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Topochemical Studies. VII. The Crystal and Molecular Structures of Tetrachlorophthalic Acid Hemihydrate and Tetrabromophthalic Anhydride

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The crystal structures of tetrachlorophthalic acid hemihydrate (TCPH) and tetrabromophthalic anhydride (TBPA) have been determined from visually estimated Cu$K\alpha$ data. The crystals of TCPH are monoclinic, space group A2/a, $a=19.81(1)$, $b=7.091(5)$, $c=16.22(1)$ Å, $\beta=101.2(2)°$ and $Z=8$. Those of TBPA are monoclinic, space group $P2_1/n$, $a=13.39(3)$, $b=6.19(2)$, $c=12.66(3)$ Å, $\beta=91.1(3)°$ and $Z=4$. The structures of TCPH and TBPA were solved from the sharpened Patterson maps, and refined by the block-diagonal least-squares method to R values of 0.112 and 0.112 for 1287 and 1278 non-zero reflections, respectively. The molecules of TCPH related by a twofold screw axis are linked together by hydrogen bonds between the carboxylic groups to form a chain along the b axis and the chains are held together by hydrogen bonds through water molecules to form a sheet parallel to the (100) plane. The sheets are stacked by van der Waals forces. The dihedral angles of the carboxylic groups with the benzene ring are 68.2 and 48.9°. The crystals of TBPA are isomorphous to those of tetrachlorophthalic anhydride. The benzene ring of TBPA are distorted by the attachment of five membered ring. There is considerable molecular overlap in TCPH, while in TBPA there is no overlap.

The conformation of the benzene ring overcrowded with halogen atoms is of considerable interest. Coulson and Stocker[1)] have discussed the planarity of *o*-dihalogenobenzenes on calculations of potentials between halogen atoms, but the problem for more overcrowded benzenes has not always been settled. Strand[2)] has shown that the planar molecule of *o*-dibromobenzene belongs to C_{2v} symmetry but the angle between the C–Br bonds is enlarged. Gafner and Herbstein[3)] have noted that the intramolecular Br···Br distance of 1,2,4,5-tetrabromobenzene is significantly shorter than the usual van der Waals separation in different molecules. Rudman[4)] has determined the structure of tetrachlorophthalic anhydride (TCPA) and pointed out that an anisotropic van der Waals radius plays an important role in the contacts of the halogen atoms. It is of additional interest that some multi-halogenated benzoic acids bear a distinct parallelism between the superdelocalizability for nucleophilic reaction and auxin activity or carcinogenic activity,[5)] but the parallelism involves some conflicts to be solved in view of the detailed molecular structures.

Previous work on the topochemical studies has been carried out with 2,5-pyridinedicarboxylic acid–*N*,*N*-dimethylformamide complex monohydrate[6)] in order to study the role of π-electron interaction and hydrogen bonding in molecular stacking and overlap on crystal structure formation. The present investigation was undertaken in order to compare the overlappings of the title overcrowded molecules and to study the effects of

TABLE 1. CRYSTALLOGRAPHIC DATA AND EXPERIMENTAL DETAILS

	Tetrachlorophthalic acid hemihydrate	Tetrabromophthalic anhydride
Chemical formula	$C_8H_2O_4Cl_4\cdot 1/2H_2O$	$C_8O_3Br_4$
F.W.	312.9	463.7
mp (°C)	*ca.* 98 (anhydrated)	280
Crystal system	monoclinic	monoclinic
Space group	A2/a-C_{2h}^6, No. 15	$P2_1/n$-C_{2h}^5, No. 14
Systematic absences	hkl $h+l$ odd	$h0l$ $h+l$ odd
	$h0l$ h odd	$0k0$ k odd
a(Å)	19.81(1)	13.39(3)
b(Å)	7.091(5)	6.19(2)
c(Å)	16.22(1)	12.66(3)
β(°)	101.2(2)	91.1(3)
Z	8	4
D_x (g/cm³)	1.859	2.935
D_m (g/cm³)	1.88	2.90
Flotation mixture	$ZnBr_2$ aq. soln.	HCOOTl aq. soln.
μ (cm⁻¹) for Cu $K\alpha$	97.8	209
F(000)	1240	828
Dimensions of crystal used (mm)	0.1×0.3×0.2	0.08×1.1×0.05
Layers photographed	$h0l$ to $h5l$	$h0l$ to $h4l$
No. of observed reflections	1287	1278
Percent to Cu$K\alpha$ sphere	50	52
B (Å²) from Wilson's plot	4.04	3.27

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overcrowding on the conformation of the benzene rings.

