New Organic 'Metals': Naphthaceno[5,6-*cd*:11,12-*c′d′*]bis[1,2]dithiolium Iodides

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Summary The new, *quasi*-1-dimensional organic 'metals,' the naphthaceno[5,6-*cd*:11,12-*c′d′*]bis[1,2]dithiolium (NBDT) iodides, (NBDT)I_x (x = *ca.* 1 and 1·5), have been synthesised and their crystal structures determined.

Recently, an intensive investigation was performed on *quasi*-1-dimensional organic 'metals' containing anion-radical stacks.[1–3] However, there is little information on the possibility of creating high conductivity metal-type systems on the basis of cation-radical chains only.

It is known that naphthaceno[5,6-*cd*: 11,12-*c′d′*]bis[1,2]-dithiole (NBDT) is a powerful donor which forms cation radical salts with different types of anions.[4,5] We have investigated the interaction of NBDT with iodine in nitrobenzene with different proportions of the initial reagents, and single crystals of two phases, (NBDT)I_x (x = *ca.* 1; **1**) and (x = 1·5; **2**) have been isolated as thin dark-green needles with a metallic lustre.

Crystal data: (**1**), $(C_{18}H_8S_4)_4I_4$, M = 1917·7, a = 13·036(2), b = 16·435(2), c = 14·582(2) Å, α = 90°42′(3), β = 83°49′(3), γ = 88°53′(3), Z = 2, D_c = 2·06 g cm^{-3}, space group $C\bar{1}$. The structural model was found by two-dimensional projection. 239 *hk*0 reflexions were recorded on a DAR-UM diffractometer with Cu-K_α-radiation. The structure was refined by full-matrix least-squares with isotropic temperature factors to R 0·093. Three-dimensional data are now being obtained and three-dimensional refinement is being performed. The existence of parallel stacks of NBDT and I along the c-axis is characteristic of the structure.

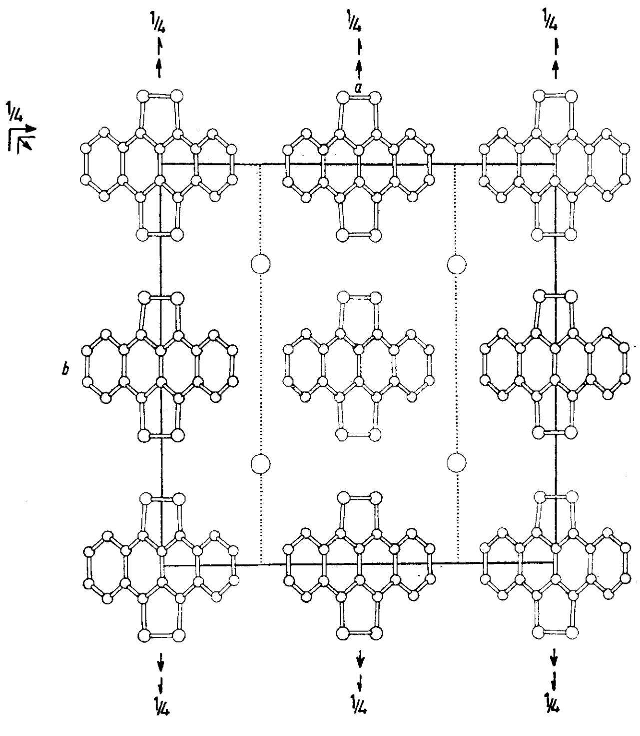

Figure 1. Projection down [001] of structure (**2**).

Crystal data: (**2**), $(C_{18}H_8S_4)_2I_3$, $M = 1085{\cdot}7$, $a = 18{\cdot}464(2)$, $b = 18{\cdot}353(2)$, $c = 9{\cdot}924(1)$ Å, $Z = 4$, $D_c = 2{\cdot}16$ g cm^{-3}. Rotation photographs about the c axis showed strong layer lines with a periodic repeat length of 4·962 Å, and diffuse streaks with a repeat distance of $c = 9{\cdot}924$ Å.

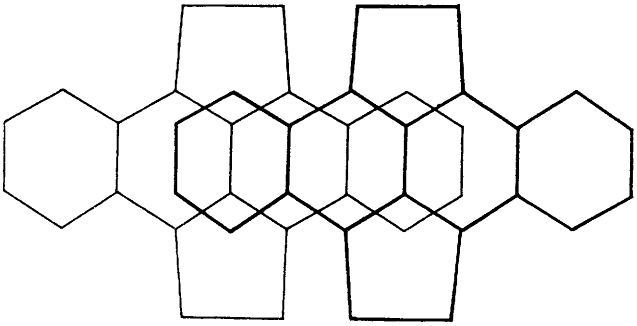

Figure 2. Overlapping of two NBDT molecules in the stack.

Detailed analysis of the crystal structure was performed in the strong subcell II: $a' = a$, $b' = b$, $c' = c/2 = 4{\cdot}962$ Å, $Z = 4$, $(\text{NBDT})I_{1{\cdot}5}$, space group $Ac2a$. A total of 632 reflections with $I \geqslant 3\sigma(I)$ were measured on a DAR-UM computer-controlled diffractometer with graphite-monochromatized Cu-K_α radiation. The structure was determined by Patterson synthesis and was refined by full-matrix least-squares with anisotropic temperature factors to R 0·055. The crystal structure viewed down the c axis is shown in Figure 1. There are the same number of NBDT and I stacks in the structure. NBDT molecules are situated on the crystallographic two-fold axis; their planes are parallel to the $(\bar{4}01)$ plane and make an angle of 42° with the (001) direction. All the NBDT–NBDT interplanar spacings in the stack are identical, 3·32 Å; this distance is substantially shorter than those in known NBDT and tetrathiafulvalene complexes.[4,6,7] The molecular overlap in the columnar stacking of the NBDT molecules is shown in Figure 2. Iodine chains are arranged in channels between the NBDT stacks. The existence of diffuse lines on the rotation photographs may be accounted for by one-dimensional ordering of the iodine chains.

The conductivity of single crystals of (**1**) along the c-direction is 30—70 Ω^{-1} cm^{-1} at room temperature for seven samples examined. On lowering the temperature the conductivity changes little down to *ca.* 200 K, then it falls rapidly.

The room temperature conductivity of crystals of (**2**) along the c-axis is very high, 600—1200 Ω^{-1} cm^{-1} for six samples examined. On lowering the temperature the conductivity increases considerably down to *ca.* 50 K but then begins to fall. Such high values of the conductivity have been observed previously only for the salts of tetracyanoquinodimethane with tetrathiafulvalene and its selenium analogue.[2,8]

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