Molecular Packing Modes of Acyl Halides.
II. The Crystal and Molecular Structure of Terephthaloyl Chloride

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Terephthaloyl chloride (TCl), $C_8H_4Cl_2O_2$, crystallizes in space group $P2_1/c$, with $a = 3\cdot902$ (3), $b = 6\cdot951$ (2), $c = 17\cdot669$ (3) Å, $\beta = 120\cdot52$ (2)°, $Z = 2$. The crystal structure was determined from diffractometer data and refined to $R = 0\cdot052$. The centrosymmetric molecule is planar within $0\cdot02$ Å, the molecular plane being tilted 14° from the *bc* plane. The bond lengths of the benzene ring show a slight quinonoid character. The exocyclic angles (123·5, 116·5°) at C(2) are distorted due probably to the in-plane 1,4 Cl$\cdots$C interaction. The bond lengths in the CCOCl group are: C–C 1·486 (4), C=O 1·185 (3), C–Cl 1·769 (3) Å. The Cl$\cdots$O intermolecular contact of 3·32 Å is accompanied by C–Cl$\cdots$O and C=O$\cdots$Cl angles of 168 and 115° respectively. The shortest Cl$\cdots$Cl and H$\cdots$O contacts are 3·72 and 2·68 Å respectively.

Introduction

Inspection of the crystal and preliminary diffraction data of the several diacyl halides deemed suitable for our study has indicated an acceptable model for the structure of TCl, conforming with the assumption that the packing of this compound is governed by the hal$\cdots$O interaction. Consequently, we have commenced our investigations by the analysis of the crystal structure of TCl.

Experimental

Three methods were used to grow suitable crystals: slow cooling from *n*-hexane solution, diffusion of benzene vapour into ethyl acetate solution, and sublimation.

It was found that only sublimation yielded crystals good enough for intensity measurements. These crystals grow either as colourless monoclinic plates showing the {10$\bar{2}$}, {010} and {001} forms, or as needles elongated along [100]. To avoid contact with moisture the crystals were sealed in lithium borate capillaries. In spite of this precaution small amounts of powder, due to hydrolysis, were gradually formed.

Cell constants were determined by least squares from 17 high-order ($\theta > 22°$) reflections measured on a Siemens diffractometer with Mo $K\alpha$ radiation.

Crystal data

Terephthaloyl chloride, $C_8H_4Cl_2O_2$, $M_r = 203\cdot03$, m.p. 83–84°C, monoclinic, $P2_1/c$, $a = 3\cdot902$ (3), $b = 6\cdot951$ (2), $c = 17\cdot669$ (3) Å, $\beta = 120\cdot52$ (2)°, $U = 412\cdot8$ Å^3, $Z = 2$, $D_c = 1\cdot632$ g cm^{-3}, $F(000) = 204$, μ(Mo $K\bar{\alpha}$) = 7·35 cm^{-1}.

The density of the crystal was not measured as no suitable flotation mixture was found.

A crystal, $0\cdot77 \times 0\cdot18 \times 0\cdot50$ mm measured perpendicular to the (10$\bar{2}$), (010) and (001) faces, was mounted along $\mathbf{a}^* - 2\mathbf{b}^*$ on an automatic Siemens diffractometer controlled by an IBM 1800 computer. 1790 reflections ($\sin\theta/\lambda < 0\cdot66$ Å^{-1}) were recorded with Mo $K\alpha$ radiation and balanced Zr and Y filters by the moving-crystal moving-counter technique. In order to avoid vignetting of the reflections, their profile widths were calculated from the observed widths of the axial reflections. Profile-width ranges were $0\cdot8$–$1\cdot2°$; time of measurement was $0\cdot3$ s per $0\cdot01°$ step interval. The background was derived from the first and last four steps in each scan. An error $\sigma(I) = [(0\cdot03I)^2 + N_o + r^2 N_b]^{1/2}$ was assigned to the net intensity $I = N_o - rN_b$ for each reflection, where N_o is the gross count, N_b the total background count and r the ratio of scan to background time. Lorentz and polarization as well as absorption corrections were applied (Coppens, Leiserowitz & Rabinovich, 1965).

The reflections were averaged to yield 899 independent reflections, 87 of which had $F_o^2 < \sigma(F_o^2)$, and were treated as unobserved.

