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Preparation and structure of the 1:2 π -molecular complex of phenothiazine with pyromellitic dianhydride

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Single crystals of the black 1:2 donor-acceptor complex of phenothiazine with pyromellitic dianhydride, PTZ:(PMDA)₂, were grown by plate sublimation at $\sim 163^\circ\text{C}$ from the zone-refined components. The 1:1 complex is produced at lower temperatures. Crystals of the 1:2 complex are monoclinic, $P2_1/c$, $Z = 4$, $a = 7.689(3)$, $b = 12.953(5)$, $c = 28.14(2)$ Å, $\beta = 104.30(2)^\circ$ at $T = 19^\circ\text{C}$. The structure was refined from 2863 x-ray diffraction reflection intensities for which $I > 2.0\sigma(I)$ to $R = 0.064$ and $R_w = 0.057$. The structure consists of continuous ... DADA ... polar stacks as does the 1:1 complex, but the stacks, which are parallel to the a axis, are separated in the c direction by the extra PMDA molecule. The overlap of adjacent molecules in the stack in the 1:2 complex is more closely related to the overlap of adjacent molecules in the π -molecular complex of PMDA with anthracene. The resultant angle between the stack axis and the normal to the planar molecules is 27.1° . The geometry of the individual molecules in the 1:2 complex is not significantly different from those in the 1:1 complex.

INTRODUCTION

Donor-acceptor (D:A) complexes of aromatic π -electron systems with nominally neutral ground states usually crystallize in the form of infinite ... DADA ... stacks with perpendicular distances between the planes of the molecules near 3.4 Å. The associated physical properties of the complex depend upon the electronic states of the constituent molecules (especially on the ionization energy of the donor and on the electron affinity of the acceptor), on their geometry and on the precise nature of the interactions of the atoms (and hence the sign and overlap of the electronic wave functions) in the donor and acceptor molecules. Variations in the nature of the interaction of adjacent molecules (and the tendency to maximize the overall molecular interactions) lead to variations in the angle between the stack axis and the normal to the planes of the molecules within the stacks; i.e., the stack angle.

In order to correlate the structural features of D:A complexes with their electrical and optical properties, it is essential that very pure material be used because the influence of impurities on these properties may be substantial. We report here on studies of the binary system composed of phenothiazine (PTZ) and pyromellitic dianhydride (PMDA) where both components were first purified separately by multipass zone refining. We have described previously the details of the purification procedure;¹ further, we have reported on the growth of single crystals by plate sublimation,² and on structure, optical and electrical properties of the 1:1 complex ($\text{C}_{12}\text{H}_9\text{SN}:\text{C}_{10}\text{H}_2\text{O}_6$).¹ In addition, UV-photoelectron spectra have

been measured³ and compared with those obtained with the neat donor crystal. There is also a 1:2 complex [$\text{C}_{12}\text{H}_9\text{SN}:\text{2}(\text{C}_{10}\text{H}_2\text{O}_6)$] formed in the binary PTZ/PMDA system which we discuss in this publication.

The structures of several other D:A π -molecular complexes containing PMDA as acceptor have been reported. In these cases the donor molecules have been acridine,⁴ anthracene,^{5,6} carbazole,⁷ fluorene,⁸ naphthalene,^{9,10} phenanthrene,¹¹ phenazine,^{12,13} pyrene,¹⁴ perylene,⁵ and thianthrene.¹⁵ Whereas the individual components absorb in the near UV and are therefore colorless or weakly yellow, the complex crystals are brightly colored or in some cases, black, because of light absorption in a broad more or less unstructured band in the visible part of the spectrum. This is due to an optical transition with charge transfer from the donor to the acceptor. Both the 1:1 and 1:2 complexes between PTZ and PMDA are black.

The black appearance of the 1:1 and 1:2 complexes is related to the low ionization potential of PTZ, leading to a small energy requirement for the transfer of an electronic charge from the highest occupied molecular orbital of PTZ to the lowest unoccupied orbital of PMDA. The charge transfer energy and hence the energy of the excited charge transfer state is low enough to overlap with high lying combinations and overtones of molecular vibrations, thus explaining the absence of any emission between 4.2 and 300 K¹ of the 1:1 complex. The energy of the excited state may preferentially be dissipated through strong coupling with "butterfly" molecular motions of PTZ along its $\text{N} \cdots \text{S}$ fold axis. In the 1:1 complex the fold angle of planes through the atoms of the two moieties

of the central ring was found to be 173.8° ¹ which is taken as an indication that the (ground state) molecule, which is much more flat here than in the neat PTZ crystal (153.3°),¹⁶ has gained binding energy by increasing its aromaticity and concomitantly decreasing its ionization threshold upon flattening. Hence the butterfly flapping motion would be expected to be strongly coupled to the charge transfer transition.

