2-hexanone while the lifetime of the 2-hexanone-5,5-d_2 triplet state is over seven times longer!

In order to account for this observed increase in quantum yields from the triplet states of 5-deuterio-2-hexanones, at least three factors may be considered. (1) It may be noted in Table I that deuterium substitution retards the photochemical reactions of the excited singlet states. Thus, one would expect a more efficient intersystem crossing in the 5-deuterio-2-hexanones resulting in an increase in the steady-state concentration of the triplet state. (2) Evidence has accumulated to support the possibilities that the photochemical reactions of ketones possessing γ hydrogens proceed through a biradical intermediate (II) and that this intermediate may also revert back to the ground-state ketones.[8,15,17] Deuterium substitution at the 5 position will reduce the rate of this reverse reaction (k_{-r}) since it will require the breaking of an O–D bond instead of an O–H bond, whereas it will have a negligible isotope effect on the rates of product formation. (3) It is possible that the γ-C–D and γ-C–H bonds may interact strongly with the excited carbonyl group in a manner analogous to hydrogen bonding in the ground state. This interaction could cause a reduction in the rates of radiationless decay upon deuterium substitution due to the participation of the Franck-Condon factor.[6] The relative importance of these factors will depend upon the relative magnitude of the rates of radiationless decay (k_{-t}) compared to those of γ-hydrogen or -deuterium abstraction. If the rates of decay (k_{-t}) are small compared to those of abstraction, the efficiency of intersystem crossing (factor 1) and the rate of reverse reaction from II (factor 2) will assume more important roles in enhancing the quantum yields from the triplet states. However, since these explanations could not be differentiated by kinetic analysis, it is not possible to choose among them. In fact, it is possible that all these factors may be operating.

A preliminary investigation on 2-hexanone-d_{12} indicated that perdeuteration of 2-hexanone had no measurable increase in isotope effect over the case of 2-hexanone-5,5-d_2 (Table I). Another interesting observation is that over 90% of cyclobutanol formation from 2-hexanones may be quenched by triplet-state quenchers. Therefore, cyclobutanol formation in saturated aliphatic ketones may be primarily a triplet-state reaction. The effects of deuterium substitution on other photochemical reactions are currently under progress in our laboratory.

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The Crystal and Molecular Structure of $B_9C_2H_9(CH_3)_2$

Sir:

A detailed investigation by three-dimensional single-crystal X-ray diffraction techniques has established the molecular structure of $B_9C_2H_9(CH_3)_2$ shown in Figure 1. We believe this to be the first example of a carborane in which carbon atoms within a cage framework are nonvicinal. The carbon atoms are in the 6 and 9 positions and have methyl substituents, clearly distinguishing them from boron. We emphasize this structural feature since, as pointed out by Lipscomb,[1] the possibility of an isomeric configuration with carbon atoms in the 2 and 4 positions could not be eliminated on a basis of previous physical and chemical evidence.

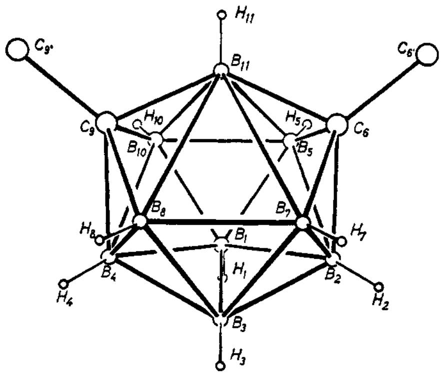

Figure 1. The structure and labeling convention for the designation of atoms in Table I. The methyl group hydrogen atoms have been omitted from $C_{6'}$ and $C_{9'}$.

We conclude from our results that the unsubstituted carborane, $B_9C_2H_{11}$, and the isoelectronic anion, $B_{11}H_{11}^{2-}$, have the structure shown in Figure 2 as proposed by Hawthorne and co-workers[2,3] with the B_{11} atom effectively bridging a decaborane-like framework.

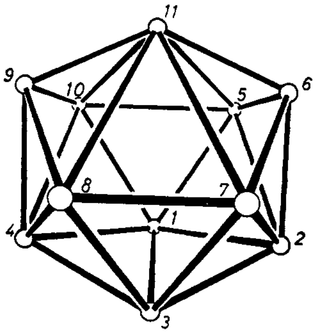

Figure 2. The structure of $B_9C_2H_{11}$ or $B_{11}H_{11}^{2-}$. For $B_9C_2H_{11}$ positions 6 and 9 are occupied by C–H units and all other positions represent B–H units. For $B_{11}H_{11}^{2-}$ all positions represent B–H units.

A colorless crystal, grown from the melt of a small sample sealed in a capillary, gave 668 out of an estimated 695 possible unique reflections in the Cu Kα

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(1) See referee's comments in footnote 3 of ref 2.