Experimental

Tetrachlorophthalic acid hemihydrate (TCPH) was recrystallized from a hot aqueous solution by cooling as thin plates elongated along the b axis. Crystals of tetrabromophthalic anhydride (TBPA) were obtained from a hot acetone solution by evaporation as prisms elongated along the b axis. Crystallographic data and experimental details are listed in Table 1. The intensity data were collected by the equi-inclination Weissenberg method using Cu*K*α radiation (λ= 1.5418 Å). Intensities were estimated visually and corrected for Lorentz and polarization factors and for spot shape, but not for absorption. The structure of TCPH was assumed to be centric from the distribution of normalized structure factors and the space group A2/a was confirmed by the analysis.

Structure Determination and Refinement

The structures were solved from three-dimensional sharpened Patterson maps. The hydrogen atoms of TCPH were located by a difference Fourier synthesis. Parameters of all the atoms were refined by the block-diagonal least-squares method. The weighting scheme used was:

$$w = 1.0 \quad \text{for} \quad 0 < |F_o| \leq F_{\max}$$

$$\text{and} \quad w = (F_{\max}/|F_o|)^2 \quad \text{for} \quad |F_o| > F_{\max},$$

where $F_{\max}$=16.0 and 30.0 for TCPH and TBPA, respectively. The final R value of TCPH was 0.112 for 1287 non-zero reflections and that of TBPA 0.112 for 1278. The observed and calculated structure factors are listed in Table 2,** and the final atomic parameters in Table 3.

The atomic scattering factors were taken from International Tables for X-ray Crystallography.[7] The computations were carried out on an NEAC 2200-500 computer at the Okayama University Computer Center. The programs used were HBLS-5 and DAPH.[8]

