

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

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Abstract. C₁₂H₉N·C₁₀H₂O₆, monoclinic, space group *P*2₁/*c*, *a* = 6.9778 (7), *b* = 9.301 (1), *c* = 13.366 (1) Å, β = 104.679 (8)°, *V* = 839.15 Å³ at *T* ~ 120 K; *Z* = 2, ρ_{cal} = 1.524 g cm⁻³. At *T* = 297 (1) K, *a* = 7.1232 (7), *b* = 9.328 (1), *c* = 13.389 (1) Å, β = 104.08 (1)°, *V* = 862.89 Å³. Of the 3680 unique reflections measured (sin θ/λ ≤ 0.816 Å⁻¹), 3037 contributed to the refinement of 230 variables to give *R* = 0.045, *R*_w = 0.055 and σ, the e.s.d. of an observation of unit weight, = 0.93. The donor and acceptor molecules are required by crystallographic symmetry to lie on inversion centres; consequently, the non-centrosymmetric carbazole molecules are dipolarly disordered.

Introduction. This and the following reports (Binder, Karl & Stezowski, 1982; Karl, Ketterer & Stezowski, 1982; Karl, Binder, Kollat & Stezowski, 1982) describe structure determinations for a series of donor–acceptor complexes between pyromellitic dianhydride, PMDA, and selected heterocyclic donors with very similar molecular shapes and sizes (carbazole, acridine and phenazine). Carbazole, Cb, was chosen for study for several reasons. Cb, as well as PMDA, can be purified by zone refining (*cf.* Karl, 1980). Crystals of the donor–acceptor complex could be grown by high-vacuum sublimation ('plate sublimation' *cf.* Karl, 1980) thus maintaining the high chemical purity obtained by zone refining. The complex was found to emit charge-transfer fluorescence which makes it of

interest for spectroscopic investigations of donor–acceptor interactions. The chemical structure of Cb provides an inherent dipole moment. Further, the molecular symmetry of the donor is lower than that of the acceptor. The latter two properties presented the potential for formation of a crystalline donor–acceptor complex with a polar crystal axis.

Experimental. A red 0.5 × 0.5 × 0.6 mm parallelepiped crystal, grown by vacuum sublimation, was sealed in a thin-walled glass capillary. Diffraction data were measured with monochromatized Mo *K*α radiation (λ = 0.71069 Å) using a Syntex P1 auto-diffractometer equipped with a Syntex LT-1 low-temperature device that maintained the crystal at ~120 K. Lattice parameters were refined (Stewart, Machin, Dickinson, Ammon, Flack & Heck, 1976) with automatically centred 2θ values for 56 reflections (35.1 ≤ 2θ ≤ 50.6°) for the crystal at ~120 and 297 (1) K. Intensities were measured for all unique reflections with an ω-scan technique [scan range = 0.75°, scan rate = 2.0 to 24.0° min⁻¹; background measured at each side (Δω = 1.0°) of the reflection for one half the scan time]. Data were corrected for Lorentz and polarization effects and for a systematic 20% decrease in the intensity of the three reference reflections, but not for absorption, μ = 1.22 cm⁻¹.

The initial model was determined by direct methods and developed by difference Fourier techniques. Even though the systematic extinctions (*h*0*l*, *l* = 2*n* + 1; 0*k*0, *k* = 2*n* + 1) correspond uniquely to space group *P*2₁/*c*, calculations were made using the non-centrosymmetric space group *Pc* to test the possibility of an ordered structure or one with a population different from 50:50 for the disordered sites. When one Cb molecule was placed in the cell, difference Fourier maps revealed the second orientation. A subsequent series of least-squares refinements of isotropic temperature factors with fixed population parameters from 80:20 to 20:80 for the

