

Fig. 2. Stereoscopic view of the molecular packing. The *z* axis is vertical, the *y* axis horizontal, and the origin is in the lower right-hand front corner.

isoquinuclidine rings are in a slightly distorted boat conformation. The top of the isoquinuclidine cage [atoms C(3), C(14) and C(16)] is twisted by  $10.5^\circ$  (mean value) relative to the bottom [atoms N(4), C(19) and C(17)]. The similar alkaloid ibogaine (Arai *et al.*, 1960) shows a less-twisted cage, with mean value  $5.5^\circ$ . As can be seen in the stereoscopic view of the molecular packing shown in Fig. 2, the greater twist of the isoquinuclidine cage in epiheyneanine is possibly due to the hydrogen bond between O(3) and the solvated acetone molecule.

The present X-ray analysis confirmed the relative configuration at C(20) but did not reveal the presence of the intramolecular hydrogen bond between O(3) and N(4) [distance  $N \cdots O = 3.761 \text{ \AA}$ ] proposed by Wenkert *et al.* (1976).

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## Structure of the 1:1 $\pi$ -Molecular Complex of Tetracene with 1,2:4,5-Pyromellitic Dianhydride\*

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**Abstract.**  $C_{18}H_{12} \cdot C_{10}H_2O_6$ ,  $M_r = 446.42$ , triclinic,  $P\bar{1}$ ,  $a = 6.719$  (1),  $b = 7.342$  (2),  $c = 10.734$  (2)  $\text{\AA}$ ,  $\alpha = 82.52$  (2),  $\beta = 79.51$  (2),  $\gamma = 104.06$  (2)°,  $V =$

$496.6$  (2)  $\text{\AA}^3$ ,  $Z = 1$ ,  $D_x = 1.49 \text{ g cm}^{-3}$ ,  $\lambda(\text{Mo K}\alpha) = 0.71069 \text{ \AA}$ ,  $\mu(\text{Mo}) = 0.99 \text{ cm}^{-1}$ ,  $F(000) = 230$ ,  $T = 295 \text{ K}$ ,  $R = 0.029$  for 1375 observed reflections [ $I > 3\sigma(I)$ ]. Centrosymmetric planar component molecules are stacked alternately in columns parallel to **a**. Both molecular planes are perpendicular to **a**, the interplanar separation being  $3.36 \text{ \AA}$ .

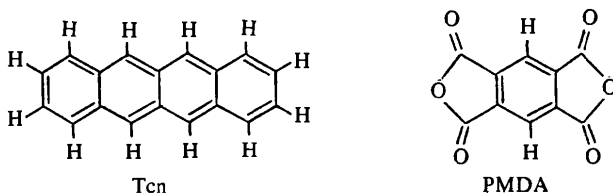
\* Tetracene = naphthacene; 1,2:4,5-pyromellitic dianhydride = 1*H*,3*H*-benzo[1,2-*c*:4,5-*c'*]difuran-1,3,5,7-tetrone.

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**Introduction.** Donor-acceptor (*D:A*) or charge-transfer (CT) complexes between pyromellitic dianhydride (PMDA) and some electron donors such as aromatic hydrocarbons are known to be rather good photoconductors. As a rule the efficiency of photoconduction of the complex can be associated with the efficiency of the carrier generation process in the regions of singlet absorption of the components and the region of CT absorption owing to intermolecular electronic transitions with charge transfer from the donor to the acceptor. The dark red 1:1 complex between PMDA and tetracene, Tcn, acting as an electron donor, is an attractive system for examining its photoconductive properties because of more promising photoconductive characteristics of Tcn compared with its structural analogues with a smaller number of rings such as naphthalene and anthracene (Silinsh, 1980). Owing to the low ionization potential of the solid Tcn [value for the crystalline state 5.40 eV (Silinsh, 1980)] the CT transition energy  $E_{CT}$  of the complex is low ( $E_{CT} = 1.90$  eV). To provide a structural basis for interpretation of the spectroscopic data and other physical properties we have undertaken an X-ray analysis of the title compound.



