are very short lived.[12] The similarities of the chemical shifts (see Figure 2) of the various types of protons as they occur in these compounds clearly establish the proposed quinonoid structures.

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A New Carborane Cage System, 1,2-$C_2B_3H_7$

Sir:

We wish to report the isolation and characterization of 1,2-dicarba-*nido*-pentaborane(7), $C_2B_3H_7$ (I), for which the structure shown in Figure 1 is proposed. This molecule is isoelectronic and isostructural with pentaborane(9), B_5H_9, and as such represents a new class of small carboranes. Compound I is produced in 3-4% yield in the 50° gas-phase reaction of tetraborane(10) and acetylene, with the latter reagent in tenfold excess (I has not been observed in experiments involving equimolar B_4H_{10}–C_2H_2 mixtures). The purification of I was accomplished by fractionation through a trap at −95° and condensation at −128° on the vacuum line, followed by glpc at 25° on a 9.8 ft × 0.25 in. column of 30% Kel-F on Chromosorb-W (retention time = 0.70 relative to B_5H_9).

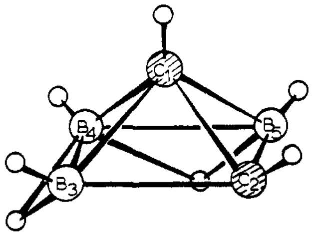

Figure 1. Proposed structure of 1,2-$C_2B_3H_7$.

The assigned structure of I is based upon the infrared spectra, ^{11}B and ^{1}H nmr spectra, and mass spectra of both I and its C-deuterated analog $D_2C_2B_3H_5$ (II), the latter compound having been obtained from the reaction of C_2D_2 and B_4H_{10} under identical conditions. The mass spectra of I and II contain sharp cutoffs at *m/e* 64 and 66, respectively, and are compatible with the presence of three boron atoms as shown by calculated monoisotopic spectra. Very little fragmentation other than hydrogen abstraction is evident in either spectrum, suggesting a compact cage structure.

The ^{11}B nmr spectrum of I (Figure 2a) supports the proposed structure, as shown by close agreement with a computer-drawn spectrum (Figure 2b) based upon the following interpretation. A doublet of area 1.0 is assigned to the B_4–H_t coupling (J = 172 Hz), each peak of which is further split into a 1:2:1 triplet by coupling with the two adjacent bridge protons (J = 48 Hz). Superimposed on these peaks is a doublet of area 2.0 assigned to the equivalent B_3–H_t and B_5–H_t groups (J = 172 Hz), each peak of which is further split into a doublet by coupling with the single adjacent bridge hydrogen (J = 34 Hz).

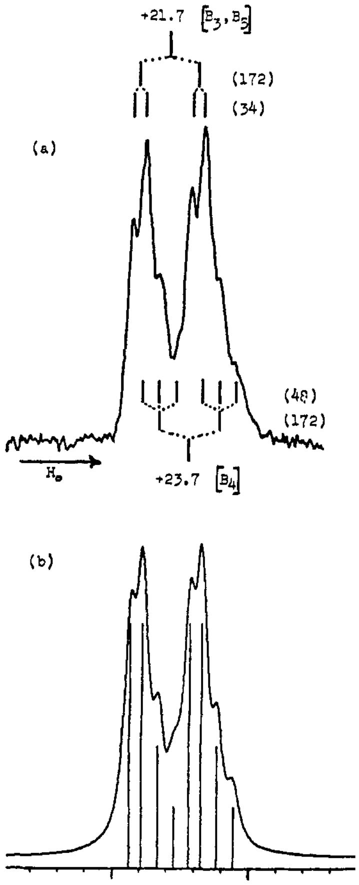

Figure 2. (a) The 32.1-MHz ^{11}B nmr spectrum of 1,2-$C_2B_3H_7$ ($CDCl_3$ solution). Chemical shifts are in ppm relative to external $BF_3 \cdot O(C_2H_5)_2$, and coupling constants (Hz) are given in parentheses. (b) Computer simulation.

