Stable Free Radicals as NMR Spin Probe for Studying Intermolecular Interactions. 12. ^{13}C Contact Shifts and Electron Spin Delocalization Induced by Charge Transfer Interaction between Halogenated Molecules and Stable Free Radicals[1]

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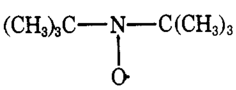
Abstract: ^{13}C and ^{1}H contact shifts induced by some stable organic free radicals were observed for various halogenated molecules. The sensitively induced downfield ^{13}C contact shifts for the carbon bonded directly to halogen (C–X) were generally of the order of X = I > Br > Cl > F. Linear relations between observed ^{13}C contact shifts and half-wave reduction potentials of various halogenated molecules were obtained as evidence for electron donor–acceptor character of this interaction. It is also shown that the π-stacking interaction between halobenzenes and the di-*p*-anisyl nitroxide radical may be responsible for anomalous upfield contact shifts for the substituted carbon (C_i) in halobenzenes. INDO MO calculations were also performed for the halomethane/nitroxide bimolecular system. The mechanism of intermolecular electron spin transmission associated with charge transfer and hydrogen bonding interactions involving nitroxide radicals was analyzed in terms of the MO theoretical method. It was revealed that intermolecular spin delocalization (SD), which corresponds to the charge transfer interaction, is predominant for the halogenated molecule–nitroxide bimolecular system, but spin polarization (SP) mechanism plays an essential role in the hydrogen bonding with nitroxide radical. The free radical induced halogen abstraction reaction was also briefly discussed in relation to this charge transfer interaction between halogenated molecules and stable free radicals.

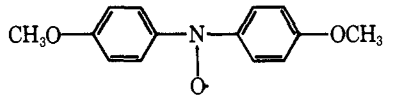
We are currently interested in the studies of the interaction between open-shell and closed-shell molecules and the mechanism of intermolecular electron spin transmission associated with hydrogen bond,[2-5] charge transfer[6] and π-stacking interactions[7] involving open-shell molecules such as free radical and excited state molecules. We have so far studied nuclear magnetic resonance (NMR) contact shifts for the diamagnetic solvent molecules induced by the hydrogen bond, charge transfer, and π-stacking interactions with nitroxide or other stable free radicals.[2-7] In the previous preliminary papers[6] we reported that ^{13}C NMR contact shifts induced by the addition of di-*tert*-butyl nitroxide radical (DTBN) were observed for several halogenated molecules. The downfield ^{13}C contact shifts for the carbon bonded directly to the halogen were more pronounced for iodide than for bromide and chloride. These shifts were interpreted in terms of the charge transfer interaction between DTBN radical and halogenated molecules with the aid of molecular orbital calculations of electron spin densities. However, it was concerned with a limited number of halogenated molecules and the charge transfer character of the DTBN–halomethane interaction was open to further studies. In order to elucidate the intrinsic nature of this interaction and to gain further insight into electron donor–acceptor interaction involving the free radical, more comprehensive studies on the interaction between free radical and various halogenated molecules are desirable.

In the present work we have measured ^{13}C and ^{1}H contact shifts for various halogenated molecules induced by the addition of di-*tert*-butyl nitroxide radical (DTBN), di-*p*-anisyl nitroxide radical (DANO), and galvinoxyl radical. The sign and magnitude of induced spin densities on the carbon and proton atoms of the halogenated molecules are concerned here in relation to the features of halide–free radical interaction. To substantiate our discussion, we have also performed MO calculations for halide–nitroxide bimolecular systems and examined the mechanism of intermolecular electron spin transfer through this charge transfer interaction. Here we are particularly concerned with the theoretical understanding of the mechanism of this spin transmission. In addition, we will comment briefly on the nature of the halogen abstraction reaction by free radical along with the theoretical understanding of the mechanism of electron spin transfer between free radical and halogenated molecules with the aid of molecular orbital calculations.

