaken. This paper presents the three-dimensional X-ray structure analysis of *p*-bromobenzoic acid.

Experimental

Crystals obtained by slow evaporation from ether solution were monoclinic needles elongated along the *c*-axis. Cell constants were determined from Weissenberg and oscillation photographs, and calibrated with sodium chloride.

Crystal data: *p*-bromobenzoic acid, $C_7H_5O_2Br$; M=201.0; mp=251°C, monoclinic, $a=29.59(5)$, $b=6.15(1)$, $c=3.98(1)$ Å, $\beta=95.5(1)°$, $U=720.4$ Å^3, $D_m=1.859$, $D_x=1.854$ g·cm^{-3}, $Z=4$.

Linear absorption coefficient for Cu $K\alpha(\lambda=1.5418$ Å); $\mu=76.5$ cm^{-1}. $F(000)=392$.

Absent spectra: *h*0*l* when *h* is odd, 0*k*0 when *k* is odd. Space group is $P2_1/a$.

The cell dimensions are substantially identical with those of Toussaint.[2]

Reflections were recorded with Cu $K\alpha$ radiation (1.5418 Å) by means of the equi-inclination Weissenberg technique, for the layers of *hk*0 to *hk*2, using a crystal of $0.19\times0.20\times1.5$ mm. 837 independent non-zero reflections were measured visually, whose intensities ranged from 1 to 10165. The spot shape of the Weissenberg photographs of the *h*0*l* layer was unsuitable for intensity measurement so that these reflections were omitted in the refinement. Corrections were made for the Lorentz and polarization factors, and for the spot shape.

Structure Determination

Approximate positional parameters of all non-hydrogen atoms were obtained from two-dimensional sharpened Patterson projections onto (010) and (001). The structure thus obtained was refined by the block-diagonal least-squares method,[3] first with isotropic thermal parameters and then with anisotropic ones for the bromine and oxygen atoms. The weighting scheme used was:

$$\sqrt{w} = 0.0, \text{ if } F_o \leq F_{min}(2.0),$$

and

$$\sqrt{w} = 1.0, \text{ if } F_{min} < F_o \leq F_{max}(20.25),$$
$$\sqrt{w} = F_{max}/F_o, \text{ if } F_o > F_{max},$$

but zero weight was given for two strong reflections, 201 and 211, because they were seriously affected by extinction.

The *R* index became 0.102. At this stage, no atomic parameters shifted by as much as 0.3 σ, hence the refinement was terminated. The difference synthesis

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2) J. Toussaint, *Mém. Soc. Sci. Liège*, **12** (3), 1 (1952).

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revealed only broad peaks corresponding to five hydrogen atoms.

Finally structure factors were calculated for all atoms including the hydrogen atoms, on the assumption of the C–H bond length of 1.08 Å, the O–H bond length of 1.05 Å, the normal bond angles, and the same isotropic temperature factors as those of the carbon or oxygen atoms to which they are attached. The final R index was 0.096 for 837 non-zero reflections.

The atomic scattering factors used in the calculation were those of Hanson, Herman, Lea, and Skillman.[4] The numerical calculations were performed with the aid of a HITAC 5020E computer of the Computer Center of The University of Tokyo.

Results and Discussion

The final atomic parameters are given in Table 1 and bond lengths and angles are listed in Table 2. Arrangement of molecules in a crystal, the selected intermolecular contacts, and the numbering of atoms are shown in Fig. 1.

Table 1. Final atomic parameters along with their estimated standard deviations within parentheses

Atom	x/a	y/b	z/c	B(Å^2)
C(1)	0.0900(3)	0.3165(15)	0.8197(32)	2.24(15)
C(2)	0.0814(3)	0.5151(15)	0.6558(33)	2.67(17)
C(3)	0.1178(3)	0.6452(16)	0.5907(32)	2.79(18)
C(4)	0.1619(3)	0.5780(15)	0.6691(32)	2.48(16)
C(5)	0.1710(3)	0.3743(15)	0.8370(32)	2.49(17)
C(6)	0.1348(4)	0.2460(15)	0.9149(39)	2.93(19)
C(7)	0.0508(3)	0.1713(17)	0.8938(33)	2.78(17)
O(8)	0.0579(2)	0.0056(11)	1.0602(24)	a)
O(9)	0.0103(3)	0.2388(12)	0.7786(32)	a)
Br(10)	0.2115(1)	0.7577(2)	0.5769(4)	a)

a) The anisotropic thermal parameters are expressed as: $\exp(-B_{11}h^2-B_{22}k^2-B_{33}l^2-B_{12}hk-B_{13}hl-B_{23}kl)$. All values of B_{ij} should be multiplied by 10^{-4}.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(8)	8(1)	224(19)	701(98)	6(6)	−35(13)	371(62)
O(9)	6(8)	293(25)	1316(151)	3(7)	−23(16)	539(76)
Br(10)	10(0)	328(4)	690(25)	−36(1)	25(3)	37(11)

