bonds must be offset between 0.1 and 0.15 Å. Bond angles are also given well with errors usually less than 4°.

However, force constants are on the order of 50% too high. While this is somewhat regrettable, we have reduced the CNDO/2 values which are from two to three times the experimental values. There is some satisfaction in that our values seem consistent in that trends within and between groups of bonding pairs are reproduced. For example, as we go from C_2H_2 to C_2H_4 to C_2H_6 the C–H force constants decrease and in going from C–H to N–N to O–H the force constants increase, as they should.

At this point we would like to compare the results of this MC–SCF approach with those for a single determinant using the same parameters. For the molecules calculated in this paper, the equilibrium geometries are predicted with about the same accuracy with either the single or multiconfiguration approach. The force constants were improved between 6 and 10% with the MC–SCF method. And, of course, the calculated heats of atomization are too small for the single determinant case, since the parameter optimization took into account the CI energy, which ranged from 0.027 to 0.125 au. It seems likely that by using the formulas for β_{pq} and V_{AB} given in this paper and a different set of optimized parameters one could get results comparable to ours for equilibrium geometry calculations using only a single determinant. However, it should be emphasized that the principle advantage of this MC–SCF approach is that it allows potential curves to be calculated up to the dissociation limit, which cannot be done using any single determinant Hartree–Fock method.

IV. Conclusion

As was stated in the introduction our objective is to develop a semiempirical model accurate enough to be of use in chemical problems. Clearly at this early stage we still have a way to go. However, it is encouraging that we have been able to do as well as we have with only eight parameters and by neglecting all differential overlap in two-electron integrals. While MINDO/2 presently gives more accurate results for heats of atomization and force constants, it requires 20 parameters and calculation of integrals involving monatomic differential overlap.

To improve our model it is particularly important to predict heats of atomization more reliably. Perhaps a different form of V_{AB} is necessary. Another possibility is the inclusion of integrals used in the INDO approximation. However, these changes are of a minor nature and fit easily in the MC–SCF pair-replacement formalism. More restrictive at the present time is the fact that we can only treat closed shell systems. Another limitation is that the model does not conveniently handle delocalized electrons as occur in aromatic systems. The difficulty with bonds between two atoms with lone pairs is perhaps not too serious given the few molecules involved.

It seems reasonable that these improvements can and will be made to this MC–SCF procedure. The flexibility in adequately treating a variety of reactions processes and the ease of interpreting "chemically" localized orbitals makes this approach particularly appealing and useful.

Mechanisms of Spin Delocalization.
An Experimental Study of γ and δ Proton Contact Shifts

Graham R. Underwood* and Howard S. Friedman

Contribution from the Department of Chemistry, New York University, Washington Square, New York, New York 10003. Received November 10, 1973

Abstract: Nickel-induced pmr contact shifts have been determined for the γ and δ protons of a variety of amines in which the molecular geometries are constrained to rigidly fixed conformations. For γ protons, it is concluded that homohyperconjugation, which places α spin at the protons in question, is dominant for those protons obeying the W plan. This mechanism falls off approximately as $\cos^6 \theta_\gamma{}^H$ and allows spin polarization to dominate for a wide range of conformations, resulting in β spin at the protons. Finally, for protons in the conformation $\theta_\beta{}^C = 0°$ and $\theta_\gamma{}^H = 0°$, another resonance contribution leads to small positive spins. For δ hydrogens, the largest positive spin densities result for those protons in the W-plan geometry and are attributed to an extended σ-bond resonance phenomenon. Smaller spin densities are induced at δ protons not conforming to the W plan.

The subject of spin delocalization in organic free radicals has attracted considerable attention in recent years. An understanding of this subject is naturally of value in interpreting esr spectroscopic data, but a further incentive for elucidating these mechanisms has been provided by the recent recognition that the chemical behavior of both open and closed shell systems is intimately associated with the spin density distributions in related radicals.[1–3] Epiotis,[2] for ex-

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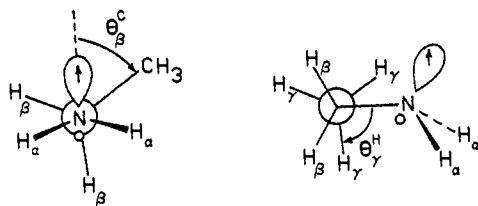
Figure 1. Definition of the dihedral angles $\theta_\beta{}^C$ and $\theta_\gamma{}^H$ in terms of a nonplanar radical site (at nitrogen).

