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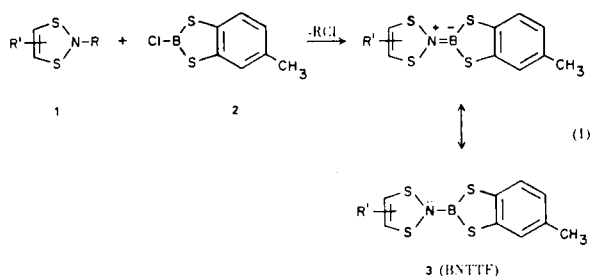
The novel heterocycles 5-methyl-1,3,2-benzodithiazoles (**7**) were prepared in 30-50% yields from toluene-3,4-dithiol (**6**) and appropriate primary amines in the presence of 2 equivalents of triethylamine under high-dilution conditions. These compounds, which exhibit one reversible oxidation potential around +0.90 V vs. SCE, serve as a model study in the quest of synthesizing a new donor, the "boron-nitrogen" analog of tetrathiafulvalene (BNTTF).

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The heterocyclic 1,3,2-dithiazole system **A** is electronically equivalent to a 1,3-dithiole carbanion of the type **B**.

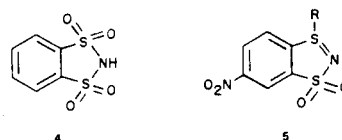


One can envisage that, in the presence of a suitable Lewis acid such as 5-methyl-1,3,2-benzodithiaborole (**2**) (1), a properly substituted 1,3,2-dithiazole **1** could react according to equation 1 to produce the unknown "boron-nitrogen"-tetrathiafulvalene **3** (BNTTF). This class of compounds is of interest because it is isoelectronic to TTF whose charge-transfer salts with TCNQ have been



known to display interesting metallic characteristics (2). Furthermore, Dewar (3) reported that a boron-nitrogen bond, in many aspects, is analogous to the carbon-carbon double bond, exhibiting similar physical and chemical properties. We now report, as model studies, the synthesis and properties of the novel heterocycle 5-methyl-1,3,2-benzodithiazole **7**.

In the early literature there are reported only two types of compounds bearing a similar ring system, *i.e.*, **4** (**4**) and **5** (**5**). Both of these compounds, however, are sulfonamides which have higher oxidation states than **7**,



and their methods of preparation are inapplicable to our system. Our successful approach toward the synthesis of **7** is shown in equation 2.

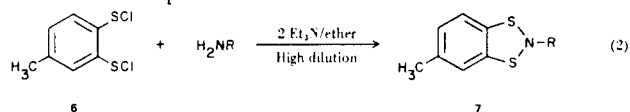


Table I

Synthesis of 5-Methyl-1,3,2-benzodithiazoles (**7**)

Compounds	R	C	Calcd. %			C	Found %			M.p. °C	% Yield
			H	N	S		H	N	S		
<b>7a</b>	Phenyl	63.7	4.5	5.7		63.3	4.7	5.6		87-89	33
<b>7b</b>	Benzyl	64.8	5.1	5.4		64.7	5.0	5.6		75.0	58
<b>7c</b>	<i>tert</i> -Butyl	58.6	6.7	6.2		58.7	6.5	6.0		Oil (a)	53
<b>7d(c)</b>	Anisyl	61.1	4.8	5.1	23.3	61.0	4.5	5.0	23.6	52-54	38
<b>7e(b)</b>		66.3	3.9	7.7	17.7	66.1	3.9	7.8	17.4	285-290	24
<b>7f</b>		55.6	3.3	9.3		55.4	3.7	9.7		161.6	27

(a) Purified by column chromatography, silica gel (benzene:hexanes = 2:1). (b) Reaction was run in THF and ether (v/v = 2:3). (c) This compound appears to be light sensitive.