Postulated model and structure determination

A model of the crystal structure based on packing considerations was proposed as follows: it was assumed that the centrosymmetric molecules form a sheet-like structure in the *bc* plane, as suggested by the strong *h*00 reflections. In constructing the intermolecular arrangement in the *bc* plane, the twofold screw axis which lies in this plane was utilized as the vehicle for generating continuous C–Cl$\cdots$O contacts in which the C–Cl vector pointed towards the O atoms with a C=O$\cdots$Cl

angle of approximately $120°$. In such an arrangement the calculated $Cl\cdots O$ distance was $2\cdot8$ Å and the intermolecular van der Waals contacts within the sheet ($H\cdots H = 2\cdot2$, $H\cdots O = 3\cdot1$, $H\cdots Cl = 3\cdot5$ Å) were acceptable.

This model was tested at low resolution ($\sin \theta/\lambda < 0\cdot2$ Å^{-1}) by a rigid-body least-squares program in which only the scale factor and the three Eulerian angles were adjusted. This approach, however, proved futile, apparently because the postulated model was too far from the correct structure.

Eventually, the structure was solved by the program *SEARCH* (Rabinovich & Schmidt, 1966). This program yielded 11 trial structures which were tested at low resolution by the rigid-body least-squares program; one of the models yielded $R = \sum|kF_o - |F_c||/\sum kF_o = 0\cdot13$. The H atoms were now removed; isotropic refinement of individual atoms with all $F(hkl)$ followed by reinsertion of the H atoms and anisotropic refinement of the other atoms led to $R = 0\cdot052$ and $R_w = [\sum w(k^2 F_o^2 - F_c^2)^2/\sum wk^4 F_o^4]^{1/2} = 0\cdot12$, where $w = 1/\sigma^2(F_o^2)$. Reflection 100 which was affected by extinction and 58 unobserved reflections for which $F_o < k\sigma(F_o^2)^{1/2}$ were excluded from the refinement.*

Standard deviations of all parameters were estimated by the usual least-squares procedure, the number of observations n and the number of parameters s being 811 and 62 respectively. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Results and discussion

Table 1 lists the atomic parameters. The e.s.d.'s of the positional parameters are nearly isotropic and average $0\cdot001$ for Cl, $0\cdot003$ for C and O, and $0\cdot03$ Å for H atoms.

Molecular shape

The molecular is nearly planar and the carbonyl group is rotated only $1\cdot25°$ from the planar phenyl ring. Equations of the best planes through all non-hydrogen atoms of the molecule (A), the phenyl ring (B) and the COCl group with attached C atom (C), and the deviations of atoms from these planes are in Table 2.

Thermal-motion analysis

Rigid-body-motion analysis of the vibration tensors of the non-hydrogen atoms was carried out with the program *TMA* (Shmueli, 1972) based on the method of Schomaker & Trueblood (1968). The results are summarized in Table 3. The r.m.s. discrepancy $\langle \Delta U^{ij} \rangle$ ($0\cdot0039$ Å^2) is significantly higher than the r.m.s. of the estimated standard deviations ($0\cdot0010$ Å^2) of the observed U^{ij}, suggesting that the molecular motion

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

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

$$-3\cdot5281x - 1\cdot4933y + 2\cdot489z = 0$$

[C(1) 17, C(2) −3, C(3) −11, C(4) −7, O(1) −10, Cl 15, H(1) −47, H(3) −32]

Plane B: through the benzene ring

$$-3\cdot5317x - 1\cdot5553y + 2\cdot6145z = 0$$

[C(1) 3, C(2) −3, C(3) 3, C(4) −8, O −23, Cl 33]

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

$$-3\cdot5223x - 1\cdot4454y + 2\cdot3622z + 0\cdot0063 = 0$$

[C(2) 1, C(4) −4, O 2, Cl 1, C(1) 34, C(3) −19, C(1') −22, C(2') 11, C(3') 31]

Table 3. *Results of rigid-body-motion analysis*

The eigenvectors of L and T are referred to the molecular system of inertia I (in terms of direction cosines) whose centroid is at $x,y,z = (0,0,0)$ and whose eigenvectors are referred to the reciprocal vectors a*, b* and c*.