Figure 2. Esr hfsc's calculated for γ hydrogen of the propyl radical as a function of the dihedral angle $\theta_\gamma{}^H$, the angle $\theta_\beta{}^C$ being kept constant at $0°$.

ample, has used the esr hyperfine splitting constants of radical ions to predict the preferred orientation of substitution reactions in polysubstituted aromatic hydrocarbons where chemical intuition would be insufficient for making confident predictions. Similar reasoning is of course applicable to the more complex problem of predicting reactivity and substitution in totally saturated molecules.

We have also used arguments based upon spin delocalization[3] to rationalize why the irradiation of β,γ-unsaturated ketones produces two totally distinct products depending upon the multiplicity of the excited state involved.

The mechanisms of spin delocalization to hydrogens located α or β to the radical site[4] are now relatively well understood.[5] For the γ hydrogens, however, the situation is somewhat more complex. For convenience in discussing these mechanisms it is appropriate to define first the two angles necessary in describing the location of the γ hydrogen relative to a radical site. This is done in the Newman projections of Figure 1. A diversity of frequently conflicting mechanisms has been proposed for spin delocalization to γ hydrogen. Kreilick[6] and de Boer,[7] on the basis of nmr contact shifts obtained in flexible radicals, have presented persuasive evidence that conformation-independent spin polarization I is the dominant mechanism for transporting spin to this position.

Russell and coworkers,[8] on the other hand, in a number of closely related studies of rigid bicyclic semidiones, have pointed out that the unusual conformational requirement ($\theta_\beta{}^C = 180°$, $\theta_\gamma{}^H = 180°$) for long-range esr hfsc's strongly implicates homohyperconjugation II as being most important.

A similar mechanism, III, but necessitating a different conformation ($\theta_\beta{}^C = 0°$, $\theta_\gamma{}^H = 0°$), had been

(4) The location of atoms relative to the radical site is defined as follows.

$$\mathrm{H_\alpha{-}N{-}C_\alpha{-}C_\beta{-}C_\gamma}$$

with $\mathrm{H_\beta}$, $\mathrm{H_\gamma}$, $\mathrm{H_\delta}$ above.
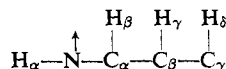
(5) (a) J. E. Wertz and J. R. Bolton, "Electron Spin Resonance Elementary Theory and Practical Applications," McGraw-Hill, New York, N. Y., 1972; (b) "Radical Ions, E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N. Y., 1968; (c) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance with Applications to Chemistry and Chemical Physics," Harper and Row, New York, N. Y., 1967.
(6) (a) W. G. Espersen and R. W. Kreilick, Mol. Phys., 16, 577 (1969); (b) R. W. Kreilick, ibid., 14, 495 (1968); (c) J. Amer. Chem. Soc., 88, 5284 (1966); (d) ibid., 90, 2711 (1968); (e) ibid., 90, 5911 (1968); (f) J. Chem. Phys., 45, 1922 (1966); (g) ibid., 46, 4260 (1967); (h) F. Yamaguchi and R. W. Kreilick, J. Amer. Chem. Soc., 91, 3429 (1969).
(7) (a) E. de Boer and C. McLean, Mol. Phys., 9, 191 (1965); (b) E. de Boer and J. P. Colpa, J. Phys. Chem., 71, 21 (1967); (c) E. de Boer and C. McLean, J. Chem. Phys., 44, 1334 (1966).
(8) (a) G. A. Russell, Science, 161, 423 (1968), and references cited therein; (b) G. A. Russell, G. Holland, K.-Y. Chang, and L. H. Zalkow, Tetrahedron Lett., 1955 (1967).
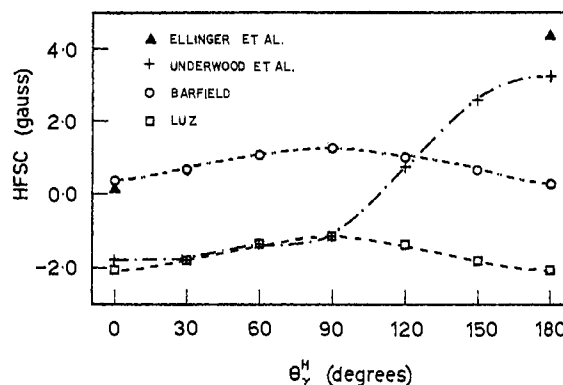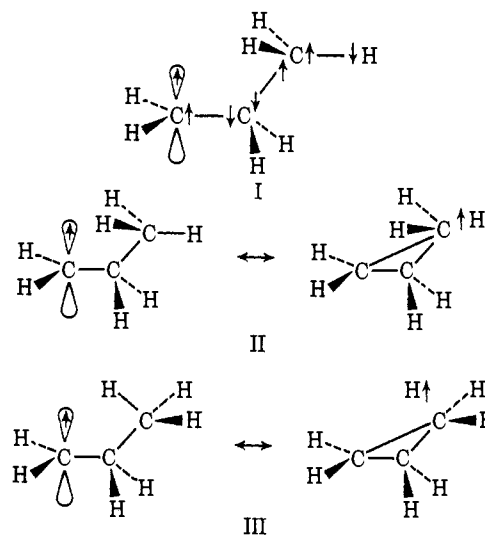
proposed also by Eaton[9] in order to account for the observed chemical shifts in the nmr studies of nickel aminotroponimine complexes.

