

from deep yellow to orange and red. It is suggested that these shifts in color from pale yellow result from anion deformation or from anion-cation charge transfer. Crystallographic studies have shown that (aromatic) $N-H \cdots X$ ($X = Cl$ or Br) interactions can significantly deform an anion.^{5c,11} Deformation of an ion may induce a perturbation of its energy levels causing absorption bands to shift in wavelength or causing one or more new bands to emerge. Presence of charge-transfer may be important in situations involving short van der Waals contacts between Br^- ligands and the cations. A short donor-acceptor distance, accompanied by specific spatial orientations, may provide a favorable situation for the transfer of electrons from a donor orbital of the halogen to the π -acceptor orbital of the pyridinium ring. An example of a closely related system is the black N,N' -dimethyl-4,4'-bipyridylium salt of $[CuCl_2]_n^{n-}$.¹²

In order to gain an insight into the various types of anions one might find in the $RSbBr_4$ and R_2SbBr_5 salts, it is profitable to examine structures of other group V nontransition metal halides having similar formulas. Five such compounds are $C_5NH_6SbCl_4$,¹³ $C_6NH_8BiBr_4$,¹⁴ $C_6NH_8BiI_4$,¹⁴ $(C_5NH_{11})_2BiBr_5$,¹⁵ and $(NH_4)_2SbCl_5$.¹⁶ In the first three examples MX_4^- anions (actually $M_2X_8^{2-}$ dimers) bind together *via* pairs of halogen bridges, linking neighboring metal atoms together. Such an arrangement enables the metal atom to adopt a distorted octahedral environment. In $(C_5NH_{11})_2BiBr_5$ a distorted octahedral configuration is also adopted by the central metal atom (Bi in this case) by forming infinite chains of $BiBr_5^{2-}$ ions *via* bromine bridges. By contrast, $SbCl_5^{2-}$ in $(NH_4)_2SbCl_5$ exists only as an isolated ion. It adopts an octahedral configuration of six electron pairs in which a lone pair of electrons occupies one of the octahedral sites in the antimony(III) coordination sphere. The same stereochemical configurations, including a hypothetical straight-chain polymeric variation of the observed zigzag $BiBr_5^{2-}$ form, are logical possibilities for the $RSbBr_4$ and R_2SbBr_5 series. There is a striking similarity in crystal data of the 2-methylpyridinium salts $C_6NH_8BiBr_4$,^{14,17} and $C_6NH_8BiI_4$,^{14,19} with the 1-methyl-, 2-methyl- and 3-methylpyridinium salts in Table I, indicating that all five structures are probably isomorphous.²⁰ Similar remarks cannot be made unequivocally about the pyridinium analogs $C_5NH_6SbCl_4$ ¹³ and $C_5NH_6SbBr_4$, however, owing to their dissimilar cell parameters.

The $Sb_2Br_9^{3-}$ ion is possibly present in the $R_3Sb_2Br_9$ series.

This anion has previously been found in the structures of $(C_5NH_6^+)_5(Sb_2Br_9^{3-})(Br^-)_2$ ^{6a} and $[(CH_3)_4N^+]_3(Sb_2Br_9^{3-})(Br_2)$.^{6b} It comprises two $SbBr_6^-$ octahedra sharing a face. Alternate considerations for $R_3Sb_2Br_9$ include $SbBr_4^-$ chains or discrete $Sb_2Br_8^{2-}$ dimers, with interstitial bromide ions for charge balance.

Of the 19 salts synthesized, nine fall into four sets of isomorphous groups having the following cations: (i) 1-methylpyridinium, 2-methylpyridinium and 3-methylpyridinium; (ii) 2-chloropyridinium and 2-bromopyridinium; (iii) 3-bromopyridinium²¹ and 3-iodopyridinium; and (iv) quino-
linium²² and isoquinolinium.