In the structure of PTZ:SbCl₆¹⁷ the ground state of PTZ is a free radical with approximately unit positive charge as it would be in the excited state of a PTZ donor-acceptor complex with PMDA. Here the fold angle at the N-S vector is 177.1° . In conjunction with the near 180° fold angle, the S-C and N-C bonds strengths are enhanced to bond lengths of 1.71(2) and 1.38(2) Å from 1.758(1) and 1.403(2) Å in PTZ:PMDA¹ suggesting enhanced delocalization through the center of the molecule. Therefore, it is reasonable to also expect further flattening of the PTZ molecule in the CT-excited state of complexes with a near neutral ground state, such as PTZ:PMDA. The further flattening of the CT-excited PTZ molecule, should also be connected with increased aromaticity and S-C and N-C bond length contraction. This consideration further contributes toward concluding that a strong coupling of the PTZ CT transition to phonons should exist.

π -Molecular complexes with D:A ratios other than 1:1 usually consist of "sandwiches" formed by two molecules of one species and by one of the other, such as in the 2:1 complex of acridine with PMDA¹⁸ or in the complex [(perylene)₂-perylene]:TCNQ.¹⁹ The unit of three sandwich molecules may pack in linear stacks as in the latter case, or the units may pack in a herringbone zig-zag pattern (commonly encountered with simple aromatic compounds such as naphthalene, anthracene) without a common axis, as in the former case. In the latter, the third perylene molecule lies approximately orthogonal to the molecules in the stack and separates neighboring stacks of DAD units.

The DAD units allow CT transitions within themselves and the appearance of crystals containing such units is not significantly different from those with infinite \cdots DADA \cdots stacks.

In consideration of the foregoing discussion, crystals of PTZ:(PMDA)₂ might reasonably be expected to contain sandwiched ADA units; infinite \cdots DADA \cdots stacks, however, with the extra PMDA acceptor molecules excluded from the stacks, might also form the basis of the structure of the 1:2 complex phase, but this seemed less likely. In either case, a comparison of the optical and electrical properties of the two PTZ/PMDA phases and their correlation with structural geometry of the two phases should promise closer insight into the physics of π -molecular interactions.

EXPERIMENTAL

From an equimolar (1:1) starting mixture of zone-refined phenothiazine and pyromellitic-dianhydride and with the growth temperature kept at $\sim 163^\circ\text{C}$, black crystals were obtained by plate sublimation² which were

different from the 1:1 complex¹ which grows at $\sim 150^\circ\text{C}$ and below. The lattice parameters of the new phase in conjunction with the chemical composition determined by elemental analysis suggested that the crystals contained units of PTZ:(PMDA)₂ in the unit cell. Whereas the 1:1 phase is triclinic, the 1:2 phase is monoclinic, space group $P2_1/c$ from systematic extinctions [(OkO) , $k = 2n$; (hol) , $l = 2n$]. Mass spectrometry yielded PTZ and PMDA entities, proving that no chemical reaction had taken place between the components. Very thin cleaved crystals (or solution-grown platelets) of the 1:1 complex are green in transmission and exhibit strongly different absorption for the two principal polarizations (in conjunction with directional pleochroism). In contrast, thin fragments of the other complex appear brownish and exhibit only weak dichroism as a function of the E and k vector.

A crystal with dimensions $0.4 \times 0.4 \times 1.0\text{ mm}^3$ was used for x-ray diffraction on a modified Picker diffractometer. Lattice constants ($a = 7.689(3)$, $b = 12.953(5)$, $c = 28.14(2)$ Å, $\beta = 104.30(2)^\circ$, $V = 2716.0\text{ Å}^3$) were determined from the centered positions of 70 reflections in the range $46^\circ \leq 2\theta \leq 55^\circ$ (MoK α_1) $\lambda = 0.70926$ Å, $T = 19^\circ\text{C}$). The long axis of the crystal corresponded to the c axis of the unit cell and to the axis of the fiber with which the crystal was mounted on the goniometer. The large relative error in the value of c arises from imprecision in the crystal height adjustment and in the radius of the goniostat. For $Z = 4$, $\rho_{\text{cal}} = 1.554\text{ g cm}^{-3}$; $1.55 < \rho_{\text{obs}} < 1.59\text{ g cm}^{-3}$.

The integrated intensities of 6258 reflections with $3^\circ \leq 2\theta \leq 55^\circ$ were measured in the θ - 2θ scan mode with MoK α radiation, using a highly oriented graphite monochromator, a scan width of $(1.60 + 0.692 \tan \theta)^\circ$, and minimum background times of 0.40 peak time. Data for which $3^\circ \leq 2\theta \leq 45^\circ$ were collected with a scan speed of 2° min^{-1} . Data for which $45^\circ < 2\theta \leq 55^\circ$ were collected with a scan speed of 1° min^{-1} .

The intensities of three standard reflections decreased by 4% during the period of the data collection. The data were corrected for this decrease in intensity and the individual intensities were reduced to structure factors using standard procedures. Corrections for the effects of absorption ($\mu = 2.00\text{ cm}^{-1}$) were not made. The standard deviations of the individual structure factors were calculated from the counting statistics associated with their measurement, with an additional contribution (approximately proportional to the square of the intensity) derived from the extent to which the scatter of the intensities of the standard reflections exceeded those expected from the statistics of their measurement.

