

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS]

## Reduction Potentials and Electronic Structures of Phenyl-Substituted Borazines

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Reduction potentials were observed at the dropping mercury electrode for a series of borazines in nonaqueous, aprotic solvents (dimethylformamide and glyme). Conventional polarograms and oscillopolarograms for the B-phenylborazines indicate the reductions involve reversible one-electron transfer to form the radical anion. This is followed by first-order decomposition ( $k \sim 40 \text{ sec}^{-1}$ ). On the basis of this information, and by analogy with conjugated hydrocarbons, these reductions are interpreted in terms of the addition of an electron to the lowest empty  $\pi$ -orbital of the borazines. Neither borazine nor benzene could be reduced within the potential range available in our systems; thus reduction of phenylborazines offers a good illustration of extensive conjugation through the borazine group. The order of decreasing ease of reduction is 1,3,5-triphenylbenzene, *m*-terphenyl, biphenyl, B,B',B''-triphenylborazine, B,B'-diphenylborazine, B-phenylborazine, and N,N',N''-triphenylborazine. The relative order of B-triphenylborazine to N-triphenylborazine apparently arises because, unlike the bonding orbitals, the nonbonding orbitals of borazines involve higher probability densities on boron than nitrogen, and this leads to stronger B-C interactions than N-C interactions in the lowest empty MO. Choice of a single parameter (the coulomb integral of boron) leads to good correlation between reduction potentials and calculated energies for the lowest empty molecular orbitals of the borazines. Solvent effects and finer details of the reduction potentials are also discussed.

## Introduction

Maccoll,<sup>1</sup> Hoihtink,<sup>2</sup> Streitwieser,<sup>3</sup> and others<sup>4</sup> have found good correlations between polarographic reduction potentials of aromatic hydrocarbons and MO calculations for the energy of the lowest empty  $\pi$ -orbitals. In view of the simple electrochemical behavior of the hydrocarbons in aprotic solvents, the correlations are not surprising. The first polarographic reduction wave (the one of primary interest) involves rapid, reversible transfer of one electron to the first unfilled molecular orbital of the hydrocarbon to form the anion radical,<sup>1,2,5-11</sup> which is relatively long-lived in aprotic solvents. As a result, the polarographic wave is diffusion controlled, and the half-wave potential essentially is equal to the  $E^0$  value<sup>12</sup> for the hydrocarbon-hydrocarbon anion radical system relative to the reference electrode employed. If solvent effects do not change greatly over the series of compounds under investigation, then the half-wave potentials are simply related to the relative electron affinities for the series of compounds,<sup>3</sup> and this parameter is given by the MO calculations. These successes prompted us to investigate the polarography and molecular orbital description of substituted borazines. A molecular orbital discussion of borazine was first given by Roothaan and Mulliken,<sup>13</sup> who were concerned with its vacuum ultraviolet spectrum. The same problem has been treated more recently by Paris-

er-Parr-Pople self-consistent field calculations.<sup>14</sup> Also, Hückel calculations and approximate perturbation treatments of borazine and similar boron-nitrogen systems have appeared.<sup>15</sup> We are unaware of polarographic studies of borazine and its derivatives.<sup>16</sup>

It is qualitatively well known from thermal stability and reactivity<sup>17</sup> of borazine derivatives that substituent effects are important, and a quantitative treatment of such effects was one goal of this research. A variety of physical evidence<sup>15b,17-20</sup> indicates that borazine is significantly aromatic. However, quantitative measures of this aromaticity are difficult to obtain because the B-N system lacks sufficient simple model compounds like acetylene and ethylene in the carbon series. Therefore, another objective was to obtain quantitative measure of the conjugation for borazine.

For the correlation of energies and half-wave potentials to be valid, reduction of the borazines must proceed nearly reversibly. Also, the change in free energy of solvation upon reduction must not vary greatly over the series of compounds being investigated. In order to ensure reversibility, we chose solvents of very low

(1) A. Maccoll, *Nature*, **163**, 178 (1949).(2) G. J. Hoihtink, *Rec. trav. chim.*, **74**, 1525 (1955).(3) A. Streitwieser, Jr., and I. Schwager, *J. Phys. Chem.*, **66**, 2316 (1962).

(4) For a summary see A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

(5) (a) G. J. Hoihtink, J. van Schooten, E. de Boer, and W. I. Aalbersberg, *Rec. trav. chim.*, **73**, 355 (1954); (b) G. J. Hoihtink, E. de Boer, P. H. van der Meij, and W. P. Weijland, *ibid.*, **75**, 487 (1956).(6) A. Pullman, B. Pullman, and G. Berthier, *Bull. soc. chim. France*, 591 (1950).(7) (a) H. A. Laitinen and S. Wawzonek, *J. Am. Chem. Soc.*, **64**, 1765 (1942); (b) S. Wawzonek and H. A. Laitinen, *ibid.*, **64**, 2365 (1942); (c) S. Wawzonek and J. W. Fan, *ibid.*, **68**, 2541 (1946); (d) S. Wawzonek, E. W. Blaha, and M. E. Runner, *J. Electrochem. Soc.*, **102**, 235 (1955).(8) (a) P. H. Given, *ibid.*, **105**, 2684 (1958); (b) P. H. Given and M. E. Peover, *Collection Czech. Chem. Commun.*, **25**, 3195 (1960).(9) D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).(10) T. L. Chu and S. C. Yu, *ibid.*, **76**, 3367 (1954).(11) A. C. Aten, C. Büthker, and G. J. Hoihtink, *Trans. Faraday Soc.*, **55**, 324 (1959).

(12) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, pp. 55, 56.