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Toluene-3,4-disulfonyl chloride (**6**) was conveniently prepared by passing chlorine through a cooled solution ( $-20^{\circ}$ ) of toluene-3,4-dithiol in carbon tetrachloride (**6**). Slow addition of an ether solution of **6** to a cooled ( $-10^{\circ}$ ), well-stirred ether solution of an appropriate primary amine in the presence of 2 equivalents of triethylamine under high-dilution conditions (**7**) yielded the desired 1,3,2-dithiazole **7** in about 30-50% yield. The structures of **7** (**a-f**) are fully supported by their nmr spectra, mass spectra, and elemental analyses (Table I). These compounds **7a-e** exhibit one reversible oxidation potential around  $E^{\circ} = +0.9$  V (vs. SCE in methylene chloride with tetrabutylammonium fluoroborate as the supporting electrolyte). Two irreversible oxidation potentials around  $E_p = +1.3$  V and  $+2.0$  V are also observed (Table II). No oxidation or reduction, however, was observed on a platinum electrode for compound **7f**. The reversible oxidation

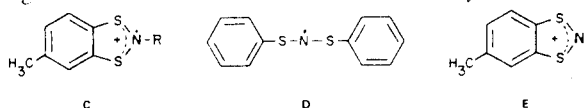
Table II

Oxidation Potentials (Volts) of 5-Methyl-1,3,2-benzodithiazoles (**7**)

Compound	Solvent	I (a) $E^{\circ}$	II (b) $E_p$	III (b) $E_p$
<b>7a</b>	$\text{CH}_2\text{Cl}_2$	+0.92	+1.39	+2.18 (S) (c)
<b>7b</b>	$\text{CH}_2\text{Cl}_2$	+0.93	+1.27	
<b>7c</b>	$\text{CH}_3\text{CN}$	+0.72	+1.05	
<b>7d</b>	$\text{CH}_2\text{Cl}_2$	+0.86	+1.39	+1.89
<b>7e</b> (d)	$\text{CH}_3\text{CN}$	+0.90	+1.31	+1.52

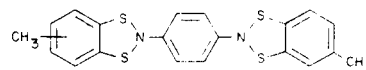
(a)  $E^{\circ}$  = The potential midpoint between forward and reverse peaks for reversible system. (b)  $E_p$  = The peak potential of the cyclic voltammogram for irreversible system. (c) S = Shoulder wave. (d) An irreversible potential at  $-1.55$  V was also recorded.

step presumably is due to the one-electron process forming the stabilized radical cation **C**. Recently, a stable nitrogen-centered radical, dibenzenesulfonamidyl radical **D**,



was reported through esr studies to have a life of a week in nonpolar solvents (**8**). It is of interest to note that the mass spectra of 5-methyl-1,3,2-benzodithiazoles (**7a-7f**) all exhibit a common intense ion of  $m/e$  168 ( $\text{C}_7\text{H}_6\text{NS}_2$ ), for which we proposed the structure **E**, presumably formed by the fragmentation of their corresponding molecular ions of the structure **C**.

Attempts to prepare other derivatives using formamide, triphenylmethylamine, *p*-nitroaniline, 2-aminothiazole, *N*-aminophthalimide, and hydrazine were not successful. Upon treating *p*-phenylenediamine with **6** in THF and ether under the same conditions, we isolated an insoluble reddish crystalline product in 28% yield, m.p.  $295-300^{\circ}$  (benzene:hexanes), to which we assigned the structure **8** on the basis of its  $^1\text{H}$ -nmr spectrum ( $\text{DMSO-d}_6/\text{TMS}$ )  $\delta$  2.3 (s, 3H,  $\text{CH}_3$ ) and 6.7-7.5 (m, 10H, ArH) and mass spectrum:  $m/e$  412,  $\text{M}^+$  for  $\text{C}_{20}\text{H}_{16}\text{N}_2\text{S}_4$  (with thermal decomposition). A good elemental analysis, however, was not obtained for this compound even after repeated recrystallization.



