

Table 3. *Some intermolecular C—H...O distances (Å with e.s.d. 0.08 Å)*

Molecule 1	H...O	Symmetry position of O
C(12)—H(12)...O(22)	2.51	-x, -y, 2-z
C(14)—H(14)...O(11)	2.71	0.5-x, y-0.5, 2.5-z
C(15)—H(15)...O(12)	2.61	1-x, -y, 2-z
C(17)—H(17)...O(21)	2.58	-x, -y, 2-z
Molecule 2		
C(22)—H(22)...O(12)	2.62	1-x, -y, 2-z
C(23)—H(23)...O(22)	2.82	0.5-x, y-0.5, 1.5-z
C(24)—H(24)...O(21)	2.74	0.5-x, y-0.5, 1.5-z
C(25)—H(25)...O(22)	2.61	-x, -y, 1-z
C(26)—H(26)...O(11)	2.86	x, y, z-1
C(26)—H(26)...O(22)	2.77	-x, -y, 1-z

pericyclic formation of an electrophilic ethylene seleninic acid intermediate. This seleninic acid species would be expected to be a soft highly polarizable electrophile, that provides one explanation for the very high nucleophilic selectivities of alkylating aryl selenones.

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## Structure of the Molecular Complex of Anthracene with 1,8:4,5-Naphthalenetetracarboxylic Dianhydride

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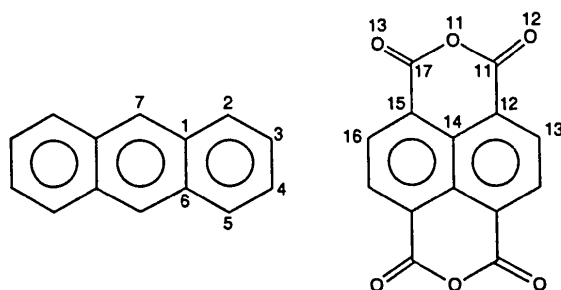
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**Abstract.**  $C_{14}H_{10} \cdot C_{14}H_4O_6$ ,  $M_r = 446.42$ , monoclinic,  $P2_1/a$ ,  $a = 17.572$  (10),  $b = 7.727$  (4),  $c = 7.398$  (4) Å,  $\beta = 101.90$  (4)°,  $V = 982.9$  (9) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.508$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.100$  mm<sup>-1</sup>,  $F(000) = 460$ ,  $T = 293$  K,  $R = 0.050$  for 1429 unique reflections with  $I > 3\sigma(I)$ . The molecules stack with alternating rows of anthracene and dianhydride molecules. The two types of molecule do not lie parallel to each other in these stacks, possibly as a result of interactions between the peripheral H atoms of the anthracene and O atoms of the anhydride.

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**Introduction.** Crystal structures of complexes of polycyclic aromatic hydrocarbons with many flat molecules such as trinitrobenzene, pyromellitic dianhydride and 1,8:4,5-naphthalenetetracarboxylic dianhydride are nicely crystalline and the structures of many of these have been investigated by X-ray diffraction techniques (Prout & Wright, 1968; Foster, 1969; Herbstein, 1971; Mayoh & Prout, 1972; Munnoch & Wright, 1974, 1975; Foster, Iball, Scrimgeour & Williams, 1976). The general feature of such molecular complexes of polycyclic aromatic hydrocarbons is the parallel stacking of alternate donor and acceptor molecules. The planes in which these molecules lie are approximately 3.4-3.5 Å apart,

although this may be decreased to 3.2–3.3 Å as a result of stronger interaction between donor and acceptor. Such  $\pi$  complexes are so-called because they imply an interaction between delocalized  $p$  orbitals of each partner of the complex. Many 'charge-transfer complexes' crystallize in this way with an alternate arrangement of the two molecular species within the stacks. In such complexes one type of molecule (such as the polycyclic aromatic hydrocarbon) has electron-donor (Lewis base) properties, whereas the other (such as the complexing agent which contains electron-withdrawing groups, e.g. trinitrobenzene) has electron-acceptor (Lewis acid) properties. We report here the crystal structure of anthracene complexed with 1,8:4,5-naphthalenetetracarboxylic dianhydride in which the two types of molecule alternate in stacks throughout the crystal.



