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1:1 Donor–Acceptor Complex between Phenazine and Pyromellitic Dianhydride at ~120 K

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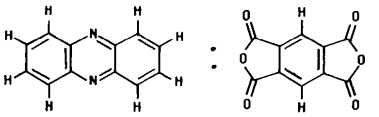
Abstract. $C_{12}H_8N_2.C_{10}H_2O_6$, triclinic, space group $P\bar{1}$, $a = 6{\cdot}930\ (3)$, $b = 10{\cdot}869\ (4)$, $c = 7{\cdot}093\ (3)$ Å, $\alpha = 116{\cdot}67\ (3)$, $\beta = 111{\cdot}21\ (2)$, $\gamma = 98{\cdot}47\ (4)°$, $V = 413{\cdot}11$ Å^3 at $T \sim 120$ K; $Z = 1$, $\rho_{calc} = 1{\cdot}60$ g cm^{-3}. At 297 (1) K, $a = 7{\cdot}031\ (2)$, $b = 10{\cdot}898\ (1)$, $c = 7{\cdot}214\ (1)$ Å, $\alpha = 116{\cdot}47\ (1)$, $\beta = 111{\cdot}57\ (1)$, $\gamma = 98{\cdot}36\ (1)°$, $V = 427{\cdot}24$ Å^3. Of the 6808 unique reflections measured to a resolution of $\sin\theta/\lambda < 0{\cdot}995$ Å^{-1} ($\lambda = 0{\cdot}71069$ Å), 6339 contributed to the refinement of 156 variables to give $R = 0{\cdot}042$, $R_w = 0{\cdot}083$ and $\sigma = 1{\cdot}01$. The crystal structure is isomorphous with those of the 1:1 donor–acceptor complexes between anthracene and pyromellitic dianhydride, and between acridine and pyromellitic dianhydride. The mixed donor:acceptor phase diagram demonstrates complete miscibility of the three complexes.

Introduction. Phenazine, Ph, is structurally related to and isoelectronic with acridine, Ac, and anthracene, A, but differs in ionization energy [values for the crystalline state are $I_c = 5{\cdot}75\ (10)$, ~6·2, and 6·9 (2) eV for A, Ac, and Ph, respectively, *cf.* Probst & Karl, 1975]. We have determined the crystal structure of the 1:1 donor–acceptor complex Ph:PMDA (PMDA = pyromellitic dianhydride) to determine if it is isomorphous with those of A:PMDA (Robertson & Stezowski, 1978) and Ac:PMDA (Binder, Karl & Stezowski, 1982). Our interest was stimulated by the hope that, if the crystal structures are sufficiently isomorphous, it might be possible to prepare single crystals of donor–acceptor complexes with mixed donors over a broad range of stoichiometry.



Ph PMDA

Experimental. A yellow 0·5 × 0·5 × 1·0 mm parallelepiped crystal, grown from zone-refined components by high-vacuum plate sublimation, was sealed in a thin-walled glass capillary and cooled to ~120 K. Lattice parameters, presented in the *Abstract*, were refined with 45 automatically centred 2θ values in the angular range $40{\cdot}0 < 2\theta < 45{\cdot}8°$ for the crystal at ~120 and 297 (1) K. Intensities were measured for the cooled crystal as described for Cb:PMDA (Stezowski, Binder & Karl, 1982). No significant variations were observed in three periodically measured reference reflections. Corrections were applied for Lorentz and polarization effects, but not for absorption, $\mu = 1{\cdot}29$ cm^{-1}.

The structural model was developed from the coordinates of A:PMDA. H-atom coordinates were determined by difference Fourier methods. The structure

Table 1. *Fractional atomic coordinates and isotropic temperature factors*

	x	y	z	U_{eq} or U (Å^2)
C(P1)	−0·19664 (9)	0·03829 (6)	−0·0281 (1)	0·01557
C(P2)	0·00954 (8)	0·13867 (5)	0·05505 (9)	0·01404
C(P3)	0·19781 (8)	0·10157 (5)	0·08212 (9)	0·01372
C(P4)	0·0760 (1)	0·29578 (6)	0·1272 (1)	0·01753
C(P5)	0·38501 (9)	0·23563 (6)	0·1753 (1)	0·01577
O(P4)	−0·02981 (9)	0·37269 (5)	0·1260 (1)	0·02708
O(P6)	0·30377 (7)	0·34817 (5)	0·20085 (8)	0·01825
O(P5)	0·57483 (7)	0·25458 (6)	0·22283 (9)	0·02163
N(Ph9)	−0·17916 (7)	0·05072 (5)	0·48794 (8)	0·01473
C(Ph11)	0·02294 (8)	0·14072 (5)	0·55966 (9)	0·01310
C(Ph12)	0·20398 (8)	0·08909 (5)	0·57156 (9)	0·01297
C(Ph1)	0·05906 (9)	0·29002 (6)	0·6235 (1)	0·01593
C(Ph2)	0·2641 (1)	0·38246 (6)	0·6962 (1)	0·01595
C(Ph3)	0·44336 (9)	0·33123 (6)	0·7088 (1)	0·01585
C(Ph4)	0·41544 (9)	0·18856 (6)	0·6474 (1)	0·01542
H(P1)	−0·324 (2)	0·066 (2)	−0·045 (2)	0·033 (3)
H(Ph1)	−0·059 (2)	0·324 (1)	0·615 (2)	0·022 (3)
H(Ph2)	0·274 (2)	0·486 (2)	0·728 (3)	0·037 (3)
H(Ph3)	0·580 (2)	0·399 (2)	0·754 (3)	0·040 (4)
H(Ph4)	0·534 (2)	0·153 (2)	0·655 (2)	0·025 (3)

