

Fig. 3. Molecular overlapping diagram.

phenanthrene (Evans & Robinson, 1977), phenazine (Bulgarovskaya, Vozzhennikov, Krasavin & Kotov, 1982). The dimensions of the Crs molecule compare well with those of the free Crs (Burns & Iball, 1960) and of Crs in the complexes with 7,7,8-tetracyanoquinodimethane (Munnoch & Wright, 1974) and fluoranil (Munnoch & Wright, 1975). The PMDA molecule is planar, the maximum deviation from the least-squares best plane through the molecule being 0.008 Å. The Crs molecule is approximately planar. The individual rings are each planar; the maximum deviation from the best planes is 0.019 Å.

In the crystal the component molecules are arranged in mixed stacks extending along the *c* axis. The molecular planes are parallel to each other (the dihedral angle between the planes of the PMDA and Crs molecules is 2.0°) and make angles of 31.2 and 30.4° respectively with the *c* axis. The mean separation

between the PMDA and Crs planes is 3.32 Å. The overlap diagram is shown in Fig. 3. A particular PMDA molecule is located above one portion of the neighbouring Crs molecule; the next PMDA molecule in the stack takes up an analogous position and orientation with respect to the other centrosymmetric portion of the Crs molecule sandwiched between them, and so on along the stack.

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Structure of the 1:1 π -Molecular Complex of 9,10-Dibromoanthracene with 1,2:4,5-Pyromellitic Dianhydride*

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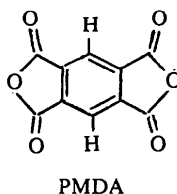
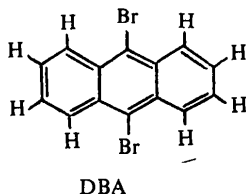
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Abstract. $C_{14}H_8Br_2 \cdot C_{10}H_2O_6$, $M_r = 554.15$, monoclinic, $A2/m$, $a = 7.134$ (2), $b = 9.740$ (3), $c = 14.310$ (4) Å, $\gamma = 90.53$ (2)°, $V = 994.3$ (3) Å³, $Z = 2$, $D_x = 1.85$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 40.85$ cm⁻¹, $F(000) = 544$, $T = 295$ K, $R = 0.026$ for 755 observed reflections [$I > 3\sigma(I)$]. The crystal structure consists of stacks of alternating 9,10-dibromoanthracene and pyromellitic dianhydride molecules 3.36 Å apart. Both molecules are situated in special positions of the $2/m$ symmetry.

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

Introduction. In recent years a number of crystal structures of donor–acceptor (*D:A*) complexes based on pyromellitic dianhydride (PMDA) as an acceptor have been reported. The 1:1 complex between PMDA and anthracene was a first choice among a number of possible combinations with donor molecules. This complex possesses interesting physical properties extensively studied and characterized. Substituted anthracene-like materials such as 9,10-dibromoanthracene (DBA) are known to possess photoconductive and luminescence characteristics different from those of the parent hydrocarbon, anthracene (Smith & Bock, 1962). As physical properties of the complex

strongly depend on the molecular properties of constituent molecules it seemed to us important to study the way DBA forms *D:A* complexes. Single crystals of a 1:1 complex of this compound (DBA) with PMDA were therefore grown and the crystal structure analysis of this complex was undertaken in order to obtain information about the influence of chemical substitution around the aromatic ring in the donor molecule on the packing arrangement of the components.



