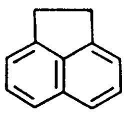
Molecular Complexes. Part XVIII.[1] Crystal and Molecular Structure of Acenaphthene–Tetrachloro-*p*-benzoquinone Molecular Complex

By **Ian J. Tickle** and **C. Keith Prout,*** Chemical Crystallography Laboratory, South Parks Road, Oxford OX1 3QS

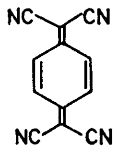
Crystals of the title 1 : 1 molecular complex are monoclinic, a = 14·66, b = 13·44, c = 8·26 Å, γ = 94·4°, space group $I2/b$, Z = 4. The structure has been determined from diffractometer data by Patterson methods and refined by least squares to R 0·063 for 959 reflections. The dimensions of the component molecules are stacked alternately plane-to-plane along the a axis of the crystal, with a mean perpendicular separation 3·41 Å. The mode of donor–acceptor overlap does not correspond to a maximum in the calculated charge-transfer stabilisation energy, possibly owing to repulsive non-bonded intermolecular Cl · · · H interaction in the expected orientation.

VERY few solid-state complexes of naphthalene with aromatic electron acceptors are known, presumably owing to its relatively high ionisation potential and unfavourable solubility properties. The crystal structures of the 1,2,4,5-tetracyanobenzene[2] and tetracyanoethylene[3] complexes have been reported in detail and the *sym*-trinitrobenzene in outline.[4] These have structures in which the charge-transfer interaction is almost maximised.[5] No structures of solid-state complexes of naphthalene with quinonoid acceptors are known although an unstable complex of naphthalene with 7,7,8,8-tetracyanoquinodimethane (II) has been prepared.[6] Structures of the complexes of the naphthalene-like donor 8-hydroxyquinoline and its chelate complexes have been reported but the donor–acceptor interaction is modified by hydrogen-bonding effects (8-hydroxyquinoline–chloranil)[7] or metal acceptor interactions [bis-(8-hydroxyquinolinato)palladium(II)–chloranil].[8]

Simple alkylnaphthalenes, which are in general more soluble than naphthalene itself, offer a better prospect of obtaining valid information about naphthalene–quinonoid electron-acceptor interactions in crystalline complexes. Those of acenaphthene (I) with chloranil (tetrachloro-*p*-benzoquinone)[9] and (II) giving crystals suitable for X-ray work, may be prepared. Here we report the crystal and molecular structure of the chloranil complex; that of the complex with (II) is reported in the following paper.



(I)



(II)

EXPERIMENTAL

Laboratory-grade acenaphthene and chloranil were recrystallised from ethanol and 1,4-dioxan respectively. The complex was prepared by the method described in ref. 9. In the absence of free acenaphthene the crystals decomposed slowly in air, apparently by sublimation of the more volatile acenaphthene. A crystal, of dimensions *ca.* 0·7 × 0·4 × 0·4 mm was mounted in a borosilicate glass capillary for the collection of intensity data.

Crystal Data.—$C_{18}H_{10}Cl_4O_2$, M = 400·1. Monoclinic prismatic, $a = 14·66 \pm 0·02$, $b = 13·49 \pm 0·02$, $c = 8·26 \pm 0·01$ Å, $\gamma = 94·4 \pm 0·1°$, U = 1630 Å^3, D_m = 1·63 (by flotation in aqueous zinc chloride), Z = 4, D_c = 1·630. Systematic extinctions: hkl, $h + k + l$ odd and $hk0$, k odd (h odd). Space group $I2/b$ [non-standard setting of $B2/b$ (C^6_{2h}, No. 15)] †; general positions $(0,0,0, \frac{1}{2},\frac{1}{2},\frac{1}{2}) \pm (x,y,z,\ \ x,\frac{1}{2} + y,\bar{z};)$. Mo-$K_\alpha$ radiation, λ = 0·7107 Å; μ(Mo-K_α) = 7·3 cm^{-1}.

Unit-cell dimensions were measured and three-dimensional X-ray intensity data [961 independent reflections significantly (3σ) above background, of the layers hk0—10] collected on a Hilger and Watts linear diffractometer. Lorentz and polarisation, but not absorption, corrections were applied. Systematic extinctions indicated space group Ib or $I2/b$. The latter was confirmed by the structure refinement.