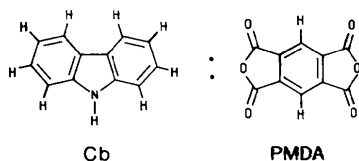


Table 1. Fractional atomic coordinates and isotropic temperature factors

	x	y	z	U_{eq} or $U(\text{\AA}^2)$	PP
C(P1)	0.9237 (1)	0.4821 (1)	0.38906 (7)	0.02156	1.0
C(P2)	0.9963 (1)	0.6118 (1)	0.43443 (7)	0.02012	1.0
C(P3)	1.0694 (1)	0.6291 (1)	0.54066 (7)	0.02034	1.0
C(P4)	1.0124 (1)	0.7530 (1)	0.38532 (8)	0.02530	1.0
O(P4)	0.9675 (1)	0.78875 (9)	0.29690 (6)	0.03410	1.0
O(P6)	1.0959 (1)	0.84976 (8)	0.46361 (6)	0.02876	1.0
C(P5)	1.1325 (1)	0.7813 (1)	0.55954 (8)	0.02634	1.0
O(P5)	1.2031 (1)	0.84413 (9)	0.63764 (6)	0.03710	1.0
N(Cb9)	0.3903 (3)	0.0173 (2)	-0.1418 (1)	0.02355	0.5
C(Cb13)	0.4047 (3)	0.1189 (2)	0.0639 (2)	0.02150	0.5
C(Cb12)	0.4965 (3)	0.0545 (2)	0.0318 (1)	0.01990	0.5
C(Cb10)	0.5372 (2)	-0.0925 (2)	0.0101 (1)	0.01785	0.5
C(Cb11)	0.4695 (3)	-0.1098 (2)	-0.0976 (1)	0.01857	0.5
C(Cb4)	0.4892 (3)	-0.2422 (2)	-0.1447 (2)	0.02997	0.5
C(Cb3)	0.5785 (3)	-0.3537 (2)	-0.0821 (2)	0.03561	0.5
C(Cb2)	0.6467 (3)	-0.3376 (3)	0.0260 (2)	0.03298	0.5
C(Cb1)	0.6254 (3)	-0.2079 (2)	0.0719 (2)	0.02518	0.5
C(Cb8)	0.5307 (3)	0.1365 (2)	0.1224 (2)	0.02771	0.5
C(Cb7)	0.4704 (3)	0.2767 (3)	0.1172 (2)	0.03862	0.5
C(Cb6)	0.3790 (3)	0.3388 (2)	0.0223 (2)	0.03792	0.5
C(Cb5)	0.3434 (3)	0.2620 (2)	0.0702 (2)	0.03098	0.5
H(P1)	0.875 (2)	0.468 (1)	0.3147 (9)	0.026 (3)	1.0
H(Cb9)	0.320 (4)	0.029 (3)	0.207 (2)	0.043 (8)	0.5
H(Cb4)	0.439 (3)	0.251 (3)	0.224 (2)	0.033 (7)	0.5
H(Cb3)	0.583 (4)	0.445 (3)	0.113 (2)	0.043 (7)	0.5
H(Cb2)	0.703 (4)	0.429 (3)	0.073 (2)	0.047 (8)	0.5
H(Cb1)	0.677 (3)	-0.198 (3)	0.142 (2)	0.028 (6)	0.5
H(Cb8)	0.585 (4)	0.105 (3)	0.186 (2)	0.047 (8)	0.5
H(Cb7)	0.492 (4)	0.334 (3)	0.182 (2)	0.052 (8)	0.5
H(Cb6)	0.328 (4)	0.440 (3)	0.016 (2)	0.040 (7)	0.5
H(Cb5)	0.275 (5)	0.307 (4)	0.142 (2)	0.07 (1)	0.5

PP is the population parameter.

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

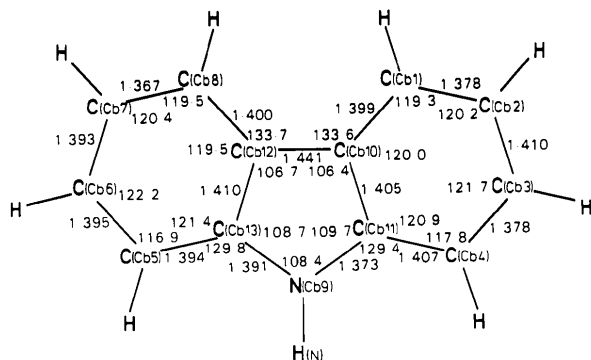


Fig. 1. Bond distances (Å) and bond angles (°) for carbazole. E.s.d.'s in bond distances are <0.004 Å and in bond angles $<0.2^\circ$.

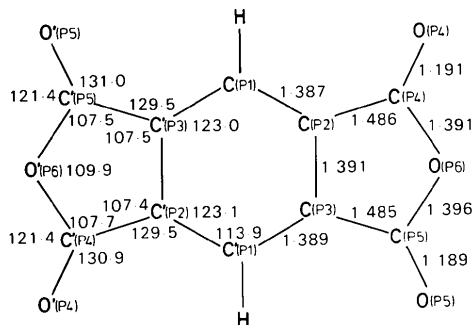


Fig. 2. Bond distances (Å) and bond angles (°) for PMDA. E.s.d.'s in bond distances are ≤ 0.003 Å and in bond angles $<0.2^\circ$.

two Cb sites gave results consistent with a 50:50 distribution. Further refinement was carried out in space group $P2_1/c$. Initial H-atom coordinates were calculated from known geometry.

All fractional atomic coordinates (Table 1) were refined as were anisotropic temperature factors for C, N, and O atoms, isotropic temperature factors for H atoms and a single scale factor.* The weighting scheme employed was: $w = \{\sigma^2(F_o) + 0.0125|F_o| + 0.0001|F_o|^2 + 0.000001|F_o|^4\}^{-1}$. The conventional R values are contained in the *Abstract*, bond angles are displayed in Figs. 1 and 2 for Cb and PMDA.

Discussion. Rather unexpectedly, crystalline Cb:PMDA does not present a well ordered structure with a polar crystal axis but instead one in which the donor (Cb) molecules occupy two sites related by a crystallographic inversion centre. Fortunately, the molecular structure of Cb differs so markedly from being centrosymmetric that little problem was encountered in resolving the disorder. In fact, the high resolution, low-temperature data set allowed refinement of individual atoms, including H atoms.