The ^{1}H nmr spectrum of I (Figure 3a), obtained at 100 MHz, displays one H–B quartet of area 3.0, a broad band of area 2.0 arising from bridge hydrogen coupling, and two nonequivalent H–C resonances. The ^{1}H nmr spectrum of II (Figure 4a) contains a similar H–B quartet and bridge hydrogen signal but lacks the H–C bands, indicating that the deuterium atoms are bonded to carbon. The computer-simulated spectra of I and II (Figures 3b and 4b), which closely approximate the actual spectra, are based on the areas indicated above (the small expected contributions from the ^{10}B isotope are not included). The bridge proton simulation, using J values measured from the ^{11}B nmr spectrum, assumes coupling of each H_b with B_4 and with B_3 (or B_5) to give 16 overlapping peaks, each of area 2/16 (two equivalent H_b protons). Both the proton and boron nmr data suggest that the boron atoms are in very similar electronic environments; significantly, no high-field resonance (such as is assigned to apical boron atoms in the spectra of the related molecules B_5H_9,[1] CB_5H_9,[2] $C_2B_4H_8$,[3] and $C_3B_3H_7$[4]) is observed in the ^{11}B nmr spectrum of I.

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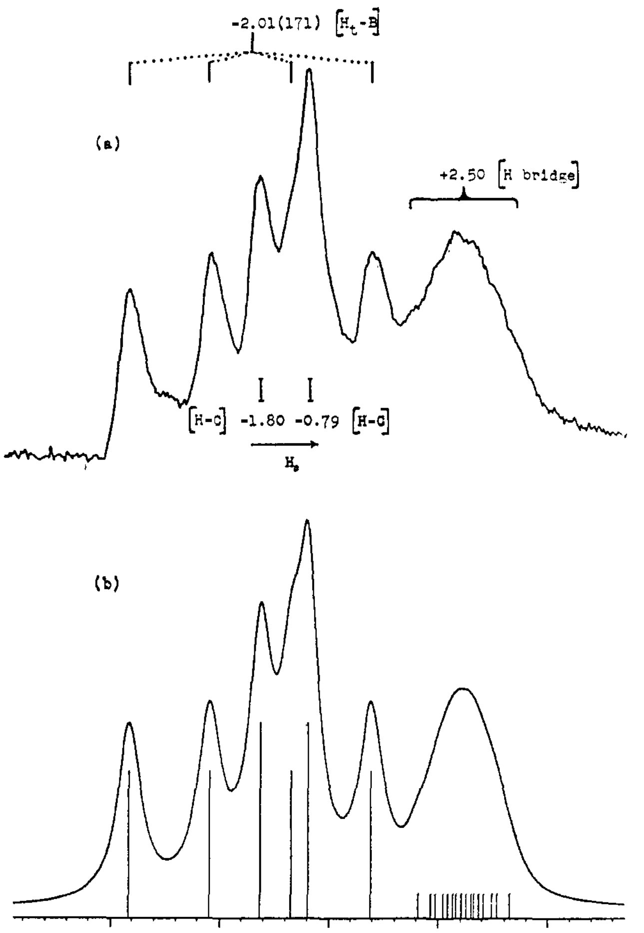

Figure 3. (a) The 100-MHz ^1H nmr spectrum of $1,2\text{-}C_2B_3H_7$ (CS_2 solution). Chemical shifts are in ppm relative to external tetramethylsilane, and coupling constants (Hz) are given in parentheses. (b) Computer simulation.

