

limited extent of the data precludes useful further discussion of the bond lengths and bond angles.

The molecular packing is illustrated in Fig. 3. The molecules are well separated, the only intermolecular contacts not involving H and less than 3.5 Å being O(61)–C(31) (3.36 Å) and S(1a)–O(51) (3.43 Å).

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The Charge-Transfer Complex Phenanthrene–Pyromellitic Acid Dianhydride (PMDA)

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Abstract. C₂₄H₁₂O₆, $M_r = 396.36$. Monoclinic $P2_1/c$, $a = 7.046$ (3), $b = 13.494$ (2), $c = 19.396$ (7) Å, $\beta = 97.4$ (3)° (refined diffractometer data), $Z = 4$, D_m (flotation) = 1.40 (5), $D_c = 1.44$ g cm⁻³. Least-squares refinements using 2105 reflexion intensities have converged with $R = 0.066$. The crystal structure consists of stacks of alternating phenanthrene and PMDA molecules 3.36 Å apart with an angle of 4.11° between the normals to their planes. These normals make angles of 15.52 and 14.35° with the x axis respectively.

Introduction. π - π organic charge-transfer compounds are a class of compounds currently subject to intensive study. Such physical properties as exciton motion (Möhwald & Sackmann, 1974), photoconductivity (Haarer & Möhwald, 1975), electron mobility (Bergman & Jortner, 1974; Möhwald, Haarer & Castro, 1975) and fluorescence (Kepler, Caris,

Avakian & Abramson, 1963) are being investigated. Techniques in use include electron spin resonance (Dalal, Haarer, Bargon & Möhwald, 1975), emission and absorption spectroscopy (Haarer & Karl, 1973) and conductivity measurements (Batt, Braun & Hornig, 1968). A review of crystallographic work has been made by Herbstein (1971). The commonly occurring features he discusses are (1) the donor–acceptor separation distance of ~3.5 Å, (2) stacking of the donor and acceptor molecules in semi-infinite columns, (3) disorder, (4) centrosymmetric molecules, (5) the dihedral angle between adjacent molecules and (6) the non-perpendicularity of the planes of the component molecules with respect to the stack axis.

In the complex phenanthrene–PMDA, phenanthrene acts as an electron donor and PMDA as an electron acceptor. The physical properties of this complex have been measured by Haarer & Möhwald (1975). In their studies they have encountered a new phenomenon

which they call field-induced charge-carrier trapping. Their discussion of the photoconductivity in terms of a hopping model enables them to argue that this new phenomenon is a consequence of the quasi one-dimensional nature of the phenanthrene-PMDA structure.

Crystals were supplied by D. Haarer. They are yellow in colour and had been grown by the Bridgman method from chromatographed and zone-refined phenanthrene and PMDA (Möhwald, Haarer & Castro, 1975). Preliminary precession photographs of these crystals exhibited monoclinic symmetry and the systematic absences $0k0$ k odd, $h0l$ l odd uniquely indicate that the space group is $P2_1/c$. The density of the crystal was measured by flotation, $D_m = 1.44$ g cm⁻³. Least-squares refinement of the cell constants (using 12 centred reflexions) as $a = 7.046$ (3), $b = 13.494$ (2), $c = 19.396$ (7) Å, $\beta = 97.4$ (3)° yields a

Table 1. Positional parameters ($\times 10^4$; for H $\times 10^3$) for phenanthrene-PMDA