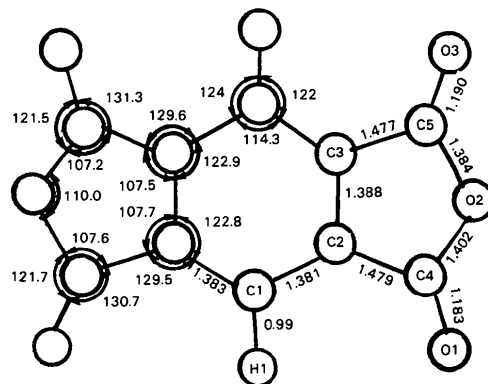
**Experimental.** Dark red crystals  $0.25 \times 0.23 \times 0.30$  mm grown by high-vacuum plate sublimation.  $D_m$  not measured. Lattice parameters refined using a least-squares fit to the settings for 15 reflections. Syntax  $P\bar{1}$  diffractometer, graphite-monochromated Mo  $K\alpha$  radiation,  $\theta/2\theta$  scan mode,  $2\theta < 50^\circ$ . During data collection three standard reflections (402, 306 and  $4\bar{2}0$ ) showed only statistical variation within  $\pm 2\%$ . 1456 unique reflections collected, range of  $hkl$ :  $h \pm 7$ ,  $k \pm 8$ ,  $l \rightarrow 12$ , 1375 significant with  $I > 3\sigma(I)$ . Structure determined by direct methods and refined (on  $F$ ) by full-matrix least squares with anisotropic thermal parameters for C and O atoms: final  $R = 0.029$ ,  $wR = 0.038$ ,  $w = 1/[\sigma^2(F) + 0.0005F^2]$ . Positions of H atoms calculated; their positional and isotropic thermal parameters were refined. Atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974), except that for H which was taken from Stewart, Davidson & Simpson (1965).  $(\Delta/\sigma)_{\max} = 0.07$ .  $(\Delta\rho)_{\max} = 0.15$  e  $\text{\AA}^{-3}$ . Calculations carried out with *SHELXTL* (Sheldrick, 1978) on the Nova 3 computer incorporated in the Nicolet R3 system.

Table 1. Fractional atomic coordinates (and e.s.d.'s) of non-hydrogen atoms ( $\times 10^4$ ) and hydrogen atoms ( $\times 10^3$ ), and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^4$ )

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i a_j a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$ Or $U_{iso}$
O(1)	3983 (2)	5203 (2)	8546 (1)	648 (7)
O(2)	3452 (2)	2300 (2)	7974 (1)	501 (6)
O(3)	3226 (2)	-68 (2)	6827 (1)	578 (7)
C(1)	5207 (2)	6709 (2)	5552 (1)	380 (7)
C(2)	4571 (2)	4897 (2)	6292 (1)	357 (7)
C(3)	4365 (2)	3253 (2)	5762 (1)	353 (7)
C(4)	4009 (2)	4301 (2)	7709 (2)	451 (9)
C(5)	3638 (2)	1600 (2)	6835 (2)	429 (9)
C(6)	-147 (2)	4169 (2)	4699 (1)	350 (7)
C(7)	-848 (2)	2353 (2)	5488 (1)	394 (7)
C(8)	-1260 (2)	2108 (2)	6823 (1)	396 (7)
C(9)	-1957 (2)	264 (2)	7637 (2)	501 (9)
C(10)	-2348 (3)	83 (3)	8933 (2)	599 (10)
C(11)	-2099 (3)	1715 (3)	9522 (2)	609 (10)
C(12)	-1449 (2)	3488 (2)	8804 (1)	515 (7)
C(13)	-983 (2)	3770 (2)	7423 (1)	396 (7)
C(14)	-285 (2)	5572 (2)	6654 (1)	399 (8)
H(1)	533 (3)	789 (4)	592 (3)	619 (15)*
H(7)	-107 (4)	121 (4)	507 (3)	504 (20)*
H(9)	-215 (3)	-87 (4)	721 (4)	624 (24)*
H(10)	-281 (4)	-124 (4)	946 (3)	684 (32)*
H(11)	-240 (4)	158 (4)	1048 (3)	658 (35)*
H(12)	-128 (3)	463 (4)	920 (3)	714 (14)*
H(14)	-5 (4)	675 (4)	707 (3)	465 (20)*

\*  $U_{iso}$ .



