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The Crystal Structure of the α Phase of N-(p-Tolyl)tetrachlorophthalimide

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Crystals of the title compound are orthorhombic, space group *Cmca*, $a = 6.906$ (4), $b = 25.191$ (13), $c = 17.020$ (9) Å, $Z = 8$. The crystal structure was solved by direct methods and refined to $R = 0.030$ (goodness of fit 0.99). The molecule occupies the space-group mirror (m) special position. The tetrachlorophthalimide part lies in the mirror plane and is necessarily planar; the p-tolyl part is bisected by this plane and is somewhat bow-shaped, presumably because of packing forces. The short $Cl\cdots O$ intermolecular contact of 2.984 Å suggests a charge transfer between the O atom as the donor and the Cl atom as the acceptor.

Introduction

N-(p-Tolyl)tetrachlorophthalimide (I) forms inclusion compounds (Pratt & Perkins, 1918) which are of special interest because it appears that only aromatic molecules of particular shapes can act as guests. Three different polymorphic forms of the host compound have been found during a study of the crystal chemistry and thermal stability of the system (Herbstein & Kaftory, 1977). The crystal structure of the stable polymorph (α phase) is reported here.

(I)
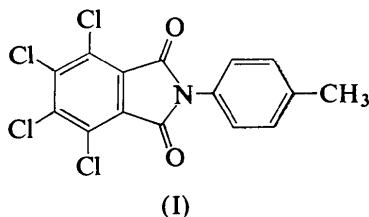
Experimental

Colourless needles, elongated along [100], may be obtained by the slow cooling of decalin, cyclo-

pentanone, cyclohexanone or N,N-dimethylformamide solutions. Intensities from a crystal, $0.40 \times 0.25 \times 0.30$ mm, were collected on an automated Hilger & Watts Y290 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å, $\mu = 4.80$ cm^{-1}); 1433 independent reflexions were measured, of which 1230 were above background $[F_o > 1.2\sigma(F_o)]$. Crystal data are summarized in Table 1. The systematic absences indicate space groups *Cmca* or *C2ca*; intensity and E statistics suggest the presence of a centre of symmetry.

The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971). The E map of the best set of 205 phases (ABS FOM = 1.283) revealed the correct structure. The structure was refined by full-matrix

Table 1. *Crystal data for the α phase of N-(p-tolyl)-tetrachlorophthalimide*

$C_{15}H_7NO_2Cl_4$	$M_r = 375.03$
Orthorhombic	μ(Mo $K\alpha$) = 4.80 cm^{-1}
$a = 6.906$ (4) Å	Space group conditions:
$b = 25.191$ (13)	$hkl: h + k = 2n$
$c = 17.020$ (9)	$h0l: l = 2n; (h = 2n)$
$V = 2960.9$ Å^3	$hk0: h = 2n; (k = 2n)$
$Z = 8$	Space group *Cmca* (No. 64) or *C2ca*
$D_m = 1.630$ g cm^{-3}	
$D_x = 1.683$	

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least squares. The weighting scheme was $w(hkl)$ $= 1/\sigma^2(F_{hkl})$. H atoms were included during the later stages.

Scattering factors for C, N, O and Cl were taken from *International Tables for X-ray Crystallography* (1962) and for H from Stewart, Davidson & Simpson (1965). R and R_w were 0·030 and 0·033 respectively; the 'goodness of fit' was 0·99.

Table 2. *Atomic coordinates* (×10⁵; *for* H ×10³)
with e.s.d.'s in parentheses

	x	y	z
Cl(1)	0	30895 (3)	31200 (4)
Cl(2)	0	41200 (3)	20977 (5)
Cl(3)	0	40502 (3)	2854 (5)
Cl(4)	0	29507 (3)	−5523 (4)
O(1)	0	18630 (9)	27164 (12)
O(2)	0	17737 (9)	374 (14)
N	0	16831 (10)	13903 (14)
C(1)	0	30478 (11)	21090 (17)
C(2)	0	35091 (12)	16519 (17)
C(3)	0	34796 (12)	8358 (18)
C(4)	0	29884 (12)	4578 (17)
C(5)	0	25379 (12)	9163 (17)
C(6)	0	25669 (12)	17323 (16)
C(7)	0	20091 (12)	20467 (18)
C(8)	0	19666 (12)	6840 (18)
C(9)	0	11083 (12)	13966 (18)
C(10)	17124 (50)	8416 (10)	13634 (18)
C(11)	16988 (50)	2929 (10)	12543 (18)
C(12)	0	183 (13)	11754 (18)
C(13)	0	−5647 (14)	9647 (24)
C(10)	291 (5)	101 (1)	146 (2)
H(11)	291 (5)	13 (1)	125 (2)
H(131)	0	−59 (1)	44 (2)
H(132)	119 (5)	−74 (1)	120 (2)

