

Polarography of some 2,1,3-Benzothiadiazoles, Benzofurazans,  
2,1,3-Benzoselenadiazoles, and 3,4-Disubstituted and Fused 1,2,5-Thiadiazoles

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The redox behavior has been determined in acetonitrile solutions at a mercury and platinum electrode for 2,1,3-benzo(group VI)diazoles, and 3,4-disubstituted and fused 1,2,5-thiadiazoles. The derivatives studied contained alkyl, phenyl, bromo, chloro, cyano, nitro, methylsulfonyl, and trifluoromethylsulfonyl groups. All ring systems and their derivatives are reversibly reduced initially in a one-electron step, to their respective radical anion, but the nitro and bromo derivatives are reduced preferentially at the substituent group. The potential at which the production of the radical anion occurred became more anodic as the electron withdrawing ability of the substituent and the number of substituents increased.

Living plants utilize the energy which is made available from oxidation of glucose and other substrates to supply the energy required for cell existence and growth. Energy is made available in a series of controlled oxidation-reduction reactions which synthesize molecules having "high-energy" phosphate bonds. In the oxidative metabolic pathway, a number of chemically diverse oxidation-reduction components serve as electron-transfer agents (mediators) to provide for ATP synthesis. Artificial mediators such as the methyl viologen-methyl viologen cation radical couple (paraquat) can catalyze photosynthetic phosphorylation when added to illuminated chloroplasts in the presence of ADP and inorganic phosphate (4), and in this role may be considered to replace a part of the normal redox system such as ferredoxin. As oxygen is necessary for rapid phototoxic action in light, it would appear that during the re-oxidation of the free radicals very strong fast-acting cell poisons, such as reactive peroxide radicals or hydrogen peroxide, are formed (5) and subsequently disrupt the cell.

Investigations in these laboratories showed that 2,1,3-benzothiadiazole- and benzofurazan-carbonitriles were active as herbicides (6). Since little is known about the mode of herbicidal action of these compounds, a study of their redox behavior was undertaken. Polarography was chosen as a convenient method for determining the formal potentials of these compounds, and for elucidation of the reduction products.

#### EXPERIMENTAL

An ORNL Model 1988-A controlled-potential polarograph (Indiana Instruments and Chemical Corp.) was used to obtain the polarograms at both a dropping mercury and a platinum electrode. A linear voltage sweep rate of 200 mV/minute was used with the mercury electrode and 1000 mV/minute with the platinum. The experiments were carried out in conventional polarographic cells suitable for maintaining an inert atmosphere of nitrogen over the test solution. The temperature of all solutions was maintained at  $25.00 \pm 0.05^\circ$ .

Anhydrous acetonitrile (7) was used as the polarographic solvent and tetraethylammonium perchlorate (8) as the supporting electrolyte for all measurements. Test solutions were prepared in a dry box to maintain the anhydrous condition of the solvent.

The dropping mercury electrode was conventional in design and had the following flow characteristics (m 2/3 t 1/6): 1.57, 1.59, 1.58, 1.48 and 1.38 mg. 2/3 sec  $^{-1/2}$  at 0, -0.5, -1.0, -2.0 and -2.5 volts, respectively. The apparent electrochemical area of the spherical platinum electrode (9) was determined (10,11) to be 0.0134 cm<sup>2</sup>. The estimated accuracy of the electrochemically active area is  $\pm 3\%$ .

A silver/0.1 M silver nitrate in acetonitrile reference electrode was used throughout. The potential of this Ag/Ag<sup>+</sup> electrode with respect to an aqueous saturated calomel electrode was  $+0.353 \pm 0.002$  volts (12). All potentials in this paper are referred to the Ag/Ag<sup>+</sup> electrode.

The heterocyclic compounds used in the present work were prepared according to methods published in the literature.

#### Results.

At the dropping mercury electrode, most of the 2,1,3-benzothiadiazoles behaved in a similar manner. Only nitro

and bromo derivatives gave current-voltage curves that were markedly different from those of other members in the series, and the behavior of these substances is discussed separately. The remaining compounds were reduced in a number of steps. Typical polarograms are shown in Figure 1. The initial reduction wave was well defined and diffusion-controlled in each case, but the reduction waves that occurred at the higher cathodic potentials varied as to number, height, and shape depending on the number and type of substituent. No attempt was made to determine the successive electrochemical reactions which occur during these latter reduction waves since generally these waves were poorly resolved. However, it is evident that the most cathodic waves arise both from the reduction of substituent groups and from electrochemical attack on the ring system itself. S. I. Zhdanov *et al.* (13) report that 2,1,3-benzothiadiazole is reduced at a dropping mercury electrode in dimethylformamide in a stepwise manner. In the second step, five electrons are transferred indicating that this proceeds *via* intermediate formation of *o*-benzoquinone diimine.