Table 2. Bond lengths (Å) and angles (°) along with their estimated standard deviations within parentheses

Bond	Length	Bond	Angle
Br(10)–C(4)	1.902(10)	C(2)–C(1)–C(6)	121.3(9)
O(8)–C(7)	1.225(14)	C(2)–C(1)–C(7)	119.8(8)
O(9)–C(7)	1.307(13)	C(6)–C(1)–C(7)	118.9(9)
C(1)–C(7)	1.517(14)	C(1)–C(2)–C(3)	118.8(9)
C(1)–C(2)	1.400(14)	C(2)–C(3)–C(4)	121.4(9)
C(2)–C(3)	1.388(14)	Br(10)–C(4)–C(3)	120.9(8)
C(3)–C(4)	1.377(13)	Br(10)–C(4)–C(5)	119.1(7)
C(4)–C(5)	1.436(14)	C(3)–C(4)–C(5)	120.0(9)
C(5)–C(6)	1.391(15)	C(4)–C(5)–C(6)	119.2(8)
C(6)–C(1)	1.411(14)	C(1)–C(6)–C(5)	119.3(10)
		O(8)–C(7)–O(9)	124.0(10)
		O(8)–C(7)–C(1)	120.1(9)
		O(9)–C(7)–C(1)	115.8(9)

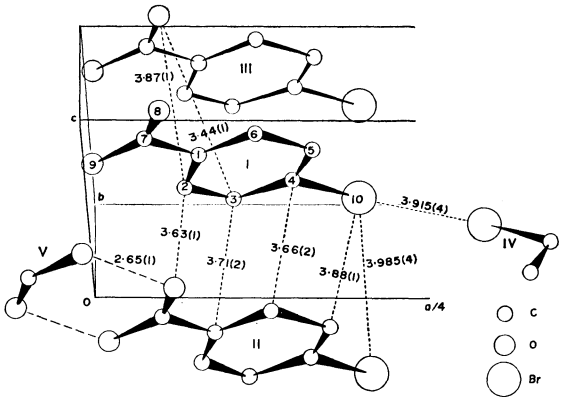

Fig. 1. Arrangement of the molecules in the crystal, the selected intermolecular contacts (Å), and the numbering of atoms.
Key for molecules I: x, y, z II: $x, y, z-1$
III: $x, 1+y, z$ IV: $1/2-x, 1/2+y, 1-z$
V: $-x, -y, 1-z$
Molecules unnecessary for illustration are omitted.
------ Intermolecular contact, ----- Hydrogen bond.

Pairs of molecules are linked through O–H–O hydrogen bonds (2.646±0.012 Å) forming dimers, and are stacked along the c-axis. Values for the O–H–O hydrogen bond length of *para*-substituted benzoic acids[5–9] range from 2.61 Å for *p*-aminobenzoic acid[5] to 2.65 Å for *p*-nitrobenzoic acid,[6] but no influence of *para*-substituents on the hydrogen bond length is discernible.

Unlike aliphatic carboxylic acids, *para*-substituted benzoic acids have no remarkable difference between the two C–O bond lengths in the carboxyl group. For example, those of terephthalic acid,[7] benzoic acid,[8] and *p*-toluic acid[9] are 1.262 and 1.272 Å, 1.24 and 1.29 Å, and 1.292 and 1.292 Å, respectively. However, *p*-bromobenzoic acid has two significantly different C–O bond lengths (1.225±0.014 and 1.307±0.013 Å) as found in *p*-nitrobenzoic acid[6] (1.222 and 1.319 Å), while *p*-bromobenzoate ion[1] has nearly equal bond lengths (1.255±0.011 and 1.281±0.011 Å).

Except the carboxyl C–O bond length, the remaining structural features of a *p*-bromobenzoic acid molecule are very similar to those of a *p*-bromobenzoate ion in the addition compound of *p*-bromobenzoic acid and piperidine.[1] The bond length of C(1)–C(7) (1.517 Å) is significantly shortened compared with the standard single bond value of 1.54 Å. The aromatic C–Br distance (1.902 Å) is slightly longer than the normally accepted value of 1.85 Å.[10] The carboxyl group is twisted out of the plane of the benzene ring by 5.8°.

Including intermolecular Br–Br distances (3.92 and 3.98 Å), all the intermolecular contacts correspond to normal van der Waals distances. The bromine atoms are in the *bc* cleavage plane.

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