Final positional parameters are listed in Table 2.* Corresponding bond distances and angles are shown in Fig. 1; C—H bond distances (not shown) lie in the range 0·90–1·02 Å. Fig. 2 shows a stereoscopic view of a molecule.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32983 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
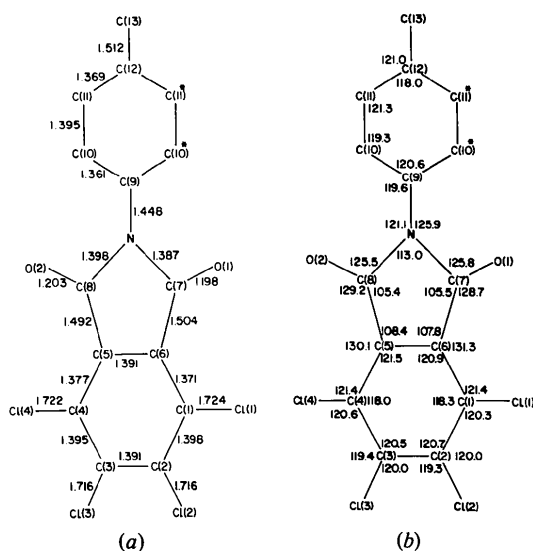

Fig. 1. (*a*) Bond distances (Å) and (*b*) bond angles (°) in the α phase of *N*-(*p*-tolyl)tetrachlorophthalimide. The e.s.d.'s of bond distances are typically 0·003–0·004 Å, of bond angles 0·2–0·3°.
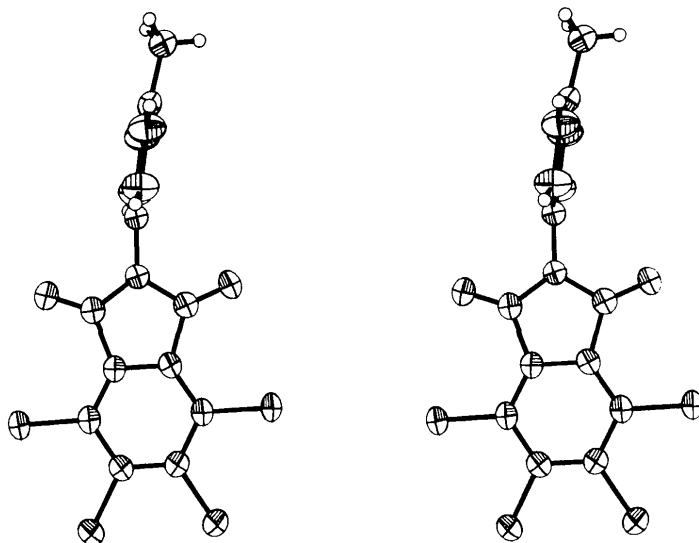

Fig. 2. The α phase of *N*-(*p*-tolyl)tetrachlorophthalimide. A stereoscopic view of the molecule, showing vibration ellipsoids at the 50% probability level (Johnson, 1965).
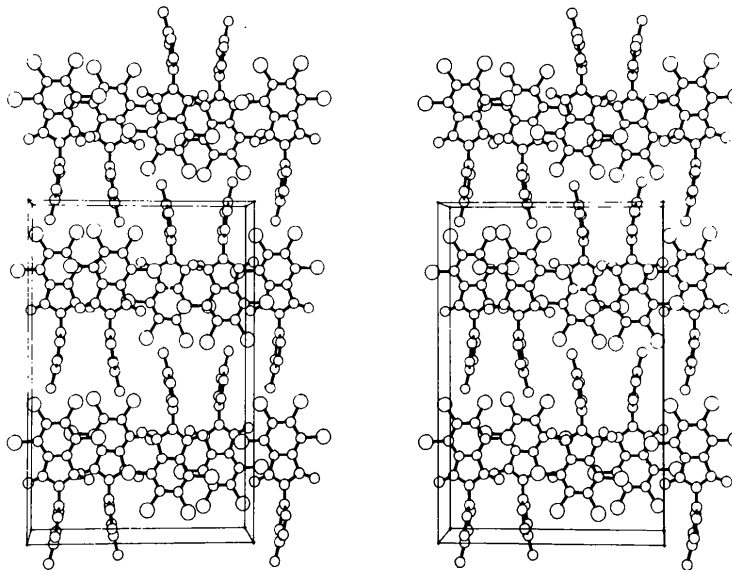
Fig. 3. A stereoscopic view of the crystal structure of the α phase of N-(p-tolyl)tetrachlorophthalimide. The reference molecule (coordinates in Table 3) is at the lower left-hand corner of the unit cell. The a axis runs into the paper, b is vertical and c horizontal.
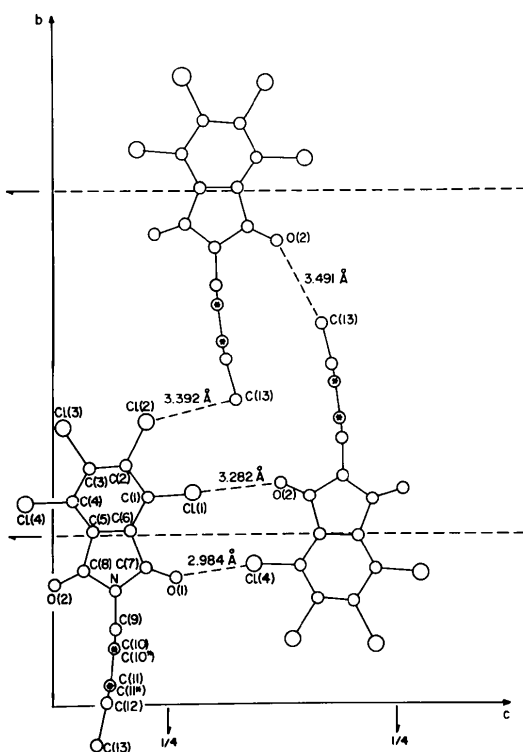

