and the 1,4-addition reaction with α,β-unsaturated carbonyl compounds,[7] as well as in their preparation.[3]

Although we have not established the precise physical basis for these facile ring opening reactions, the strain present in the borolane ring, attributable largely to the sp^2 hydridization of the boron atom, appears to be primarily responsible for the greater reactivity. However, the possibility must also be considered that the additional stability of the double hydrogen bridge of 1,2-tetramethylenediboranes (**2** and **8**), as evidenced by its relatively low reactivity toward terminal olefins, may also be playing an important role in the ease of the ring opening reaction with borane.

---

(7) A. Suzuki, S. Nozawa, M. Itoh, H. C. Brown, E. Negishi, and S. K. Gupta, *Chem. Commun.*, 1009 (1969).

(8) (a) Postdoctorate research associate on a research grant (DA 31-124 ARO(D) 453) supported by the U. S. Army Research Office (Durham). (b) Graduate assistant on a research grant (GM 10937) supported by the National Institutes of Health.

* Address correspondence to this author.

Herbert C. Brown,* Ei-ichi Negishi,[8a] Patrick L. Burke[8b]
Richard B. Wetherill Laboratory, Purdue University
Lafayette, Indiana 40907

Received July 17, 1970

Nuclear Magnetic Resonance in Paramagnetic Solution. Carbon-13 Contact-Shift Studies of Pyridine, Aniline, and Triphenylphosphine Complexed with Nickel(II) Acetylacetonates

Sir:

Recently nmr contact shifts have been extensively studied for various paramagnetic systems, including transition metal complexes and organic free radicals.[1] Most of these studies have dealt with the proton shift, and major problems in this area involve the interpretation of the mechanism of electron spin delocalization onto the ligand molecule and the determination of the sign and magnitude of the electron spin density on the proton. The present report deals with the ^{13}C contact shifts for pyridine- and aniline-type bases, induced by the formation of complexes with paramagnetic nickel(II) acetylacetonate ($Ni(AA)_2$). These molecules have been shown by proton contact-shift studies to be typical σ- and π-type bases,[1d,2] respectively. It is hoped that ^{13}C contact-shift studies will yield useful information about the electron spin distribution on the carbon skeleton, thus providing a powerful new tool for investigating the molecular and electronic structures of paramagnetic complexes.

We have observed ^{13}C chemical shifts for the σ-type bases pyridine, methyl-substituted pyridines, and piperidine, and for the π-type bases aniline and triphenylphosphine, perturbed by $Ni(AA)_2$. The perturbation of the ^{13}C nmr spectra of pyridine and triphenylphosphine by $Ni(AA)_2$ is shown in Figures 1 and 2. The spectra were measured at room temperature on a JEOL-C60-HL spectrometer at 15.1 MHz using a fully proton-decoupled ^{13}C nmr technique.[3] In the spectra of the diamagnetic solution a, each carbon

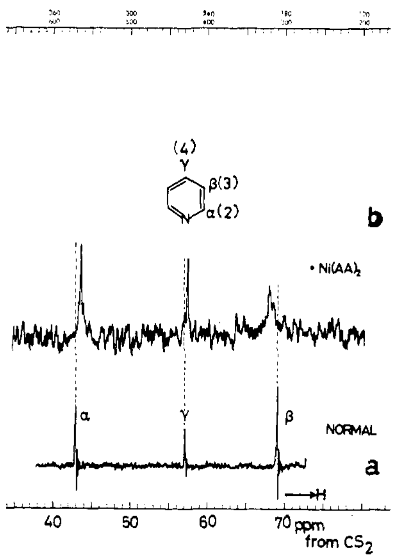


Figure 1. Proton-decoupled ^{13}C nmr spectra (at 15.1 MHz) of pyridine: (a) pyridine alone (single scan), (b) in the presence of $Ni(AA)_2$ (0.3 *M*).