**Discussion.** The atomic coordinates are listed in Table 1,\* bond distances and bond angles are displayed in Figs. 1 and 2 for PMDA and Tcn. The bonding geometry of the PMDA molecule agrees well with that found for the acceptor in quite a number of 1:1 *D:A* complexes with donors such as anthracene (Robertson & Stezowski, 1978), phenazine (Bulgarovskaya, Vozzhennikov, Krasavin & Kotov, 1982), carbazole (Stezowski, Binder & Karl, 1982). Tcn bond distances and bond angles may be compared with the average values found in the free Tcn (Robertson, Sinclair & Trotter, 1961). Each of the component molecules is planar. The maximum deviations from the mean planes of the PMDA and Tcn molecules (neglecting H atoms) are 0.021 and 0.012 Å respectively.

The structure of the complex consists of columns of alternately stacked molecules of Tcn and PMDA. The *a* axis of the crystal is the stack axis. The molecular planes are parallel to each other and perpendicular to *a* (the angle between the plane normals is 1.7°, those between the normals to the Tcn and PMDA planes and the *a* axis are 0.7 and 1.5°, respectively), the interplanar separation being 3.36 Å. Because the stacks are not shifted with respect to one another along the *a* axis, the structure can also be described in terms of alternating sheets of Tcn and PMDA molecules. Adjacent Tcn and PMDA molecules are orientated in such a manner that the bonds of the Tcn molecule common to two rings lie over (or under) the centres of the rings of the neighbouring PMDA molecule, Fig. 3.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43514 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

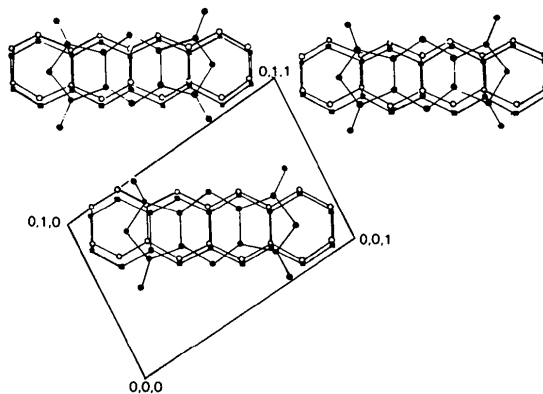


Fig. 3. Molecular packing in Tcn.PMDA viewed normal to the PMDA molecular plane.

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## Structure of the 1:1 $\pi$ -Molecular Complex of Chrysene with 1,2:4,5-Pyromellitic Dianhydride\*

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**Abstract.**  $C_{18}H_{12} \cdot C_{10}H_2O_6$ ,  $M_r = 446.4$ , monoclinic,  $P2_1/n$ ,  $a = 8.093$  (3),  $b = 16.479$  (5),  $c = 7.746$  (2) Å,  $\gamma = 97.62$  (3)°,  $V = 1023.9$  (6) Å<sup>3</sup>,  $Z = 2$ ,  $D_x =$

\* 1,2:4,5-Pyromellitic dianhydride = 1*H*,3*H*-benzo[1,2-*c*:4,5-*c'*]-difuran-1,3,5,7-tetrone.

1.45 g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu(\text{Mo}) = 0.96$  cm<sup>-1</sup>,  $F(000) = 460$ ,  $T = 295$  K,  $R = 0.041$  for 845 observed reflections [ $I > 3\sigma(I)$ ]. Alternate planar centrosymmetric molecules form stacks along *c*. The mean separation of the molecular planes is 3.32 Å, the interplanar angle is 2.0°.

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