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sphere. Weissenberg photographs of levels hkL for $0 \leq L \leq 6$ using Cu Kα radiation and precession photographs of levels Hkl for $0 \leq H \leq 2$ and of levels hKl for $0 \leq K \leq 2$ using Mo Kα radiation were collected. All photographs were taken at low temperature by cooling the crystal with a conventional nitrogen vapor cold stream in order to reduce thermal motion in the crystal and to eliminate a tendency for the sample to sublime at room temperature. The crystal is orthorhombic, space group Pmn2$_1$, $a = 7.21 \pm 0.02$, $b = 9.30 \pm 0.03$, $c = 7.62 \pm 0.02$ A at approximately −135°, with two molecules per unit cell.

The carbon and boron atoms were located with some difficulty from analyses of the Patterson, symmetry minimum,[4] vector verification,[5] and Patterson superposition functions. Difference Fourier maps established all hydrogen atom positions except the methyl hydrogens which appear disordered. Least-squares refinement with isotropic thermal parameters has reached a residual of 0.11 for a structure in which the methyl

$$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

hydrogens have been omitted.

The bond distances, shown in Table I, are in general agreement with similar bonds in other carboranes.

Table I. Bond Distances

Bond	Distance, A	Bond	Distance, A
B_1–B_3	1.85	B_5–B_{11}	2.05
B_1–B_2	1.79[a]	B_{10}–B_{11}	2.06
B_1–B_4	1.81	C_6–C_6'	1.51
B_1–B_5	1.78	C_9–C_9'	1.53
B_1–B_{10}	1.78	C_6–B_{11}	1.68
B_2–B_5	1.81	C_9–B_{11}	1.66
B_4–B_{10}	1.83	B_1–H_1	1.15
B_2–C_6	1.70	B_2–H_2	0.97
B_4–C_9	1.70	B_4–H_4	0.94
B_5–B_{10}	1.87	B_5–H_5	1.20
B_5–C_6	1.59	B_{10}–H_{10}	0.96
B_{10}–C_9	1.60	B_{11}–H_{11}	1.25

[a] Distances for the half-molecule within the crystallographic asymmetric unit are given. The bonds in brackets are related by a molecular plane of symmetry not required by crystal symmetry. The estimated errors are ±0.01 A for C–C, B–C, and B–B, and ±0.11 A for B–H.

The molecule has mm-C_{2v} symmetry. Crystal symmetry requires the molecule to have at least m-C_s symmetry (the molecular plane containing atoms B_2, B_4, C_6, C_9, and B_{11} in Figure 1), and a second plane, the perpendicular bisector of a C_6–C_9 vector, is apparent from the bond lengths. The molecule resembles $B_{10}H_{12}(CH_3CN)_2$[6] and $B_{10}H_{12}(S(CH_3)_2)_2$[7] in geometrical and valence structures. The most notable difference is a shortening of the 6–9 interatomic distance due to bonding with the apical B_{11} atom and the fact that some B–B bonds have been replaced with shorter B–C bonds. We observe a 6–9 distance of 3.09 A as compared with 3.32 A in $B_{10}H_{12}(CH_3CN)_2$, 3.21 A in $B_{10}H_{12}(S(CH_3)_2)_2$, and a much longer 3.55 A in decaborane.[8,9] Perhaps a more discriminating comparison is seen in the ratio of the parallel distances, B_2–B_4/B_6–B_9, which is nearly constant in the three compounds above (0.833, 0.865, and 0.858 respectively) whereas in $B_9C_2H_9(CH_3)_2$ the corresponding B_2–B_4 and C_6–C_9 distances are nearly equal with a ratio of 0.969.

The results of refinement with anisotropic thermal parameters, an approximation for the disordered methyl hydrogens, and other more complete details will be reported later.

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Electron Spin Resonance Study of Mono- and Dimeric Cations of Aromatic Hydrocarbons[1]

Sir:

Lewis and Singer[2] recently investigated the electron spin resonance spectra of cation radicals formed by oxidation with antimony pentachloride of a variety of aromatic hydrocarbons dissolved in methylene chloride. Of particular interest was the observation of a spectrum from naphthalene that appeared to be caused by two sets of eight equivalent protons, each having approximately one-half the hyperfine splitting constant of the naphthalene negative ion radical, which these investigators assigned to a singly charged positive ion dimer. With a slight modification of the techniques, including the use of a concentration gradient in the sample tube,[3] we have confirmed this as well as some of their other results and at the same time have obtained well-resolved spectra from compounds for which spectra were previously either poorly resolved or not observed at all.

The cation dimer formed by naphthalene is not an isolated result. We have found spectra attributable to singly charged dimers on oxidation of both 2,3,6,7-tetramethylnaphthalene and anthracene when an excess of the hydrocarbon is present. In the latter case, a black paramagnetic precipitate is formed at −100° (perhaps the tetrachloroantimonate salt of the hydrocarbon ion). At −85° enough of this dissolves to form a green solution whose spectrum consists of a pattern of narrow lines attributable to the monopositive ion dimer superimposed onto a central asymmetric line about 1 gauss wide resulting from the solid. The green solution is unstable, decaying into a blue, diamagnetic solution, but an approximately steady-

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[1] This research was supported in part through U. S. Air Force Office of Scientific Research Grant No. AF-AFOSR-285-65.

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