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	231 (3)	3929 (2)	6295 (1)
C(2)	-374 (3)	3199 (2)	5819 (1)
C(3)	-352 (3)	2207 (2)	5984 (1)
C(4)	-1093 (4)	3282 (3)	5072 (1)
C(5)	-1099 (4)	1655 (2)	5344 (2)
C(11)	244 (3)	1857 (2)	6642 (1)
C(12)	859 (3)	2577 (2)	7127 (1)
C(13)	847 (3)	3574 (2)	6959 (1)
C(14)	1613 (4)	2487 (2)	7863 (1)
C(15)	1592 (4)	4121 (2)	7594 (1)
O(1)	-1365 (4)	3993 (2)	4702 (1)
O(2)	-1505 (3)	2342 (2)	4820 (1)
O(3)	-1315 (3)	780 (2)	5261 (1)
O(11)	1884 (3)	1773 (2)	8225 (1)
O(12)	2011 (3)	3433 (2)	8122 (1)
O(13)	1827 (3)	4988 (2)	7690 (1)
C(21)	4553 (4)	894 (2)	734 (2)
C(22)	5257 (4)	471 (2)	1328 (2)
C(31)	5876 (3)	1049 (2)	1938 (1)
C(32)	6642 (4)	615 (3)	2578 (2)
C(33)	7157 (5)	1159 (3)	3141 (2)
C(34)	6979 (4)	2193 (3)	3112 (2)
C(35)	6262 (4)	2658 (2)	2501 (1)
C(36)	5695 (3)	2098 (2)	1893 (1)
C(41)	4368 (3)	1941 (2)	657 (1)
C(42)	3617 (4)	2406 (3)	19 (1)
C(43)	3435 (4)	3417 (3)	-30 (2)
C(44)	4012 (4)	3995 (3)	536 (2)
C(45)	4760 (4)	3585 (2)	1151 (2)
C(46)	4943 (3)	2545 (2)	1239 (1)
H(1)	22 (3)	454 (2)	612 (1)
H(11)	18 (4)	129 (2)	674 (2)
H(21)	403 (5)	37 (3)	36 (2)
H(22)	525 (4)	-38 (2)	131 (2)
H(32)	653 (4)	-12 (3)	251 (2)
H(33)	752 (4)	87 (2)	350 (2)
H(35)	598 (4)	333 (2)	245 (2)
H(34)	716 (4)	253 (2)	350 (2)
H(42)	319 (4)	203 (2)	-38 (2)
H(43)	291 (4)	369 (2)	-46 (2)
H(44)	393 (4)	456 (2)	45 (2)
H(45)	510 (4)	385 (2)	159 (2)

calculated density of 1.44 g cm⁻³ with four molecular pairs in the unit cell.

Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) was used, reflexions being observed from a crystal of dimensions $0.5 \times 0.6 \times 0.8$ mm having the planes (012), (012), (100), (012), (211), (012) as its bounding faces.

Data were collected for one quadrant of reciprocal space with $\theta < 57^\circ$ using a Hilger & Watts automatic diffractometer. The intensities of the diffracted X-rays were measured with a 72-step 0.01° scan with 18 s background counts at each end of the scan. Attenuators were used when the monitored pulses exceeded 8000 s⁻¹. The intensities of three standard reflexions were monitored every 100 reflexions and the data scaled accordingly. Lorentz and polarization corrections were applied and of the unique reflexions measured 1951 had intensities $>5\sigma$ and 2105 had intensities $>3\sigma$. No absorption corrections were made as test calculations showed them to be unnecessary.

25 of the 30 non-hydrogen atoms were located by use of the direct-methods program *MULTAN* (Main, Woolfson & Germain, 1971) with the 500 reflexions with highest E values. The positions of the remaining five atoms were calculated and three cycles of refinement of positional and thermal parameters by full-matrix least squares gave a conventional R of 0.203. Further refinement, with anisotropic thermal parameters for all non-hydrogen atoms, reduced R to 0.092 and refinement of the H atom positions with isotropic thermal parameters finally gave $R = 0.066$. Shifts in all parameters were less than 0.5 of their standard deviations in the final cycle of refinement.

A final difference Fourier synthesis revealed no anomalously large peaks. The scattering-factor tables used for C and O were those of Cromer & Waber (1965) and for H those of Stewart, Davidson & Simpson (1965). Atomic coordinates are given in Table 1.*

Discussion. The structure of the complex consists of columns of alternately stacked molecules of phenanthrene and PMDA. Figs. 1 and 2 define the atom labelling scheme used throughout this paper. Fig. 3 shows the spatial relations between the molecular pairs related by the symmetry elements of the space group. The x axis of the crystal is described as the stack axis and the phenanthrene-PMDA repeat distance along the stack axis is 3.52 Å whereas the perpendicular distance between these molecules is 3.36 Å. The angle between the normals to the molecular planes of a phenanthrene-PMDA pair, shown in Fig. 3, is 4.11° and these same normals make angles of 15.52 and

