SYNTHESIS OF BIS(o-XYLYLENEDITHIO)TETRATHIAFULVALENE

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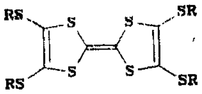
UDC 547.738'895:542.953.5.07

Radical-cation salts of tetrathiafulvalenes have the properties of metals and superconductors [1]. Condensed heterocyclic tetrathiafulvalenes with five-, six-, and seven-membered dithiaheterocycles (I-III) have now been obtained:

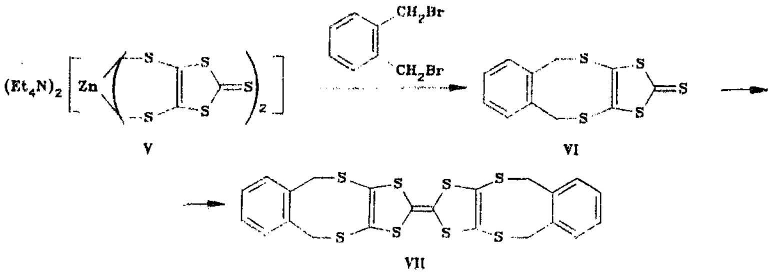


I-IV

I $R{-}R{=}CH_2$; II $R{-}R{=}(CH_2)_2$; III $R{-}R{=}(CH_2)_3$; IV $R{=}Me$

The change of the geometry of the heterocycle condensed with the tetrathiafulvalene system leads to a change of the type of intermolecular interactions in crystals of radical-cation salts, which, in its turn, determines their electrophysical properties [2].

We obtained bis(o-xylylenedithio)tetrathiafulvalene (VII), tetrathiafulvalene with condensed eight-membered dithiaheterocycles, by condensation of tetraethylammonium bis(2-thioxo-1,3,-dithiolo-4,5-dithiolato)zincate (V) with o-xylene dibromide and subsequent dimerization of the resulting dithiolo-2-thione VI [68% yield, mp 206-208°C (from dioxane). IR spectrum (KBr): 1046 cm^{-1} (C=S)] in trimethyl phosphite with boiling:



The yield of compound VII was 50%, mp 270°C (with decomposition, from pyridine). IR spectrum (KBr): 1625 (C=C), 753 cm^{-1} ($S_2C{=}CS_2$). UV spectrum (1,1,2-trichloroethane), λ_{max}, nm (log ε): 275 (4.04), 340 (4.09), 380 (3.70), 408 (3.11). Mass spectrum, m/z: 536 (M^+), 312, 224, 190.

The elemental analysis of compounds VI and VII corresponded to the calculated analysis.

In the series of compounds I-IV, with ring expansion (decrease of angular strain), hypochromic shift of the long-wave absorption band occurred: 542 (I, CH_2Cl_2 [3]), 467 (II), 400 (III), 378 pL (IV). Compound VII, with an eight-membered ring, occurs in this series between compounds with six- and seven-membered rings. Such a shift of the absorption band indicates the expansion of the highest occupied molecular orbital of the system, with a greater contribution of sulfur atoms in the 4 and 5 positions, with the decrease in ring size [4, 5].

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Branch Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka 142432. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 855-856, June, 1986. Original article submitted November 12, 1985.