The bonding geometry obtained for the Cb molecule is consistent with expectation (Kurahashi, Fukuyo & Shimada, 1969), and that of the PMDA molecule is in good agreement with that found in the low-temperature crystal-structure determination for anthracene:PMDA (Robertson & Stezowski, 1978). Thus, though the crystal structure of Cb:PMDA is disordered, we conclude that the distribution of PMDA molecules is well ordered and that there are two well defined energetically equivalent sites for the Cb molecules. These conclusions are supported by the appearance of an electron density map calculated in the plane of the Cb molecule, Fig. 3, which clearly

* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36926 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

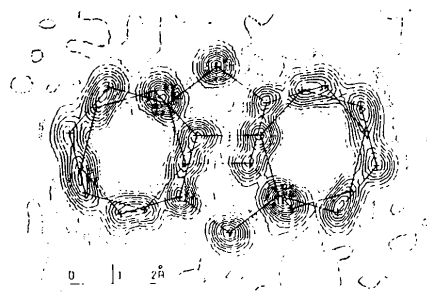


Fig. 3. An F_o -Fourier (electron density) plot through the plane of the disordered carbazole molecule, contoured at $1 \text{ e } \text{\AA}^{-3}$ intervals.

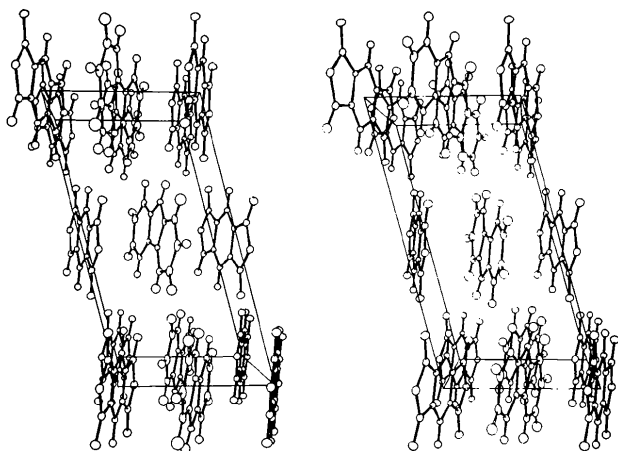


Fig. 4. A stereoscopic projection (Johnson, 1971) on the ac plane displaying crystal packing. Carbazole molecules in the left image were generated with symmetry operations $\bar{x}, \bar{y}, \bar{z}$ and $x, \frac{1}{2} - y, \frac{1}{2} + z$. Those in the right image were generated with operations x, y, z and $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$.

indicates the (\pm) dipolar disorder defined by the vector from atom N(Cb9) to the midpoint between atoms C(Cb10) and C(Cb12). The map provides an indication of the resolution of the respective atomic sites for the two Cb orientations. The closest approach between atoms of the two sites is 0.41 Å for atoms C(Cb2) and C'(Cb5); the prime indicates an atom generated by the inversion operator. The fact that atoms C(Cb2) and C(Cb5) could be refined independently is traceable to the high resolution of the data set. The nearly circular electron density contours for well resolved atoms [e.g. N(Cb9), C(Cb10), C(Cb11) and C(Cb13)] indicate that the lattice site for the donor molecule is well defined. No evidence for a phase transition between room temperature and 120 K was found.

Crystal packing, Fig. 4, consists of infinite stacks of alternating planar $-D-A-D-A$ molecules. The intra-stack-interplanar distance between donor and acceptor mean planes is 3.30 (1) Å; the interplanar angle is 2.9 (1)°. The angle between the stack axis (a axis) and the plane normal for PMDA is 17.5°. The equation for least-squares mean planes [orthogonal axis system \mathbf{a}, \mathbf{b}^* , ($\mathbf{a} \times \mathbf{b}^*$)] are for PMDA: $0.9665x - 0.2445y - 0.0784z = 0.0$ ($\sigma = 0.004$ Å) and for Cb: $0.9536x -$

$0.27967y - 0.11124z = 3.299$ ($\sigma = 0.009$ Å). A characteristic feature of this crystal structure is the packing of alternating sheets containing solely donor or acceptor molecules. Donor and acceptor molecules lie on inversion centres in bc planes separated by translations of $\mathbf{a}/2$. The space-group symmetry operators give rise to adjacent sheets of complexes in which respective plane normals are related by mirror symmetry (\perp to \mathbf{b}); the interplanar angle between PMDA molecules in adjacent sheets is 28.3° (for Cb 32.5°). The centroid of a disordered Cb molecule (neglecting H atoms) is displaced from the nearest inversion centre by fractional coordinates $\pm(0.0106, 0.0107, 0.0152)$.

In contrast to the crystal structure of the 1:1 complex between Cb and trinitrobenzene (Bechtel, Chasseau & Gaultier, 1976), in which the Cb molecules are ordered, there is no hydrogen bonding in Cb:PMDA. The H atom bonded to N(Cb9) displays equal contact distances, 2.67 (3) Å, to carbonyl O atoms O(P4) and O(P5), depending on which of the disordered carbazole molecules is present.

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