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Registry No. $C_5H_5NHSbBr_4$, 52279-30-8; $1-CH_3C_5H_5NSbBr_4$, 52279-29-5; $2-CH_3C_5H_5NHSbBr_4$, 50284-20-3; $3-CH_3C_5H_5NHSbBr_4$, 52279-31-9; $2,6-Cl_2C_5H_3NHSbBr_4$, 52279-32-0; $C_6H_7NHSbBr_4$, 52279-33-1; $i-C_6H_7NHSbBr_4$, 52279-34-2; $(4-CH_3C_5H_4NH)_2SbBr_5$, 52279-35-3; $(2-ClC_5H_4NH)_2SbBr_5$, 52279-36-4; $(2-BrC_5H_4NH)_2SbBr_5$, 52279-37-5; $(3-BrC_5H_4NH)_2SbBr_5$, 52279-38-6; $(3-IC_5H_4NH)_2SbBr_5$, 52279-39-7; $(3-HO_2CC_5H_4NH)_2SbBr_5$, 52279-40-0; $(3,5-Cl_2C_5H_3NH)_2SbBr_5$, 52279-41-1; $[2,6-(CH_3)_2C_5H_3NH]_2Sb_2Br_9$, 52486-72-3; $[2,4,6-(CH_3)_3C_5H_2NH]_2Sb_2Br_9$, 52486-73-4; $(2-FC_5H_4NH)_2Sb_2Br_9$, 52486-74-5.

Supplementary Material Available. A listing of infrared frequencies in the region 1700-250 cm^{-1} will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24X reduction, negatives) containing all the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-2767.

(21) The 3-bromopyridinium crystals contain a B-centered unit cell (dimensions $a = 35.90$ (11), $b = 11.98$ (4), $c = 9.35$ (3) Å; $\beta = 92.2$ (2)°) which, according to Weissenberg photographs, is similar in shape and orientation to the primitive unit cell in the 3-iodopyridinium analog (dimensions given in Table I), indicating that there exists a subtle similarity in ionic packing for the two materials.

(22) The quino-
linium crystals contain a body-centered unit cell (dimensions $a = 13.45$ (4), $b = 14.04$ (4), $c = 7.44$ (2) Å; $\beta = 90.8$ (2)°) which, according to Weissenberg photographs, is similar in shape and orientation to the primitive unit cell in the isoquinolinium analog (dimensions given in Table I), indicating that there exists a subtle similarity in ionic packing for the two materials.

(11) See, for example: M. L. Hackert and R. A. Jacobson, *Acta Crystallogr., Sect. B*, 27, 1658 (1971); S. Koda, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Jap.*, 44, 1597 (1971); R. E. DeSimone and G. D. Stucky, *Inorg. Chem.*, 10, 1808 (1971); R. C. Gearhart, T. B. Brill, W. A. Welsh, and R. H. Wood, *J. Chem. Soc., Dalton Trans.*, 359 (1973); S. L. Lawton, E. R. McAfee, J. E. Benson, and R. A. Jacobson, *Inorg. Chem.*, 12, 2939 (1973).

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(17) Monoclinic, space group $P2_1/c$, with lattice parameters $a = 12.91$, $b = 13.40$, $c = 7.63$ Å, and $\beta = 107.2^\circ$.¹⁸

(18) Lattice parameters correspond to those reported in ref 14 but transformed with the matrix $(\frac{1}{2}, 0, \frac{1}{2})/(0, \bar{1}, 0)/(0, 0, \bar{1})$.

(19) Monoclinic, space group $P2_1/c$, with lattice parameters $a = 13.65$, $b = 14.06$, $c = 8.03$ Å, and $\beta = 106.7^\circ$.¹⁸

(20) The structure of a sixth salt, $C_6NH_8SbI_4$, is isomorphous with the $C_6NH_8BiBr_4$ and $C_6NH_8BiI_4$ crystals, according to a preliminary study reported in ref 14.

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Atropisomerism in Aryl-Substituted Borazines¹

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There is much evidence^{2,3} to suggest that in the most stable conformation the aromatic rings of triaryl-substituted borazines are perpendicular to the plane of the borazine ring.

(1) Presented in part at the 165th National Meeting of the American Chemical Society, Dallas, Tex., April 1973.

(2) E. F. Mooney, *Spectrochim. Acta*, 18, 1355 (1962), and papers quoted therein.

(3) I. M. Butcher, W. Gerrard, J. B. Leane, and E. F. Mooney, *J. Chem. Soc.*, 4528 (1964).

