

binding for ring and hydrogen moieties in this compound.

The N<sub>2</sub> complex described here, however, is so strikingly similar in composition, stability, and color to that formed from N<sub>2</sub> and decamethyltitanocene<sup>1</sup> that there can be no reasonable doubt about its structural assignment as a *bone fide* (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti derivative. Formulation of the complex as (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TiN<sub>2</sub>Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> is also supported by the ir spectrum of the solid complex. The spectrum exhibits only the plain metallocene bands mentioned above. The lack of an absorption attributable to the coordinated N<sub>2</sub> moiety is unfortunate for our curiosity about the effects of coordination on the strength of the N–N bond, but of course entirely in accord with the symmetry of this structure. The intermediacy of this nitrogen complex in N<sub>2</sub> reduction reactions will be reported upon in a separate communication.

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### Studies on Nuclear Magnetic Resonance Contact Shifts Induced by Hydrogen Bonding with Organic Radicals. I. <sup>1</sup>H and <sup>13</sup>C Contact Shifts of Protic Molecules in the Presence of the Nitroxide Radical

Sir:

During the last 20 years considerable interest has been manifested in the study of the hydrogen bond (H bond).<sup>1</sup> A great majority of phenomena connected with the H bond can be explained if this bond is considered as describing an interaction in which the electrostatic charge-migration (covalent bond) as well as the short-range repulsion effects are simultaneously important. The fundamental similarity between the H-bond and charge-migration (or charge-transfer or covalent bond) interaction has been emphasized.<sup>1c</sup> Recently MO theoretical studies have been performed for various H-bond systems and proved to be successful in producing H-bond energies, charge distributions, and most stable conformations.<sup>2</sup> All these studies are associated with closed-shell molecules. In the present work we are concerned with the H bond between closed-shell and open-shell molecules which has been studied less experimentally and theoretically. We wish to report here preliminary results of nmr contact-shift and MO theoretical studies for the H bonding in the protic molecule–nitroxide radical system.<sup>3</sup>

(1) (a) G. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960; (b) D. Hadzi, Ed., "Hydrogen Bonding," Pergamon Press, Oxford, 1959; (c) S. Bratoz, *Advan. Quantum Chem.*, **3**, 209 (1966).

(2) K. Morokuma, H. Kato, T. Yonezawa, and K. Fukui, *Bull. Chem. Soc. Jap.*, **38**, 1263 (1965); K. Morokuma and L. Pederson, *J. Chem. Phys.*, **48**, 3275 (1968); P. Kollman and L. C. Allen, *ibid.*, **51**, 3286 (1969); A. S. N. Murthy and C. N. R. Rao, *Chem. Phys., Lett.*, **2**, 123 (1968); W. Adam, A. Grimison, R. Hoffmann, and G. Zuazaga de Ortiz, *J. Amer. Chem. Soc.*, **90**, 1509 (1968), and other recent papers.

(3) To our knowledge, study of the nmr contact shifts of solvent molecules in the presence of organic radicals has been quite limited

In order to assess the importance of covalent bonding in the XH···Y H-bonding system, we have studied proton and <sup>13</sup>C contact shifts for various proton donor molecules, XH, induced by the presence of di-*tert*-butyl nitroxide (DTBN), the proton acceptor. We have also carried out unrestricted Hartree–Fock (UHF) calculations using Pople's INDO method<sup>4</sup> for the above H-bond system to substantiate the observed contact shifts. The observation of the XH proton contact shift is expected to reflect directly the electron spin density transferred through the H bond from DTBN. This H-bond contact shift will serve as a measure of covalent character or strength of the XH···Y H-bond interaction. In addition, the contact shifts for other protons and carbons in the XH molecule will allow us to see the mode of electron spin distribution in the XH molecule.

