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# UNUSUAL 1:1 MOLECULAR COMPLEXES OF 2,5-DIARYL-1,4-DITHIINS WITH 2,4-DIARYLTHIOPHENES

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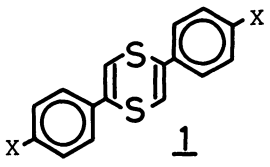
The title compounds have been found to form the crystalline 1:1 molecular complexes wherein distinct intermolecular interaction such as hydrogen bonding, charge transfer interaction, or clathrate inclusion was not found as studied by an X-ray analysis.

Intensive current interest has been focused on engineering the crystal structure of organic molecular complexes to packing modes that provide a desired function toward solid-state reactions,[1] selective molecular complexations,[2] and organic conductors.[3] Hydrogen bonding or charge transfer interaction is usually required to bound crystalline molecular complexes composed of organic components. Otherwise, clathrate inclusion in which guest species are enclosed in channel or cages given by host lattice is responsible for the formation of stable molecular complexes. We now report a novel type of molecular complex, where such intermolecular interaction is not responsible for bonding the components, along with the structural characterization by an X-ray crystallographic study.

The stable 1:1 molecular complexes are generally formed in a variety of combinations of 2,5-diaryl-1,4-dithiin (1) and 2,4-diarylthiophene (2) listed in Table 1. When the dithiin and thiophene components of approximately equimolar quantities were dissolved in ethanol and allowed to stand at room temperature for a few days, the 1:1 complex exclusively separated out; neither of the component species crystallized alone. Thus nine varieties of the complexes[4] were obtained in good yields, all of which gave satisfactory elemental analyses as 1:1 complex and HPLC

Table 1. 1:1 Molecular Complexes of 2,5-Diaryl-1,4-dithiin (1) and 2,4-Diarylthiophene (2) and their Melting Points

| (2) \ (1) | X=H | X=Cl | X=$CH_3$ |
|---|---|---|---|
| Y=H | 128-129 °C | 153-155 °C | 116-117 °C |
| Y=Cl | 168-169 | 134-135 | 176-177 |
| Y=$CH_3$ | 123-124 | 175-178 | 136 |

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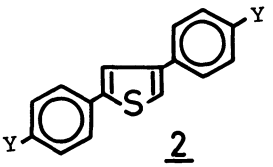


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peaks due to 1:1 composition as corrected by the absorbance. The uv spectra of the complexes are the superposition of these of the constituent species. Thus yellow colour of the 1,4-dithiins remains unchanged by complexation with the thiophenes.

Obviously both components posess no functional group to participate in hydrogen bonding. The formation of the complex regardless of electron-donating and electron-accepting properties of the para-substituents indicates that charge transfer interaction is not essential for the complexation. Intrigued as to the origin of the complexation, the crystal and molecular structure was studied by an X-ray analysis for the complex of 2,5-diphenyl-1,4-dithiin and 2,4-diphenylthiophene.

Crystal data were as follows: $C_{16}H_{12}S_2 \cdot C_{16}H_{12}S$, Mw=504.72, triclinic, $P\bar{1}$, a=27.078(2), b=5.714(1), c=8.195(2) Å, $\alpha$=93.40(1), $\beta$=92.11(1), $\gamma$=93.64(1)°, V=1262.1(4) Å$^3$, Z=2, $D_x$=1.328 Mgm$^{-3}$. Intensity data were collected on a Rigaku four-circle diffractometer using graphite-monochromated CuK$\alpha$ ($2° \leq 2\theta \leq 130°$). A total of 3682 reflections were obtained with $|Fo| \geq 3\sigma(Fo)$. The structure was solved by the direct method with MULTAN78.[5] The E-map and subsequent refinements showed the structure of thiophene to be orientationally disordered with the pseudo mirror symmetry. The positions of the disordered atoms S(1B), C(5B), S(5B) and C(1B) were located from a difference Fourier map. The fixed occupancy factors, 0.5, for these atoms were estimated from their peak heights. H(3B) in thiophene and the hydrogen atoms for all the phenyl groups were found on a difference map. The other hydrogen positions were assumed and also included in the refinements. All atoms were refined by block-diagonal least-squares with anisotropic temperature factors for non-H atoms and isotropic ones for H atoms. The tentative R value is 0.116 and further refinements are in progress.

