TABLE VI

Values of b, For Equation 1, $k' = k[H^+] \exp b$

Solvent	T, °C.	b, mole^{-1}, from Table I	b, mole^{-1}, from Table III
H_2O, HCl	34.98	0.76	.....
H_2O, H_2SO_4	34.98	.79[a]	.....
H_2O, HCl	37.27	.87	.....
H_2O, HCl	...	..	0.82 ± 0.08
20% Dioxane, HCl	34.98	0.80	
20% Dioxane, HCl	...	..	0.66 ± 0.05
80% Dioxane, H_2SO_4	34.98	2.1[a]	.....

[a] From Table II.

values is only about 10%, and the difference in the values should not be considered significant for the water and 20% dioxane solution. b is increased in 80% dioxane but less than predicted. The effect on the rate when NaCl or $(CH_3)_3N \cdot HCl$ is added is in accord with expectations, decreasing in the order H^+, Na^+, $(CH_3)_3NH^+$ (Table V).

Acknowledgment.—Financial assistance in this work by the Research Corporation is gratefully acknowledged.

Experimental

Materials.—Several different lots of trimethylamine borane were kindly supplied by Callery Chemical Corporation. The samples were 98–100% pure based on iodate titration and were used without further purification. Only peroxide-free 1.4 dioxane was used after drying and distillation from calcium hydride. All other materials were reagent grade.

Kinetic Procedure.—All experiments were carried out at temperatures held constant to ±0.005°. Temperature intervals were measured with a Beckmann thermometer. In making an experiment, 50 ml. of an aqueous borane solution was pipetted into the reaction vessel and diluted either with 50 ml. of distilled water or with 50 ml. of 50.0% by volume aqueous dioxane. Then 25 ml. of standardized aqueous HCl were added and the mixture was thoroughly shaken. All solutions were thermostated and concentrations were calculated from the dilution ratios. The borane concentrations were about 0.01 M. At intervals 10-ml. aliquots were pipetted for analysis.

Analysis.—Samples were added to a measured amount of standard KIO_3 solution. In the acidic solution excess oxidant was converted to iodine which was titrated with sodium arsenite to the starch end-point after adding excess $NaHCO_3$.

[CONTRIBUTION FROM CHEMICAL DEPARTMENT, NAGOYA UNIVERSITY, CHIKUSA NAGOYA, JAPAN]

The Diamagnetic Anisotropy of a Borazole Ring

BY HARUYUKI WATANABE,[1] KAZUO ITO AND MASAJI KUBO

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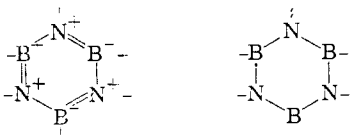
The diamagnetic susceptibilities of borazole and some of its derivatives were measured at room temperature. From these data and the diamagnetic susceptibility calculated from Pascal's constants along a direction parallel to the molecular plane, the diamagnetic anisotropy of a borazole ring was estimated at about -36×10^{-6}. Theoretical calculations based on molecular orbitals for the π-electron system of a borazole ring were carried out in order to evaluate the diamagnetic anisotropy as a function of molecular parameters. Comparison between the observed and calculated diamagnetic anisotropies led to the conclusion that the extent of contribution of the donor–acceptor double bond structure to the normal state of borazole is 24% and that the π-electron bond order of BN bonds in a borazole ring is 0.45.

Introduction

Borazole is isoelectronic with benzene. In fact, a number of physical properties of this compound and its derivatives bear fairly close resemblance to those of benzene and corresponding benzene derivatives.[2] For instance, the approximately planar hexagon form of a borazole ring in the molecules of borazole and some of its derivatives has been confirmed by electron diffraction[3–5] as well as by X-ray analysis,[6] the BN bond distance being intermediate between the B–N single bond distance and the B=N double bond distance.[7] The ultraviolet absorptions of borazole and its derivatives are similar to those of benzene and the corresponding benzene derivatives, respectively.[7–10] The infrared absorptions and Raman spectra of the former group of compounds can be interpreted on the basis of results on the latter group of compounds,[11–13] the force constant of BN stretching vibrations being intermediate between those for a B–N single bond and a B=N double bond. The dipole moment data also suggest a nearly planar hexagon structure of a borazole ring.[14,15]