We have observed the effect on <sup>1</sup>H and <sup>13</sup>C resonance positions of several XH molecules upon addition of increasing amounts of DTBN.<sup>5</sup> The hydroxyl proton of methanol, for example, in CCl<sub>4</sub> experienced an upfield shift and broadening when a small amount of DTBN was added, while methyl protons were almost unaffected. This upfield shift is proportional to the concentration of added DTBN and is more pronounced for a more acidic XH proton such as in phenol. The observed upfield shifts of the XH proton in the various proton donor molecules are plotted against the DTBN concentration (Figure 1).<sup>6</sup>

The upfield shift is most likely caused by the Fermi contact interaction for the XH proton of that fraction of the XH molecule which is specifically H bonded to DTBN. We have also examined the temperature dependence of this upfield shift. The resulting linear dependence of the shift on 1/T (Curie law behavior) may be characteristic of the contact shift.<sup>7,8</sup>

[see N. A. Sysoeva, A. U. Stepanyants, and A. L. Buchachenko, *Zh. Strukt. Khim.*, **9**, 311 (1968)]. Very recently, de Boer, *et al.*, have reported contact shift data for the solvent molecule (tetrahydrofuran) dissolving radical anions: E. de Boer, A. M. Grotens, and J. Smid, *J. Amer. Chem. Soc.*, **92**, 4742 (1970); *Chem. Commun.*, 1035 (1970).

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

(5) Pmr spectra were obtained at various temperatures on a Jeolco high-resolution nmr spectrometer (60 MHz) using TMS as an internal standard. The concentration of all XH molecules was 2.5 × 10<sup>-3</sup> M in CCl<sub>4</sub> solution. To this solution, DTBN was added drop by drop (from 3.3 × 10<sup>-6</sup> to 16.5 × 10<sup>-5</sup> M) until the XH proton signal was too broad to be observed. Natural-abundance <sup>13</sup>C nmr spectra were recorded with a Jeolco C-60HL spectrometer (15.1 MHz) using a complete proton-decoupling technique.

(6) Since the exchange of the proton donor molecules between H-bonded and nonbonded sites is rapid on the nmr time scale, the spectra are time averaged, the various proton resonances being shifted from their normal diamagnetic values by an amount which is proportional to the concentration of the H-bonded species. Thus as DTBN is added, the proton resonances of the XH molecule shift toward the resonance position of the H-bonded species. The relative values of this shift for various XH molecules are of significance in the present study. The relative values of the slope in the linear relation for various XH molecules may approximately correspond to the relative H-bonding contact shifts in this labile molecular interaction.

(7) This temperature dependence of the shift is, of course, partly caused by the temperature dependence of the equilibrium of the H-bond interaction.

(8) In the diamagnetic solution, the XH proton signal is displaced to lower field by H bonding;<sup>1a,b</sup> this usual downfield shift and upfield contact shift occur simultaneously for the present H-bond systems. However, the contact shift appears to be predominant in the observed DTBN-induced shift; addition of a diamagnetic proton acceptor, in place of DTBN, to the solution of the XH molecule had no substantial effect on the XH proton shift. Therefore, DTBN-induced upfield shifts strongly suggest negative electron spin density on the XH proton induced by H bonding with DTBN, although the apparent values of the relative shifts obtained from Figure 1 are not quantitatively related to the relative values of the induced spin densities.

Inspection of Figure 1 shows that H-bonding contact shifts fall generally in the order of proton-donating ability of the X-H group, which is well established<sup>1a,b</sup> by various spectroscopic methods. However, it is interesting to note that the C-H proton in chloroform experiences a substantial contact shift, comparable with that for other more acidic O-H groups. The acid strength determined by ir spectroscopy (the shift of the X-H stretching frequency) is in the order acetic acid > phenol > methanol > amine > chloroform.<sup>1a,9a</sup> Therefore, the large contact shift for chloroform appears to imply that the covalent character in the H bond is quite large for the C-H group, as compared with the N-H and O-H groups.<sup>9b,10</sup> This is also seen in the sizable contact shift for the acetylenic proton in phenylacetylene in comparison with diethylamine.<sup>9b,12</sup> Another feature apparent from the data in Figure 1 is the unexpectedly small contact shift for acetic acid. This may be due to the self-association (dimer formation) of acetic acid, which is less sensitive to the H bond.

