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The Crystal Structure of 1,6-Dithiapyrene(DTP)-7,7,8,8-Tetracyano-P-Quinodimethane(TCNQ)

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THE CRYSTAL STRUCTURE OF 1,6-DITHIAPYRENE(DTP)-7,7,8,8-TETRACYANO-P-QUINODIMETHANE(TCNQ)

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Abstract The crystal structure of the charge-transfer complex between 1,6-dithiapyrene(DTP) and 7,7,8,8-tetracyano-p-quinodimethane(TCNQ) is reported. The structure correlates well with the observed physical properties.

INTRODUCTION

The charge-transfer complex between DTP and TCNQ (1:1 stoichiometry) has recently been prepared[1]. This material exhibits metallic conductivity down to 4 K with no apparent metal-insulator transition (σ(300 K) = 130 ohm^{-1}cm^{-1}). In order to obtain a better understanding of its physical properties a crystal structure study was initiated.

CRYSTALLOGRAPHIC RESULTS

The crystals are triclinic, space group $P\bar{1}$, with a = 3.833, b = 8.106, c = 15.605 Å, α = 89.77, β = 83,96, γ = 84.77°. V = 480.1 Å^3, Z = 1. Refinement to R = 0.044. Atomic coordinates are listed in Table I[2]. The resulting bond lengths are given in Figs. 1 and 2.

TABLE I Fractional coordinates

Atom	x	y	z
S	0.2339(2)	0.5826(1)	0.7001(1)
N1	0.4360(6)	0.4812(3)	0.1077(1)
N2	0.4505(6)	0.0447(3)	0.2675(1)
C1	0.1502(6)	0.3815(3)	0.7212(2)
C2	0.0328(6)	0.2808(3)	0.6680(2)
C3	-0.0367(5)	0.3236(2)	0.5794(1)
C4	0.0292(5)	0.4821(2)	0.5435(1)
C5	0.1521(5)	0.6077(3)	0.5932(1)
C6	0.2172(6)	0.7604(3)	0.5567(2)
C7	-0.1641(6)	0.2074(3)	0.5280(2)
C8	0.2983(5)	0.1777(3)	0.1249(1)
C9	0.3723(5)	0.3465(3)	0.1142(1)
C10	0.3822(6)	0.1036(3)	0.2034(1)
C11	0.0578(5)	0.1664(3)	-0.0156(1)
C12	0.1494(5)	0.0900(3)	0.0626(1)
C13	0.0852(5)	-0.0802(3)	0.0753(1)

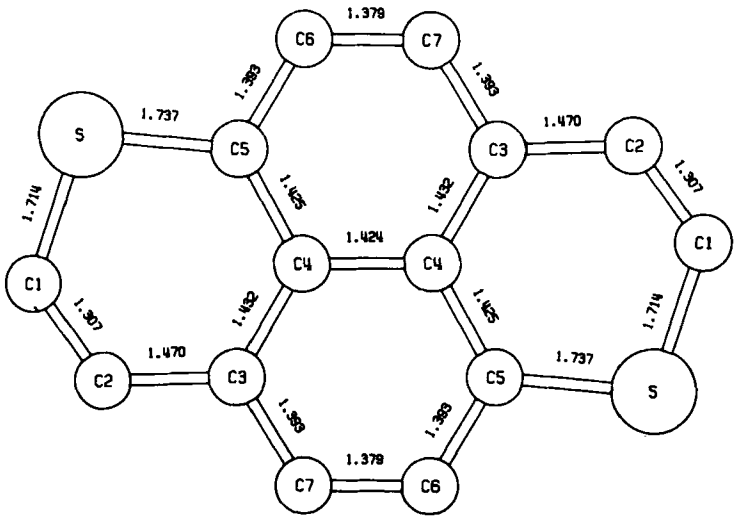

FIGURE 1 Bond lengths (Å) in DTP (centrosymmetric). Esd's ≃ 0.03 Å.

