Highly Conducting Charge Transfer Complexes of Benzo-1,3,2-dithiazol-2-yl and Its Derivatives with Tetracyanoquinodimethane

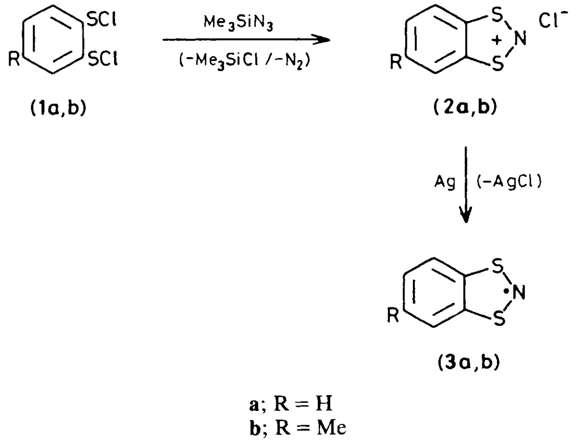
Gotthelf Wolmershäuser,* Martin Schnauber, and Thomas Wilhelm

Fachbereich Chemie der Universität Kaiserslautern, Erwin-Schrödinger-Strasse, D-6750 Kaiserslautern, Federal Republic of Germany

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

The intense search for new highly conducting 'organic metals' has led to a wide variety of charge transfer complexes based on tetracyanoquinodimethane (TCNQ) as acceptor.[1] A comparison of the best donors shows most of them [*e.g.* tetrathiafulvalene (TTF), hexamethylenetetraselenafulvalene (HMTSF), tetrathiotetracene (TTT)] to contain flat five membered heterocycles with two chalcogen atoms. To sustain this basic feature two chemical variations are feasible: introduction of substituents or exchange of ring atoms.

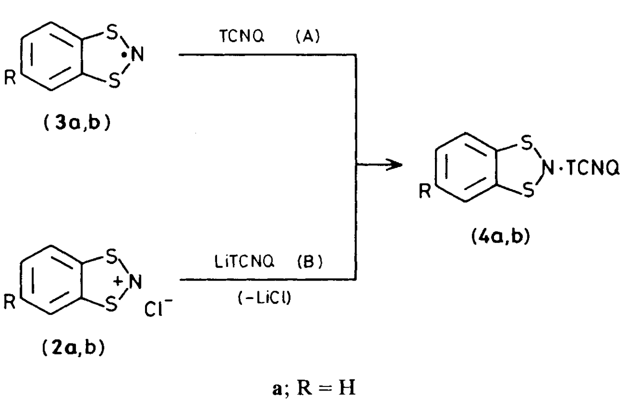
We report a simple and versatile synthesis of benzo-1,3,2-dithiazol-2-yl (BDTA) derivatives containing a five membered C_2S_2N ring skeleton (Scheme 1). The first step in the synthesis is the selective reaction of the benzene-1,2-disulphenyl chlorides (**1a, b**) with trimethylsilylazide to give the benzo-1,3,2-dithiazolium chlorides (**2a, b**) respectively. These reactions were carried out at 0 °C in dichloromethane. The yellow compounds (**2a, b**) precipitated in almost quantitative yields as analytically pure solids. The salts, with naphthalene-like odour, are insoluble in nonpolar solvents but readily soluble in protic polar solvents, *e.g.* water or alcohols. The i.r., and ^1H and $^{13}C\{^1H\}$ n.m.r. spectra are consistent with the proposed symmetric ionic structures. Isomerization to give benzo-1,2,3-dithiazolium salts[2] (Herz compounds) was not observed.



a; R = H
b; R = Me

Scheme 1

In the second step (**2a, b**) were reduced with silver powder in acetonitrile at room temperature to give the corresponding radicals (**3a, b**). Evaporation of the solvent and repeated recrystallization from pentane yielded thin golden, lustrous platelets or needles [(**3a**)] or black crystals [(**3b**)]. These air



a; R = H
b; R = Me

Scheme 2

sensitive compounds dissolve readily in nonpolar solvents to form red solutions.

The e.s.r. spectra of (**3a, b**) consist of 1 : 1 : 1 triplets with almost no hyperfine splitting due to spin coupling with the aromatic protons. Thus most of the spin density seems to be localized on the heterocyclic five membered ring. The g-factors and coupling constants ($g = 1.990$—2.003; $a^N = 1.101$—1.150 mT) agree well with those reported for 2,3-norbornyl-1′,3′,2′-dithiazolidin-2′-yl and similar compounds.[3,4] In contrast to comparable open chain radicals, *e.g.* $(PhS)_2N$,[5] (**3a, b**) exhibit no tendency to dimerize on evaporation of the solvent.

Highly conducting TCNQ complexes of these novel donors were prepared *via* two different routes (Scheme 2). Route (A) involved mixing acetonitrile solutions of (**3a, b**) and TCNQ together at room temperature. In reaction (B) the laborious isolation of (**3a, b**) was avoided: solutions of (**2a, b**) and LiTCNQ in water were mixed together at 20 °C. In both reactions (A) and (B) 1 : 1 complexes [(**4a, b**)] precipitated as blue–black solids which were washed with the corresponding solvent and dried *in vacuo*. Both reactions yielded virtually identical substances with satisfactory elemental analysis data. The pressed powder conductivities of the complexes (**4a, b**) are 1.1 and 3.0 Ω^{-1} cm,† respectively, compared with that reported for TTF–TCNQ of 10 Ω^{-1}/cm.[6]

Single crystals for an X-ray structure determination have so far not been obtained. However, we think there are separate areas of stacking of donors and acceptors within these crystals with incomplete charge transfer between these species. Some idea of the degree of charge transfer is given by the i.r. spectra of the powdered samples dispersed in KBr. A broad band centred at *ca.* 2900 cm^{-1} may be ascribed to a mixed valence charge transfer transition,[7] characteristic of salts such as TTF–TCNQ which exhibit incomplete charge transfer.

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