

Tetrachlorophthalic Anhydride: a Study of the Carbon-Chlorine Bond

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The crystal and molecular structure of tetrachlorophthalic anhydride (TCPA) was determined by single-crystal X-ray diffraction methods. It crystallizes in space group $P2_1/n$, $a = 13.37$ (2), $b = 5.760$ (8), $c = 12.32$ (2) Å, $\beta = 91.03$ (10) $^\circ$ with four molecules per unit cell. Molecular overcrowding causes the chlorine atoms to be distorted 1.0 to 2.6 $^\circ$ from the benzene ring plane. The average carbon-chlorine bond distance is 1.709 Å. It is suggested that, in aromatic compounds, the C-Cl bond distance is significantly shorter for two *ortho* bonds than for *meta*, *para* or isolated bonds.

Introduction

The tetrahalophthalic anhydrides, TXPA (X = Cl, Br, I), are known to form charge-transfer complexes with a number of polycyclic compounds (Buu-Hoi & Jacquignon, 1957; Chowdhury & Basu, 1960; Chowdhury, 1961; Czekalla & Meyer, 1961; Short, 1968). The TXPA compounds contain no hydrogen atoms and complexes containing these molecules should be free of hydrogen bonds between the molecules constituting the complex, thus permitting a study of the structural effects of complex formation relatively free of other complicating factors. Prior to undertaking a general study of these complexes, it was considered advisable to determine the structure of the uncomplexed TXPA molecules, so that the effects of any complex formation (e.g. distortion from planarity) could be recognized. A preliminary examination of the three TXPA molecules revealed that they crystallize in different space groups. It is quite possible that the effects of molecular overcrowding become progressively more severe as the size of the halogen atom increases. The question of molecular overcrowding has been studied by a number of investigators (Bastiansen & Hassel, 1947; Coulson & Stocker, 1959; Ferguson & Sim, 1961; Strel'cova & Struchkov, 1961; Gafner & Herbstein, 1962).

However, few systematic investigations of related compounds using X-ray diffraction techniques have been reported. The study of TCPA was undertaken as the initial step in the investigation of the tetrahalophthalic anhydrides and their charge-transfer complexes.

Crystal data

Crystals of TCPA were prepared in three ways: crystallization from benzene, crystallization from nitrobenzene, and sublimation. In the latter case, a sample of TCPA, in an evacuated (10^{-3} mm) glass tube was placed in a tube furnace set at 100 $^\circ$; crystals grew at the end of the tube extending from the furnace. Subsequent analysis of crystals from all three sources

showed that they formed the same crystalline modification.

Crystal data are found in Table 1. McCrone (1951) determined the unit-cell dimensions of TCPA. These values, as reported by Donnay & Donnay (1963) ($a = 13.45$, $b = 5.834$, $c = 12.34$ Å, $\beta = 90.97^\circ$) are in satisfactory agreement with those reported here, which were refined with powder data.

Table 1. *Crystal data*

Name:	Tetrachlorophthalic anhydride, C ₈ Cl ₄ O ₃
Formula weight:	285.90 (based on ¹² C)
Crystal system:	monoclinic
Systematic absences:	0k0, k odd; h0l, h + l odd
Space group:	$P2_1/n$ (No. 14, C_{2h}^5) $a = 13.37$ (2), $b = 5.760$ (8), $c = 12.32$ (2) Å, $\beta = 91.03$ (10) $^\circ$
Unit-cell volume:	948.9 Å ³
Density:	Z = 4
	X-ray 2.00 ₁ g.cm ⁻³
	Experimental 1.970 g.cm ⁻³ (McCrone, 1951)

Needle-shaped crystals growing along the **b** direction were used for collecting data at room temperature (24 ± 2). Integrated Weissenberg photographs using the multiple-film technique were taken of layers hkl , $K = 0-3$. Each exposure was taken for 170 hours using Ni-filtered Cu $K\alpha$ radiation. Three layers ($hk0$, $hk1$, $0kl$) of non-integrated, timed precession photographs were taken for scaling purposes with Zr-filtered Mo $K\alpha$ radiation. A total of 628 reflections (548 Weissenberg and 80 precession) were used in the refinement of the structure.

