Studies on the Nuclear Magnetic Resonance Contact Shifts induced by Interaction with Free Radicals. Part IV.[1] Utility of ^{13}C Contact Shifts for the Study of Weak Hydrocarbon–Radical Interaction

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^{13}C N.m.r. contacts shifts induced by the addition of the di-t-butyl nitroxide radical have been observed for various aprotic molecules and are shown to be useful as a sensitive probe for detecting the weakly acidic or the active site with respect to the free radical in hydrocarbons and for the study of weak solvent–radical interactions.

We have previously reported the ^{1}H and ^{13}C contact shifts for protic molecules induced by hydrogen bonding with nitroxide radicals.[2] Hydrogen bonding between protic molecules (X–H) and di-t-butyl nitroxide (DTBN) induces an upfield contact shift (*i.e.* negative spin density) of the X–H proton (X = O, N, or C) and a downfield contact shift (positive spin density) of the C–H carbon atom (X = C). These contact shifts were in agreement with the predictions of INDO–MO calculations;[1,3] a spin-polarization mechanism plays an important role in electron spin transfer through the hydrogen bond.[1]

We now report substantial ^{13}C contact shifts of aprotic molecules in the presence of DTBN. Proton shifts of these molecules, however, were hardly affected. The ^{13}C n.m.r. shift was more sensitive to the interaction with DTBN than the proton shift. We show that DTBN-induced ^{13}C contact shifts can be used as a sensitive probe for detecting the weakly acidic or the active site with respect to the radical in hydrocarbons or aprotic molecules and for studying weak solvent–solute interactions. DTBN-Induced ^{13}C shifts are given in Figures 1 and 2 for various molecules.

Addition of DTBN to acetonitrile shifted the methyl ^{13}C resonance to lower field and the nitrile carbon atom resonance to slightly higher field by an amount proportional to the concentration of DTBN (Figures 1 and 2) while the proton shift was almost unchanged. The resonances of the methyl and carbonyl carbon atoms of acetone and acetic acid were shifted downfield and upfield, respectively, by the addition of DTBN. For ethylbenzene, the alkyl carbon atom signals were shifted downfield while those of the phenyl carbon atoms were almost unaffected or slightly shifted downfield. The signal of the methyl carbon atom of nitromethane was shifted markedly downfield by the addition of DTBN. Signals of methyl and methylene carbon atoms α to a carbonyl or an unsaturated group such as cyano or phenyl were perturbed to lower field more than those of other carbon atoms. This is evident from the fact that in cyclohexene the signal of the methylene carbon atom adjacent to the double bond undergoes a larger downfield ^{13}C contact shift than the others. However, the methyl carbon atom contact shift of toluene was larger than that of the methylene carbon atom of diphenylmethane. This is probably due to steric inhibition of the approach of DTBN to the methylene group of diphenylmethane.

The carbon atom of methanol also exhibited a downfield contact shift, indicating that DTBN partially interacts with the methyl group, which functions as a weak proton donor. If only the hydroxy-group interacts with DTBN, an upfield contact shift (*i.e.* negative spin density) would be expected for the carbon atom because the electron spin redistributes itself through the bonds by a spin-polarization mechanism which induces positive and negative spin density alternately

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[1] Part III, I. Morishima, K. Endo, and T. Yonezawa, *Chem. Phys. Letters*, 1971, **9**, 143; (*b*) *J. Chem. Phys.*, in the press.

[2] I. Morishima, K. Endo, and T. Yonezawa, *J. Amer. Chem. Soc.*, 1971, **93**, 2048.

[3] I. Morishima, K. Endo, and T. Yonezawa, *Chem. Phys. Letters*, 1971, **9**, 203.

along σ bonds.[2] In fact, the carbon atom at the 1-position of phenol, which interacts with DTBN predominantly at the hydroxy-group, showed an upfield contact shift. The upfield and downfield contact shifts for the methyl and carbonyl carbon atoms of acetic acid are possibly due to interaction with DTBN at the methyl and hydroxy-groups. For acetonitrile and acetone, the alternating ^{13}C contact shifts may be attributed to spin redistribution by spin polarization which originates from the interactions of the methyl protons and the radical. For isopropyl alcohol, the methine carbon atom shows an upfield shift, contrary to the methyl and methylene carbon atoms in methanol and ethanol, respectively. However, downfield contact shifts were observed for both methyl and methylene carbon atoms in ethanol and ethylbenzene. These observations imply that in isopropyl alcohol the interaction with DTBN at the hydroxy or methyl protons gives rise to negative spin density by spin polarization acting on the methine group and that interaction at the methine group is hindered owing to the steric effect of the two adjacent methyl groups. Similar observations were also made for cumene (Figure 2).