The shape of the current-voltage curve for a reversible process when both reactant and product are soluble is given by

$$E = E^{01} + \frac{0.059}{n} \log \frac{f_{ox} D_{red}^{1/2}}{f_{red} D_{ox}^{1/2}} - \frac{0.059}{n} \log \frac{i}{(i_d - i)}$$

where  $i$  is the instantaneous current at potential  $E$ ,  $i_d$  is the diffusion current,  $n$  is the number of electrons transferred,  $E^{01}$  is the formal reduction potential of the redox couple, and  $f$  and  $D$  are the activity and diffusion coefficients of the oxidized and reduced forms, respectively. When the current is one-half the diffusion current, the second log

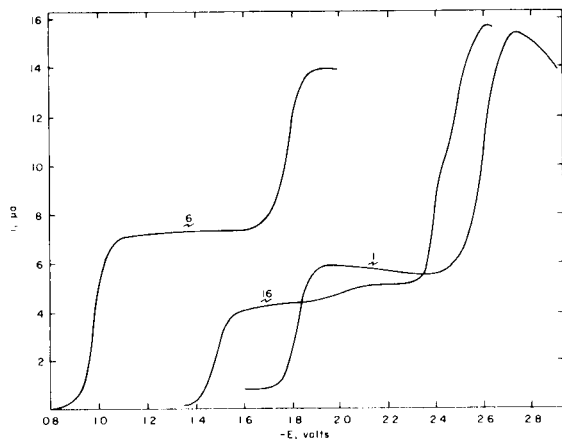


Figure 1 POLAROGRAM OF  $7.34 \times 10^{-4} M$  2,1,3-BENZOTHIADIAZOLE, 4,  $5.66 \times 10^{-4} M$  4,7-DICHLORO-2,1,3-BENZOTHIADIAZOLE, 15, and  $6.87 \times 10^{-4} M$  4,7-DICIANO-2,1,3-BENZOTHIADIAZOLE, 16

term becomes zero; and one obtains the expression for the half-wave potential.

$$E_{1/2} = E^{01} + \frac{0.059}{n} \log \frac{f_{ox} D_{red}^{1/2}}{f_{red} D_{ox}^{1/2}}$$

This equation was used to analyze the initial reduction wave

of a number of 2,1,3-benzothiadiazoles by plotting  $E$  against  $\log\left(\frac{i}{i_d - i}\right)$ . Straight lines were obtained with each compound as illustrated in Figure 2. The values of  $E_{1/2}$  and the slope

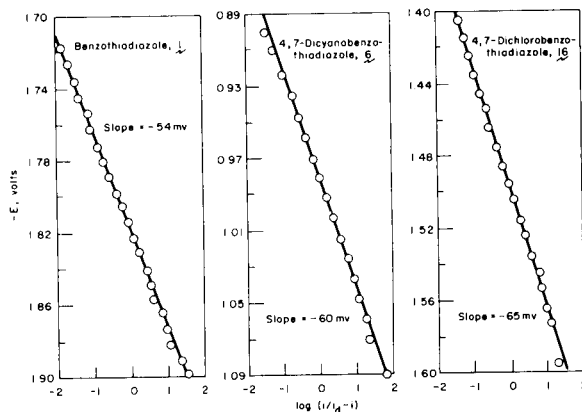


Figure 2  $E$  vs  $\text{LOG}(i/(i_d - i))$  FOR SOME BENZOTHIADIAZOLES

of the lines obtained from such plots are listed in Table I. The slope values indicate that the reduction process involves the reversible addition of one electron with the formation of the anion radical. Reductions of a similar nature have been previously observed for the reduction of aromatic systems (1,4) in aprotic solvents and of benzofurazan, 2,1,3-benzothiadiazole and 2,1,3-benzoselenadiazole in dimethylformamide (13,15) and it has been shown that the electron is added to the lowest lying vacant molecular orbital. Some of the calculated slopes deviate from the expected value of  $-59$  mV by more than the experimental error ( $\pm 2$  mV). The reversibility of these systems was further checked by examining the behavior of the 2,1,3-benzothiadiazoles at a platinum electrode.

