

be the result, not of an unusually high *exo* rate with a normal *endo* rate, as is commonly assumed, but of a normal *exo* rate with an unusually slow *endo* rate.¹¹ But what is the factor that might be responsible for the slow *endo* rate? An examination of the preferred path for the leaving group in the *endo* derivative reveals that this path brings the departing group very close to the opposite side of the rigid endocyclic system. Indeed, if one constructs an intimate ion pair with a representative anion, such as chloride, situated along the perpendicular to the face of the carbonium ion at C-2, at distances equal to the sum of the two ionic radii, the anion is observed to be severely crowded against the 5,6-bridge.¹²

It is apparent that the chloride ion must depart along some other path which is more favorable sterically, but more costly in requiring greater separation of charges in the ion pair.

In conclusion, the results clearly indicate that a high *exo-endo* rate ratio in a norbornyl derivative does not provide a unique basis for concluding that the derivative undergoes ionization with participation of the 1,6-bonding pairs to form a nonclassical norbornyl cation.

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(11) H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, pp. 140-158, 174-178.

(12) This hypothesis of steric hindrance to ionization in rigid bicyclic systems is readily susceptible to experimental test, and such tests are underway in research in progress with Dr. I. Rothberg.

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The Diamagnetic Anisotropy of a Borazine Ring. A Correction

Sir:

The importance of data on the diamagnetic anisotropy of borazines^{1,2} with respect to the problem of the aromaticity of these compounds³ renders necessary the correction of some errors made in the paper by Watanabe, Ito, and Kubo,¹ especially in the paragraph headed "Evaluation of Diamagnetic Anisotropy."

The experimental molar susceptibilities of boron compounds listed in the compilation by Foëx^{4a} clearly show that Pascal's rule concerning the additivity of atomic susceptibilities, χ_A , for obtaining the molar susceptibilities, χ_M , does not hold for boron compounds. This might be due to the fact that Pascal calculated the χ_A values^{4b} of nitrogen, oxygen, hydrogen, and chlorine from χ_M values of carbon compounds, so that these values do not reflect any effects specific to boron compounds, such as back coordination. Moreover, Pascal's value for the atomic susceptibility of boron,⁵ $\chi_B = -7.2 \times 10^{-6}$, was obtained solely from the χ_M of $B(OCH_3)_3$. It remains to be proved that this value could indeed be used as such for calculating the χ_M

values of boron compounds. It is, therefore, apparently as yet impossible to calculate the diamagnetic susceptibility of the borazine molecule, its plane parallel to the magnetic field, $\chi_{||}$, from $\chi = 3\chi_B + 3\chi_N + 6\chi_H$ as has been done.^{1,6}

The χ_B required for calculating $\chi_{||}$ was obtained from the χ_M of BCl_3 . However, the value -67.0×10^{-6} for the molar susceptibility of boron trichloride listed in this paper¹ is incorrect. According to these authors,¹ this value was taken from the compilation of Foëx,⁴ who, however, does not list the -67.0×10^{-6} value, but gives only the value -59.9×10^{-6} , this being an experimental value given by Pascal.⁵ The value¹ $\chi_M = -67.0 \times 10^{-6}$ is probably an approximation of the $\chi_M = -66.9 \times 10^{-6}$ calculated by Pascal⁵ by adding the χ_A of Cl, -19.9×10^{-6} , and the χ_A of B, -7.2×10^{-6} , i.e., $-(3 \times 19.9 + 7.2) \times 10^{-6} = -66.9 \times 10^{-6}$. It is very difficult to justify this procedure for obtaining χ_B ,¹ which amounts to estimating χ_B from an experimentally nonexistent value for the χ_M of BCl_3 , -67.0×10^{-6} .

Moreover, as a result of an arithmetical error, these authors¹ obtained $\chi_B = -3.2 \times 10^{-6}$, whereas from their values they should have obtained $\chi_B = -(67.0 - 3 \times 19.6) \times 10^{-6} = -8.2 \times 10^{-6}$. This value, $\chi_B = -8.2 \times 10^{-6}$, is the χ_B from $B(OCH_3)_3$, $\chi_B = -7.2 \times 10^{-6}$, modified by adding and subtracting different χ_A values of chlorine.

The erroneous value $\chi_B = -3.2 \times 10^{-6}$ was used by those authors¹ for calculating the $\chi_{||}$ of borazine

$$\begin{aligned}\chi_{||} &= 3\chi_B + 3\chi_N + 6\chi_H \\ &= -(3 \times 3.2 + 3 \times 3.3 + 6 \times 2.93) \times 10^{-6} \\ &= -37.1 \times 10^{-6}\end{aligned}$$

Had the value $\chi_B = -8.2 \times 10^{-6}$ been used, the $\chi_{||}$ would have amounted to -52.1×10^{-6} , whereas the value $\chi_B = -7.2 \times 10^{-6}$ would yield $\chi_{||} = -49.1 \times 10^{-6}$. It must here again be stressed that the χ_N (at least) was chosen¹ quite arbitrarily. Thus no significance at all should be attributed to the "corrected" $\chi_{||}$ values -52.1×10^{-6} or -49.1×10^{-6} .

The molar susceptibility of borazine as determined,¹ $\chi_M = -49.6 \times 10^{-6}$, and the $\chi_{||}$ values -52.1×10^{-6} or -49.1×10^{-6} , yield the following values for the diamagnetic anisotropy, $\Delta\chi$, respectively

$$\begin{aligned}\Delta\chi &= 3(\chi_M - \chi_{||}) \\ \Delta\chi &= -3(49.6 - 52.1) \times 10^{-6} = +7.5 \times 10^{-6}\end{aligned}$$

and

$$\Delta\chi = -3(49.6 - 49.1) \times 10^{-6} = -1.5 \times 10^{-6}$$

It is thus clear that the otherwise important conclusions,¹ based on the value $\Delta\chi = -36 \times 10^{-6}$,¹ are as yet unsubstantiated. On the other hand, the other values of $\Delta\chi$, $+7.5 \times 10^{-6}$ and -1.5×10^{-6} , create the impression of borazine not possessing any diamagnetic anisotropy. However, from the very moderately accurate data of Lonsdale and Toor² for the diamagnetic anisotropy of B-trichloroborazine, $\Delta\chi = -18 \times 10^{-6}$, it seems that borazine and its other derivatives would show some diamagnetic anisotropy. Obviously this problem requires further investigation.

(6) Neither can the $\chi_{||}$ of borazine be assumed to be equal to the $\chi_{||}$ of the isoelectronic benzene molecule as suggested.¹ Thus, the calculated $\chi_{||}$ -values of molecules isoelectronic with benzene, such as pyridine, pyrimidine, pyrazine, and sym-triazine, differ appreciably from the $\chi_{||}$ of benzene.

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(1) H. Watanabe, K. Ito, and M. Kubo, *J. Am. Chem. Soc.*, **82**, 3294 (1960).

(2) K. Lonsdale and E. Toor, *Acta Cryst.*, **12**, 1048 (1959).

(3) J. C. Sheldon and B. C. Smith, *Quart. Rev.* (London), **14**, 200 (1960).

(4) (a) G. Foëx, "Tables de Constantes et Données Numériques. 7. Constantes Sélectionnées. Diamagnétisme et Paramagnétisme," Masson et Cie, Paris, 1957, pp. 28-29; (b) *ibid.*, p. 222.

(5) P. Pascal, *Compt. rend.*, **218**, 57 (1944).