However, all such previous reported evidence has been circumstantial. We present the first example of an aryl-substituted borazine in which the absence of coplanarity of the aromatic and borazine rings is clearly demonstrated; it is also the first reported case of atropisomerism in borazines. *B*-Tri-*o*-tolyl-*N*-triethylborazine (I), in which the aryl substituents on the boron atoms are sterically prevented from rotating freely about the carbon-boron bonds, has been prepared. Compound I exists as a pair of diastereomers, and partial separation of the isomers was achieved. Although racemization is immeasurably slow at 0°, the isomers are thermally interconvertible. Proton nmr was used as monitor in a brief investigation of the kinetics of the interconversion at 50°. The position isomer of I, *B*-triethyl-*N*-tri-*o*-tolylborazine (II), was also prepared.

Experimental Section

General Data. All borazines were prepared under nitrogen by modifications of established procedures. In each case, a *B*-trichloro-*N*-triaryl(or trialkyl)borazine was made from BCl₃ and a primary amine, and the trichloroborazine was treated with a Grignard reagent to form the final product. Standard drybox and high-vacuum techniques were used in handling borazines and other air-sensitive substances. Solvents were dried by refluxing over LiAlH₄. Compounds I and II were characterized by proton nmr, infrared, ultraviolet, and mass spectrometry, elemental analysis, and melting point. Proton nmr spectra were recorded on a Bruker HFX-90 spectrometer and a Varian A-60 spectrometer, using samples in CDCl₃ solution, sealed under vacuum; TMS, 1,4-dioxane, and 1,1,2,2-tetrachloroethane were used as internal standards. Infrared mull spectra were recorded on a Perkin-Elmer Model 521 grating infrared spectrometer using a 0.05-mm polystyrene film for calibration. Ultraviolet spectra were recorded on a Cary 14 recording spectrophotometer. High-resolution mass spectral data were obtained on an AEI MS 902 mass spectrometer internally referenced to perfluorokerosene using a DEC PDP-8/I computer. Elemental analyses were performed by Schwarzkopf Micro-analytical Laboratory, Woodside, N. Y. Melting points were determined using a Buchi melting point apparatus, with capillaries sealed under nitrogen, and are uncorrected.

***B*-Tri-*o*-tolyl-*N*-triethylborazine (I).** A diethyl ether solution of *o*-tolylmagnesium bromide, prepared from magnesium turnings (1.64 g, 0.0675 mol) and a slight excess of *o*-bromotoluene, was added dropwise to a solution of *B*-trichloro-*N*-triethylborazine (III)^{4,5} (4.02 g, 0.015 mol) in toluene (120 ml).^{6,7} After removal of the ether by distillation, the reaction mixture was refluxed 20 hr. Magnesium salts were removed by filtration, and the toluene and excess *o*-tolylmagnesium bromide were removed by vacuum distillation; a brown solid remained. Sublimation under vacuum at 150–160° produced 3.31 g (51% based on III) of white crystals of I, mp 188–193°. *Anal.* Calcd for C₂₇H₃₆B₃N₃: C, 74.54; H, 8.34; N, 9.66. Found: C, 74.64; H, 8.50; N, 9.57. Mol wt (mass spectrum) 435.3179 (calcd 435.3187).

Separation of Isomers. The cis isomer (described below) of I, mp 198.5–199.5°, was isolated in the pure state by crystallization from a benzene-hexane mixture. Trans-enriched samples, mp 193.5–194.5°, were obtained by column chromatography, using a 22-cm alumina column with *n*-hexane as solvent.

Thermal Interconvertibility of Isomers. Sealed melting point capillaries containing samples of each isomer were heated for short periods of time in the liquid state (ca. 200°). The samples were allowed to cool and solidify, and their melting points were taken again. After each period of heating, the melting point of each sample was lower and the melting point range was wider, until finally all samples had a melting point range of 187–194°.

Racemization at 0° is immeasurably slow; nmr spectra of 1 year old samples of the cis isomer stored at 0° were indistinguishable from the spectra taken the day the samples were prepared. The intensities of the three tolyl CH₃ singlets at ca. 2.3 ppm (Figure 1) were used to follow the rate of racemization at 50°. A plot of $\ln(A_t - A_{eq})$ vs.

