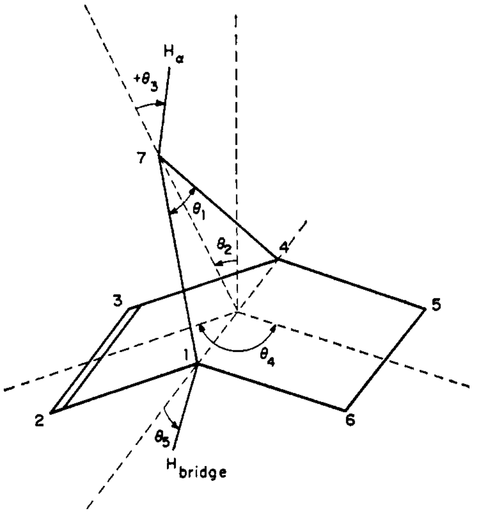

Figure 3. Structural parameters for the 7-norbornenyl radical.

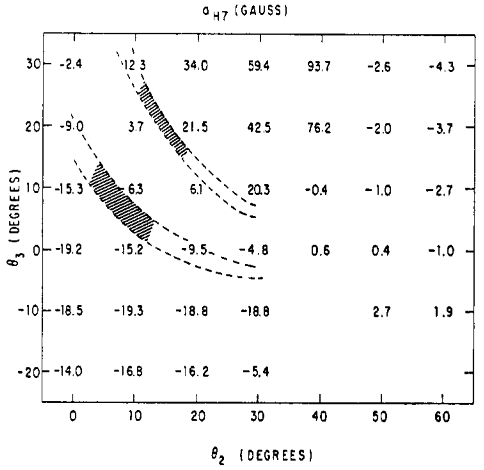

Figure 4. INDO isotropic hyperfine coupling constants for H-7 of the 7-norbornenyl radical. Shaded areas represent structures consistent with the absolute values of $a_{\mathrm{H}\text{-}7}$ and $a_{\mathrm{H}\text{-}2}$ obtained experimentally. Note that the calculated values of $a_{\mathrm{H}\text{-}7}$ are positive in the upper area and negative in the lower.

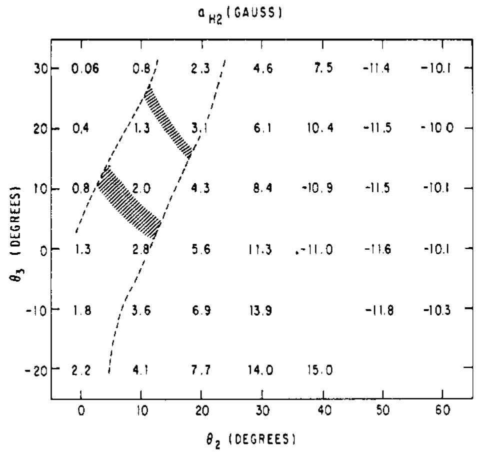

Figure 5. INDO isotropic hyperfine coupling constants for H-2 of the 7-norbornenyl radical. Shaded areas represent structures consistent with the absolute values of $a_{\mathrm{H}\text{-}2}$ and $a_{\mathrm{H}\text{-}7}$ obtained experimentally.

structures compatible with the observed couplings allowing the uncertainties of ±2 G and ±1 G in the calculated values for $a_{\mathrm{H-7}}$ and $a_{\mathrm{H-2}}$, respectively.[17] The *shaded areas* result by superposition of the two maps and further restrict the allowed structures. We assume that the α coupling constant is negative in accord with other alkyl radicals. This limits the structure of the 7-norbornenyl radical to one in which θ_2 is no more than 13° and θ_3 is less than 14° in the *anti* direction.

The calculated values for the couplings to H_{endo}, H_{exo}, and H_{bridge} (Figure 3) for structures within the shaded areas are also consistent with the experimental values. They show much less variation with structure. Bonding situations that can be termed nonclassical indeed arise in very distorted models and are characterized (Figures 3, 4, and 5) by very small α couplings and by relatively large and negative couplings to the protons attached to C-2 and C-3.[22-24] Such coupling constants, however, are clearly at variance with experiment.

The reduced value of the α coupling constant indicates that the 7-norbornyl radical is also bent at C-7 though less so than the 7-norbornenyl radical. However, all four *exo* and all four *endo* hydrogens in the 7-norbornyl radical show magnetic equivalence and, therefore, the rate of inversion of C-7 must be rapid between equivalent potential minima. The rate of inversion of the 7-norbornenyl radical should be relatively slower. The bent sites at C-7, however, are inequivalent and could account for the slight selectivity observed in hydrogen transfer from trialkylstannanes.[1-3] The latter is also supported by the quantitative analysis of the products derived from the photolysis of either pure *syn-* or *anti*-perester.