The absorption coefficients calculated for TCPA are: $\mu_{Cu} = 112$ and $\mu_{Mo} = 12$. A nearly cylindrical crystal of dimensions 0.3 mm length by 0.04 mm diameter ($\mu R = 0.2$) was selected for use on the Weissenberg goniometer. The precession data were collected from another cylindrical crystal with dimensions 0.9 by 0.15 mm

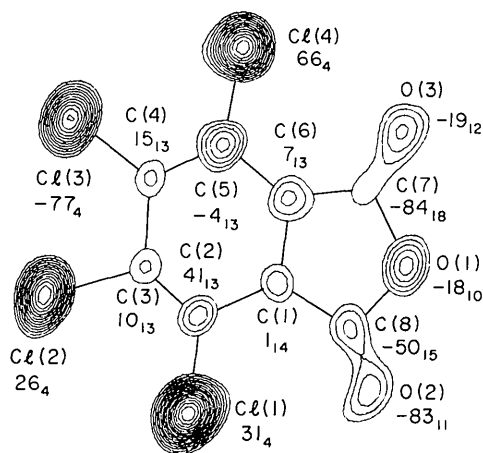


Fig. 1. Electron density map of the TCPA molecule through the weighted least-squares plane, $6.424x - 3.415y - 8.070z = 4.178$. The deviation of each atom from the plane is shown in the Figure; the e.s.d. of this deviation is shown as a subscript (all values are $\times 10^3$). The heights of the chlorinic atoms in the regular electron density map are $17-19 \text{ e.}\text{\AA}^{-3}$, those of the oxygen atoms are $7-8 \text{ e.}\text{\AA}^{-3}$ and for carbon they are $6-7 \text{ e.}\text{\AA}^{-3}$. Some of the peak heights in this Figure are misleading because of the deviations of the atoms from the plane through which the map was drawn.

($\mu R = 0.1$). The effect of absorption on the relative intensities is as follows: As a function of θ , less than 2%; as a function of the variation of crystal diameter, less than 4%. No absorption corrections were applied. Relative intensities, measured on a Nonius microdensitometer, were scaled and converted to F^2 by the application of the proper Lp factor. Standard crystallographic programs, modified for use on the Brookhaven computer, were used in the solution and refinement of this structure.

Solution and refinement

The following general position coordinates were used: $\pm(x, y, z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$. The structure was solved and refinement carried out using the form factor for Cl, O, C which will appear in Volume IV of *International Tables for X-ray Crystallography* and Cromer's (1965) anomalous dispersion corrections for chlorine.

An estimated absolute scale factor and mean isotropic temperature factor were determined from a Wilson plot and the crystal structure was solved using the symbolic addition method of direct determination of phases (Karle & Karle, 1966). Three signs and two symbols were selected. From a total of 254 E factors

Table 2. Atomic coordinates and anisotropic temperature factors of TCPA

The β values are used in the expression

$$\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})].$$

All positional and thermal parameters have been multiplied by 10^5 ; e.s.d.'s are in parentheses.

(a) Positional parameters

	x	y	z
Cl(1)	12130 (30)	9039 (58)	57226 (32)
Cl(2)	32459 (28)	18753 (63)	69349 (28)
Cl(3)	45156 (30)	60770 (59)	62939 (31)
Cl(4)	38874 (29)	91638 (60)	43138 (33)
O(1)	8613 (82)	65802 (202)	31018 (72)
O(2)	314 (73)	35202 (177)	38179 (85)
O(3)	19458 (82)	93525 (204)	27940 (92)
C(1)	16732 (108)	46246 (256)	45475 (117)
C(2)	19549 (96)	31238 (230)	53622 (103)
C(3)	28588 (102)	36361 (252)	58991 (98)
C(4)	34442 (95)	54773 (262)	55825 (113)
C(5)	31705 (97)	70061 (232)	47405 (103)
C(6)	22653 (100)	64755 (278)	42314 (107)
C(7)	17520 (137)	78210 (378)	33629 (145)
C(8)	7653 (129)	47697 (349)	38270 (139)

(b) Thermal parameters

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl(1)	540 (30)	3253 (263)	682 (37)	-372 (72)	63 (27)	116 (72)
Cl(2)	570 (34)	3803 (264)	378 (32)	28 (61)	-135 (25)	311 (62)
Cl(3)	386 (29)	5231 (277)	558 (33)	-148 (69)	-221 (26)	-44 (72)
Cl(4)	423 (28)	3626 (264)	762 (38)	-453 (72)	36 (27)	316 (74)
O(1)	533 (88)	5445 (601)	230 (72)	270 (185)	-64 (63)	729 (178)
O(2)	207 (70)	5282 (562)	864 (104)	-178 (176)	-176 (75)	-288 (184)
O(3)	427 (89)	5336 (705)	611 (96)	122 (188)	89 (72)	902 (210)
C(1)	281 (108)	2082 (756)	452 (132)	-88 (243)	-31 (99)	-178 (263)
C(2)	233 (100)	2128 (713)	344 (117)	-169 (239)	36 (91)	199 (234)
C(3)	273 (95)	3446 (752)	178 (91)	141 (248)	-115 (79)	-8 (253)
C(4)	111 (100)	2984 (746)	618 (148)	21 (225)	24 (96)	-388 (282)
C(5)	219 (105)	2593 (748)	289 (110)	314 (252)	35 (89)	332 (246)
C(6)	209 (103)	3517 (858)	252 (105)	421 (280)	56 (84)	-2 (267)
C(7)	322 (135)	4775 (1184)	669 (181)	-67 (322)	101 (127)	-143 (352)
C(8)	334 (119)	5967 (1107)	407 (128)	-202 (307)	80 (105)	-1181 (317)

greater than 1.0, phases for 247 reflections were determined after four passes through *SORTE* (Okaya & Bednowitz, 1967). All 15 atoms of the asymmetric unit were visible on the *E* map obtained using these phases.

