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# A Comparison of the High Resolution Crystal Structures of the $\pi$-Molecular Complexes of Anthracene and Phenothiazine with Pyromellitic Dianhydride†

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## INTRODUCTION

The $\pi$-molecular complexes formed by aromatic molecules with three rings tend to form crystals of high purity and are therefore ideal for solid state spectroscopic and photocurrent studies. We have therefore undertaken an investigation of the detailed structures of a number of such complexes in order to facilitate the interpretation of such data and other physical properties and in order to better understand the large changes in physical properties generated by small changes in composition and molecular packing. The

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† The details of the crystal structure of anthracene with pyromellitic dianhydride have appeared elsewhere (Robertson and Stezowski [1978]). The details of the crystal structure, and spectroscopic and electrical properties of phenothiazine with pyromellitic dianhydride will appear elsewhere (Anthonj, Karl, Robertson and Stezowski, 1979).

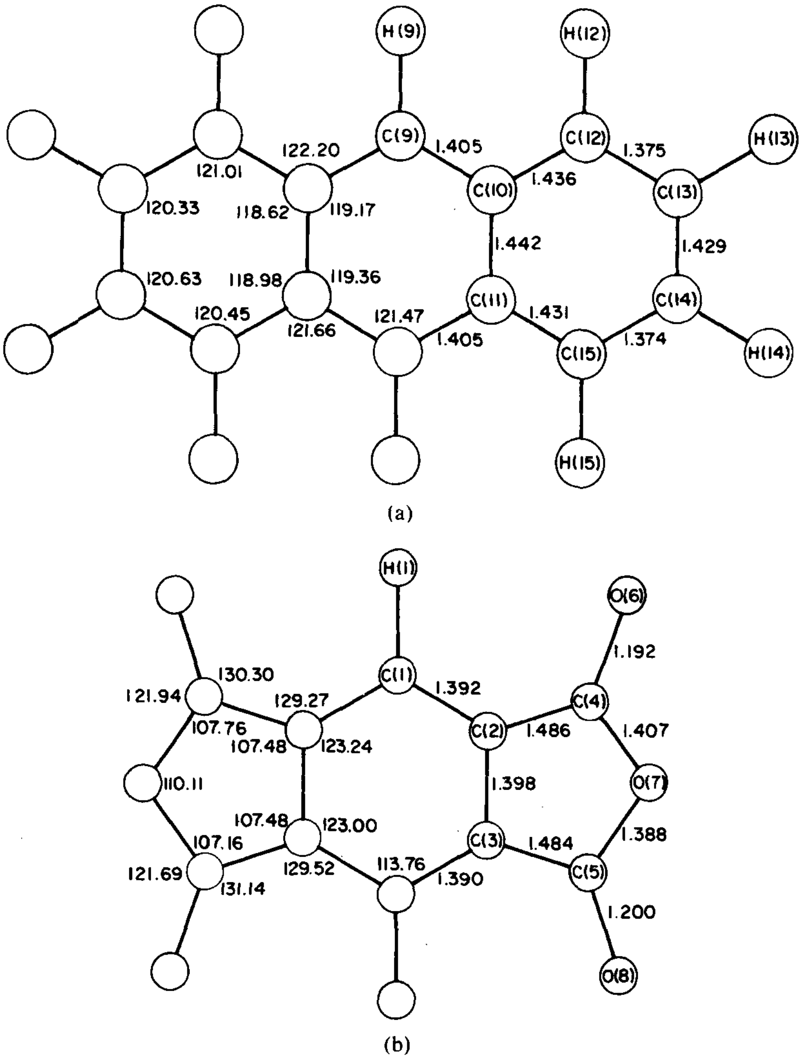


FIGURE 1 Bond lengths (Å), angles (°) and atom numbering sequence for the two molecular species in A-PMDA, *(a) anthracene and (b) pyromellitic dianhydride. The average error in bond* lengths not involving a hydrogen atom is 0.0013 A. The average error in a bond angle not involving a hydrogen atom is 0.09°.

piezoreflection spectra of the anthracene-pyromellitic dianhydride complex (A–PMDA) has been studied by Eckhardt and Merski (1973). The photocurrent excitation spectra of A–PMDA was reported by Karl and Ziegler (1975) and more recently the preparation, optical properties, absorption and photoconductivity properties of phenothiazine-pyromellitic dianhydride have also been studied. (Anthonj, Karl, Robertson and Stezowski, 1979).

