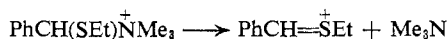


Figure 1. Plot of  $\log k_{\text{obsd}}$  against  $\log [\text{H}_3\text{O}^+]$  for the reaction  
 $\text{PhCH}(\text{NHMe}_2)\text{SEt} \rightarrow \text{PhCH}=\text{NMe}_2 + \text{EtSH}$

by eq. 3, where  $K_I = a_{\text{S}}a_{\text{H}_3\text{O}^+}/a_{\text{SH}^+}a_{\text{H}_2\text{O}}$ . The term  $a_{\text{H}_2\text{O}}f_{\text{SH}^+}/f_{\text{H}_3\text{O}^+}f_{\text{EtS}}$  should change little in the predominantly aqueous solutions used, and hence  $k_{\text{obsd}}$  should be inversely proportional to  $[\text{H}_3\text{O}^+]$ , as observed. The assigned mechanism also accounts for the lack of catalysis by formate ion or molecular formic acid.

In complete agreement with the mechanism is the finding of a solvent isotope effect ( $k_{\text{HClO}_4}/k_{\text{DClO}_4}$ ) of  $5.9 \pm 0.1$  in several acidities for the ethyl sulfide (Figure 1). Since equilibrium 1 lies far to the left, the concentration of S should be significantly greater in protio than in deutero acid of the same molarity.<sup>4</sup> It can reasonably be assumed that the solvent isotope effect on [S] is comparable to that on the acid dissociation constant of trimethylammonium ion. This is reported to be 4.0 but is more likely 5.0.<sup>5</sup> The second step probably has a small positive isotope effect.<sup>7,10</sup> The closest model is the reaction



for which  $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$  is 1.2.<sup>11</sup> Thus the estimated total solvent isotope effect agrees well with that observed.

The transition state of the rate-controlling step of the assigned mechanism has sulfide ion character. In agreement with this, the relative rates for various  $\alpha$ -dimethylaminobenzyl thio ethers are: Ph (398),  $\text{PhCH}_2$  (4.6), Et (1.0), *t*-Bu (0.8). A plot of  $\log k$  vs.  $\log K_{\text{RSH}}$ , where  $K_{\text{RSH}}$  is the acidity constant of the thiol in water, is linear with slope  $-0.57$ .

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(5) In 1936, Schwarzenbach and Epprecht reported the following  $K_{\text{HA}}/K_{\text{DA}}$  values:  $\text{H}_2\text{O}$  (5.4),  $\text{NH}_4^+$  (3.1),  $(\text{CH}_3)_2\text{NH}^+$  (4.0),  $\text{CH}_3\text{CO}_2\text{H}$  (2.9), and  $\text{H}_2\text{PO}_4^-$  (2.9).<sup>6</sup> No later values for  $(\text{CH}_3)_2\text{NH}^+$  were found, but the generally accepted values for all the other acids are consistently larger than the earlier values, by a factor of  $1.25 \pm 0.05$ :  $\text{H}_2\text{O}$  (6.5),<sup>7,8</sup>  $\text{NH}_4^+$  (4.06),<sup>9</sup>  $\text{CH}_3\text{CO}_2\text{H}$  (3.33),<sup>7,8</sup> and  $\text{H}_2\text{PO}_4^-$  (3.62).<sup>8</sup> Applying this factor to the early value for  $(\text{CH}_3)_2\text{NH}^+$  gives  $K_{\text{HA}}/K_{\text{DA}} = 5.0$ .

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Mechanisms in which the transition state contains the hydroxide ion and the elements of  $\text{SH}^+$  (such as in an  $\text{S}_{\text{N}}2$  attack of  $\text{OH}^-$  on the sulfur-conjugate acid) are not ruled out by the acidity dependence of  $k_{\text{obsd}}$ . However, they are inconsistent with the other results obtained.

A literature search failed to reveal any unambiguous example of the  $\text{S}_{\text{N}}1$  solvolysis of a neutral sulfide. Carbon-sulfur bond cleavage in general is much more difficult to achieve than carbon-oxygen bond cleavage.<sup>12-14</sup> However, in this instance the "carbonium" ion formed,  $\text{I}^+$ , has a relatively high stability. The iminium ion character of the transition state no doubt is of great assistance in promoting the  $\text{S}_{\text{N}}1$  heterolysis of the carbon-sulfur bond.