Refinement continued through various stages, until the final refinement was carried out with a full-matrix least-squares calculation using 143 variables. These included 7 scale factors, three positional and six thermal parameters for each of the fifteen atoms, and an isotropic extinction factor as suggested by Zachariasen (1968) and as treated by Coppens & Hamilton (1970). The discrepancy factors,

$$R = \frac{\sum |F_o - F_c|}{\sum |F_o|}$$

and

$$R' = \frac{[\sum w||F_o| - |F_c||^2 / \sum w|F_o|^2]^{1/2}}$$

before and after the extinction correction are:

	Before	After
<i>R</i>	0.090	0.055
<i>R'</i>	0.097	0.054

The weighting scheme employed in the least-squares program used $\sigma^2 = (0.08F)^2 + (20F/I)^2$, where *F* is the observed structure factor and *I* the observed intensity. Final positional and thermal parameters are found in

Table 3. *Observed and calculated structure factors* ($\times 10$)
Reflections marked with a dot were obtained from precession photographs.

K* 0		H L		F OBS	F CALC	H L		F OBS	F CALC	H L		F OBS	F CALC
0 0	2	708	672	10	10	133	118	4	-4	407	403	13	3
0 0	2	712	672	10	10	259	251	4	-2	553	553	13	4
0 0	4	755	731	10	-2	516	504	4	0	728	735	13	5
0 0	6	672	731	10	0	231	257	4	0	723	735	14	-7
0 0	6	468	471	10	0	158	158	4	0	1861	1558	14	-5
0 0	6	659	471	10	4	256	264	4	1	1610	1546	14	-1
0 0	6	596	438	10	0	118	297	4	3	91	87	14	5
0 0	8	661	638	10	6	474	474	4	2	1097	1073	14	0
-1 5	146	149	11	-7	132	208	4	4	4	427	435	14	2
-1 1	232	197	11	1	191	218	4	5	758	771	14	6	
-1 1	232	197	11	3	128	103	4	6	136	113	15	1	
-1 9	211	107	11	5	184	233	4	7	308	304			
1 -3	132	165	12	-4	278	295	4	10	248	233			
1 1	166	137	11	7	334	336	4	9	140	52			
1 3	111	105	12	-4	553	548	4	11	267	238			
1 5	208	212	12	2	476	451	5	-11	134	130			
1 7	199	184	12	6	269	288	5	-9	181	192			
1 9	193	197	12	6	308	277	5	-5	208	186			
1 15	87	16	12	8	183	182	5	-3	266	298			
-2 4	223	221	13	-3	154	154	5	-2	389	396			
-2 12	331	354	13	-3	378	408	5	0	200	192			
-2 10	337	321	13	1	285	300	5	0	199	192			
-2 8	492	432	13	-5	149	149	5	1	593	597			
-2 6	175	151	14	-6	235	261	5	1	611	597			
-2 2	579	637	14	-2	185	188	5	2	168	169			
-2 0	433	408	14	4	176	166	5	6	408	427			
-2 0	420	408	14	6	215	200	5	10	195	126			
2 2	464	446	14	8	114	115	5	11	146	113			
2 4	2343	2311			6	-12	276	288	0	10			
2 2	501	519			6	-10	198	174					
2 10	171				6	-11	275	260	0	13			
2 12	188	137			6	-9	428	403	1	-9			
2 14	173	181			6	-8	255	230	1	-6			
3 15	130	130			6	-8	183	191	1	-4			
3 13	252	243			6	-5	393	384	1	-4			
3 11	155	163			6	-4	361	367	1	-2			
3 9	145	145			6	-3	596	613	1	-1			
3 7	365	366			6	-1	403	385	1	0			
3 5	140	136			6	-1	374	385	1	0			
3 3	171	171			6	-1	202	267	1	0			
3 3	360	350			6	-1	281	267	1	0			
3 1	264	264			6	0	955	1003	6	3			
3 11	314	356			6	0	967	1003	6	4			
4 12	174	136			6	0	639	654	6	5			
4 10	323	323			6	0	767	654	6	6			
4 8	911	918			6	0	183	158	6	3			
4 6	295	297			6	0	245	241	6	8			
4 4	894	865			6	0	434	416	6	13			
4 2	717	291			6	0	111	180	6	11			
4 0	865	865			6	0	230	197	6	11			
4 0	826	826			6	0	284	179	6	7			
4 4	184	139			6	1	222	225	7	1			
4 6	465	467			6	1	182	187	7	2			
4 8	962	962			6	1	304	298	7	4			
4 10	523	509			6	1	184	172	7	6			
4 14	126	85			6	1	148	129	7	7			
4 11	198	208			6	1	211	190	7	8			
5 9	390	370			6	1	188	190	7	9			
5 5	478	477			6	1	132	120	7	10			
5 3	400	400			6	1	131	120	8	-12			
5 1	176	165			6	1	107	128	8	-8			
5 7	289	324			6	1	176	158	8	-4			
5 9	502	539			6	1	139	140	8	-1			
5 11	265	299			6	1	190	200	8	-1			
5 13	198	219			6	1	121	142	8	1			
6 10	244	223			6	1	142	90	8	1			
6 8	295	285			6	1	205	142	8	3			
6 6	331	298			6	1	379	8	4	231			
6 4	126	91			6	1	308	302	8	5			
6 2	1268	1311			6	1	485	477	8	6			
6 0	413	386			6	1	352	368	8	6			
6 0	395	396			6	1	189	157	8	12			
6 2	1042	1027			6	1	2211	2145	8	13			
6 4	602	605			6	1	2032	2017	8	9			
6 6	211	164			6	1	902	556	8	284			
6 8	467	448			6	1	560	556	9	-3			
6 12	297	297			6	1	245	227	9	0			
6 14	167	191			6	1	238	227	9	229			
7 7	219	219			6	1	666	632	9	5			
7 9	296	296			6	1	845	832	9	9			
7 7	186	140			6	1	190	185	9	9			
7 5	1	506			6	1	565	593	9	10			
7 3	576	571			6	1	151	107	10	-8			
7 1	316	307			6	1	509	516	10	10			
7 1	245	307			6	1	425	394	10	-3			
7 3	213	236			6	1	190	140	10	-2			
7 5	179	172			6	1	245	235	10	1			
7 7	168	130			6	1	155	112	10	0			
7 9	241	242			6	1	133	113	10	3			
7 11	247	215			6	1	147	158	10	7			
7 13	189	194			6	1	220	227	10	6			
8 12	316	329			6	1	349	367	10	10			
8 8	352	347			6	1	404	226	10	4			
8 6	640	626			6	1	521	527	11	-3			
8 4	289	325			6	1	472	456	11	-2			
8 2	174	135			6	1	426	456	11	1			
8 0	284	290			6	1	135	104	11	0			
8 0	294	303			6	1	123	91	12	-7			
8 2	835	866			6	1	136	122	-8	124			
8 6	448	456			6	1	178	184	12	-4			
8 12	202	192			6	1	155	125	12	-2			
9 1	442	530			6	1	143	143	12	272			
9 1	538	530			6	1	225	210	12	2			