## ANTHRACENE PYROMELLITIC DIANHYDRIDE

The structure of (A–PMDA) was determined from X-ray data collected at −120°C using a Syntex P$\bar{1}$ autodiffractometer. The crystals are bright red transparent needles with well formed faces. The structure was solved by direct methods using the X-ray 76 system of crystallographic programs (Stewart *et al*., 1976). The unit cell parameters are $a = 7.2812(6)$, $b = 10.7684(7)$, $c = 7.1246(7)$Å, $\alpha = 117.516(7)$, $\beta = 111.513(8)$, $\gamma = 97.437(8)°$. The space group is P$\bar{1}$ with one formula unit per unit cell. The structure has been previously determined at room temperature by Boeyens and Herbstein (1969). The results reported here are substantially in agreement with those of the latter authors but are of much greater accuracy. The bond lengths and bond angles for the individual molecules are given in Figure 1.

The geometry of A has been corrected for the effects of thermal motion, assuming rigid body motion, while that of PMDA has not because its thermal motion was found to be not unequivocally rigid. These bond lengths were obtained from a refinement using diffraction data collected between the limits of 0.478 and 0.910 Å$^{-1}$ in sin $\theta/\lambda$.

The PMDA molecules are situated at the centers of symmetry at cell origins. The A molecules are at the centers of symmetry at the points ($00\frac{1}{2}$) of each cell, thus forming mixed stacks of donor and acceptor molecules running in the $c$ direction. The overlap of adjacent molecules is of the "ring double bond" type (Herbstein, 1971). The resultant packing of the molecules is shown in Figure 2.

Crystals of A–PMDA cleave on the (1$\bar{1}$0) and (010) planes which, from examination of Figure 2, corresponds to the separation of adjacent stacks

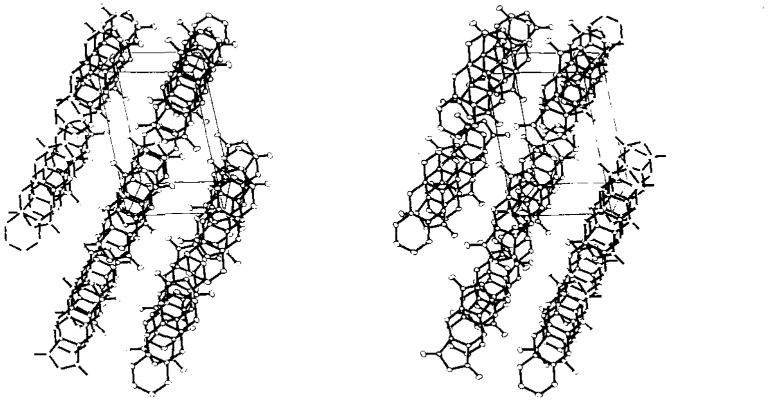


FIGURE 2 Molecular packing in A–PMDA. The origin is in the back left lower corner. The *a* axis points to the right and the *b* axis points up. The $c^*$ axis is therefore out the plane of the page approximately normal to it. The hydrogen atoms have been omitted for clarity.

either on their long or short edges respectively. Crystals grown by sublimation are also prone to twinning on the $(1\bar{1}0)$ planes.

Assuming the basic Mulliken theory of 1 : 1 $\pi$-molecular complexes (Mulliken, 1956) we expect that slightly less than one unit of electronic charge is transferred from the donor to the acceptor species in the ground state of radical-ion salts and in the ground state of formally neutral complexes, some fraction, usually small, of one unit of electronic charge is transferred. Tanaka and Tanaka (1978) have recently estimated that 0.105 units of electronic charge are transferred in anthracene-7,7,8,8-tetracyanoquinodimethane (TCNQ). The effect on the bond lengths of TCNQ resulting from the transfer of one electron have been tabulated by Ashwell *et al.*, (1977) and average to 0.023 Å. The electron affinity of PMDA is half that of TCNQ. Therefore, we would expect transfer of less charge in A-PMDA than in A-TCNQ. Making some simple assumptions, including the assumption that the average change in bond length varies as no less than the first power of transferred charge, we would expect an average change in bond length in either species of A-PMDA of no more than 0.002 Å. The present crystal structure determination is perhaps the most accurate to date of a $\pi$-molecular complex. The structure of pure perdeuterioanthracene has also been determined to a high degree of accuracy by neutron diffraction by Lehmann and Pawley (1972). Table I compares the symmetry averaged bond lengths of anthracene in A-PMDA with those from perdeuterioanthracene. The numbering sequence is given in Figure 1. The bond lengths listed in Table I are averages of thermally corrected bond lengths.

