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Benzo-1,3,2-Dithiazol-2-YL and its Derivatives: A New Class of Donor Molecules for Highly Conducting Charge Transfer Complexes

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BENZO-1,3,2-DITHIAZOL-2-YL AND ITS DERIVATIVES: A NEW CLASS OF DONOR MOLECULES FOR HIGHLY CONDUCTING CHARGE TRANSFER COMPLEXES

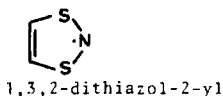
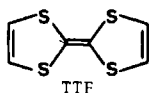
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Abstract Benzo-1,3,2-dithiazol-2-yl and its derivatives form charge transfer complexes with tetracyanoquinodimethane; their powder conductivities are as high as $3 \Omega^{-1} \text{ cm}^{-1}$.

INTRODUCTION

Among the wide variety of conducting charge transfer complexes, TTF·TCNQ is one of the best known compounds. Chemical modifications of the donor were achieved either by introducing substituents in 4,4',5,5' position or by exchange of the sulfur atoms by other chalcogen atoms¹. Replacement of the central carbon by nitrogen atoms would lead to "azaanalogue" TTF which is expected to be non-planar. In addition the N-N single bond should be cleaved by oxidation.

The monomer 1,3,2-dithiazol-2-yl² is expected to meet the basic requirements for a building block in conducting CT complexes such as planarity and size and may also have an appropriate redox-potential. As a test of this assumption we prepared the easily accessible benzo- and methylbenzo derivatives of this heterocycle³. The synthesis of CT complexes formed by this new class of persistent free radicals will be presented in this paper together with the results of cyclic voltammetry and conductivity measurements.



SYNTHESIS

The synthetic pathway which permits convenient entry into this novel donor system³ is illustrated in Figure 1.

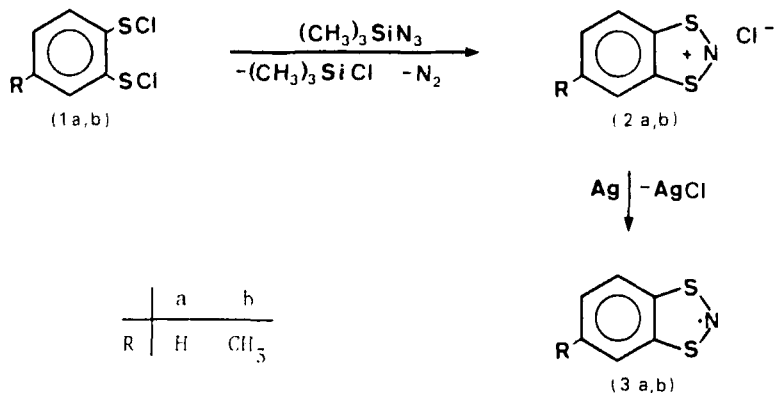


FIGURE 1 Synthesis of Benzo-1,3,2-dithiazol-2-yl derivatives

The central step in the synthesis is the selective reaction of 1 a, b with trimethylsilylazide to give yellow salts 2 a, b. Crystals of these compounds can be obtained by carrying out the reactions in a diffusion cell.

Highly conducting TCNQ complexes of these novel donors were prepared via three different routes (Figure 2).

Route (A) affords mixing of acetonitrile solutions of 3 a, b and TCNQ, route (B) mixing of water solutions of 2 a, b and LiTCNQ together. The electrocrystallization method (route C) involves the application of an electric current (5μA, 0.15 V) to a 1:1 acetonitrile mixture of 2 a, b and TCNQ in an electrochemical cell. Clusters of small shiny black crystals were harvested at both platinum electrodes in the course of a few days. However, single crystals, suitable for x-ray structure determination and conductivity measurements have not so far been obtained. All reactions yielded virtually identical substances with satisfactory elemental analy-

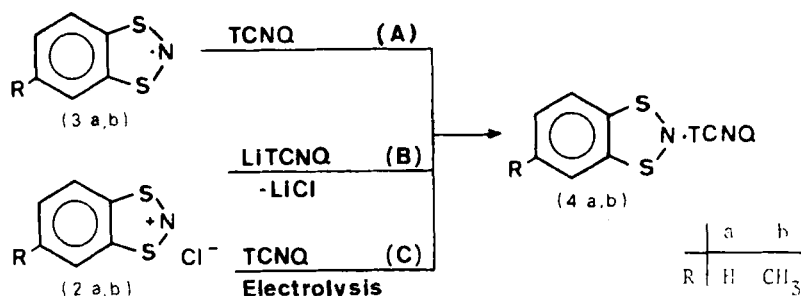


FIGURE 2 Synthesis of charge transfer complexes

sis data.

PROPERTIES

The results of the conductivity measurements of BDTA·TCNQ (4 a) and MBDTA·TCNQ (4 b) are compared with TTF·TCNQ⁴ in Table I.

TABLE I Pressed powder conductivities (measured by four probe technique) at 300 K for 4 a, b and TTF·TCNQ.

	(4 a)	(4 b)	TTF·TCNQ
σ ($\Omega^{-1} \text{ cm}^{-1}$)	1.1	3	10

Cyclic voltammetry shows the peak reduction potentials to be approximately 0.1 eV lower than the value of TTF (0.31 eV). They are well within the limits given by Torrance for mixed valence CT complexes⁴.

On the basis of these results we suggest segregated stacking of donors and acceptors and incomplete charge transfer between these species is likely. Some additional hints about the degree of charge transfer can be gained from the IR-spectra of the powdered

samples dispersed in KBr. A band centered at ca. 2900 cm^{-1} may be ascribed to a mixed valence charge transfer transition, characteristic of salts such as TTF-TCNQ which exhibit incomplete charge transfer.

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