Table 2; the calculated and observed structure factors are in Table 3.

The final isotropic extinction parameter corresponds to a mosaic spread of approximately 2.67 sec or a spherical domain radius of 3.36 microns depending upon whether a Zachariasen (1968) type I or type II description is chosen. The calculated structure factors have been multiplied by the extinction correction

$$E = \left[1 + \frac{2\bar{T}F_{\text{calc}}^2 g \lambda^3}{V^2 \sin 2\theta} \right]^{-1/4},$$

where F_{calc}^2 is on an absolute scale, λ is in Å, the cell volume, V , is in Å³, $\bar{T}=0.005$ cm is the average path length in the crystal and g (the refined extinction parameter) has the value 2.18×10^4 . The extinction parameter corrected for deviations between F_{obs} and F_{calc} as extreme as $F_{\text{obs}}/F_{\text{calc}}=0.37$.

The equation of the weighted least-squares plane through the plane of the molecule is:

$$6.424x - 3.415y - 8.070z = 4.178,$$

where x, y and z are the fractional coordinates in the monoclinic cell. The electron density map of this plane is shown in Fig. 1; the deviation of each atom from the least-squares plane is indicated in the diagram. The highest electron density in the difference electron density ($F_{\text{obs}} - F_{\text{calc}}$) map was 0.37 e.Å^{-3} , about 6% of the height of a benzene ring carbon atom in this structure.

Thermal 'riding' correction

The chlorine and carbonyl oxygen atoms are vibrating anisotropically with a maximum root-mean-square amplitude of vibration of about 9° for chlorine and 16° for oxygen. Bond corrections for these motions have been calculated assuming that the chlorine and carbonyl oxygen atoms 'ride' on the carbon atoms to which they are attached (Busing & Levy, 1964). The corrected bond lengths are used in the following discussion and are listed in Table 4.

Table 4. Selected interatomic distances in TCPA

All distances are in ångströms, with the e.s.d. in parentheses.