These facts have led to the presumption that the electronic structure of a borazole molecule may well be represented by a resonance hybrid between the two electronic states.[7,8]



This suggests that a borazole ring shows diamagnetic anisotropy due to π-electrons as does a benzene ring. However, the effective number of π-electrons contributing to the diamagnetic anisotropy of a borazole molecule is presumed to be

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smaller than that of a benzene molecule depending upon the importance of the electronic structure involving single bonds alone relative to that having donor–acceptor double bonds. In addition, unlike a benzene molecule belonging to a point group D_{6h}, a borazole molecule has a symmetry of D_{3h}. For these reasons, the diamagnetic anisotropy of borazole will be appreciably different from that of benzene, and the determination of its value will give a clue to the elucidation of the electronic state of a borazole ring.

The present investigation has been undertaken in an effort to discuss this problem based on the measurements of the magnetic susceptibilities of borazole and its derivatives.

Materials.—The samples of borazole and N-trimethylborazole were supplied from Dr. R. Schaeffer of Indiana University. Other derivatives listed in Table I were synthesized by the methods already reported.[15]

TABLE I

MOLAR DIAMAGNETIC SUSCEPTIBILITIES OF B-triX-N-triY-BORAZOLES AT ROOM TEMPERATURE AND THE DIAMAGNETIC ANISOTROPY OF A BORAZOLE RING

Compound			
X	Y	$\chi_M \times 10^6$	$\Delta\chi \times 10^6$
H	H	− 49.6	−36
H	CH_3	− 78.6	
CH_3	CH_3	−119	−37
C_2H_5	CH_3	−146	
C_2H_5	C_2H_5	−189	−40
CH_3	C_6H_5	−234	
C_2H_5	C_6H_5	−264	

Experimental Method and Results

The magnetic susceptibility was determined at room temperature by means of a Gouy magnetic balance described elsewhere.[16] The results are shown in Table I.

Evaluation of Diamagnetic Anisotropy.—The diamagnetic anisotropy $\Delta\chi$ of borazole is related to the molar susceptibility χ_M by

$$\chi_M = \frac{1}{3}(2\chi_{||} + \chi_\perp) = \chi_{||} + \frac{1}{3}\Delta\chi$$

where $\chi_{||}$ and $\chi_\perp$ denote the magnetic susceptibilities of a borazole molecule with its molecular plane parallel and perpendicular to the external magnetic field, respectively. The factor $^1/_3$ takes into account all possible orientations of the molecule in space. Accordingly, provided that $\chi_{||}$ is properly estimated, $\Delta\chi$ can be evaluated from the observed susceptibility. The estimation of $\chi_{||}$ presents a fairly difficult problem. However, because π-electrons revolving along the ring are not involved in $\chi_{||}$, one may safely assume that $\chi_{||}$ of borazole is not very different from that of isoelectronic benzene, -37.7,[17–19] yielding $\Delta\chi = -36$.[20] This assumption is supported by these several considerations.

In calculating $\chi_{||}$ by Pascal's additivity rule

$$\chi_{||} = 3\chi_B + 3\chi_N + 6\chi_H$$

no suitable data of Pascal's constants can be found in the literature, except that for hydrogen,[21] -2.93. The only datum available for the estimation of χ_B is the magnetic susceptibility of boron trichloride, -67.0.[22] Fortunately, B–Cl bonds in this molemolecule, like BN bonds in a borazole molecule, are known to have some degree of double bond character.[23–25] Accordingly, the contribution of a chlorine atom to molar diamagnetic susceptibility was evaluated from the data of compounds, such as tetrachloroethylene, *trans*-dichloroethylene, chlorobenzene and *sym*-trichlorobenzene,[22] having partial double bond character in their C–Cl bonds, as -19.6, instead of the usual Pascal constant. -20.1, for chlorine. Therefore χ_B was estimated at about -3.2.

