plicated and troublesome, development toward this direction should be made in the future because of the importance of the configuration interaction in the calculation of the rotational strength of many molecules. Another possible development of this analysis is to increase the number of the molecular fragments for analysis by more than two. For example, methylcyclohexanone can be divided into the methyl group, the carbonyl group, and the remaining part. In this case, the contribution of each part cannot be represented in matrix form, although the results may sometimes be very convenient in order to see the effect of a substituent on a chromophore. But development toward this direction would be rather trivial, since the precedure of calculation would be quite similar to that described in this paper and the obtained results may be expected to be essentially similar to those given here.

Finally, it should be noted that the method presented here can also be applied by using the molecular orbitals obtained by INDO approximation.

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Interaction between Closed-Shell and Open-Shell Molecules.[1] Nuclear Magnetic Resonance Contact Shift Studies on the π-Hydrogen Bonding Involving Stable Hydrocarbon π Radicals

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Abstract: ^{1}H and ^{13}C nmr shifts induced by the π-hydrogen bond between the BDPA radical (stable hydrocarbon π radical) and various proton donor molecules have been studied. The preferential upfield ^{1}H shift of the XH proton, as compared with the shift induced by BDPP (the corresponding closed-shell hydrocarbon molecule), was attributed to the contact shift characteristic of negative spin density on the XH proton. The experimental results were also substantiated by MO theoretical calculation.

We are currently interested in the use of a stable free radical induced nmr contact shift as a potential probe for studying weak molecular interactions involving free radicals. Our recent studies[2] on the ^{1}H and ^{13}C nmr contact shifts have shown that nitroxide radical (di-*tert*-butyl nitroxide, DTBN) can be used to probe chemical phenomena associated with molecular interactions such as hydrogen bond and charge-transfer interactions involving free radicals. We have also been studying the features and mechanism of intermolecular electron spin transmission associated with these interactions in the light of elucidating the intrinsic nature of the interaction between closed- and open-shell molecules.[2,3]

Concerning the hydrogen bond involving free radicals, we have observed nmr contact shifts for a variety of the proton donor molecules, XH, induced by the presence of DTBN radical which serves as a proton acceptor. It was found that the X–H···DTBN hydrogen bond produces quite sensitively upfield contact shift for the X–H proton. MO (molecular orbital) theoretical studies have also been performed for the H-bonding in the protic molecule–nitroxide radical bimolecular system.[3] MO calculations (UHF-INDO method) have shown that in the H-bonding between XH and DTBN, the observed *upfield* contact shift (characteristic of negative spin density) of the XH proton is reproduced only for the π model in which the XH proton is directly over the oxygen or nitrogen pπ orbital (the π-hydrogen bonding), while the σ model fails to explain the observed DTBN-induced ^{1}H and ^{13}C contact shifts (Figure 1).

In order to obtain more confirmative evidence for the π model responsible for DTBN-induced negative spin density on the XH proton and to get further insight into the π-hydrogen bond involving free radicals, we used here the stable hydrocarbon π radical, α,γ-bis-diphenylene-β-phenylallyl (BDPA) (Figure 2), as a proton acceptor (the π base) in the π-hydrogen bonding and followed the ^{1}H and ^{13}C contact shifts for various proton donor molecules, XH, induced by the presence of BDPA. This contact shift would serve as a sensitive probe for elucidating the chemical phenomena involved in the very weak interaction of the π-hydrogen bonding.[4]

Experimental Section

Materials. We tried to observe the ^{1}H shifts of various XH molecules caused by the addition of varying amounts of BDPA

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(1) Part IX in this series. Part VIII, see I. Morishima, *et al.*, *J. Amer. Chem. Soc.*, **94**, 6555 (1972).