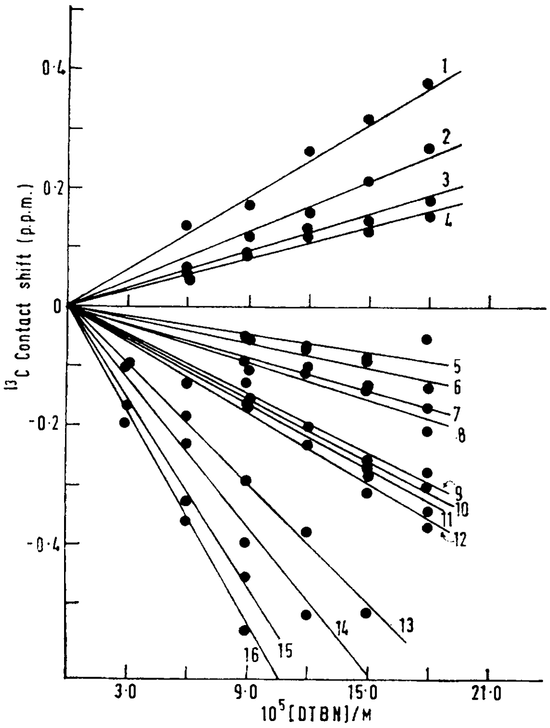

FIGURE 1 ^{13}C Contact shifts vs. [DTBN] for 1, $CH_3{}^{13}CO_2H$; 2, $(CH_3)_2{}^{13}CO$; 3, $CH_3{}^{13}CN$; 4, $(CH_3)_2{}^{13}CH\cdot OH$; 5, $^{13}CH_3\cdot CH_2\cdot OH$ and $CH_3\cdot{}^{13}CH_2\cdot OH$; 6, $(^{13}CH_3)_2CH\cdot OH$; 7, $(CH_3\cdot{}^{13}CH_2)_2O$; 8, $^{13}CH_3\cdot OH$; 9, $(^{13}CH_3\cdot CH_2)_2O$; 10, $^{13}CH_3\cdot CO_2H$; 11, $C_6H_5\cdot{}^{13}CHO$; 12, $(^{13}CH_3)_2CO$; 13, $CH_3\cdot{}^{13}CHO$; 14, $^{13}CH_3\cdot CHO$; 15, $^{13}CH_3\cdot CN$; and 16, $^{13}CH_3\cdot NO_2$

For acetaldehyde, both the methyl and carbonyl carbon atoms show downfield ^{13}C contact shifts (Figure 1), indicating that the methyl and formyl protons interact directly with DTBN. A downfield ^{13}C contact shift of the formyl group was also found for benzaldehyde. This result corresponds to the occurrence of hydrogen abstraction from the formyl group. In dimethylformamide, the formyl carbon atom exhibited a downfield contact shift. It is interesting that the *trans*- (with respect to the C=O group) methyl carbon atom contact shift is larger than the *cis*-one, implying that the *trans*-methyl group has a larger interaction with DTBN than the *cis*. It is known that the reaction between dimethylformamide and the hydroxyl radical produces three radical species resulting from abstraction of a hydrogen atom from a methyl or a formyl group.[4]

The ring carbon atoms of benzene were shifted to lower field by the addition of DTBN. This may be also due to a C–H · · · DTBN interaction in which the aromatic proton acts as a weak proton donor. For toluene and ethylbenzene, all the ring carbon atom resonances showed downfield ^{13}C contact shifts except the carbon atom at the 1-position which exhibited an upfield contact shift, as for phenol. The negative spin density at the 1-position may be induced by spin polarization from the methyl (for toluene), methylene (for ethylbenzene), and hydroxy- (for phenol) groups interacting with DTBN. It is not likely that the benzene carbon atoms act as a π-electron acceptor, because π donor–acceptor interactions would induce alternative upfield and downfield ^{13}C contact shifts of the ring carbon atoms. All the ring ^{13}C contact shifts are downfield and comparable in magnitude, implying that the aromatic protons interact with DTBN in the same manner as $CHCl_3$ · · · DTBN hydrogen-bond interactions.[2]