In order to look at the manner of electron spin distribution on the various parts of XH molecule, we have observed <sup>13</sup>C contact shifts for CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>OH, and C<sub>6</sub>H<sub>5</sub>C≡CH as well as proton shifts induced by the presence of DTBN (Table I).<sup>13</sup> Addition of DTBN

**Table I.** Proton and Carbon Contact Shifts and Spin Densities Induced by Hydrogen Bonding with DTBN

Molecule	Nucleus	Obsd contact shift <sup>a</sup>		Rel spin density
		Obsd, ppm	Rel value	
CH <sub>3</sub> OH	OH	+1.12	+1.00	-1.00
	CH <sub>3</sub>	-0.23	-0.205	+0.205
CHCl <sub>3</sub>	<sup>13</sup> C	-1.0	-0.893	+0.148
	H	+0.69	+1.00	-1.00
CH <sub>2</sub> Cl <sub>2</sub>	<sup>13</sup> C	-9.4	-13.6	-2.31
	H	+0.20	+1.00	-1.00
C <sub>6</sub> H <sub>5</sub> C≡CH	<sup>13</sup> C	-2.4	-12.0	+1.99
	H	+0.15	+1.00	-1.00
	<sup>13</sup> C <sub>1</sub>	-2.21	-14.7	-2.44
	<sup>13</sup> C <sub>2</sub>	-0.40	-2.65	-0.44

<sup>a</sup> Measured as neat liquid in the presence or absence of DTBN (1 × 10<sup>-4</sup> M).

shifts the <sup>13</sup>C resonances of these molecules to lower field, indicating positive spin density on the carbon. This <sup>13</sup>C downfield shift for CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and C<sub>6</sub>H<sub>5</sub>-C≡CH is more pronounced in its magnitude than are

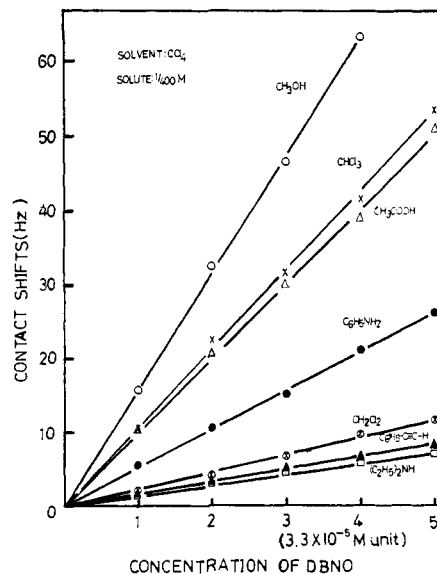
(9) (a) This order of acid strength determined by the ir frequency shift corresponds to that of the H-bond energy (see C. A. Coulson, "Valence," Oxford University Press, London, 1961); (b) the apparent contact shifts are affected by the shift of the H-bonded species and by the equilibrium constant. Therefore, one should not take the observed shift as the shift directly proportional to the H-bond contact shift. However, one may be allowed to take the relative value of the shifts as proportional to the H-bond shift.

(10) The contribution of the covalent bond structure in the XH...Y H-bond system has been theoretically shown to be 6% at most for the OH...O system.<sup>10,11</sup> The above finding would be acceptable if the covalent bond contribution in the CH...O system is more important than in the OH...O and the NH...O systems.

(11) C. A. Coulson and V. Dannielson, *Ark. Fys.*, **8**, 239, 245 (1954).

(12) Although the concomitant downfield shift of the XH proton due to H-bond formation is considered to reduce the apparent upfield contact shift, particularly for protons more acidic than C-H protons, the contribution of this downfield shift is minor, as evidenced by the diamagnetic solution with corresponding concentration of the diamagnetic proton acceptor such as trimethylamine oxide or dimethyl sulfoxide.

(13) In order to obtain the relative magnitudes of the <sup>1</sup>H and <sup>13</sup>C contact shifts (Table I), we have measured <sup>1</sup>H and <sup>13</sup>C spectra for neat liquids of these molecules in the absence or presence of DTBN.



**Figure 1.** Plots of the proton shift induced by di-*tert*-butyl nitroxide (DBNO) vs. concentration of DBNO for various protic substances. The solute concentration is  $2.5 \times 10^{-3}$  M in CCl<sub>4</sub>.

the proton contact shifts in these molecules. This <sup>13</sup>C shift is evidently due to the Fermi contact interaction, not to the effect of bulk susceptibility. This is apparent from the fact that the phenyl ring carbons in phenylacetylene are hardly affected by the addition of DTBN. It should also be noted that the addition of the diamagnetic proton acceptor does not change the <sup>13</sup>C shift.