(2) I. Morishima, K. Endo, and T. Yonezawa, *ibid.*, **93**, 2408 (1971); *Chem. Phys. Lett.*, **9**, 203 (1971); I. Morishima, T. Inubushi, K. Endo, T. Yonezawa, and K. Goto, *J. Amer. Chem. Soc.*, **94**, 4812 (1972); *Chem. Phys. Lett.*, **14**, 372 (1972); I. Morishima, T. Matsui, T. Yonezawa, and K. Goto, *J. Chem. Soc., Perkin, Trans. 2*, 633 (1972).

(3) I. Morishima, K. Endo, and T. Yonezawa, *Chem. Phys. Lett.*, **9**, 143 (1971); *J. Chem. Phys.*, **58**, 3146 (1973).

(4) The study of intermolecular hydrogen bonding involving a π base as the proton acceptor has been most extensively carried out by the ir method; see R. West, *J. Amer. Chem. Soc.*, **81**, 1614 (1959); Z. Yoshida and E. Osawa, *ibid.*, **87**, 1467 (1965); **88**, 4019 (1966).

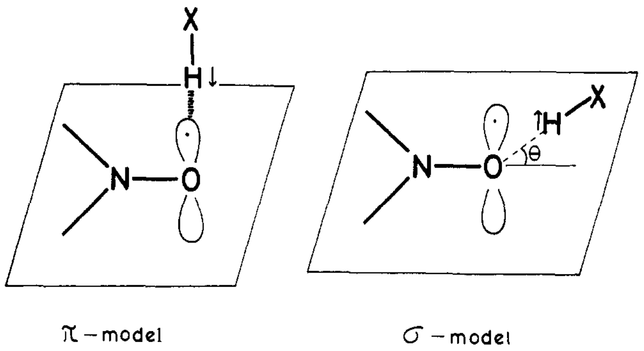

Figure 1. The π and σ models for the hydrogen bond between nitroxide radical and X-H proton donor. (For details of these models, see ref 3.)

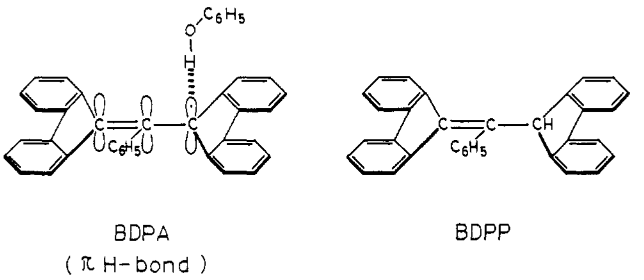

Figure 2. The π-hydrogen bond involved in the BDPA radical.

radical and α,γ-bisdiphenylene-β-phenylpropylene (BDPP), the corresponding diamagnetic hydrocarbon molecule (see Figure 2), and to figure out BDPA-induced "contact shift" contribution by estimating the contribution of diamagnetic ring current effect to the observed BDPA-induced shift.

BDPA radical and BDPP were prepared by referring to Kuhn and Neugebauer.[5] BDPA recrystallized from the benzene solution contained one molecule of benzene which could be removed by heating at 90° *in vacuo* for 8 hr. *Anal.* Calcd for $C_{33}H_{21}$ (BDPA): C, 94.9; H, 5.1. Found: C, 94.8; H, 5.2. All other chemicals used in this study were commercially available.

Pmr Measurement. Pmr spectra were obtained at room temperature with a Varian HR-220 spectrometer (220 MHz) to detect sensitively BDPA- and BDPP-induced shifts of the XH proton using cyclohexane as an internal reference. Samples were made 1 mol % in CCl_4 solution in the absence or presence of the given amount of BDPA and BDPP, while samples used for the determination of the equilibrium constant were made in CCl_4 solution with various concentrations of XH molecules.

^{13}C Nmr Measurement. ^{13}C nmr spectra were also obtained at room temperature on a JEOLCO PFT-100 spectrometer in a Fourier transform mode using cyclohexane as an internal standard. The spectra were measured in 10 mol % in CCl_4 containing the given amount of BDPA radical.