Table 3. Final atomic parameters and estimated standard deviations ($\times 10^4$)
The anisotropic thermal parameters are defined as: $\exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-\beta_{12}hk-\beta_{13}hl-\beta_{23}kl)$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Tetrachlorophthalic acid hemihydrate (TCPH)									
Cl(1)	834(1)	1619(4)	435(1)	39(1)	297(8)	33(1)	60(4)	7(1)	−9(4)
Cl(2)	187(1)	5045(4)	1158(2)	31(1)	221(8)	51(1)	52(3)	−1(1)	21(4)
Cl(3)	422(1)	5641(4)	3083(2)	34(1)	172(8)	56(1)	32(3)	28(2)	−39(4)
Cl(4)	1368(1)	2905(4)	4288(1)	37(1)	232(8)	36(1)	−10(3)	19(1)	−38(3)
O(1)	1671(3)	−1277(10)	3943(4)	30(2)	267(20)	39(3)	−19(9)	17(4)	44(11)
O(2)	2621(3)	−288(9)	3515(4)	24(2)	210(18)	47(3)	2(8)	11(3)	19(10)
O(3)	1695(3)	−2475(9)	2070(4)	35(2)	138(16)	52(3)	0(9)	37(4)	17(11)
O(4)	2101(4)	−714(10)	1148(4)	45(3)	236(20)	51(3)	54(11)	53(5)	81(12)
C(1)	1536(4)	1033(12)	2896(5)	25(2)	103(22)	34(3)	−14(10)	12(4)	10(11)
C(2)	1434(4)	755(12)	2034(5)	24(2)	130(24)	37(3)	5(10)	16(4)	−6(12)
C(3)	1010(4)	2010(13)	1494(5)	20(2)	194(28)	35(3)	4(10)	7(4)	9(12)
C(4)	708(4)	3524(13)	1830(5)	21(2)	181(25)	35(3)	13(9)	6(4)	−7(12)
C(5)	803(4)	3774(13)	2681(6)	20(2)	121(24)	52(4)	7(9)	16(5)	−22(14)
C(6)	1219(4)	2545(13)	3216(6)	21(2)	173(26)	48(4)	−3(10)	18(4)	−7(15)
C(7)	2001(5)	−256(12)	3484(5)	28(2)	151(24)	29(3)	1(11)	8(4)	−4(11)
C(8)	1765(5)	−890(13)	1695(5)	27(3)	212(26)	31(3)	25(12)	15(4)	−5(13)
O(5)	2500(0)	−3414(13)	5000(0)	32(3)	177(24)	35(3)	0(0)	19(5)	0(0)
H(1)	2063(64)	−2271(178)	4383(86)	B=5.8(3.3) Å^2					
H(2)	1981(73)	−3619(207)	1802(91)	7.8(4.1)					
H(3)	2736(83)	−4135(220)	4503(100)	8.5(4.3)					
Tetrabromophthalic anhydride (TBPA)									
Br(1)	1174(2)	805(4)	5670(2)	50(1)	191(10)	51(1)	−54(5)	−6(2)	17(5)
Br(2)	3279(2)	1940(4)	6960(2)	60(1)	176(9)	40(1)	−9(5)	−30(2)	49(5)
Br(3)	4564(2)	6208(4)	6335(2)	48(1)	231(10)	46(1)	−58(5)	−38(2)	12(5)
Br(4)	3882(2)	9139(5)	4247(2)	61(1)	201(11)	53(1)	−74(5)	−11(2)	52(5)
O(1)	832(11)	6281(28)	3106(11)	44(8)	246(61)	45(9)	10(34)	−33(14)	−9(37)
O(2)	−7(13)	3391(35)	3837(15)	56(10)	384(81)	68(13)	−114(45)	−21(19)	31(50)
O(3)	1931(16)	8945(36)	2755(14)	103(16)	302(85)	57(12)	−7(52)	−8(23)	169(46)
C(1)	1644(13)	4579(33)	4489(13)	39(10)	40(74)	26(9)	13(36)	−7(15)	−52(35)
C(2)	1925(14)	3187(34)	5304(12)	39(10)	107(77)	19(9)	−23(38)	−23(14)	−3(35)
C(3)	8243(12)	3715(37)	5822(13)	25(9)	213(84)	26(9)	−56(38)	−27(14)	−2(39)
C(4)	3406(14)	5440(37)	5528(15)	36(10)	141(86)	39(11)	23(40)	−34(17)	−82(43)
C(5)	3126(13)	6807(36)	4697(13)	33(10)	141(81)	25(9)	−27(38)	−6(15)	−16(38)
C(6)	2223(14)	6247(41)	4185(13)	42(11)	318(95)	13(8)	−70(47)	−34(16)	39(41)
C(7)	1751(20)	7331(44)	3300(15)	95(19)	164(95)	23(10)	−1(61)	−20(22)	1(44)
C(8)	774(12)	4583(38)	3837(13)	20(8)	256(86)	26(9)	−49(39)	−9(14)	30(42)

** Table 2 is kept as Document No. 7524 at the Chemical Society of Japan.

Results and Discussion

Figure 1 shows the crystal structures of TCPH (a) and TBPA (b) viewed along b axes. The molecular overlappings are shown in Fig. 2. Bond lengths and angles are shown in Fig. 3 for TCPH (a) and TBPA (b) together with intramolecular distances. The least-squares planes and deviations of the atoms from the re-