Agreement is no better between the various theoretical approaches to this question. In fact, four recent papers[10-13] have led to widely different conclusions. Figure 2 summarizes the esr hfsc's calculated for the γ hydrogen in the propyl radical as a function of the dihedral angle $\theta_\gamma{}^H$ ($\theta_\beta{}^C = 0°$) by using the four different theoretical models. The lack of agreement is obvious.

Because of the diversity of proposals concerning the mechanisms of long-range spin delocalization, it appeared essential to us to make an experimental approach to this problem. The technique we have chosen involves the study of a series of cyclic and bicyclic systems in which there is a high degree of confidence concerning the geometric relationship between the hydrogens in question and the radical site. Furthermore we have used the method of nickel-induced nmr contact shifts which provides not only the relative

(9) D. R. Eaton, A. D. Josey, and R. E. Benson, J. Amer. Chem. Soc., 89, 4040 (1967).
(10) M. Barfield, J. Phys. Chem., 74, 621 (1970).
(11) Z. Luz, J. Chem. Phys., 48, 4186 (1968).
(12) G. R. Underwood, V. L. Vogel, and J. M. Iorio, Mol. Phys., 25, 1093 (1973).
(13) Y. Ellinger, A. Rassat, R. Subra, and G. Berthier, J. Amer. Chem. Soc., 95, 2372 (1973).

magnitudes of the spin densities but also its *sign*.[14] A knowledge of the sign of the spin density can be definite in deciding between several delocalization mechanisms. For example, if a negative spin density (β spin) is observed this can only arise from a dominant spin polarization mechanism whereas a resonance mechanism such as homohyperconjugation demands the observation of positive (or α) spin.

We have chosen a series of amines in which the nitrogen atom is constrained to be nonplanar. This provides us with additional information by virtue of the fact that the geometries defined by $\theta_\beta{}^C$ and $180° - \theta_\beta{}^C$ are nonidentical and allows an examination of our earlier proposal[15] that spin delocalization should be most facile along the pathway for which $\theta_\beta{}^C = 180°$ rather than $\theta_\beta{}^C = 0°$.