(a) Intramolecular distances

(i) Bond lengths corrected for thermal motion (uncorrected values are in Fig. 2)

Cl(1)–C(2)	1.700 (13)
Cl(2)–C(3)	1.717 (13)
Cl(3)–C(4)	1.718 (13)
Cl(4)–C(5)	1.684 (13)
O(3)–C(7)	1.177 (17)
O(2)–C(8)	1.227 (17)

(ii) Non-bonded intramolecular distances

	No 'riding' correction	'Riding' correction
Cl(1)···Cl(2)	3.129 (5)	3.144 (5)
Cl(2)···Cl(3)	3.068 (5)	3.090 (5)
Cl(3)···Cl(4)	3.122 (5)	3.134 (5)
Cl(1)···O(2)	3.185 (10)	
Cl(4)···O(3)	3.176 (12)	

Table 4 (cont.)

(b) Intermolecular distances

(i) Adjacent molecules related by center of symmetry

Cl(1)···O(2)	3.101 (11)
Cl(3)···Cl(4)	3.563 (5)

(ii) Distance between parallel molecular planes*

3.451 (14)

(iii) Adjacent molecules (a) x, y, z and (b) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$

a	b
O(3)···C(7)	3.024 (18)
O(3)···C(6)	2.989 (17)

* Cl(1) is nearly directly over C(6) of the molecule parallel to it; the vector drawn between these two atoms forms an angle of 87.3° with the molecular plane containing C(6).

Planarity of the molecule

A number of other molecules containing polyhalogenated benzene rings have been studied in an attempt to determine whether or not molecular overcrowding can distort molecules that should otherwise be planar (e.g. Gafner & Herstein, 1962). In the absence of steric distortions, all the atoms in a molecule of TCPA should lie on the same plane. The present data (Fig. 1) show that molecular overcrowding in TCPA does cause a small, but significant, deviation from planarity.

No distortion is noted in the benzene ring, nor is there any significant bending of the molecule along the C(1)–C(6) axis (the angle between the two planes defined by C(2), C(3), C(4) and by O(1), C(7), C(8) is 2.0° with an e.s.d. of 1.3°). However, most of the atoms not in the benzene ring are not located on the weighted least-squares plane. The relative displacements of the Cl(1), C(8) and Cl(4), C(7) pairs of atoms agree with those observed in *o*-chlorobenzoic acid (Ferguson & Sim, 1961).

The data for the chlorine atoms correspond to a bending from the plane of between 1.0 and 2.6°, with a puckered effect observed over the molecule. The two outer atoms, Cl(1) and Cl(4), are bent away from the adjacent chlorine atoms toward the oxygen atoms which also appear to maintain this puckered effect.

The relatively small displacements of the chlorine atoms from the molecular plane are consistent with the observations of a number of other investigators: Sakurai and co-workers (Dean, Richardson & Sakurai, 1961; Sakurai, 1962*b*) found the out-of-plane bending of a number of tetrachlorobenzene derivatives to be of the order of 1°. Morino, Toyama, Itoh & Kyono (1962) reported in a footnote that a re-evaluation of hexachlorobenzene by Bastiansen (private communication to them) showed it to be planar, in contradiction with the earlier work of Bastiansen & Hassel (1947) which indicated a deviation of 12°. Finally, Daševskij, Avoyan & Davydova (1966), calculated that the energy minima in *ortho* tetrahalogenated benzene compounds correspond to the planar configurations. This calculation is compatible with the experimental results showing a small 1–2° deviation from planarity.

Intramolecular distances

Bartell (1960, 1962) reported an intramolecular non-bonded Cl...Cl distance of 2.88 Å for chlorine atoms attached to the same carbon atom. However, the average value observed for chlorine atoms attached to adjacent carbon atoms on an aromatic ring is 3.14 Å (Table 5). The intramolecular nonbonded contact distances in TCPA are presented in Table 4(a).

From the data in Table 5, it is possible to differentiate between compounds containing two or more *ortho* carbon-chlorine bonds and those containing 'isolated' carbon-chlorine bonds. In the former case the average value is 1.709 Å, while in the latter it is 1.737 Å.* This leads to the important conclusion that, in the case of aromatic compounds, each of two adjacent carbon-chlorine bonds is shorter than a single carbon-chlorine bond.

In any given molecule, local bonding conditions are likely to cause slight deviations from these values, while cases of severe molecular overcrowding can

result in gross changes in the Cl...Cl or C-Cl distances and may even distort the molecule. Thus in 1:4:5:8-tetrachloronaphthalene (Gafner & Herbstein, 1962) and 5,6-dichloroacenaphthene (Avoyan & Struchkov, 1961) the closely spaced, theoretically parallel carbon-chlorine bonds cause molecular distortions and abnormal interatomic distances (Table 5). Less severe molecular overcrowding, such as is found in TCPA, results in small molecular distortions with normal interatomic distances.