The relative contact shifts ( $\Delta\delta_C/\Delta\delta_H$ ) of the proton and <sup>13</sup>C are related to the relative value of the spin densities ( $\rho_{SC}/\rho_{SH}$ ) on the proton 1s and the carbon 2s atomic orbitals by the relation

$$\frac{\rho_{SC}}{\rho_{SH}} = \frac{|\phi_{SH}(\gamma_H)|^2 \Delta\delta_C}{|\phi_{SC}(\gamma_C)|^2 \Delta\delta_H}$$

where  $|\phi_{SN}(\gamma_N)|^2$  is the square of the 1s or 2s atomic orbital at the nucleus N.<sup>4</sup> The relative spin densities obtained by this relation are also given in Table I. Nonlocal distribution of the spin densities on the proton and carbon atoms is clearly seen.

In order to substantiate the observed <sup>1</sup>H and <sup>13</sup>C contact shifts, INDO calculations were performed for dimethyl nitroxide (DMN)-methanol and DMN-acetylene systems. We assumed that the nitrogen, oxygen, and carbon atoms in DMN were coplanar. The bond distances used are NO, 1.215 and NC, 1.550 Å and the CNC bond angle is assumed to be 120°. The corresponding values for donor molecules methanol and acetylene were obtained from Sutton's compilation.<sup>14</sup> The geometrical structures for the H-bond system adopted here are the  $\pi$  and  $\sigma$  type, where the XH proton is directly over the  $p_\pi$  orbital of the oxygen atom with the X-H bond axis perpendicular to the N-O bond and in the  $\sigma$  plane, respectively. The spin densities calculated for each H-bond model were obtained for the structure with energy optimization. The results are summarized in Table II. The experimental trend of the induced spin densities on the <sup>1</sup>H and <sup>13</sup>C nuclei is well reproduced only for the  $\pi$  model both for DMN-methanol and DMN-acetylene systems. The  $\sigma$  model fails to explain the observed <sup>1</sup>H and <sup>13</sup>C contact shifts in these

(14) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. 11 (1958).

**Table II.** Results of INDO Calculations for Proton Donor... Nitroxide Systems

Proton donor	$R_{O\cdots H},^a$ (Å)		Calcd spin densities <sup>b</sup> and stabilization energies <sup>c</sup>	
			$\pi$ model	$\sigma$ model <sup>d</sup>
Methanol	1.50	$\rho_{OH}$	-0.016	0.002
		$\rho_C$	0.000	0.000
		$\Delta E, \text{kcal/mol}^e$	8.87	10.10
Acetylene	1.75	$\rho_{H1}$	-0.010	0.002
		$\rho_{C2}$	0.008	-0.002
		$\rho_{C3}$	0.000	0.000
		$\rho_{H4}$	0.001	0.000
		$\Delta E, \text{kcal/mol}^e$	1.29	1.20

<sup>a</sup> Obtained by energy optimization. <sup>b</sup> Spin densities on the hydrogen 1s and carbon 2s atomic orbitals. <sup>c</sup> Energy differences between two conformations for finite and infinite separations of proton donor and dimethyl nitroxide. <sup>d</sup> Calculated for the model where  $\angle NOH = 120^\circ$ . <sup>e</sup> Numbering of the atoms:  $(CH_3)_2N-O\cdots H_1-C_2\equiv C_3-H_4$ .

two systems; the downfield  $^{13}C$  contact shifts in two acetylenic carbons ( $C_1$  and  $C_2$ ) require the  $\pi$  model.

The appearance of negative and positive spin densities in the C-H group can be explained by a spin polarization mechanism. Because positive spin density is residing on the oxygen  $p_\pi$  orbital, the transfer process will preferentially involve an electron in the  $O\cdots H$  bond with a spin antiparallel to that of the oxygen electron. This results in a slight excess of positive electron spin density on another site (carbon) of the C-H bond, leading to a slight amount of unpairing of the electrons in the C-H bond. This may also be the case for other  $XH\cdots DTBN$  systems. As is inferred from the above discussion, polarization of electron spins may propagate through the bonds and induce positive or negative spin density on the various parts of the  $XH$  molecule. Therefore, the way in which electron spin distributes itself in  $XH$  molecules is expected to follow the trend of nuclear spin coupling constants. The relative  $^{13}C$  contact shift, *i.e.*, the relative spin densities, for acetylenic carbons ( $C_1$  and  $C_2$ ) in phenylacetylene ( $\rho_{C_2}/\rho_{C_1} = 0.18$ ) is well correlated with the relative values of the  $^{13}C_1-H$  and  $^{13}C_2\equiv C_1-H$  nuclear spin coupling constants ( $J_{C_2-C-H}/J_{C_1-H} = +251/+49 = 0.20$ ). This correlation appears to hold for the trend in the directly bonded  $^{13}C-H$  coupling constants in  $CHCl_3$ ,  $CH_2Cl_2$ , and  $C_6H_5C\equiv CH$ .<sup>15</sup>

