Molecular Complexes. Part XX.[1] Crystal and Molecular Structure of 9-Methylanthracene–Tetrachloro-*p*-benzoquinone Molecular Complex

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Crystals of the title 1 : 1 complex are monoclinic, $a = 7.29$, $b = 13.83$, $c = 9.53$ Å, $\gamma = 103.35°$, space group $P2/b, Z = 2$. The structure was determined from diffractometer data by direct methods and refined by least squares to R 0.052 for 860 reflections. The molecules are stacked alternately characteristically plane-to-plane along the a axis. The 9-methylanthracene is disordered, so that the methyl group appears to be distributed randomly between two possible positions related by an inversion centre. The mode of overlap of the electron-donor and -acceptor molecules is very close to the orientation which is expected to produce maximum donor–acceptor charge-transfer interaction.

In the absence of any complex of naphthalene itself with a quinone, probably owing to the relatively low solubility of the hydrocarbon in suitable solvents, the structure of acenaphthene–chloranil was determined [2] as a possible representative naphthalene–*p*-benzoquinone electron-donor–acceptor system. Similarly, solid-state complexes of a *p*-benzoquinone with anthracene have not been prepared although under rigorous conditions Diels–Alder adducts are produced.[3] Monosubstituted anthracenes have considerably lower melting points, and hence higher solubilities than the parent hydrocarbon.

In particular, the 9-methyl derivative has m.p. 81·5 °C (*cf.* anthracene, 216 °C) and offers better prospects for the preparation of crystalline quinone complexes. We report here the preparation and the crystal and molecular complex of the 1 : 1 complex of 9-methylanthracene and chloranil (tetrachloro-*p*-benzoquinone).

EXPERIMENTAL

9-Methylanthracene was prepared by a Grignard reaction from anthrone,[4] purified by column chromatography on alumina with light petroleum (b.p. 60—80°) as eluant, and recrystallised from 96% ethanol (m.p. 78—79 °C).

[1] Part XIX, I. J. Tickle and C. K. Prout, preceding paper.
[2] Part XVIII, I. J. Tickle and C. K. Prout, *J.C.S. Perkin II*, 1973, 724.
[3] E. Clar, *Ber.*, 1931, **64**, 1676.
[4] A. Sieglitz and R. Marx, *Ber.*, 1923, **56**, 1620.

The complex was prepared by co-crystallisation from a solution in glacial acetic acid of 9-methylanthracene and chloranil in the molar ratio 4 : 1. The excess of 9-methylanthracene is necessary to prevent crystallisation of the less soluble chloranil. Intensely coloured dark green needles were produced on slow evaporation of the solution. The complex is unstable in the absence of the free hydrocarbon, which apparently sublimes away, even if a crystal is sealed in a glass capillary. Decomposition could, however, be very effectively prevented by coating the crystal with a thin film of 'Durafix' cement. No adequate elemental analysis could be obtained.

anthracene and chloranil molecules in the unit-cell must lie about two of the four pairs of inversion centres, the noncentrosymmetric 9-methylanthracene must be randomly distributed about two possible equally occupied positions to give a mean apparent centre of inversion. In the E map the non-hydrogen atoms were clearly identifiable and the two anthracene skeletons appeared to be superposed with half a methyl group in each of the 9- and 10-positions. The atomic parameters of a model from the E map, in which it was assumed that the anthracene skeletons of the two 9-methylanthracene molecules were exactly superposed, were refined by full-matrix least-squares initially with unit

