

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

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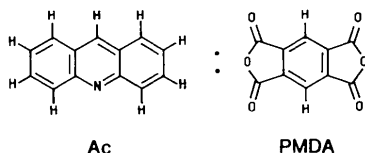
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(Received 1 September 1981; accepted 10 May 1982)

Abstract. $C_{13}H_9N \cdot C_{10}H_2O_6$, triclinic, space group $P\bar{1}$, $a = 7.092$ (2), $b = 10.886$ (1), $c = 7.111$ (1) Å, $\alpha = 117.31$ (1), $\beta = 110.69$ (1), $\gamma = 98.36$ (1)°, $V = 423.97$ Å³ at $T \sim 120$ K; $Z = 1$, $\rho_{\text{calc}} = 1.55$ g cm⁻³. At 297 (1) K, $a = 7.160$ (2), $b = 10.917$ (1), $c = 7.209$ (1) Å, $\alpha = 117.27$ (1), $\beta = 110.70$ (1), $\gamma = 98.34$ (1)°, $V = 435.43$ Å³. Of the 5181 unique reflections measured ($\sin \theta/\lambda \leq 0.9005$ Å⁻¹), 4558 contributed to the refinement of 156 variables to give $R = 0.050$, $R_w = 0.075$, and $\sigma = 1.49$. The donor and acceptor molecules are required by crystallographic symmetry to lie on inversion centres; consequently, the acridine molecule is disordered.

Introduction. Similar reasons to those given in the preceding contribution for carbazole:pyromellitic dianhydride, Cb:PMDA, (Stezowski, Binder & Karl, 1982) prompted us to study the structure of the 1:1 donor–acceptor complex between acridine, Ac, and PMDA.



Experimental. A yellow 0.5 × 1.0 × 0.8 mm parallelepiped crystal, grown from zone-refined components by high-vacuum plate-sublimation techniques, was sealed in a thin-walled glass capillary and used for all diffraction measurements. Lattice parameters for the crystal at room temperature and at ~120 K were refined with 45 automatically centred 2θ values in the range $31.5 < 2\theta < 45.4^\circ$ ($\lambda = 0.71069$ Å). Intensities were measured in the manner described for Cb:PMDA (Stezowski *et al.*, 1982). Three periodically monitored reference reflections displayed no significant variations in their intensities. Corrections were made for Lorentz and polarization effects. Absorption corrections, $\mu =$

1.24 cm⁻¹, were estimated to give rise to a maximum error of less than 6% in F_o and were neglected.

The crystal structure was derived from that of the analogous anthracene complex, A:PMDA (Robertson & Stezowski, 1978), by isomorphous replacement. Initial refinement was carried out in space group $P1$. H atoms, except that bonded to the unique C atom of the central Ac ring, were located in difference Fourier maps. The model was refined to an R value of 5.2%, at which point a difference electron density map (calculated without H-atom contributions), Fig. 1, was examined. Subsequent refinement, carried out as described for Cb:PMDA, was effected in space group $P\bar{1}$. The N scattering factor was used for the symmetry-equivalent central-ring atoms of Ac and the associated H atom was neglected. Conventional residuals* are presented in the *Abstract*; fractional atomic coordinates are contained in Table 1; bond distances and bond angles are depicted in Figs. 2 and 3.

* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36927 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

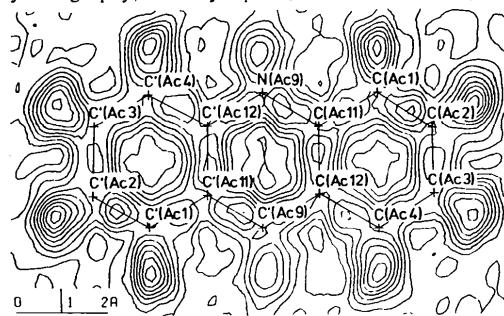


Fig. 1. A ΔF -Fourier (difference electron density) plot through the plane of the disordered acridine molecule calculated with space-group symmetry $P1$. H-atom contributions were not included in the calculated structure factors. Electron density is contoured at 0.1 e Å⁻³ intervals beginning with 0.1 e Å⁻³.

Table 1. Fractional atomic coordinates and isotropic temperature factors

	x	y	z	U_{eq} or $U(\text{Å}^2)$
C(P1)	-0.1890 (2)	0.0417 (1)	-0.0272 (2)	0.01892
C(P2)	0.0128 (2)	0.1390 (1)	0.0537 (2)	0.01664
C(P3)	0.1943 (2)	0.0991 (1)	0.0804 (2)	0.01626
C(P4)	0.0803 (2)	0.2960 (1)	0.1240 (2)	0.02118
O(P4)	-0.0198 (2)	0.3746 (1)	0.1233 (2)	0.03259
O(P6)	0.3029 (2)	0.34511 (9)	0.1953 (2)	0.02226
C(P5)	0.3791 (2)	0.2307 (1)	0.1715 (2)	0.01915
O(P5)	0.5645 (2)	0.2475 (1)	0.2200 (2)	0.02519
N(Ac9)	0.1758 (2)	-0.0496 (1)	0.4741 (2)	0.02132
C(Ac11)	-0.0269 (2)	-0.1433 (1)	-0.5546 (2)	0.01808
C(Ac12)	-0.2053 (2)	-0.0925 (1)	-0.5806 (2)	0.01634
C(Ac4)	-0.4129 (2)	-0.1920 (1)	-0.6623 (2)	0.01976
C(Ac3)	-0.4420 (2)	-0.3334 (1)	-0.7149 (2)	0.02113
C(Ac2)	-0.2656 (2)	-0.3837 (1)	-0.6894 (2)	0.02452
C(Ac1)	-0.0643 (2)	-0.2924 (1)	-0.6123 (2)	0.02389
H(P1)	-0.315 (3)	0.066 (2)	-0.042 (3)	0.034 (5)
H(Ac4)	-0.530 (3)	-0.161 (2)	-0.680 (3)	0.031 (5)
H(Ac3)	-0.597 (3)	-0.400 (2)	-0.779 (4)	0.040 (5)
H(Ac2)	-0.300 (4)	-0.486 (3)	-0.739 (4)	0.052 (6)
H(Ac1)	0.054 (3)	-0.321 (2)	-0.585 (4)	0.041 (6)