The structure was solved by direct methods using the NRCC program package.²⁰ Further calculations used the X-RAY 76 system of programs.²¹ Only 2863 reflections showed $I < 2.0 \sigma(I)$ and were used in the blocked full-matrix least-squares calculations. Of these, three strong reflections were believed to be affected by secondary extinction and were excluded from the refinement. An analysis of the weighting scheme based on $\sigma^{-2}(F)$ showed a strong bias toward the stronger reflections. Therefore final cycles of least squares used constant weights. Refine-

ment converged with anisotropic temperature factors applied to all atoms, except hydrogen atoms, to $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o| = 0.064$ and $R_w = \{\Sigma(|F_o| - |F_c|)^2/\Sigma F_o^2\}^{1/2} = 0.057$ with an average shift to error ratio of 0.04. The fractional atomic coordinates, anisotropic temperature factors for nonhydrogen atoms, and isotropic temperature factors for hydrogen atoms are listed in Tables I, II, and III. Figure 1 shows the atom labeling, the bond lengths, and bond angles in the three molecules of the asymmetric unit. The equations of relevant molecular planes and lines are given in Table IV.²²

TABLE I. Positional parameters with estimated standard deviations ($\times 10^4$) for carbon, oxygen, nitrogen, and sulfur atoms.

| PMDA 1 | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> |
|--------|------------|------------|------------|
| C (1) | 1641 (4) | 6112 (2) | 348 (1) |
| C (2) | 2386 (3) | 6382 (2) | 828 (1) |
| C (3) | 2112 (3) | 7336 (2) | 1020 (1) |
| C (4) | 1021 (4) | 8097 (2) | 746 (1) |
| C (5) | 273 (3) | 7808 (2) | 265 (1) |
| C (6) | 553 (3) | 6859 (2) | 73 (1) |
| C (7) | -926 (4) | 8423 (2) | -130 (1) |
| C (8) | -409 (4) | 6853 (2) | -452 (1) |
| C (9) | 3590 (4) | 5778 (2) | 1226 (1) |
| C (10) | 3181 (4) | 7379 (3) | 1536 (1) |
| O (1) | -1559 (3) | 9248 (2) | -140 (1) |
| O (2) | -1267 (2) | 7802 (1) | -560 (1) |
| O (3) | -509 (3) | 6199 (2) | -756 (1) |
| O (4) | 3398 (3) | 8048 (2) | 1829 (1) |
| O (5) | 4029 (3) | 6423 (2) | 1639 (1) |
| O (6) | 4167 (3) | 4928 (1) | 1234 (1) |
| PMDA 2 | | | |
| C (11) | -3997 (3) | 8248 (2) | 2874 (1) |
| C (12) | -5584 (3) | 8075 (2) | 2956 (1) |
| C (13) | -5716 (4) | 7131 (2) | 3180 (1) |
| C (14) | -4121 (4) | 6591 (2) | 3310 (1) |
| C (15) | -2537 (3) | 6942 (4) | 3225 (1) |
| C (16) | -2416 (3) | 7884 (2) | 2998 (1) |
| C (17) | -1135 (5) | 6162 (2) | 3405 (1) |
| C (18) | -3737 (5) | 5578 (2) | 3563 (1) |
| C (19) | -6973 (4) | 8866 (2) | 2772 (1) |
| C (20) | -4387 (4) | 9443 (2) | 2618 (1) |
| O (7) | 405 (3) | 6130 (2) | 3403 (1) |
| O (8) | -1927 (3) | 5359 (1) | 3614 (1) |
| O (9) | -4672 (3) | 5022 (2) | 3725 (1) |
| O (10) | -8522 (3) | 8879 (2) | 2772 (1) |
| O (11) | -6178 (3) | 9669 (1) | 2573 (1) |
| O (12) | -3443 (3) | 9998 (2) | 2458 (1) |
| PTZ | | | |
| C (21) | 7565 (3) | 6474 (2) | 973 (1) |
| C (22) | 7236 (4) | 7460 (2) | 1123 (1) |
| C (23) | 5209 (4) | 7975 (2) | 327 (1) |
| C (24) | 5357 (3) | 7062 (2) | 86 (1) |
| C (25) | 4494 (5) | 6956 (2) | -405 (1) |
| C (26) | 3433 (5) | 7737 (3) | -654 (1) |
| C (27) | 3276 (5) | 8646 (3) | -413 (2) |
| C (28) | 4134 (4) | 8768 (2) | 76 (1) |
| C (29) | 8120 (4) | 7776 (3) | 1601 (1) |
| C (30) | 9257 (4) | 7105 (3) | 1907 (1) |
| C (31) | 9542 (5) | 6122 (3) | 1765 (1) |
| C (32) | 8717 (5) | 5817 (3) | 1294 (2) |
| N | 6030 (4) | 8115 (2) | 824 (1) |
| S | 6553 (1) | 5983 (1) | 381 (1) |

TABLE II. Anisotropic thermal parameters with estimated standard deviations ($\times 10^3$) for carbon, oxygen, nitrogen, and sulfur atoms.

