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# THE CRYSTAL STRUCTURE OF THE 1:2 COMPLEX OF 3,3-DIMETHYLTHIACYANINE AND 7,7,8,8-TETRACYANOQUINODIMETHANE, $(C_{17}H_{15}N_2S_2)^+(C_{12}H_4N_4)^-(C_{12}H_4N_4)$

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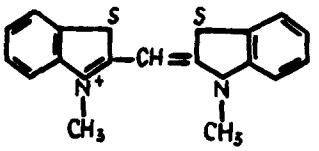
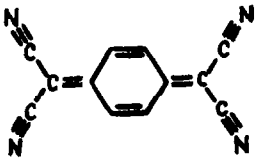
Anion-radical salts of the powerful electron acceptor 7,7,8,8-tetracyanoquinodimethane (TCNQ) show interesting electrical and magnetic properties. These salts can be classified into three types: the high-conductivity complexes ($\rho \approx 10^{-1} - 10^{-2}$ ohm.cm at room temperature), the intermediate-conductivity ones, and the effective insulators. In order to find the relationship between crystal structure and electrical properties X-ray studies of a number of TCNQ molecular complexes with different cations are being carried out.

The present paper deals with the 1:2 complex of the organic dye



and TCNQ



Crystal data:

a= 34.670 ± 0.010 Å
b= 13.205 ± 0.008 Å
c= 7.842 ± 0.005 Å
$\beta$ =102°01' ± 03'
V= 3511.5 Å$^3$
Space group P $2_1$/ a

$C_{41}H_{23}N_{10}S_2$
F(000) =1484
M = 719.8
$d_{calc.}$ =1,37g./cm$^3$
$\mu$ =17.1 cm$^{-1}$(CuK$\alpha$ )
Z = 4

Intensity data for 2146 independent non-zero reflections were collected on a DRON-1 diffractometer (Cu radiation).Because of the small size of the crystal the absorption could be ignored.

The crystal structure was determined by the application of the direct method [1,2] .The signs of 419 reflections with $|E| \geq 1.47$ have been calculated from twelve initial reflections $3k + 9a_i$. From three-dimensional E-map computed with the 419 determined phases 45 of the 53 non-hydrogen atoms have been localized , the remaining eight atoms are readily revealed by the first Fourier electron-density distribution.

Refinement was carried out by means of a full matrix least-squares calculation with isotropic temperature factors giving a final R value of 0.082. The positions of the 17 hydrogen atoms (excluding the methyl hydrogen atoms) were deduced from a difference synthesis.

The [001] projection of the structure is shown in Figure 1.Isolated stacks of TCNQ molecules parallel to the $b$ axis are essential features of the structure of this complex.The TCNQ planes are nearly parallel( dihedral angle 3° ) and they are approximately perpendicular to the $b$ axis.The interplanar spacings of TCNQ molecules in stacks are 3.25Å for 1-11;3.38Å for 11-1'. There are two modes of overlapping of neighbouring TCNQ molecules within a stack (Figure 2a and 2b).The overlap configurations are very similar to those found in the structure of 1:1 complex $Rb^+TCNQ^-$ [3].

The complex salt of TCNQ and the cyanine dye is an intermediate-conductivity complex(specific resistance $\rho$ =2.3 $10^3$ ohm.cm,with activation energy $E_a$=0.11ev*)

*)I.F.Shchegolev,L.I.Buravov(private communication)

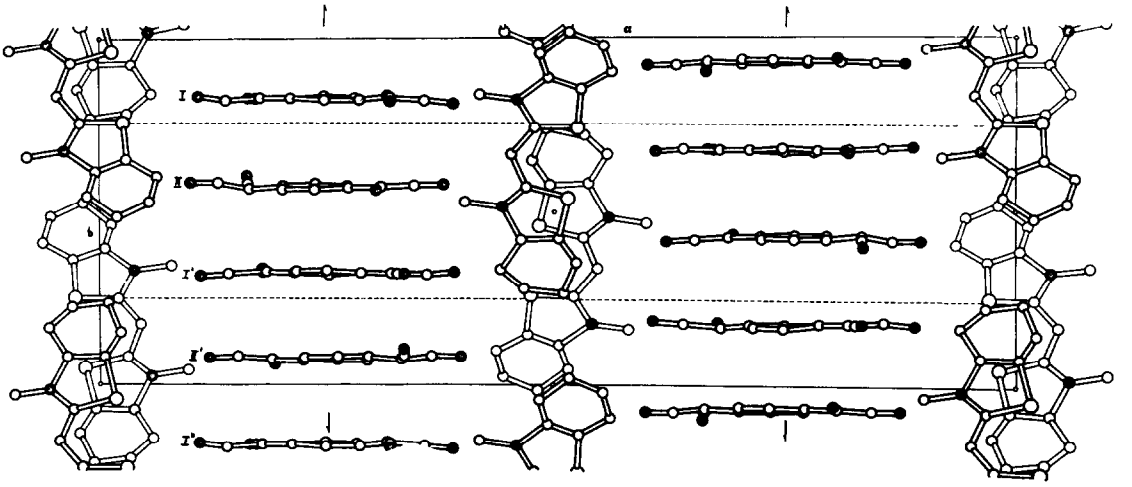


Fig.1 The [001] projection of the structure.

The molecule of the cyanine dye is not planar, the dihedral angle between the planes of the two benzothiazole cycles is 9°40'.

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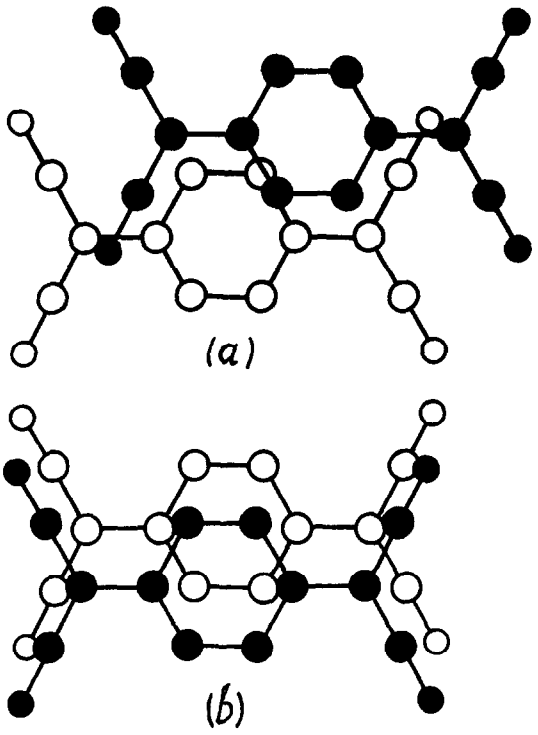


Fig.2 a)Overlapping of adjacent TCNQ molecules 1-11
b)Overlapping of adjacent TCNQ molecules 11-1'