The temperature factor has the form of $\exp(-T)$ where $T = 8\pi^2 U(\sin\theta/\lambda)^2$ for isotropic atoms. The e.s.d. of the last significant digit is given in parentheses.

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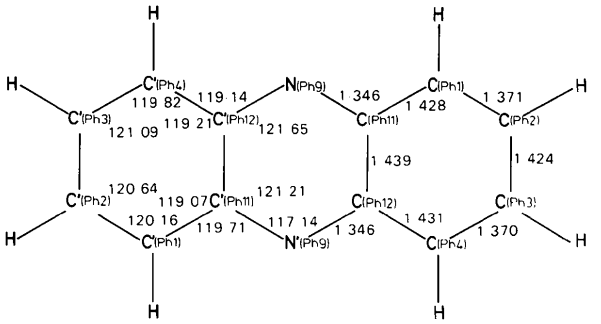

Fig. 1. Bond distances (Å) and bond angles (°) for Ph. E.s.d.'s in bond distances are <0·002 Å and in bond angles are <0·1°.

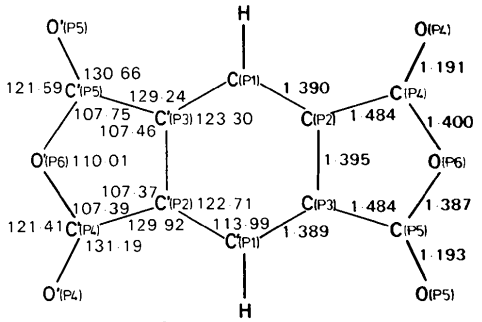

Fig. 2. Bond distances (Å) and bond angles (°) for PMDA. E.s.d.'s in bond distances are <0·002 Å and in bond angles <0·1°.

was refined in a similar manner to that described for Cb:PMDA, but with a slightly different weighting scheme: $w = \{\sigma^2(F_o) + 0{\cdot}01|F_o| + 0{\cdot}002|F_o|^2 + 0{\cdot}00002|F_o|^3\}^{-1}$. The conventional residuals* are presented in the *Abstract*. Fractional atomic coordinates are reproduced in Table 1. Bond distances and bond angles are displayed in Figs. 1 and 2.

Discussion. The crystal structure of the Ph:PMDA complex is, as expected, very similar to those of A:PMDA (Robertson & Stezowski, 1978) and Ac:PMDA (Binder *et al.*, 1982). The bonding geometry in PMDA agrees well with that in the other examples. Ph bond distances and bond angles are in close agreement with values between chemically identical atoms in A:PMDA and Ac:PMDA as well as in the 2:1 Ac complex with PMDA (Karl, Binder, Kollat & Stezowski, 1982).

The equations for least-squares mean planes (coordinate system described for Cb:PMDA, Stezowski *et al.*, 1982) are for Ph: $-0{\cdot}1716x + 0{\cdot}2919y + 0{\cdot}9409z = 3{\cdot}3313$ ($\sigma = 0{\cdot}001$ Å) and for PMDA: $-0{\cdot}2211x + 0{\cdot}2908y + 0{\cdot}9309z = 0{\cdot}0$ ($\sigma = 0{\cdot}017$ Å). The maximum deviations from the mean planes of the Ph and PMDA molecules (neglecting H atoms) are 0·004 and 0·029 Å, respectively. The interplanar–intrastack distance between donor and acceptor molecules is 3·33 Å. The angle between the plane normals is 2·9°, that between the normal to the Ph plane and the *c* axis is 20·0°. The crystal packing is shown in Fig. 3.

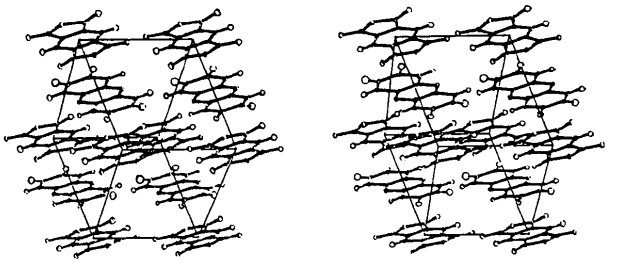

Fig. 3. A stereoscopic packing diagram of Ph:PMDA, which is representative of the crystal structures for Ac:PMDA and A:PMDA as well. The *a* axis runs horizontally.

