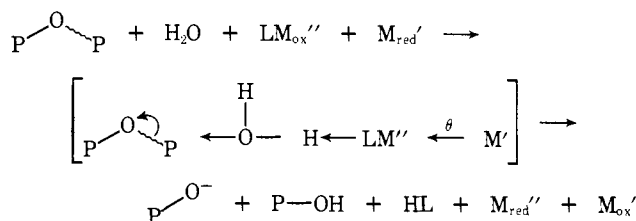


product (e.g., BH_3 , $\text{BH}(\text{OH})_3^-$ etc.¹⁴) is more active than the initial BH_4^- in reaction with Mo-SH complexes.

Another possibility is that the protonation of the ligand, connected with the Mo atom by the acid added or formed during BH_4^- decomposition, could facilitate hydride transfer from BH_4^- to the Mo-SH complex and the following reaction with the complexed C_2H_2 .

We believe that, if the latter possibility is the case, the mechanism of acid action in stimulation of Mo-SH systems bears in fact some resemblance with ATP action in enzymes. ATP, when hydrolyzed, can also provide an active proton to a substrate.¹⁵ One may visualize the following enzymatic mechanism of ATP hydrolysis coupled with electron (or H^-) transfer from the M' atom to the M'' atom (M'' then can reduce a substrate).



It is evident that this mechanism requires a very specific spatial arrangement of substrates which has not been achieved so far in model experiments.

(14) K. N. Mochalov, V. S. Khain, and G. G. Gilmanshin, *Dokl. Akad. Nauk SSSR*, **162**, (1965).

(15) It has been suggested that "ATP hydrolysis could be required as a site-specific proton source for the conversion of N_2 to NH_3 "; D. Y. Jeng, J. A. Morris, and L. E. Mortenson, *J. Biol. Chem.*, **245**, 2809 (1970).

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 Received April 4, 1974

Spin Delocalization in 7-Norbornenyl-Type Radicals

Sir:

The 7-norbornenyl radical poses some interesting problems regarding its structure,^{1,2} stereoselective reactions,^{1,3} and possible nonclassical nature.^{3,4} The recent studies on this¹⁻³ and related^{5,6} radicals prompt us to make a preliminary report on the systems we have been studying.

The work reported here involves an examination of the nmr paramagnetic contact shifts induced in 7-azabenzonorbornene (I) and 7-azabenzonorbornadiene (II) and derivatives by the addition of bis(acetylacetonato)nickel (II).⁷ These shifts, resulting from posi-

(1) P. Bakuzis, J. K. Kochi, and P. J. Krusic, *J. Amer. Chem. Soc.*, **92**, 1434 (1970).

(2) J. K. Kochi, P. Bakuzis, and P. J. Krusic, *J. Amer. Chem. Soc.*, **95**, 1516 (1973).

(3) J. Warkentin and E. Sanford, *J. Amer. Chem. Soc.*, **90**, 1667 (1968).

(4) H. O. Ohorodnyk and D. P. Santry, *J. Amer. Chem. Soc.*, **91**, 4711 (1969); *Chem. Commun.*, 510 (1969).

(5) D. J. Kosman, *Tetrahedron Lett.*, 3317 (1972).

(6) I. Morishima, K. Yoshikawa, K. Bekki, M. Kohno, and K. Arita, *J. Amer. Chem. Soc.*, **95**, 5817 (1973).

(7) The theory and experimental details of this technique have been adequately discussed elsewhere: D. H. Geske, *Progr. Phys. Org. Chem.*,

