TRICYANOMETHANIDES OF CATION–RADICAL SALTS OF DERIVATIVES OF TETRATHIAFULVALENE AND TETRATHIOTETRACENE

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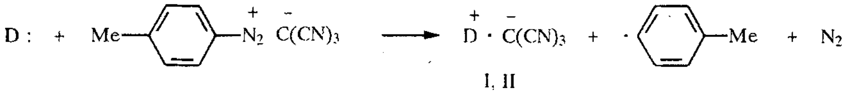
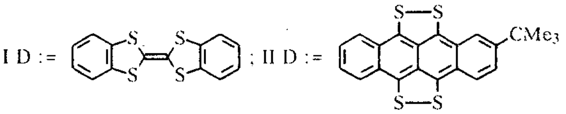
In the preparation of new organic metals and superconductors among the cation–radical salts of tetrathiafulvalene derivatives the method of electrocrystallization has been largely used [1, 2]. We have shown previously [3] that arenediazonium salts can be used with advantage as one-electron oxidants in the preparation of cation–radical salts of strong electron donors. Employing this method, and using 4-methylbenzenediazonium tricyanomethanide as oxidant, we have prepared for the first time, for the examples of dibenzotetrathiafulvalene and 2-(tert-butyl)tetrathiotetracene, the tricyanomethanides of cation–radical salts by a straightforward chemical route





The electron spectra of the salts prepared show characteristic absorption for the corresponding cation–radicals [3].

4-Methylbenzenediazonium tricyanomethanide was prepared by the reaction of 4-methylbenzenediazonium salts and tricyanomethanide; this will be the subject of a separate communication.

A solution of 0.5 mmole 4-methylbenzenediazonium tricyanomethanide in 1 ml acetonitrile was added, dropwise with stirring, to a solution of 0.5 mmole dibenzotetrathiafulvalene in 20 ml dry benzene. The precipitate was filtered off and washed with benzene and ether to give a 52% yield of dibenzotetrathiafulvalene tricyanomethanide (I). IR spectrum (cm^{-1}): $\nu_{C\equiv N}$ 2156 (72); 2176 (88). UV spectrum in dichloroethane in the 400-800 nm range [λ_{max} nm (ε)]: 425 (9700); 446 (10172); 514 (inflection); 644 (6941).

The tricyanomethanide of 2-(tert-butyl)tetrathiotetracene (II) was prepared in a similar manner. Yield 61%. IR spectrum (cm^{-1}): $\nu_{C\equiv N}$ 2164. UV spectrum in dichloroethane in the 400-800 nm range [λ_{max} nm (ε)]: 469 (9660); 547 (inflection); 586 (14956).

The results of elemental analyses for compounds I and II were in agreement with those calculated.

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