Cyclic voltammograms were obtained with the same test solutions used for polarography at the dropping mercury

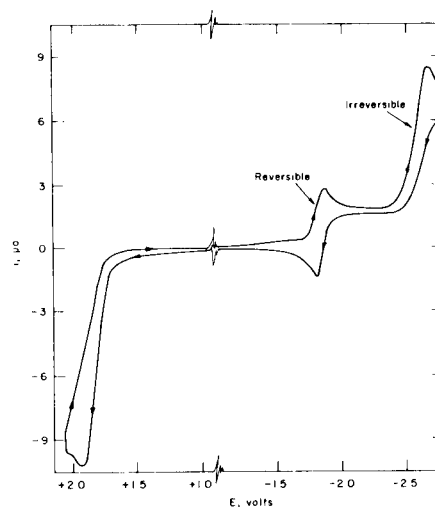
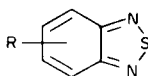


Figure 3 CYCLIC VOLTAMMOGRAM OF BENZOTHIADIAZOLE, 4

Table 1

Comparison of Voltammetric and Polarographic Half-wave Potentials ( $E_{1/2}$ ) for some 2,1,3-Benzothiadiazoles

Compound No.	R	Concentration (M) X 10 <sup>4</sup>	$\langle E_{1/2} \rangle_{\text{red}}$ (volt)	$\langle E_{1/2} \rangle_{\text{ox}}$ (volt)	$\langle E_{1/2} \rangle_{\text{vol}}$ (volt)	$\langle E_{1/2} \rangle_{\text{pol}}$ (volt)	$\langle \text{Slope} \rangle$ (m volt)
<b>1</b>	H	7.34	1.828	1.818	1.823	1.818	54
<b>15</b>	4,6-Cl <sub>2</sub>	4.88	1.685	1.697	1.691	1.686	65
<b>13</b>	4-Cl	11.2	1.653	1.655	1.654	1.645	64
<b>17</b>	5,6-Cl <sub>2</sub>	4.88	1.572	1.564	1.568	1.556	61
<b>16</b>	4,7-Cl <sub>2</sub>	5.66	1.505	1.500	1.503	1.496	65
<b>23</b>	5-CH <sub>3</sub> SO <sub>2</sub>	5.42	1.495	1.484	1.490	1.475	57
<b>18</b>	4,5,6-Cl <sub>3</sub>	5.68	1.453	1.451	1.452	1.445	59
<b>2</b>	4-CN	5.46	1.421	1.422	1.422	1.410	62
<b>19</b>	4,5,7-Cl <sub>3</sub>	4.85	1.412	1.410	1.411	1.394	66
<b>20</b>	4,5,6,7-Cl <sub>4</sub>	4.84	1.328	1.323	1.326	1.311	60
<b>23</b>	5-CF <sub>3</sub> SO <sub>2</sub>	4.93	1.251	1.250	1.251	1.243	62
<b>6</b>	4,7-(CN) <sub>2</sub>	6.87	0.982	0.987	0.980	0.982	60

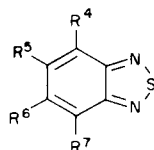
electrode and are illustrated by a typical example in Figure 3. The single irreversible oxidation peak in the region of -2.0 volts was not observed with the 4,7-dicyano, **6**, and 6-trifluoromethylsulfonyl, **24**, derivatives. This oxidation peak also shifted to slightly more positive values as the number of substituents was increased. In general, the reduction peaks paralleled in potential and number the polarographic waves observed at the dropping mercury electrode. However, polarographic waves that occurred at potentials more cathodic than -2.6 volts were not detectable with the platinum electrode. It is readily apparent that reversible processes are distinguished from irreversible ones by an oxidation peak (Figure 3), which occurs in the same potential region as the reduction peak, when the direction of potential sweep is reversed. This oxidation process does not become apparent until the parent compound has first been reduced. Nicholson and Shain (10) have quantitatively treated reversible processes at stationary electrodes. They found that for a completely reversible system the half-wave potential occurs at 85.17% of the way up the reduction or oxidation peak. It was also shown that  $E_{1/2}$  from either the oxidation or the reduction peak should be identical and should be equal to the  $E_{1/2}$  determined with a dropping mercury electrode.