The errors in an individual uncorrected bond length not involving a hydrogen atom, as determined by the least-squares analysis is 0.0013 Å for A in A-PMDA. The estimated standard deviations quoted in Table I reflect some additional arbitrary uncertainty associated with the corrections for thermal effects. We must also point out that some of the differences between the pure compound and the complex may reflect the fact that one set of numbers measures nuclear-nuclear separations (neutron diffraction data) and

TABLE I

Comparison of Bond Lengths of Anthracene in Perdeuterioanthracene and A-PMDA

| | Perdeuterioanthracene | A-PMDA |
|---|---|---|
| C(9)-C(10), C(9)-C(11′) | 1.402(2) | 1.405(2) |
| C(10)-C(11) | 1.439(3) | 1.442(2) |
| C(10)-C(12), C(11′)-C(15) | 1.433(2) | 1.434(2) |
| C(12)-C(13), C(15)-C(14) | 1.368(2) | 1.375(2) |
| C(13)-C(14) | 1.432(3) | 1.429(2) |

the other measures distances between centers of negative charge (X-ray diffraction data). Nevertheless, the values are remarkably similar and despite the high resolution of the two crystal structure determinations, we are not able to observe the effect of charge transfer in neutral ground state $\pi$-molecular complexes with any significance. We note in passing, however, that the largest difference, 0.007(3) Å, though less than three standard deviations, is consistent with expectations. The highest occupied molecular orbital (HOMO) of anthracene has been identified by Clark *et al.*, (1972) as a $B_{2g}$ state. The Hückel coefficients for that state, as listed by Heilbronner and Bock (1976), give the largest (and the only positive) product of coefficients for the C(12)–C(13) and C(14)–C(15) bonds, which implies that the loss of an electron from the HOMO should lengthen these bonds and decrease all others but by a lesser amount.

The packing arrangement in A–PMDA brings the end bond C(13)–C(14) of A directly over the end of the anhydride ring of the PMDA molecule below it. Each molecule in the structure sits at a center of symmetry and therefore the other end of A sits directly below the end of the anhydride ring of the PMDA molecule above it. The interatomic distances [C(13)–C(14)] and [C(4)–C(5)] are 3.315 and 3.331 Å respectively. These are among the shortest intrastack contacts; the contacts on the oppositive side of A are significantly longer. It appears therefore that the two ends of an acceptor molecule are involved in localized interactions, one with the end of the donor below and the other with the oppositive end of the donor above. Because the donor and acceptor molecules are not of the same length, the individual molecules in the stack are tilted with respect to the stack direction in order to facilitate this

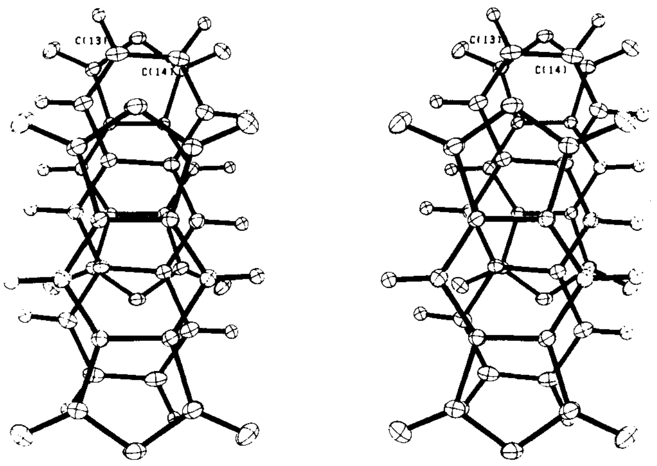


FIGURE 3 Intrastack neighbours of a donor molecule in A–PMDA.

interaction. The angle between the normal to the A molecule and the stack axis (c) is 20.7°. A further consequence is that successive donor or acceptor molecules along the stack are offset from one another by the width of one six membered ring as is illustrated in Figure 3.