Experimental Section

Materials. Nickel bisacetylacetonate, hereafter referred to as Ni(Acac)$_2$, was purchased from Alfa Inorganics and was obtained in an anhydrous form by heating *in vacuo* at 61° for at least 15 hr. Chloroform-d was obtained from Merck Sharp and Dohme of Canada Limited. Tetramethylsilane (TMS) was obtained from Stohler Isotope Chemicals. Pyridine, α-picoline, 2-ethylpyridine, and 2-benzylpyridine were purchased from Aldrich Chemical Co. 2-(1-Ethylpropyl)pyridine and diphenyl-2-pyridylmethane were purchased from Alfred Bader Chemicals. All commercial samples were used without further purification. 2-Methylene-3-quinuclidinone was synthesized by the procedure of Hansen and Bader[16] and 1-azabicyclo[2.2.2]octene by the procedure of Grob, *et al.*[17] Both compounds had physical and spectral properties in agreement with the literature values.

Nmr Measurements. All spectra were recorded on a Perkin-Elmer R20B spectrometer with a probe temperature of 35°. The proton resonance shifts were measured relative to internal TMS reference to eliminate bulk susceptibility shifts, and measurements were made using a Takeda-Riken TR-3824X frequency counter. Two methods were used for determining the contact shifts. For compounds 1–3 and 7–12 a solution of the amine in chloroform-d (*ca.* 1 *M*) was prepared, and its spectrum was recorded. To this were added increasing amounts of Ni(Acac)$_2$ and each time the spectrum was recorded. Relative shifts were obtained by plotting the chemical shifts against the Ni(Acac)$_2$:amine ratio for at least six different concentrations. A linear least-squares regression analysis of the data provided a slope which was equated with the relative contact shifts, and hence the spin densities. The second method employed for compounds 4–6 and 12 shows linearity over the complete range of concentrations. This procedure involves the measurement of the chemical shifts of each proton in solutions at a constant Ni(Acac)$_2$ concentration, but with different amine concentrations. The contact shift δ_{cs} for each proton in the various solutions is obtained by subtracting the measured chemical shift in the presence of Ni(Acac)$_2$ from that obtained in the absence of Ni(Acac)$_2$. The data can then be fitted to an equation of the form

$$[\text{amine}]_0 = [\text{Ni}]_0 \Delta_{cs} \delta_{cs}{}^{-1} - K^{-1}$$

where [amine]$_0$ and [Ni]$_0$ are the initial concentrations of the amine and of Ni(Acac)$_2$, respectively, Δ_{cs} is the contact shift of the paramagnetic species produced, and K is the equilibrium constant for formation of the paramagnetic species.[18] For these measurements

the Ni(Acac)$_2$ concentration range was 0.03 to 0.04 *M* and the amine concentrations were varied from 0.1 to 2.0 *M*. At least six different concentrations were used for each amine. The best straight lines were obtained by a linear least-squares regression analysis. In all compounds where a direct comparison of these two procedures has been made the same relative spin densities were obtained.

Results and Discussion

Table I lists the experimental normalized values of the proton contact shifts for the amines discussed in this section. It is well known that the contact shifts induced in organic amines by the addition of nickel bisacetylacetonate, Ni(Acac)$_2$, arise as a result of spin density (α spin) introduced into the nitrogen nonbonding orbital.[14] Therefore, our discussion will center around the relative spin densities at hydrogens located γ to the nitrogen, as a function of the angles $\theta_\beta{}^C$ and $\theta_\gamma{}^H$ relating the nonbonding orbital and the hydrogen in question.

Since the contact shift technique does not normally yield absolute spin densities, but rather relative spin densities, it is necessary to use a reference shift (or reference spin density) within each molecule in order that valid comparisons can be made from one molecule to another. We have used the pyridine two-proton shifts as our arbitrary reference (relative shift = 100) for those compounds under examination (1–8) in which a pyridine moiety is present. It is desirable to be able to make comparisons of the relative spin densities in these molecules with other molecules in which the pyridine nucleus is not present. To this end we have synthesized and examined the shifts in 1-azabicyclo-[2.2.2]oct-2-ene (9).
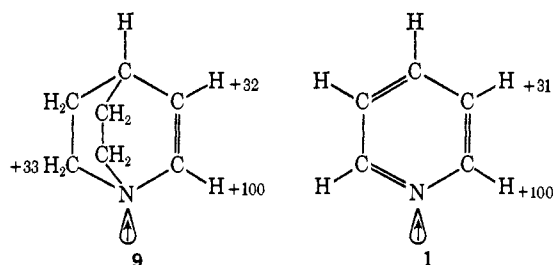
We propose that since there is a similar geometric relationship between the nitrogen lone pair, C$_2$ and H$_2$ in this molecule and the corresponding atoms in pyridine ($\theta_\beta{}^H = 0°$ for both), then for a given spin density in the nonbonding orbital, the amount of spin delocalized to this hydrogen should be comparable with that delocalized to H$_2$ in pyridine. In view of the expected difference in hybridization of the nitrogen nonbonding orbital in 9 and in pyridine we examine the plausibility of this proposal. To do this we note the similar locations of H$_3$ in 9 and H$_3$ in pyridine ($\theta_\gamma{}^H = 180°$ and $\theta_\beta{}^C = 180°$ for both) and compare the ratio of the