| PMDA 1 | <i>U</i> ₁₁ | <i>U</i> ₂₂ | <i>U</i> ₃₃ | <i>U</i> ₁₂ | <i>U</i> ₁₃ | <i>U</i> ₂₃ |
|--------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| C (1) | 66 (2) | 47 (2) | 55 (2) | -0 (1) | 16 (1) | -2 (1) |
| C (2) | 63 (2) | 59 (2) | 48 (2) | -5 (1) | 17 (1) | 8 (1) |
| C (3) | 56 (2) | 72 (2) | 40 (2) | -14 (2) | 15 (1) | -3 (1) |
| C (4) | 67 (2) | 54 (2) | 56 (2) | -7 (1) | 24 (2) | -14 (1) |
| C (5) | 55 (2) | 52 (2) | 54 (2) | -4 (1) | 16 (1) | 2 (1) |
| C (6) | 56 (2) | 52 (2) | 45 (2) | -8 (1) | 11 (1) | -6 (1) |
| C (7) | 59 (2) | 70 (2) | 66 (2) | -5 (2) | 11 (2) | 9 (2) |
| C (8) | 65 (2) | 60 (2) | 58 (2) | -3 (2) | 10 (2) | -1 (2) |
| C (9) | 65 (2) | 74 (2) | 65 (2) | -8 (2) | 14 (2) | 17 (2) |
| C (10) | 68 (2) | 84 (2) | 47 (2) | -14 (2) | 16 (2) | -1 (2) |
| O (1) | 85 (2) | 67 (1) | 106 (2) | 20 (1) | 15 (1) | 10 (1) |
| O (2) | 73 (1) | 74 (1) | 59 (1) | 2 (1) | 0 (1) | 4 (1) |
| O (3) | 115 (2) | 86 (2) | 56 (1) | -6 (1) | 4 (1) | -19 (1) |
| O (4) | 114 (2) | 107 (2) | 51 (1) | -14 (1) | 11 (1) | -24 (1) |
| O (5) | 78 (1) | 95 (2) | 50 (1) | -5 (1) | 4 (1) | 11 (1) |
| O (6) | 92 (1) | 77 (1) | 83 (1) | 14 (1) | 12 (1) | 21 (1) |
| PMDA 2 | | | | | | |
| C (11) | 61 (2) | 49 (2) | 41 (2) | -6 (1) | 5 (1) | 1 (1) |
| C (12) | 55 (2) | 53 (2) | 47 (2) | -1 (1) | 9 (1) | -16 (1) |
| C (13) | 66 (2) | 66 (2) | 49 (2) | -23 (2) | 17 (1) | -12 (1) |
| C (14) | 63 (2) | 49 (2) | 42 (2) | -9 (1) | 12 (1) | -4 (1) |
| C (15) | 59 (2) | 50 (1) | 46 (2) | -3 (1) | 5 (1) | -5 (1) |
| C (16) | 55 (2) | 61 (2) | 43 (2) | -12 (1) | 9 (1) | 15 (1) |
| C (17) | 75 (2) | 66 (2) | 59 (2) | -7 (2) | 3 (2) | 1 (2) |
| C (18) | 93 (2) | 58 (2) | 41 (2) | -18 (2) | 8 (2) | 4 (1) |
| C (19) | 65 (2) | 68 (2) | 64 (2) | -6 (2) | 8 (2) | -21 (2) |
| C (20) | 74 (2) | 53 (2) | 45 (2) | -8 (2) | 2 (2) | -1 (1) |
| O (7) | 64 (1) | 88 (2) | 121 (2) | 4 (1) | 9 (1) | 17 (1) |
| O (8) | 86 (2) | 62 (1) | 72 (1) | -3 (1) | -1 (1) | 11 (1) |
| O (9) | 122 (2) | 65 (1) | 75 (2) | -28 (1) | 32 (1) | 11 (1) |
| O (10) | 63 (1) | 82 (2) | 128 (2) | 5 (1) | 19 (1) | -15 (1) |
| O (11) | 72 (1) | 58 (1) | 68 (1) | 2 (1) | 0 (1) | -3 (1) |
| O (12) | 100 (2) | 66 (1) | 76 (2) | -7 (1) | 15 (1) | 15 (1) |
| PTZ | | | | | | |
| C (21) | 51 (2) | 66 (2) | 75 (2) | -5 (1) | 19 (1) | -15 (2) |
| C (22) | 49 (2) | 71 (2) | 86 (2) | -4 (2) | 20 (2) | -24 (2) |
| C (23) | 57 (2) | 57 (2) | 89 (2) | -6 (1) | 28 (2) | -12 (2) |
| C (24) | 60 (2) | 58 (2) | 68 (2) | -3 (1) | 24 (2) | -3 (2) |
| C (25) | 101 (3) | 68 (2) | 77 (2) | -4 (2) | 48 (2) | -3 (2) |
| C (26) | 107 (3) | 106 (3) | 67 (2) | -6 (2) | 34 (2) | 12 (2) |
| C (27) | 92 (3) | 86 (3) | 103 (3) | 6 (2) | 42 (2) | 29 (2) |
| C (28) | 76 (2) | 58 (2) | 106 (3) | 1 (2) | 36 (2) | 4 (2) |
| C (29) | 71 (2) | 95 (2) | 88 (3) | -11 (2) | 25 (2) | -41 (2) |
| C (30) | 80 (2) | 120 (3) | 72 (2) | -20 (2) | 17 (2) | -13 (2) |
| C (31) | 91 (3) | 101 (3) | 77 (3) | -7 (2) | 19 (2) | -1 (2) |
| C (32) | 87 (2) | 67 (2) | 99 (3) | -11 (2) | 22 (2) | -10 (2) |
| N | 89 (2) | 68 (2) | 113 (2) | 14 (2) | 4 (2) | -44 (2) |
| S | 76.4 (5) | 59.0 (5) | 87.9 (6) | 7.1 (4) | 5.6 (5) | -27.7 (5) |

