

CIDNP arises from a smaller triplet-born radical pair component which is undetected in scavenging and quenching attempts; (b) the reaction is mainly concerted,¹¹ with a smaller singlet radical pair component giving rise to free radicals in which CIDNP is produced during diffusive encounters.

Attempts to distinguish a and b by adding known triplet quenchers such as *cis*-piperylene have so far proven ambiguous because such additives also either absorb light or act as free-radical scavengers. It is observed, however, that photolysis of I produces enhancement of the aldehyde proton which is twice as large (and lasts $\sim 15\%$ longer) in benzene as in pentane. This suggests that benzene acts as a triplet sensitizer which increases the production of triplet-born radical pairs.¹² Further, the enhancement of the aldehyde proton of I is larger during photolysis in acetone despite the fact that the rate of disappearance of I is half that in pentane.

2-Methyl-2-(1-naphthyl)propanal and 1-naphthylacetaldehyde photolyze in benzene at a rate comparable to I and II but give no CIDNP in either the decarbonylation products or the aldehydes themselves. Although both the carbonyl and naphthalene groups in these compounds absorb light (to give excited singlet states), the naphthalene triplet state is of sufficiently low energy to accept energy from the carbonyl triplet. Consequently the lowest, preferentially populated triplet state probably is predominantly naphthalene-like and therefore unlikely to react to form triplet radical pairs by cleavage of the C-C bond of the carbonyl group.

Finally, if mechanism b were responsible for the observations, the cage effect for geminate recombination of cumyl and formyl radicals would have to be lower than that for recombination of the free radicals diffusively encountering each other. In the present case this might be expected if the fragments formed in the initial photodissociation possessed excess kinetic energy. However, this would be at least partially compensated by the fact that a significant portion of the cumyl radicals escaping from a geminate cage recombine with each other and therefore decrease the number of cumyl-formyl diffusive encounters.

For the above reasons we presently consider mechanism a to be the most likely explanation for all of the experimental results.

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(11) A singlet radical pair which reacts with a cage effect of unity would not be distinguished from a concerted reaction by our techniques.

(12) Low concentrations of *cis*-piperylene substantially quench both toluene formation and the disappearance of II when the photolysis is conducted in benzene solution.

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Interactions between Closed- and Open-Shell Molecules.¹ ¹³C Contact Shift Studies on the Interaction between Aromatic Hydrocarbons and Nitroxide Radical

Sir:

Recently we have been studying the nmr contact shifts for diamagnetic solvent molecules induced by weak interactions with stable organic free radicals.¹⁻⁴ Quite-sensitive induced contact shifts were proved to be a potential probe for studies of the hydrogen bond² and charge-transfer interactions^{1,3} involving free radicals. In the X-H...DTBN (di-*tert*-butyl nitroxide radical) hydrogen bond, the proton and X (carbon, for example) nuclei of the proton donor molecules sense negative and positive electron spin densities, respectively, which have been interpreted in terms of a spin polarization mechanism.^{2,4} On the other hand, in the charge-transfer interaction between halogenated molecules and DTBN, positive spin densities are induced on both the halogen atom and on the carbon atom which is bonded directly to the halogen atom through a spin delocalization mechanism.^{1,3} These studies were associated with saturated molecules. In the present study we are concerned with ¹³C contact shift studies of weak interactions between aromatic hydrocarbons and nitroxide radical where a π -type interaction as well as σ -type one is expected to be involved.⁵ The evidence for ground-state complexing between DTBN and aromatic hydrocarbons could be also of value in understanding recent studies on the DTBN-induced quenching of the photoexcited state of aromatic hydrocarbons.⁶

Addition of DTBN radical to benzene in cyclohexane solution caused substantial downfield shift of the ring carbon resonances.⁷ For naphthalene, however, the junction carbon (C₉) exhibited an upfield contact shift while the ternary carbons (C₁ and C₂) experienced downfield contact shifts.⁸ In substituted benzenes, such as nitro- and fluorobenzene, the ring carbons showed sizable downfield DTBN-induced contact shifts while the substituted one (junction carbon) exhibited an upfield contact shift. From these results it is likely that the aromatic C-H proton can serve as a weak proton donor

(1) Part VIII in this series. Part VII: I. Morishima, T. Inubushi, K. Endo, T. Yonezawa, and K. Goto, *J. Amer. Chem. Soc.*, **94**, 4812 (1972).