This nonlocal distribution of electron spin density is also seen in the stereospecific proton contact shifts for various protons in the  $XH$  molecules. We have examined the proton nmr spectrum of 4-methylpiperidine, for example, in the presence of DTBN. Quite different values of the downfield contact shifts for  $\alpha$ -axial and  $\alpha$ -equatorial protons were observed, while the NH proton exhibited a pronounced upfield shift. The observation of a greater downfield contact shift for an  $\alpha$ -axial proton than for an equatorial one ( $\Delta\delta_{ax}/\Delta\delta_{eq} = 5$ ) is in accord with the conformation of the N-H group located preferentially at the axial position,<sup>16</sup> in which these protons are separated by the "zig-zag" route, the favorable arrangement for electron spin distribution and nuclear spin coupling.<sup>17</sup>

(15) I. Morishima, K. Endo, and T. Yonezawa, *Chem. Phys. Lett.*, in press.

(16) T. Yonezawa, I. Morishima, and Y. Ohmori, *J. Amer. Chem. Soc.*, **92**, 1267 (1970); I. Morishima, K. Okada, M. Ohashi, and T. Yonezawa, *Chem. Commun.*, 33 (1971).

(17) I. Morishima and T. Yonezawa, *J. Chem. Phys.*, in press.

From the present work we can conclude that the contact shifts induced by H bonding between protic substances and the nitroxide radical serve as a sensitive probe for elucidation of the covalent character of the H bond and of the mode of electron spin distribution on the proton donor molecules. Further theoretical studies on this H-bonding system will appear elsewhere.<sup>18</sup>

(18) I. Morishima, K. Endo, and T. Yonezawa, *Chem. Phys. Lett.*, in press.

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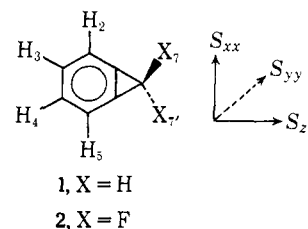
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## Nuclear Magnetic Resonance Spectra of Oriented Benzocyclopropene and 7,7-Difluorobenzocyclopropene

Sir:

It is well established that nmr spectra of small molecules oriented in a nematic phase yield valuable structural information on proton-proton distances.<sup>1</sup> We wish to report such information for the benzocyclopropene system, the smallest benzo-annulated cycloalkene.

$^1H$  and  $^{19}F$  nmr spectra of benzocyclopropene (**1**)<sup>2</sup> and its 7,7-difluoro derivative **2**<sup>3</sup> were observed in



*N*-(*p*-ethoxybenzylidene)-*p*-*n*-butylaniline<sup>4</sup> as nematic solvent at normal magnet temperature (30°). Measurements were made on a Varian HA-100 spectrometer, operated in the HR mode. Calibration was achieved by the usual side-band technique,<sup>5</sup> using tetramethylsilane as internal reference compound.

The spectra of **1** and **2** are of the AA'BB'C<sub>2</sub> and AA'BB'X<sub>2</sub> type, respectively. For the analysis the following steps were taken. (1) trial spectra were calculated using direct coupling constants  $D_{ij}$  based on assumed geometries and orientation parameters  $S_{ki}$ . Input data for the indirect H,H- and H,F-coupling constants were obtained from the results in isotropic media.<sup>6,7</sup> (2) Iterative computer analysis was performed with the program LAOCOONOR<sup>8</sup> using the data of the best trial spectrum as starting parameters. In addition, the  $^1H$  aa'bb' subspectra of **2**, belonging to fluorine spin states  $F_2(X_2) = +1, 0, \text{ and } -1$ , have

(1) For a recent review see: P. Diehl and C. L. Khetrapal, "NMR—Basic Principles and Progress," Vol. 1, Springer-Verlag, West Berlin, 1969.

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(6) M. A. Cooper and S. L. Manatt, *J. Amer. Chem. Soc.*, **92**, 1605 (1970).

(7) H. Günther and J. B. Pawliczek, *Org. Magn. Resonance*, in press.

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