DISCUSSION

Contrary to expectations, the structure of PTZ:(PMDA)₂ contains infinite DADA stacks as does the 1:1 complex. The *a* axis is the stack axis. The extra acceptor PMDA molecule (PMDA II) sits outside the stack with its length and the normal to the plane of the molecule approximately perpendicular to the stack axis (67.9° and 89.5°, respectively). The packing is represented in Fig. 2. The sides of the stacks are in van der Waals contact along the *b* direction, but the extra acceptor molecules completely separate the stacks in the *c* direction.

TABLE III. Positional and isotropic thermal parameters ($\times 10^3$) for hydrogen atoms.

| PMDA 1 | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> | <i>U</i> |
|--------|------------|------------|------------|----------|
| H (1) | 178 (2) | 545 (2) | 23 (1) | 55 (6) |
| H (4) | 83 (2) | 879 (1) | 85 (1) | 56 (6) |
| PMDA 2 | | | | |
| H (13) | -691 (3) | 688 (2) | 322 (1) | 71 (2) |
| H (16) | -127 (2) | 815 (1) | 296 (1) | 56 (6) |
| PTZ | | | | |
| H (25) | 463 (3) | 633 (1) | -57 (1) | 47 (6) |
| H (26) | 271 (3) | 753 (2) | -101 (1) | 98 (9) |
| H (27) | 253 (3) | 915 (2) | -58 (1) | 73 (7) |
| H (28) | 405 (3) | 944 (2) | 26 (1) | 80 (8) |
| H (29) | 793 (3) | 851 (2) | 166 (1) | 99 (9) |
| H (30) | 990 (3) | 734 (2) | 226 (1) | 86 (8) |
| H (31) | 1032 (4) | 557 (2) | 203 (1) | 130 (10) |
| H (32) | 871 (3) | 519 (2) | 118 (1) | 49 (8) |
| H (N) | 595 (3) | 869 (1) | 93 (1) | 62 (7) |

In the 1:1 complex the stacks are in good contact both on their broad and on their narrow side.

The nature of the overlap of adjacent molecules in the stack is shown in side view in Fig. 3 and as viewed along the stack axis in Fig. 4. The increased stack angle causes a greater repeat distance [$a = 7.689(3)$ Å] along the stack in the 1:2 complex than in the 1:1 complex [$c = 6.886(1)$ Å]. However, the interplanar spacing between molecules (half the separation between two consecutive PMDA molecules in the stack along the normals to the planes of the molecules) are identically 3.425 Å. Also the folding of the PTZ molecules is similar in the two structures. The angle between the two planes of the two phenyl rings of PTZ are 175.7° and 176.4°. As in the 1:1 complex all PTZ molecules in one stack are folded in the same direction, thus giving rise to noncentrosymmetric, polar ("pyroelectric") stacks. Point group symmetry, 2/m, is fulfilled by pairs of stacks with mutually opposite polarity, related by interstack inversion centers.

Among the factors that influence the overlap of adjacent aromatic molecules in π -molecular complexes, the tendency for bonds common to two rings to lie over or under the centers of the rings of neighboring molecules is important. Such a tendency seems to play a role in the overlap of adjacent molecules in both stacking modes observed for PTZ and PMDA. However, the steric requirements of the sulfur atom are also important. In the stack found in the 1:1 complex the sulfur atom fits into one of the four clefts of the PMDA molecule above and below formed by a carbonyl group and a central CH group. (H-C-C-C=O). In the 1:1 complex the two clefts are equivalent, related by a cell translation along the stack axis. As a result the line of centers of the PTZ molecules is offset from the line of centers of the PMDA molecules, and the longer PTZ molecules protrude from the stack at one end. Also, the angle between the stack axis and the normal to the plane of the PMDA molecule is small at 5.9°.