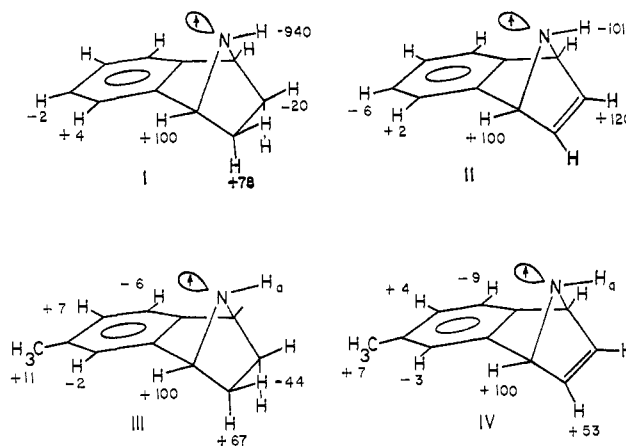


Figure 1. Nickel-induced contact shifts in the 7-azabornenes and -norbornadienes. The signs given refer to the signs of the spin densities at the protons in question. The numbers given are obtained by a least-squares analysis of data obtained over at least six different concentrations. (a) Insufficient data could be obtained for these -NH absorptions to allow reliable analyses. (b) The assignments of the aromatic protons are based upon the general observation that alkyl substitution causes a slight upfield shift for protons ortho to the substitution site: L. M. Jackman, Q. N. Porter, and G. R. Underwood, *Aust. J. Chem.*, **18**, 1221 (1965). The assignments of the exo and endo protons are made by direct comparison with the nmr spectra of the carbocyclic analogs: K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Lett.*, **9** (1966); N. Inamoto, S. Masuda, K. Tori, K. Aono, and H. Tanida, *Can. J. Chem.*, **45**, 1185 (1967); K. Tori, Y. Yoshimura, and R. Muneyuki, *J. Amer. Chem. Soc.*, **93**, 6324 (1971). (c) The contact shifts obtained for the bridgehead protons of the above molecules were as follows: (I, 20.5; II, 78.1; III, 689; IV, 71.7 ppm)/[Ni]/[amine].

tive spin density in the nitrogen nonbonding orbital, have been shown to be accurate probes of the spin distributions in the corresponding hydrocarbon radicals.⁸ The present study, however, offers several advantages over the conventional esr experiments; these are (a) unequivocal assignment of the spin densities to specific atoms, (b) direct determination of the *sign* of the spin density, and (c) the determination of spin densities which normally would give rise to unobservably small esr hyperfine splitting constants.

The results for the molecules under investigation are given in Figure 1 in which all values are normalized with respect to the spin densities at the bridgehead protons.⁹ Several interesting points can be noted from these data. First, all -NH protons exhibit upfield shifts resulting from negative (or β) spin densities. This is a typical result for cyclic amines, although in this case, where substantial nonplanarity at the radical site is expected,¹⁰ the result was not a foregone conclusion. That the radical site is in fact nonplanar can be deduced from the

4, 125 (1967); W. D. Horrocks, R. C. Taylor, and G. N. LaMar, *J. Amer. Chem. Soc.*, **86**, 3031 (1964).

(8) (a) R. H. Holm, G. W. Everett, Jr., and W. D. Horrocks, Jr., *J. Amer. Chem. Soc.*, **88**, 1071 (1966); (b) E. E. Zaev, Y. N. Molin, G. M. Zhidomiron, and V. V. Voevodskii, *Dokl. Phys. Chem.*, **173**, 285 (1967); (c) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, *J. Amer. Chem. Soc.*, **93**, 3922 (1971); (d) I. Morishima, K. Okada, and T. Yonezawa, *ibid.*, **94**, 1425 (1972).

(9) We prefer this reference to the more frequently used -NH protons which often cannot be monitored over a sufficiently wide range of concentrations and which may be subject to substantial medium and concentration effects.

(10) For the 7-norbornenyl radical² and for the analogous nitroxides,^{5,6} ring strain is proposed to cause substantial nonplanarity at the radical site.

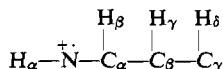
magnitude of the bridgehead hydrogen¹¹ spin densities relative to the remaining protons. A planar radical would result in these protons being located in the nodal plane of the nonbonding orbital and would lead to extremely small shifts.¹²

A nonplanar radical site raises the question of the stereochemistry of the $-NH$ bond relative to the benzene ring (syn or anti). This subject has received considerable attention recently^{2,5,6} and is related to possible stabilization of the radical site by interaction with the ethylenic or benzene π -electrons.¹⁷ In the present systems, with the availability of both signs and relative magnitudes of the spin densities, it is possible to make definitive statements as to the location of the protons in question. Experimentally we find the ratio of spin densities $H_{2(\text{endo})}:H_{2(\text{exo})}$ in I to be -3.9 . Based upon the theoretical results for the 7-norbornenyl radical,² this can only be compatible with the location of the proton being anti to the benzene ring.¹⁹

In the unsaturated analog II the bridgehead and vinylic protons have comparable spin densities. The ratio of spin densities is $+1.20$, remarkably close to the value of 1.28 observed for the 7-norbornenyl radical (H_7 syn to the double bond²). If the hydrogen atom were located anti to the double bond, a much smaller value would be anticipated.⁶ Hence we conclude that *the $-NH$ bond lies anti to the aromatic ring in both the saturated and unsaturated molecules in this series.*

The observation of substantial shifts for the vinylic protons raises the question as to how spin is transmitted to this location. Similar observations have been noted in studies of unsaturated semidiones,¹⁴ semiquinones,¹⁵ and semifuraquinones.^{13,20,21} The knowledge of the sign of this spin density allows a unique solution: of the four spin delocalization mechanisms which have been proposed to account for spin at the vinylic proton (through-bond spin polarization, electron transfer, homoconjugation, and homohyperconjugation) *only homohyperconjugation can account for the observed positive spin densities* and for the magnitude of the interaction.²²

(11) We use the usual esr convention for describing the location of an atom relative to the radical site



(12) This subject has been discussed in some detail.¹³⁻¹⁶

(13) S. F. Nelsen and E. D. Stepanen, *J. Amer. Chem. Soc.*, **89**, 5740 (1967).