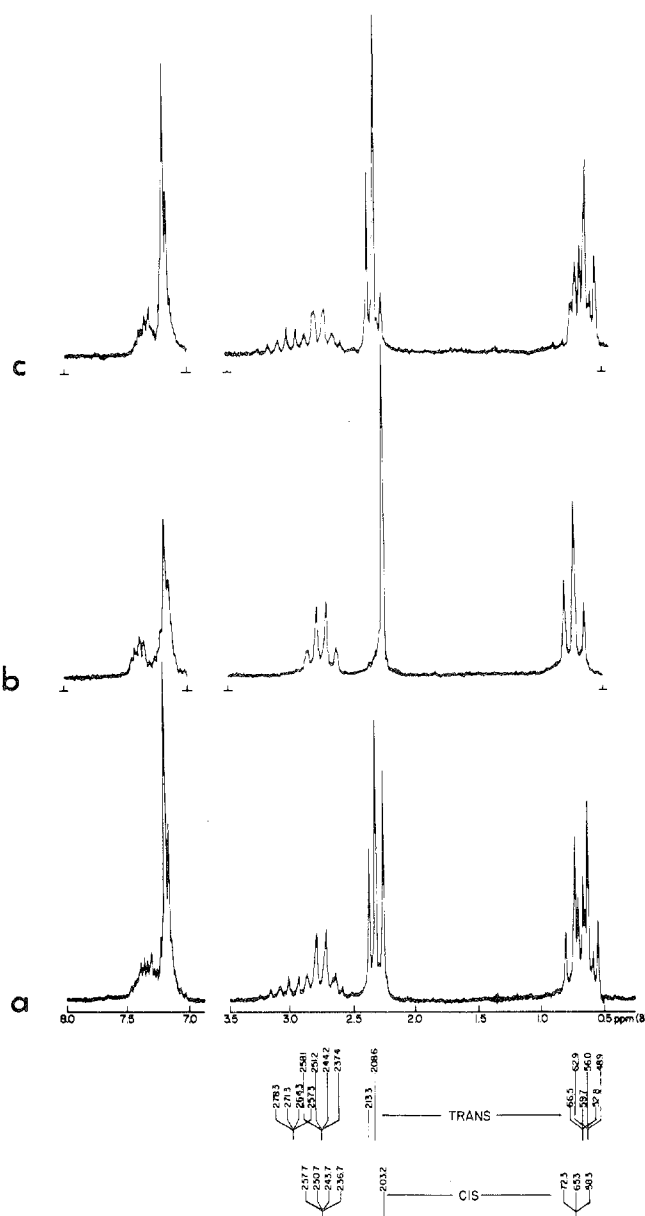


Figure 1. The 90-MHz proton nmr spectra of *B*-tri-*o*-tolyl-*N*-triethylborazine. The numbers in the lower section of the figure marked "TRANS" and "CIS" are chemical shifts in hertz downfield from TMS: (a) reaction product mixture; (b) cis isomer; (c) trans-enriched sample.

time ($A = [\text{trans}]$) was linear over 4 half-lives of reaction. From the slope of the line and the value of K_{eq} at 50°, the first-order rate constant for the conversion of the cis isomer at that temperature is $3.47 \times 10^{-5} \text{ sec}^{-1}$; for the conversion of the trans isomer it is $2.61 \times 10^{-5} \text{ sec}^{-1}$.

***B*-Triethyl-*N*-tri-*o*-tolylborazine(II).** An ether solution of ethylmagnesium bromide (0.045 mol) was added to a solution of *B*-trichloro-*N*-tri-*o*-tolylborazine (IV)^{4,5} (5.30 g, 0.0117 mol) in toluene (120 ml); the ether was removed by distillation, and the mixture was refluxed 17 hr. After removal of toluene by vacuum distillation, II was isolated by the saturated aqueous NH₄Cl method followed by crystallization from an ether-methanol solution.⁶ The yield was 0.70 g (14% based on IV) of white crystals, mp 130–132°. *Anal.* Calcd for C₂₇H₃₆B₃N₃: C, 74.54; H, 8.34; N, 9.66. Found: C, 74.83; H, 8.47; N, 10.01. Mol wt (mass spectrum) 435.3153 (calcd 435.3187).

Infrared and Visible-Uv Spectral Data. The strongest bands in the ir spectra recorded in this study are as follows (cm⁻¹): I, 1415 sh, s, 1408 vs; II, 1383 vs, in agreement with the observation^{8,9} that

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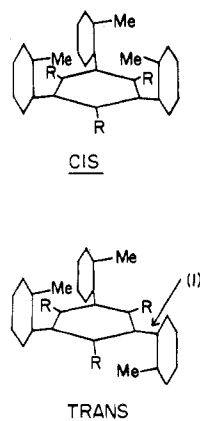


Figure 2. Configurations of cis and trans isomers of tri-*o*-tolylborazines.

the strongest band in the ir spectra of *B*-arylborazines is at higher frequency than the corresponding band in the spectra of *N*-arylborazines.

