SYNTHESIS AND PROPERTIES OF A HEXADECYL DERIVATIVE OF BIS(ETHYLENEDITHIO)TETRATHIAFULVALENE (HEXADECYL BEDT-TTF)

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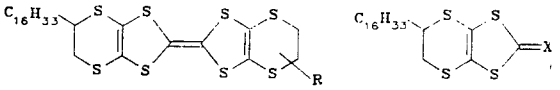
The discovery of superconductivity in bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) cation-radical salts at temperatures of 1.2-11°K has prompted the synthesis of a number of compounds of this type. At the same time, considerable advances have been made in the development of conductive Langmuir-Blodgett films using organic ion-radical salts (see conference proceedings [1]). We have now obtained for the first time an analog of BEDT-TTF containing a long-chain substituent, viz., hexadecyl BEDT-TTF (I).



I, IV II, III

I R=H, IV R=$C_{16}H_{33}$; II X=S, III X=O

Polymeric 1,3-dithio-2,4,5-trithione reacts with 1-octadecene as described in [2] to give 4,5-hexadecylethylenedithio-1,3-dithiol-2-thione (II) [mp 72-73°C (from hexane), IR spectrum: 2952, 2920, 2848, 1060, 1040, 720 cm^{-1}], which reacts with mercury acetate as described in [3] to give the 2-oxo-compound (III) [yield 50%, mp 56-57°C (from alcohol). IR spectrum: 2950, 2924, 2852, 1618, 720 cm^{-1}].

A solution of 1.38 mmole of the oxo-compound (III) and 1.73 mmole of 4,5-ethylenedithio-1,3-dithiol-2-one [3] in 20 ml of triethyl phosphite was boiled under argon for 2 h, cooled, and 90 ml of ethanol added to precipitate a mixture of (I), (IV), and BEDT-TTF (yield 78%). The mixture was dissolved in benzene, filtered from the insoluble BEDT-TTF, and chromatographed on a column of silica gel (eluent hexane-chloroform, 2:1) to give 13% of (I) (orange plates from hexane, mp 92-93°C) and 10% of (IV) (orange crystals from hexane, mp 109-110°C). Compounds (I) and (IV) were readily soluble in benzene and chloroform, sparingly soluble in acetonitrile, and insoluble in alcohol. The UV spectra of (I), (IV), and BEDT-TTF were identical. Cyclic voltammetry showed definite differences in the electron-donor properties of (I) and BEDT-TTF, evidently owing to the different extents of solvation of these compounds and the corresponding cation-radicals and dications. For example, in acetonitrile solution, for (I) E_1^{Ox} = 0.63; E_2^{Ox} = 0.90; E_2^{Red} = 0.81; E_1^{Red} = 0.51 V, and for BEDT-TTF 0.56, 0.87, 0.81, and 0.51 V respectively. In benzonitrile solution, for (I) E_1^{Ox} = 0.59; E_2^{Ox} = 0.89; E_2^{Red} = 0.71; E_1^{Red} = 0.40 V; for BEDT-TTF, 0.61, 0.93, 0.86, and 0.56 V (relative to s.c.e., glass-graphite electrode).

LITERATURE CITED

1. Thin Solid Films, 160, Nos. 1-2 (1988).
2. O. Ya. Neiland, Ya. Ya. Katsens, and Ya. N. Kreitsberga, Author's Cert. (USSR), No. 1,428,753; Byull. Izobret., No. 37 (1988).
3. K. Hartke, T. Kissel, J. Quante, and R. Matusch, Chem. Ber., 113, 1898 (1980).

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