In the 1:2 complex the sulfur atom of the PTZ molecule is similarly oriented with respect to the PMDA molecule on the "outside" of the slight fold of the PTZ molecule. The distances from the sulfur atom to the atoms forming the cleft, H(1), C(1), C(2), C(9), O(6) are 3.65(2), 3.758(3), 3.756(3), 3.688(4), and 3.630(3) Å, respectively. However, the cleft of the PMDA molecule on the "inside" of the fold of the PTZ molecule which is

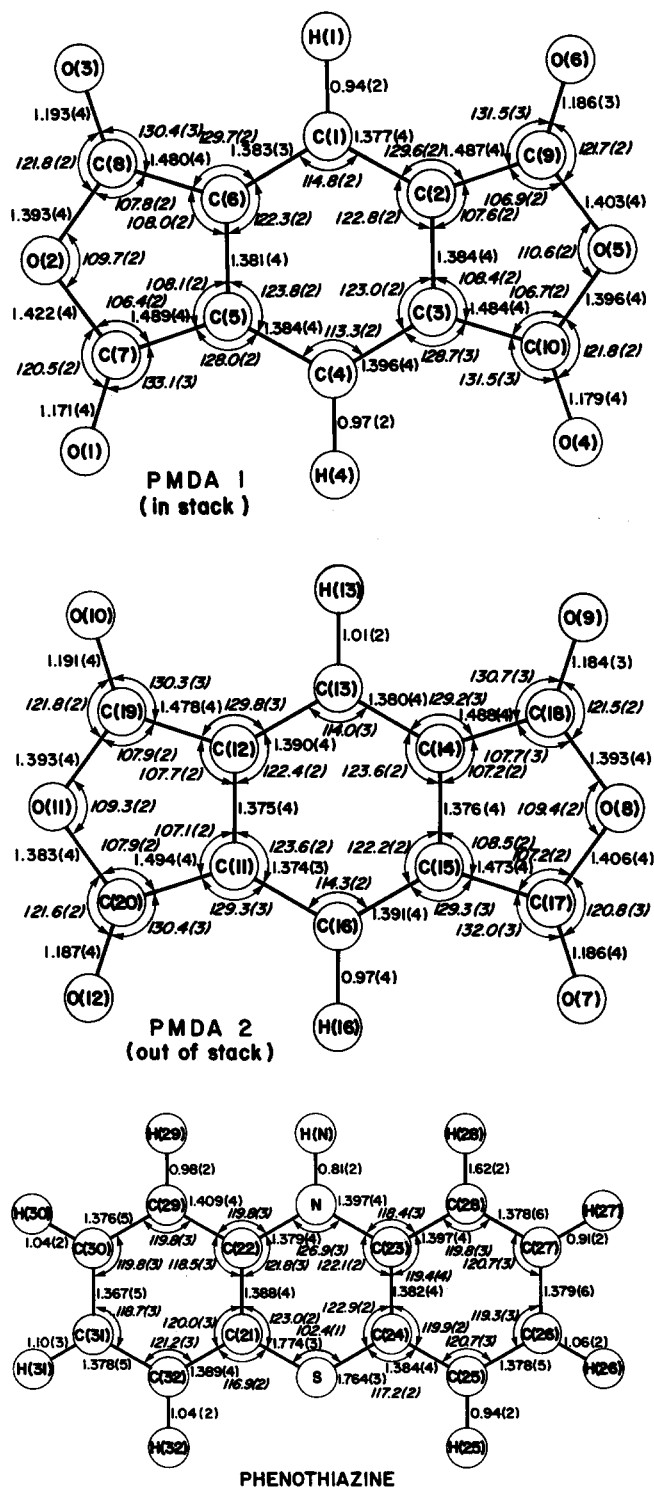


FIG. 1. Atom labeling, bond lengths (Å), and bond angles (°) for PTZ:2PMDA, with estimated standard deviations in parentheses. (a) PMDA(I) (in stack), (b) PMDA(II) (out of stack), (c) PTZ.

TABLE IV. Equations of the least-squares planes and lines.

The x , y , and z axes of the orthogonal coordinate system are in the directions a , b , and c^* , respectively. In that coordinate system:

The plane of the nonhydrogen atoms of the PMDA molecule in the stack (PMDA I) is given by

$$-0.8901x - 0.3673y + 0.2699z = -3.5650.$$

The plane of the nonhydrogen atoms of the PMDA molecule not in the stack (PMDA II) is given by

$$0.0080x + 0.4544y + 0.8908z = 11.8861.$$

The line of the long axis of the PMDA molecule in the stack is given by

$$x = 0.6865 + 0.3764t,$$

$$y = 9.2130 - 0.2645t,$$

$$z = 1.4719 + 0.8879t.$$

The line of the long axis of the molecule PMDA not in the stack is given by

$$x = -5.2667 - 0.3764t,$$

$$y = 9.7329 + 0.8259t,$$

$$z = 8.4357 - 0.4198t.$$

The plane of the phenyl ring of PTZ formed by atoms C (23) to C (28) is given by

$$-0.8888x - 0.3737y + 0.2653z = -6.9736.$$

The plane of the phenyl ring of PTZ formed by atoms C (21), C (22), C (29)–C (32) is given by

$$-0.8796x - 0.3404y + 0.3324z = -6.4880.$$

The plane of PTZ formed by atom C (23), C (24), N, and S is given by

$$-0.9123x - 0.3376y + 0.2317z = -6.7328.$$

The plane of PTZ formed by atoms C (21), C (22), N, and S is given by

$$-0.8600x - 0.3706y + 0.3507z = -6.6080.$$

In terms of a , b , and c and in terms of the unit vectors along x , y , and z (i.e. \hat{i} , \hat{j} , and \hat{k}) the unit normal to the central ring of the PMDA molecule in the stack may be expressed as

$$N = -0.1068a - 0.0284b + 0.0099c,$$

$$N = -0.8901\hat{i} - 0.3673\hat{j} + 0.2699\hat{k}.$$

The angle between this normal and the c axis is 27.1° .