Experimental. Red crystals $0.05 \times 0.10 \times 0.08$ mm grown by high-vacuum plate sublimation technique. D_m not determined. Syntex $P\bar{1}$ diffractometer. Unit-cell parameters determined by least-squares refinement of 14 reflections. Data set ($\pm h$, $+k$, $+l$) up to $2\theta = 52^\circ$, $\theta/2\theta$ scan mode, graphite-monochromated $Mo K\alpha$ radiation. 848 independent reflections of which 755 significant with $I > 3\sigma(I)$ (index range $h - 8 \rightarrow 8$, $k 0 \rightarrow 12$, $l 0 \rightarrow 17$). Three reference reflections (122, 102, 011), measured every 100 steps, remained constant to within 2% of their initial intensities. Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods. Full-matrix refinement (on F) of a scale factor, positional and anisotropic thermal parameters (isotropic thermal parameters for H atoms, calculated using geometric considerations) converged to $R = 0.026$, $wR = 0.028$, $w = 1/[\sigma^2(F) + 0.0005F^2]$. International scattering factors for Br, O, C from *International Tables for X-ray Crystallography* (1974), for H from Stewart, Davidson & Simpson (1965).

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 ($\text{\AA}^2 \times 10^3$)

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

| | <i>x</i> | <i>y</i> | <i>z</i> | U_{eq} or U_{iso} |
|------|----------|----------|----------|-----------------------|
| Br | 0 | 0 | 2289 (1) | 55 (1) |
| C(1) | 0 | 0 | 961 (3) | 31 (1) |
| C(2) | 608 (4) | 1190 (3) | 506 (2) | 29 (1) |
| C(3) | 1240 (5) | 2400 (3) | 974 (3) | 37 (1) |
| C(4) | 1801 (5) | 3530 (3) | 497 (3) | 43 (1) |
| O(1) | 6609 (6) | 3260 (4) | 0 | 78 (2) |
| O(2) | 6475 (5) | 2939 (4) | 1549 (3) | 96 (2) |
| C(5) | 5000 | 0 | 1000 (5) | 56 (2) |
| C(6) | 5563 (5) | 1118 (4) | 484 (3) | 50 (1) |
| C(7) | 6234 (6) | 2491 (4) | 792 (4) | 68 (2) |
| H(3) | 129 (7) | 238 (5) | 176 (4) | 78 (18)* |
| H(4) | 230 (6) | 438 (4) | 80 (3) | 47 (13)* |
| H(5) | 500 | 0 | 162 (6) | 107 (32)* |

* U_{iso} .

$(\Delta/\sigma)_{max} = 0.16$. $(\Delta\rho)_{max} = 0.21 e \text{\AA}^{-3}$. Calculations carried out with *SHELXTL* (Sheldrick, 1978) on the Nova 3 computer incorporated in the Nicolet R3 system.

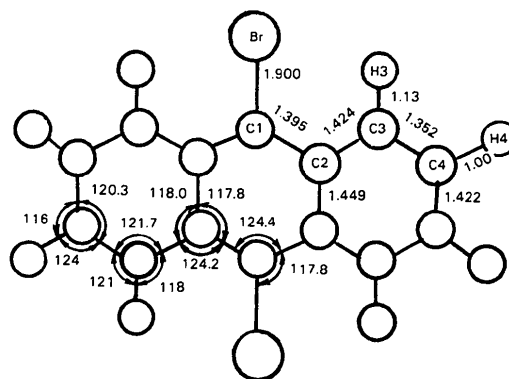


Fig. 1. Bond distances (\AA) and bond angles ($^\circ$) for DBA. E.s.d.'s in bond distances are 0.004 – 0.005 \AA and in bond angles 0.2 – 0.3° (0.03 – 0.05 \AA for C–H bonds and 3 – 6° for C–C–H angles).

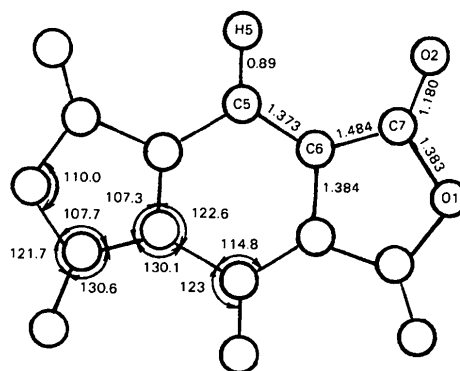


Fig. 2. Bond distances (\AA) and bond angles ($^\circ$) for PMDA. E.s.d.'s in bond distances are 0.005 – 0.007 \AA and in bond angles 0.3 – 0.5° (0.03 – 0.05 \AA for C–H bonds and 3 – 6° for C–C–H angles).