(14) G. A. Russell, G. W. Holland, and K. Y. Chang, *J. Amer. Chem. Soc.*, **89**, 6629 (1967).

(15) D. Kosman and L. M. Stock, *J. Amer. Chem. Soc.*, **91**, 2011 (1969).

(16) L. M. Stock and J. Suzuki, *J. Amer. Chem. Soc.*, **87**, 3909 (1965); (b) E. G. Janzen and J. L. Gerlock, *J. Org. Chem.*, **32**, 820 (1967); (c) T. W. McKinney, *J. Amer. Chem. Soc.*, **90**, 3879 (1968); (d) R. D. Allendoerfer, P. E. Gallagher, and P. T. Lansbury, *ibid.*, **94**, 7702 (1972); (e) L. M. Stock and M. R. Wasielewski, *ibid.*, **95**, 2743 (1973).

(17) It has been concluded that the 7-proton lies syn to the double bond in 7-norbornenyl^{2,4,18} while the oxygen atom is proposed to lie syn to the aromatic ring in 7-azabenzonorbornen-7-oxyl but anti to the ring in the unsaturated analog.⁶ These statements refer, of course, to the more stable minimum of what is presumably a double well potential.

(18) M. Shanshal, *Z. Naturforsch. A*, **26**, 1336 (1971).

(19) Based upon the magnitude alone this ratio could be regarded as evidence for either a syn or an anti proton, but the sign of this ratio eliminates any possible doubt.

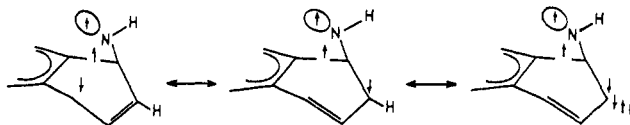
(20) S. F. Nelsen and E. D. Stepanen, *J. Amer. Chem. Soc.*, **92**, 6216 (1970).

(21) S. F. Nelsen, E. F. Travecedo, and E. D. Stepanen, *J. Amer. Chem. Soc.*, **93**, 2913 (1971).

Small spin densities are observed at the aromatic protons and several mechanisms have been forwarded to account for corresponding results in similar systems.^{14,15} The almost equal magnitudes for the aromatic proton shifts tend to favor spin transfer *via* the aromatic π -system. Electron transfer from the symmetric benzene π -orbital, Ψ_3 , to the electron deficient nitrogen currently appears to be an attractive possibility. Involvement of the aromatic π -system is also strongly implicated by the results obtained for the methyl derivatives III and IV. The shifts observed for these methyl protons (separated from the radical site by six σ -bonds) are of opposite sign but comparable magnitude to the aromatic protons they replace—a good diagnostic for spin transfer through the π -system rather than through the σ framework.^{14,15,21,23} More concrete statements as to the exact nature by which spin is transferred to the aromatic π -system awaits further studies. Such studies are in progress.

Acknowledgments. We thank Professor R. N. Warriner (Australian National University) for details of the preparation of the compounds used in this research and for generous samples. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

(22) A referee has suggested that the negative spin density at the vinylic hydrogens might arise by spin polarization of the electrons in the C_1-N_7 bond, followed by allylic conjugation leading to negative spin density on the vinyl carbons. This would be transmitted to the vinyl hydrogens with the sign inversion common to π - σ interactions of this type



While this mechanism may contribute, we consider that it would not account for the magnitude of the interaction, particularly since an identical polarization of the C_1-N_7 bond would result in a (lesser) negative spin at the same hydrogen.

(23) G. A. Russell, T. Ku, and J. Lokensgard, *J. Amer. Chem. Soc.*, **92**, 3833 (1970).

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Total Synthesis of Talatisamine, a Delphinine Type Alkaloid

Sir:

Some time ago we have completed a stereospecific synthesis of compound 1.¹ We wish to disclose now the first formal total synthesis of a hexacyclic polysubstituted aconite alkaloid (talatisamine, 7) starting with this atisine type intermediate.

Treatment of compound 1 with NaH in refluxing dioxane (24 hr) followed by cooling and addition of dibenzoyl peroxide² yielded 65% of the oily benzoate 2 isolated by preparative tlc (ir 1720, 1735 cm^{-1} (benzoate, CO); nmr singlet (1 H) τ 4.73 (H unshielded by

(1) K. Huber, Ph.D. Thesis, University of New Brunswick, 1973. Experimental details are available on microfilm (U.N.B. Library) and will be published in the full paper.

(2) S. O. Lawesson, T. Busch, and C. Berglund, *Acta Chem. Scand.*, **15**, 260 (1961).