Acknowledgments. We thank Dr. Claibourne Smith and Dr. James Wilt for helpful suggestions on synthesis. P. B. also wishes to thank the National Science Foundation for generous financial support.

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[22] The C-7 hyperfine coupling constant is also strongly dependent on θ_2 and θ_3. For very distorted structures ($\theta_2 > 35°$), $a_{\mathrm{C-7}}$ becomes negative, indicating that the unpaired electron is no longer localized on C-7.

[23] We have also calculated the partial derivatives of the proton hyperfine coupling contants with respect to all structural parameters of our model for a representative structure within the shaded areas (θ_2 = 7.5° and θ_3 = 7.5°). The largest values were obtained for $\partial/\partial\theta_2$ and $\partial/\partial\theta_3$ justifying our parametrization.

[24] Small values for $a_{\mathrm{H-2}}$ do not, by themselves, invalidate a nonclassical structure for this radical. Such values would be expected if H-2 and H-3 were below the $C_1C_2C_3$ plane rather than in the plane as in the assumed structure (*cf.* ref 19). We are indebted to a referee for bringing to our attention this possibility.

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Nuclear Magnetic Resonance Spectra of Quinodimethanes

Sir:

The chemistry of *p*-xylylene or quinodimethane, **1**, has been extensively studied[1-4] since the species was

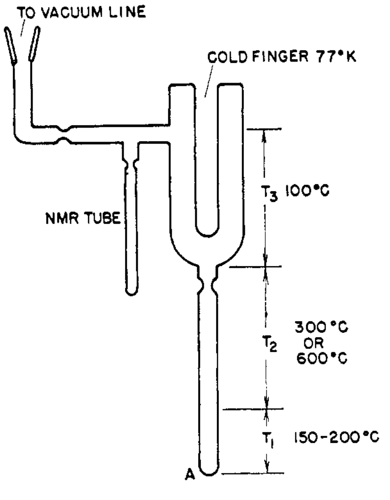
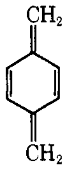


Figure 1. Pyrolysis unit for preparing nmr samples.

first reported by Szwarc.[5] Errede[2] showed that solutions of the quinodimethane could be prepared at low temperatures (−78°) and their reactions with a variety of molecules were studied. Very little is known about the 1,4-naphthaquinodimethane,[6] **2**, or the 9,10-anthraquinodimethane,[7,8] **3**, species.



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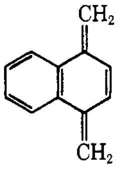

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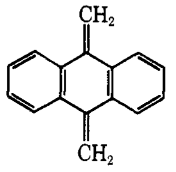

3

Their existence as intermediates in certain reactions was established, *e.g.*, in the synthesis of the corresponding paracyclophanes and polymers.[6,7] They have also been shown to form mixed cyclophanes and to react with other dienophiles to form Diels–Alder adducts.[9,10] The labile nature of these species and their tendency to polymerize very rapidly at ambient temperatures necessitates the use of special procedures in their generation and subsequent investigations of their reactions. Phenyl substitution at the 1, 4, 5, and 8 positions has been shown to increase the stability of the anthraquinodimethane species due to steric hindrance of the methylene–methylene interactions.[11a] We have succeeded in preparing solutions of **1**, **2**, and **3** in tetrahydrofuran and have observed for the first time their nmr spectra, which unequivocally establish their structures.

Solutions of all three compounds were prepared by pyrolytic cleavage of the corresponding paracyclophanes and trapping the intermediates at low temperature.

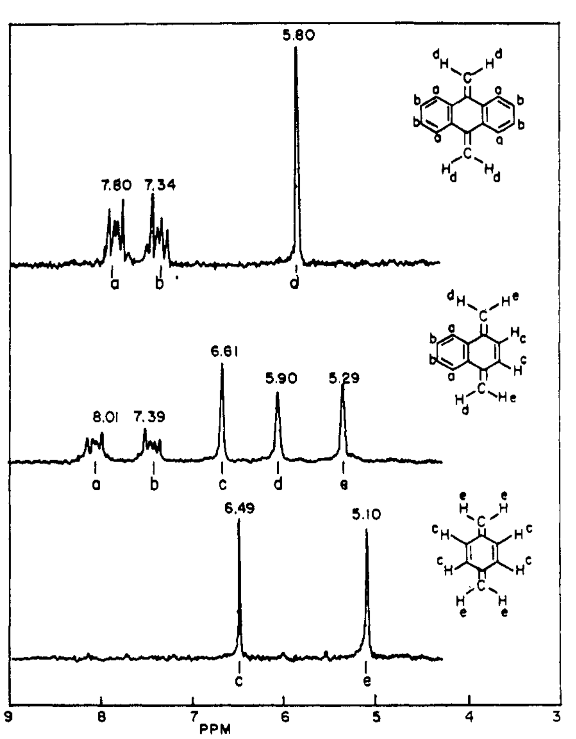

Figure 2. The 60-MHz ^1H nmr spectra of the quinodimethanes measured relative to TMS.