(2) I. Morishima, K. Endo, and T. Yonezawa, *ibid.*, **93**, 2048 (1971); *Chem. Phys. Lett.*, **9**, 143, 203 (1971); *J. Chem. Phys.*, in press.

(3) I. Morishima, T. Inubushi, K. Endo, and T. Yonezawa, *Chem. Phys. Lett.*, **14** 372 (1972).

(4) I. Morishima, T. Matsui, T. Yonezawa, and K. Goto, *J. Chem. Soc., Perkin Trans. II*, 633 (1972).

(5) Here the π -stacking interaction between aromatic hydrocarbon and nitroxide radical is referred to as a π -type interaction and the C-H...DTBN hydrogen bond as a σ -type interaction.

(6) R. A. Caldwell and R. E. Schwerzel, *J. Amer. Chem. Soc.*, **94**, 1035 (1972), and references cited therein.

(7) Proton-decoupled ¹³C nmr spectra were obtained at 15.1 MHz on a JEOL-C-60HL spectrometer. The spectra were measured in 15 mol % solutions in cyclohexane or CS₂ containing varying amounts of DTBN radical ranging from 0 to 7.0×10^{-4} M. The DTBN-induced ¹³C contact shifts, the shift from the diamagnetic solution to the paramagnetic one, were proportional to the concentration of DTBN. Cyclohexane was most insensitive to DTBN and was used as an internal reference for ¹³C chemical shift measurements, the precision being ± 0.05 ppm. Addition of DTBN (4.0×10^{-4} M) to a C₆H₁₂ solution (15 mol %) of benzene caused a -0.45 ppm downfield shift for the benzene carbons but had no effect on the ¹³C shift of C₆H₁₂ within an experimental error.

(8) We used CS₂ as the solvent for polycyclic aromatic hydrocarbons. Actual contact shifts were -0.25 , -0.26 , and $+0.20$ ppm for C₁, C₂, and C₉, respectively, in the presence of 3.0×10^{-4} M DTBN.

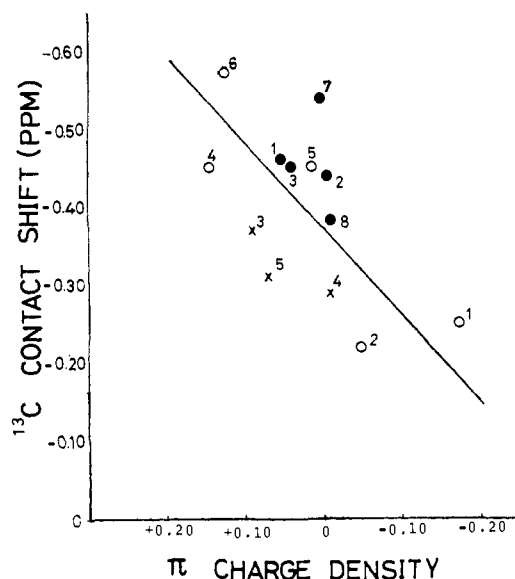
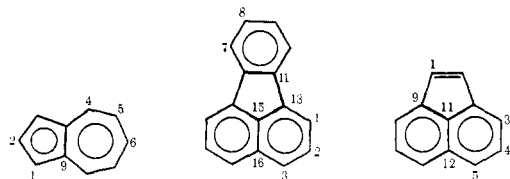