Further indications of a significant difference between *ortho* carbon-chlorine bonds and single, *meta*-, or *para*-carbon-chlorine bonds are available from nuclear quadrupole resonance data. Bersohn (1954), in a discussion of the double-bond character of conjugated carbon-chlorine bonds, states that the decrease of double-bond character and consequent increase of the nuclear quadrupole coupling constant of a carbon-chlorine bond upon the introduction of another chlorine atom in a resonating system is a small high-order effect. He does not distinguish between *ortho*, *meta*, and *para* substitution. However, if we use nuclear quadrupole resonance data as a measure of the double bond and/or ionic character of the bond, then an increase in the resonance frequency will indicate a decrease in the ionic character of the bond, an increase in the double-bond character and a shortening

* Palenik, Donohue & Trueblood (1968) presented a table of aromatic C-Cl bonds, although they did not make the distinction that is made here. With one exception, the data in their table are in agreement with the present conclusions.

Table 5. Average carbon-chlorine bond lengths and chlorine-chlorine non-bonded contact distances in several aromatic compounds.

Compound	C-Cl	Cl...Cl	Reference
5,6-Dichloroacenaphthene	1.76 Å	(3.12) Å ^a	Avoyan & Struchkov (1961)
2,5-Dichloroaniline	1.744		Sakurai, Sundaralingam & Jeffrey (1963)
1-(2,6-Dichlorobenzyl)-6-hydroxy-1,4,5,6-tetrahydropyridinamide	1.743		Hope (1969)
Ammonium chloranilate monohydrate	1.741		Krogh-Anderson (1967)
1:4:5:8-Tetrachloronaphthalene	1.740	(2.98) ₇ ^a	Gafner & Herbstein (1962)
4-Acetyl-2'-chlorobiphenyl	1.738		Sutherland & Hoy (1968)
<i>o</i> -Chlorobenzoic acid	1.737		Ferguson & Sim (1961)
<i>trans-p,p'</i> -Dichloroazobenzene	1.737		Hope & Victor (1969)
4-4''-Dichlorodiphenylsulphone	1.736		Sime & Abrahams (1960)
Tetrachlorohydroquinone (X-ray)	1.733	3.15	Sakurai (1962a)
TMPD-Chloranil ^b	1.714	3.16	de Boer & Vos (1968)
Tetrachloro- <i>p</i> -benzoquinone	1.714	3.17	Chu, Jeffrey & Sakurai (1962)
Tetrachlorohydroquinone (neutron)	1.712	3.14	Sikka & Chidambaram (1967)
Pentachlorophenol	1.707	3.12	Sakurai (1962b). Corrected in Sakurai <i>et al.</i> (1963)
TCPA	1.705	3.12 ₃	This work
TCPC ^c	1.705	(3.35) ^e	Shimanouchi, Sasada, Ashida, Kakudo, Murata & Kitahara (1969)
TCBF ^d	1.705	(3.35) ^e	Nishi, Sasada, Ashida & Kakudo (1966)
	Average	3.14	

^a Not attached to adjacent carbon atoms, not included in average.

^b *N,N,N',N'*-Tetramethyl-*p*-diaminobenzene-chloranil.

^c 1,2,3,4-Tetrachloro-5,6-di-*n*-propyl calicene.

^d 1,2,3,4-Tetrachlorobenzo[*g*]sesquifulvalene.

^e Five-membered ring, not included in average.

of the bond length. The data for a series of chlorinated benzene compounds (Table 2 in Bersohn, 1954) show that there is a small increase for the *meta* and *para* substituted dichlorobenzenes, and a significantly larger increase for *o*-dichlorobenzene.

The observed shortening of the C-Cl bond can be due to an actual shortening of this bond because of halogen-halogen interactions as discussed by Coulson (1962) and by Bastiansen & Traetteberg (1962), or it can be due to an induction effect (Morino *et al.*, 1962). The comparison of accurate neutron and X-ray diffraction data would be of help in clarifying this point.

A (partial) search of the literature revealed only one suitable compound that had been studied by neutron diffraction. Sikka & Chidambaram (1967) found that the C-Cl bond lengths in tetrachlorohydroquinone (TCHQ) have an average bond length of 1.712 (8) Å

and that all carbon-carbon bond lengths are within one e.s.d. of 1.390 Å. The X-ray diffraction investigation of this compound (Sakurai, 1962*a*) revealed a longer C-Cl distance and a shorter C-C distance. The neutron diffraction data place tetrachlorohydroquinone in the same category as TCPA and other polychlorinated aromatic compounds; there is no evidence of any difference between the various C-C bonds in TCHQ. On this basis, the observed C-Cl bond lengths, which are within one e.s.d. of 1.709 Å, are in agreement with those observed for TCPA and related compounds. However, it is felt that these data are not sufficient to permit one to distinguish between actual shortening of the bond and apparent shortening due to electron-cloud distortion. Neutron diffraction investigations of other polychlorinated compounds are needed.