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

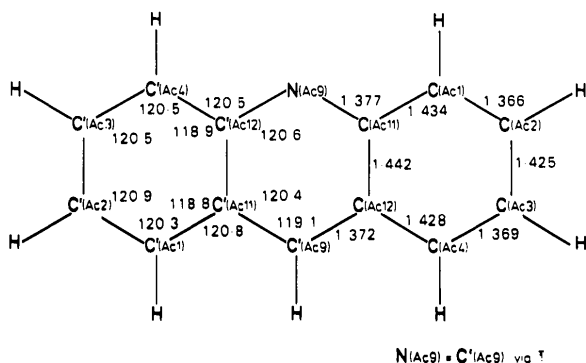


Fig. 2. Bond distances (Å) and bond angles ($^\circ$) for acridine. E.s.d.'s in bond distances are < 0.003 Å and in bond angles $< 0.2^\circ$.

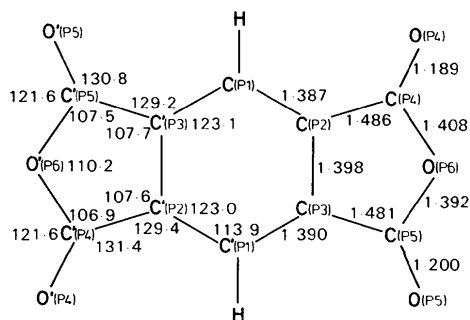


Fig. 3. Bond distances (Å) and bond angles ($^\circ$) for PMDA. E.s.d.'s in bond distances are < 0.003 Å and in bond angles $< 0.2^\circ$.

Discussion. The difference electron density map presented in Fig. 1 was taken as convincing evidence that the correct space group is $P\bar{1}$. The electron density corresponding to the disordered H atom is consistent with equal occupancy of the two sites.

The refined model presents a PMDA molecule with bonding geometry that is in excellent agreement with that in the isomorphous A:PMDA complex. The bonding geometry of the disordered Ac molecule is particularly interesting. The bond distances and bond angles in the unique terminal ring are nearly identical (to within 0.005 Å) with those found for the 2:1 Ac:PMDA complex (Karl, Binder, Kollat & Stezowski, 1982) in which no evidence of disorder has been found. The unique bond distances and angles for the central ring are very nearly equal to the average of the C—C(Ac10) and C—N(Ac9) bond distances in the 2:1 complex. The relevant cross-ring nonbonded C...C distance in the 1:1 complex is 2.370 (2) Å, which can be compared with C(Ac11)...C(Ac14) = 2.325 (2) and C(Ac12)...C(Ac13) = 2.423 (2) Å in the 2:1 complex; the value for the disordered Ac molecule is the average.

The free energy of crystal packing is the sum of enthalpy and entropy contributions. Both Cb and Ac possess static dipole moments oriented parallel to their short intraplanar molecular symmetry axis. An ordered structure with these dipoles aligned antiparallel (preferably intra- and interstack) would provide a favourable enthalpy component but an unfavourable entropy one. From the crystal-structure determinations for Cb:PMDA and Ac:PMDA, it appears that entropy dominates the crystal packing of these complexes. The interesting problem of short- and mid-range dipolar order (*i.e.* statistical correlations) among the disordered donor molecules remains unsolved.

In the Ac:PMDA 1:1 complex, the Ac molecules are planar to within a standard deviation of 0.004 Å. The maximum deviation from the mean plane fit to the PMDA atomic coordinates (neglecting H atoms) is 0.024 Å. The equations of the mean planes in the coordinate system described for Cb:PMDA (Stezowski *et al.*, 1982) are for PMDA: $-0.2238x + 0.3095y + 0.9242z = 0.0$ ($\sigma = 0.014$ Å) and for Ac: $-0.2248x + 0.3256y + 0.9180z = 3.344$. The angle between the respective plane normals is 0.98° ; the angle between the plane normal for Ac and the *c* axis is 20.0° . The interplanar distance is 3.36 Å.

A detailed description of the crystal packing has been presented for the isomorphous A:PMDA complex (Robertson & Stezowski, 1978).

Financial assistance from the Stiftung Volkswagenwerk (contract No. I/35974) is gratefully acknowledged.

References

- KARL, N., BINDER, W., KOLLAT, P. & STEZOWSKI, J. J. (1982). *Acta Cryst.* **B38**, 2919–2921.
 ROBERTSON, B. E. & STEZOWSKI, J. J. (1978). *Acta Cryst.* **B34**, 3005–3011.
 STEZOWSKI, J. J., BINDER, W. & KARL, N. (1982). *Acta Cryst.* **B38**, 2912–2914.