All significant maxima in a Patterson synthesis sharpened to ' point atoms at rest ' lie close to the $(4,\bar{2},0)$ plane and can be interpreted in terms of acenaphthene and chloranil molecules at special two-fold positions in the centrosymmetric space group $I2/b$, the former about the two-fold rotation axis at $(0,\frac{1}{4},z)$ and the latter at the inversion centre at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$. If the planes of the molecules are parallel to the $(4,\bar{2},0)$ plane, crystal packing forbids location of chloranil molecules at the non-equivalent inversion centre at (0,0,0). The co-ordinates of the two independent chlorine atoms were then derived from the two double-weight intramolecular Cl · · · Cl vectors. An F_o synthesis, with phases computed from these co-ordinates showed the remainder of the chloranil molecule and the acenaphthene.

The atomic co-ordinates were refined by full-matrix least squares, initially with isotropic temperature factors and unit weights for all observations to give R 0·17. Two intense reflections, (3,0,1) and $(4,\bar{2},0)$ appeared to be suffering from extinction and were given zero weight; the latter reflection has an abnormally high amplitude since it corresponds to near in-phase scattering from the entire contents of the unit cell. The hydrogen atoms were located in a difference-Fourier synthesis and in the subsequent refine-

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† The non-standard setting reflects the habit of the crystal.

[1] Part XVII, I. J. Tickle and C. K. Prout, preceding paper.

[2] S. Kumakura, F. Iwasaki, and Y. Saito, *Bull. Chem. Soc. Japan*, 1967, **40**, 1826.

[3] R. M. Williams and S. C. Wallwork, *Acta Cryst.*, 1967, **22**, 899.

[4] S. C. Wallwork, *J. Chem. Soc.*, 1961, 494.

[5] B. Mayoh and C. K. Prout, *J.C.S. Faraday II*, 1972, 1072.

[6] J. D. Wright, personal Communication.

[7] C. K. Prout and A. G. Wheeler, *J. Chem. Soc.* (*A*), 1967, 469.

[8] B. Kamenar, C. K. Prout, and J. D. Wright, *J. Chem. Soc.*, 1965, 4851.

[9] O. Dimroth and C. Bamberger, *Ann. Chem.*, 1924, **438**, 67.

ment, their isotropic temperature factors were held invariant, while their space parameters were constrained so that the hydrogen atoms were allowed to move only over the surface of a sphere radius 1·05 ± 0·02 Å centred on the parent carbon atom, according to the method described in ref. 10. Full-matrix refinement, with anisotropic temperature factors for all but hydrogen and the weighting scheme $w = [1 + (|F_o| - 7{\cdot}0)^2/200]^{-1}$, converged at R 0·063 for 959 reflections. In a final difference-Fourier synthesis (estimated standard deviation of the electron density 0·16 e Å^{-3}) the only significant features were troughs and peaks of 0·48—0·60 e Å^{-3} density at the extrema, located *ca.* 0·75 Å from the chlorine atoms. The observed structure amplitudes and structure factors calculated from the final atomic parameters in Table 1 are given in Supplementary Publication No. SUP 20629 (10 pp. 1 microfiche).†

The estimated standard deviations in Table 1 were calculated from the diagonal elements of the inverse of the normal matrix. Either Rollett's NOVTAPE system, as modified by Hodder [11] or Rollett and Ford's ALGOL system [12] were used for all calculations. Atomic scattering factors were those for the uncharged atoms taken from ref. 13. The real part of the anomalous dispersion correction was applied to the values for chlorine.

TABLE 1

Atomic parameters * with standard deviations in parentheses. Hydrogen atoms are numbered according to the carbon atom to which they are attached

