The relative configuration of the two hydroxyl groups in **5a** was not determined.

Treatment of **5a** with excess methanesulfonyl chloride in pyridine at room temperature for 16 hr gave the dimethanesulfonate **5b** [75% yield; mp 205 dec;[10] $\lambda_{\max}^{\mathrm{CH_3CN}}$ 227 mμ (ε 1520), 240 (1140), and 254 (720)],[7] which was then boiled with potassium hydroxide in aqueous methanol and dimethyl sulfoxide for 1 hr. This reaction effected elimination and rearrangement[12] to give a mixture of products from which a tridehydro[26]annulene could be separated in *ca.* 2% yield by preparative thin layer chromatography on silica gel.[13] The positions of the three acetylenes or the stereochemistry of the double bonds in this compound cannot be assigned at present, and the 1,9,17-tridehydro structure **6** is one of many possibilities. The [26]annulene formed red-brown crystals (red in concentrated solution), decomposing on attempted melting point determination; mol wt 332.156[6] (calcd for $C_{26}H_{20}$, 332.156); $\lambda_{\max}^{\mathrm{ether}}$ 237 mμ (ε 23,000), 291 (33,700), 300 (33,400), 383 (119,000),[14] and 451 (12,300); infrared bands (KBr) 2140 (w) (acetylene) and 988 (s) cm^{-1} (*trans* double bond), no allene band at *ca.* 1950 cm^{-1}. The monocyclic nature of the substance was established by catalytic hydrogenation in ethyl acetate over platinum, which led to cyclohexacosane (mol wt 364).[6]

The nmr spectrum of tridehydro[26]annulene at room temperature (100 Mc/sec, in $CDCl_3$ or CD_3COCD_3, TMS used as internal standard) exhibited a very broad multiplet at *ca.* 2.0–4.5, no discrete inner or outer protons being recognizable. Cooling to −60° caused essentially no change. The spectrum was similar to that of tridehydro[30]annulene[3b] and pentadehydro[30]annulene,[3b] as well as that of a long-chain linear polyene-polyyne.[16] It appears therefore that dehydroannulenes containing $(4n + 2)$ out-of-plane π electrons show no ring current and resemble a linear analog when $n \geqslant 6$. As regards lower members of this series, the five known dehydro[14]annulenes ($n = 3$) and the three known dehydro[18]annulenes ($n = 4$) have all been found to sustain a diamagnetic ring current.[3] It is now of interest to synthesize and study the behavior of members belonging to the unknown dehydro[22]annulene ($n = 5$) series.

Regarding dehydroannulenes containing $4n$ out-of-plane π electrons, the largest member to be investigated is tetrahydro[24]annulene ($n = 6$).[17] This substance was found to possess a paramagnetic ring current,[3b,18] as do the lower known members containing 12, 16, and 20 out-of-plane π electrons ($n = 3$, 4, and 5, respectively).[3b] It will be of interest to prepare and study the behavior of a dehydro[28]annulene, the next higher member of this series ($n = 7$), in order to find the limiting size for the existence of a paramagnetic ring current.

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(12) The base treatment under similar conditions of a cyclic compound containing the 1,6-heptadiyn-4-ol methanesulfonate grouping to give cyclic conjugated systems has been described by us previously (J. Mayer and F. Sondheimer, *J. Am. Chem. Soc.*, **88**, 602, 603 (1966)).

(13) The only other highly colored substance eluted [*ca.* 2% yield; red-brown powder; main $\lambda_{\max}^{\mathrm{ether}}$ 390 mμ (ε 131,000)] showed mol wt 428.[6] The formula therefore appears to be $C_{27}H_{24}O_3S$ (calcd mol wt 428), derived from the dimethanesulfonate **5b** by elimination of *one* molecule of methanesulfonic acid. It is possible that this substance is the methanesulfonate of a monohydroxybisdehydro[26]annulene, but it has not been investigated further.

(14) By comparison, tetradehydro[24]annulene showed the principal $\lambda_{\max}^{\mathrm{isooctane}}$ 340 mμ (ε 225,000),[15a] and tridehydro[30]annulene showed the principal $\lambda_{\max}^{\mathrm{isooctane}}$ 397 mμ (ε 114,000).[15b]

(15) (a) F. Sondheimer and R. Wolovsky, *J. Am. Chem. Soc.*, **84**, 260 (1962); (b) F. Sondheimer and Y. Gaoni, *ibid.*, **84**, 3520 (1962).