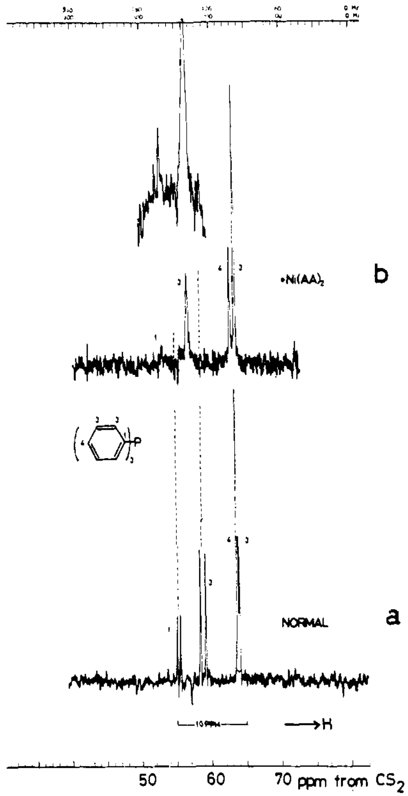


Figure 2. Proton-decoupled ^{13}C spectra (at 15.1 MHz) of triphenylphosphine in $CDCl_3$: (a) the diamagnetic solution (3 *M* in $CDCl_3$, single scan) [the splittings are due to P–C spin coupling ($J_{P-C_1} = 10, J_{P-C_2} = 16, J_{P-C_3} = 5$, and $J_{P-C_4} = 0$ Hz]; (b) in the presence of 0.3 *M* $Ni(AA)_2$ (single scan) (the P–C couplings disappear due to decoupling by paramagnetic complex formation).

---

(1) (a) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965); (b) E. De Boer and H. Nan Willigen, "Progress in NMR Spectroscopy," Vol. 2, Pergamon Press, Oxford, 1967, p 111; (c) T. Yonezawa, I. Morishima, and Y. Ohmori, *J. Amer. Chem. Soc.*, **92**, 1267 (1970); (d) T. Yonezawa, I. Morishima, Y. Akana, and K. Fukuta, *Bull. Chem. Soc. Jap*, **43**, 379 (1970); (e) I. Morishima and T. Yonezawa, *J. Chem. Phys.*, in press.

(2) W. D. Horrocks, Jr., R. C. Taylor, and G. N. La Mar, *J. Amer. Chem. Soc.*, **86**, 3031 (1964).

(3) Completely proton-decoupled ^{13}C nmr spectra were obtained at 15.1 MHz on a JEOL-C60-HL spectrometer equipped with an IS-60 field-frequency synchronous sweep system of the proton irradiation frequency and an SD-HC heteronuclear spin decoupler. Spectra were also measured with the external field locking mode. Samples were made in 50% (v/v) $CDCl_3$ solution in 8-mm sample tubes. For the

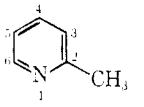
Table I. Relative ^{13}C Contact Shifts

Ligand	1	2 (α)	3 (β)	4 (γ)	5 (β′)	6 (α′)	CH_3
Pyridine		10.0	−16.7	4.5	−16.7	10.0	
α-Picoline		10.0	−13.7	2.5	−8.1	10.0	−6.0
β-Picoline		10.0	−15.0	6.7	−12.0	10.0	−1.5
γ-Picoline		10.0	−16.5	4.2	−16.5	10.0	∼0
Piperidine		10.0	−16.0	∼0	−16.0	10.0	
Aniline	10.0	−8.9	3.6	−5.4	3.4	−8.9	
α-Methyl-aniline	10.0	−3.6	5.0	−2.4	5.2	−3.1	∼0
Triphenyl-phosphine	−10.0	−8.8	−3.8	∼0	−3.8	−8.8	

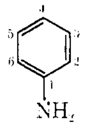
Relative ^{13}C contact shifts[a] — Carbon position[b]

[a] Values are relative to the position 1 or 2 (α). Accuracies are within ±1.0. [b] Numbering is shown in **1** and **2** (see text).