Results and Discussion

^1H Contact Shifts. We observed the ^1H nmr chemical shifts of various XH molecules caused by the addition of varying amounts of BDPA radical and BDPP, the corresponding closed-shell hydrocarbon molecule. We examined the BDPP-induced shift to estimate the contribution of diamagnetic ring current induced shift to the observed BDPA-induced shift and to figure out BDPA-induced contact shift contribution. The XH protons of phenol, alcohol, chloroacetic acids, and chloroform in CCl_4 solution experienced substantial upfield shift and broadening by the addition of BDPA, while the protons other than the OH and acidic CH protons were hardly affected. This upfield shift was proportional to the concentration of the added BDPA radical. Figure 3 shows the BDPA- and BDPP-induced upfield shifts for the XH proton of various proton donors.[6] It is revealed that the BDPA-induced upfield shift is more pronounced than the BDPP-induced shift. These upfield shifts appear to reflect the trend of proton donating ability of the XH groups.[7] This preferential upfield shift for the BDPA system could be attributable to the presence of the Fermi contact shift for the XH proton induced by the π-hydrogen bonding with BDPA radical.

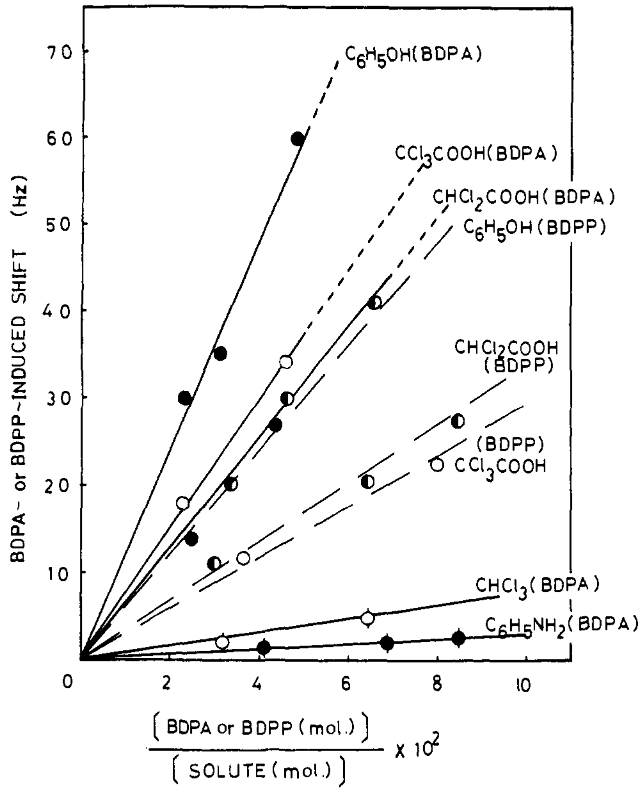

Figure 3. BDPA- and BDPP-induced ^1H shifts at 220 MHz varying with the concentration of BDPA and BDPP for various proton donor molecules in CCl_4 solution (1 mol %).

The frequency shifts of ν_{OH} of phenol in the ir spectra were obtained[8] to afford the evidence for hydrogen bond formation involving BDPA and BDPP, as has been always the case for hydrogen bonding of phenol to aromatics and olefins.[4]

^{13}C Contact Shifts. In order to study further the intrinsic nature of this BDPA-induced shift, we observed the BDPA-induced ^{13}C shifts for $^{13}CHCl_3$ and $C_6H_5C{\equiv}{}^{13}CH$ in CCl_4 solution (10 mol %). The downfield ^{13}C shifts were observed for these CH carbons; -0.12 and -0.19 ppm downfield ^{13}C shifts were obtained with the addition of BDPA = 1.3×10^{-5} mol.

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(5) R. Kuhn and F. A. Neugebauer, *Monatsh. Chem.*, **95**, 3 (1964).

(6) BDPA and BDPP were slightly soluble in CCl_4 and the concentration of aromatic molecules was quite limited. The dotted line shown in Figure 3 indicates the region beyond the solubility limitation. In Figure 3 BDPP-induced shifts for $CHCl_3$ and aniline were negligibly small.