Pascal's constant of a nitrogen atom in a closed ring as in piperidine and piperazine is known to be equal to -4.61.[21,26] The correction for the partial double bond character of BN bonds can be made in the following way. The constitutive correction constant for N==C is $+8.2$.[21] Subtracting from this value half an amount of the constitutive correction constant for C==C, $+5.5$, one obtains a constitutive correction constant for a double-bonded nitrogen atom in a ring. This multiplied by the degree of BN double bond character gives a correction to be applied to the ordinary Pascal's constant mentioned above. The degree of BN double bond character is nothing but the fractional contribution of the donor–acceptor double bond structure to the normal state of a borazole molecule, *i.e.*, the π-electron density on a boron atom in a borazole ring, and is estimated at 0.24, as described below. Thus, we have

$$\chi_N = -4.61 + 0.24\left(8.2 - \frac{1}{2}\times 5.5\right) = -3.3$$

Therefore

$$\chi_{||} = -3\times 3.2 - 3\times 3.3 - 6\times 2.93 = -37.1$$

in good agreement with -37.7 for benzene.

Analogous calculations are feasible for some of the borazole derivatives investigated and give almost concordant results, as shown in Table I. However, with increasing complexity of molecules, the calculated values of anisotropy are less reliable than that for borazole. One may presume that the diamagnetic anisotropy of a borazole ring is not far from -36, which is considerably smaller than -54 for benzene.[17–19]

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Discussion

The quantum mechanical treatment of diamagnetic anisotropy due to the ring current of π-electrons has been carried out by London[27,28] and led to satisfactory results for a variety of aromatic ring compounds.[29] Later, McWeeny[30] gave a general formulation for the solution of a secular equation appearing in the London theory. According to his results, the diamagnetic anisotropy of benzene as well as of borazole is expressed by

$$\Delta\chi = -\frac{1}{18}\left(\frac{2\pi e}{hc}\right)^2 \Omega^2|\beta|\left[\sum_{(rs)} p_{rs} + \beta \sum_{(rs)}\sum_{(tu)} \bar{\pi}_{(rs)(tu)}\right] \quad (1)$$

Here, Ω denotes the area of the ring. β is a parameter defined by[31]

$$\beta = \gamma - s\alpha \quad (2)$$

where γ and s are the resonance integral and the overlap integral between neighboring atoms, respectively, while α is the coulomb integral of a carbon atom and the mean of the coulomb integrals of boron and nitrogen, respectively, for benzene and borazole. p_{rs} is the bond order of the rs bond. $\bar{\pi}_{(rs)(tu)}$ is defined by[32]

$$\bar{\pi}_{(rs)(tu)} = \pi_{rs,\,tu} - \pi_{rs,\,ut} + \pi_{sr,\,ut} - \pi_{sr,\,tu} \quad (3)$$

$$\pi_{rs,\,tu} = 2\sum_{J}^{\text{occ.}}\sum_{K}^{\text{unocc.}} \frac{c_{rJ}c_{sK}c_{tK}c_{uJ}}{E_J - E_K} \quad (4)$$

where c_{rJ} is the coefficient of the rth atomic orbital ϕ_r ($r = 1, \ldots 6$) in the Jth zero-field molecular orbital having an energy E_J, real wave functions being used throughout. Other notations have similar significances. The LCAO molecular orbitals of benzene are available in the literature.[33] Those of borazole have the forms shown in Table II. Calculations show that irrespective of numerical values of c, the following summation vanishes for both benzene and borazole.

$$\sum_{(tu)} \pi_{(rs)(tu)} = 0 \quad (5)$$

TABLE II

MOLECULAR ORBITALS OF BORAZOLE

Species	Molecular orbitals
A_1	$c_{11}(\phi_1 + \phi_3 + \phi_5) + c_{21}(\phi_2 + \phi_4 + \phi_6)$
E	$c_{12}(\phi_1 - \phi_5) + c_{22}(\phi_2 - \phi_4)$ $c_{12}(\phi_1 - 2\phi_3 + \phi_5) - c_{22}(\phi_4 - 2\phi_6 + \phi_2)$
E	$c_{14}(\phi_1 - \phi_5) + c_{24}(\phi_2 - \phi_4)$ $c_{14}(\phi_1 - 2\phi_3 + \phi_5) - c_{24}(\phi_4 - 2\phi_6 + \phi_2)$
A_1	$c_{16}(\phi_1 + \phi_3 + \phi_5) + c_{26}(\phi_2 + \phi_4 + \phi_6)$