Carbon-oxygen distances

Although the differences between chemically equivalent carbon-oxygen interatomic distances in TCPA [Fig. 2 and Table 4(*a*)] are only about three e.s.d.'s, they are larger than the differences found between other chemically equivalent bonds in this molecule. The possibility that the least-squares refinement had reached a false minimum was considered. Coordinates of C(7) and C(8) corresponding to equal and 'usual' carbon-oxygen interatomic distances were determined and refined using the least-squares procedure. After three cycles of refinement, the coordinates returned to their original values (Table 2). A function and error analysis showed that there are no significant differences between chemically equivalent bond lengths and angles in the TCPA light-atom skeleton.

The rather large discrepancies between the two pairs of $>C=O$ and $>C-O$ bonds in TCPA may be due to the fact that, even though two pairs of bonds are chemically equivalent, they are located in non-equivalent crystalline environments. The O(2) atom of a molecule in general position x, y, z is related to a second O(2) atom across a center of symmetry at $\bar{x}, \bar{y}, \bar{z}$, while the O(3) atom of this molecule is directed at the five-membered ring of a molecule at $\frac{1}{2} - x, \frac{1}{2} + y,$

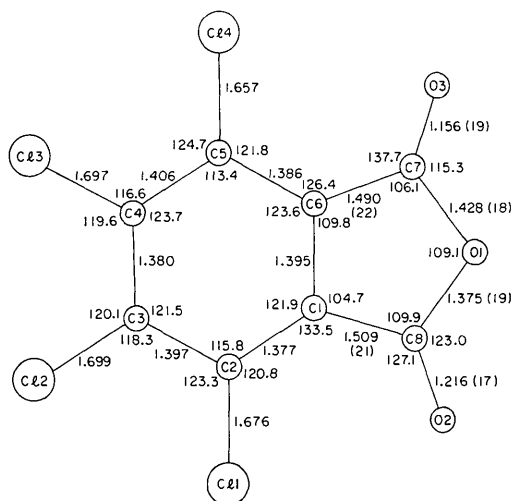


Fig. 2. Intramolecular bond distances in TCPA. The e.s.d.'s are 0.013 Å for C-Cl; 0.016 Å for C-C (benzene); 2° for angles around C(7) and C(8); and 1.2° for other angles. The remainder of the e.s.d.'s are shown in parentheses. All values shown are not corrected for thermal vibration; the corrections are found in Table 4 (*a*).

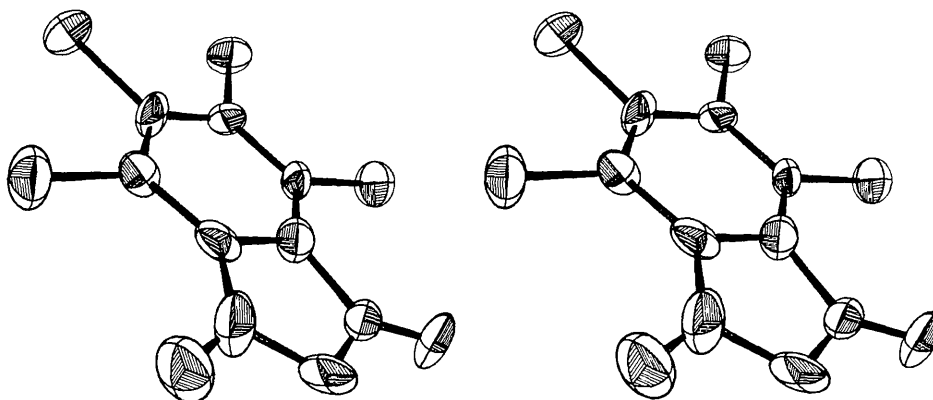


Fig. 3. Stereo pair of the TCPA molecule.

$\frac{1}{2}-z$. These different environments will result in different thermal and vibrational modes which may give rise to the observed differences in bond lengths. A similar effect was noted by Boeyens & Herbstein (1965) in the perylene complex of pyromellitic dianhydride, in which $>C=O$ bond lengths of 1.230 and 1.178 Å (after thermal corrections) were determined. However, in a structure determination of the pyrene-pyromellitic dianhydride complex at 110°K, a value of 1.193 Å with an e.s.d. of 0.006 Å was determined for all four crystallographically non-equivalent $>C=O$ bonds (Herbstein & Snyman, 1969). Quite clearly the effects due to molecular motions of atoms in anisotropic environments were removed at low temperatures.

A comparison of C=O, C-O and C-C (non-benzene) bond lengths in TCPA and related molecules is found in Table 6. The chlorine-oxygen intramolecular distances are discussed in the following section.

A stereo view of the molecule is presented in Fig. 3.

Crystal structure

The molecules pack together in interpenetrating and parallel rows, with each molecular plane lying along the row-axis. One row is formed by molecules related to each other by a center of symmetry, while parallel rows in adjacent unit cells are related by a translation vector. Molecules related to the x, y, z positions by $\frac{1}{2}+x$,

$\frac{1}{2}-y$, $\frac{1}{2}+z$ form a similar set of parallel rows which lie at an angle of 106.7(2.0)° to the first set. This is shown in the stereo packing diagram found in Fig. 4. This packing diagram was drawn perpendicular to the molecular plane of TCPA; for purposes of identification, Cl(1) is marked with an asterisk in each molecule shown.