**Experimental.** Crystals of the complex of anthracene and 1,8:4,5-naphthalenetetracarboxylic dianhydride were prepared by warming equimolar amounts of the two components in anhydrous 2-butanone and allowing the solvent to evaporate slowly. The crystal used was a black prism,  $0.30 \times 0.12 \times 0.75$  mm in dimensions. The X-ray diffraction data were collected on a Nicolet/Siemens P3 four-circle automated diffractometer using variable  $\omega$  scans in the range  $2.02$ – $58.6^\circ \text{ min}^{-1}$ , depending on reflection intensity. Graphite-monochromatized radiation was used. The lattice parameters were determined, using a least-squares procedure, from 14 centered reflections in the  $2\theta$  range  $10$  to  $30^\circ$ . All measurements were made at the ambient temperature of the instrument room ( $293 \text{ K}$ ). The index ranges of the data were  $h = -22$  to  $22$ ,  $k = 0$  to  $10$  and  $l = 0$  to  $9$ . The total number of unique data, 2265, was measured to max.  $\sin\theta/\lambda$  of  $0.65 \text{ \AA}^{-1}$  ( $2\theta = 55^\circ$ ). Of these, 1429 were considered observed [ $I \geq 3.0\sigma(I)$ ]. Four standard reflections, measured at periodic intervals, showed a variation of less than 1% and therefore no correction for intensity decay was necessary. An empirical absorption correction was derived from a  $\psi$  scan of a reflection near  $\chi = 90^\circ$  in  $5^\circ$  increments of the  $\varphi$  angle. Correction factors ranging from 0.91 to 1.00 were applied to the data as a function of  $\varphi$ . The range of transmission factors was 0.912 to 1.000. The data were

corrected for Lorentz and polarization effects. The weights for reflections used in the least-squares refinements,  $w = 1/\sigma^2(F)$ , were derived from counting statistics using the relation  $\sigma(F) = (F/2)[\sigma^2(I)/(I^2 + \delta^2)]^{1/2}$  in which  $\delta$  ( $=0.021$ ) is an instrumental uncertainty based on the variation in the intensities of the standard reflections monitored throughout the data collection. Equivalent reflections agreed within  $R_{\text{int}} = 0.02$  (for 171 sets of two equivalent reflections each). The structure was found from the Patterson map by comparing the vector maps constructed from the molecular formulae of each of the two components. This was done by displaying the Patterson map of more than one unit cell on a graphics system (Evans and Sutherland PS 390) by use of the computer program *FRODO* (Jones, 1978). Since both the anthracene and anhydride lie on centers of symmetry, the orientations and locations of each molecule could readily be found in this way from the Patterson map. For all other crystallographic calculations in-house programs were used (Carrell, Shieh & Takusagawa, 1981). The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). No correction was made for anomalous scattering. All structure refinements on  $F$  were carried out using a least-squares procedure, first with isotropic and then anisotropic thermal parameters. 1429 reflections with  $I \geq 3\sigma(I)$  were used. Initially, only C- and O-atom parameters were refined. Then the positions of H atoms were calculated. Further refinement was done with anisotropic temperature factors for C and O atoms and isotropic temperature factors for H atoms. The final  $R$  factors and weighted  $R$  factors were  $R_{\text{obs}} = 0.050$ ,  $R_{\text{all}} = 0.078$ ,  $wR_{\text{obs}} = 0.052$ ,  $wR_{\text{all}} = 0.057$ . The number of parameters refined was 182,  $S$  was 2.10,  $(\Delta/\sigma)_{\text{max}}$  was 0.22,  $(\Delta\rho)_{\text{max}}$  and  $(\Delta\rho)_{\text{min}}$  were 0.17 and  $-0.25 \text{ e \AA}^{-3}$ , respectively. The refined atomic coordinates are listed in Table 1.

A diagram of the thermal ellipsoids, produced with the computer program *SNOOPI* (Johnson, 1965; Davies, 1983), is given in Fig. 1. The packing and overlap diagrams were produced with the computer program *VIEW* (Carrell, 1976).

**Discussion.** Bond lengths are listed in Table 2. A table of interbond angles has been deposited.\* Molecules pack, as shown as a stereopair in Fig. 2, with alternating rows of anthracene and dianhydride molecules. In this way the crystal structure resembles

\* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles, torsion angles and least-squares-planes calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55573 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1003]

Table 1. Atomic coordinates and isotropic or equivalent isotropic thermal parameters ( $\text{\AA}^2$ )