## EXPERIMENTAL

Melting points (uncorrected) were obtained on a Mettler FPI instrument and a Thomas-Hoover capillary melting point apparatus. Nmr spectra were recorded on a Varian T-60 spectrometer using tetramethylsilane as internal standard. Uv spectra were recorded on a Cary-17 spectrophotometer. Mass spectra were obtained on a Hitachi RMS-1 mass spectrometer. Cyclic voltammograms were obtained on a Heath Polarography System Model EUW-401. Elemental analyses were done by Analytical Sciences Division, Kodak Research Laboratories. Thin layer chromatography was done on silica gel plates (0.25 mm thick). Toluene-3,4-disulfonyl Chloride (**6**) (**6**).

Chlorine gas was bubbled through a cooled ( $-20^{\circ}$ ) solution of 10 g. of toluene-3,4-dithiol in carbon tetrachloride. When the solution became dark orange, an nmr sample was taken to check the disappearance of the -SH doublet at  $\delta$  3.8. The solvent,

Table III

Spectroscopic Data of 5-Methyl-1,3,2-benzodithiazoles (**7**)

Compound	Formula	Uv (methylene chloride)		Mass	$^1\text{H-Nmr}$ (deuteriochloroform)
		$\lambda$ max (nm)	$\epsilon$		
<b>7a</b>	$\text{C}_{13}\text{H}_{11}\text{NS}_2$	248	21,200	245 ( $\text{M}^+$ ), 168	$\delta$ 2.3 (s, 3H), 6.7-7.4 (m, 8H, arom.)
<b>7b</b>	$\text{C}_{14}\text{H}_{13}\text{NS}_2$	245	30,800	259 ( $\text{M}^+$ ), 168	$\delta$ 2.3 (s, 3H), 3.95 (s, 2H), 6.6-7.2 (m, 8H, arom.)
<b>7c</b>	$\text{C}_{11}\text{H}_{15}\text{NS}_2$	246	22,300	225 ( $\text{M}^+$ ), 168	$\delta$ 1.2 (s, 9H), 2.3 (s, 3H), 6.8-7.4 (m, 3H, arom.)
<b>7d</b>	$\text{C}_{14}\text{H}_{13}\text{NOS}_2$	247	16,800	275 ( $\text{M}^+$ ), 168	$\delta$ (b) 2.3 (s, 3H), 3.65 (s, 3H), 6.5-7.3 (m, 7H, arom.)
<b>7e</b>	$\text{C}_{20}\text{H}_{14}\text{N}_2\text{OS}_2$	315	35,720	362 ( $\text{M}^+$ ), 168	$\delta$ 2.3 (s, 3H), 6.7-8.2 (m, 11H, arom.)
<b>7f</b>	$\text{C}_{14}\text{H}_{10}\text{N}_2\text{S}_3$	224 (a)	26,600	302 ( $\text{M}^+$ ), 168	$\delta$ (c) 2.2 (s, 3H), 6.8-7.7 (m, 7H, arom.)

(a) In THF. (b) In acetone- $d_6$ . (c) In  $\text{DMSO-d}_6$ .

excess chlorine and hydrogen chloride were stripped under vacuum, and the residue was used directly:  $^1\text{H-nmr}$  (deuteriochloroform):  $\delta$  2.3 (s, 3H), 6.8-7.5 (m, 3H, arom.).

5-Methyl-2-phenyl-1,3,2-benzodithiazole (**7a**).

A solution of 10.0 g. (0.044 mole) of **6** in 75 ml. of ether was added dropwise over 1 hour to a vigorously stirred mixture (cooled to  $-10^\circ$ ) of aniline (4.14 g., 0.044 mole), triethylamine (9.0 g., 0.088 mole), and 500 ml. of anhydrous diethyl ether. The temperature was kept at  $-10^\circ$  for 2 hours, then allowed to warm to room temperature as the tlc showed a disappearance of aniline. After filtration and evaporation of the filtrate the residue was column chromatographed on silica gel, eluting with hexane, to give 3.2 g. (33%) of pure material, m.p.  $87-89^\circ$ .

Other compounds were prepared similarly. Their spectroscopic data are presented in Table III.

Acknowledgment.

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