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
Cl(1)	0·1680(1)	0·0310(1)	0·2142(2)	0·084(1)	0·035(1)	0·073(1)	0·009(1)	−0·012(2)	−0·011(1)
Cl(2)	0·2091(1)	0·1662(1)	−0·0956(2)	0·085(1)	0·055(1)	0·045(1)	−0·012(1)	−0·004(2)	−0·001(2)
O(1)	0·2072(4)	0·1409(3)	0·5100(6)	0·091(3)	0·045(3)	0·051(3)	0·030(4)	0·014(5)	−0·011(4)
C(1)	0·2112(4)	0·1505(4)	0·2255(7)	0·048(3)	0·030(3)	0·049(3)	0·000(4)	0·007(5)	0·002(4)
C(2)	0·2301(4)	0·2075(4)	0·0957(7)	0·047(3)	0·036(3)	0·046(3)	−0·010(5)	0·004(5)	0·010(5)
C(3)	0·2283(4)	0·1895(4)	0·3893(7)	0·047(3)	0·034(3)	0·050(3)	0·018(4)	0·003(5)	0·011(5)
C(4)	0	0·25	0·3443(10)	0·035(4)	0·043(4)	0·048(4)	0	0	0·015(6)
C(5)	0	0·25	0·1786(11)	0·033(4)	0·064(6)	0·056(5)	0	0	0·024(7)
C(6)	0·0379(5)	0·3384(6)	0·1029(10)	0·064(4)	0·071(5)	0·062(4)	0·027(8)	0·020(8)	0·032(7)
C(7)	0·0722(5)	0·4160(5)	0·1978(10)	0·072(4)	0·049(4)	0·069(5)	0·037(7)	0·014(8)	0·011(6)
C(8)	0·0709(5)	0·4147(5)	0·3662(11)	0·064(4)	0·042(4)	0·085(5)	0·000(6)	−0·001(7)	−0·011(6)
C(9)	0·0343(4)	0·3301(4)	0·4426(8)	0·040(3)	0·045(3)	0·061(4)	−0·001(5)	0·000(5)	0·005(5)
C(10)	0·0218(5)	0·3037(6)	0·6176(9)	0·066(4)	0·063(4)	0·056(4)	−0·022(6)	−0·013(7)	0·001(7)

	x/a	y/b	z/c	U_{iso}		x/a	y/b	z/c	U_{iso}
H(6)	0·042(6)	0·336(7)	−0·024(4)	0·065	H(10a)	0·079(4)	0·298(8)	0·691(11)	0·070
H(7)	0·107(6)	0·473(5)	0·131(11)	0·070	H(10b)	−0·013(6)	0·352(6)	0·689(11)	0·070
H(8)	0·090(6)	0·482(4)	0·420(12)	0·070					

* The temperature factor T is exp $[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$.

TABLE 2

Analysis of rigid-body thermal motion

	Directional cosines relative to:					
Principal axes	Inertial axes			Orthogonal crystal axes		
(*a*) Acenaphthene						
$\boldsymbol{T}$ Tensor/Å^2	X	Y	Z	a	b^*	c
0·044(3)	0·998	0	0·061	0·422	0·907	0
0·051(3)	0	1	0	0	0	1
0·031(5)	−0·061	0	0·998	0·907	−0·422	0
$\boldsymbol{\omega}$ Tensor/deg.^{2}						
16(4)	0·730	0	0·684	0·903	0·430	0
18(4)	0	1	0	0	0	1
18(4)	−0·684	0	0·730	0·430	−0·903	0
(*b*) Chloranil						
$\boldsymbol{T}$ Tensor/Å^2						
0·046(2)	0·822	−0·492	−0·287	0·419	0·256	0·871
0·037(2)	0·212	0·732	−0·648	0·793	0·365	−0·488
0·026(2)	0·529	0·471	0·706	−0·443	0·895	−0·050
$\boldsymbol{\omega}$ Tensor/deg.^{2}						
28(2)	0·995	−0·032	−0·091	0·358	0·710	0·606
15(1)	0·051	0·976	0·210	−0·023	0·656	−0·754
9(1)	0·082	−0·213	0·974	−0·933	0·256	0·252

RESULTS AND DISCUSSION

Interatomic distances and interbond angles, derived from the atomic parameters in Table 1, are shown, with their estimated standard deviations in Figure 1.

Table 2 gives the results of a rigid-body analysis of

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† See note about Supplementary Publications in Notice to Authors No. 7, in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[10] J. Waser, *Acta Cryst.*, 1963, **16**, 1091.

[11] O. J. R. Hodder and J. S. Rollett, unpublished work.

[12] J. S. Rollett and G. Ford, unpublished work.