Figure 1. A correlation between DTBN-induced ^{13}C contact shifts and π -charge densities for nonalternant hydrocarbons: azulene (○), fluoranthene (●), and acenaphthylene (×). ^{13}C contact shifts are for 15 mol % CS_2 solutions containing $4.0 \times 10^{-4} M$ DTBN radical. π -Charge densities were taken from simple Hückel calculations. The numbering of the carbon is as follows:



in the $\text{C}-\text{H} \cdots \text{DTBN}$ hydrogen bond as is the case for the aliphatic $\text{C}-\text{H}$ group.⁴ One may, therefore, expect that DTBN-induced ^{13}C contact shifts are proportional to the proton donor ability of the $\text{C}-\text{H}$ group (or acidity of the $\text{C}-\text{H}$ bond) in aromatic hydrocarbons. We examined here this correlation for some nonalternant hydrocarbons. It has been shown⁹ that the electron density on the $\text{C}-\text{H}$ proton is proportional to the π -electron density on the $\text{C}-\text{H}$ carbon in aromatic hydrocarbons. Consequently, a linear relation between the DTBN-induced ^{13}C contact shift and the π -electron density on the periphery carbon might be expected. Figure 1 shows that this relation is roughly realized. For alternant hydrocarbons, however, ^{13}C contact shifts for various $\text{C}-\text{H}$ carbons in a molecule were not so different from each other when compared to contact shifts for $\text{C}-\text{H}$ carbons on nonalternant hydrocarbons. These findings show that the $\text{C}-\text{H} \cdots \text{DTBN}$ weak hydrogen bond interaction is important at the periphery $\text{C}-\text{H}$ group of the aromatic hydrocarbon in the presence of DTBN radical.

The upfield contact shifts for the substituted ring carbon or the junction carbon are possibly due to the negative spin density on the carbon transmitted from the adjacent $\text{C}-\text{H}$ group hydrogen bonded with DTBN. A polarization mechanism allows transmission of positive and negative spin densities alternatively along the bond. This σ -type interaction could induce a downfield contact shift for C_{15} in pyrene and for C_{11} in acenaphthylene. However, observed substantial upfield contact

(9) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, **82**, 5846 (1960).

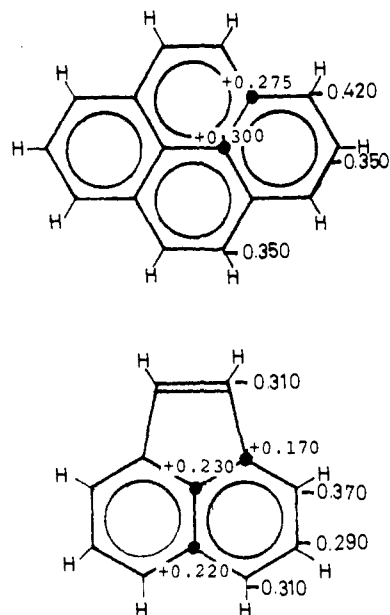
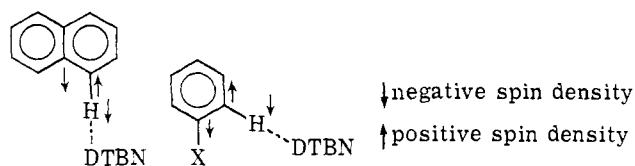
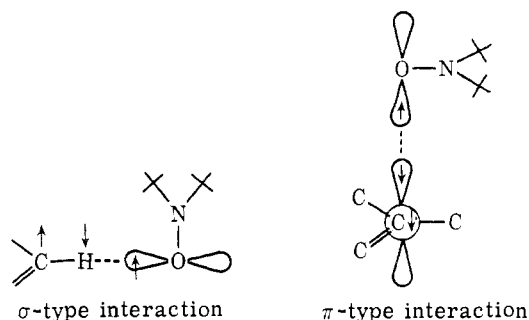