signal is easily assigned to ring carbons.[4] Addition of $Ni(AA)_2$ to the diamagnetic solution shifts the carbon resonances upfield or downfield and is accompanied by signal broadening. The extent of the broadening is approximately proportional to the shift.[5] The various carbon resonances are shifted from their normal diamagnetic values by an amount which is proportional to the concentration of added $Ni(AA)_2$. This linear relation implies that the exchange of ligand between complexed and uncomplexed sites is rapid on the nmr time scale and that the spectra are time averaged. Thus the ^{13}C resonances of the ligand shift toward the resonance position of the complex as $Ni(AA)_2$ is added to the diamagnetic solution, and the relative values of these paramagnetic shifts are of significance in the present study. The relative values for various carbons in a ligand molecule were obtained from the slopes of the linear plot of the paramagnetic shifts *vs.* the concentration of $Ni(AA)_2$, with the value for the particular carbon normalized to 10.0. It has been firmly established that the isotropic proton paramagnetic shift in the $Ni(AA)_2$-ligand complex is caused mainly by the Fermi contact interaction, which is related to the electron spin density on the proton. This should also be true for the ^{13}C shift (*vide infra*).[6] The relative ^{13}C contact shifts for various ligand molecules are summarized in Table I. Numbering of the positions for Tables I and II is shown in **1** and **2**. The plus and minus of these values denote the upfield and downfield contact shifts which correspond to the negative and positive spin densities (or positive and negative hyperfine coupling constants, $a_{^{13}C}$), respectively, induced on the carbon s atomic orbital.



1



2

All the downfield contact shifts for α, β, and γ methyl carbons in methylpyridines (picolines) are similar to the proton contact shifts for pyridine.[7] This can be interpreted as due to the dominant mechanism of electron spin delocalization through σ orbitals (predominantly through the lone-pair orbital), as is also the case for protons in pyridine.[7,8] However, ^{13}C contact shifts were observed to alternate in sign for the ring carbons in pyridine and methylpyridines. Similar alternating shifts were also seen for piperidine with a σ skeleton, although the shift attenuates quite rapidly at the γ carbon. The relative contact shift for the β carbon is almost the same in pyridine and in piperidine. A similar trend was encountered with pyrollidine (α:β = 10.0:−16.0). The larger contact shift for the β carbon than for the α carbon is characteristic of the σ-type spin distribution in pyridine, piperidine, and pyrollidine. This may easily be recognized by comparison with the result for aniline (*vide infra*), in which π-type spin distribution occurs and induces ^{13}C contact shifts of $C_1:C_2$ = 10.0:−8.9. Thus it seems likely that the alternating ^{13}C contact shifts for the pyridine ring carbons can be explained by a contribution from the σ spin-polarization mechanism. However, slow attenuation of the contact shifts at the γ carbon in pyridine does not rule out the possibility that the π polarization mechanism makes a contribution.

In order to examine the σ nature of the binding between pyridine and $Ni(AA)_2$, it should be of interest to compare the relative $a_{^{13}C}$ (which is proportional to the ^{13}C contact shift) for the phenyl radical with the ^{13}C contact shifts for a pyridine–$Ni(AA)_2$ complex which has a similar electronic structure. Because of a lack of experimental $a_{^{13}C}$ data for this radical, the MO theoretical values found by Pople's INDO calculations[9] are compared with the ^{13}C contact shifts (Table II). Comparison is also made for the protons. The agreement between observed contact shifts and theoretical hyperfine coupling constants is fairly close. This result provides further evidence for the assump-

---

diamagnetic solution, spectra were recorded by single scan; for the paramagnetic solution, spectra were scanned 4–16 times using a JEOL spectrum computer RA-5 to obtain enhanced *S/N* values. The concentration of $Ni(AA)_2$ ranged from 0.2 to 2 *M*.