The intensities and frequencies of the uv absorptions of these compounds are as follows: I, $3.7 \times 10^3 \text{ cm}^{-1}$, $\log \epsilon = 3.0$, $3.8 \times 10^3 \text{ cm}^{-1}$, $\log \epsilon = 3.1$; II, $3.3 \times 10^3 \text{ cm}^{-1}$, $\log \epsilon = 1.9$, $3.7 \times 10^3 \text{ cm}^{-1}$, $\log \epsilon = 3.1$, $3.8 \times 10^3 \text{ cm}^{-1}$, $\log \epsilon = 3.2$. These values corroborate earlier suggestions¹⁰ about the dependence of uv spectral bands on average dihedral angles in phenyl-substituted borazines.

Discussion

Even in *B*-triphenylborazine and *N*-triphenylborazine, there is some overlapping of the borazine ring hydrogen atoms and the phenyl ring ortho hydrogen atoms; this crowding results in van der Waals repulsion between these hydrogen atoms and a small energy barrier to free rotation about the C-B or C-N bonds. When there are additional substituents on the borazine ring and in the ortho positions of the phenyl rings, the average dihedral angles are increased, and the energy barriers to rotation are increased.¹⁰ If the substituents are bulky enough, a triaryl-substituted borazine has sufficient steric hindrance to prevent rotation about the C-B or C-N bonds; and if the aromatic rings have no σ_v plane (*i.e.*, have different substituents in the two ortho or in the two meta positions of each ring), such a compound should exist as a pair of separable diastereomers, or atropisomers.

Compound I satisfies these criteria. The six substituents provide sufficient steric hindrance to prevent rotation, and a methyl group in an ortho position on each phenyl ring provides the asymmetry. The cis isomer has all three of the tolyl CH_3 groups on the same side of the plane of the borazine ring, while the trans isomer has two tolyl CH_3 groups on one side of the borazine ring plane and the third on the opposite side (Figure 2, R = Et). Compound I was prepared and the isomers were separated as described above.

The proton nmr spectra (Figure 1) of the isomers and of the reaction product mixture are easily predicted from the structures. Assuming rapid (on the nmr time scale) rotation about the C-N bonds, the three ethyl groups of the cis isomer are equivalent, as are the three tolyl groups; therefore the first-order spectrum consists of one A_2X_3 ethyl pattern, one tolyl CH_3 singlet, and a phenyl ring multiplet. In the trans isomer, two ethyl groups are equivalent and the third is different; two tolyl groups are equivalent and the third is different. Therefore the spectrum of this isomer consists of two triplets, two quartets, two singlets, and two phenyl multiplets, with one resonance of each type being of twice

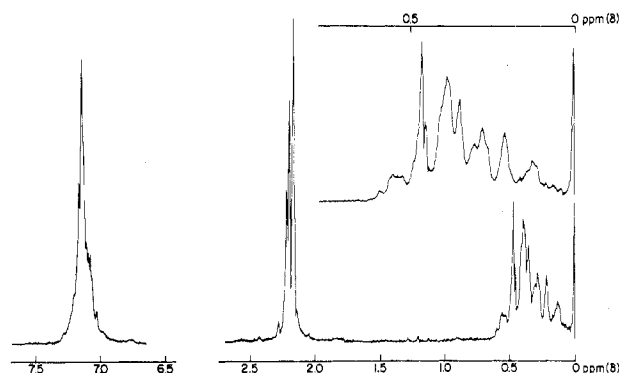


Figure 3. The 90-MHz proton nmr spectrum of *B*-triethyl-*N*-tri-*o*-tolylborazine.

the intensity of the other. The reaction product mixture spectrum is a superposition of the other two; the three phenyl ring resonances coincide.