(14) The theory of paramagnetic shifts has been adequately outlined: D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, 1, 105 (1965); E. de Boer and H. van Willigen, *Progr. Nucl. Magn. Resonance Spectrosc.*, 2, 111 (1967).

(15) G. R. Underwood and R. S. Givens, *J. Amer. Chem. Soc.*, 90, 3713 (1968).

(16) A. R. Hansen and H. Bader, *J. Heterocycl. Chem.*, 3, 109 (1966).

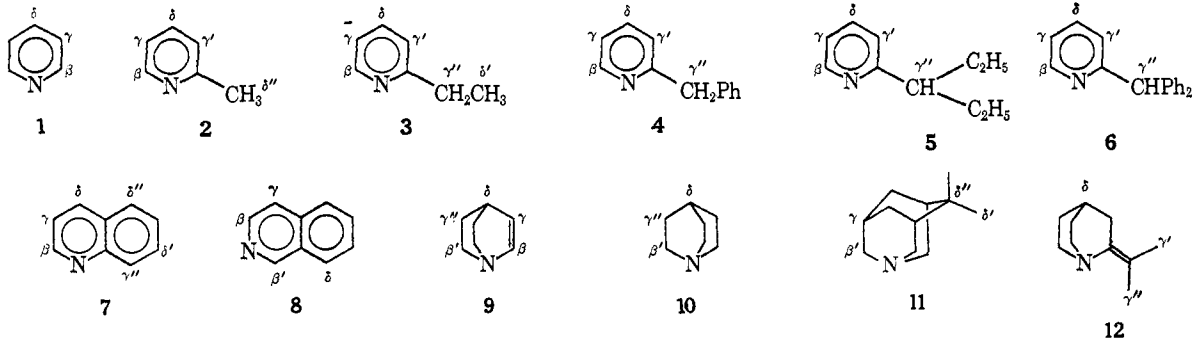(17) C. A. Grob, A. Kaiser, and E. Renk, *Helv. Chim. Acta*, 40, 2170 (1957).

(18) A similar expression has been derived for pseudo-contact shifts by I. Armitage, G. Dunmore, L. D. Hall, and A. G. Marshall, *Chem. Commun.*, 1281 (1971); I. M. Armitage, V. Gibb, L. D. Hall, and A. G. Marshall, 2nd International Symposium on Nmr Spectroscopy, Guildford, England, June 1972. A referee has requested the derivation of

this expression. Let the total concentrations of amine and nickel (complexed and uncomplexed) be A_0 and N_0, respectively. Assuming 1:1 complexation between the amine and nickel, the concentration of the complexed amine, [AN], is given in the equilibrium expression: $K = [\text{AN}](A_0 - [\text{AN}])^{-1}(N_0 - [\text{AN}])^{-1} \approx [\text{AN}]A_0{}^{-1}(N_0 - [\text{AN}])^{-1}$, since $A_0 \gg N_0$. Rearranging this expression yields $[\text{AN}] = KA_0N_0(1 + KA_0)^{-1}$. The observed contact shifts, δ_{obsd}, relative to the shifts of the uncomplexed amine, are then $\delta_{obsd} = \Delta_{cs}[\text{AN}]A_0{}^{-1} = \Delta_{cs}KN_0(1 + KA_0)^{-1}$, where Δ_{cs} is the contact shift of the complex, and rearrangement yields $A_0 = N_0\Delta_{cs}\delta^{-1} - K^{-1}$. The assumption of a 1:1 complex appears valid since reproducible results are obtained irrespective of the experimental concentration N_0 used. This expression gives Δ_{cs} with satisfactory accuracy, but due to the extrapolation necessary the equilibrium constants have large errors. Generally the value of K is in the range 1 to 10.