H atoms were refined isotropically; for non-H atoms  $B_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $B_{ij}$  tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{iso}}/B_{\text{eq}}$
C(1)	0.0617 (1)	-0.1154 (3)	0.5687 (2)	4.02 (9)
C(2)	0.1280 (1)	-0.2215 (3)	0.6373 (3)	5.2 (1)
C(3)	0.2006 (1)	-0.1578 (4)	0.6516 (3)	6.3 (1)
C(4)	0.2136 (1)	0.0109 (4)	0.6008 (4)	6.5 (1)
C(5)	0.1542 (1)	0.1153 (3)	0.5360 (3)	5.4 (1)
C(6)	0.0760 (1)	0.0612 (3)	0.5158 (2)	3.92 (9)
C(7)	0.0141 (1)	0.1707 (3)	0.4499 (3)	4.45 (9)
O(11)	0.04031 (7)	0.4078 (2)	-0.1637 (2)	4.22 (6)
O(12)	-0.08409 (8)	0.4706 (2)	-0.2432 (2)	5.00 (7)
O(13)	0.16666 (7)	0.3609 (2)	-0.0871 (2)	5.49 (8)
C(11)	-0.0373 (1)	0.3653 (3)	-0.1761 (3)	3.68 (9)
C(12)	-0.05411 (9)	0.1944 (2)	-0.1042 (2)	3.14 (8)
C(13)	-0.12959 (9)	0.1456 (3)	-0.1073 (3)	3.66 (9)
C(14)	0.00822 (9)	0.0828 (2)	-0.0326 (2)	2.90 (8)
C(15)	0.08641 (9)	0.1306 (2)	-0.0245 (2)	3.13 (8)
C(16)	0.1458 (1)	0.0171 (3)	0.0428 (3)	3.71 (9)
C(17)	0.1037 (1)	0.3029 (3)	-0.0899 (3)	3.92 (9)
H(2)	0.161 (1)	0.235 (3)	0.503 (3)	6.0 (6)
H(3)	0.272 (2)	0.051 (4)	0.631 (4)	10.3 (9)
H(4)	0.243 (1)	-0.234 (4)	0.700 (4)	10.1 (9)
H(5)	0.116 (1)	-0.333 (4)	0.666 (3)	7.3 (7)
H(7)	0.022 (1)	0.283 (3)	0.413 (3)	5.3 (6)
H(13)	-0.169 (1)	0.215 (3)	-0.152 (3)	4.6 (5)
H(16)	0.198 (1)	0.058 (3)	0.050 (3)	5.2 (5)

Table 2. Bond distances ( $\text{\AA}$ )

C(1)—C(7)	1.380 (2)	C(11)—O(11)	1.387 (2)
C(1)—C(2)	1.429 (3)	C(11)—O(12)	1.190 (2)
C(2)—C(3)	1.349 (3)	C(17)—C(15)	1.470 (3)
C(3)—C(4)	1.389 (4)	C(11)—C(12)	1.476 (3)
C(4)—C(5)	1.328 (3)	C(14)—C(15)	1.412 (2)
C(5)—C(6)	1.415 (2)	C(12)—C(14)	1.409 (2)
C(1)—C(6)	1.455 (3)	C(12)—C(13)	1.375 (2)
C(6)—C(7)	1.385 (3)	C(15)—C(16)	1.376 (2)
C(17)—O(13)	1.190 (2)	C(13)—C(16)	1.395 (3)
C(17)—O(11)	1.395 (2)		

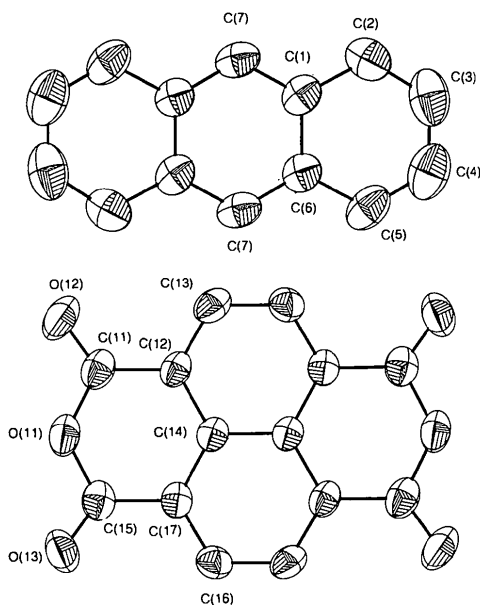


Fig. 1. Thermal ellipsoid (50%) representation.