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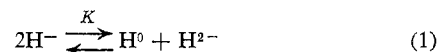
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### Comments on the Proposed Dibenzocyclobutadiene Dianion

Sir:

We wish to report results of our spectroscopic measurements of equilibrium constants for disproportionation of anthracene ( $a^0$ ) and biphenylene ( $b^0$ ) radical anions in tetrahydrofuran (THF) solution (sodium gegenion)



Equilibrium data have been reported for disproportionation of the radical anions of stilbene,<sup>1</sup> tetraphenylethylene,<sup>2</sup> 1,2,3,4-tetraphenylbutadiene,<sup>3</sup> and cyclooctatetraene,<sup>4</sup> but no direct measurements of equilibrium constants for disproportionation of aromatic radical anions have been reported. Polarographic<sup>5,6</sup> and potentiometric titrations<sup>7,8</sup> indicate disproportionation of aromatic radical anions is small.

It was recently reported,<sup>9</sup> based on visible spectral measurements, that in THF solutions biphenylene radical anion ( $b^-$ ) (sodium gegenion) undergoes extensive disproportionation, but the equilibrium constant was not measured. The authors interpreted their observed disproportionation of  $b^-$  as evidence that biphenylene dianion ( $b^{2-}$ ) derives a special stability from being the closed shell  $4n + 2$   $\pi$ -electron molecule dibenzocyclobutadiene dianion.

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The equilibrium constant measurements given here are based on electronic absorption spectra in the ultraviolet and visible using methods described previously.<sup>10</sup> THF solutions of  $b^0$  and  $a^0$  were exposed to a Na mirror, then poured off the metal surface prior to making spectral readings. Biphenylene radical anion has strong absorption maxima at 382 (log  $\epsilon$  4.72) and 270 m $\mu$  (log  $\epsilon$  4.69).<sup>11</sup> Biphenylene dianion<sup>12</sup> has an absorption maximum of 345 m $\mu$  (log  $\epsilon$  4.64). The strong absorptions of biphenylene at 249 (log  $\epsilon$  4.99) and 241 m $\mu$  (log  $\epsilon$  4.74) were used to obtain the concentration of  $b^0$  in equilibrium with  $b^-$  and  $b^{2-}$ . Similarly the absorptions of anthracene radical anion ( $a^-$ ) at 258 (log  $\epsilon$  4.90), 325 (log  $\epsilon$  4.54), and 364 m $\mu$  (log  $\epsilon$  4.38), of anthracene dianion ( $a^{2-}$ ) at 325 (log  $\epsilon$  4.77) and 605 m $\mu$  (log  $\epsilon$  4.28), and of the absorption maxima of anthracene at 245 (log  $\epsilon$  4.97) and 253 m $\mu$  (log  $\epsilon$  5.29) were used to evaluate equilibrium data for the anthracene system.<sup>13</sup> Because we find that the two low extinction absorption maxima in the visible (*i.e.*, 595 and 565 m $\mu$ ) are characteristic only of  $b^-$ , which is contrary to the recent assignment<sup>9</sup> that the shorter wave length 565 m $\mu$  absorption arises from  $b^{2-}$ , we have illustrated our spectra for  $b^-$ ,  $b^{2-}$ , and  $b^0$  in Figure 1.

Successive spectral measurements following the progress of these reactions have established that in experiments having initial  $b^0$  or  $a^0$  concentrations of  $4 \times 10^{-3}$  to  $2 \times 10^{-2}$  M disproportionation of both  $b^-$  and  $a^-$  is so small it is not possible to simultaneously measure spectroscopically all three species *i.e.*,  $H^0$ ,  $H^-$ , and  $H^{2-}$ . These experiments establish the effective  $K$  (disproportionation) of  $b^-$  must be less than  $1.5 \times 10^{-2}$ , which is in agreement with previous conclusions.<sup>11</sup> A similar small value of  $K$  (*i.e.*,  $<5 \times 10^{-3}$ ) is found for anthracene radical anion, which is in agreement with  $K \sim 10^{-6}$  calculated from the first and second reduction potentials of anthracene for both sodium cation in THF<sup>7,8</sup> and tetrabutylammonium cation in 96% dioxane-water<sup>5</sup> or acetonitrile.<sup>6</sup>

The tendency of a radical anion to disproportionate is believed to be determined by a balance between relative solvation energies of the radical anion and dianion and electron repulsion energy in the dinegative ion.<sup>7,14</sup> Competition between electron repulsion energy and solvation energy should be both counterion and solvent dependent. Shatenshtein, *et al.*,<sup>15</sup> demonstrated that counterion and solvent are major factors controlling the disproportionation equilibrium of naphthalene radical anion. The importance of solvent and gegenion is also illustrated by the finding that the equilibrium constant for disproportionation of stilbene radical anion varies from  $10^{-3}$  to  $10^3$  with changes of solvent and gegenion.<sup>1</sup> Similarly the equilibrium