(7) The ethanol hydroxyl proton experienced BDPA- and BDPP-induced upfield shifts of 50 and 20 Hz, respectively, at the concentration of [BDPA(BDPP)]/[solute] = 0.06, less than those for phenol but comparable with those for chloroacetic acid. Dimer association of chloroacetic acids may be responsible for limited magnitude of upfield shift induced by the π-hydrogen bonding.

(8) The hydrogen bonded frequency shift $\Delta\nu_{OH}$ of the hydroxyl stretching vibration of phenol was 160 cm^{-1} at the concentration of 2.4×10^{-4} *M* phenol and 4.8×10^{-3} *M* BDPA in CCl_4.

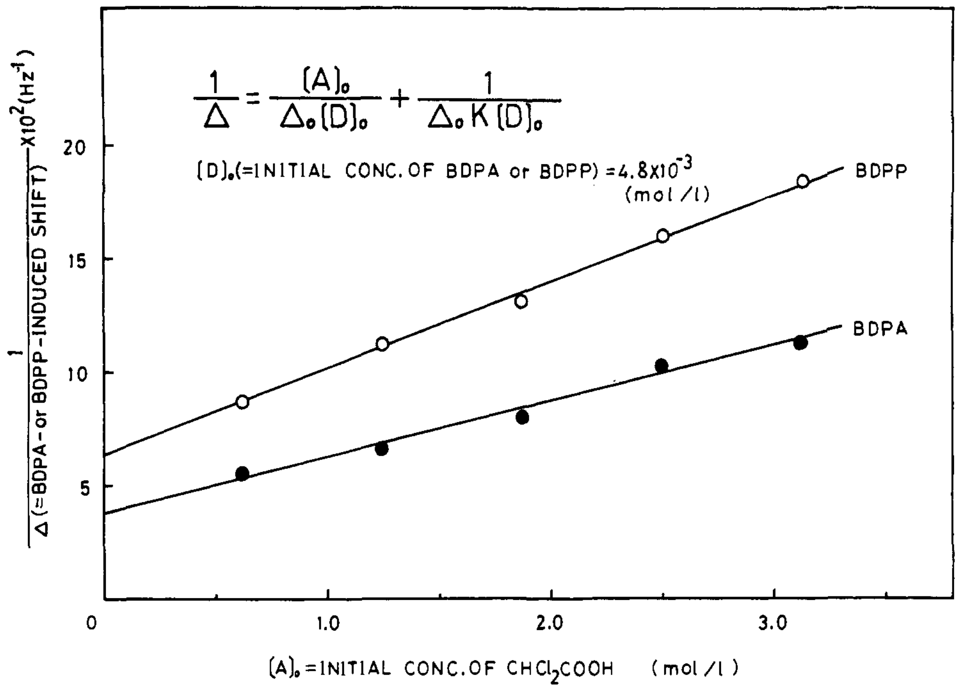
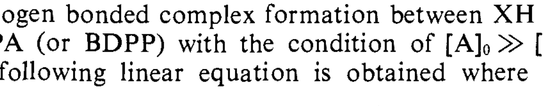


Figure 4. Plots of the inverse of the BDPA- and BDPP- induced ^1H shifts against the initial concentration of $CHCl_2COOH$ at room temperature.

The phenyl ring carbons in phenylacetylene were hardly affected by the addition of BDPA. The alternation of the BDPA-induced shifts for the proton and carbon in these carbon acids is quite similar to the DTBN-induced contact shifts,[2] implying that the upfield bias of the BDPA-induced proton shift and downfield ^{13}C shift for the C–H carbon result from the contact shift characteristic of negative and positive spin densities on the proton and carbon atoms, respectively, transmitted by the spin polarization mechanism from DBPA radical.[3]



$\underset{\uparrow}{Cl_3C}—\underset{\downarrow}{H}\cdots BDPA$ ↑ positive spin density