Half-wave potentials were calculated from the reduction and oxidation peaks observed for the initial redox reaction of the 2,1,3-benzothiadiazoles. In Table I,  $E_{1/2}$  obtained from the reduction peak,  $(E_{1/2})_{\text{red}}$ , is compared with that obtained from the oxidation peak,  $(E_{1/2})_{\text{ox}}$ ; and the average of these values,  $(E_{1/2})_{\text{vol}}$ , is also compared with the polarographic half-wave potential,  $(E_{1/2})_{\text{pol}}$ . Although the half-wave potentials obtained from the oxidation and reduction peaks agreed with each other within experimental

error ( $\pm 5$  mV), the agreement between the voltammetric  $E_{1/2}$  and the polarographic  $E_{1/2}$  was only fair. These data indicate that most of the systems are not perfectly reversible; but are much closer to being reversible than irreversible. The correlation of the voltammetric and polarographic half-wave potentials for the 4,7-dicyano analog, **6**, shows that this compound forms the most stable radical anion. Chemical reactions of the radical anion with trace impurities, (water, oxygen, etc.) or with the solvent could give rise to the observed degree of irreversibility.

When the potential of the platinum electrode was held at a value slightly cathodic to the first reduction peak, a discoloration of the solution boundary layer at the electrode interface became evident especially for the more easily reduced 2,1,3-benzothiadiazoles. The color detected was green or a light yellow-green and presumably arose from the formation of the radical anion. Additional evidence to support the production of the radical anion during the reduction process was obtained from the ESR spectrum of the reduction product of **6**. A  $2 \times 10^{-3}$  M solution of **6** was electrolyzed at constant potential with a large mercury cathode. Both the anode and the reference electrode were isolated from the electrolysis solution by fritted glass discs. The dark green solution obtained after electrolysis was stable in the absence of oxygen. When air was brought into contact with the green solution, it rapidly became reddish-brown. The green solution produced a spectrum which was complicated by excessive overlapping of the hyperfine structure from the protons and ring nitrogens. The total breadth of the spectrum was 14.1 gauss which agrees reasonably well with a value of 13.6 gauss calculated from the published splitting constants (16) for 2,1,3-benzothiadiazole, **1**. This is taken as qualitative evidence that the radi-

Table 2  
Comparison of Experimental and Calculated Half-Wave Potentials for 2,1,3-Benzothiadiazoles



No.	R <sup>4</sup>	R <sup>5</sup>	R <sup>6</sup>	R <sup>7</sup>	Reference	-E <sub>1/2</sub> (Volts)		-ΔE <sub>1/2</sub> (Volts)
						Found	Calcd.	
1	---	---	---	---	22	1.818	---	---
2	CN	---	---	---	23	1.410	---	0.408 (a)
3	---	CN	---	---	23	1.460	---	0.358 (a)
4	CN	CN	---	---	23	1.001	1.052	0.817
5	CN	---	CN	---	23	1.066	1.052	0.752
6	CN	---	---	CN	23	0.982	1.002	0.836
7	---	CN	CN	---	23	1.151	1.102	0.667
8	CN	Cl	---	---	(b)	1.287	1.269	0.531
9	CN	Cl	---	Cl	23	1.155	1.096	0.663
10	CN	CH <sub>3</sub>	---	CN	23	1.074	1.081	0.744
11	CN	CH <sub>3</sub>	CH <sub>3</sub>	CN	23	1.147	1.160	0.671
12	---	CH <sub>3</sub>	---	---	24	1.897	---	-0.079 (a)
13	Cl	---	---	---	17	1.645	---	0.173 (a)
14	---	Cl	---	---	17	1.677	---	0.141 (a)
15	Cl	---	Cl	---	25	1.686	1.504	0.132
16	Cl	---	---	Cl	25	1.496	1.472	0.322
17	---	Cl	Cl	---	25	1.556	1.532	0.262
18	Cl	Cl	Cl	---	26	1.445	1.363	0.373
19	Cl	Cl	---	Cl	26	1.394	1.331	0.424
20	Cl	Cl	Cl	Cl	27	1.311	1.190	0.507
21	CO <sub>2</sub> CH <sub>3</sub>	---	---	CO <sub>2</sub> CH <sub>3</sub>	28	1.272	---	0.546
22	---	CF <sub>3</sub>	---	---	26	1.579	---	0.239
23	---	CH <sub>3</sub> SO <sub>2</sub>	---	---	(c)	1.475	---	0.343
24	---	CF <sub>3</sub> SO <sub>2</sub>	---	---	(d)	1.243	---	0.575
25	---	NO <sub>2</sub>	---	---	17	1.137	---	0.681