(4) For the assignment of ^{13}C signals of methylpyridines, see H. L. Retcofsky and R. A. Friedel, *J. Phys. Chem.*, **71**, 3592 (1967); **72**, 290 (1968); for aniline, see P. C. Lauterbur, *J. Chem. Phys.*, **38**, 1415 (1963).

(5) In the proton nmr spectra, signal broadening is greatest for the ortho proton which is closest to the coordinated paramagnetic metal.[1c,2,7] This has been attributed to a dipolar broadening effect which falls off as the sixth power of the metal–proton distance.[1] However, in the ^{13}C nmr spectra of pyridine, piperidine, and pyrollidine, the β carbon rather than the α carbon experiences the greater broadening effect. This observation shows that the contact interaction is of major importance in the relaxation effect of the ^{13}C resonance: I. Morishima, manuscript in preparation.

(6) The ^{13}C paramagnetic shifts for $Co(AA)_2$ complex systems show upfield bias due to the pseudocontact contribution: unpublished results in this laboratory.

(7) J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).

(8) R. H. Holm, G. W. Everett Jr., and W. D. Horrocks, Jr., *J. Amer. Chem. Soc.*, **88**, 1071 (1966).

(9) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.*, **90**, 4201 (1968).

Table II. Comparison between ^{13}C and ^{1}H Contact Shifts for $Ni(AA)_2$ Complexes and Corresponding Hyperfine Coupling Constants for Radicals with Isoelectronic Structure

Ligand	Position	Obsd[a] contact shift ^{13}C	Obsd[a] contact shift ^{1}H	Radical	Calcd[a,b] $a_{^{13}C}$	Calcd[a,b] $a_{^{1}H}$
Pyridine[c]	α (2)	10.0	−10.0[d]	Phenyl	−10.0	10.0
	β (3)	−16.7	−2.9[d]		22.3	3.3
	γ (4)	4.5	−0.8[d]		−5.4	2.1
Aniline[e]	1	10.0		Benzyl	−10.0	
	2	−8.9	10.0[f]		9.5	−10.0
	3	3.4	−4.2[f]		−6.9	5.6
	4	−5.6	10.0[f]		8.3	−8.7

[a] Values are relative to position 1 or 2. A positive hyperfine coupling contant corresponds to a negative contact shift (see ref 1). [b] Taken from ref 9. [c] Numbering as in **1**. [d] Taken from ref 7. [e] Numbering as in **2**. [f] Taken from ref 1d.

tion that metal–ligand binding is essentially σ in character and that the Fermi contact shift provides a dominant contribution to the isotropic ^{13}C paramagnetic shifts in the $Ni(AA)_2$–pyridine complex.

The ^{13}C contact shifts for aniline follow the pattern (alternating signs and magnitudes) expected for a π mechanism in which the electron spin on the pπ orbital induces spin density on the carbon s orbital, the orbital responsible for the ^{13}C contact shift. The proton contact shift is related to the π spin density on the carbon to which the proton is attached.[10] The linear relation between relative ^{13}C contact shifts and relative proton contact shifts[1d] for aniline (positive ^{13}C shifts correspond to negative proton shifts) provides further evidence for a π-delocalization mechanism (see Table II). The agreement between relative ^{13}C contact shifts in the aniline–$Ni(AA_2)$ complex and relative $a_{^{13}C}$ values obtained theoretically for the corresponding radical, the benzyl radical, is also close as was the case for pyridine.

When triphenylphosphine, an aniline-type base,[2] was used as the ligand, unexpected downfield ^{13}C contact shifts of all the ligand carbons were observed (Table I). The study of proton contact shifts has shown that the odd electron distributes itself on the phenyl ring *via* π orbitals as in the case of aniline. Therefore with triphenylphosphine, ^{13}C contact shifts alternating in sign and magnitude might be expected. All the downfield ^{13}C contact shifts observed show the predominance of spin delocalization through the σ bond, as occurs with σ delocalization on the proton in pyridine. The structure most likely to account for σ spin delocalization in triphenylphosphine appears to be a skew conformation[11] of the phenyl ring in which the lone-pair orbital on the P atom is nearly parallel to the plane of the phenyl ring. It then follows that alternating proton contact shifts[2] reflect the small amount of the π spin density on the carbon p orbital, which conjugates slightly with the lone-pair orbital on the P atom, while the ^{13}C resonance is insensitive to this low π spin density and reflects the positive spin density delocalized on the carbon 2s atomic orbital.