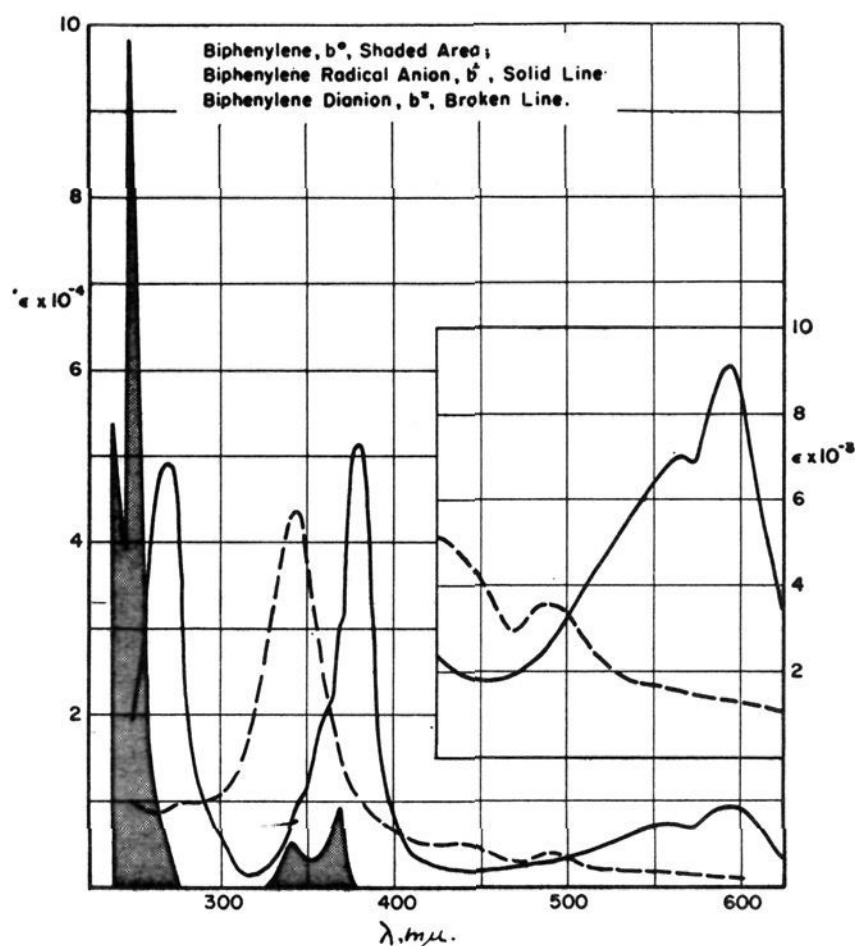


Figure 1. Absorption spectra in tetrahydrofuran.

constant for disproportionation of tetraphenylethylene radical anion was shown to depend on cation<sup>16</sup> and solvent<sup>2</sup> and to increase with increasing concentration.<sup>2</sup>

Based on our measurements of the equilibrium constants for disproportionation of biphenylene and anthracene, in addition to cation, solvent, and concentration sensitivity of such disproportionations, it is our conclusion that disproportionation of  $b^-$  should not be cited as evidence that biphenylene dianion derives enhanced stability as a result of being a closed shell  $4n + 2$   $\pi$ -electron cyclobutadiene dianion.

On the other hand  $K$  is reported to be  $5 \times 10^8$  for planar cyclooctatetraene radical anion.<sup>4,17</sup> Planar cyclooctatetraene is a monocyclic conjugated olefin in which the two extra electrons in the dianion are presumed to fill completely the degenerate nonbonding orbitals and produce a closed shell ground state.<sup>18</sup> Analogous behavior would be anticipated for a monocyclic cyclobutadiene and some substituted cyclobutadienes.<sup>18,19</sup> In contrast, the calculated energy levels of biphenylene<sup>20</sup> are like those of typical alternant aromatics; the highest occupied level is bonding and not degenerate. Similarly, the  $\pi$ -electron levels of biphenylene dianion, calculated using the  $\omega$  technique<sup>21</sup>

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(21) A. Streitwieser and P. M. Nair, *Tetrahedron*, 5, 149 (1959).

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to compensate for the decreased effective electronegativity of the carbon cores in  $b^{2-}$ , do not show degeneracy of the highest occupied  $\pi$  orbital. Also, bond length measurements indicate biphenylene is essentially devoid of cyclobutadiene character.<sup>22</sup>

Further evidence inferring  $b^{2-}$  does not derive special stability from being a closed shell  $4n + 2$   $\pi$ -electron molecule is obtained from the proton magnetic resonance spectrum of  $b^{2-}$ . The chemical shift difference between the centers of  $b^0$  and  $b^{2-}$  patterns indicates that partitioning of electron density in the dianion<sup>23</sup> between C-1-C-8 and C-9-C-12 is essentially identical with that determined for  $b^-$  by electron spin resonance.<sup>24,25</sup> The electron distribution in this latter species was best explained by assuming unequal bond lengths in the 4-C ring, *i.e.*, C-C of 9-10 and 11-12 are long,<sup>25</sup> thus indicating a lack of aromaticity for these species.