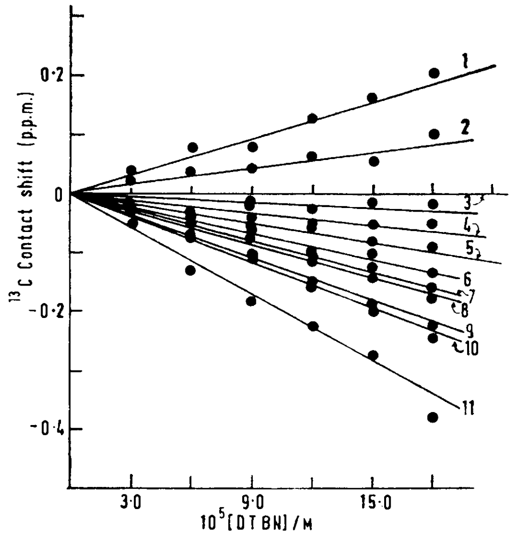

FIGURE 2 ^{13}C Contact shifts vs. [DTBN] for 1, [1-^{13}C]toluene; 2, $(CH_3)_2{}^{13}CH\cdot C_6H_5$; 3, [1-^{13}C]cyclohexene; 4, [4-^{13}C]cyclohexene; 5, [3-^{13}C]cyclohexene; 6, $(C_6H_5)_2{}^{13}CH_2$; 7, $CH_3\cdot{}^{13}CH_2\cdot C_6H_5$; 8, [$^{13}C_1$]benzene; 9, $(^{13}CH_3)_2CH\cdot C_6H_5$; 10, $^{13}CH_3\cdot CH_2\cdot C_6H_5$; and 11, $C_6H_5\cdot{}^{13}CH_3$

The downfield ^{13}C contact shifts of carbon atoms

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[4] T. Yonezawa, I. Noda, and T. Kawamura, *Bull. Chem. Soc. Japan*, 1969, **42**, 650.

may be correlated with the acidity of the corresponding protons[5] or with the relative ease of hydrogen abstraction, although there are a few exceptions for molecules with an isopropyl group which prevents DTBN from interacting with the methine protons. The C–H carbon atoms in $C_6H_5{\cdot}C{\equiv}CH$, $CHCl_3$, and CH_2Cl_2, which are strong carbon acids, exhibit substantial ^{13}C contact shifts in the order $CHCl_3 > CH_2Cl_2 > C_6H_5{\cdot}C{\equiv}CH$.[2] Methyl, methylene, and phenyl systems, which are much weaker carbon acids, show correspondingly much smaller ^{13}C contact shifts. The methyl or methylene protons adjacent to C=C, C_6H_5, C≡C, C≡N, and C=O groups are more acidic or more prone to hydrogen abstraction and exhibit greater downfield ^{13}C contact shifts on addition of DTBN. The large downfield ^{13}C contact shift for nitromethane, a strong carbon acid, corresponds to the small pK_a value.[6] The result that benzene exhibits a larger DTBN-induced ^{13}C contact shift than cyclohexane is in qualitative agreement with its greater acidity (determined by tritium exchange[5]).

The downfield ^{13}C contact shift of an alkyl group interacting with DTBN is in agreement with the predictions of INDO calculations of the electron spin density of the carbon 2*s* orbital. Only a π model[1,2] in which the C–H bond approaches the oxygen or the nitrogen orbital perpendicularly to the N–O bond of DTBN produces positive spin density on the carbon 2*s* orbital, in agreement with the observed trend of the downfield ^{13}C contact shift.

The fact that an alkyl carbon atom exhibits a DTBN-induced ^{13}C contact shift which is related to its acidity means that this is a sensitive probe for the investigation of weak molecular interactions of hydrocarbons or aprotic molecules. In this sense, DTBN could be termed a *spin label reagent* for the study of weak molecular interactions. More quantitative studies on equilibrium constants and thermodynamic data for hydrocarbon–DTBN interactions are under way.

EXPERIMENTAL

Natural abundance proton noise-decoupled ^{13}C n.m.r. spectra for most compounds were obtained at room temperature with a JEOL C-60-HL spectrometer equipped with ^{13}C n.m.r. assembly (at 15·1 MHz).[2] The spectra were measured for neat liquids containing varying amounts of DTBN (0—$3{\cdot}0 \times 10^{-4}$ M). ^{13}C Chemical shifts were accurate to within 0·05 p.p.m. Proton spectra were recorded with a Varian HR-220 spectrometer at 220 MHz. The DTBN-induced ^{13}C shift for nitromethane follows the Curie law behaviour,[2] characteristic of the Fermi contact shift. Cyclohexane was most insensitive to DTBN and was used as an internal reference for ^{13}C chemical shift measurements. The DTBN-induced ^{13}C shift for cyclohexane was less than the shift of the vinyl carbon atoms of cyclohexene.

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[5] A. Streitwieser, jun., W. R. Young, and R. A. Caldwell, *J. Amer. Chem. Soc.*, 1969, **91**, 527.

[6] D. J. Cram, ' Fundamentals of Carbon Chemistry,' Academic Press, New York, 1965; E. M. Kosower, ' An Introduction to Physical Organic Chemistry,' Wiley, New York, 1968.