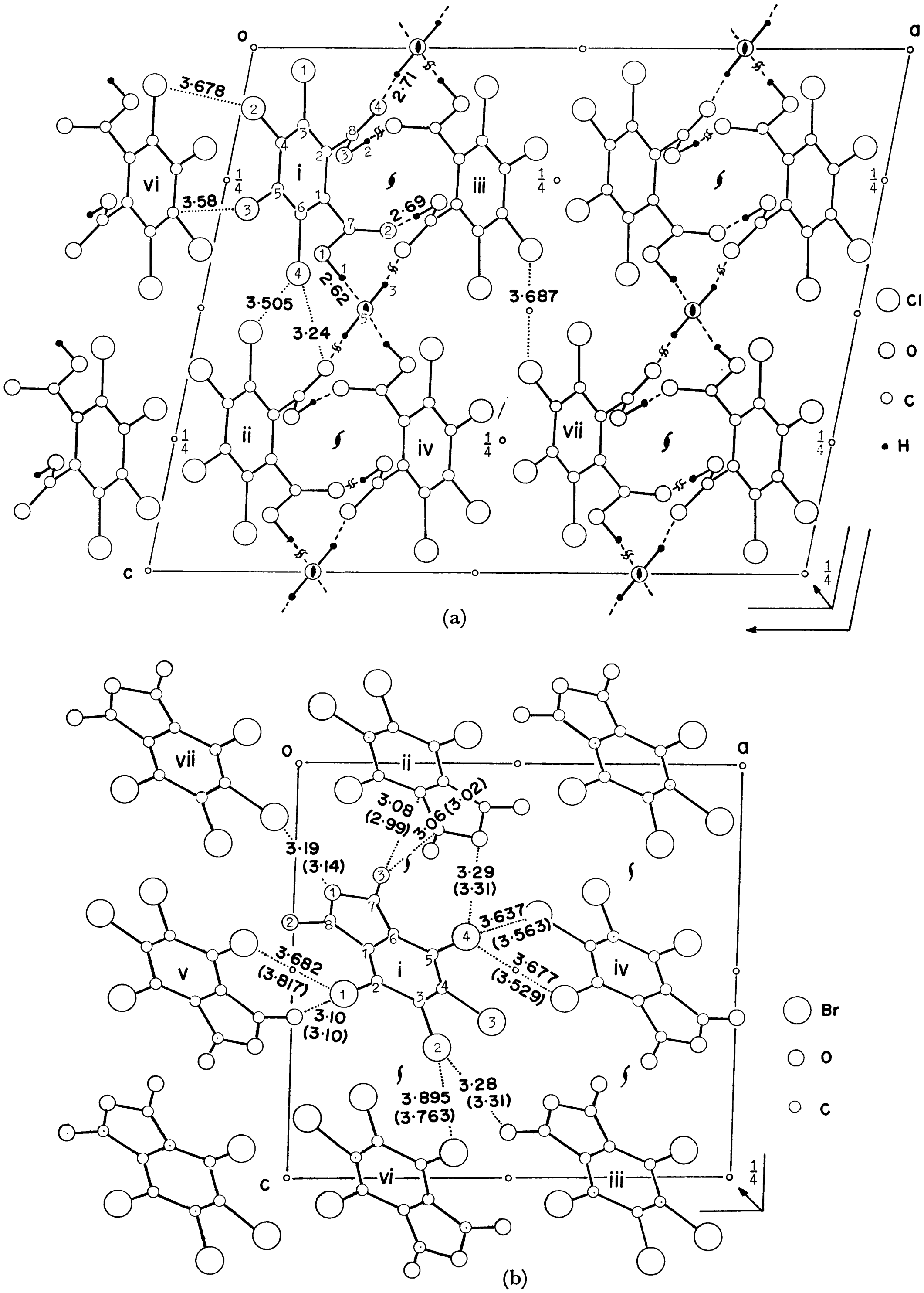

Fig. 1. Projections of the crystal structures of (a) TCPH and (b) TBPA along b axes, together with intermolecular contacts. Figures for TCPA are shown in parentheses for comparison.

Symmetry code: For TCPH, i x, y, z; ii x, $1/2+y$, $1/2+z$; iii $1/2-x$, $1/2+y$, $1/2-z$; iv $1/2-x, y, 1-z$; v x, $-1/2+y$, $1/2+z$; vi $-x$, $1/2-y$, $1/2-z$; vii $1/2+x$, $3/2-y$, $1/2+z$; viii $1/2-x$, $-1/2+y$, $1/2-z$.

For TBPA, i x, y, z; ii $1/2-x$, $1/2+y$, $1/2-z$; iii $1/2+x$, $1/2-y$, $1/2+z$; iv $1-x$, $2-y$, $1-z$; v $-x$, $-y$, $1-z$; vi $1/2-x$, $1/2+y$, $3/2-z$; vii $-1/2+x$, $3/2-y$, $-1/2+z$; viii $1-x$, $1-y$, $1-z$; ix $-x$, $1-y$, $1-z$; x x, $1+y$, z.