(13) C. C. J. Roothaan and R. S. Mulliken, *J. Chem. Phys.*, **16**, 118 (1948).(14) (a) D. W. Daves, *Trans. Faraday Soc.*, **56**, 1713 (1960); (b) O. Chavet, R. Daudel, and J. J. Kaufman, *Advances in Chemistry Series*, No. 42, American Chemical Society, Washington, D. C., 1963, p. 251.(15) (a) J. C. Patel and S. Basu, *Naturwissenschaften*, **47**, 302 (1960); (b) H. Watanabe, K. Ito, and M. Kubo, *J. Am. Chem. Soc.*, **82**, 3294 (1960); (c) M. J. S. Dewar and H. Rogers, *ibid.*, **84**, 395 (1962); (d) R. Hoffmann, *Advances in Chemistry Series*, No. 42, American Chemical Society, Washington, D. C., 1963, p. 78; (e) J. J. Kaufman and J. R. Hamann, *ibid.*, p. 95.(16) D. Chapman, S. H. Glarum, and A. G. Massey (*J. Chem. Soc.*, 3140 (1963)) have mentioned that they obtained polarographic waves for some inorganic heterocyclic compounds but it is unclear whether borazines were studied. These same authors failed to observe e.s.r. spectra for a series of borazines in the presence of K or Na-K. The rather short half-life observed for borazine radical anions in the present study may explain their failure to observe an electron spin resonance signal.(17) (a) H. C. Newsom, W. D. English, A. L. McCloskey, and W. G. Woods, *J. Am. Chem. Soc.*, **83**, 4134 (1961); the following reviews also contain information on substituent effects: (b) L. F. Hohnstedt and G. W. Schaeffer, *Advances in Chemistry Series*, No. 32, American Chemical Society, Washington, D. C., 1961, p. 232; (c) J. C. Sheldon and B. C. Smith, *Quart. Rev. (London)*, **14**, 200 (1960); (d) E. K. Mellon, Jr., and J. J. Lagowski, in "Advances in Inorganic Chemistry and Radiochemistry," Vol. 5, H. J. Emeléus and A. G. Sharpe, Ed., Academic Press, Inc., New York, N. Y., 1963, p. 259.(18) (a) C. W. Rector, G. W. Schaeffer, and J. R. Platt, *J. Chem. Phys.*, **17**, 460 (1949); (b) J. R. Platt, H. B. Klevens, and G. W. Schaeffer, *ibid.*, **15**, 598 (1947); (c) L. Jacobs, J. R. Platt, and G. W. Schaeffer, *ibid.*, **16**, 116 (1948).(19) J. Goubeau, *Advances in Chemistry Series*, No. 42, American Chemical Society, Washington, D. C., 1963, p. 87.(20) (a) K. Ito, H. Watanabe, and M. Kubo, *J. Chem. Phys.*, **34**, 1043 (1961); (b) K. P. Coffin and S. H. Bauer, *J. Phys. Chem.*, **59**, 193 (1955).

proton availability and reactivity—dimethylformamide (DMF) and 1,2-dimethoxyethane (glyme). To check reversibility of the reductions, conventional d.c. polarography was supplemented with oscillopolarography employing triangular wave applied potentials (cyclic voltammetry).<sup>21</sup> We hoped that by the use of two solvents with appreciable polarity differences (dielectric constants: DMF, 37.65; glyme, 3.49) we might detect peculiarities due to variations of  $\Delta G$  of solvation. The use of glyme as a solvent for electrochemical studies has been reported previously.<sup>22,23</sup> It presented significant difficulties which are discussed in the next section. Examination of correlations between polarographic half-wave potentials and MO calculations has never been reported for glyme. While there seemed no reason to expect glyme to differ from other aprotic solvents in this respect, we did examine the polarographic behavior of several aromatic hydrocarbons to ensure that glyme possesses no unusual properties.

### Experimental

Conventional polarograms and oscillopolarograms were obtained with the aid of an all-electronic instrument employing operational amplifier circuitry with a three-electrode configuration. Details of construction and performance of such instrumentation have been discussed at length in the literature.<sup>24-28</sup> This type of electronic polarograph is essential for automatic recording of polarograms with little distortion by ohmic resistance in low conductance solvents such as glyme. The operational amplifier—three-electrode configuration eliminates effects of most of the ohmic resistance in solvent and external circuitry. The only uncompensated ohmic potential drop exists in the solution between the tip of the reference electrode probe and the working electrode. In the work reported here, ohmic potential drop distortion was negligible in dimethylformamide, while in glyme an uncompensated resistance of approximately 10,000 ohms resulted in small, but noticeable, distortion of the polarograms and oscillopolarograms. All data reported for glyme are corrected for this effect.

Readout for conventional polarograms was to a Sargent Model SR recorder. A Tektronix Model 502A oscilloscope was employed as the readout device for the oscillopolarograms with a Tektronix Model C-13 oscilloscope camera providing for permanent recording of "scope" traces. The triangular wave potential source was a Hewlett-Packard Model 202A low frequency function generator. The electrolysis cell was a Sargent Model S-29390. A silver-saturated silver nitrate electrode in the solvent under investigation was employed as reference electrode. The working electrode was a dropping mercury electrode. A platinum wire served as auxiliary electrode. Tetrabutylammonium perchlorate (0.1 M) was used as supporting electrolyte. Preparation of solutions and polarographic experiments were performed in a dry, inert atmosphere glove box for two reasons: (1) dry glyme reacts with atmospheric oxygen with the formation of polarographically reducible peroxides, and (2) borazines display varying sensitivity to the atmosphere. This box and the transfer port were purged with water-pumped nitrogen which was purified by passing it successively through columns of silica gel, magnesium perchlorate, hot active copper, and finally calcium hydride.

Polarograms were run at ambient temperature as thermostating the polarographic cell in the drybox was inconvenient, and the temperature coefficients of the half-wave potentials were insignificant for these studies. Because the laboratory was air conditioned, ambient temperature never varied greatly ( $26 \pm 1^\circ$ ).

Solvent purification in the case of glyme was performed by dehydration with calcium hydride and lithium aluminum hydride, followed by a 16-hr. reflux and a fractional distillation from lithium aluminum hydride through a 5-ft. glass helix-packed column under a dry, oxygen-free nitrogen atmosphere. The distillate collector was designed so that solvent could be collected and removed from the column without exposure to the atmosphere. Dimethylformamide was purified by initial dehydration with calcium hydride followed by distillation from phthalic anhydride at 10 to 15 mm.

Aromatic hydrocarbons were obtained from departmental stock and standard commercial sources. When melting point or color indicated the presence of impurities, the compound was recrystallized twice from ethanol or toluene and then sublimed. Final melting ranges fell within  $1^\circ$  of the reported value(s), and the ranges were  $1^\circ$  or less. Hexaphenylbenzene was prepared by the method of Dilthey and Hurtig<sup>30</sup>; m.p. 415–417° (obsd.), 416–418° and 425° (reported).<sup>29,30</sup>

The borazines were prepared by published methods and purity was checked using melting points (vapor pressure for borazine), infrared spectra, and in some cases X-ray powder patterns. A sample of 1,3,5-trimethylborazine<sup>31</sup> was obtained from Callery Chemical Co., and one sample of 2,4,6-trichloroborazine was kindly donated by the U. S. Borax Research Corp. These compounds were used as received, but other samples were prepared and characterized as indicated by the following references: 2,4,6-trichloroborazine<sup>32</sup>; 1,3,5-triphenyl-2,4,6-trichloroborazine,<sup>33</sup> m.p. 269–270° (reported 273–275°); 1,3,5-triphenylborazine,<sup>33</sup> m.p. 157–158° (reported 160–161°); 2,4,6-triphenylborazine,<sup>34</sup> m.p. 180° (reported 179–182°) (in the synthesis we obtained a 50% yield without the use of triethylamine); 2-phenylborazine,<sup>35</sup> m.p. 72–73° (reported 73–75°); 2,4-diphenylborazine,<sup>36</sup> m.p. ca. 100° (reported 120–122°); and borazine,<sup>33</sup> vapor pressure at 0°, 84.8 mm. (reported 85 mm). Judging from polarograms, the melting point of 2,4-diphenylborazine was depressed by the presence of 2-phenylborazine despite the fact that we employed fractional sublimation and zone melting techniques in the purification. In any case, our X-ray powder patterns and infrared spectra agreed with those of Moews and Laubengayer.<sup>35</sup> Our problem with the purification probably arose from the small size of our sample. Presence of traces of 2-phenylborazine presented no problems in the electrochemistry of 2,4-diphenylborazine because the polarographic waves were easily resolved.

