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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triles,[2] arylnitriles,[3] and heterocyclic amine N-oxides,[4] as well as in some octahedrally coordinated nickel(II)–salicylaldimine complexes,[5] where again no direct π-type interaction is expected because of symmetry. The present study involves pseudo-tetrahedrally coordinated diiodobis(pyridine)nickel(II) and the analogous picoline compounds[6] wherein the unpaired electrons occupy orbitals of proper symmetry for π (and σ) bonding. All tetrahedral nickel(II) complexes studied to date have exhibited π spin delocalization. The ratios ($\alpha:\beta:\gamma$ = 1:0.297:0.0664 for pyridine) of isotropic shifts (Table I) are almost identical with those reported[1] for an octahedral coordination situation. Isotropic shifts[7] can arise from the Fermi contact interaction (dependent on spin density distribution) or the pseudo-contact interaction[8] (dependent on g-tensor anisotropy and the geometrical position of the resonating nucleus with respect to the paramagnetic center and the ligand field axes). Octahedrally coordinated nickel(II) is magnetically isotropic, and no pseudo-contact shifts are expected. However, for a tetrahedrally coordinated nickel(II) complex, the presence of a pseudo-contact shift has been demonstrated,[9] although it is apparently absent in the dihalobis(triphenylphosphine)nickel(II) compounds,[10] perhaps due to an accidental cancelling of opposing shifts.

Table I. Isotropic Shifts[a] for L_2NiI_2 Molecules

Resonance/L	Pyridine	β-Picoline	γ-Picoline
α-H	-8861 ± 30[b]	-9351 ± 60[c]	-8744 ± 75[b]
β-H	-2631 ± 8	-2830 ± 12	-2508 ± 40
γ-H	-589 ± 10	-564 ± 8	. . .
CH_3	. . .	-403 ± 12	$+550 \pm 50$

[a] Measured in deuteriochloroform solution at 25° in cps at 60 Mc sec^{-1} from the diamagnetic ligand resonances (in order: α-, β-, γ-, CH_3) pyridine: −516, −433, −453, . . .; β-picoline, −504, −427, −443, −136; γ-picoline, −506, −422, . . ., −136 (all in cps from TMS). [b] Very broad. [c] Very broad, doublet.

Using the pseudo-contact shift equation for C_{2v} symmetry,[11] assuming the maximum possible g-tensor anisotropy consistent with the observed magnetic moments[6] and a reasonable geometry for the complex, an upper limit for the pseudo-contact shift of the α-proton resonance was estimated to be ±900 cps. A value of about half of this was obtained for the β and γ protons. The considerably greater magnitude of the observed shifts (Table I) indicates that the pseudo-contact interaction is not the dominant effect here.

The observed isotropic shifts must therefore be due primarily to a contact interaction and, in an attempt to determine the mode of unpaired-electron spin delocalization in the ligand and the exact orbitals involved, an analysis of the results of an extended Hückel molecular orbital calculation[12] (EHMO) for pyridine was made. As noted,[12] the highest filled MO in pyridine is one of σ symmetry (the highest filled and lowest vacant orbitals are of π symmetry in all previously studied ligands) although there is another filled σ and a filled π level (π_b) within 1 ev of this in energy. The lowest three antibonding levels are π MO's, the lowest (π_a) lying about 3 ev above the highest filled level. Delocalization of spin in π_b is expected to be slight since this MO has a nodal plane through the nitrogen perpendicular to the ring. The calculations show that delocalization of α spin (unpaired electron aligned with the applied magnetic field) onto the ligand *via* π_a should produce moderately large upfield shifts for the α and γ protons and much smaller shifts, perhaps downfield if spin correlation is important, for the β proton. A methyl resonance shift of sign opposite to that of a proton attached to the same position is expected for π delocalization.[10,13] The ratio of isotropic hyperfine coupling constants, $|A_\gamma/A_\alpha| = 2.6$, obtained by esr for the 3,5-lutidine anion radical,[14] is in reasonable agreement with the EHMO calculation of the pyridine π_a MO for which this ratio is predicted to be 2.0. Our nmr data are at variance with these results, indicating that a π spin delocalization mechanism does not predominate in these coordinated pyridine systems. However, the γ-methyl resonance of the γ-picoline complex is shifted upfield, indicative of some π delocalization which becomes apparent only at the γ position.