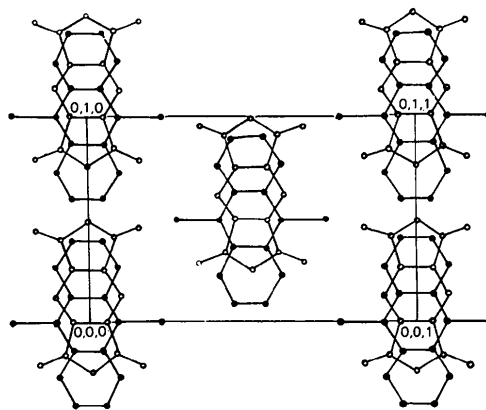


Fig. 3. Projection of the structure on the plane of the DBA molecule at the origin.

Discussion. The atomic coordinates are listed in Table 1,* bond distances and bond angles are given in Figs. 1 and 2 for DBA and PMDA. The bonding geometry obtained for the PMDA molecule is in good agreement with that found in the low-temperature crystal structure determination for anthracene-PMDA (Robertson & Stezowski, 1978). The bond lengths in the DBA molecule are different from those given by Trotter (1958) for uncomplexed DBA, but because of the low accuracy of the latter work this comparison is not useful. The C—C bond distances in the DBA molecule are close to those found in unsubstituted uncomplexed anthracene (Lehmann & Pawley, 1972). Both molecules are planar, the maximum deviations from the mean planes of DBA and PMDA molecules (neglecting H atoms) being 0.007 and 0.009 Å respectively.

The crystal is built up of stacks along *a* of alternating donor DBA and acceptor PMDA molecules charac-

teristic of π - π D:A complexes. The intrastack interplanar distance between donor and acceptor mean planes is 3.36 Å; the interplanar angle is 0.5°, those between the normals to the DBA and PMDA planes and the *a* axis are 20.1 and 19.6° respectively. The relative orientation of the molecules (Fig. 3) is very similar to that found in PMDA-anthracene (Robertson & Stezowski, 1978).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43515 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of *tert*-Butoxycarbonyl-L-alanyl-L-asparaginy-L-proline Benzyl Ester

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Abstract. C₂₄H₃₄N₄O₇, *M_r* = 490.56, orthorhombic, *P*2₁2₁2₁, *a* = 15.874 (5), *b* = 18.080 (8), *c* = 9.015 (2) Å, *V* = 2588 (2) Å³, *Z* = 4, *D_m* = 1.253 (2), *D_x* = 1.259 g cm⁻³, λ(Cu Kα) = 1.5418 Å, μ = 7.35 cm⁻¹, *F*(000) = 1048, *T* = 297 K, *R* = 0.058 for 2516 independent reflections. The molecule adopts a folded conformation with Ala-Asn at the corner, although no intramolecular hydrogen bond is present. The proline ring has a type *B* conformation ($\chi_1 = 19.4^\circ$). Cylindrical columns are formed along a diad screw axis by hydrogen bonds between the carbamoyl group of Asn and the backbone peptide groups.

Introduction. The tandemly repeating structure of Asn-Ala-Asn-Pro is found in the circum sporozoite (CS) protein of the human malaria parasite *Plasmodium falciparum* (Enea, Ellis, Zavala, Arnot, Asavanich, Masuda, Quakyi & Nussenzweig, 1984; Dame, Williams, McCutchan, Weber, Wirtz, Hockmeyer, Maloy, Haynes, Schneider, Roberts, Sanders, Reddy, Diggs & Miller, 1984) and is essential for the biological function of the CS protein (Ballou, Rothbard, Wirtz, Gordon, Williams, Gore, Schneider, Hollingdale, Beaudoin, Maloy, Miller & Hockmeyer, 1985). Three-dimensional studies of this repeating structure can provide useful information on conformational characteristics and on the possible application of artificial vaccines against *Plasmodium malariae*.

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