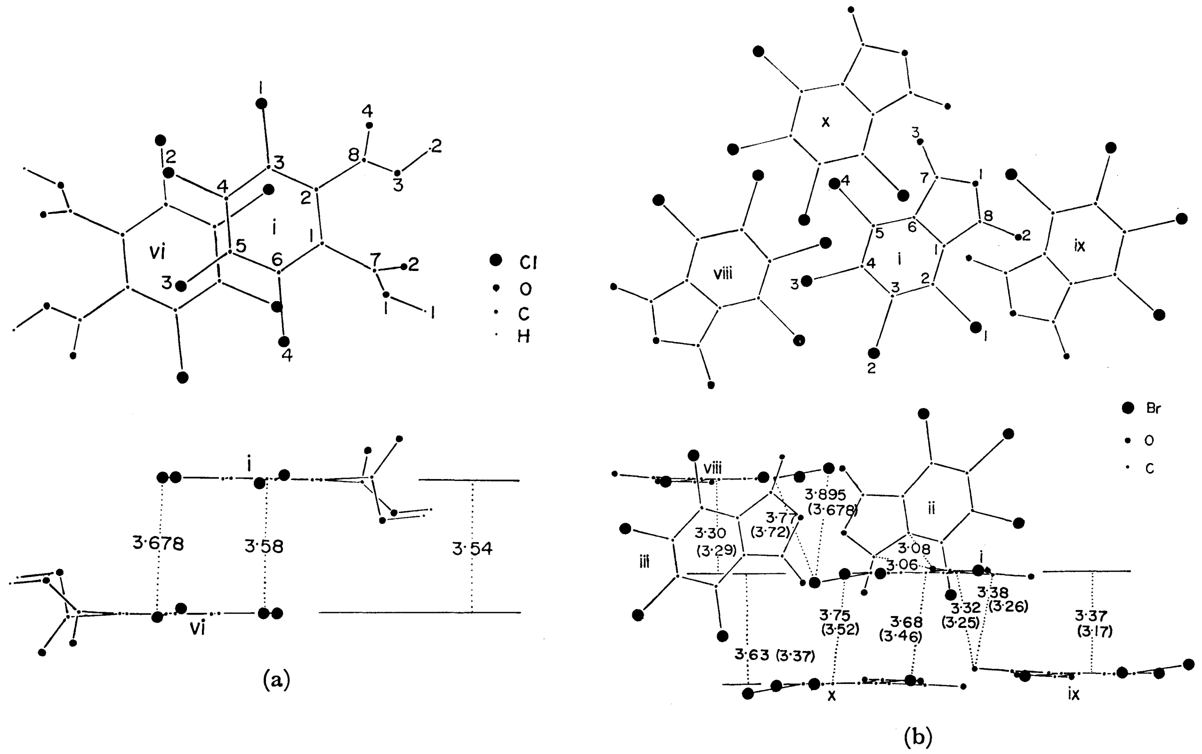

Fig. 2. The molecular overlappings for (a) TCPH and (b) TBPA. Figures are intermolecular distanes (Å). Values for TCPA are shown in parentheses for comparison. Symmetry code is given in the legend of Fig. 1.

spective planes are listed in Table 4.

Crystal Structures. *(a) TCPH*: The molecules related by the twofold screw axis at $x=1/4$ and $z=1/4$ are linked by the hydrogen bonds between the carboxylic groups to form a chain along the b axis. The chains are held together by the hydrogen bonds through the water molecules on the twofold axis at $x=1/4$ and $z=1/2$ to form a sheet parallel to the (100) plane, which is in accordance with the observed cleavage. The sheets are stacked along the a axis by van der Waals forces.

Geometry of the hydrogen bonds are listed in Table 5. It can be seen that the O–H······O bonds are nearly linear and the O······O······O angles are close to the tetrahedral angle.

As seen from Fig. 2 (a), the perpendicular spacing between the adjacent benzene-ring planes is close to that found in hexachlorobenzene (3.52 Å)[9] and in 1,2,3-trichlorobenzene (3.53 Å).[10]

TABLE 4. THE LEAST-SQUARES PLANES AND DEVIATIONS FROM THE PLANES
$X=ax+cz\cos\beta$, $Y=by$, $Z=cz\sin\beta$ (Å).

