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## Molecular Packing Modes of Acyl Halides.

### VI. The Crystal and Molecular Structure of Terephthaloyl Bromide

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The structure of terephthaloyl bromide (TBr) has been refined to  $R = 0.059$ ,  $R_w = 0.14$ . Crystals are monoclinic, space group  $P2_1/c$ , with  $a = 4.0632$  (4),  $b = 10.9096$  (4),  $c = 10.2214$  (6) Å,  $\beta = 96.43$  (1)°,  $Z = 2$ . The molecules are nearly planar, the carbonyl bromide group being rotated only 7.7° from the phenyl ring. The molecular structure (excluding the C–Br bond) is essentially identical to that of TCl, the only exception being the exocyclic C–C bond which is 0.02 Å longer in the present case. Bond lengths of the CCOBr group are: C–C 1.502, C=O 1.181, C–Br 1.931 Å. Short intermolecular Br···O contacts are not observed; there is a short Br···Br contact of 3.57 Å, accompanied by a C–Br···Br angle of 159°. The shortest H···O contact is 2.54 Å.

#### Introduction

Amongst the four acyl chloride structures analysed thus far, the only one that exhibited a hal···O interaction similar to that found in oxalyl bromide was TCl.

Since hal···O interactions are stronger for Br than for Cl (Bent, 1968), it was expected that replacement of Cl by Br in a structure having a Cl···O interaction would result either in an isomorphous structure or at least in one showing Br···O interactions.

The space group of TBr is the same as that of TCl; however, the cell constants are different. In order to determine whether the packing modes are similar in both compounds, the structure analysis of TBr was undertaken.

#### Experimental

Crystals of TBr grown by sublimation are colourless monoclinic plates showing the {012}, {021} and {10 $\bar{1}$ } forms.

Cell constants were determined by least squares from 13 medium- and high-order reflections ( $57 < \theta < 70^\circ$ ) measured on a Siemens diffractometer with Cu  $K\alpha$  radiation.

#### Crystal data

Terephthaloyl bromide,  $C_8H_4Br_2O_2$ ,  $M_r = 291.93$ , m.p. 84°C, monoclinic,  $a = 4.0632$  (4),  $b = 10.9096$  (4),  $c = 10.2214$  (6) Å,  $\beta = 96.43$  (1)°,  $U = 450.25$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 2.154$  g cm<sup>-3</sup>,  $F(000) = 276$ ,  $\mu(\text{Cu } K\alpha) = 121.7$  cm<sup>-1</sup>, space group  $P2_1/c$ .

A crystal, 0.11 × 0.24 × 0.33 mm measured normal to the faces (021), (0 $\bar{1}2$ ) and (10 $\bar{1}$ ), was mounted along  $a^*$  on an automatic Siemens diffractometer controlled by an IBM 1800 computer. 1834 reflections ( $\sin \theta/\lambda < 0.61$  Å<sup>-1</sup>) were recorded with Cu  $K\alpha$  radiation filtered by Ni foil and the  $\omega$ -2 $\theta$  scan technique. Scan ranges varied from 0.57 to 1.1° in  $\theta$ . The background was measured over the same range with an  $\omega$  offset of 0.6°; time of measurement was 0.2 s per 0.01° step interval.

for both scans. The data were processed as for TCl. The reflections were averaged to yield 850 independent reflections, 48 of which had  $F_o^2 < \sigma(F_o^2)$  and were treated as unobserved.

### Structure determination

The structure was solved by the *SEARCH* program (Rabinovich & Schmidt, 1966) which yielded 11 trial structures; the molecular model was the same as that of TCl with the Cl atom replaced by Br.

The relative intensities of the  $h00$ ,  $0k0$  and  $00l$  reflections (100 and 300 weak, 200 strong; 020 and 060 weak, 040 and 080 strong; 004 very weak, 002, 006, and 008 strong) yielded the following approximate Br coordinates:  $x = \frac{1}{4}$ ,  $y = \frac{3}{8}$  and  $z = \frac{1}{16}$ . Only one trial structure had the Br atom near this position ( $x = 0.30$ ,  $y = -0.36$ ,  $z = 0.06$ ). Least-squares refinement of the positional parameters of the non-hydrogen atoms and an overall isotropic temperature factor of this trial structure led to  $R = 0.26$ . The refinement proceeded with individual anisotropic thermal parameters; H atoms were introduced and their positions were held fixed while their temperature factors were allowed to refine isotropically. The final  $R = 0.059$  and  $R_w = 0.14$ .\*

### Results and discussion

Table 1 lists the atomic parameters. The e.s.d.'s in the positional parameters are nearly isotropic and average  $0.001 \text{ \AA}$  for Br and  $0.005 \text{ \AA}$  for C and O.