### Calculations

Energy values and coefficients of atomic orbitals were determined on a digital computer. Failure to include overlap may lead to incorrect results with heteroatomic systems, so calculations were carried out for both Hückel and overlap included approximations. In the latter case the secular equation is

$$HC = SCE_d \quad (1)$$

where **H** contains coulomb integrals on the diagonal and resonance integrals as off-diagonal elements, and **S** is the overlap matrix. **C** and **E<sub>d</sub>** are, respectively, the coefficient and energy matrices. In the Hückel approximation **S** = **1** so the diagonal energy matrix and the coefficient matrix are found by diagonalization of **H** by

(21) (a) Z. Galus, H. Y. Lee, and R. N. Adams, *J. Electroanal. Chem.*, **5**, 17 (1963); (b) J. Heyrovsky in "Advances in Polarography," Vol. 1, I. S. Longmuir, Ed., Pergamon Press, New York, N. Y., 1960, Chapter 1.

(22) A. K. Hoffman, W. G. Hodgson, and W. H. Jura, *J. Am. Chem. Soc.*, **83**, 4676 (1961).

(23) D. L. Maricle, W. H. Jura, A. K. Hoffman, and W. G. Hodgson, Division of Analytical Chemistry, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., 1963.

(24) D. D. DeFord, Division of Analytical Chemistry, 133rd National Meeting of the American Chemical Society, San Francisco, Calif., April, 1958.

(25) (a) G. L. Booman, *Anal. Chem.*, **29**, 213 (1957); (b) G. L. Booman and W. B. Holbrook, *ibid.*, **35**, 1793 (1963).

(26) W. M. Schwarz and I. Shain, *ibid.*, **35**, 1770 (1963).

(27) W. L. Underkoffler and I. Shain, *ibid.*, **35**, 1778 (1963).

(28) D. E. Smith, *ibid.*, **35**, 1811 (1963).

(29) R. Breslow and P. Dowd, *J. Am. Chem. Soc.*, **85**, 2729 (1963).

(30) W. Dilthey and G. Hurtig, *Chem. Ber.*, **67**, 2004 (1934).

(31) Numbering of the borazine ring begins on the nitrogen atom.

(32) L. F. Hohnstedt and D. T. Haworth, *J. Am. Chem. Soc.*, **82**, 89 (1960).

(33) S. J. Grosszos and S. F. Stafiej, *ibid.*, **80**, 1357 (1958).

(34) W. D. English and A. L. McClosky, U. S. Patent 3,000,937; *Chem. Abstr.*, **56**, 1479h (1962).

(35) P. C. Moews, Jr., and A. W. Laubengayer, *Inorg. Chem.*, **2**, 1072 (1963).

the Jacobi method.<sup>36</sup> When a nonorthogonal basis set was employed, the Schmidt orthogonalization procedure<sup>37</sup> was first employed to find a matrix  $\mathbf{R}$  such that

$$\mathbf{R}^T \mathbf{S} \mathbf{R} = \mathbf{1}$$

Equation 1 may be multiplied by  $\mathbf{R}^T$  and rewritten

$$\mathbf{R}^T \mathbf{H} \mathbf{R} \mathbf{R}^{-1} \mathbf{C} = \mathbf{R}^T \mathbf{S} \mathbf{R} \mathbf{R}^{-1} \mathbf{C} \mathbf{E}$$

Let

$$\mathbf{R}^T \mathbf{H} \mathbf{R}^{-1} = \mathbf{J} \quad (2)$$

and

$$\mathbf{R}^{-1} \mathbf{C} = \mathbf{U}$$

then

$$\mathbf{J} \mathbf{U} = \mathbf{U} \mathbf{E}_d$$

Transformation 2 is carried out to yield  $\mathbf{J}$  which is then diagonalized by the Jacobi routine to yield energies and the  $\mathbf{U}$  matrix. The coefficient matrix  $\mathbf{C}$  for atomic orbital basis functions is then found by

$$\mathbf{C} = \mathbf{R} \mathbf{R}^{-1} \mathbf{C} = \mathbf{R} \mathbf{U}$$

This program also contained optional charge and bond-order subroutines based on Chirgwin and Coulson's formulation.<sup>38</sup> Provision was also made for iterative adjustment of coulomb integrals by Streitwieser's  $\omega$ -technique. In order to conserve computer time, initial calculations were carried out using symmetry orbital basis functions, and once the "best" fit to experimental energies was obtained, an atomic orbital basis set was employed, and charges and bond orders were determined.

In an effort to explain some of the finer details of our experiments, two additional programs were written. One was based on Hush and Pople's approximate treatment which accounts for electron-electron repulsion.<sup>39</sup> The other was designed to calculate resonance integrals between all B, N, and C  $p_z$  orbitals. These were determined by use of the Wolfsberg-Helmholtz approximation<sup>40</sup>; for this purpose overlap integrals between all atoms were determined by the program using standard formulas based on Slater atomic orbitals.<sup>41</sup> The  $\mathbf{H}$  and  $\mathbf{S}$  matrices generated by this program were used as input for the general molecular orbital program. This procedure closely resembles Hoffmann's "Extended Hückel Theory."<sup>15d, 42</sup>

(36) The Jacobi subroutine was one written by F. J. Corbato and M. Merwin, "Eigenvalues and Eigenvectors of a Real Symmetric Matrix," M.I.T., 1963.

(37) H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., New York, N. Y., 1943, pp. 296-298.

(38) B. H. Chirgwin and C. A. Coulson, *Proc. Roy. Soc. (London)*, **A201**, 196 (1950).

(39) N. S. Hush and J. A. Pople, *Proc. Faraday Soc.*, **51**, 600 (1955).

(40) M. Wolfsberg and L. Helmoltz, *J. Chem. Phys.*, **20**, 837 (1952).

(41) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *ibid.*, **17**, 1248 (1949).

(42) (a) R. Hoffmann, *ibid.*, **39**, 1397 (1963); (b) G. Klopman, *Tetrahedron*, **19**, 111 (1963).