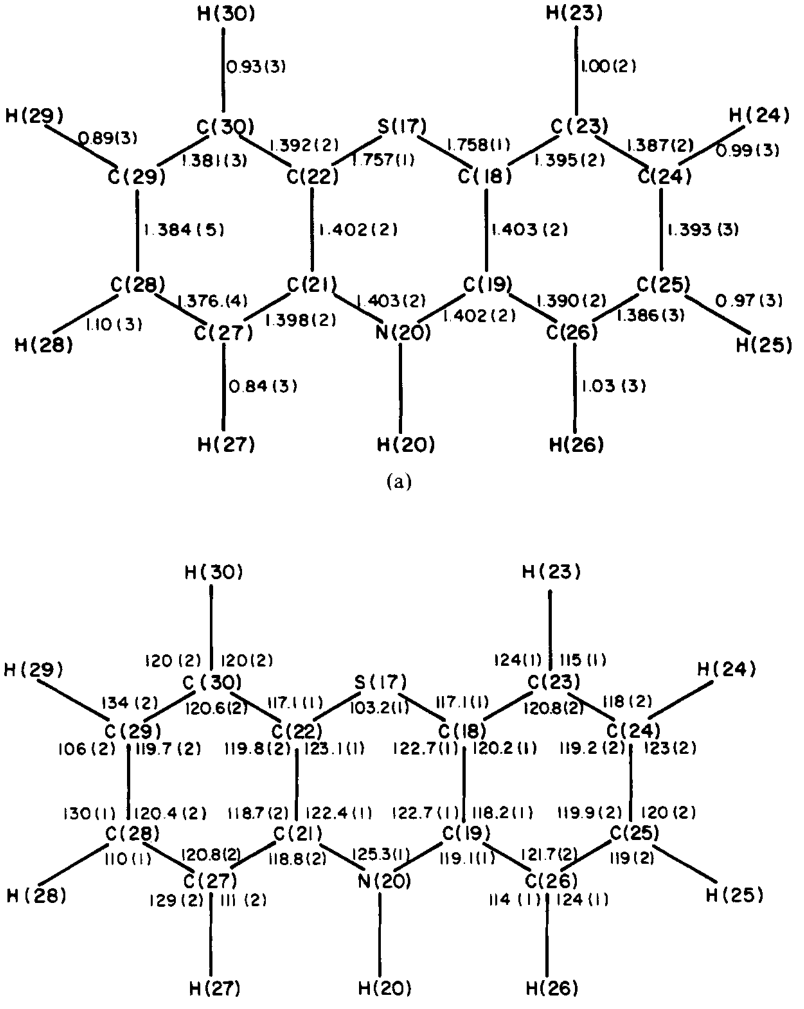
This aspect of the molecular overlap in A–PMDA appears to be relevant to its charge-transfer properties. Recent spectroscopic results of Eckhardt and Merski (1978) suggest a first charge-transfer transition dipole corresponding to the stacking vector ($\frac{1}{2}c$), which also corresponds to the vector from molecular center to molecular center, and a second charge-transfer transition dipole which would appear to involve the ends of the molecules.

## PHENOTHIAZENE PYROMELLITIC DIANHYDRIDE

The structure of PTZ–PMDA was determined from data collected at room temperature and solved by direct methods. The unit cell constants are $a$ = 6.885(1), $b$ = 19.072(5), $c$ = 7.197(1) Å, $\alpha$ = 84.79(1), $\beta$ = 72.98(1), $\gamma$ = 85.72(2)°. The space group is $P\bar{1}$ with two formula units per unit cell. PTZ–PMDA crystals are black with well formed faces but are less prone than A–PMDA to form needles. The structure is similar to that of A–PMDA though the molecules cannot sit at centers of symmetry as in A–PMDA because one of them (PTZ) is itself not centrosymmetric. The unit cell is therefore approximately twice as large as that of A–PMDA. The structure was refined with data with sin $\theta/\lambda$ between 0.0 and 0.807. The bond lengths and bond angles for PTZ are given in Figure 4. Those for PMDA are not significantly different from the values obtained for PMDA in A–PMDA although they reflect the difference in temperature at which the two structures were determined and the method by which they were refined.

The PTZ molecule is slightly folded with an angle of 176.4° between the planes of the two phenyl rings. The equivalent angle in the structure of pure PTZ (McDowell, 1975) is 158.5°. The flattening of the PTZ molecule does not appear to significantly change the bond lengths of carbon to the sulfur or nitrogen atoms.

A peak in electron density *ca.* 0.5 Å from the N atom suggests that approximately one in fifty of the PTZ molecules are disordered, with the positions of the S and N atoms reversed. Unfortunately the disorder obscures the N-hydrogen atom. The peak in the electron density map which we have interpreted as evidence for disorder of the S atom, is not symmetric. It shows a shoulder on its side further removed from the normal position of the N atom. If the symmetric part of the peak is removed, a very weak residual electron density is left at a position roughly 1.0 Å from the N atom. The asymmetry of the secondary S peak, and the short (3.189 Å) distance from the N atom to a



(b)

FIGURE 4 (a) Bond lengths (Å), and (b) bond angles (°) for PTZ.

carbonyl 0 atom on a neighbouring PMDA molecule suggests that a weak N—H · · · 0 hydrogen bond is formed and the H atom is *intra* to the fold of the PTZ molecule as predicted by Malrieu and Pullman (1964).