The stereoscopic view looking down the a axis and the crystal structure projected along the b axis are shown in Figs. 1 and 2, respectively. As is clearly shown in Fig. 1 the molecules are closely packed in the bc plane and the components are arranged alternatively along the [0$1\bar{1}$] and [011] directions. The molecular plane of thiophene ring, which is almost planar, and the mean plane of dithiin ring, which is slightly distorted to the twisted boat conformation, are not parallel; the angle between these planes is 76°. Thus there is no evidence for $\pi$-$\pi$ overlapping between thiophene and dithiin rings. The phenyl substituents on both

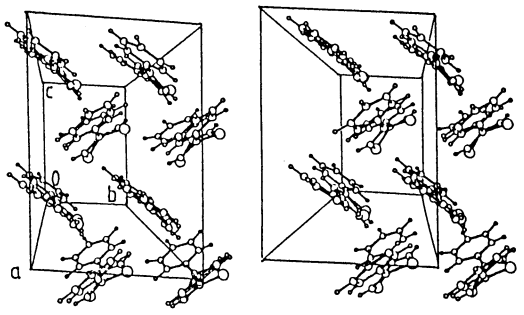


Fig. 1. Stereoscopic view of the crystal structure of the complex (X=Y=H) looking down the a axis.

components also show no serious intermolecular overlapping.[6] Some short intermolecular distances are S(1)···C(3B) 3.458, S(1)···C(2B) 3.382, C(2)···S(1B$^{i}$) (i= x, y, z+1) 3.507, C(21)···S(1B$^{i}$) 3.500 Å. These might be regarded as van der Waals contacts. The length of S(1)···H(3B) is 3.68 Å and far longer than S···H distance in S···HC hydrogen bonding. It is also evident that the complex differs basically from the host-guest type of the complexes in having no cavity, channel, nor layer inclusion.

Although the origin of the intermolecular forces requires further investigation to be disclosed, it seems most likely that van der Waals interaction associated with the similarity of the molecular shape in both components brings about such particular molecular packing as characterized herein.[7] Recently it has been suggested that three dimentional shape similarity is important factor for specific molecular recognition.[9] There is one report, to our knowledge, describing a similar molecular complex in which no distinct intermolecular interaction is recognized.[10]

As to the molecular structure, it is interesting to note that the 1,4-dithiin ring in the complex has slightly twisted boat conformation, while all the 1,4-dithiin derivatives so far reported[11] and uncomplexed 2,5-diphenyl-1,4-dithiin[8] have the boat conformation. This finding would suggest that the 1,4-dithiin ring system is conformationaly so mobile enough to subject the conformational change by packing forces of the crystal. Recent theoretical calculations show the boat and planar conformations of 1,4-dithiin ring are virtually identical energies.[12]

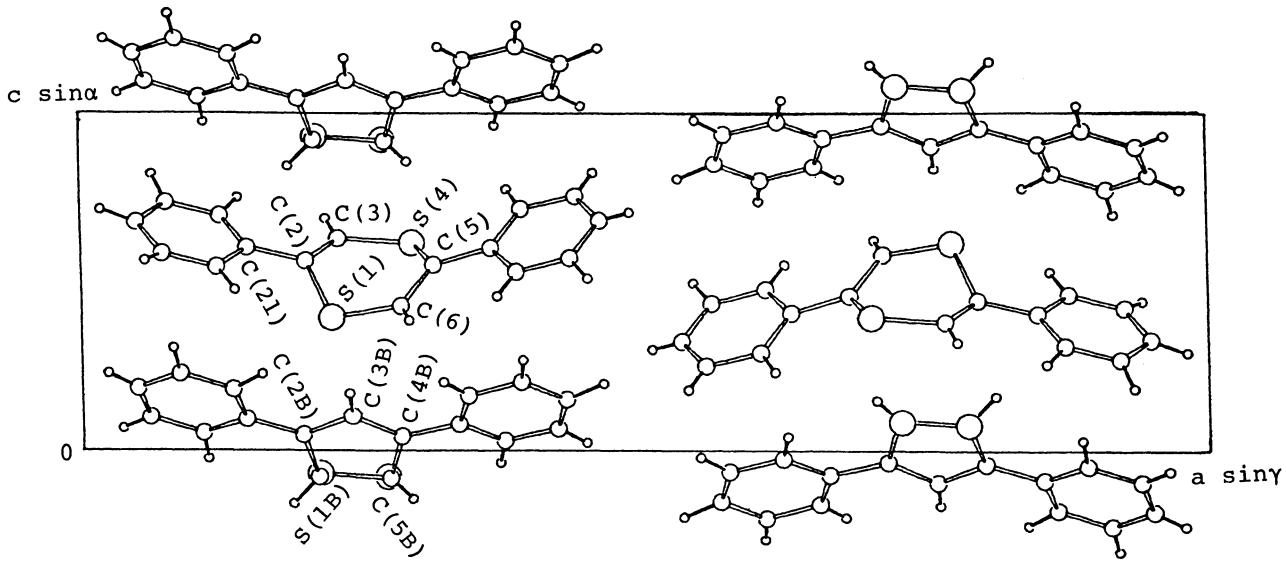


Fig. 2. Projection of the crystal structure of the complex (X=Y=H) along the b axis with the atom-numbering of the 1,4-dithiin and thiophene rings.

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