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32671 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

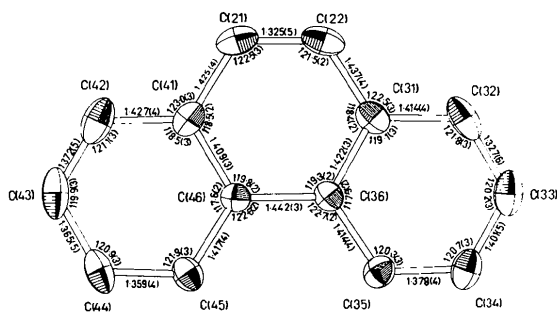


Fig. 1. Bond distances and angles in phenanthrene.

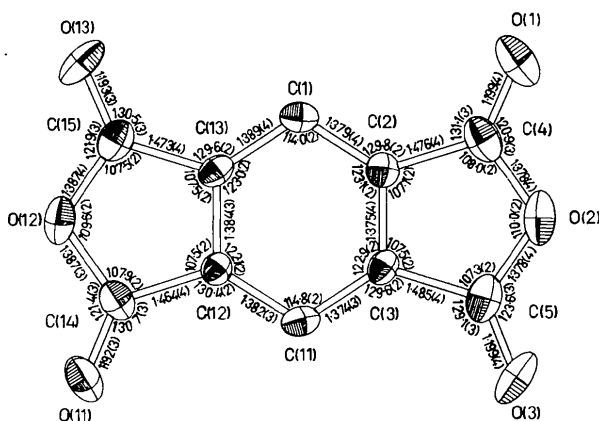


Fig. 2. Bond distances and angles in PMDA.

14.35°, respectively, with the stack axis. The non-parallelism of the phenanthrene and PMDA molecules and the manner in which they overlap indicate localized interactions (Goldberg, 1975). The extent of such interactions is apparent in Fig. 3. It is interesting to note that when a molecular pair is viewed in projection the O atoms in PMDA do not lie above regions of electron density (be they bonds or atoms) in the adjacent phenanthrene molecule. In fact, in this view five of the six oxygen atoms lie 'outside' the phenanthrene molecule. The sixth O atom lies centrally above one of the end phenyl rings in phenanthrene. This feature is common to complexes of PMDA with anthracene, naphthalene, perylene, pyrene (Herbstein, 1971) and fluorene (Evans & Robinson, 1977). It appears then that the C atoms and their concomitant H atoms are the atoms involved in the intermolecular binding and charge interactions.

The bond distances and angles calculated from the atomic coordinates (Table 1) are given on Figs. 1 and 2. These figures illustrate the anisotropic thermal vibrations of the atoms. There is no evidence of disorder in the structure.

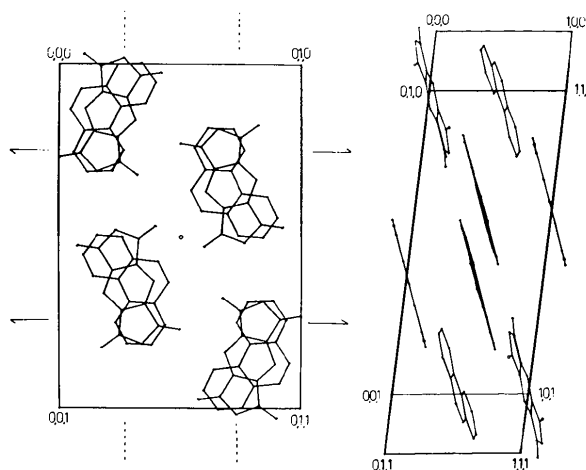


Fig. 3. Crystal packing of phenanthrene and PMDA molecules viewed down the stack axis and viewed edge-on to one of the PMDA molecules.

The bond C(36)–C(46) is 1.442 (3) Å in length – longer than any other C–C bond in phenanthrene. MO calculations (Banerjee & Basak, 1975) indicate that π -electron delocalization in phenanthrenoids is the main cause of this lengthening rather than steric overcrowding of H atoms.

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