[13] 'International Tables for X-Ray Crystallography,' vol. **3**, Kynoch Press, Birmingham, 1962.

the thermal motion of the acenaphthene and chloranil molecules. The inertial axes, together with the deviations from the molecular mean planes, weighted in proportion to the atomic weights, are defined in Figure 2. The centre of libration of the chloranil molecule necessarily coincides with its inversion centre, but that of the acenaphthene molecule is only restricted to lie on the two-fold rotation axis; its position was refined by minimisation of $\Sigma[V_{ij}(\text{obs}) - V_{ij}(\text{calc})]^2$ where each V_{ij} is obtained from the corresponding U_{ij} by orthogonalisation relative to the molecular inertial axes. The centre of libration of the acenaphthene molecule is indicated by w in Figure 2. The value of $\Sigma[V_{ij}(\text{obs}) - V_{ij}(\text{calc})]^2/N$, where N is the number of V_{ij} terms less the number of rigid-body parameters determined, was 0·0055 for acenaphthene and 0·0031 Å for chloranil, compared with $\sigma(U_{ij})$ of 0·003—0·005 for acenaphthene and 0·001—0·003 for chloranil. The rigid-body approximation therefore gives a reasonable fit to the data although, as expected, internal vibrations appear to be more significant for the chlorine atoms.

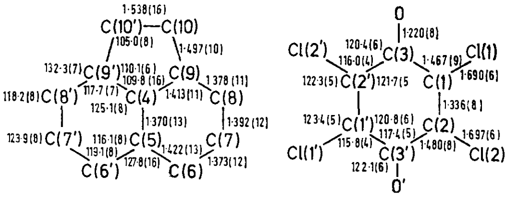

FIGURE 1 Interatomic distances (Å; before libration correction) and interbond angles (deg.) with standard deviations in parentheses

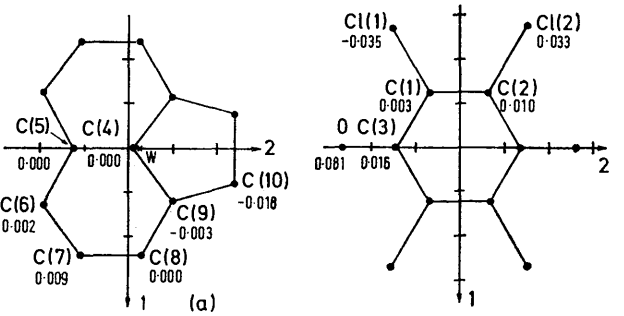

FIGURE 2 Molecular inertial axes of (a) acenaphthene (crystal symmetry 2) and (b) chloranil (crystal symmetry $\bar{1}$), with deviations from the mean planes

The libration of the acenaphthene molecule is isotropic within experimental error. This is contrary to expectation because, almost without exception, we have observed that other aromatic hydrocarbons, in their molecular complexes, undergo anisotropic libration with maximum amplitude in the plane of the molecule. In general the electron-acceptor molecule librates with maximum amplitude about one of the other inertial axes, as is observed for the chloranil. Table 3 lists the interatomic distances to which Cruickshank's libration correction [14] has been applied. The interbond angles in the acenaphthene molecule, which differ from the corresponding angles in naphthalene [15] because of the dislocation produced by the bridging dimethylene group, agree well with those found in free acenaphthene [16] but the alteration in bond lengths that was observed in the structure of free acenaphthene, 1,8-dinitrosonaphthalene,[17] and naphthalene, is less evident in the present determination: the bonds C(4)–C(5) 1·376 and C(7)–C(8) 1·397 Å are significantly shorter. The maximum difference between a bond length (after libration correction) in the chloranil molecule in the complex and that of the corresponding bond observed in a recent accurate refinement of the structure of chloranil itself,[18] is 2σ, but on the whole the agreement is much better than this. It is therefore possible, but it is not thought probable, that there is a modification of the bond lengths of the electron donor in this π–π* electron-donor–acceptor complex.

TABLE 3

Bond lengths (Å) corrected for rigid-body thermal motion. Uncorrected bond lengths and bond angles are given in Figure 1

(*a*) Chloranil		(*b*) Acenaphthene	
Cl(1)–C(1)	1·696	C(4)–C(5)	1·376
Cl(2)–C(2)	1·703	C(4)–C(9)	1·420
O(1)–C(3)	1·224	C(5)–C(6)	1·427
C(1)–C(2)	1·341	C(6)–C(7)	1·379
C(1)–C(3)	1·474	C(7)–C(8)	1·397
C(2)–C(3′)	1·486	C(8)–C(9)	1·383
		C(9)–C(10)	1·504
		C(10)–C(10′)	1·545

The co-ordinates of the primed and unprimed atoms are related by the molecular inversion centre for chloranil and two-fold axis for acenaphthene.