## Results and Discussion

**Electrochemistry.**—Initial assessment of glyme as a solvent was made by examining the polarographic reductions of fifteen hydrocarbons. Conventional polarograms of all hydrocarbons yielded well-formed first reduction waves with both wave heights and linear  $\log(i_d - i)/i$  vs. potential plots<sup>12</sup> of slope 0.06 v. indicative of one-electron reduction. Triangular-wave oscillograms showed that these reductions involve reversible charge transfer with the anion radical stable to chemical decomposition (half-life  $\gg$  mercury drop life). These combined results substantiate that the hydrocarbons are reduced through a diffusion controlled one-electron process. Thus, the polarographic half-wave potential is related to the  $E^\circ$  value for the hydrocarbon-hydrocarbon anion radical oxidation-reduction couple by

$$E^\circ = E_{1/2} - \frac{RT}{F} \ln \left( \frac{f_o}{f_r} \right) \left( \frac{D_r}{D_o} \right)^{1/2} \quad (3)$$

where  $f_o$  and  $f_r$  are activity coefficients of the oxidized and reduced forms, respectively,  $D_o$  and  $D_r$  are their diffusion coefficients, and  $R$ ,  $T$ , and  $F$  have their usual thermodynamic significance. The log term is usually negligible so that the polarographic  $E_{1/2}$  can be taken equal to the  $E^\circ$  value of the oxidation-reduction system, relative to the reference electrode employed. Electrochemical data of interest for these hydrocarbons in glyme, as well as for the borazines, are given in Table I. Some of the hydrocarbons showed second reduction

TABLE I  
POLAROGRAPHIC DATA IN GLYME

Compound	$-E_{1/2}$ , <sup>a</sup> v.	Product decomposition rate, sec. <sup>-1</sup>
B,B',B''-Triphenylborazine	3.33	35 ± 3
B,B'-Diphenylborazine	3.37	48 ± 4
B-Phenylborazine	3.40	39 ± 5
N,N',N''-Triphenylborazine	≥ 3.6	≥ 500
B,B',B''-Trichloroborazine	1.45	Complicated process
B,B',B''-Trichloro-N,N',N''-triphenylborazine	1.75	Complicated process
Azulene	2.21	Negligible
Perylene	2.26	Negligible
Fluoranthene	2.36	Negligible
Anthracene	2.50	Negligible
1,2,5,6-Dibenzanthracene	2.66	Negligible
Pyrene	2.70	Negligible
Chrysene	2.88	Negligible
<i>p</i> -Terphenyl	3.00	Negligible
Phenanthrene	3.01	Negligible
Triphenylene	3.06	Negligible
1,3,5-Triphenylbenzene	3.08	Negligible
Naphthalene	3.16	Negligible
<i>m</i> -Terphenyl	3.17	Negligible
Biphenyl	3.24	Negligible
<i>o</i> -Terphenyl	3.25	Negligible

<sup>a</sup> First reduction wave vs. Ag-AgNO<sub>3</sub> electrode.

waves, presumably corresponding to the addition of a second electron, yielding a dianion.<sup>5,7</sup> We did not attempt a detailed examination of the second waves.

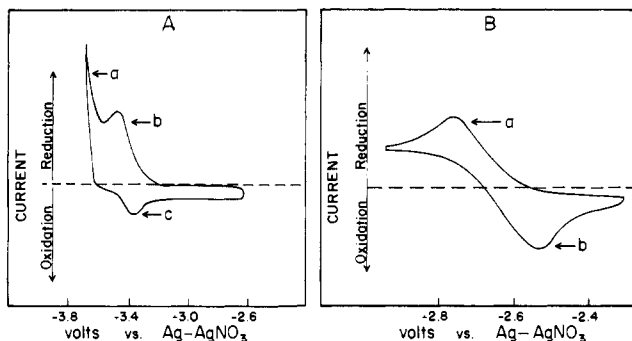


Fig. 1.—Oscillopolarograms of B, B', B''-triphenylborazine in DMF (A) [wave a, supporting electrolyte reduction; wave b, borazine reduction; wave c, oxidation of borazine anion radical (frequency, 5 c.p.s.)] and 1,2,5,6-dibenzanthracene in glyme (B) [wave a, hydrocarbon reduction; wave b, hydrocarbon anion-radical oxidation (frequency, 2.0 c.p.s.)].

The electrochemical behavior of the hydrocarbons, together with the correlation between half-wave potentials illustrated in Fig. 3, parallels observations in other nonaqueous, aprotic solvents<sup>4</sup> suggesting no unusual features for glyme with regard to reduction processes.

Conventional polarograms of the B- and N-phenyl-substituted borazines in glyme indicated behavior essentially identical with that exhibited by the hydrocarbons, *i.e.*, well-formed reduction waves, linear  $\log(i_d - i)/i$  vs.  $E$  plots of slope 0.06 v., and diffusion currents consistent with a one-electron reduction. None of the borazines showed second waves. The oscillopolarograms of the B-phenylborazines indicated reversible charge transfer, but unlike the hydrocarbons, relatively rapid decomposition of the anion radical was evident. Typical oscillopolarograms of a hydrocarbon and a B-phenylborazine are illustrated in Fig. 1. The relatively small oxidation wave of the borazine indicates decomposition of the anion radical. Employing the foot-of-wave oscillopolarographic method,<sup>43</sup> the decompositions of the anion radicals were found to be first order, and the rate constants were assessed at about 40 sec.<sup>-1</sup> (see Table I) for the B-phenylborazines. No reoxidation wave could be detected from the oscillopolarograms of N, N', N''-triphenylborazine. This fact coupled with the conventional polarographic data is consistent with two mechanisms: (a) reversible one-electron transfer at the mercury electrode followed by decomposition of the anion radical which was too rapid to permit detection of reoxidation, (b) irreversible one-electron transfer with a charge-transfer coefficient of nearly 1.<sup>44</sup> In view of the behavior of the B-phenylborazines, the latter alternative is extremely unlikely for these systems, and we interpret the N, N', N''-triphenylborazine reduction process to be the same as for the B-substituted derivatives except that the anion radical is considerably more reactive. Because the reduction wave of N, N', N''-triphenylborazine overlaps the foot of the supporting electrolyte reduction wave, reaction of the anion radical with products of supporting electrolyte electrolysis may contribute to the decomposition rate. This, rather than some more fundamental difference in the stability, may account for the difference in reac-

tivity of the B- and N-substituted anion radicals. Because of rapid decomposition of primary reduction products, the relation between the polarographic  $E_{1/2}$  and the  $E^\circ$  value for the phenylborazine-phenylborazine anion radical couples are not given by eq. 3 but by<sup>45,46</sup>