Other structures have been reported which contain PTZ and PTZ$^+$ as a member of a charge transfer complex. However, in all but one, the PTZ species is disordered. In the complex of PTZ$^+$ with *cis*-bis(trifluoromethylethylene) nickel$^-$ (Singhabhandhu *et al.*, 1975), the PTZ$^+$ species is folded with the

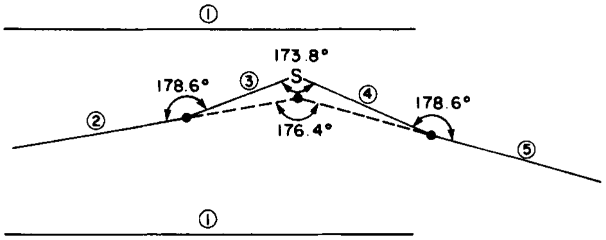


FIGURE 5 Exaggerated representation of the non-planarity of phenothiazine in PTZ–PMDA. Plane 1 is fitted to the ring of PMDA. The dihedral angles between plane 1 and planes 2, 3, 4 and 5 are 1.4°, 2.6°, 5.0° and 3.6° respectively.

value of the angle between the phenyl rings at 172.8°. The additional electron in PTZ could be expected to increase the resistance of the molecule to being flattened. Therefore, the further approach of PTZ to planarity in PTZ–PMDA than in PTZ$^+$-*cis*-bis(trifluoromethylethylene)nickel$^-$ suggests that the forces associated with the $\pi$-molecular interaction in PTZ–PMDA are greater than those in PTZ$^+$-*cis*-bis(trifluoromethylethylene)nickel$^-$. The ionization energy of PTZ has been shown to be 0.70 eV lower than that of A (Anthonj, Karl, Robertson and Stezowski, 1979) which implies that it should be a somewhat better electron donor than A.

As is illustrated in Figure 5, one half of the PTZ molecule sits between two neighbouring acceptors and is nearly parallel to them and the other half protrudes out of the stack and deviates slightly from being coplanar with the acceptors. As a result the lower PMDA molecule is not offset by the width of one six membered ring as in A–PMDA but is directly below the PMDA molecule above it. Thus the angle between the stack and the plane normals is

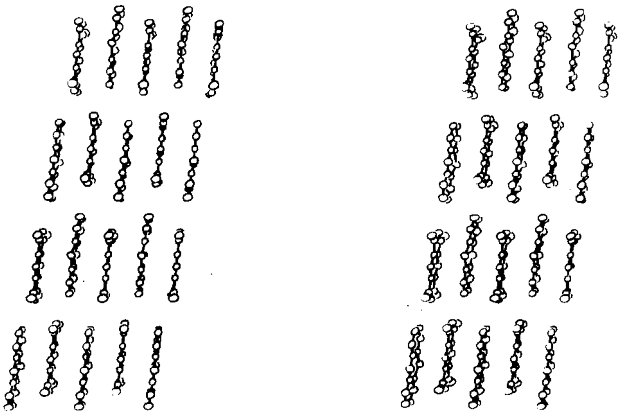


FIGURE 6 Molecular packing in PTZ–PMDA.

only 5.9° in PTZ–PMDA. Also the channels formed by the abutment between the long ends of the stacks at the protruding ends of the PTZ molecules tend to interlock while the channels at the other ends of the stacks are relatively smooth, as is illustrated in Figure 6.

In both the structures discussed above, one of the independent C=O bonds is shorter than the other. In each case the oxygen atom forming the shortened bond is involved in a short O—O interstack intermolecular contact. It is reasonable to suggest that this contact decreases the charge on the O atom and thereby increases the double bond character of the C=O bond.

## CONCLUSIONS

The structures of A–PMDA and PTZ–PMDA are similar but the lack of a center of symmetry in the PTZ molecule and its tendency to be non-planar leads to a different mode of stacking in PTZ–PMDA from that in A–PMDA. This and the lower ionization energy of PTZ lead to the differences in the physical properties of the two complexes. The changes in the bond lengths of anthracene in A–PMDA from those in the pure compound are small and not inconsistent with those predicted from Hückel theory. The structure of A–PMDA suggests the presence of localized interactions associated with the ends of the donor and acceptor molecules.

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