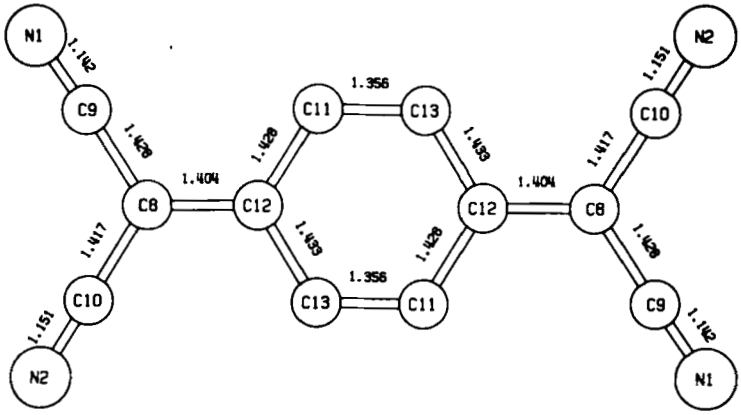

FIGURE 2 Bond lengths (Å) in TCNQ (centrosymmetric) Esd's ≃ 0.03 Å.

The structure consists of regular, segregated stacks of DTP and TCNQ as shown in Figs 3 and 4. The molecules are nearly parallel with their normals inclined about 30° to the stacking axis (a). The interplanar spacing is 3.39 Å for DTP and 3.27 Å for TCNQ. The shortest transverse contacts between stacks are two S-N distances of 3.40 and 3.41 Å.

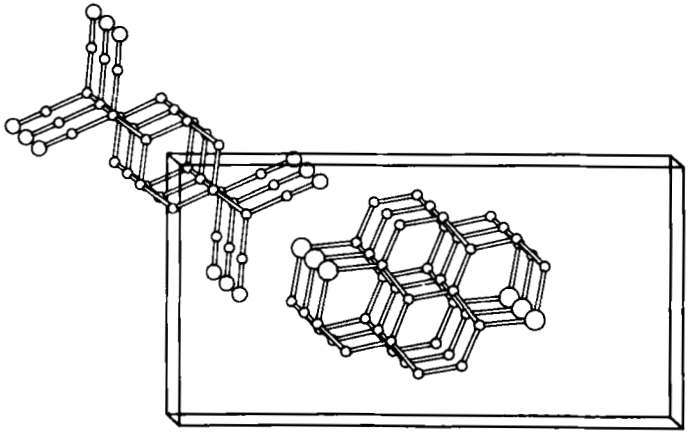

FIGURE 3 Top view (along a) of stacks.

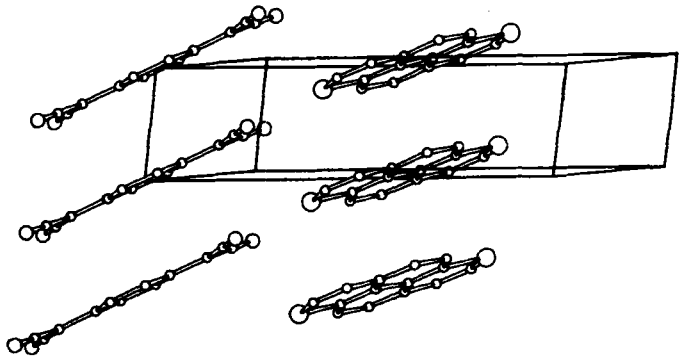

FIGURE 4 Side view of stacks.

DISCUSSION

The two S-N contacts just mentioned are longer than the normal van der Waals distance of 3.35 Å. These weak interactions indicate a fairly high degree of one-dimensionality, which is corroborated by the observed ESR linewidth (ΔH = 5.3 G). The charge transfer from DTP to TCNQ can be estimated from the bond lengths in $TCNQ^3$ yielding a value of 0.66 e in good agreement with a value of 0.64 e derived from IR measurements. The negative thermopower ($S(300\ K) = -34\ \mu V \cdot K^{-1}$) suggests dominance of acceptor stacks. An optic plasma frequency of 8500 cm^{-1} points to a sligthly smaller molecular overlap than in TTF-TCNQ, which is in accord with the interplanar distances (3.27 Å vs. 3.17 Å[4] for TCNQ stacks).

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