TABLE 1

Final atomic parameters * with standard deviations in parentheses

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Cl(1)	0·3249(2)	−0·1018(1)	0·2753(2)	0·059(1)	0·106(1)	0·073(1)	0·058(2)	0·027(2)	0·022(2)
Cl(2)	0·4502(2)	0·1337(1)	0·2541(2)	0·065(1)	0·091(1)	0·078(1)	−0·067(2)	−0·011(2)	0·045(2)
O(1)	0·3968(7)	−0·1955(3)	0·0181(6)	0·090(3)	0·043(3)	0·104(4)	0·008(5)	0·008(5)	0·009(4)
C(1)	0·4208(7)	−0·0419(4)	0·1285(6)	0·040(3)	0·058(4)	0·050(3)	0·013(5)	0·000(5)	0·012(5)
C(2)	0·4420(8)	−0·1059(4)	0·0091(7)	0·046(3)	0·046(4)	0·067(4)	0·012(6)	−0·012(5)	0·019(5)
C(3)	0·4733(7)	0·0560(4)	0·1199(6)	0·041(3)	0·055(4)	0·055(3)	−0·027(5)	−0·012(5)	0·030(5)
C(4)	−0·0287(7)	0·0471(4)	0·1251(7)	0·040(4)	0·076(4)	0·056(4)	0·003(6)	−0·006(5)	0·044(5)
C(5)	−0·0575(10)	0·0922(7)	0·2548(9)	0·063(4)	0·117(6)	0·071(5)	−0·032(10)	−0·010(7)	0·075(8)
C(6)	−0·1387(13)	0·0357(10)	0·3628(10)	0·073(6)	0·196(11)	0·063(6)	0·002(13)	0·005(8)	0·115(13)
C(7)	−0·1937(11)	−0·0658(11)	0·3533(11)	0·060(5)	0·200(11)	0·076(7)	0·090(14)	0·028·8)	0·067(13)
C(8)	−0·1676(8)	−0·1141(6)	0·2339(9)	0·045(3)	0·114(6)	0·083(6)	0·078(10)	0·013(7)	0·035(7)
C(9)	−0·0839(7)	−0·0578(4)	0·1140(7)	0·035(3)	0·066(4)	0·065(4)	0·034(6)	−0·010(5)	0·011(5)
C(10)	−0·0536(8)	−0·1041(4)	−0·0093(7)	0·047(3)	0·053(4)	0·071(4)	0·006(6)	−0·026(6)	0·029(5)
C(11) †	−0·0986(18)	−0·2075(8)	−0·0143(16)	0·074(8)	0·029(7)	0·095(10)	−0·007(12)	−0·013(14)	0·010(10)

	x/a	y/b	z/c	U_{iso}		x/a	y/b	z/c	U_{iso}
H(1)	−0·017(10)	0·169(2)	0·256(10)	0·080	H(3)	−0·273(11)	−0·107(6)	0·431(7)	0·100
H(2)	−0·157(12)	0·070(6)	0·456(6)	0·100	H(4)	−0·217(10)	−0·192(3)	0·219(10)	0·080

* The temperature factor T is given by $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}hla^*c^* + 2U_{12}hka^*b^*)]$.
† C(11) has occupancy 0·5.

With fluoranil an intense blue colouration was produced on mixing the components in solution, but this faded completely within 48 h at 18 °C. Rapid evaporation of solvent produced a deep blue solid but this too was rapidly transformed into a colourless compound when set aside. This reaction, possibly of the Diels–Alder type, was not further investigated.

Crystal Data.—$C_{21}H_{12}Cl_4O_2$, $M = 438·2$. Monoclinic prismatic, $a = 7·29 \pm 0·02$, $b = 13·83 \pm 0·03$, $c = 9·53 \pm 0·02$ Å, $\gamma = 103·4 \pm 0·1°$, $U = 935$ Å^3, $D_m = 1·535$, $Z = 2$, $D_c = 1·556$. Space group $P2_1/b$ (C_{2h}^5, No. 14). Mo-K_α radiation, $\lambda = 0·7107$ Å; $\mu(\text{Mo-}K_\alpha) = 6·5$ cm^{-1}.

Unit-cell dimensions were measured, the intensities of 860 independent reflections, significantly (3σ) above background, from layers $hk0$—10, were collected on a Hilger and Watts linear diffractometer. Lorentz and polarisation corrections were applied but no correction was made for absorption.

Normalised structure amplitudes were computed and the phases for 319 reflections were determined by the symbolic addition method,[5] with the CSSA[6] program. From the 349 independent reflections with $E > 1·0$, the program chose 6 starting phases, 2,0,1, 3,$\overline{10}$,4, and 6,$\overline{13}$,6 to fix the origin and 8,4,0, 8,$\overline{4}$,4, and 8,$\overline{12}$,0 from Σ_1 relationships. In the course of the phase-determination symbolic phases were assigned to 4,$\overline{2}$,2, 0,4,4, 4,$\overline{1}$,2, and 2,9,3 all of which were positive in the highest probability solution, which proved to be correct. Since in $P2_1/b$ the two 9-methyl-

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

weights and isotropic temperature factors and then with anisotropic temperature factors and the weighting scheme $w = (1 + F_o^2/2000)^{-1}$. The hydrogen atom positions were poorly resolved in a difference-Fourier synthesis and except for those of the methyl group and C(10) which were not included in any of the calculations, they were placed geometrically. The refinement converged at R 0·052 for 860 observed reflections. Various more sophisticated approaches to the disorder of the 9-methylanthracene were less satisfactory than the system reported. The observed structure amplitudes and structure factors calculated from the atomic parameters in Table 1 are given in Supplementary Publication No. SUP 20631 (8 pp., 1 microfiche).‡ The estimated standard deviations in Table 1 are derived from the diagonal elements of the inverse of the normal matrix.