$$E_{1/2} = E^\circ + \frac{RT}{nF} \ln \left[ \frac{12kt}{7} \right]^{1/2}$$

where  $k$  is the first-order or pseudo-first-order rate constant,  $t$  is drop life, and the other parameters have their usual significance. This expression applies to the measurement of instantaneous currents. For the B-phenylborazines, the term  $RT/nF \ln(12kt/7)^{1/2}$  can be calculated from the decomposition rate data found in Table I. The half-wave potentials given in Table I are corrected for the effect of product decomposition and represent the half-wave potentials which would be observed if the primary products were stable, *i.e.*, essentially the  $E^\circ$  value for the oxidation-reduction system. The magnitude of the correction for chemical kinetic effects is  $\sim 0.06$  v. Because the apparent rapidity of the decomposition of the N, N', N''-triphenylborazine prevented evaluation of the rate of decomposition, only a lower limit on the correction term and corrected half-wave potential can be given. The lower limit is based on our estimate that a rate constant  $\geq 500$  sec.<sup>-1</sup> would be required to prevent detection of the reoxidation wave value due to unreacted anion radical. The lower limit on the correction term is thus  $-0.10$  v. It should be noted that if the true rate constant were three orders of magnitude larger than 500 sec.<sup>-1</sup>, the corrected half-wave potential would be only 0.1 v. more negative than the lower limit given in Table I.

In addition to investigating the reductions of the phenyl-substituted borazines, borazine, N, N', N''-trimethylborazine, B, B', B''-trichloroborazine, and B, B', B''-trichloro-N, N', N''-triphenylborazine were also studied. Borazine and N, N', N''-trimethylborazine were not reduced in the available potential range.

The B-chloroborazines were easily reduced at the dropping mercury electrode. The half-wave potentials are given in Table I. From the conventional polarograms and oscillopolarograms it was evident that the electrode reactions were considerably more complicated than found for the phenyl-substituted compounds. The reductions appear to involve at least three electrons. The data suggest a mechanism involving reversible charge transfer followed by B-Cl bond cleavage yielding chloride ion and borazine free radical. This radical may be reduced further and/or couple with a similar fragment; also the coupling products may undergo reduction at the same potential. This mechanism has precedent in the reported reaction of B-chloroborazine with sodium metal<sup>47</sup> and in the electrode reduction processes of analogous halogenated hydrocarbon aromatics.<sup>48,49</sup> The complicated behavior of the chloro-

(45) (a) J. Koutecky, *Collection Czech. Chem. Commun.*, **18**, 597 (1953); (b) *ibid.*, **20**, 116 (1955).

(46) T. J. Katz, W. H. Reinmuth, and D. E. Smith, *J. Am. Chem. Soc.*, **84**, 806 (1962); note misprint in eq. 4 of this reference.

(47) R. J. Brotherton, L. L. Petterson, and A. L. McCloskey, Division of Inorganic Chemistry, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

(48) S. Wawzonek and J. H. Wagenknecht, *J. Electrochem. Soc.*, **110**, 420 (1963).

(43) (a) D. E. Smith and W. H. Reinmuth, Division of Analytical Chemistry, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961; (b) D. E. Smith, Ph.D. Thesis, Columbia University, New York, N. Y., 1961.

(44) L. Meites and V. Israel, *J. Am. Chem. Soc.*, **83**, 4903 (1961).

borazines suggested that the observed half-wave potentials would not be simply related to  $E^\circ$  values for the chloroborazine-chloroborazine anion-radical system so no attempt was made to include these compounds in the correlation with MO calculations.

The reductions of borazine and phenyl-substituted borazines were studied in dimethylformamide together with several analogous hydrocarbon aromatics. Except for differences in half-wave potentials, the polarographic behavior of these compounds was the same as observed in glyme. The stabilities of the B-phenylborazine anion radicals were substantially the same as found in glyme. Another similarity to glyme was the rapid decomposition of the N,N',N''-triphenylborazine radical which prevented observation of a reoxidation wave in the oscillopolarograms. Data for DMF are given in Table II. Except for the relative instability of the anion radical, the qualitative electrochemical behavior of the borazines closely parallels that of hydrocarbon aromatics in these solvents. The chloroborazines can be included in this statement, despite the apparent complexities of the reduction process, as reduction of halogenated benzenes often leads to bond cleavage and halide ion formation.<sup>48,49</sup> While the preparation of hexaphenylborazine is reported in the literature, we did not include the compound in our study because its adjacent phenyl groups are expected to deviate greatly from planarity. Since the twist angle is unknown, we could not correct for it in our calculations. The effect of such a twist is to make reduction more difficult than would be expected for a planar or nearly planar molecule. Such deviations have been demonstrated by others<sup>4</sup> and were clearly evident in our study of *o*-terphenyl (Fig. 3a) and hexaphenylbenzene.

TABLE II  
POLAROGRAPHIC DATA IN DIMETHYLFORMAMIDE

Compound	$-E_{1/2}^a$ , v.	Product decomposition rate, sec. <sup>-1</sup>
B,B',B''-Triphenylborazine	3.29	~40
B,B'-Diphenylborazine	3.32	~40
B-Phenylborazine	3.37	~40
N,N',N''-Triphenylborazine	≥ 3.45	≥ 500
<i>p</i> -Terphenyl	2.82	Negligible
1,3,5-Triphenylbenzene	2.93	Negligible
<i>m</i> -Terphenyl	3.02	Negligible
Biphenyl	3.05	Negligible
<i>o</i> -Terphenyl	3.10	Negligible
Hexaphenylbenzene	3.10	Negligible

<sup>a</sup> First reduction wave vs. Ag-AgNO<sub>3</sub> electrode.

**Solvent Effects.**—Comparison of data in Tables I and II indicates a specific solvent effect. The three phenylbenzenes reduce about 0.16 v. more negative in glyme than in DMF, but each of the corresponding borazines reduces only 0.04 v. more negative in glyme than DMF. This effect is qualitatively explainable in terms of the charge distribution in the borazines. In solvents of appreciable polarity, a borazine-solvent interaction should arise from dipole or weak donor acceptor interaction between solvent molecules and the polar B-N groups. Because of proximity to the sol-

vent, it is probable that  $\pi$ -charge densities are more influential on solvation than  $\sigma$ -charge densities. Inspection of charge densities given in Table III shows that  $\pi$ -electrons of the various borazines are concentrated on nitrogen atoms at the expense of adjacent borons, and it is this variation in charge density which leads to polar interaction with the solvent. However, the situation is reversed for the antibonding levels. When an electron is added to the lowest  $\pi^*$ -orbital it becomes more localized on boron than nitrogen; thus the polar part of the solvent interaction is reduced. The net effect is to make more difficult the reduction of phenylborazines relative to phenylbenzenes in solvents of high polarity than in solvents of low polarity.