Fig. 4. Some short distances between molecules in the same crystallographic mirror plane at $x = 0$. The symmetry elements are marked.

An attempt to refine the structure in space group $C2ca$ gave essentially the same parameters as for $Cmca$, but there was a high correlation between matrix elements; the noncentrosymmetric space group was therefore rejected.

Discussion

Crystal structure

The crystal structure can be described in terms of sheets of antiparallel planar tetrachlorophthalimide groups piling up along the [100] direction and pairs of antiparallel p-tolyl groups running along the [001] direction (Fig. 3).

The molecules within a sheet along [001] are paired by short $Cl\cdots O$ intermolecular contacts (Figs. 3 and 4). The distance of 2·984 Å between O(1) (at x,y,z) and Cl(4) (at $x, \frac{1}{2} - y, \frac{1}{2} + z$) is significantly shorter than the sum of the van der Waals radii, 3·2 Å (Pauling, 1960). A similar arrangement of paired molecules is also found in the crystal structure of tetrachlorophthalic anhydride (Rudman, 1971) where two molecules are related by a centre of symmetry with a non-bonded $Cl\cdots O$ distance of 3·101 Å. An even shorter contact of 2·88 Å found in the crystal structure of N-chlorosuccinimide (Brown, 1961) was attributed to charge separation on more negative O and more positive Cl. Bent (1968) suggests that such short linear (or nearly linear) $Cl\cdots O$ inter-

molecular interactions (when the substituent attached to the halogen atoms is an organic group) are a result of charge transfer between the O atom as the donor and the Cl atom as the acceptor. Short contacts between Cl and O atoms are also observed when the atoms involved are partially charged, as in pentachloronitrobenzene (3·01 Å) (Tanaka, Iwasaki & Aihara, 1974) and 2-chloro-4,6-dinitrophenol (3·054 Å) (Andersen & Andersen, 1975). In both cases the O has a partial negative charge.

The shortest Cl···Cl intermolecular distance of 3·46 Å is between Cl(1) (at *x,y,z*) and Cl(4) (at *x*, $\frac{1}{2}-y$, $\frac{1}{2}+z$). A shorter distance (3·36 Å) has been observed in decachlorophenanthrene (Herbstein, Kapon & Merksamer, 1976). The shortest Cl···Cl intermolecular contact in hexachlorobenzene is 3·52 Å (Brown & Strydom, 1974).

Molecular dimensions

The molecule possesses crystallographic *m* symmetry with the tetrachlorophthalimide part in the mirror plane and the *p*-tolyl bisected by this plane. Tetrachlorophthalimide also has non-crystallographic *m* symmetry perpendicular to the crystallographic symmetry. The differences between chemically equivalent bond lengths and angles are less than 3σ (Fig. 1).

Tetrachlorophthalimide

The C—Cl bond lengths [mean 1·720 (3) Å] are in good agreement with the values found in hexachlorobenzene [1·722 (2) Å] (Brown & Strydom, 1974). This is in qualitative but not quantitative agreement with Rudman's (1971) proposal that C—Cl bonds are shorter when *ortho* to one another (1·709 Å) than when isolated (1·737 Å).

The intramolecular distances Cl(1)···Cl(2)··· Cl(3)···Cl(4) are 3·125, 3·098 and 3·115 Å respectively and in good agreement with the values found in tetrachlorophthalic anhydride (3·129, 3·068, 3·122 Å; Rudman, 1971) and with the 3·11 Å found in hexachlorobenzene (Brown & Strydom, 1974).