Looking to the σ MO's one finds a σ level lying 1 ev below the highest filled MO which has no s or p orbital component on the nitrogen in the direction of the metal atom, leaving the highest lying filled σ level the only likely candidate for spin delocalization. The isotropic shifts due to unpaired-electron delocalization in a σ orbital are expected to be proportional to the squares of the coefficients of the hydrogen 1s orbitals defining the MO.[15] The EHMO calculation leads us to expect the isotropic shift ratios: $\Delta\nu_\beta/\Delta\nu_\alpha = 0.291$ and $\Delta\nu_\gamma/\Delta\nu_\alpha = 1.97$, while observed ratios for pyridine are 0.297 and 0.0664, respectively. Nor could agreement between observed and calculated isotropic shift ratios be obtained by assuming any amount of π-type delocalization in addition to the σ-delocalization using the EHMO coefficients. The recent report of the esr spectrum of the phenyl radical, which is *isoelectronic* with the pyridine cation radical, has significant bearing on our contention that the unpaired electron is principally delocalized in the highest filled bonding orbital. These workers[16] observe hyperfine interaction constants, A_i, of 18.1, 6.4, and ~0 gauss for the α, β, and γ protons, respectively. The A_β/A_α ratio of 0.354 is in moderately good agreement with our nmr results, and the fact that no splitting due to the γ proton was observed is con-

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sistent with the small isotropic nmr shift for the resonance of the corresponding proton in pyridine. An EHMO calculation for the phenyl radical is again in poor agreement with experiment for the γ proton where a hyperfine constant somewhat larger than for the α proton is predicted. The approximate MO treatment of Dixon[15] for the phenyl radical predicts A_i's for the α, β, and γ protons of 23.3, 4.2, and 17.9 gauss, respectively. However, he states that if negative overlap integrals are neglected the constants become 19.2, 3.1, and 0.1 for the protons in the above order. This latter result is more in agreement with the phenyl radical esr[16] and the present pyridine nmr data.

We must conclude that EHMO calculations yield inaccurate σ-orbital eigenvectors, that the σ contribution to the isotropic shift at the γ position is actually quite small, and that the indirect π-delocalization mechanism predominates here, at least for methyl substitution. It is apparent that the mode of spin delocalization, in pyridine-type ligands at least, is more a function of the ligand than of the symmetry of the complex as a whole. The relative energies and perhaps overlap characteristics of the ligand and metal orbitals probably determine the mode of spin delocalization. This conclusion is in accord with ideas presented recently concerning spin density transferral in octahedral transition metal acetylacetonate complexes.[17]

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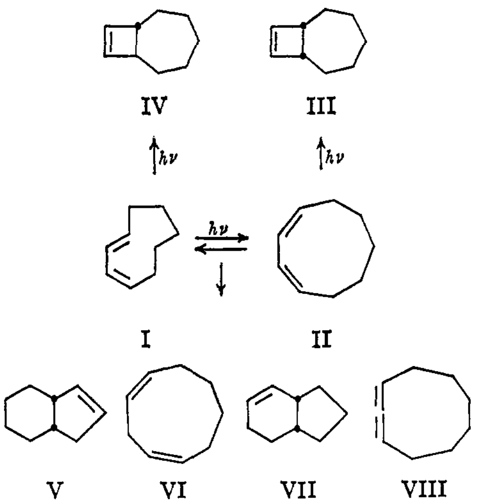
Photochemical Reactions of Medium Ring 1,3-Dienes

Sir:

Having recently[1] noted the unusual electrocyclic reactions of medium ring conjugated dienes in the electronic ground state, we now wish to report on processes which are presumed to arise from the electronic excited state of such systems.

Irradiation of ether solutions of *cis,trans*-1,3-cyclononadiene (I) with ultraviolet light of <3000 A gives rise to rapid isomerization to an approximate steady state in which the isomeric *cis,cis*-1,3-cyclononadiene predominates. Slower processes which accompany the *cis–trans* isomerization lead to the formation of a complex mixture of III, IV, V, VI, VII, and VIII in the approximate distribution ratio of 25:14:23:4:6:1.



Structures have been assigned on the basis of physical property and spectral identity with authentic samples of III,[1] VI,[2] VII,[3] and VIII.[4] The structure of IV is assigned on the basis of its nmr spectrum (τ 3.90, 7.1, 8.5; area ratio 2:2:10) and hydrogenation to the known[5] *trans*-bicyclo[5.2.0]nonane. The structure of V is assigned on the basis of its identity with the primary olefin obtained by a Bamford–Stevens reaction[6] of the tosylhydrazone of *cis*-2-hydrindanone and its hydrogenation to *cis*-hydrindane.

It is our conviction that III results from a disrotatory cyclization arising from the excited state of II, and that IV arises similarly from the excited state of I. Such stereoselectivity would be in complete accord with the postulated[7] orbital symmetry control of such electrocyclic reactions and would bear witness of the anticipated reversal of stereochemistry of such cyclizations upon proceeding from the ground state to the excited state. In this respect 1,3-cyclononadiene is the first example of a diene system in which the complimentary modes of electrocyclization have been observed in both the electronic ground and excited states.

The formation of V, VI, VII, and VIII are postulated to result from photochemically induced hydrogen shifts and cyclizations of the sigmatropic type.[8] The photochemically induced formation of V and VII from cyclononadiene is without precedent, and the process accordingly represents a new photochemical process. The complexity of the photochemistry of cyclononadiene is unrivaled among dienes heretofore studied. Preliminary studies of the photolysis of higher members of the medium ring conjugated diene suggest that these may rival the C_9 diene in product complexity and afford similar structurally altered products.

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