Table I. Relative Proton Nmr Contact Shifts

	β^j	$\beta'^{\,i}$	γ	γ'	$\gamma''^{\,i}$	δ	δ'	δ''
1	$+100^{a,b}$		$+30.9 \pm 0.3^c$			$+9.4 \pm 0.2$		
2	$+100^d$		$+20.4 \pm 0.8^i$	$+40.5 \pm 0.8^i$	-11.4 ± 0.1	$+6.8 \pm 0.4$		
3	$+100$		$+23 \pm 4^i$	$+43 \pm 4^i$	-5.7 ± 0.5	$+3 \pm 3$	$+0.2 \pm 0.8$	
4	$+100$		$+29 \pm 6^i$	$+26 \pm 5^i$	-10 ± 2	e		
5	$+100$		$+18 \pm 4^i$	$+61 \pm 6^i$	$+3.1 \pm 0.8$	$+0.6 \pm 0.2$		
6	$+100$		e	e	$+2.9 \pm 0.7$	e		
7	$+100^f$		$+23$		$+8$	$+8$	$+4$	$+18$
8	$+100^f$					$+3$		
9	$+100$	$\underline{+33 \pm 2}$	$+32 \pm 3$		$+3.3 \pm 0.6$	-17 ± 2		
10		$\underline{+33^g}$			$+4$	-4		
11		$\underline{+33^h}$	$+25$				$+1$	$+10$
12				-9 ± 2	$\underline{+8}$	-4 ± 2		

^{a} Positive values represent downfield shifts corresponding to α spin. ^{b} D. Doddrell and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 6839 (1970), reported the values 100, 30.3, and 9.1. ^{c} All errors reported are standard deviations. ^{d} D. Doddrell and J. D. Roberts, footnote b, reported 100, 24.9, 49.8, −16.0, and 8.2. ^{e} These protons are obscured at least partly by the phenyl absorptions. ^{f} Taken from I. Morishima, K. Okada, and T. Yonezawa, *J. Amer. Chem. Soc.*, **94**, 1425 (1972). Errors were not reported. ^{g} Taken from T. Yonezawa, I. Morishima, and Y. Ohmori, *ibid.*, **92**, 1267 (1970). Errors were not reported. ^{h} Taken from I. Morishima, K. Okada, and T. Yonezawa, *ibid.*, **93**, 3922 (1971). Errors were not reported. ^{i} The assignment of the shifts of the two γ protons in the substituted pyridines is tentative and based upon analogy with 2,3-disubstituted pyridines. However, further investigation may result in a reversal of these assignments. ^{j} The underlined numbers apply to shifts for the reference protons in each molecule.

contact shifts for H_2 and H_3 in both molecules. The fact that these two ratios are similar, $+0.32$ and $+0.31$, respectively, lends some credence to our model.

Furthermore, based on the use of H_2 in **9** ($\theta_\beta^{\,H} = 0°$) as the reference, one obtains the relative shift of H_6 ($\theta_\beta^{\,H} = 60°$) to be $+33$. In turn, these hydrogens have the same geometrical relationship to the nonbonding orbital ($\theta_\beta^{\,H} = 60°$) as do the H_2 hydrogens in 1-azaadamantane (**11**). Therefore, by using the H_2 hydrogens in **11** as a reference ($+33$) for the shifts in that molecule, the relative shift of H_3 in **11** is measured to be $+25$. When it is recognized that these protons have the same geometry ($\theta_\beta^{\,C} = 180°$ and $\theta_\gamma^{\,H} = 180°$) as the H_3 in pyridine, these two protons would be predicted to have the same relative shifts if the above assumptions are all valid. The exceptional agreement between these two sets of numbers ($+25$ and $+31$, respectively) certainly appears to justify these otherwise doubtful assumptions.