All calculations used either Rollett's NOVTAPE system as modified by Hodder or Rollett and Ford's ALGOL system, unless otherwise stated. The atomic scattering factors were those for neutral atoms taken from ref. 7. Those for chlorine were corrected for the real part of the anomalous dispersion.

RESULTS AND DISCUSSION

Interatomic distances and interbond angles with standard deviations in parentheses, derived from the

[5] J. Karle and I. L. Karle, *Acta Cryst.*, 1966, 21, 849.
[6] O. J. R. Hodder, C. K. Prout, and J. S. Rollett, unpublished work.
[7] 'International Tables for X-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

parameters in Table 1 (uncorrected for thermal motion) are given in Figure 1. Table 2 details the analysis of the thermal parameters in terms of rigid body motion. The poorly resolved probably because the two disordered molecules are not exactly superposed. The lack of resolution is consistent with the abnormally high mean-
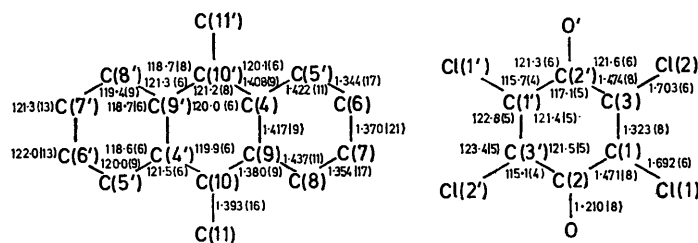

FIGURE 1 Interatomic distances and interbond angles with standard deviations in parentheses. C(11) has occupancy 0·5

TABLE 2

Analysis of apparent rigid-body thermal notion

|	Direction cosines relative to:					
Principal axes	Inertial axes			Orthogonal crystal axes		
(a) 9-methylanthracene						
T Tensor/Å²	X	Y	Z	a	b*	c
0·066(2)	0·716	−0·694	−0·072	0·130	−0·644	−0·754
0·047(2)	0·675	0·715	−0·183	0·077	0·764	−0·640
0·030(4)	0·179	0·082	0·980	0·988	0·026	0·149
ω Tensor/deg.²						
12(8)	0·967	0·220	0·128	0·442	0·267	−0·856
7(1)	−0·218	0·976	−0·031	−0·054	0·961	0·272
36(1)	−0·132	0·002	0·991	0·895	−0·074	0·440
(b) Chloranil						
T Tensor/Å²						
0·051(2)	0·992	−0·080	−0·102	0·222	−0·160	−0·962
0·045(2)	0·055	0·973	−0·223	−0·141	0·971	−0·194
0·030(3)	0·117	0·216	0·969	0·965	0·179	0·193
ω Tensor/deg.²						
32(2)	0·963	0·001	0·271	0·568	−0·087	−0·818
6(1)	0·024	0·996	−0·088	−0·023	0·992	−0·121
25(1)	−0·270	0·091	0·959	0·822	0·088	0·562
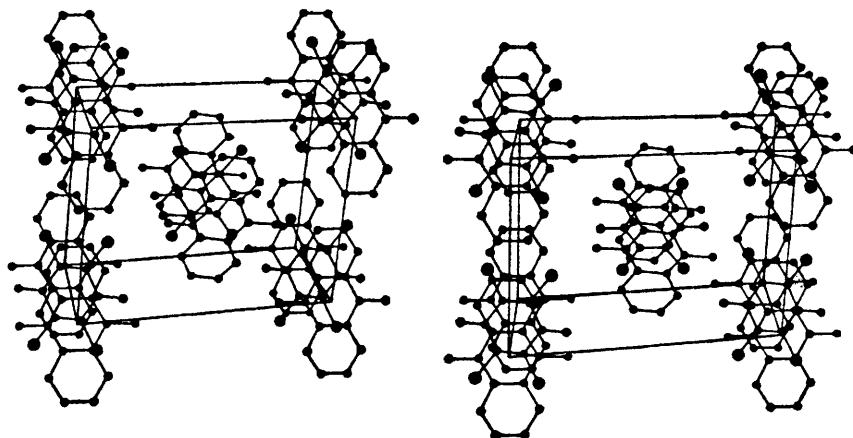
FIGURE 2 Stereoscopic projection. Rotation matrix (for conversion of orthogonal crystal co-ordinates relative to a, $b*$, c to plotter co-ordinates):

