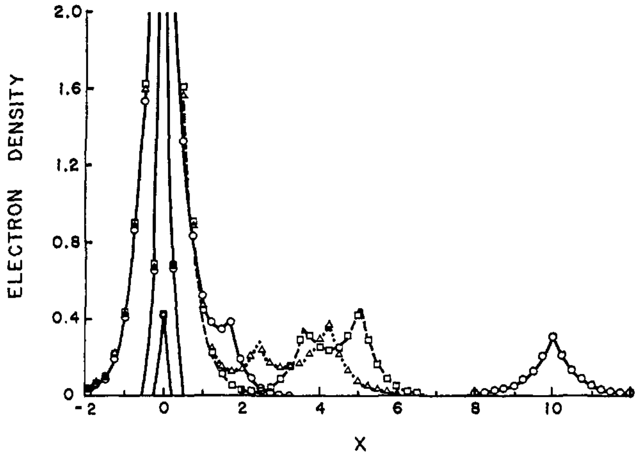

Figure 1. Electron density along the internuclear axis for three different linear configurations of FHH^-: circles refer to HF and H^- at infinite separations; triangles refer to r(HF) = 2.40 and r(HH) = 1.8 au; squares refer to r(HF) = 3.60 and r(HH) = 1.45 au. The density about F is shown with three different scales, differing by a factor of 10.

linear with fluorine in a terminal position, showed no barrier, indicated an intermediate complex stable by 55 kcal/mole, and served to define clearly the reaction coordinate. Further calculations were then carried out with an extended basis set of ten s-type and six of each p-type bases on fluorine, and five s-type and two of each p-type bases on each of the hydrogens. These calculations were limited to points along the minimum energy path found in the preliminary investigation, except for occasional checks to be sure that the minimum path was being reproduced. Exponential parameters were kept constant for all calculations. It is doubtful, however, that significantly different results could be obtained by reoptimization at each point since we are within 0.03 au of the estimated Hartree–Fock limits at both ends of the reaction coordinate. The results of the calculations are shown in Table I.

Table I. Potential Energies for the Linear H_2F^- System[a]

d_{FH}	d_{H-H}	Energy
1.74	∞	−100.517
1.85	3.00	−100.569
1.95	2.35	−100.574
1.80[b]	2.20[b]	−100.567[b]
2.20[b]	2.10[b]	−100.574[b]
2.20	1.90	−100.575
2.40	1.80	−100.577
2.70	1.60	−100.582
2.70[b]	1.40[b]	−100.577[b]
3.00[b]	1.80[b]	−100.577[b]
3.10	1.50	−100.585
3.60	1.45	−100.586
∞	1.40	−100.574

[a] Internuclear distances and energies are in atomic units. [b] These points are off the reaction coordinate.

Again no barrier is observed. A stable intermediate is still indicated, but the energy difference between intermediate and separated products is now only 8 kcal/mole. The bond lengths are also drastically different from that found with the smaller basis set.

Long-range attraction between H_2 and F^- is to be expected, but the attraction persists to smaller separations than are typically found[8] experimentally and theoretically for ion–molecule interactions. For example, H_2 and H^- are calculated[9] to be strongly repulsive in the range of our broad minimum. The flat curve we observe is the result of several opposing effects as is indicated by the electron-charge shifts. In Figure 1 the low electron density at the central hydrogen nucleus at about the middle of the reaction coordinate is particularly noticeable.

The energy difference between the highest occupied and the lowest unoccupied orbitals remains nearly constant from point to point along the reaction coordinate. Thus, it appears unlikely that configuration interaction calculations would drastically alter the present results.

It is possible that the basis set used gives better results for the intermediate than for reactants or products. As mentioned above, however, we are within 0.03 au of the Hartree–Fock limit at both ends of the reaction coordinate. It does not, therefore, appear likely that significant changes in the shape of the curve would result from this source.

An accurate *ab initio* calculation of electron correlation energy has never been carried out for a system of this complexity. An estimate of correlation energies based on method I of Sinanoglu's recent paper[10] indicates that these effects may stabilize the intermediate relative to the products by approximately 6 kcal. Thus, consideration of correlation effects may actually cause a larger dip in the reaction coordinate than that shown by the Hartree–Fock calculation. In view of the extreme approximations involved, however, it is possible that the effect may actually be in the opposite direction. In any case we do not expect any change large enough to introduce a barrier along the coordinate.

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A New Isomer of $C_2B_3H_5$, C,3-Dimethyl-1,2-dicarbaclovopentaborane(5)

Sir:

Although three isomers having a trigonal bipyramidal structure are theoretically possible for the carborane $C_2B_3H_5$, only the 1,5 isomer, in which the carbons occupy the apical positions, has been prepared.[1] We now report the isolation of a dimethyl derivative (I) of a second isomer, 1,2-dicarbaclovopentaborane(5), from the reaction of acetylene and diborane in an electric discharge.