(a) Values used for calculation of E<sub>1/2</sub>'s. (b) Prepared according to Reference 23; m.p. 173-175°. (c) From corresponding diamine with *N*-thionylaniline; m.p. 116-117°. (d) From corresponding diamine with *N*-thionylaniline; m.p. 97-99°.

cal anion is the major reduction product. The absence of an intense central spectral line was surprising and indicated that there is non-equivalence in one or both pairs of atoms. Possible causes for this non-equivalence are solvent effects or some kind of association in solution.

5-Nitro-2,1,3-benzothiadiazole (17), **25**, gives an initial reduction wave which is reversible at both the dropping mercury and platinum electrodes. A plot of E vs log i/(i<sub>d</sub>-i) was linear with a slope of 60 mV, and E<sub>1/2</sub> was determined to be -1.137 volts. Comparison of the E<sub>1/2</sub> for **25** with the E<sub>1/2</sub>'s of the other compounds in Table 2 shows that **25** is reduced more easily than all the compounds except the dicyano compounds **4**, **5**, **6** and **10**. This value seems very low when one considers the magnitude of shift in E<sub>1/2</sub> brought about by single Cl, CN, CF<sub>3</sub>, CH<sub>3</sub>SO<sub>2</sub> or CF<sub>3</sub>SO<sub>2</sub> substituents. Holleck and Becher (18) have determined that aromatic nitro compounds are initially reduced in a reversible one electron step in acetonitrile or dimethylformamide yielding anion radicals characterized by effective

electron localization on the nitro group. It is suggested that **25** is itself reduced accordingly. The E<sub>1/2</sub> of **25** compares almost identically to those reported by Holleck and Becher for nitrobenzene substituted in the para-position by CN or CHO or in the meta-position by NO<sub>2</sub>. The electron withdrawing ability of these substituents could be expected to approximate that of the heterocyclic ring of the 2,1,3-benzothiadiazoles.

4-Bromo- (19), **26**, and 4,7-dibromo-2,1,3-benzothiadiazoles (19), **27**, differed from other benzothiadiazoles studied in that the initial reduction wave of these compounds was irreversible. Also, for comparable concentration of depolarizer, the initial wave was approximately twice as high. At the dropping mercury electrode, the series of waves for **26** and **27** was poorly defined, but better resolution was obtained with the platinum electrode. The peak potentials obtained at a platinum electrode for **26** and **27** are compared with that of **1** in Table 3. The peak observed at -1.86 to -1.88 volts was reversible for each com-

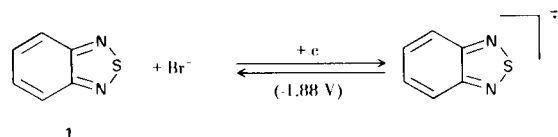
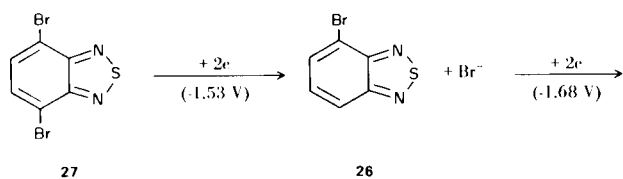


Table 3

Ep For 2,1,3-Benzothiadiazole, **1**,  
4-Bromo-2,1,3-benzothiadiazole, **26**, and  
4,7-Dibromo-2,1,3-benzothiadiazole, **27**

No.	Compound Structure	-Ep (Volts)		
<b>1</b>		1.86		
<b>26</b>		1.88	1.68	
<b>27</b>		1.88	1.68	1.53

found. The following scheme is proposed on the basis of the data in Table 3 for the reduction of **26** and **27**. It has been assumed that the solvent or traces of water present in the solvent serve as a proton source in these reactions.