We believe that ^{13}C contact-shift studies can provide an additional tool for the elucidation of the electron spin distribution on the ligand molecule and of the geometric structure of the paramagnetic metal complexes.

---

(10) H. M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956); H. M. McConnell and D. B. Chesnut, *ibid.*, **28**, 107 (1958).

(11) For the skew conformation of triphenylphosphine, see G. R. Miller, A. W. Yankowsky, and S. O. Grim, *ibid.*, **51**, 3185 (1969).

* Address correspondence to this author.

Isao Morishima,* Teijiro Yonezawa
Department of Hydrocarbon Chemistry,
Faculty of Engineering
Kyoto University, Kyoto, Japan

Kojitsu Goto
Japan Electron Optics Laboratory Co. Ltd.
Akishima, Tokyo, Japan

Received June 23, 1970

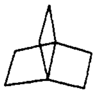
A New Model for the Bonding in Bicyclobutanes

Sir:

Bicyclobutane (I) is a most unusual molecule.[1] The dipole moment (0.675 ± 0.01 D),[2] bridgehead ^{13}C–H coupling constant (205 Hz),[3] and strain energy (64 kcal/mol) are especially large. The 1,3-diphenyl derivative has a uv spectrum suggesting conjugated phenyls, and 3-methylbicyclobutane-1-carboxylate has an uv extinction coefficient (λ_{max} 210, ε 6800) more akin to an α,β-unsaturated ester than to methylcyclopropanecarboxylate.[1] Bicyclobutanes are readily attacked by acids, bases,[4] halogens, carbenes, and radicals, many of these leading to addition across the central bond.[1] They do *not*, however, undergo facile Diels–Alder reaction.[4]

Excluding the latter instance, it is tempting to regard the bicyclobutane central bond as ethylenic or even acetylenic;[5] the latter accounts for the highly acidic bridgehead hydrogen.[1] However, a more appropriate model becomes apparent from *ab-initio* SCF calculation,[6] interpreted by Mulliken population analysis.[7] The new bonding model which emerges is consonant both with physical properties and reactivity.

I



II

A minimum basis set of contracted Gaussian-type functions[8] was employed and the microwave-determined geometry assumed.[2b] The SCF wave function (obtained with all integrals computed, without approximation) furnished a dipole moment of 0.686 D (along the C_2 axis, with positive end pointing up through the bridgehead carbons, I), in excellent agreement with the microwave value (0.695).[2,9] This lends credence to the

---

(1) K. B. Wiberg, G. M. Lampman, R. P. Cuila, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965).

(2) (a) M. D. Harmony and K. Cox, *J. Amer. Chem. Soc.*, **88**, 5049 (1966); (b) K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *J. Chem. Phys.*, 50, 1976 (1969).

(3) K. Wuthrich, S. Meiboom, and L. C. Snyder, *ibid.*, **52**, 230 (1970).

(4) E. P. Blanchard, Jr., and A. Cairncross, *J. Amer. Chem. Soc.*, **88**, 487, 496 (1966).

(5) M. Pomerantz and E. W. Abrahamson, *ibid.*, **88**, 3970 (1966).

(6) For maximum overlap and CNDO treatments see Z. Maksić, L. Klasinc, and M. Randić, *Theor. Chim. Acta*, **4**, 273 (1966), and K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968), respectively.

(7) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

(8) J. M. Schulman, C. J. Hornback, and J. W. Moskowitz, manuscript in preparation.

(9) The phenomenal agreement with experiment is, to some extent, fortuitous, but suggests a well-balanced basis. These calculations are presently being performed at the double ζ level with localized orbitals.