Figure 2. ^{13}C contact shifts (ppm) for pyrene and acenaphthylene in 15 mol % CS_2 solution induced by the addition of $4.0 \times 10^{-4} M$ DTBN radical. Contact shifts are linearly proportional to the concentration of DTBN (footnote 7).



shifts (see Figure 2) for these carbons rule out the above possibility and lead us to expect direct π -type interactions with DTBN at C_{15} or C_{11} , respectively. The fact that the upfield contact shift for C_{15} is more prominent than that for C_{11} in pyrene also seems to support the π -type interaction because spin density transmitted by a spin polarization mechanism in the σ -type interaction attenuates rapidly. This upfield contact shift for cross-linked carbons was also encountered for C_{11} in acenaphthylene, for C_{15} in fluoranthene, and for C_{15} in pyrene.¹⁰ We conclude that a direct π -type inter-



action appears to be responsible for the substantial upfield contact shift for the cross-linked carbons in polycyclic aromatic hydrocarbons.

In order to substantiate theoretically ^{13}C contact shifts associated with the π - and σ -type interactions between aromatic hydrocarbons and DTBN radical, we

(10) The observed contact shifts were $+0.26 \sim +0.30$ ppm for these cross-linked carbons (for $[\text{DTBN}] = 4.0 \times 10^{-4} M$), slightly greater than those for the adjacent junction carbons in each molecule.

have performed unrestricted Hartree-Fock (INDO method) MO calculations¹¹ for the ethylene-DNMO (dimethyl nitroxide) bimolecular system with various geometries. Calculated spin densities on the carbon 2s AO for the σ - and π -type interactions were positive and negative, respectively, in agreement with the observed trend.¹²

The interaction with DTBN radical at the cross-linked carbon can be further characterized from a study of ¹³C spin-lattice relaxation time (T_1) for solutions involving the DTBN radical. We have therefore measured T_1 for ¹³C in pyrene on a JEOL PFT-100 spectrometer (at 25.1 MHz) in a Fourier transform mode using the 180°- τ -90° pulse method. T_1 's for pyrene in CS₂ solution (15 mol %) were 7.1 (C₁), 8.7 (C₂), 9.1 (C₄), 47.2 (C₁₁), and 60.3 (C₁₅) sec.¹³ T_1 's for C₁₅ and C₁₁, the cross-linked carbons, are most strikingly affected by the addition of DTBN radical (3.0×10^{-5} M)(27.2 (C₁₅), 25.5 sec (C₁₁)), while the T_1 's for the other C-H carbons changed only slightly.¹⁴ These results appear to be in accord with a direct π -type interaction between DTBN and the cross-linked carbons in pyrene.

From the present study we conclude that measurement of ¹³C contact shifts and relaxation times are promising for the elucidation of weak interactions involving free radicals.

Acknowledgment. The authors are thankful to K. Yoshikawa and K. Matsushita for help in the experiment of pulse and Fourier transform ¹³C nmr.

(11) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967); *J. Amer. Chem. Soc.*, **90**, 4201 (1968).

(12) MO theoretical calculations for the σ -type interaction have been well studied (see ref 2). The C-H bond perpendicular to the oxygen or nitrogen π orbital of DMNO radical senses negative and positive spin densities on the H 1s and C 2s AO's. The four-centered π -stacking interaction induced +0.015 and +0.010 spin densities on the 2s AO of the ethylene carbons close to the O and N atoms of DMNO, respectively, for an intermolecular distance of 2.0 Å.

(13) The experimental error is ± 1.0 sec.

(14) The study of ¹³C relaxation time in the paramagnetic solution is now under way.

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Evidence for a Guanosine-Calcium(II) Complex. A Specific Nucleoside-Metal Interaction

Sir:

There is a wealth of information published on nucleic acid-metal ion interactions. A closer examination, however, indicates that most interactions are due to metal-phosphate complexation.¹ Recently, some base-metal interactions have been reported with Ag⁺,^{2a} Co²⁺, Hg²⁺, and Zn²⁺.^{2b}

We would like to report evidence concerning the existence of a 1:1 Ca²⁺-guanosine complex, to our knowledge the first example of an alkaline earth metal-guanine base interaction.