many such molecular complexes of polycyclic aromatic hydrocarbons (Herbstein, 1971; Mayoh & Prout, 1972). The stacking of the anthracene and dianhydride molecules takes place with a distance of approximately  $3.52 \text{ \AA}$  between the planes through different molecules. The overlap of molecules is shown in Fig. 3. The anthracene and anhydride molecules are, however, not precisely parallel, as shown in Fig. 3(b). The anthracene molecules lie so that the distances between some of the peripheral H atoms of the anthracene and the O atoms of the anhydride are shorter than other intermolecular contacts. These distances are  $\text{O}(11)\cdots\text{H}(7)$   $3.23 (3)$ ,  $\text{O}(12)\cdots\text{H}(5)$   $3.24 (3)$  and  $\text{O}(13)\cdots\text{H}(2)$   $3.17 (3) \text{ \AA}$ . The average distance between molecules is longer than that seen in charge-transfer complexes, but the

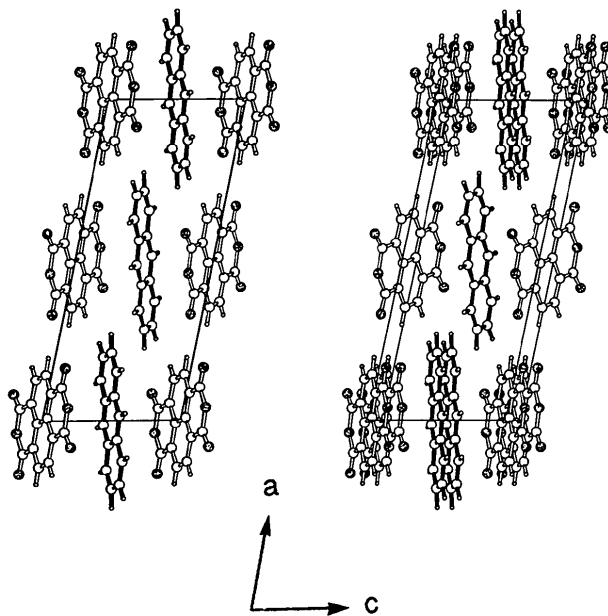
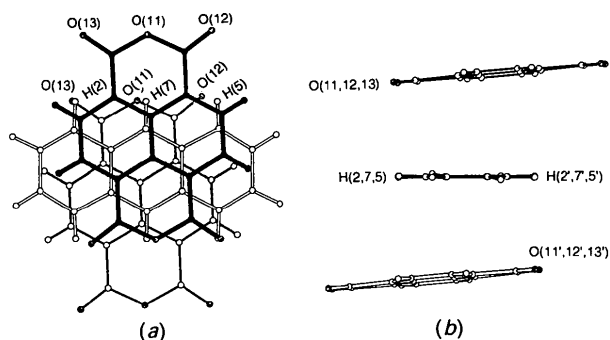
Fig. 2. Stereoview along *b* of the packing in the unit cell. Anthracene molecules are drawn with black bonds. O atoms are stippled.

Fig. 3. Overlap of molecules in the unit cell shown by (a) a view onto the plane of the anthracene molecule and (b) a view along the plane of the anthracene molecule.

observed dark color of the crystals may indicate some transfer of charge. The r.m.s. deviation of C atoms from the plane of the anthracene ring system is 0.003 (1) Å, while for the dianhydride it is 0.027 Å. Atoms O(12), O(13), C(13) and C(16) deviate most from the plane.

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## Structure of 4-(5-Cyano-2-furyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarbonitrile

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**Abstract.** C<sub>14</sub>H<sub>10</sub>N<sub>4</sub>O, *M<sub>r</sub>* = 250.26, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 13.293 (3), *b* = 8.099 (2), *c* = 13.815 (3) Å, β = 120.474 (5)°, *V* = 1281.9 (5) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.26 (2), *D<sub>x</sub>* = 1.297 Mg m<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ = 0.08 mm<sup>-1</sup>, *F*(000) = 520, *T* = 299 K, final *R* = 0.0442 for 2081 unique reflections with *F* > 2σ(*F*). The crystal structure consists of single molecules. The substituted 1,4-dihydropyridine ring has a flat boat conformation with the N(1) and C(4) atoms displaced by 0.100 (1) and 0.141 (1) Å, respectively, from the plane through the other four C atoms which defines the base of the boat. The plane of the furyl ring makes an angle of 76.7 (1)° with the

plane of the base of the boat. No significant intermolecular interactions are observed.

**Introduction.** Numerous newly synthesized 1,4-dihydropyridines have been studied as models of NADH coenzymes in 'hydrogen-transfer' reactions (Eisner & Küthan, 1972). In order for a 1,4-dihydropyridine to act as a reducing agent, the H atom in the 4-position [H(3)] and that at the N atom should assume an antiperiplanar arrangement.

X-ray studies on 1,4-dihydropyridines have shown a great dependence of the geometry of the skeleton on the attached substituents, especially those in the 4