The aromatic part of the acenaphthene group is planar (Figure 2) within experiental error, but the bridging methylene group is significantly twisted out of the plane. The chloranil molecule is decidedly non-planar. This effect is discussed in the earlier structure determinations of chloranil.[19,20]

Figure 3 shows a stereo-projection viewed normal to the (4,$\bar{2}$,0) plane, in which all the electron density is concentrated. The molecules are stacked alternately in characteristic plane-to-plane fashion along the crystal *a* axis. The angle between the mean planes of adjacent molecules is 2·7° and the mean perpendicular separation is 3·41 Å. This is slightly less than expected for a van der Waals contact between an aromatic hydrocarbon and chloranil, which, in general, appears to have a somewhat greater 'thickness' than most

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[14] D. W. J. Cruickshank, *Acta Cryst.*, 1956, **9**, 757.

[15] D. W. J. Cruickshank, *Acta Cryst.*, 1957, **10**, 504.

[16] H. W. W. Ehrlich, *Acta Cryst.*, 1957, **10**, 699.

[17] C. K. Prout, T. S. Cameron, R. M. A. Dunn, O. J. R. Hodder, and D. Viterbo, *Acta Cryst.*, 1971, *B*, **27**, 1310.

[18] K. J. van Weperen and G. J. Visser, *Acta Cryst.*, 1972, *B*, **28**, 338.

[19] I. Veda, *J. Phys. Soc. Japan*, 1961, **16**, 1185.

[20] S. C. Chu, G. A. Jeffrey, and T. Sakurai, *Acta Cryst.*, 1962, **15**, 661.

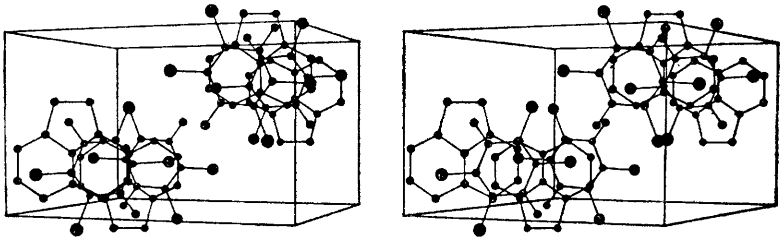

FIGURE 3 Stereoscopic view of the crystal packing. Rotation matrix (from orthogonal co-ordinate system based on *a*, *b**, *c* to plotter co-ordinates):

$$\begin{matrix} 0\cdot000 & 0\cdot000 & -1\cdot000 \\ 0\cdot365 & 0\cdot931 & 0\cdot000 \\ 0\cdot931 & -0\cdot365 & 0\cdot000 \end{matrix}$$

π^* acceptors. However, it appears that the non-planarity of the chloranil molecule allows a closer approach of the hydrocarbon. It is unlikely that charge-transfer forces, although undoubtedly significant, are strong enough in this system to cause an approach closer than the van der Waals contact, as is observed in the *NNN'N'*-tetramethyl-*p*-phenylenediamine–chloranil complex.[21] Figure 4 shows the projection of the chloranil molecule on the least-squares best plane of the carbon skeleton of the acenaphthene. Semi-empirical calculations [5] indicate that charge-transfer effects would be maximised if the centroid of the chloranil were superposed on the mid-point of the C(4)–C(5) bond with the molecular two-fold axes parallel. According to this [5] the observed orientation has *ca.* 84% of the maximum charge-transfer stabilisation and does not correspond to a local potential minimum. It is thought that the position of maximum charge-transfer stabilisation is not achieved owing to mutual repulsion between the out-of-plane hydrogen atoms attached to C(10) and C(10′) and the atoms of the acceptor. This repulsion prevents any movement of the acceptor from observed position towards the centroid of the acenaphthene which would improve the charge-transfer stabilisation.

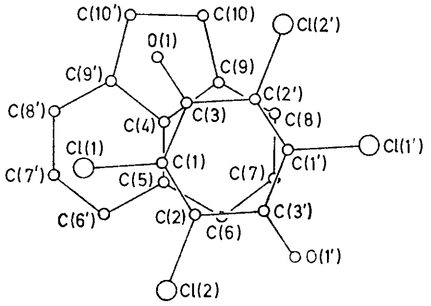

FIGURE 4 Projection of an acenaphthene molecule on the mean plane of the adjacent chloranil

We thank the S.R.C. for a studentship (to I. J. T.).

[2/2366 *Received*, 16*th October*, 1972]

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[21] J. L. de Boer and A. Vos, *Acta Cryst.*, 1968, *B*, **24**, 720.