associated with the sulfur atom is that on the opposite side of C(1). This is essentially the stacking mode of PMDA and anthracene in the 1:1 π -molecular complex formed by them.⁶ In anthracene:PMDA the stack angle

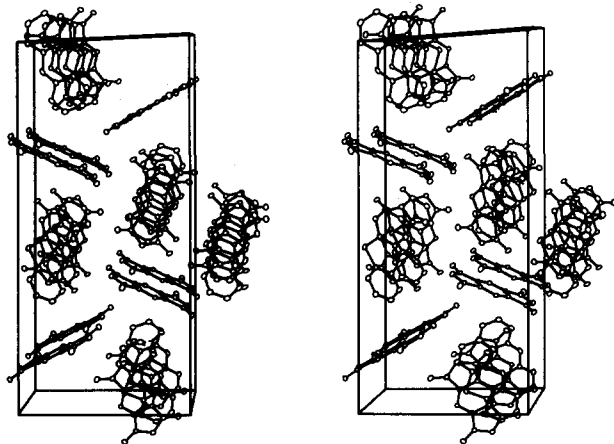


FIG. 2. Stereoscopic drawings of the molecular packing. The c axis points up, the b axis is to the right of the a axis is the stack axis and points out of the page.

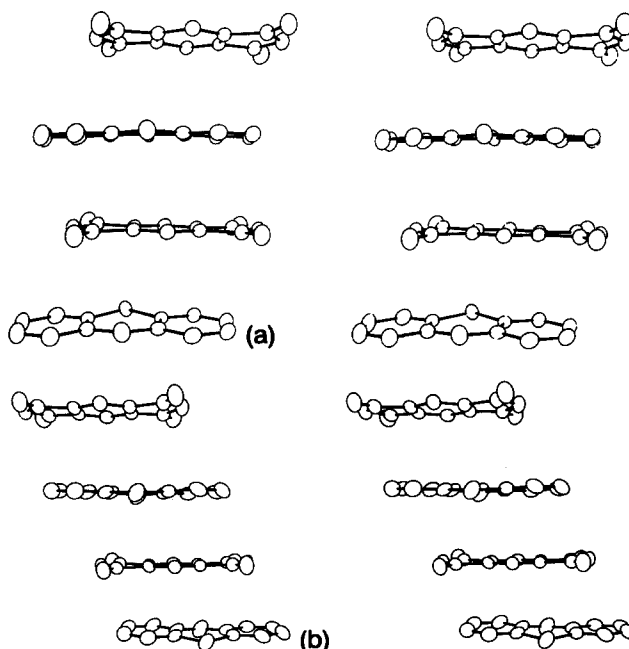


FIG. 3. Side view of the molecular packing and overlap within the stacks (a) 1:1 complex, (b) 1:2 complex.

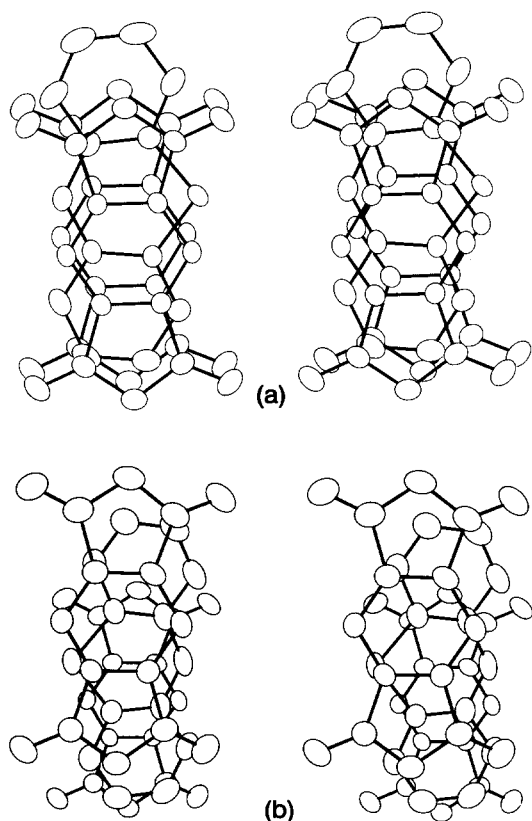


FIG. 4. Stereoscopic drawings of the molecular overlap looking normal to the PMDA molecular plane. (a) 1:1 complex, (b) 1:2 complex.

is 20.7° and the tilt of the molecules is nearly entirely along their long axis. In the 1:2 complex of PTZ with PMDA, the stack angle (between the normal to the PMDA molecule and the stack axis) is greater at 27.1° . However, this tilt contains a significant component of 15.8° along the breadth of the PMDA molecule. The component of the tilt along the long axis of the molecule is 22.1° , similar to the value in the 1:1 complex. The component along the breadth is evident in Figs. 3(b) and 4(b). As a result of the latter component, the sulfur atom of PTZ is brought near the apex of the cleft of the PMDA molecule on the inside of the fold and $[S-C(6)] = 3.580(3) \text{ \AA}$.