A further test of these assumptions can be made by comparing the reasonableness of the value of $+0.33$ obtained experimentally for the ratio $a_\beta^{\,H}(\theta_\beta^{\,H} = 60°)/a_\beta^{\,H}(\theta_\beta^{\,H} = 0°)$ with that calculated by the INDO method for nonplanar radicals. The ratio obtained theoretically is 0.26, again in satisfactory agreement with the experimental value. In view of the above arguments, the following discussions will be based upon all relative shifts of β hydrogens at $\theta_\beta^{\,H} = 0°$ being $+100$ and those with $\theta_\beta^{\,H} = 60°$ being $+33$.

The most striking feature of the shifts obtained for the γ hydrogens is that the largest positive shifts are invariably obtained at $\theta_\beta^{\,C} = 180°$ and $\theta_\gamma^{\,H} = 180°$. These results are compatible only with the INDO and *ab initio* calculations of Figure 2 and are at complete variance with the valence bond calculations of Barfield[10] and of Luz.[11] From a simple mechanistic viewpoint they are best described by homohyperconjugation II. The naive description of homohyperconjugation as II makes it tempting to speculate as to whether the smaller value of the γ-hydrogen shift for 1-azaadamantane than for pyridine is related to the poorer alignment of the C_β–H_γ bond with the nonbonding orbital or to the assumptions discussed above.

An estimate can be obtained for the sensitivity of the γ-hydrogen spin density to changes in $\theta_\gamma^{\,H}$ by a comparison of the data at $\theta_\beta^{\,C} = 180°$ for $\theta_\gamma^{\,H} = 180$ and $120°$. The former are available from pyridine ($+31$), 1-azabicyclooctene (**9**) ($+32$), and 1-azaadamantane (**11**) ($+26$), while the latter are from **9** ($+3$) and 1-azabicyclooctane (**10**) ($+4$). Obviously the small change in the angle $\theta_\gamma^{\,H}$ of $60°$ has a drastic effect on the magnitude of the γ-hydrogen spin density, again totally compatible with the simple description II of homohyperconjugation and with the results of the INDO calculations. It is unfortunate that we do not have suitable models to test further the dependence of spin density as a function of $\theta_\gamma^{\,H}$ at this value of $\theta_\beta^{\,C}$.

In the region $\theta_\beta^{\,C} = 0°$ we have several sightings on the spin density for a variety of values of $\theta_\gamma^{\,H}$. The eight proton in quinoline, **7**, is located at $\theta_\beta^{\,C} = 0°$ and

$\theta_\gamma{}^H = 0°$ and has a small positive relative spin density (+8). Likewise, compound 12 has a proton similarly located which also is found to have a small positive spin density. However, complexation of 12 with Ni(Acac)$_2$ is such that the induced shifts are extremely small and as a result we are unable to separate the absorptions of the five and six protons sufficiently to allow the use of the six-proton shifts for reference. Presumably this is due to weak complexation of 8 and also of 12 and is associated with steric shielding of the nitrogen lone-pair orbital from the bulky Ni(Acac)$_2$.

The side-chain protons in 5 and 6 are expected to adopt, more or less, the conformation $\theta_\beta{}^C = 0°$ and $\theta_\gamma{}^H = 0°$, particularly when it is remembered that contact shifts result only upon interaction between the nitrogen atom and the Ni(Acac)$_2$. The values of +3.1 and +2.9 are consistent with their proposed geometry, modified by a certain amount of libration about the $\theta_\gamma{}^H = 0°$ position. The effect of increasing the angle $\theta_\gamma{}^H$ from 0° in the region $\theta_\beta{}^C = 0°$ is thus deduced to decrease the spin density. As the angle is increased further, spin polarization may be expected to dominate since neither of the two resonance mechanisms II or III should contribute substantially to the spin distribution. This is borne out well by the data for compounds 3 and 4 ($\theta_\gamma{}^H \sim 60°$) where negative spin densities (-5.8 and -9.7, respectively) are observed. Furthermore, for the freely rotating methyl group in α-picoline, 2, in which all values of $\theta_\gamma{}^H$ ($\theta_\beta{}^C = 0°$) are encompassed, a negative spin (-11) is observed.