#### Molecular shape

Table 2 lists the best planes passing through the non-hydrogen atoms of the molecule (*A*), the phenyl ring

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33415 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* ( $\times 10^4$  for C and O;  $\times 10^5$  for Br;  $\times 10^3$  for H) and their e.s.d.'s

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	-1811 (12)	-125 (5)	-1228 (4)
C(2)	-1474 (10)	1016 (5)	-618 (4)
C(3)	359 (12)	1142 (4)	605 (4)
C(4)	-3181 (12)	2074 (5)	-1351 (4)
O	-5063 (13)	1974 (5)	-2312 (3)
Br	-22991 (17)	36787 (6)	-5944 (7)
H(1)	-316	-21	-209
H(3)	69	196	106

Table 2. *Equations of planes in the form*  $Ax + By + Cz + D = 0$ , where  $x, y, z$  are the fractional coordinates; distances ( $\times 10^3 \text{ \AA}$ ) of atoms from the planes are given in square brackets

Plane *A*: through all non-hydrogen atoms of the molecule

$$-3.4810x - 1.4004y + 6.0537z = 0$$

[C(1) -96, C(2) -3, C(3) 82, C(4) -0, O 86, Br -75, H(1) -137, H(3) 128]

Plane *B*: through the benzene ring

$$-3.5815x - 1.8198y + 5.4955z = 0$$

[C(1) -4, C(2) -4, C(3) 4, C(4) 20, O 184, Br -173]

Plane *C*: through the atoms of the carbonyl bromide group and C(2)

$$-3.3742x - 1.1069y + 6.5136z + 0.0219 = 0$$

[C(2) 5, C(4) -14, O 6, Br 3, C(1) -153, C(3) 169, C(1') 197, C(2') 39, C(3') -125]

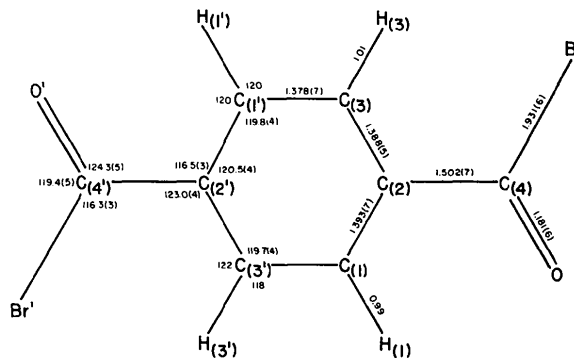


Fig. 1. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) and their e.s.d.'s.

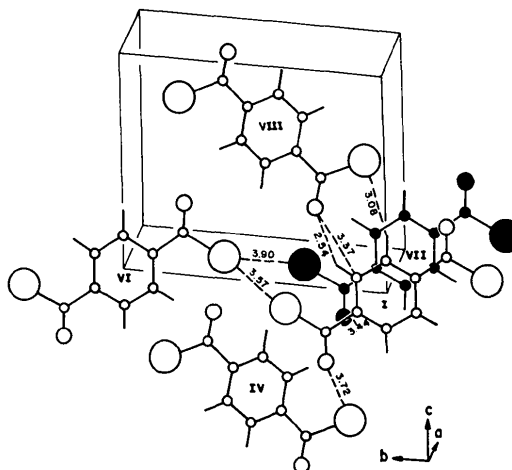


Fig. 2. Packing seen along the normal to the benzene ring plane.

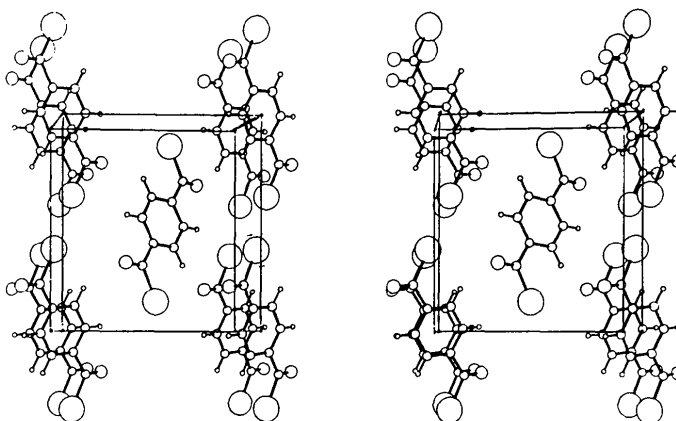


Fig. 3. Stereoscopic view (Johnson, 1971) of the packing along [100]. The origin of the unit cell is at the bottom left-hand corner with *b* vertical and *c* horizontal.