The N atom of PTZ forms close contacts $[N-C(3)] = 3.349(4) \text{ \AA}$, $[N-C(10)] = 3.448(5) \text{ \AA}$ to the PMDA molecule on the outside of the fold. The closest C-C contacts in the stack are $[C(26)-C(8)] = 3.345(5) \text{ \AA}$, $[C(24)-C(1)] = 3.356(4) \text{ \AA}$, and $[C(28)-C(5)] = 3.380(4) \text{ \AA}$, all between PTZ and the PMDA molecule on the outside of the fold. The close S-C(6) contact seems to prevent a close approach of other atoms to the PMDA molecule on the inside of the fold.

The shortest contact between the atoms in the stack and those in the extrastack PMDA II molecule is $[O(4)-O(11)] = 2.926(3) \text{ \AA}$. All of the oxygen atoms in PMDA I enter into close contacts with oxygen and carbon atoms of PMDA II, but O(4) forms the shortest contacts. Others are to C(19) $[2.937(4)]$, to C(20) $[3.037(4)]$, to C(12) $[3.074(4)]$, and to C(11) $[3.160(4) \text{ \AA}]$. Other important intrastack contacts are $[S-S] = 3.775(2) \text{ \AA}$, $[S-H(1)]$

$= 3.02(2) \text{ \AA}$, $[O(1)-O(1)] = 3.093(3) \text{ \AA}$, and $[O(6)-O(3)] = 3.159(3) \text{ \AA}$. The shortest intramolecular PMDA II to PMDA I contacts are $[O(9)-O(12)] = 3.285(4) \text{ \AA}$, $[O(12)-C(14)] = 3.231(3) \text{ \AA}$, and $[O(12)-C(18)] = 3.232(3) \text{ \AA}$.

The bond lengths and angles within the donor and acceptor molecules are similar in both stacks. The S-C bonds are slightly larger in the 1:2 complex and the N-C bonds are slightly shorter, but the differences are only marginally significant. In both structures the nitrogen atom is hydrogen bonded to an oxygen atom on a PMDA molecule. In the present case the oxygen atom involved is O(9) on the extrastack PMDA molecule. The relevant parameters are $[N-O(9)] = 3.077(4) \text{ \AA}$, $[H(N)-O(9)] = 2.31(2) \text{ \AA}$, and $[N-H(N) \cdots O(9)] = 158(1)^\circ$. The equivalent N-O distance in the 1:1 complex is $3.189(2) \text{ \AA}$. The electron density in the 1:2 complex shows no evidence of limited disorder (by $N \leftrightarrow S$ interchange) as in the 1:1 complex. Within the available resolution the extrastack PMDA molecule also exhibits no significant geometric difference from the intrastack one.

The presence of the near orthogonal extra acceptor molecule between the $\cdots DADA \cdots$ stacks raises several interesting questions with respect to molecular interactions, energy and charge transfer, and charge carrier mobility. It will be important to find out if the extra acceptor molecule, though nearly orthogonal, tends to decrease the energy of the charge transfer transition. Indications that charge transfer interaction is not necessarily dependent upon parallel arrangement of planes containing conjugated π electrons has been obtained recently by a crystal structure analysis of the black-red 1:2 complex between PTZ and phenazine²³ (both forming light yellow crystals in their one-component phases).

Further, since the $[100]$ -oriented $\cdots DADA \cdots$ stacks are "isolated" from one another by the extra PMDA molecules in one dimension ($[001]$) in the 1:2 complex it is possible to study how the interstack interactions differ in the close contact $[010]$ and the isolated $[001]$ directions; e.g., by measuring the interstack hopping rates of charge transfer excitons. Another interesting but conceptually different problem concerns the anisotropy of the electron and hole mobility tensors. The significance of this question lies in the fact that it has been argued²⁴ that in D:A complexes the hole band might essentially originate from the highest occupied molecular orbital (HOMO) of the donor molecule, whereas the electron band should be formed by the lowest unoccupied orbitals (LUMO) of the acceptor. Hence in the D:A complexes with extra acceptor (or extra donor)¹⁹ molecules the electron and hole mobility tensors may differ much more in their anisotropy than generally encountered with one-component organic molecular crystals; cf. Ref. 25. UV-photoelectron spectroscopy of PTZ:PMDA and other PMDA complexes has recently established³ that, besides a small acceptor-induced shift of $\sim 0.25 \text{ eV}$, the hole band is in fact due to the donor HOMOs.

Finally, the apparent absence of disorder in this complex, in contrast to the situation in the 1:1 complex will afford the opportunity to draw conclusions from experimental results on the effect of intrastack disorder

on the intrastack motion of elementary excitations such as excitons or charge carriers.

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