The crystal structures of the 1:1 donor–acceptor complexes: Ph:PMDA, A:PMDA and Ac:PMDA are very nearly isomorphous. Consequently, it was conjectured that these three complexes should form mixed donor–acceptor crystals of the kind $(A_xAc_yPh_{1-x-y})_1$:$PMDA_1$ with a wide range of miscibility in the donors. The corresponding ternary phase diagram has been studied (Karl & Ketterer, 1981, unpublished results) by differential scanning calorimetry (DSC). From the solidus curves so obtained and from the continuity of lattice-parameter changes as a function of composition (Guinier photographs), complete miscibility in the whole range of stoichiometries has been inferred. The phase diagrams of the ternary and of the three binary systems are reproduced in Fig. 4.

In conclusion, the fact that the crystal structures of the three 1:1 donor–acceptor systems A:PMDA,

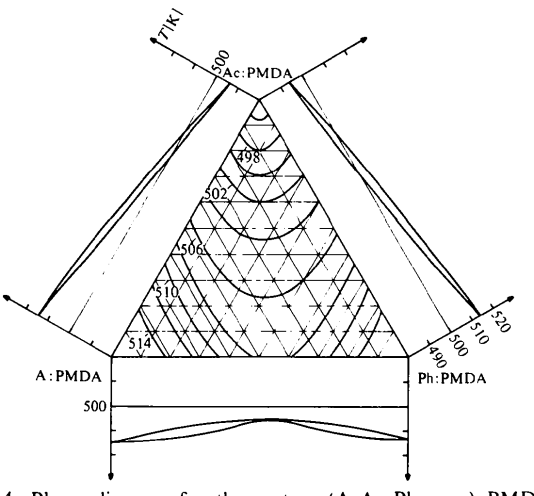

Fig. 4. Phase diagram for the system $(A_xAc_yPh_{1-x-y})$:PMDA. The ternary solidus surface has been omitted.

* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36928 (62 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Ac:PMDA and Ph:PMDA are isomorphous explains why the mixed-donor system exhibits complete miscibility in any ratio, Fig. 4. Two of the complexes, A:PMDA and Ac:PMDA, fluoresce strongly and in one, Ac:PMDA, the donor is dipolarly disordered. In the mixed crystals this orientational disorder combines with substitutional disorder. Since zone refining is possible for all components, high-purity crystals can be obtained (Karl & Ziegler, 1975; Ziegler & Karl, 1979; Karl, 1980). We believe that this is a unique system for studying details of charge transfer, and of excitonic and electric energy and charge transport in donor–acceptor crystals.

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2:1 Donor–Acceptor Complex between Acridine and Pyromellitic Dianhydride at ~120 K

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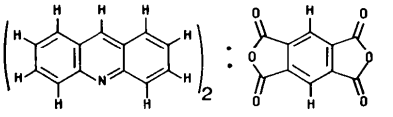
Abstract. $2C_{13}H_9N.C_{10}H_2O_6$, monoclinic, space group $P2_1/c$, $a = 9{\cdot}807$ (5), $b = 7{\cdot}581$ (2), $c = 17{\cdot}835$ (5) Å, $\beta = 100{\cdot}18$ (3)°, $V = 1305{\cdot}10$ Å^3 at $T \sim 120$ K; $Z = 2$, $\rho_{calc} = 1{\cdot}47$ g cm^{-3}. At 297 (1) K, $a = 9{\cdot}820$ (2), $b = 7{\cdot}721$ (1), $c = 17{\cdot}883$ (2) Å, $\beta = 100{\cdot}15$ (1)°, $V = 1336{\cdot}03$ Å^3. Of the 6078 unique reflections measured ($\sin\theta/\lambda$ <0·857 Å^{-1}, $\lambda = 0{\cdot}71069$ Å) 4946 contributed to the refinement of 239 parameters to give $R = 0{\cdot}062$, $R_w = 0{\cdot}089$ and $\sigma = 0{\cdot}94$. Crystallographic symmetry requires the pyromellitic dianhydride molecule to occupy an inversion centre; the acridine molecule is in a general position. The crystals consist of discrete *D*–*A*–*D* sandwiches.

Introduction. The existence of a 2:1 donor–acceptor complex, in addition to the 1:1 complex (Binder, Karl & Stezowski, 1982) between acridine, Ac, and pyromellitic dianhydride, PMDA, was inferred from phase-diagram data for the binary system Ac–PMDA. Crystals of the fluorescing 2:1 complex were grown from solution (methyl ethyl ketone) and by sublimation. The crystal-structure determination was undertaken to characterize the interaction between donor and acceptor molecules in different molecular environments.



Ac PMDA

Experimental. A yellow 0·6 × 0·4 × 0·2 mm parallelepiped crystal, sealed in a thin-walled glass capillary was cooled to ~120 K without encountering a phase change. Lattice parameters were refined with 56 automatically centred 2θ values in the range $31 \le 2\theta \le 52°$ for the crystal at 297 (1) and ~120 K. Intensities

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