The effects of factors influencing disproportionation of polyacene radical anions are under investigation, as is the analysis of  $b^{2-}$  and other dianion p.m.r. spectra.

(22) T. C. W. Mak and J. Trotter, *Proc. Chem. Soc.*, 161 (1961).

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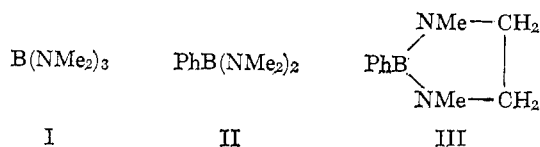
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## Doubly Charged Ions in the Mass Spectra of Some Organoboron Derivatives<sup>1</sup>

Sir:

We wish to report the appearance of very intense peaks, due to doubly charged ions, in the mass spectra of tris(dimethylamino)borane (I), bis(dimethylamino)phenylborane (II), and 1,3-dimethyl-2-phenyl-1,3,2-diazaborolidine (III).



The intensities of peaks due to doubly charged ions in the mass spectra of organic compounds rarely exceed 1-2% of the base peak intensity.<sup>2</sup> If the molecule, or part of it, is aromatic or heteroaromatic, the ability of the molecule, or some of its fragments, to sustain two positive charges can be considerably increased.<sup>3</sup> Mass spectra of substituted indoles<sup>2</sup> and of some alkaloids<sup>3</sup> show abundant peaks due to doubly charged ions, some of which correspond to 10% or more of the base peak intensity. The presence of abundant double charged ions in the mass spectrum of a compound is invariably connected with the presence of aromatic rings or high unsaturation in the molecule.<sup>3</sup>

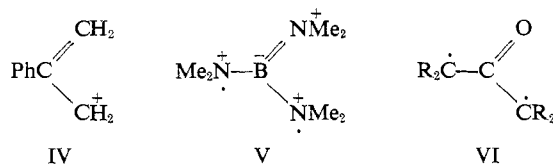
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The boron amides were prepared by standard methods: I, b.p. 33° (5.5 mm.), lit.<sup>4</sup> 43° (12 mm.),  $n_D^{25}$  1.4450; II, b.p. 56° (0.5 mm.), lit.<sup>5</sup> 59° (3 mm.),  $n_D^{25}$  1.5155; III, b.p. 66.5° (0.5 mm.), lit.<sup>5</sup> 73° (3 mm.),  $n_D^{25}$  1.5350. The mass spectra were measured by Mr. F. C. Maseles in the Mass Spectrometry Laboratory of The University of Texas, using a Consolidated Electroynamics Corp. Type 21-103C mass spectrometer with an ionization potential of 70 v. and 50- $\mu$ a. current. The doubly charged ions could be identified by the presence of peaks corresponding to half-integral mass number, either for the <sup>10</sup>B or <sup>11</sup>B isotopic species. The total contributions of doubly charged species to the mass spectra of I, II, and III were 6.6, 6.15, and 11.1%  $\Sigma_{50}$ , respectively. The largest peaks for doubly charged ions corresponded in each case to ions derived from the parent molecules by loss of two electrons. The appearance potentials for the relevant peaks in the spectra of I and III were found to be  $21 \pm 1$  and  $23.5 \pm 1$  e.v., respectively, using xenon calibration. Although the facilities available to us did not permit these to be measured with any great accuracy, the results are sufficient to indicate that the species involved have high energies and must almost certainly be doubly charged. At the same time these values are considerably less than those commonly observed<sup>3</sup> for multiple ion formation, a further indication of the unusual stability of the dipositive ions in our case.

Previous compounds yielding abundant dipositive ions have invariably been aromatic<sup>3</sup>; in this case aromaticity is clearly not a factor, given that I and II form a comparable percentage of such ions. The ready formation of dipositive ions at relatively low ionizing potentials indicates clearly that the ions are unusually stable. This is not surprising in the case of II and III, which are isoconjugate with the stable  $\beta$ -phenylallyl-carbonium ion IV. The case of V is interesting; this is isoconjugate with the "nonclassical" system VI, which was postulated<sup>6</sup> some time ago by Burr and Dewar on the basis of MO calculations to be an intermediate in the Favorskii reaction, a conclusion later confirmed experimentally by Fort.<sup>7</sup>



The ease with which V was formed in the mass spectrometer suggests that it might conceivably be isolable in the form of stable salts; however, treatment of I with antimony pentachloride led to decomposition.

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