1,2,5-Thiadiazole, **28**, acenaphtho[1,2-c]-1,2,5-thiadiazole, **33**, and phenanthro[9,10-c]-1,2,5-thiadiazole, **34**, show reversible reduction at potentials more negative than that of 2,1,3-benzothiadiazole, **1** (Table 4), whereas 2,1,3-benzoselenadiazole, **35**, and benzofurazan, **36**, have half-wave potentials slightly more positive than that of **1** (Table 5). The  $E_{1/2}$ 's of the series containing group VI elements, **36**, **1**, and **35**, are anomalous, being different from the order according to electronegativity of the heteroatom. 2,1,3-Benzothiadiazole, **1** ( $E_{1/2} = -1.818$  V), was the most resistant to reduction and 2,1,3-benzoselenadiazole, **35** ( $E_{1/2} = -1.694$  V) the least so. The initial one-electron reduction of both **35** and **36** yielded yellow anion radicals in acetonitrile that in the absence of oxygen were relatively stable.

#### Discussion

The half-wave potentials of the 2,1,3-benzothiadiazoles

Table 4

Half-wave Potentials for other 1,2,5-Thiadiazoles

No.	Group Attached to Basic Structure	Reference	$-E_{1/2}$ (Volts)
<b>28</b>	H H	29	2.52
<b>29</b>	CH <sub>3</sub> CH <sub>3</sub>	29	2.66
<b>30</b>	C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub>	(a)	2.50
<b>31</b>	C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub>	30	2.39(b)
<b>32</b>		31	1.44
<b>33</b>		30	1.44
<b>34</b>		30	1.95

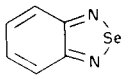
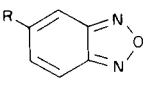
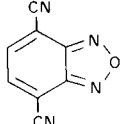
(a) Prepared in 14% yield from 1-amino-1-phenylbutane and S<sub>4</sub>N<sub>4</sub> in refluxing xylene (6 hours); b.p. 70-71° (0.01 mm); nmr:  $\delta$  1.4 (CH<sub>3</sub>), 3.0 (CH<sub>2</sub>), and circa 7.5 ppm (CH=); Anal. Calcd. for C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>S: N, 14.7; S, 16.8. Found: N, 14.7; S, 16.7. (b) With  $-E_{1/2} = 2.17$  volts, the half-wave potential of 2,5-diphenyl-1,3,4-thiadiazole (**32**) is somewhat less cathodic.

(Table 2), 3,4-disubstituted and fused 1,2,5-thiadiazoles (Table 4), and 2,1,3-benzoselenadiazole and benzofurazans (Table 5) became more anodic when either the electron withdrawing ability or the number of substituent groups increased. Addition of electron withdrawing substituents decreased the electron density in the ring systems and, hence, facilitated the addition of an additional electron to the ring systems during the reduction process.

Since half-wave potentials are related to the standard free energy change between the oxidized and reduced forms, a number of linear free energy relationships have been proposed to correlate the shift in half-wave potential

Table 5

Half-wave Potentials of 2,1,3-Benzoselenadiazole and some Benzofurazans

No.	Structure	Reference	$-E_{1/2}$ (Volts)	
35		33	1.694	
36		(R = H)	34	1.780
37		(R = CH <sub>3</sub> )	34	1.855
38		(R = Cl)	35	1.616
39		(R = CN)	36	1.318
40		36	0.802	

with respect to the unsubstituted compound,  $\Delta E_{1/2}$ , with the number and type of substituent (20). More recently the energy of the lowest lying vacant molecular orbital has been directly correlated with the reduction half-wave potentials of carbocyclic aromatic (21a) and nitrogen- and sulfur-containing heterocyclic (21b) systems as well.

For systems having a single polarographically active group to which the substituents are attached, the linear free energy relationship takes the form of a modified Taft equation,

$$\Delta E_{1/2} = \rho^* \cdot \sigma^*$$

where  $\rho^*$  is the reaction constant and  $\sigma^*$  is the Taft substitution constant. The equation is most applicable for substituents without pronounced steric or mesomeric effects. Multiple substitution of the polarographically active group may be correlated with this equation by summing Taft substituent constants for the respective substituents. It was found, however, that the shift in half-wave potentials correlated very poorly with the Taft substituent constants. The large positive deviation observed with the cyano derivatives and the large negative shift observed with 4,6-dichloro-2,1,3-benzothiadiazole, **15**, indicates that the shift in half-wave potentials is not only the result of inductive effects, but also contains a large resonance contribution.