Tensor	r.m.s. amplitude	Eigenvalues	Eigenvectors		
I		210 at. wt Å^2	1·6723	−3·2271	−15·6308
		1637	−0·0284	−5·9770	7·8347
		1848	−3·5278	−1·4817	2·4398
L	9·0°	246 × 10^{-4} rad^2	0·9963	−0·0818	−0·0283
	3·3	34	0·0865	0·9524	0·2925
	2·4	17	0·0030	−0·2938	0·9559
T	0·233 Å	542 × 10^{-4} Å^2	−0·9945	0·0137	0·1038
	0·208	433	−0·0136	0·9660	−0·2583
	0·169	287	−0·1038	−0·2583	−0·9605

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

	x	y	z
C(1)	−10015 (68)	19180 (34)	−2021 (15)
C(2)	−665 (54)	12010 (29)	6150 (14)
C(3)	9128 (67)	−7253 (33)	8113 (14)
C(4)	−2033 (64)	25919 (36)	12382 (15)
O	−9913 (76)	42496 (30)	11029 (14)
Cl	8671 (19)	16170 (10)	22603 (4)
H(1)	−1485 (85)	3301 (47)	−311 (21)
H(3)	1569 (69)	−1225 (40)	1361 (16)

cannot be regarded as that of an ideal rigid body. The principal axes of translation and libration are nearly parallel to the principal axes of inertia. The translational vibrations are nearly isotropic with the largest vibration along the longest molecular axis, which corresponds to the smallest moment of inertia. The librational motion is highly anisotropic with the largest vibration (9·0°) again about the long axis of the molecule.

Bond lengths and angles

The observed bond lengths and angles are shown in Fig. 1. C(1)—C(3') is 1·373 Å, while the average of the other two aromatic bonds is 1·389 Å. Similar shortening of the central bond was also found in a series of benzene derivatives having electron donor and acceptor groups in *para* positions, *e.g.* *p*-toluic acid (1·379 Å) (Takwale & Pant, 1971), *p*-aminobenzoic acid (1·375 Å) (Lai & Marsh, 1967), *p*-nitroaniline (1·375 Å) (Trueblood, Goldish & Donohue, 1961), *β-p*-nitrophenol (1·380 Å) (Coppens & Schmidt, 1965), and *β*-sulphanilamide (1·381 Å) (O'Connell & Maslen, 1967). The shortening of the central bond in these compounds is attributed to cooperative electronic interaction between the donor and acceptor groups in the *para* positions. An analysis of 15 published structures of terephthalic acid derivatives yielded 1·380 (2) and 1·395 (3) Å as the mean lengths of the central and outer bonds of the phenyl ring respectively. This difference is highly significant and displays a quinonoid character of these centrosymmetric compounds. It rules out the donor–acceptor explanation, at least in this case. C(2)—C(4), 1·486 Å, agrees well with other values of C(phenyl)—C(carbonyl) bond lengths, *e.g.* terephthalic acid (1·483) (Bailey & Brown, 1967), benzoic acid (1·48) (Sim, Robertson & Goodwin, 1955), and the mean value of 1·489 ± 0·012 Å found for a series of chalcone derivatives (Rabinovich & Shakked, 1974). The bond angles in the benzene ring are all equal to 120·0°; on the other hand, the
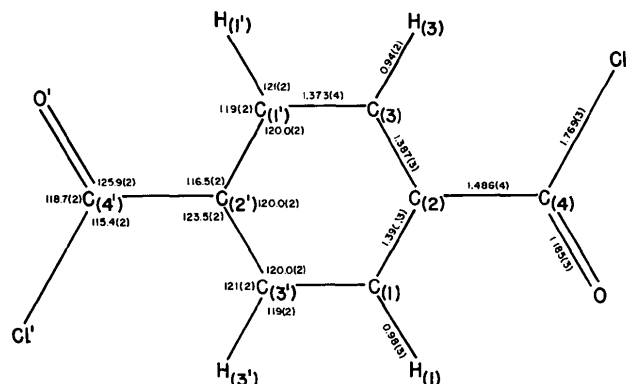
exocyclic angles at C(2) (123·5, 116·5°) deviate significantly from 120·0°. This distortion is attributed to the in-plane 1,4 Cl···C(3) (3·04 Å) repulsion. The C=O length of 1·185 Å agrees well with the values obtained for other acyl chlorides by electron diffraction and microwave spectroscopy (Simonetta & Beltrame, 1972), varying from 1·166 in phosgene to 1·21 (4) Å in chloroacetyl chloride. On average this distance is shorter in acyl halides than in carboxylic acids, esters, ketones or aldehydes (Simonetta & Carrá, 1969), indicating more double-bond character. The C—Cl length of 1·769 Å is longer than the accepted value of 1·736 Å for Cl-bonded sp^2 C atoms (Dewar & Schmeising, 1960). A similar lengthening is also observed in the acyl chlorides listed by Simonetta & Beltrame (1972), varying from 1·746 in phosgene to 1·789 (5) Å in acetyl chloride.