Table 3. Short intermolecular contacts (Å)

C(2)···C(3) <sup>II</sup>	3.68	Br···Br <sup>VI</sup>	3.57
C(1)···C(1') <sup>II</sup>	3.81	C(2)···C(4) <sup>VI</sup>	3.71
C(1)···C(2') <sup>II</sup>	3.62	C(2)···O <sup>VII</sup>	3.44
C(1)···C(3') <sup>II</sup>	3.77	C(3)···C(4) <sup>VII</sup>	3.62
C(2)···C(2') <sup>II</sup>	3.94	C(4)···O <sup>VII</sup>	3.55
Br···Br <sup>III</sup>	3.90	Br···Br <sup>VII</sup>	4.06
C(4)···H(3) <sup>IV</sup>	3.39	C(3)···O <sup>VIII</sup>	3.37
O···Br <sup>IV</sup>	3.72	H(3)···O <sup>VIII</sup>	2.54
C(1')···Br <sup>V</sup>	4.03	H(1')···Br <sup>VIII</sup>	3.08

Roman numeral superscripts refer to the molecules in the following equivalent positions.

(I)	<i>x</i> ,	<i>y</i> ,	<i>z</i>	(V)	<i>x</i> ,	$\frac{1}{2}-y$ ,	$\frac{1}{2}+z$
(II)	$-1+x$ ,	<i>y</i> ,	<i>z</i>	(VI)	<i>x</i> ,	$1+y$ ,	<i>z</i>
(III)	$-1+x$ ,	$1+y$ ,	<i>z</i>	(VII)	$1+x$ ,	<i>y</i> ,	<i>z</i>
(IV)	<i>x</i> ,	$\frac{1}{2}-y$ ,	$-\frac{1}{2}+z$	(VIII)	$1+x$ ,	$\frac{1}{2}-y$ ,	$\frac{1}{2}+z$

(*B*) and the carbonyl bromide group (*C*). The phenyl ring is planar within 0.004 Å. C(4), Br and O lie respectively at 0.02, -0.17 and 0.18 Å from this plane. The carbonyl bromide group plus C(2) is planar to within 0.01 Å and is rotated 7.7° from the phenyl ring.

### Bond lengths and angles

Fig. 1 shows the bond lengths and angles. The bond lengths of the phenyl ring which show a small amount of quinonoid character and the exocyclic angles at C(2) are similar to those found in TCl. C(2)–C(4) (1.502 Å) is significantly longer than that in TCl. The C=O length and the angles at C(2) are similar to those found in the other acyl halides. The C–Br length (1.931 Å) is longer than the accepted value (1.89 Å) for Br bonded to an *sp*<sup>2</sup> C atom (Dewar & Schmeising, 1960). This lengthening of 0.04 Å is nearly the same as the lengthening of C–Cl in acyl chlorides (1.736 to 1.771 Å), indicating identical changes in the amount of *s* character of the C atom.

### Packing arrangement

Fig. 2 shows the packing seen along the normal to the benzene ring. A stereoscopic view of the packing along [100] is shown in Fig. 3. The best plane of the molecule is tilted from the (100) plane by 37.3°. The molecules are stacked along [100] approximately parallel to the (102) plane. The benzene rings in a stack overlap partially and the distance between their planes is 3.48 Å. Short intermolecular distances are listed in Table 3. The shortest O···H and C···O distances are 2.54 and 3.37 Å respectively, and the former is shorter than the sum of the van der Waals radii (2.72 Å, Bondi, 1964); however, the C=O···H angle (148°) is different from the mean (120°) found in *cis*-dibenzoyl-ethylenes (Rabinovich, Schmidt & Shakked, 1970).

In contrast to TCl, no short hal···O interactions are present. On the other hand, there are short Br···Br contacts of 3.58 Å (van der Waals distance = 3.70 Å) which form C–Br···Br–C angles of 159°; these angles are similar to those found in MCl and in a series of chloroaromatic compounds with short Cl···Cl contacts.

The fact that, in addition to the non-isomorphism, the interactions in TBr are different is rather surprising. This point will be discussed in part VII.

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