(16) W. H. Okamura and F. Sondheimer, unpublished observations.

(17) A hexadehydro[36]annulene ($n = 9$) has been obtained in impure form, but the nmr spectrum was not determined.[15a]

(18) See J. A. Pople and K. G. Untch, *J. Am. Chem. Soc.*, **88**, 4811 (1966); F. Baer, H. Kuhn, and W. Regel, *Z. Naturforsch.*, **22a**, 103 (1967); H. C. Longuet-Higgins, Special Publication No. 21, The Chemical Society, London, in press.

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On Triplet States of Flavins

Sir:

We have observed anaerobically the phosphorescence of riboflavin (RF) at 6650 A (uncorrected) in a 0.8% glucose–water matrix,[1] while others reported the emission at shorter wavelengths (6030–6100 A) under aerobic conditions and in an organic matrix.[2–4]

Recently, Steele and Cusachs[5] proposed the spin-conserved energy-transfer process given by eq 1 to account for the apparent oxygen requirement in the phosphorescence emission from RF. Ironically, oxygen is a rather well-known triplet quencher.[6]

$$O_2{}^{\mathrm{t}} + \mathrm{RF}^{\mathrm{s}} \underset{h\nu(6030\ \mathrm{A})}{\overset{h\nu(4500\ \mathrm{A})}{\rightleftarrows}} O_2{}^{\mathrm{s}*} + \mathrm{RF}^{\mathrm{t}} \qquad (1)$$

We investigated flavin triplets theoretically in an attempt to establish singlet–triplet intervals in RF. Reasonably reliable values for triplet states can be computed by means of the SCF–ASMO–CI method in the Pariser–Parr–Pople semiempirical framework.[7,8]

Several flavins were investigated. Methyl groups were treated by means of the group orbital and heteroatom approximations.[9] Different sets of semiempirical integrals were used and most of these were taken from published sources.[10] The assumed geometry of the basic isoalloxazine ring was the same as in ref 11.

Results are shown in Table I. Several conclusions can be made from the results presented. (1) The sets of integrals used by Grabe[11] gave triplet states of considerably low energies. The calculated singlet–singlet transition energies were also too low to compare favorably with the experimental absorption spectrum. Notice also that the first triplet is below the singlet ground state in the case of C. Therefore, we conclude that the results for A, B, and C are questionable due to the use of inappropriate integrals.

(2) Values obtained for D and E appear to be reasonable with respect to the bond-order matrix and singlet–

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(1) P. S. Song and D. E. Metzler, *Photochem. Photobiol.*, in press.

(2) R. H. Steele, *Biochemistry*, **2**, 529 (1963).

(3) J. M. Lhoste, A. Haug, and P. Hemmerich, *ibid.*, **5**, 3290 (1966).

(4) J. Posthuma and W. Berends, *Biochim. Biophys. Acta*, **122**, 422 (1966).

(5) R. H. Steele and L. C. Cusachs, *Nature*, **213**, 800 (1967).

(6) K. Kawaoka, A. U. Khan, and D. R. Kearns, *J. Chem. Phys.*, **46**, 1842 (1967).

(7) R. Pariser and R. G. Parr, *ibid.*, **21**, 466, 767 (1953).

(8) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

(9) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 131, and references therein.

(10) A complete list of semiempirical integrals used in methods A–R in Table I is available upon request. Some of the parameters are tabulated in P. S. Song and T. A. Moore, *J. Quantum Chem.*, in press.

(11) B. Grabe, *Biopolymers Symp.*, **1**, 283 (1964).

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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[12] P. S. Song, submitted for publication.

[13] (a) J. L. Fox, K. Nishimoto, and L. S. Forster, *Biochim. Biophys. Acta*, **109**, 626 (1965); (b) J. L. Fox, S. P. Laberge, K. Nishimoto, and L. S. Forster, *ibid.*, **136**, 544 (1967).

[14] A. Denis and A. Pullman, *Theoret. Chim. Acta*, **7**, 110 (1967).

[15] L. W. Bader and E. A. Ogryzlo, *Discussions Faraday Soc.*, **37**, 46 (1964).

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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[3] D. N. Kendall, Ed., "Applied Infrared Spectroscopy," Reinhold Publishing Corp., New York, N. Y., 1960, p 50.