Some of the more interesting intermolecular interatomic distances are listed in Table 4(b). All distances of closest approach are within a few e.s.d.'s of the sum of the van der Waals radii (Bondi, 1964). Bondi has emphasized the distinction between the van der Waals radius of a singly-bonded oxygen atom (1.5 Å), doubly-bonded oxygen atom in the direction parallel to the double bond (1.4 Å) and doubly-bonded oxygen atom in the direction perpendicular to the double bond (1.6 Å). Using Bondi's van der Waals radius of 1.70 Å for chlorine we would expect a chlorine to oxygen distance of 3.3 Å perpendicular to the carbonyl double bond and 3.1 Å parallel to it.

In TCPA we find a verification of these predicted trends. The intramolecular chlorine-oxygen contact is nearly perpendicular to the double bond of oxygen and the observed interatomic distance is 3.18 Å [Table 4(a)]. On the other hand, the intermolecular contact direction of these two atoms, across a center of symmetry, is nearly parallel to the double bond [the C(8)-O(2)···Cl(1) angle is 157°] and the interatomic

Table 6. Carbon-oxygen and (nonbenzene) carbon-carbon average bond distances (Å) in TCPA and related molecules

Molecule	C=O	C-O	C-C	Reference
TCPA	1.202	1.402	1.500	This work
Phthalidimide	1.215	—	1.482	<i>a</i>
Maleic anhydride	1.195	1.402	1.481	<i>b</i>
Pyromellitic dianhydride	1.204	1.393	1.465	<i>c</i>
Pyromellitic dianhydride (110°K)	1.193	1.396	1.485	<i>d</i>

a Post (1969).

b Marsh, Ubell & Wilcox (1962), corrected for thermal motion in reference *c*.

c Boeyens & Herbstein (1965) in perylene-PMDA complex.

d Herbstein & Snyman (1969) in pyrene-PMDA complex.

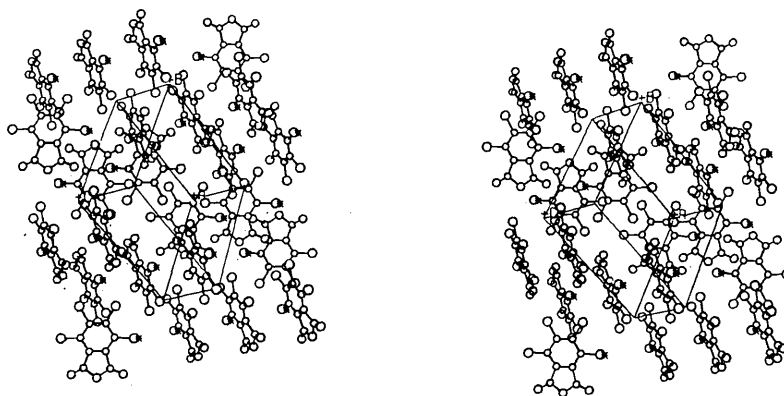


Fig. 4. Stereo pair of the crystal packing in TCPA. The view is perpendicular to the plane of the molecule in position x, y, z . One unit-cell, showing +A, +B, +C directions, is outlined. For purposes of identification, each Cl(1) atom is marked with an asterisk.

distance is $3 \cdot 10 \text{ \AA}$ [Table 4(b)]. Similarly, the distances between O(3) of a molecule in position x, y, z and C(7) and C(6) of a molecule in position $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$, average $3 \cdot 01 \text{ \AA}$.

Conclusions

It is concluded that the TCPA molecule contains chlorine and oxygen atoms that are distorted from the molecular plane in a puckered arrangement. All intra- and intermolecular bond lengths and contact distances are 'normal' if localized environmental and bonding effects are taken into consideration. The molecules in the crystal are independent of each other.

The interesting effect of a shortened C-Cl bond length in the presence of two *ortho* carbon-chlorine bonds has been noted and discussed.

Finally, the point is stressed that if the usual Pauling (1961) values of the van der Waals radii were used, with no distinction being made with respect to the direction of bonding and contact, different conclusions would have been reached concerning the interatomic interactions, particularly in the case of $\text{Cl}(1) \cdots \text{O}(2)$. In general, one must be careful that any conclusions based on a discussion of van der Waals or non-bonding radii take into account the many factors that contribute to the van der Waals radius. The electron cloud surrounding each atom is subject to distortion from a variety of forces and very often this leads to an anisotropic van der Waals radius. This important fact is often overlooked in discussions of molecular structure and packing.

Note added in proof: In agreement with the conclusions of this paper, the average carbon-chlorine distance in 1,2,3,4-tetrachloro-5,7-diphenylcalicene has recently been reported as 1.709 \AA by Kennard, Kerr, Watson & Fawcett (1970).

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