(a) TCPH

I. Benzene ring

$0.8193X+0.5720Y-0.0395Z=1.9827$

Atom	Shift (Å)	Atom	Shift (Å)	Atom	Shift (Å)
Cl(1)	0.112	O(3)	0.898	C(5)*	0.006
Cl(2)	0.004	O(4)	−0.771	C(6)*	0.001
Cl(3)	−0.003	C(1)*	−0.004	C(7)	−0.047
Cl(4)	−0.044	C(2)*	0.000	C(8)	0.021
O(1)	1.050	C(3)*	0.007	H(1)	0.96
O(2)	−1.030	C(4)*	−0.010	H(2)	0.81

II. 1-Carboxyl group

$-0.0113X+0.7132Y+0.7009Z=3.7275$

O(1)*	−0.001	C(1)*	−0.001	H(1)	0.02
O(2)*	−0.001	C(7)*	0.003		

III. 2-Carboxyl group

$0.7127X+0.1743Y+0.6795Z=3.8561$

O(3)*	−0.007	C(2)*	−0.006	H(2)	−0.04
O(4)*	−0.008	C(8)*	0.020		

Dihedral angle I and II 68.2°, I and III 48.9°

(b) TBPA

I. Benzene ring

$-0.4979X+0.5857Y+0.6396Z=4.2372$

Br(1)	0.07	O(2)	−0.15	C(4)*	−0.00
Br(2)	0.00	O(3)	0.02	C(5)*	−0.01
Br(3)	−0.18	C(1)*	−0.02	C(6)*	0.02
Br(4)	0.02	C(2)*	0.01	C(7)	0.04
O(1)	−0.04	C(3)*	0.00	C(8)	−0.06

II. Five-membered ring

$-0.4661X+0.6108Y+0.6400Z=4.4007$

Br(1)	0.17	O(2)	−0.04	C(4)	−0.07
Br(2)	−0.00	O(3)	−0.04	C(5)	−0.08
Br(3)	−0.30	C(1)*	0.01	C(6)*	−0.01
Br(4)	−0.12	C(2)	0.04	C(7)*	0.01
O(1)*	−0.01	C(3)	−0.01	C(8)*	−0.00

Dihedral angle I and II 2.3°

* Atoms with asterisks were used for calculations of the planes.