The chemical shift differences between the three tolyl CH_3 peaks were too small to permit integration to be used to determine isomeric abundance, but curve analysis of these peaks with a Du Pont 310 curve resolver indicated that the ratio for the reaction product mixture was approximately 66% trans to 34% cis *vs.* a ratio of 75% trans to 25% cis predicted from simple statistics. We believe that the reason for the nonstatistical distribution is the thermal interconvertibility of the isomers. The kinetic data are consistent with a unimolecular mechanism of interconversion involving rotation about C-B bonds. Rotation about any one of the three C-B bonds converts the cis isomer to trans; either rotation about one specific C-B bond [(1) in Figure 2] or sequential (or simultaneous) rotations about the other two C-B bonds converts the trans isomer to cis. Prolonged heating of either isomer produces a mixture; the equilibrium mixture at 50° is 57% trans and 43% cis, and the equilibrium constant is essentially invariant as a function of temperature over the range 50 – 90° . We suggest that the final step of the synthesis, stepwise replacement of the three chlorine atoms of *B*-trichloro-*N*-triethylborazine by the tolyl groups of the Grignard reagent,^{7,11} could yield the statistical ratio of three trans molecules for every cis molecule; but since the process involved refluxing the reaction mixture in toluene for 20 hr, the original ratio was shifted in the direction of the 57:43 equilibrium ratio.

The question of how much bulk in the substituents is necessary to prevent free rotation of the aromatic rings is unanswered. The nmr spectrum (Figure 3) of II indicates the probability that it also exists as a pair of diastereomers which could be separated; the three peaks at *ca.* 2.2 ppm are not unlike the three tolyl CH_3 peaks in the spectrum of I. As described above, *B*-trichloro-*N*-tri-*o*-tolylborazine (IV; Figure 2, R = Cl) was prepared as an intermediate in the synthesis of II. The nmr spectrum of IV consists of one very sharp tolyl CH_3 singlet and a phenyl ring multiplet, indicating probable equivalence of the three tolyl groups. A logical extension of this investigation would be an attempt at the resolution of atropisomers of sterically similar borazines, such as *B*-trimethyl-*N*-tri-*o*-tolylborazine and its position isomer, *B*-tri-*o*-tolyl-*N*-trimethylborazine^{12,13} (Figure 2,

(11) J. H. Smalley and S. F. Stafiej, *J. Amer. Chem. Soc.*, **81**, 582 (1959).

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R = Me), to determine the minimum size of substituents in the blocking positions on the borazine ring for prevention of free rotation of tolyl groups.

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Registry No. *o*-Tolylmagnesium bromide, 932-31-0; *B*-trichloro-*N*-triethylborazine, 2608-99-3; *B*-tri-*o*-tolyl-*N*-triethylborazine, 52176-10-0; ethylmagnesium bromide, 925-90-6; *B*-trichloro-*N*-tri-*o*-tolylborazine, 5775-58-6; *B*-triethyl-*N*-tri-*o*-tolylborazine, 52176-11-1.

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Observations Regarding Cu-H-B Interactions in $\text{Cu}^{\text{I}}_2\text{B}_{10}\text{H}_{10}$

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In 1962 Dobrott and Lipscomb^{5,6} confirmed the D_{4d} symmetry of the $\text{B}_{10}\text{H}_{10}^{2-}$ anion by an X-ray diffraction study of $\text{Cu}^{\text{I}}_2\text{B}_{10}\text{H}_{10}$ (shown in Figure 1), and the nature of the covalent interactions of the copper atoms with the borane aggregate was discussed in detail.⁵ The authors postulated either an sp hybridized Cu^I forming three-center bonds with B-B edges or a tetrahedrally hybridized Cu^I interacting with the four nearest B atoms. The latter interpretation was discounted since the B-Cu-B angles were acute (44.6–46.9°, uncorrected for rigid-body motion). A third interpretation of the covalent bonding, not mentioned by Dobrott and Lipscomb, is the possible involvement of the borane terminal hydrogen atoms with sp³ hybridized copper orbitals, thus forming three-center Cu-H-B bridge bonds.

We have recently found that enough Cu-H-B interaction exists in $\text{Cu}^{\text{I}}_2\text{B}_{10}\text{H}_{10}$ to affect its ir spectrum substantially. In addition to the four terminal B-H stretching bands observed at 2510, 2535, 2560, and 2570 cm⁻¹ (Nujol mull), there is a broad absorption at 2100–2300 cm⁻¹. Muetterties⁷ made note of this broad band and also observed that the bands characteristic of $\text{B}_{10}\text{H}_{10}^{2-}$ at 1015 and 1070 cm⁻¹ had vanished. Lippard and Ucko⁸ reported bridging Cu-H-B stretching frequencies of 2045 (broad) and 2100 cm⁻¹ (broad, Nujol mull) for $(\text{PPh}_3)_2\text{Cu}^{\text{I}}\text{B}_3\text{H}_8$; the ir band at 2300–2100 cm⁻¹ of $\text{Cu}^{\text{I}}_2\text{B}_{10}\text{H}_{10}$ is comparable.