**Energy Correlation.**—The foregoing considerations led us to use only the results obtained in glyme in attempting a correlation between molecular orbital calculations and reduction potentials. Hydrocarbons were included along with borazines in the correlation, and in addition we required that calculated reduction potentials for borazine and benzene fall outside the available potential range. The heteroatom parameters are conveniently scaled in terms of the carbon resonance integral<sup>4</sup>

$$\alpha_X = \alpha_C + h_X \beta_{CC} \quad (4)$$

$$\beta_{XY} = k_{XY} \beta_{CC} \quad (5)$$

where  $\alpha$ 's are coulomb integrals and  $\beta$ 's are resonance integrals. The problem is to determine values of  $h_X$  for boron and nitrogen and  $k_{XY}$  for B-N, B-C, and N-C bonds. We clearly do not have enough reduction potentials to empirically determine all of the parameters. The Wolfsberg-Helmholtz approximation (eq. 6) has proved adequate for a variety of MO calculations on heteroatom systems.<sup>15d,40</sup>  $K$  is a constant, and  $S_{XY}$  is

$$\beta_{XY} = K S_{XY} \frac{(\alpha_X + \alpha_Y)}{2} \quad (6)$$

the overlap integral for the XY bond. Combination of eq. 4 through 6 yields

$$k_{XY} = \frac{S_{XY}}{S_{CC}} \left[ 1 + (h_X + h_Y) \frac{\beta_{CC}}{2\alpha_C} \right] \quad (7)$$

The ratio  $\beta_{CC}/2\alpha_C$  was estimated to be 0.40 from data for aromatic hydrocarbons. Another relation which reduces the number of variables is  $h_B \cong -h_N$ . Roothaan and Mulliken have pointed out that this relation is indicated by Pauling electronegativities.<sup>13</sup> Only one independent variable is left with which to fit the observed reduction potentials, and a value of  $h_B = -0.89$  was found to give a good correlation. When we applied eq. 7 to an inter-ring bond, we assumed a 20° twist from planarity which has been determined by Suzuki for biphenyl in hexane solution.<sup>50</sup> Bond distances for the calculation of  $k_{XY}$  were estimated from published values of closely analogous compounds: B-C (inter-ring) = 1.55, N-C (inter-ring) = 1.46, C-C (inter-ring) = 1.50, and B-N = 1.43 Å. Energies of the lowest unfilled  $\pi$ -molecular orbitals, total  $\pi$ -energies, conjugation

(49) T. Kitagawa, T. P. Layloff, and R. N. Adams, *Anal. Chem.*, **35**, 1086 (1963).

(50) H. Suzuki, *Bull. Chem. Soc. Japan*, **32**, 1340 (1959).

TABLE III  
MOLECULAR PARAMETERS FOR BORAZINE AND PHENYL-SUBSTITUTED BORAZINES

Compound	Total $\pi$ -energy <sup>a</sup>	Conjugation energy <sup>a,b</sup>	Lowest empty MO energy <sup>d</sup>	Atomic orbital <sup>c</sup>	Charged <sup>d</sup>	Bond <sup>c</sup>	$\pi$ -Bond order				
Borazine	8.79	0.0	-1.23	1	1.63	1,2	0.527				
				2	0.37						
B-Phenylborazine	16.91	0.125	-0.832	1	1.635	1,2	0.514				
				2	0.395	1,6	0.528				
				4	0.366	4,5	0.526				
				5	1.635	2,7	0.214				
				7	1.016	7,8	0.651				
				8	0.982	8,9	0.670				
				9	1.001	9,10	0.665				
				10	0.986						
				B-Diphenylborazine	25.04	0.250	-0.799	1	1.635	1,2	0.513
								2	0.395	1,6	0.528
				3	1.635	2,3	0.516				
				6	0.367	2,7	0.214				
				7	1.016	7,8	0.651				
				8	0.982	8,9	0.670				
				9	1.001	9,10	0.665				
				10	0.986						
B-Triphenylborazine	33.17	0.376	-0.799	1	1.635	1,2	0.515				
				2	0.396	2,7	0.214				
				7	1.016	7,8	0.651				
				8	0.982	8,9	0.669				
				9	0.001	9,10	0.665				
				10	0.986						
N-Triphenylborazine	33.60	0.808	-0.968	1	1.570	1,2	0.502				
				2	0.363	1,7	0.312				
				7	0.967	7,8	0.633				
				8	1.037	8,9	0.674				
				9	0.998	9,10	0.662				
				10	1.039						

<sup>a</sup> The energy scale is based on  $\alpha_C = 0.0$ , and the unit of energy is  $\beta_{CC}$ . <sup>b</sup> Conjugation energy =  $E(\text{total } \pi) - E(\pi\text{-borazine}) - nE(\pi\text{-benzene})$ , where  $n$  is the number of benzene substituents: C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A195**, 188 (1948). <sup>c</sup> The numbering system is presented in Fig. 2. Atomic orbitals and bonds which are omitted are related by symmetry to those presented in the table. <sup>d</sup> Charge in the  $p_z$  atomic orbital.

energies, charge densities, and bond orders are presented in Table III. The correlations between calculated molecular energy levels and observed reduction potentials are presented in Fig. 3.

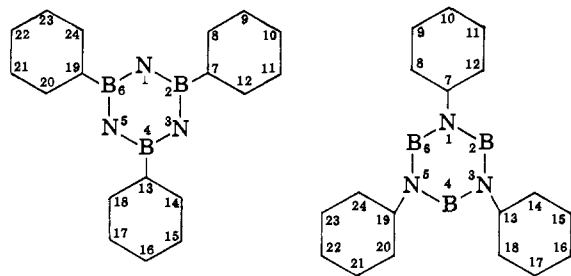


Fig. 2.—Numbering system.

The effect of removing some of the above restrictions was investigated. The value  $k_{BN} = 0.855$  calculated using eq. 7 appeared rather large; so values down to 0.6 were tried. Other authors have employed values ranging from 0.87 to 0.57.<sup>15</sup> It is possible to partially offset decreases in  $k_{BN}$  by decreases in  $h_B$ , but the best fit seemed to be obtained with  $k_{BN} \sim 0.8$ . Some improvement was obtained for the position of N-triphenylborazine in the correlation when  $h_B$  and  $h_N$  were varied independently, but the arbitrariness this introduces is not appealing. Our data do not afford a critical choice

of all parameters, so use of  $h_B = -h_N$  along with eq. 7, both of which are subject to independent justification, provides the least arbitrary approach. At the same time, this yields a good fit to experiment. In another series of calculations overlap was included; a decrease in the variable  $h_B$  below  $-0.89$  was necessary to obtain a satisfactory correlation with  $E_{1/2}$  values but no improvement of the fit was obtained. However, bond orders and charge densities derived when overlap is included are probably more significant than those calculated by the HMO method.<sup>38</sup>