$C_6H_5C\equiv \underset{\uparrow}{C}—\underset{\downarrow}{H}\cdots BDPA$ ↓ negative spin density

Equilibrium Constants and Limiting Contact Shifts. To facilitate a quantitative analysis of this weak interaction between BDPA and XH molecule, we obtained the equilibrium constant (K) and the limiting shift (Δ_0) for XH–BDPA and XH–BDPP complex formation by the procedure presented previously.[3] For the 1:1 hydrogen bonded complex formation between XH and BDPA (or BDPP) with the condition of $[A]_0 \gg [D]_0$, the following linear equation is obtained where $[A]_0$

$$1/\Delta = 1/K[D]_0\Delta_0 + [A]_0/[D]_0\Delta_0$$

and $[D]_0$ are the initial concentration of XH molecule and BDPA (or BDPP), respectively, Δ_0 is the limiting ^1H contact shift for the pure complex relative to the ^1H shift for the free XH, and Δ is the observed ^1H shift of XH in the presence of BDPA (or BDPP) relative to the free XH. However, as shown by Person[9] and Deranleau,[10] simultaneous evaluation of K and Δ_0 values for weak complex formation is difficult and these values obtained from the above straight-line fitting procedure should contain substantial uncertainty. The separation of K and Δ_0 requires special conditions that K is large and BDPA (or BDPP) is completely complexed. However, this is rarely possible. In this respect, we carried out only order estimation of K and Δ_0 values by the above standard procedure. Figure 4 shows the linear plots of $1/\Delta$ *vs.* the initial concentration of $CHCl_2COOH$, as an example, at room temperature (the probe temperature was 292°K). The results are K = 0.64 (l./mol) and Δ_0 = 39 ppm for the BDPA–$CHCl_2COOH$ system and K = 0.60, Δ_0 = 25 for the BDPP–$CHCl_2COOH$ system. The very close values of these two equilibrium constants imply that the difference in the observed upfield shifts between the BDPA and BDPP systems (see Figure 3) is due to the contribution of the contact shift for the BDPA system. The difference in the limiting shifts between two systems is expected to be absolutely attributable to this cause.

A Theoretical Study on the XH Molecules–Allyl Radical (the Model of BDPA) Bimolecular System by Molecular Orbital Calculations. In order to substantiate theoretically the BDPA-induced upfield ^1H and ^{13}C contact shifts for XH molecules and to elucidate the intrinsic nature of the π radical–XH hydrogen bond, UHF-INDO MO calculations were performed for the allyl radical (the model of BDPA)–XH (H_2O, acetylene, fluoroform) bimolecular systems. We assumed that the carbon atoms in allyl radicals were coplanar. Bond lengths for allyl radicals used in the calculations are C–C, 1.4 and C–H, 1.08 Å, and the C–C–C and C–H bond angles are assumed to be 120°. The corresponding values for the XH molecules (H_2O, acetylene, fluoroform) were obtained from Sutton's compilation.[11] The geometrical structures for the allyl radical–XH molecule systems adopted here are π model, where the X–H bond is perpendicularily over the terminal carbon

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(9) W. B. Person, *J. Amer. Chem. Soc.*, **87**, 167 (1965).

(10) D. A. Deranleau, *ibid.*, **91**, 4044 (7969).

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

Morishima, et al. / Hydrogen Bonding in Stable Hydrocarbon π Radicals

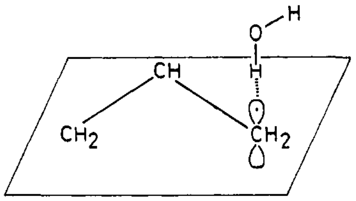

Figure 5. The π-hydrogen bond model for the allyl radical-H_2O bimolecular system.

pπ orbital of the allyl radical (Figure 5). The spin densities calculated for this π-hydrogen bond model were obtained for the structure with energy optimization. The results are summarized in Table I.