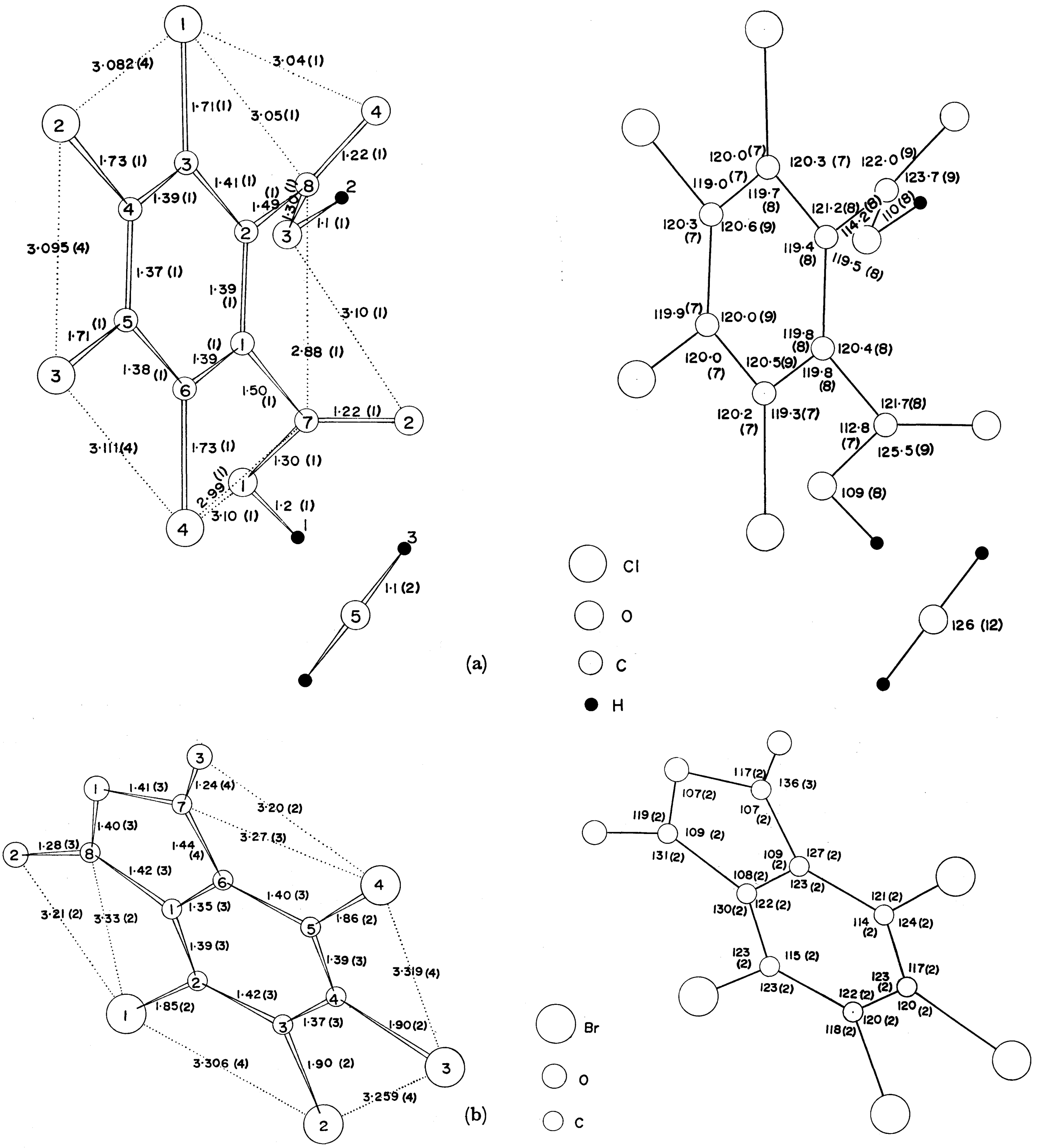

Fig. 3. Bond lengths (Å) and angles (°) of (a) TCPH and (b) TBPA, together with some intramolecular distances (Å). The estimated standard deviations are shown in parentheses.

(b) TBPA: The crystals of TBPA are isostructural with those of TCPA.[4)] The molecules related by a center of symmetry, a b translation, and a twofold screw axis pack together by van der Waals forces along the a, b, and c axes, respectively.

The distances $\mathrm{Br(1)\cdots Br(1^{v})}$ and $\mathrm{Br(1)\cdots O(2^{v})}$ are shorter than those expected from the van der Waals radii, and are unexpectedly not longer than the corresponding distances in TCPA, respectively.

As seen from Fig. 2 (b), the perpendicular distance between the planes of the benzene rings of the molecules i and x is close to the distances 3.61 and 3.63 Å found in the 1 : 1 complex of hexabromobenzene with 1,2,4,5-tetrabromobenzene.[11)] This distance is determined by the carbon-bromine contacts. On the other hand, the distance between the molecules i and viii is determined by the contacts of the O(3) atom with $\mathrm{C(6^{ii})}$ and $\mathrm{C(7^{ii})}$ atoms. The carbon-oxygen contacts are also found between the molecules i and ix.

Molecular Structures. *(a) TCPH*: The benzene ring keeps a planar form of regular hexagon within experimental error, but the Cl(1) and Cl(4) atoms are

TABLE 5. HYDROGEN-BOND DISTANCES (Å) AND ANGLES (°) IN TCPH

D–H···A	Symmetry	D···A	H···A	Angle
O(1)–H(1)···O(5)	(i, i, i)	2.616(11)	1.44(14)	173(12)
O(3)–H(2)···O(2)	(iii, iii, i)	2.686(9)	1.56(15)	176(13)
O(5)–H(3)···O(4)	(i, i, viii)	2.706(12)	1.62(16)	161(14)