Dewar and Rogers<sup>15c</sup> have investigated charge-transfer spectra for  $\pi$ -complexes formed between tetracyanoethylene and B-N containing heteroaromatic compounds. In addition they have used a perturbation method to derive resonance and coulomb integrals from the spectral data. Their parameters,  $h_B = -h_N = -1.59$ ,  $k_{BN} = 0.50$ , and  $k_{BC} = k_{NC} = 0.90$ , deviate from ours, but this is primarily due to the fact that their simple perturbation treatment does not reproduce the Hückel results when large perturbations are involved. As an example of this disparity, we calculate an energy of  $0.322\beta$  for the highest-filled orbital energy of 10,9-borazarophenanthrene when their parameters are used in a Hückel calculation, but they derived the parameters on the basis of  $0.535\beta$  for this energy. Thus we cannot make direct comparison between their parameter set and ours. Instead, our value  $h_B = -0.89$

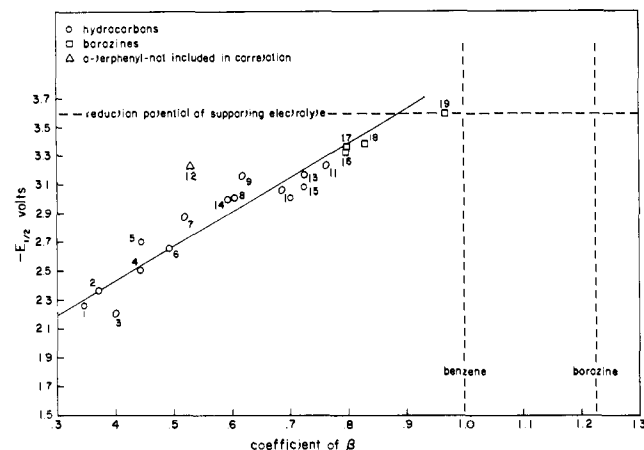


Fig. 3a.—Corrected half-wave potentials (in glyme) vs. the HMO coefficients for  $\beta$  (which are negative) for the lowest empty MO. Most of the hydrocarbon coefficients were taken from ref. 3. polyphenyl data were calculated using  $k_{CC} = 0.772$  for inter-ring bonds; borazine calculations were based on  $k_{BN} = 0.866$ ,  $k_{CN}$  (inter-ring) = 0.862, and  $k_{BC}$  (inter-ring) = 0.582. The numbers refer to the following compounds: (1) perylene, (2) fluoranthene, (3) azulene, (4) anthracene, (5) pyrene, (6) dibenzanthracene, (7) chrysenes, (8) phenanthrene, (9) naphthalene, (10) triphenylene, (11) biphenyl, (12) *o*-terphenyl, (13) *m*-terphenyl, (14) *p*-terphenyl, (15) 1,3,5-triphenylbenzene, (16) B-triphenylborazine, (17) B-diphenylborazine, (18) B-phenylborazine, and (19) N-triphenylborazine. Values for *o*- and *p*-terphenyl are not corrected for the reduced inter-ring  $k_{CC}$ .

was employed to calculate energy levels for their compounds (see Table IV). The agreement between these calculations and experimentally derived values is adequate.

TABLE IV

COMPARISON OF CALCULATED ENERGIES OF THE HIGHEST-OCCUPIED MO WITH THOSE DEDUCED FROM SPECTRAL DATA

Compound	Energy of highest occupied MO, $\beta$	
	Data of Dewar and Rogers	Calculated <sup>a</sup>
2,1-Borazonaphthalene	0.75	0.725
10,0-Borazarophenanthrene	0.535	0.623
2,7-Dibora-1,8-diazaroanthracene	0.50	0.584
2,6-Dibora-1,7-diazaropyrene	0.57	0.537

<sup>a</sup> The parameters employed were  $h_B = -h_N = -0.89$ ,  $k_{BN} = 0.855$ ,  $k_{BC} = 0.866$ , and  $k_{NC} = 0.976$ . The latter pair were calculated for B-C and N-C bond distances of 1.41 and 1.37, which were estimated from published bond distances: H. J. M. Bowen, *et al.*, "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication II, L. E. Sutton, Ed., The Chemical Society, London, 1958.

Reduction potentials and the MO calculations both show that the lowest empty  $\pi$ -orbital of N-triphenylborazine is higher in energy than the comparable orbital of B-triphenylborazine. Some insight into the physical basis for this difference may be gained by constructing a phenylborazine  $\pi$ -molecular orbital from a linear combination of molecular orbitals<sup>51</sup> for borazine and benzene. The  $m$ th molecular orbital of phenylborazine in the LCMO approximation is

$$\psi_m = a\Phi_{na} + b\Phi_{nb}$$

(51) (a) M. J. S. Dewar, *Proc. Cambridge Phil. Soc.*, **45**, 638 (1949); (b) S. Nagakura and V. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954); (c) the simple LCMO procedure used in this discussion is based on ref. 51b, and it leads to zero conjugation energies but it is useful for illustrative purposes.

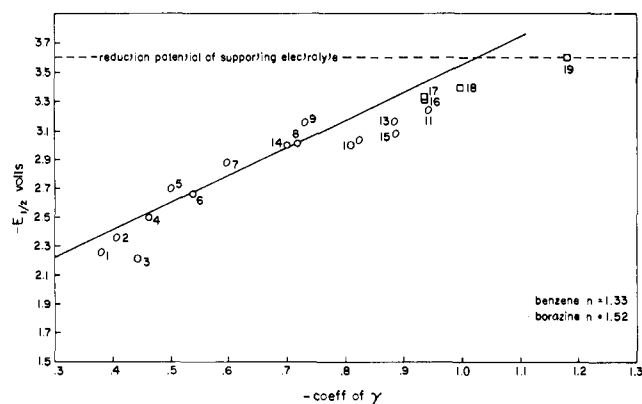


Fig. 3b.—Correlation of half-wave potentials in glyme vs. overlap included MO energy parameter. These coefficients, which are negative, were calculated for the hydrocarbons from HMO data in ref. 4. Compound numbers are given in the caption to Fig. 3a. The correlation was obtained with  $h_B = -0.95$ ; all other parameters were calculated as described in the text:  $h_N = 0.95$ ,  $k_{BN} = 0.855$ ,  $k_{BC} = 0.559$ ,  $k_{NC} = 0.878$ .

where  $\Phi_{na}$  and  $\Phi_{nb}$  are the appropriate molecular wave functions for the  $n$ th MO of borazine and benzene, and  $a$  and  $b$  are constants to be determined by a variation procedure. Neglect of overlap and solution of the secular determinant for this case yields

$$E = \frac{1}{2}(E_a + E_b) \pm \frac{1}{2}(E_a^2 + E_b^2 - 2E_aE_b + 4C_{1a}C_{1b}\beta_{ab}^2)^{1/2} \quad (8)$$