(1) R. M. Izatt, J. J. Christensen, and J. H. Rytting, *Chem. Rev.*, **71**, 439 (1971).

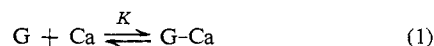
(2) (a) K. Gillen, R. Jensen, and N. Davidson, *J. Amer. Chem. Soc.*, **86**, 2792 (1964); (b) L. S. Kan and N. C. Li, *ibid.*, **92**, 4823 (1970).

Comparison of the proton magnetic resonance spectrum (taken on a Varian A-60) of guanosine in DMSO-*d*₆ with similar solutions to which varying amounts of CaCl₂ have been added indicates a gradual downfield shift only in the N(1)-H and N(2)-H₂ resonances of guanosine (almost identical shifts for both resonances) with increasing CaCl₂ concentration. The C(8)-H resonance and the ribose resonances are all unaffected in their chemical shifts by the addition of CaCl₂ implying complexation to the pyrimidine ring. That the base portion of the nucleoside is affected by complexation is further proven by the fact that the *O*-2',3',5'-triacetylguanosine exhibits identical behavior as does 8-bromoguanosine. The latter result indicates that the nucleoside conformation is most likely not responsible for the complex.³

A similar study found *no effect* of CaCl₂ on all observable resonances in adenosine, cytidine, or inosine (observation of the N(1)-H resonance of inosine even in DMSO-*d*₆ is very difficult); thus the complex appears to be *highly specific* for *guanine bases*. MgCl₂ was also employed with all above molecules and showed *no such* behavior.

The equilibrium constant (37°) for the complex was determined by monitoring the N(2)-H resonance at constant guanosine concentration varying the CaCl₂ concentration as well as by varying the guanosine concentration at a given CaCl₂ concentration.

Following Kan and Li^{2b} for a 1:1 Ca²⁺-guanosine complex



$$K = \frac{[G-Ca]}{[G][Ca]} = \frac{x}{([G]_0 - x)([Ca]_0 - x)} \quad (2)$$

where x is the concentration of complex and $[G]_0$ and $[Ca]_0$ are initial concentrations of guanosine and calcium, respectively. The observed chemical shift for the N(2)-H resonance ν_0

$$\nu_0 = \frac{x}{[G]_0} \nu_{G-Ca} + \frac{([G]_0 - x)}{[G]_0} \nu_G \quad (3)$$

where ν_{G-Ca} and ν_G are the complexed and uncomplexed N(2)-H resonances (for the same guanosine concentration), respectively. Equation 3 can be rewritten in terms of $\Delta_0 = (\nu_0 - \nu_G)$ and $\Delta_t = (\nu_{G-Ca} - \nu_G)$ as

$$\Delta_0 = (x/[G]_0)\Delta_t \quad (4)$$

Combining with eq 1 and inverting finally leads to

$$\frac{[Ca]_0}{\Delta_0} = \frac{1}{K\Delta_t} + \frac{1}{\Delta_t}([Ca]_0 + [G]_0 - x) \quad (5)$$

Plots of $[Ca]_0/\Delta_0$ vs. $([Ca]_0 - x)$ or $([G]_0 - x)$ lead to Figure 1 where x is varied in an iterated manner to give the best straight line. For a Δ_t of 46 ± 2 Hz (60 MHz) slope one obtains a $K = 17 \pm 1$ l./mol as the mean of the two results. Data used for Figure 1 are given in Table I.

Some other pertinent observations defining properties of the complex are as follows. (1) The complex exhibits great stability at elevated temperatures.

(3) D. W. Miles, L. B. Townsend, M. J. Robins, R. K. Robins, W. H. Inkeep, and H. Eyring, *ibid.*, **93**, 1600 (1971).