Table I. Triplet States of Some Flavins

Flavin	Method[a]	Lowest[b]	2nd lowest[b]
Isoalloxazine	A	0.812	1.369
	B	1.007	1.315
	C	−0.437	0.690
	D	1.712	2.670
	E	1.689	2.937
	F	1.941	2.953
6,7-Dimethyl-	G	1.673	2.828
	H	1.826	2.907
	I	1.811	2.714
	J	0.673	2.168
	K	0.515	1.314
	L	0.714	2.238
Reduced 6,7-dimethyl-	M	0.969	2.691
	N	1.083	2.660
2-Thio-	O	1.553	2.742
4-Thio-	P	1.618	2.398
Alloxazine	Q	2.548	2.944
	R	2.465	2.885

[a] See text. [b] In electron volts.

singlet transition energies.[12] The semiempirical integrals used were analogous to those employed by Fox, *et al.*,[13] who obtained the lowest triplet state of 1.541 ev, which is slightly lower than the values presented in Table I. They included more configurations than we did and used slightly erroneous molecular geometry, thus accounting for their lower value.

(3) Introduction of the methyl groups as a group orbital contribution lowers the triplet, 1.673 ev, in going from D to G, but its value depends on the integrals employed (H and I[14]).

(4) The heteroatom model (J, K, and L) does not appear to be adequate, since the dipole moment (above 20 D.) and singlet and triplet transition energies were not reasonable.

(5) Reduced isoalloxazines showed phosphorescence in the range from 2.27 to ~2.84 ev.[3] It seems that these phosphorescence emissions correspond to the calculated second lowest triplet transition. However, it is probable that reduced flavins are not planar.

(6) 2-Thio- and 4-thioflavins show lower singlet and triplet levels than those of 6,7-dimethylisoalloxazine. The experimental triplet for this molecule is not available. The singlet transition energy calculated is in agreement with experiment.[12]

(7) Alloxazine has its triplet well above that of the isomer (isoalloxazine). The calculated values are in reasonable agreement with the observed phosphorescence (2.27 ev) for lumichrome.[3]

From the above observations, it can be seen that the lowest triplets of flavins are in the region from 7000 to ~7500 A or longer. Consequently, if singlet oxygen is indeed involved in the phosphorescence emission (6030 A) *via* the Steele–Cusachs mechanism,[5] the singlet oxygen cannot be $^1\Sigma_g^+$. There is another low-lying singlet (0,0) band of the $^1\Delta_g - {}^3\Sigma_g^-$ system at 12,700 A.[15] This seems to be still too high to account for the flavin phosphorescence. However, an alternative possibility of an as yet unknown emission at a longer wavelength region may not be ruled out.

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Pill-Soon Song, William E. Kurtin
Department of Chemistry, Texas Technological College
Lubbock, Texas 79409
Received April 29, 1967

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μ-Trimethylsilyl-pentaborane(9). The First Example of a Compound Containing a B–Si–B Three-Center Bond

Sir:

In the course of studying the chemistry of the B_5H_8 ion,[1] it was found that reaction with DCl produced DB_5H_8 in which the deuterium atom was exclusively in a bridging position (μ-DB_5H_8). Further studies have resulted in the preparation of μ-trimethylsilyl-pentaborane, μ-$(CH_3)_3SiB_5H_8$, the first example of a compound containing a boron–silicon–boron three-center two-electron bond.

The μ-$(CH_3)_3SiB_5H_8$ is readily prepared by slowly warming an ether solution of LiB_5H_8[1] and $(CH_3)_3SiCl$ from −78 to −30° with stirring. Subsequent separation of the reaction mixture by high-vacuum fractional condensation[2] results in yields of up to 90% of μ-$(CH_3)_3SiB_5H_8$, which has a melting range of 16–17° and a vapor pressure of about 1 mm at room temperature.

The compound was analyzed in part by hydrolysis in dilute aqueous HCl. The calculated amounts of boron and hydrolytic hydrogen according to the reaction

$$2(CH_3)_3SiB_5H_8 + 31H_2O \longrightarrow 10B(OH)_3 + [(CH_3)_3Si]_2O + 24H_2$$

are: B, 39.9%; H, 88.7 mmoles/g. Found: B, 40.3%; H, 88.7 mmoles/g. The $(CH_3)_3Si$ moiety was recovered as $(CH_3)_3SiH$ when μ-$(CH_3)_3SiB_5H_8$ was reduced with $LiAlH_4$ in tetrahydrofuran solution. However, the highest yields of the silane were only 89% of the expected amount, and the remaining residue has thus far proved intractable. The molecular weight was determined by mass spectrometry. The most intense peak in the parent group at *m/e* 135 corresponds to $(^{12}CH_3)_3{}^{28}Si^{10}B^{11}B_4H_8^+$. The cutoff at *m/e* 138 corresponds most probably to $(^{13}CH_3)(^{12}CH_3)_2{}^{29}Si^{11}B_5H_8^+$.

The gas-phase infrared spectrum of μ-$(CH_3)_3SiB_5H_8$ contains major bands (cm^{-1}) that may be assigned as follows: C–H stretch, 2960 (w) and 2905 (vw); B–H stretch, 2600 (s) and 2570 (sh); B–H–B bridge stretch, 1820 (br, w). A broad band centered at about 1410 cm^{-1} is present in B_5H_9 and all its derivatives, and additional bands at 1255 (m), 840 (s), and 760 (w) cm^{-1} are characteristic of the $(CH_3)_3Si$ moiety.[3]

The 32.1- and 9.2-Mc ^{11}B nmr spectra of μ-$(CH_3)_3SiB_5H_8$ are shown in Figure 1. The high-field doublet, of relative area 1, occurs in a chemical shift region characteristic of an apex-type B–H group. The low-field group, of relative area 4, is composed of two equally intense B–H doublets, as shown by the collapse of the spectrum to a single doublet at the lower frequency.