Empirically, it was observed that the shift in half-wave potential could be correlated with the Hammett para-substituent constant for almost the complete series of 2,1,3-benzothiadiazoles (Figure 4). Similar correlations of the para-substituent constant with shift in half-wave potential have been observed for other aromatic systems (21), but the interpretation of such correlations is still questionable because of the manner in which the para-substituent constant is defined and because the "para" constant is

used irrespective of the actual substituent position on the aromatic rings. Qualitatively, the position of the points for the various chlorobenzothiadiazoles parallels that observed with the Taft constants and indicates that the para-substituent constant reflects a predominantly inductive effect. The good correlation of the cyano derivatives, with the exception of the sterically hindered 5,6-dicyano analog, **7**, in Figure 4 suggests that the use of the para-substituent constant has correctly represented the resonance effect of this substituent.

4,6-Dichloro-2,1,3-benzothiadiazole, **15**, exhibited a half-wave potential which was more cathodic than that of 4-chloro-2,1,3-benzothiadiazole, **13**. This was the only compound where increased substitution did not produce a more anodic half-wave potential. The more negative half-wave potential for **15** indicates that the free energy change between the oxidized and reduced forms is greater than that of the other benzothiadiazoles. The increased free energy cannot arise from a steric effect since 5,6-dichloro-2,1,3-benzothiadiazole, **17**, in which the chlorine atoms are vicinal, has a more anodic half-wave potential than 5-chloro-2,1,3-benzothiadiazole, **14**. In 2,1,3-benzothiadiazole, **1**, contributions of mesomeric forms such as A, B, C and D

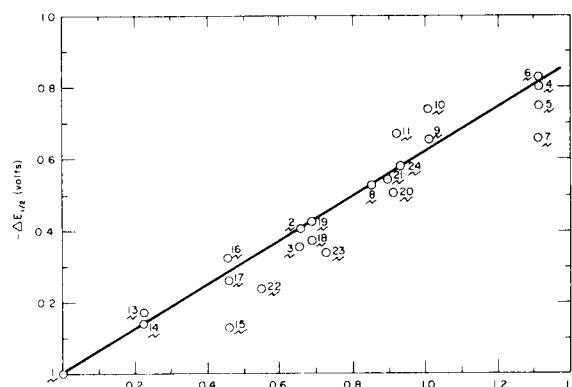
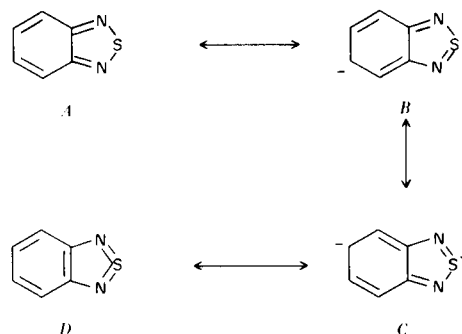
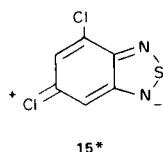


Figure 4  $-\Delta E_{1/2}$  VS SUM OF HAMMETT SUBSTITUENT CONSTANTS FOR 2,1,3-BENZOTHIADIAZOLES LISTED IN TABLE 2

might be important to its overall structure. In placing a chloro group at position 6, where resonance is not influenced by steric effects, as in **15**, it might be predicted that



the mesomeric contribution illustrated by form *B* and *C* would be reduced, causing an increase in free energy.

Group potential increments,  $\Delta E_{1/2}$ 's have been determined for a number of 2,1,3-benzothiadiazoles in Table 2 as follows:  $-(1.818 - E_{1/2} \text{ of compound}) = \Delta E_{1/2}$ . To use this series of  $\Delta E_{1/2}$ 's in the calculation of half-wave potential of the parent compound (-1.818 volts for **1**) was assigned for the group potential of that structure in all of the derivatives. The 4-CN (-0.408 V), 5-CN (-0.358 V), 5-CH<sub>3</sub> (+0.079 V), 4-Cl (-0.173 V), and 5-Cl (-0.141 V), were assigned the respective values, from **2**, **3**, **12**, **13** and **14**, respectively. Then the addition for ring substitution is easily carried out. The results showing the calculated and observed half-wave potentials are found in Table 2. In examining these data, note that the parent molecule is used for a group potential which contains much of the initial electronic distribution. Substitution of the various groups should increase or decrease the stability of various contributing structures such as *A*, *B*, *C* and *D*, and, therefore, should show apparent differences between experimental and calculated half-wave potentials.

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