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The preparation was accomplished by the continuous circulation at 25° of a 1:1 diborane–acetylene mixture, diluted with helium, through copper disk electrodes 1 cm apart between which an ac potential of 1000 to 1500 v was maintained. The 4.5-l. Pyrex reactor was grease free and contained a magnetically driven circulating propeller constructed of copper and stainless steel with which circulation velocities of approximately 50 cc/sec were maintained.

A complex mixture of volatile products consisting almost entirely of carboranes and carborane derivatives was obtained,[2] from which I was isolated in pure form by vapor phase chromatography (8.5 ft × 0.25 in. column of tricresyl phosphate on Chromosorb W, $R_v = 1.7$ relative to B_4H_{10} at 25.0°). A typical experiment in which 1.50 mmoles of C_2H_2 was consumed yielded 0.015 mmole of I, which accounted for 11.2 mole % of the total volatile products.

The infrared spectrum of I shows strong C–H (2960 and 2900 cm^{-1}), strong terminal B–H (2570 cm^{-1}), and strong $-CH_3$ (1260 and 1320 cm^{-1}) stretching frequencies. In addition, strong absorptions are found at 1197 and 1110 cm^{-1}, medium bands at 1450 and 940 cm^{-1}, and weak bands at 980 and 906 cm^{-1}. There are no appreciable absorptions between 1500 and 2500 cm^{-1}, indicating the absence of bridge hydrogen atoms.

The mass spectrum of pure I has a sharp, high-mass cutoff at m/e 90, corresponding to the $^{12}C_4{}^{11}B_3H_9{}^+$ ion. The ^{11}B nmr spectrum consists of two well-separated doublets and a singlet (δ −7.8 referred to $B(OC_2H_5)_3$, $J = 174$ cps; δ −34.9, $J = 184$ cps; δ −6.2, respectively), with a 1:1:1 area ratio. These data indicate the presence of three borons, two of which are bonded to single terminal protons which account for the observed doublets, while the third boron is not bonded to hydrogen (as indicated by the single resonance line) and may be assumed to have an attached methyl group. The two B–H units are clearly chemically different, which requires that at least one boron occupy an apical position.

Since the high-field doublet and singlet have δ values relatively near those assigned[3,4] to equatorial boron atoms in other carboranes, while the other doublet in the spectrum of I appears at considerably lower field, it is reasonable to assign the high-field doublet and singlet to equatorial borons and the low-field doublet to an apical boron. This is also consistent with the spectra obtained for cage molecules[5,6] such as $B_{10}H_{10}{}^{-2}$ and $B_{20}H_{18}{}^{-4}$ in which the apical ^{11}B resonance occurs at low field relative to the resonance of the equatorial borons.

These data are in agreement with a trigonal bipyramidal structure having one apical carbon and one equatorial carbon, with a methyl group located on one of the equatorial borons. Further support is provided by the proton nmr, which indicates a 6:1 ratio of methyl protons to the cage C–H unit, as expected. The two methyl resonances are nearly superimposed and are observed as one rather broad, slightly split peak (δ −0.3 relative to tetramethylsilane). The location of the methyl group bonded to carbon is not certain, but the ^1H nmr resonance signal from the single proton attached to a cage carbon occurs at very nearly the same field strength (δ −4.50) as do the resonances of the apical protons[7] in 1,5-$C_2B_3H_5$ (δ −4.60). It might then be inferred that the C–H group in I is similarly apical, in which case the C-bonded methyl group is in an equatorial position.

It is interesting to note that although appreciable yields of the carboranes 1,5-$C_2B_3H_5$ and 2-CH_3-1,5-$C_2B_3H_4$ were isolated in repeated experiments in which I was prepared, no dimethyl derivative of 1,2-$C_2B_3H_5$ other than I was found, nor was the parent carborane 1,2-$C_2B_3H_5$ detected. This suggests that while nonsubstituted $C_2B_3H_5$ isomers having adjacent carbons are very probably less stable than the isomer having apical carbons, as has been predicted,[8-10] it is possible that the alkyl groups in I serve to stabilize the adjacent-carbon cage structure with respect to rearrangement to the 1,5 isomer. Studies currently in progress may help to clarify this situation.

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Isotropic Nuclear Magnetic Resonance Shifts in Tetrahedral Bispyridine and Bispicoline Complexes of Nickel(II)

Sir:

For pyridine octahedrally coordinated to nickel(II) acetylacetonate, proton resonances have been reported[1] to be shifted downfield from their diamagnetic positions in the ratio $\alpha:\beta:\gamma = 1:0.294:0.077$. These results were interpreted in terms of isotropic contact shifts due to unpaired-electron spin delocalization from the metal into the σ-orbital system of the ligands. Indeed, it was pointed out that the unpaired electrons are in orbitals of $\sigma(e_g)$ symmetry, and a direct interaction with ligand π orbitals is not expected. More recently the pmr spectra of a variety of ligands octahedrally coordinated to nickel(II) acetylacetonate have provided evidence for unpaired-electron spin delocalization in the π orbitals of triarylphosphines,[2] arylisoni-

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