The minus sign applies for the lowest empty molecular orbital. Here  $E_a$  and  $E_b$  are the original energies for the  $n$ th MO of borazine and benzene, respectively,  $C_{1a}$  and  $C_{1b}$  are the corresponding coefficients in the unperturbed MO's for the atoms involved in the inter-ring bond, and  $\beta_{ab}$  is the resonance integral for this bond. It is clear from eq. 6 that, in this approximation, the difference between B-phenylborazine and N-phenylborazine must arise from the corresponding four  $C_{1a}C_{1b}\beta_{ab}^2$  terms. The Hückel MO's for borazine are (determined for  $h_N = 0.89$ ,  $h_B = -0.89$ ,  $k_{BN} = 0.855$ ) shown in Table V. The numbering scheme used here for  $p_z$  atomic orbitals ( $\phi_1 \dots$ ) is illustrated in Fig. 2.  $\Phi_{6a}$  is of the correct energy and symmetry to combine with a similar benzene molecular orbital to produce the lowest empty molecular orbital of phenylborazine. When N-phenylborazine is considered,  $\phi_1$  will be used for bonding so the coefficient  $C_{1a}$  in eq. 6 will be  $C_{1a} = (2)(0.152)$ . However, B-phenylborazine will involve bonding through  $\phi_4$ , so for this case the appropriate coefficient is  $C_{1a} = (2)(0.379)$ . In addition there is a somewhat smaller difference in resonance integrals:  $\beta_{NC} = 0.862$ , and  $\beta_{BC} = 0.582$  (for the best parameter set). The latter difference is not adequate to offset the effect of the coefficients so for the lowest empty orbital,  $E$  (N-phenylborazine)  $>$   $E$  (B-phenylborazine) because  $C_{1a}\beta_{NC}^2 <$   $C_{1a}\beta_{BC}^2$ .

For both the borazines and benzenes *sym*-triphenyl derivatives are reduced more easily than the corresponding *m*-diphenyl derivatives (see Tables I and II). By contrast, the Hückel theory produces identical energies for the *sym*-triphenyl and *m*-diphenyl compounds. This discrepancy is less than others which arise in the correlation of  $E_{1/2}$  with the coefficient of  $\beta$  for hydrocarbons, but it is interesting to speculate on its

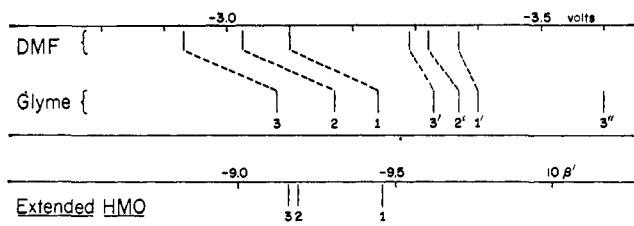


Fig. 4.—From top to bottom are reduction potentials in DMF, reduction potentials in glyme, and results of an extended Hückel calculation in which all interactions at 4 Å. or less are included. The number of phenyl substituents on benzene is indicated by 1, 2, 3. Primes denote B-substituted borazine, and 3'' indicates N-triphenylborazine. The specific solvent effect which is discussed in the text is clearly evident from variation in slope of the dashed correlation lines.

origin. While the effect may be due to solvation energy differences, the nearly identical results in glyme and DMF suggest that this is not the case. Another possible origin may be the Jahn-Teller effect<sup>52</sup> which

TABLE V

	$E, \beta_{CC}$
$\Phi_{1a} = 0.494(\phi_2 + \phi_3 + \phi_5) + 0.300(\phi_2 + \phi_4 + \phi_6)$	1.93
$\Phi_{2a} = 0.656(\phi_3 - \phi_5) + 0.264(\phi_2 - \phi_6)$	1.23
$\Phi_{3a} = 0.379(2\phi_1 - \phi_3 - \phi_5) + 0.152(\phi_2 - 2\phi_4 + \phi_6)$	
$\Phi_{4a} = 0.264(-\phi_3 + \phi_5) + 0.656(\phi_2 - \phi_6)$	
$\Phi_{5a} = 0.152(2\phi_1 - \phi_3 - \phi_5) + 0.379(-\phi_2 + 2\phi_4 - \phi_6)$	-1.23
$\Phi_{6a} = 0.300(\phi_1 + \phi_3 + \phi_5) - 0.494(\phi_2 + \phi_4 + \phi_6)$	-1.93

should arise for the *sym*-triphenyl radical anions because of their orbital degeneracy, but recent calculations by Snyder indicate that this effect should account for only 0.02-v. stabilization of the *sym*-triphenylbenzene radical anion.<sup>53</sup> Configuration interaction, conformational changes, electron-electron repulsion, and interactions between nonadjacent atomic orbitals might also be responsible for the difference between simple theory and experiment. Since the calculations are easily performed, a quantitative assessment was made of electron-electron repulsion and of nonbonded interactions.

(52) H. A. Jahn and E. Teller, *Proc. Roy. Soc. (London)*, **A161**, 220 (1937).

(53) L. C. Snyder, *J. Phys. Chem.*, **66**, 229 (1962).

Hush and Pople<sup>39</sup> have developed a semiempirical MO procedure which takes into account electron-electron repulsions, and they have shown that it yields a considerable improvement over Hückel theory in the prediction of ionization potentials and electron affinities. The procedure used by them was based on Hückel orbitals along with semiempirical values for electron-interaction integrals. We employed this method for planar *m*-terphenyl and 1,3,5-triphenylbenzene, but the resulting energy values were nearly identical; so electron-electron repulsion is not responsible for the difference between these compounds.

Nonbonded interactions are generally neglected in simple molecular orbital treatments. By including these Hoffmann has had some success in the calculation of molecular geometries.<sup>42</sup> He employed 2s and 2p basis functions and included all interactions. Only  $\pi$ -energies were pertinent to the present study, so we assumed molecular planarity and employed only a  $p_z$  basis set. This procedure is not strictly defensible since nonplanarity of the actual molecule changes the overlap and removes orthogonality of  $p_z$ -orbitals to  $\sigma$ -orbitals, but neglect of these effects is probably no more serious than the use of Slater orbitals and eq. 7. Results of this calculation are presented in Fig. 4 where it may be seen that a sizable difference is calculated between *m*-terphenyl and 1,3,5-triphenylbenzene.

Finally, we note that the HMO  $\pi$ -bond order in borazine is 0.527; this value is 79% of the corresponding  $\pi$ -bond order for benzene. When overlap is included, the bond order of borazine relative to benzene is even greater. Even though exact bond orders are sensitive to their definition and to the experimental quantities employed in their calculation, we feel that the present experiments correctly indicate a high bond order in borazines. This result is not incompatible with borazine chemistry which is dominated by other factors, the most important of which is alternating polarity in the B-N ring.

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