The apparatus is shown in Figure 1. The paracyclophane was vaporized by heating to 150–200° (zone T1), the vapor pyrolyzed[11b] (zone T2), and the product condensed on the cold finger at liquid nitrogen temperature. The remainder of the unit was heated to 100° (zone T3) to minimize condensation and polymerization on the glass surfaces. After sealing off the pyrolysis tube (A) THF (d_8) was distilled into the unit at −80° to permit the intermediate to be taken into solution. The cold solution was transferred into the nmr tube and sealed off.

Nmr spectra were recorded on a Jeolco C-60H nmr spectrometer at −80° and are shown in Figure 2. The aromatic protons in **2** and **3** constitute two sets of quartets typical of the $A'_2X'_2$ spin case. In **1** and **3** a single line is observed for the two types of methylenic protons d and e. These protons differ from each other by virtue of the deshielding of the d protons by the aromatic ring. In **2**, one proton each of types d and e can be observed. The coupling between these protons is very small and appears as a slight broadening of the lines. The olefinic protons c that appear in **1** and **2** can be clearly distinguished from the methylenic protons. The integrals of the various peaks are consistent with the proposed structures. Increasing the temperature caused the nmr signals of the compounds to disappear and was accompanied by the formation of insoluble polymer which accumulated at the top of the solution. The signal disappearance time is a measure of the stability of the three species with **3** > **2** > **1**. As the temperature was raised the amplitude of the signals decreased but the line width and chemical shifts remained unchanged. The inability to obtain an esr signal in these samples (in agreement with Errede[2]) and the lack of broadening of the nmr lines as the temperature was raised indicates that the quinonoid structure is predominant and that the biradicals, if formed,

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(11) (a) S. Carlton Dickerman, J. H. Berg, J. R. Haase, and R. Varma, *J. Amer. Chem. Soc.*, **89**, 5457 (1967). (b) The pyrolysis temperature was 300° for the anthracene derivative and 600° for the naphthalene and benzene compounds.

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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[13] Visiting Scientist on sabbatical leave from the Weizmann Institute, Rehovot, Israel.

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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).

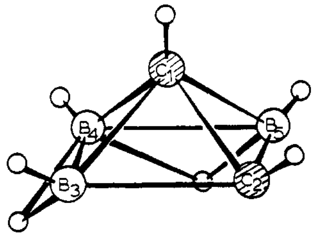

Figure 1. Proposed structure of 1,2-$C_2B_3H_7$.

The assigned structure of I is based upon the infrared spectra, ^{11}B and ^1H 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).

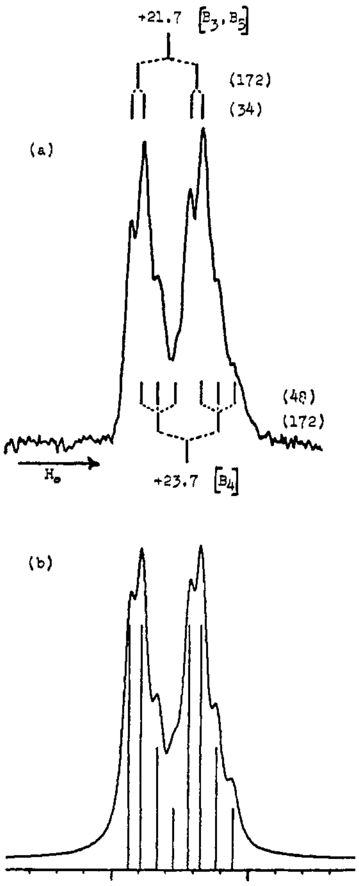

Figure 2. (a) The 32.1-MHz ^{11}B nmr spectrum of 1,2-$C_2B_3H_7$ ($CDCl_3$ solution). Chemical shifts are in ppm relative to external $BF_3 \cdot O(C_2H_5)_2$, and coupling constants (Hz) are given in parentheses. (b) Computer simulation.

The ^1H 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 ^1H 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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