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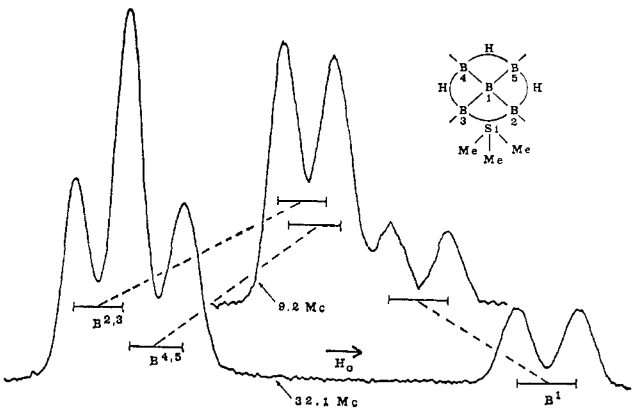

Figure 1. The ^{11}B nmr spectra of μ-Si(CH$_3$)$_3$B$_5$H$_8$ at 32.1 and 9.2 Mc. The assignments, chemical shifts (ppm from $BF_3 \cdot O(C_2H_5)_2$), and coupling constants (cps in parentheses) are: $B^{2,3}$, 8.5 (145); $B^{4,5}$, 13.2 (158); B^1, 48.0 (179).

The higher field doublet in this group has a chemical shift and coupling constant very nearly the same as that of B_5H_9 and has therefore been assigned as arising from $B^{3,4}$. The lower field doublet, arising from $B^{2,3}$, has a coupling constant somewhat smaller than usual, probably as a result of bonding of those boron atoms to the bridge silyl group. The 100-Mc ^{1}H nmr spectrum of μ-$(CH_3)_3SiB_5H_8$ agrees with the ^{11}B spectrum. Integration of the bridge and terminal hydrogen regions gives values which agree with those calculated, assuming five terminal and three bridge hydrogens.

Isomerization of μ-$(CH_3)_3SiB_5H_8$ to 2-$(CH_3)_3SiB_5H_8$ occurs at room temperature in the presence of dimethyl ether. After 1 day, 94% of the starting material was recovered as the 2 isomer, identified by its mass spectrum (which is indistinguishable from that of the bridge isomer) and by its ^{11}B and ^{1}H nmr spectra. Integration of the ^{1}H nmr spectrum agreed with that calculated, assuming four bridge and four terminal hydrogen atoms.

Bromination of μ-$(CH_3)_3SiB_5H_8$ occurs rapidly at room temperature to produce 1-Br-μ-$(CH_3)_3SiB_5H_7$ in moderate yield. A single crystal X-ray study of this compound is presently under way in the laboratory of Professor Lawrence F. Dahl.

The bonding in the silicon bridge of μ-$(CH_3)_3SiB_5H_8$ can be viewed as similar to that suggested for the carbon bridge in dimeric trimethylaluminum.[4] Thus a three-center two-electron bond is probably formed using sp^3 orbitals from the silicon and the two adjacent boron atoms. There appear to be no previous examples of compounds in which silicon atoms are thought to participate in electron-deficient bonding.

Several other preliminary investigations suggest that trialkylgermanium and -tin halides react with LiB_5H_8 in the same manner as trimethylsilyl chloride to produce the corresponding bridged pentaborane(9) derivatives. There is no evidence as yet, however, for the existence of stable pentaborane(9) derivatives having carbon bridges between boron atoms.

Further studies of group IV bridged boron hydride derivatives are in progress and will be published shortly.

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Donald F. Gaines, Terry V. Iorns
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706
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Additions and Corrections

The Donor Properties of Pyrophosphate Derivatives. III. A Colorless Copper(II) Complex [*J. Am. Chem. Soc.*, **88,** 5465 (1966)]. By MELVIN D. JOESTEN and JAMES F. FORBES, Department of Chemistry, Southern Illinois University, Carbondale, Illinois 62903.

In Table III the experimental magnetic moments should be expressed as an average magnetic moment/metal ion. This results in values of 2.04, 2.04, 5.24, and 5.24 BM for [Cu(OMPA)$_2$][CuBr$_4$], [Cu(OMPA)$_2$][CuCl$_4$], [Co(OMPA)$_3$][CoBr$_4$], and [Co(OMPA)$_3$][CoCl$_4$], respectively. The calculated magnetic moments/metal ion from the spin-only formula are 1.73 BM for Cu(II) and 3.88 BM for Co(II).

On Hydroxyalkylcobaloximes and the Mechanism of a Cobamide-Dependent Diol Dehydrase [*J. Am. Chem. Soc.*, **89,** 143 (1967)]. By G. N. SCHRAUZER and R. J. WINDGASSEN, Shell Development Company, Emeryville, California.

On page 147, the side heading in the first line should read: Degradation of β-Hydroxy-*n*-propylpyridinatocobaloxime.

Catalytic Reactions Involving Azomethines. VIII. Water and Alanine Catalysis of the Transamination of 3-Hydroxypyridine-4-aldehyde by Alanine [*J. Am. Chem. Soc.*, **89,** 2090 (1967)]. By DAVID S. AULD and THOMAS C. BRUICE, Department of Chemistry, University of California at Santa Barbara, Santa Barbara, California 93106.

Equation 12 should read as follows