Therefore, the diamagnetic anisotropies of these compounds can be expressed by

$$\Delta\chi = -\frac{1}{3}\left(\frac{2\pi e}{hc}\right)^2 \Omega^2 p|\beta| \quad (6)$$

It should be mentioned in this connection that this equation, with $p = 2/3$ due to Coulson,[34] gives $\Delta\chi$ of benzene in agreement with that obtained by solving the secular determinant of London.[28,29]

Equation 6 suggests that $p|\beta|$ of a borazole ring can be calculated from the observed diamagnetic anisotropy. However, it is hardly expected that this procedure gives useful data on the electronic state of a borazole molecule. It is because the value of β, -4.4 e.v., calculated by the present authors for benzene using eq. 6 from the observed diamagnetic anisotropy was in poor agreement with -2.6 e.v. estimated by Roothaan and Mulliken[8] from the data of ultraviolet spectra. On the other hand, London's method gives relative values for the diamagnetic anisotropies of benzene and various aromatic compounds having condensed rings in good agreement with experiments.[29] For this reason, an analysis is carried out with the relation

$$\frac{\Delta\chi_{\text{boraz}}}{\Delta\chi_{\text{benz}}} = \frac{(\Omega^2 p\beta)_{\text{boraz}}}{(\Omega^2 p\beta)_{\text{benz}}} = \frac{(r^4 p\beta)_{\text{boraz}}}{(r^4 p\beta)_{\text{benz}}} \quad (7)$$

where r denotes the BN or CC distance. The coefficients in the LCAO molecular orbitals for the π-electron system of borazole were calculated as functions of the overlap integral s and a parameter d defined by[8]

$$d = (\alpha_N - \alpha_B)/2\beta \quad (8)$$

where the numerator denotes the difference between the coulomb integrals of nitrogen and boron. The overlap integral is listed in tables compiled by Mulliken, *et al.*[35] The observed value, 1.44 Å.,[4] for the BN distance of borazole gives $s = 0.219$. The π-electron distribution on a boron atom q_B ($q_N = 2 - q_B$) and the bond order of BN bonds can be evaluated by the usual procedure from molecular orbitals. Therefore, they can be calculated in a straightforward way as functions of d. The results are shown in Table III along with the values

TABLE III

MOLECULAR PARAMETERS OF A BORAZOLE RING

d	q_B	p	$\lvert\beta\rvert$, e.v.	$\Delta\chi_{\text{boraz}}/\Delta\chi_{\text{benz}}$
0	1.000	0.667	3.30	1.415
0.5	0.531	.595	2.96	1.132
1.0	.257	.459	2.36	0.697
1.5	.124	.336	1.86	.402
2.0	.060	.239	1.50	.231

of β evaluated for the BN distance equal to 1.44 Å. by means of the following equation first proposed by Roothaan and Mulliken[8] and modified in accordance with the new assignments of ultraviolet absorption bands of benzene.[35,37]

$$\beta = -6.93/2.10(1 + 0.95d^2)^{1/2} \text{ e.v.} \quad (9)$$

From these data, $\Delta\chi_{\text{boraz}}/\Delta\chi_{\text{benz}}$ can be evaluated as a function of d by means of eq. 7 with $r_{CC} = 1.40$

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Å.,[38,39] $p = 2/3$, and $\beta = -2.6_6$ e.v. for benzene as mentioned above. The results are shown in the last column of Table III. On the other hand, the observed ratio of the diamagnetic anisotropies of the two compounds is 36/54 = 0.67. Interpolation by means of Table III gives $d = 1.0_5$, $q_B = 0.24$, $p_{BN} = 0.45$ and $\beta_{BN} = -2.3_1$ e.v. for the molecular parameters of a borazole ring.