$$0·315 \quad -0·044 \quad -0·948$$
$$0·138 \quad 0·990 \quad 0·000$$
$$0·939 \quad -0·130 \quad 0·318$$

electron density in the plane of the 9-methylanthracene, calculated with the final phases, shows the carbon atom C(11) at about half the height of the carbon atoms of the central ring. The carbon atoms C(6) and C(7) are square vibrational amplitudes of these atoms. The rigid-body ω and T tensors (Table 2) for 9-methyl-anthracene indicate that the observed anthracene skeleton (excluding the methyl groups) is quite accurately

described in terms of a rigid body executing a librational motion with a root-mean-square amplitude of $6 \cdot 0 \pm 0 \cdot 1°$ about the inertial axis normal to the molecular plane. However, because this description is demonstrably inappropriate, bond length corrections are not reported. As a result of the disorder the apparent bond-lengths in the 9-methylanthracene, particularly to the outer carbons are somewhat shorter than those in anthracene,[8] e.g. the mean of C(5)–C(6) and C(7)–C(8) is $1 \cdot 35 \pm 0 \cdot 02$ compared with $1 \cdot 375 \pm 0 \cdot 008$ and C(6)–C(7) is $1 \cdot 37 \pm 0 \cdot 02$ compared with $1 \cdot 418 \pm 0 \cdot 008$ Å. The single C–C bond C(10)–C(11) $1 \cdot 30 \pm 0 \cdot 02$ Å is considerably shorter than expected ($1 \cdot 50$ Å) as a result of the averaging effect of the disorder.

The crystal structure shown as a stereoscopic projection in Figure 2, consists of stacks of alternate donor- and acceptor-molecules with the stacking axis parallel to the crystallographic a axis. The mean separation between the molecular planes is $3 \cdot 45$ Å and the angle between the plane normals is $1 \cdot 5°$. The component molecules are planar within experimental error, with the exception of the methyl carbon which is $0 \cdot 07$ Å out of the plane of the anthracene nucleus. The near-planarity of the chloranil molecule is contrary to previous observations in chloranil itself [9] and in the acenaphthene–chloranil molecular complex,[2] where large deviations from planarity are observed [9] for the peripheral atoms; these deviations have been adequately explained in

terms of non-bonded repulsions.[10] Owing to the disorder of the 9-methylanthracene molecule, however, it is not possible in this case to say whether the planarity of the chloranil is real, or whether it is the result of averaging two nearly superposed orientations.

The acceptor projected on the least-squares best-plane of the donor is shown in Figure 3. The relative positions of donor and acceptor are those calculated [11] to maximise
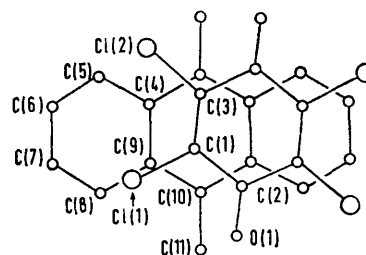

FIGURE 3   Projection of chloranil on least-squares best-plane of 9-methylanthracene.   C(11) has occupancy 0·5

the charge-transfer stabilisation of the complex. There are short intermolecular contacts between atoms in adjacent stacks; Cl(1) and C(11) at $(-x, -\frac{1}{2} - y, \frac{1}{2} + z)$ $3 \cdot 42$ Å and Cl(2) and O at $(x, \frac{1}{2} + y, \frac{1}{2} - z)$ $3 \cdot 30$ Å.

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

[8] R. Mason, Acta Cryst., 1964, 17, 547.
[9] K. J. van Weperen and G. J. Visser, Acta Cryst., 1972, B, 28, 338.
[10] I. Veda, J. Phys. Soc. Japan, 1961, 16, 1185.
[11] B. Mayoh and C. K. Prout, J.C.S. Faraday II, 1972, 1072.