In the tetrachlorobenzene ring the two bond lengths C(1)—C(6) (1·371 Å) and C(4)—C(5) (1·377 Å) are significantly shorter than the other four (mean 1·395 Å, range 1·391–1·398 Å). Similar (but not so convincing) differences were found in the crystal structure of *N*-(*p*-chlorophenyl)phthalimide (Farmer & Lando, 1974) (1·363, 1·378 Å) and the mean of the other four is 1·396 Å (range 1·381–1·411 Å).

The contraction of the chemically equivalent angles C(2)—C(1)—C(6) and C(3)—C(4)—C(5) (118·3 and 118·0° respectively) is apparent in structures where a benzene ring is fused to a smaller ring. Herbstein & Snyman (1969) have suggested a way of calculating this contraction, for example, for the values obtained in pyrene–pyromellitic dianhydride (112·9, 113·2°). In

the inclusion complex of the title compound with *o*-xylene (Herbstein & Kaftory, 1977) values of 116·2 and 117·7° have been obtained.

The explanation for the difference in the bond angles of the carbonyl groups C—C=O (mean 129·0°) and N—C=O (mean 125·7°) is that it allows O(1) and O(2) to bend away from the aromatic ring and thus achieve normal intramolecular distances for O(1)···Cl(1) (3·165 Å) and O(2)···Cl(4) (3·130 Å). The same results were also found in the inclusion complex of the title compound with *o*-xylene (Herbstein & Kaftory, 1977) (129·8 and 124·9°); other examples where H atoms replace the Cl atoms are pyrene–pyromellitic dianhydride (Herbstein & Snyman, 1969) (130·9 and 121·7°) and thalidomide (Allen & Trotter, 1971) (129·1 and 124·7°).

The difference between the bond lengths of N—C(9) (1·448 Å) and N—C(7), N—C(8) (1·387 and 1·398 Å respectively) can be ascribed to interaction of the N lone-pair electrons with the two carbonyl groups [C(7), C(8)] while there is no interaction with the perpendicular phenyl ring. Similar effects are found in many compounds such as thalidomide (Allen & Trotter, 1971) (1·455 and 1·391, 1·391 Å).

p-Tolyl

The apparently significant difference between the bond lengths of the tolyl ring [C(9)—C(10) 1·361 Å, C(11)—C(12) 1·369 Å and C(10)—C(11) 1·395 Å] may be due to the absence of a correction for thermal motion. C(10) and C(11) which are not restricted by the crystallographic special position have the highest U_{33} vibration components (perpendicular to the phenyl plane): 0·085 and 0·088 Å^2 respectively, compared with 0·035 and 0·036 Å^2 for C(9) and C(12). This parallel thermal motion does not affect the C(10)—C(11) distance but shortens C(9)—C(10) and C(11)—C(12).

The *p*-tolyl group deviates significantly from planarity. The mean-plane equation through the most planar part of the group, C(10), C(11) and their equivalent atoms C(10*) and C(11*), is 0·0*x* + 3·4024*y* + 16·8641*z* = 2·0129 (*x,y,z* are fractional coordinates); the out-of-plane displacements of the atoms are: C(10) and C(10*) 0·0 Å, C(11) and C(11*) 0·003 Å, C(9) −0·034 Å, C(12) −0·037 Å, and C(13) −0·194 Å. Furthermore, the angle C(7)—N—C(9) is 125·9° while the corresponding C(8)—N—C(9) is 121·1°.

This effect can be described as a bending of the *p*-tolyl group away from the C(7)—N bond. To account for the distortion that occurs it seems necessary to invoke the effect of crystal-packing forces. The short intermolecular contact between Cl(2) of the reference molecule and the methyl C(13) of the molecule at *x*, $\frac{1}{2}+y$, $\frac{1}{2}-z$ is 3·392 Å. This distance and the bend of the *p*-tolyl group are the result of a repulsive force

between Cl(2) and the methyl C(13) of an undistorted *p*-tolyl group (see Figs. 2, 3 and 4).

The dihedral angle between the planes of tetrachlorophthalimide and *p*-tolyl is 90°. This is an exceptional value because in most similar compounds the angle is around 60°, *e.g.* in the inclusion complex with *o*-xylene (Herbstein & Kaftory, 1977) 53°, in *N*-(4-iodophenyl)phthalimide (Ribár, Stanković, Herak, Halasi & Djurić, 1974) 56°, in *N*-(4-chlorophenyl)-phthalimide (Mornon, 1968) 60°, and in succinimide (Wong & Watkins, 1973) 71°.

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