Molecular packing

Figs. 2 and 3 show the packing seen along [100]. The nearly planar molecules form stacks along [100] which are held together by C—Cl···O and C—H···O contacts of 3·3 and 2·7 Å respectively. The in-stack benzene rings overlap partially, the interplanar distance being 3·52 Å, and the shortest C···C distance 3·55 Å. Other short intermolecular contacts are listed in Table 4. The molecular packing is essentially similar to that postulated on the grounds of Cl···O interactions and unit-cell dimensions. Nevertheless, the differences between the two are appreciable and indicate that the postulated Cl···O contact of 2·8 Å is far too short. In order to relax these short contacts the molecular plane is tilted from the (100) plane by 14°; we note, however, that the C—Cl vector is definitely pointing toward the lone-pair lobe of an O atom (the angles C—Cl···O and

Fig. 1. Bond lengths (Å) and angles (°) and their e.s.d.'s.
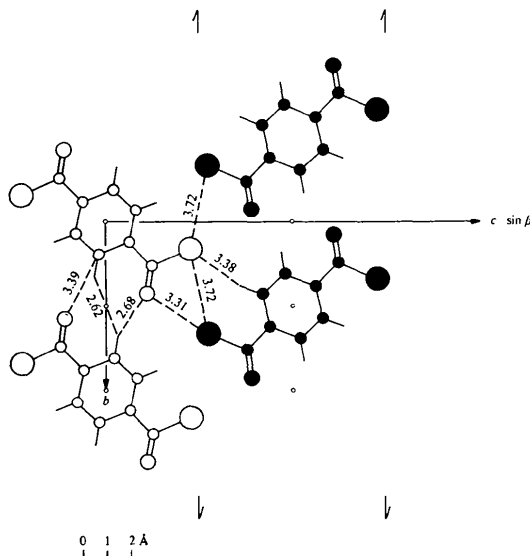

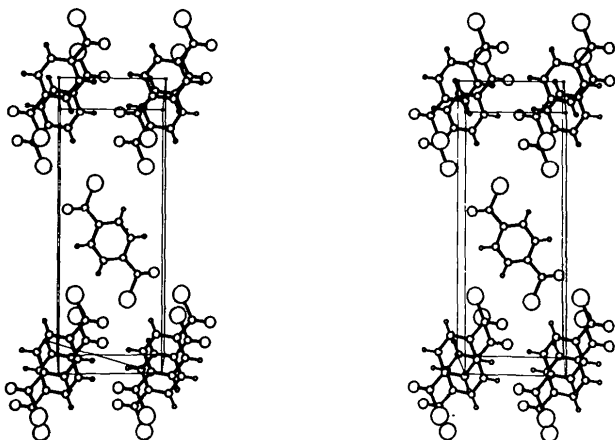Fig. 2. Packing arrangement seen along [100].

Fig. 3. Stereoscopic view of the unit cell seen along **a**, drawn by *ORTEP* (Johnson, 1971). The origin of the unit cell is at the top left-hand corner with **c** vertical and **b** horizontal.

Table 4. *Short intermolecular contacts* (Å)

C(1)···C(2)^I	3·85	Cl···H(3)^{IV}	3·38
C(1)···C(3)^I	3·55	C(1)···C(2)^V	3·78
C(2)···C(2)^I	3·72	C(1)···C(4)^V	3·68
C(2)···C(3)^I	3·68	C(2)···C(4)^V	3·56
Cl···Cl^{II}	3·72	C(2)···Cl^V	3·76
C(1)···O^{III}	3·39	C(3)···Cl^V	3·77
O···H(1)^{III}	2·68	C(4)···Cl^V	3·80
H(1)···H(1)^{III}	2·62	C(3)···Cl^{VI}	3·77
O···Cl^{IV}	3·31	Cl···H(3)^{VII}	3·10
Cl···Cl^{IV}	3·72		

Roman numeral superscripts refer to the molecules in the following equivalent positions relative to the reference molecule at x,y,z.

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

$C=O\cdots Cl$ are, respectively, 167·5 and 114·5°), thus retaining the basic idea of the hal···O affinity. The

difference between the observed and postulated structures explains the failure of the rigid-body computer program to refine the model.

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