The perdeuterated complex $\text{Cu}^{\text{I}}_2\text{B}_{10}\text{D}_{10}$ was synthesized and examined for alterations of the ir spectrum in the 1800–2500-cm⁻¹ region. Analysis revealed that the B-D stretching bands were located at 1885, 1905, 1925, and 1935 cm⁻¹, and a broad absorption was centered at 1655 cm⁻¹ (Nujol mull).

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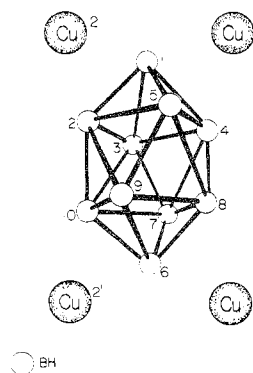


Figure 1. Structure of $\text{Cu}^{\text{I}}_2\text{B}_{10}\text{H}_{10}$ using the numbering system of ref 5. The structure only depicts the relative positions of the atoms and is not drawn to crystallographic scale.

The ratio of $\nu(\text{BH})/\nu(\text{BD})$ was determined as 1.33 (calcd 1.35) for all five ir bands; these data are consistent with Cu-H-B bonding interactions. Also synthesized was $(\text{PPh}_3)_2\text{Cu}^{\text{I}}\text{B}_{10}\text{H}_{10}$ from an alcoholic solution of triphenylphosphine and $\text{Cu}^{\text{I}}_2\text{B}_{10}\text{H}_{10}$. The ir spectrum (Nujol mull) contained two broad bands at 2230 and 2325 cm⁻¹ consistent for Cu-H-B stretching modes.

Unfortunately, the H positions in $\text{Cu}^{\text{I}}_2\text{B}_{10}\text{H}_{10}$ are not directly determined from the X-ray work⁵ and probably would not be reliable within $\sim 0.1\text{Å}$ even if they were. Clearly a neutron diffraction study of the $\text{Cu}^{\text{I}}_2\text{B}_{10}\text{H}_{10}$ structure is desirable. However, some observations can be made on the basis of the Cu and B positions.

The Cu-B distances range from 2.06 to 2.33 Å (average 2.20 Å), uncorrected for rigid-body motion. Assuming a single-bond boron radius⁹ of 0.88 Å and a Cu^I sp radius¹⁰ of 1.17 Å, we must lengthen the Cu-B single bond by about 0.15 Å to reproduce the observed average distance. The result, 2.20 Å, would be consistent with a three-center bond in which Cu is bonded to two B-B edges of the boron polyhedra. The bond order here is ~ 0.5 from Pauling's relation¹¹

$$D(n) = D(l) - 0.60A \log(n)$$

where n is the bond order. Appreciable covalent Cu-B bonding would probably still remain even at the 2.33-Å distance.

In an alternative view, we might assume a Cu^I sp³ radius¹² of 1.35 Å. We would then have almost a full (although bent) Cu-B bond of 2.23 Å if we add the B covalent radius of 0.88 Å. Large amounts of covalent Cu-B bonding would still be likely at 2.33 Å.

If the H atoms of the boron polyhedron are not grossly distorted from the local D_{4d} symmetry, we may utilize this symmetry and information from X-ray structure determinations^{13,14} of analogous compounds to estimate the H positions from the B positions. Using the numbering system from ref 5, we find four H atoms approximately 1.6–2.2 Å distant from Cu₁ and four H atoms approximately 1.7–2.1 Å distant from Cu₂ (average 1.9 Å). One of these H atoms is between two Cu atoms, at 2.1 Å from each if it is equidistant as the orientation of the B₁₀ cage suggests. This distance

(9) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 246.

(10) Reference 9, p 256.

(11) Reference 9, p 255.

(12) Reference 9, p 246.

(13) F. E. Scarbrough and W. N. Lipscomb, *Inorg. Chem.*, **11**, 369 (1972).

(14) C. H. Schwalbe and W. N. Lipscomb, *Inorg. Chem.*, **10**, 160 (1971).