Table I. Results of INDO Calculations for Proton Donor–Allyl Radical Bimolecular Systems (π model)

Proton donor (XH)	$R_{XH\cdots C}$[a] (Å)	Calcd spin densities[b] and stabilization energies[c]	
H_2O	1.6	ρ_H	−0.056
		ΔE, kcal/mol	13.96
HC≡CH[d]	1.7	ρ_{H_1}	−0.025
		ρ_{C_2}	0.026
		ΔE, kcal/mol	6.28
CHF_3	1.7	ρ_H	−0.035
		ρ_C	0.040
		ΔE, kcal/mol	7.62

[a] Obtained by energy optimization. [b] Spin densities on the hydrogen 1s and carbon 2s atomic orbitals. [c] Energy differences between two conformations for finite and infinite separations of proton donor and allyl radical. [d] Numbering of the atoms: allyl radical···H_1–H_2≡C–H.

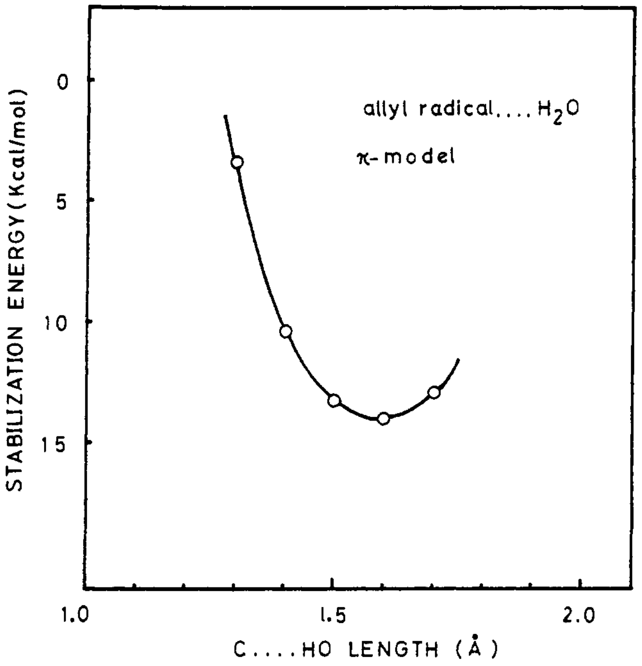

Figure 6. INDO stabilization energy curve plotted against the C···HO distance for the allyl radical-H_2O bimolecular system (π model).

Figure 6 shows the stabilization energies varying with XH···C distance for H_2O as an example. The results of calculated spin densities are in qualitative agreement with experimental trends.[12] The alternation in contact shifts (the contact shift characteristic of negative and positive spin densities on the proton and carbon atoms) is also reproduced for the π model both for the allyl radical–HC≡CH and –CHF_3 bimolecular systems and is reasonably due to spin transmission by a polarization mechanism as is the case for the DTBN–XH hydrogen bonding system.[3]

From the present work we can conclude that contact shifts serve as a sensitive probe for the very weak interaction of π-hydrogen bonding involving hydrocarbon π radicals such as BDPA.

Acknowledgment. The authors thank Mr. K. Uchino for assistance in the synthesis of the BDPA radical, and Dr. T. Funabiki for his assistance in purification of BDPA radical.

(12) Concerning the allyl radical–H_2O system, the π-hydrogen bonding at the central carbon of the allyl radical produced positive spin density, ρ_H = 0.020, with substantial stabilization. The calculated spin density for the terminal π model for the allyl radical–H_2O system amounts to 2136 ppm, greater than the observed limiting contact shift by a factor of 10^2. However, we should keep in mind that the odd electron at the allyl terminal carbon is delocalized onto the aromatic part in the BDPA radical to a large extent and results in diminution of induced spin density on the OH proton. It is also to be noted that the BDPA–XH π-hydrogen bond complex is very labile and XH would not be fixed at the allyl terminal carbon of the BDPA radical. These would be responsible for the very small value of the limiting contact shift for BDPA–XH π-hydrogen bond formation.