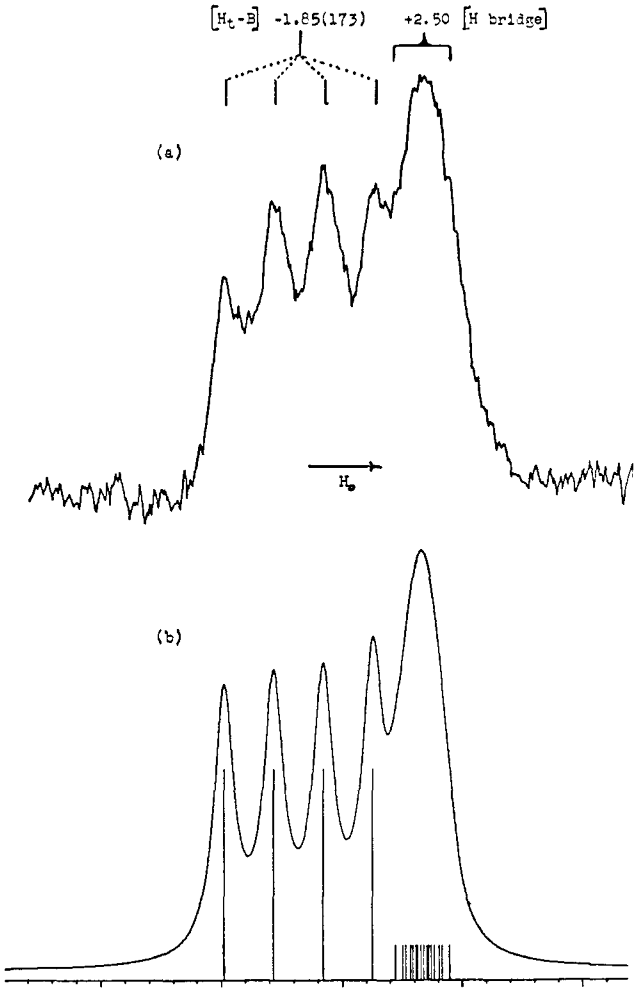

Figure 4. (a) The 100-MHz ^1H nmr spectrum of $C_2D_2B_3H_6$ (CS_2 solution). Data are given as in Figure 3a. (b) Computer simulation.

The gas-phase infrared spectrum of I includes principal bands at 3150 (m), 3075 (m), 2610 (vs), 1860 (s, b), 1800 (s), 1565 (vs), 1420 (s, sh), 1370 (vs), 1155 (s), 1050 (m), 980 (s), 895 (s), 840 (vs), 730 (vs, sh), 715 (vs), and 690 (s, sh) cm^{-1}. The bands at 3150 and 3075 cm^{-1}, each having multiplet structure, are assigned to H–C stretching modes, while the absorptions at 2610 cm^{-1} and in the region of 1800 cm^{-1} are attributed to B–H$_t$ and B–H$_b$–B stretching, respectively. The infrared spectrum of II is similar but contains no significant bands above 2610 cm^{-1}, indicating the absence of C–H bonds. A weak absorption at 2350 cm^{-1} is attributed to C–D stretching.

Compound I has shown some unusual properties. In the vapor phase at 50° it is apparently stable, but in the liquid phase it rapidly polymerizes to a white solid at room temperature. The polymerization occurs even in $CDCl_3$ or CS_2 solutions, which complicated the task of obtaining nmr spectra; these data were finally recorded from 20% solutions of I, but even these dilute mixtures became gel-like after 1 hr at room temperature. No reaction was observed between I and B_4H_{10} at 50° in the vapor phase, but I reacts rapidly with B_2H_6 at 50° to yield products as yet unidentified. Further investigations of this carborane are in progress.

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Isotope and Substituent Effects on the Interaction of Benzophenone with Simple Olefins. Apparent Insufficiency of the Schenk Mechanism

Sir:

Recent work[1-3] has demonstrated that the *cis–trans* isomerization of alkylethylenes, photosensitized by n–π* ketone triplets, does not proceed through the triplet state of the olefin as the exclusive[2] or apparently even major[1,3] pathway. Instead, a 1,4 biradical (the Schenk mechanism) has been implicated as an intermediate in this reaction as well as in oxetane forma-

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