The value of d is in excellent agreement with that given by Roothaan and Mulliken,[8] 1.0. The resulting value of $\alpha_N - \alpha_B = -4.7$ e.v. compares favorably with $\alpha_N - \alpha_C = -(1.8\text{–}2.4)$ e.v.[40] The value of β thus obtained gives the ratio, $\beta_{boraz}/\beta_{benz} = 2.31/2.66 = 0.87$ in good agreement with the ratio of overlap integrals, $s_{boraz}/s_{benz} = 0.219/0.25 = 0.88$. It is known[31] that β (or the resonance integral) of CC bonds varies with the interatomic distance in proportion to the overlap integral s. The present results confirm that the same relation is valid also for bonds involving heteroatoms.[41]

The extent of contribution of the donor–acceptor double bond structure, *i.e.*, the π-electron distribution q_B on boron atoms in a borazole molecule has been a subject of considerable dispute. Although the marked similarity of a borazole ring to a benzene ring suggests a fairly high value of q_B, the present analysis gives 0.24 in agreement with the conclusion derived by Pease[42,43] from observed interatomic distances that q_B is not very great. Rector, *et al.*,[7] have estimated the value of q_B at about 0.15 from the observed BN bond distance. However, since no reliable data are available at present for the single bond distance as well as the double bond distance of BN bonds, the value thus obtained is open to question. On the other hand, Kobayashi[44] has carried out SCF m.o. treatment on borazole and found $q_B = 0.52$.

The evaluation of the dependence of bond lengths upon the bond order of bonds between different atoms presents considerable difficulties owing to the lack of sufficient data.[45,46] The π-electron bond order $p_{BN} = 0.45$ for a BN bond distance $r_{BN} = 1.44$ Å. for borazole is consistent with the curve of CC bond lengths plotted against the bond order and suggests the adequacy of the values for the single bond distance ($r_s = 1.56$ Å.) and the double bond distance ($r_d = 1.35$ Å.) proposed by Coffin and Bauer[5] and those by Cartmell and Fowles[47] ($r_s = 1.54$, $r_d = 1.36$ Å.). On the other hand, the values of BN distances given by Rector, *et al.*,[7] ($r_s = 1.48$, $r_d = 1.30$ Å.) and by Hedberg and Stosick[48] ($r_s = 1.49$ Å.) deviate appreciably from the curve of CC bond lengths mentioned above.

Acknowledgment.——We wish to express our cordial thanks to Dr. R. Schaeffer of Indiana University for providing us with some of the materials used id the present investigation.

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[CONTRIBUTION FROM THE WESTINGHOUSE RESEARCH LABORATORIES, PITTSBURGH 35, PENNSYLVANIA]

The Sulfur Hexafluoride Clathrate of Dianin's Compound (4-*p*-Hydroxyphenyl-2,2,4-trimethylchroman): Preparation, Characterization and Thermal Decomposition

BY L. MANDELCORN, N. N. GOLDBERG AND R. E. HOFF

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The sulfur hexafluoride clathrate of Dianin's compound is obtained by recrystallization at a high pressure of sulfur hexafluoride. The amount of sulfur hexafluoride contained in the clathrate so prepared is about 13% by weight, which on the basis of volume of containing solid, is equivalent to a pressure of 25 atmospheres of gas. At temperatures below its melting point, this clathrate decomposes by sublimation of Dianin's compound. The decomposition rate is limited by the ratio of sample volume to exposed area and by the magnitude of external gas pressure. An examination of infrared spectra reveals that chemical interactions between the sulfur hexafluoride and its enclosing cages are very slight. Evidence that the guest-free form of Dianin's compound also possesses the clathrate structure is derived from density measurements.

Introduction

A review of the subject of clathrates[1] mentioned that these substances afford a convenient means for storage and for controlled release of inert gases. Generally, in clathrate systems, gases are retained under ordinary conditions and may be released easily by simple processes such as heating, dissolving or grinding. Sulfur hexafluoride is a gas that has found considerable use in electrical devices. It was felt that its range of practical applicability would be considerably enhanced if it were associated with a solid. A clathrate of sulfur hexafluoride appeared to fulfill this requirement.

Dianin's compound was selected as the host component for a clathrate of sulfur hexafluoride as a result of preliminary reports by Baker and McOmie[2] and by Powell and Wetters[3] on an extensive investigation of the properties of this solid. They showed that three series of clathrates of Dianin's compound are possible; their maximum-composition formulas being $6C_{18}H_{20}O_2 \cdot 3M_1$, $6C_{18}H_{20}O_2 \cdot 2M_2$ and $6C_{18}H_{20}O_2 \cdot M_3$ where M_1, M_2 and M_3 are molecules of the size of methanol, ethanol and hexachloroethane, respectively. Since the size of a sulfur

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