O···O···O	Symmetry	Angle
O(1)···O(5)···O(1)	(i, i, iv)	109.2(4)
O(1)···O(5)···O(4)	(i, i, viii)	97.3(4)
O(1)···O(5)···O(4)	(i, i, v)	124.3(4)
O(4)···O(5)···O(4)	(viii, i, v)	105.9(4)

Symmetry code is given in the legend of Fig. 1.

displaced to both sides of the benzene-ring plane because of the short contacts between the Cl(1) and O(4) atoms, and the Cl(4) and O(1) atoms, respectively. The average C–Cl bond length 1.716 (10) Å is near to the normal value.[4] The distances between the adjacent chlorine atoms are not far from the average value of 3.096 Å. The dihedral angles of both carboxylic groups with respect to the benzene ring are rather large because of cooperative effect of formation of the hydrogen bonds and a repulsive interaction between the O(2) and O(3) atoms.

(b) TBPA: The benzene ring is somewhat distorted from the regular hexagon, the angles C(1)–C(2)–C(3) and C(4)–C(5)–C(6) being significantly smaller than the sp^2 angle. The average C–Br bond length 1.88 (2) Å is close to the normal value.[12] The distance between the Br(2) and Br(3) atoms is shorter than that between the Br(1) and Br(2) atoms, or the Br(3) and Br(4) atoms, as found in TCPA. As seen from Table 4, the molecule is nearly planar but the Br(3) and O(2) atoms deviate from the benzene-ring plane in the same sense as in TCPA.

Comparison of the Mode of Molecular Overlapping. Different modes of overlapping are found for the overcrowded molecules; these is considerable molecular overlap in TCPH, while in TBPA these is no overlap. As noted above, this reflects in the spacings of stacking in both compounds: the spacing in TCPH is rather large and determined by the carbon-chlorine contacts, while in TBPA there are two short spacings determined by the carbon-oxygen contacts in addition to one spacing determined by the carbon-bromine contacts.

Effects of Overcrowding on the Conformation of the Benzene Rings. The observed distances between halogen atoms attached to adjacent carbon atoms on a benzene ring are much less than the sum of the van der Waals radii of the halogen atoms in both TBPA and TCPH. However, the benzene ring in TCPH is not distored. As an explanation for this fact an anisotropic van der Waals radius can be considered as follows. Let the z axis be perpendicular to the benzene ring plane, and the x axis be along the carbon-chlorine bond, then the direction of the $3p_y$ orbital, which is assumed to participate in the van der Waals interaction, deviates outward by 30 ° from the line between the chlorine atoms. On this model for usual geometry the possible extent of the $3p_y$ orbital is estimated to be 1.80 Å, which is equal to the Pauling's van der Waals radius.

TABLE 6. DECREASE IN THE BOND ANGLES OF C(1)–C(2)–C(3) AND C(4)–C(5)–C(6) IN THE BENZENE RING WITH FIVE-MEMBERED RING FUSED AT THE C(1) AND C(6) ATOMS

Compound	Angles (°)	
TBPA[a]	114	115
TCPA[4]	113.4	115.8
Xanthotoxin[13]	115.5	117.6
Dibenzofuran[14]	116.7	117.9
Alkaloid lycorine[15]	116.7	117.3
2-(*p*-Bromophenyl)indane-1,3-dione[16]	115.0	117.1
	117.5	117.7
Phthalimide[17]	116.6	116.8
5-Methoxytryptamine[18]	117.7	117.8
N-Acetyl-L-tryptophane[19]	117.9	118.7
Melatonin[20]	117.1	118.4
2-Thio-1-(*β*-D-ribofuranosyl)-3*H*-benzimidazole[21]	115.7	116.8
5-Methylbenzofurazan-1-oxide[22]	115.7	117.8
Benzotriazole[23]	114.7	115.6
	115.6	115.6
	115.0	117.0
	115.8	116.6

a) This work.

The decrease in the C(1)–C(2)–C(3) and C(4)–C(5)–C(6) bond angles as found in TBPA is commonly observed in the benzene rings attached by five-membered ring as listed in Table 6. Therefore, the decrease is not attributed to the overcrowding of the halogen atoms, but to the attachment of five-membered ring as pointed out recently by Bechtel, *et al.*[16]

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