In 12, is found a hydrogen located at $\theta_\beta{}^C = 0°$ and $\theta_\gamma{}^H = 180°$. In view of the inability to use the six protons of this molecule as an internal reference vide supra we chose for this species to use the proton at $\theta_\beta{}^C = 0°$ and $\theta_\gamma{}^H = 0°$ as the reference and assume the magnitude of its shift to be the same as for the corresponding proton (H$_8$) in quinoline 7. On this basis the proton in question has a relative spin density of -7 indicating that at this conformation spin polarization dominates, albeit slightly, over homohyperconjugation.

From these experimental spin density distributions we therefore make the following generalizations. (a) For nonplanar radicals, spin is preferentially transferred to the atoms located at $\theta_\beta{}^C = 180°$ rather than at $\theta_\beta{}^C = 0°$. (b) Spin is most efficiently transferred to those γ atoms described by the W rule[8] ($\theta_\beta{}^C = 180°$ and $\theta_\gamma{}^H = 180°$). This is α spin and arises as a result of homohyperconjugation. (c) Homohyperconjugation is sharply dependent upon $\theta_\gamma{}^H$ and falls off approximately as $\cos^6 \theta_\gamma{}^H$. (d) In the region $\theta_\beta{}^C = 0°$ and $\theta_\gamma{}^H = 0°$ the resonance contribution III barely exceeds the spin polarization contribution. (e) In all other regions, spin polarization dominates and results in β spin.

We have also obtained contact shifts for several δ protons relative to the same reference of +100 for the two-proton in pyridine. These are also given in Table I. Broadly speaking there appear to be three groupings for the δ-proton shifts, depending on the orientation of the bonds linking the proton and the nitrogen nonbonding orbital.

(a) The "zig-zag" (or 2.5 V) arrangement of 1-

azaadamantane (11) and quinoline (7) results in the
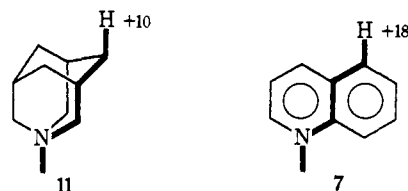
largest positive spin densities. The same large spin densities have also been reported for many benzazoles[19] and are implied by the results of the esr data on semidiones[8,20] and semiquinones.[21] These are consistent with, and in fact were anticipated from, an extended σ-bond conjugation mechanism.
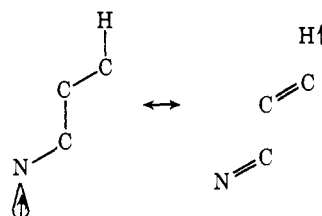
(b) When one of the terminal orbitals only fails to comply with this "zig–zig" arrangement (isoquinoline (8), 1-azaadamantane (11), and quinoline (7)) a much
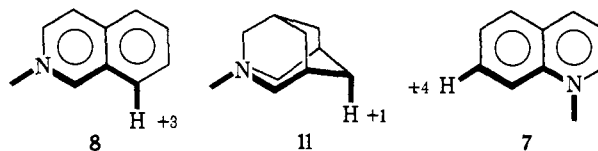
smaller positive spin density is measured indicating a less efficient mode of extended σ-bond conjugation.

(c) When one of the nonterminal bonds fails to fulfill the "zig–zag" requirement (pyridine (1), azabicyclooctane (10), and azabicyclooctene (9)) a more drastic
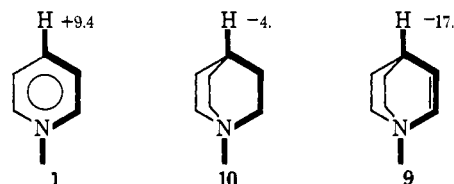
and less predictable effect on the spin density is observed. It is apparent that small changes in geometry and/or hybridization have a large effect on the relative spin densities for this arrangement of orbitals. This is possibly due to opposing effects of through-bond and through-space contributions.

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