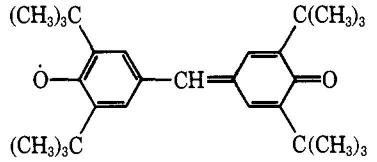


$(CH_3)_3C-\underset{\underset{O\cdot}{|}}{N}-C(CH_3)_3$

DTBN



DANO



galvinoxyl

Experimental Section

Materials. The DTBN radical was prepared by the method of Rassat[8] and was used soon after distillation (66 °C (17 mm)). DANO was prepared by the method of Meyer et al.[9] and recrystallized from ethyl acetate (mp 151–152 °C). Galvinoxyl was synthesized following the method of Kharasch and Joshi[10] or Bartlett and Funahashi.[11] It was purified by recrystallization under nitrogen from the mixed solvent of ether and alcohol (2:1) (mp 152–153 °C) and stored in a nitrogen atmosphere before use. 1-Bromo-2-iodoethane was synthesized from ethylene and BrI in glacial acetic acid after the method of Simpson.[12] A pure sample of 1-bromo-2-iodoethane was obtained by recrystallization in methanol. *tert*-Butyl iodide was prepared by the usual method.[13]

NMR Measurements. Completely proton-decoupled ^{13}C NMR spectra were obtained at 15.1 MHz on a Jeolco C-60HL spectrometer equipped with the SD-HC heterospin decoupler and IS-60 field/frequency synchronous sweep system of the proton irradiating frequency. Spectra were measured with the external locking mode. ^{13}C chemical shifts were determined on an expanded scale (18 ppm per full scale) with a precision of ±0.10 ppm. Samples were made in the liquid or other suitable solutions in the absence or presence of the given amount of stable free radical in an 8 mm sample tube. The ^{13}C

Table I. DTBN-Induced ^{13}C Contact Shifts for Halomethanes (ppm)[a]

	X =			
Halomethane	F	Cl	Br	I
CH_3X	*b*	*b*	*b*	−0.52
CH_2X_2	*b*	−0.65	−0.80	−1.04
CHX_3	*b*	−1.33	−1.50	*c*
$CXCl_3$	−0.23	−0.39	−0.90	*b*

[a] Measured at [DTBN] = 3.0 × 10^{-4} M. [b] Not measured. [c] A chemical reaction occurred with DTBN.

Table II. DTBN-Induced ^{13}C Contact Shifts for Alkyl Halides (ppm)[a]

	Cl		Br		I	
Alkyl halide	α	β	α	β	α	β
CH_3CH_2–X	*b*	*b*	−1.50	−0.64	−1.59	−0.58
$(CH_3)_2CH$–X	−0.52	−0.43	−0.62	−0.43	−0.69	−0.42
$(CH_3)_3C$–X	+0.18	−0.36	+0.13	−0.41	(+0.04)[c]	(−0.23)[c]

[a] Measured at [DTBN] = 3.0 × 10^{-4} M. [b] Not measured. [c] Slightly decomposed during NMR measurements, but the relative ratio of α to β is meaningfull.

Table III. DTBN-Induced ^{13}C Contact Shifts for Alkyl Dihalides (ppm)[a]

Alkyl Dihalide	C–Cl	C–Br	C–I
$ClCH_2$–CH_2Br	−1.12	−1.26	
$BrCH_2$–CH_2I[b]		−1.28	−1.58

[a] Measured at [DTBN] = 3.0 × 10^{-4} M. [b] Solution in cyclohexane.

chemical shift of cyclohexane was hardly affected[4] by the addition of DTBN or DANO within experimental error and was used as an internal reference for the ^{13}C chemical shift measurement of halogenated molecules in the presence of the stable free radical. The free radical induced ^{13}C contact shift is the shift variation from the diamagnetic one in the presence of a given amount of free radical. ^1H NMR spectra were measured on a Varian HR-220 spectrometer (220 MHz). The linear plots between contact shifts and the concentration of free radical were obtained for each sample.

Results

(A) **Alkyl Monohalides and Dihalides.** In the previous work,[6] we examined ^{13}C contact shifts for halomethanes induced by the addition of DTBN radical. Downfield ^{13}C contact shifts which are proportional to the concentration of added DTBN were observed for various halomethanes. Here we add newly the data of $CFCl_3$. The results are summarized and compared in Table I. Inspection of the table shows that DTBN-induced ^{13}C contact shifts are in the order of X = I > Br > Cl > F and this trend has been discussed in the previous paper. In Table II are summarized the results for ethyl, isopropyl and *t*-butyl halides. For ethyl and isopropyl halides, ^{13}C contact shifts for the carbon (C_α) bonded directly to the halogen atom follow the trend of I > Br > Cl which has been established for halomethanes. This downfield ^{13}C contact shift is decreased on going from ethyl to isopropyl halides and an unusual upfield ^{13}C contact shift was encountered for *tert*-butyl halides. Table III presents the data for alkyl dihalides, i.e., 1,2-dihaloethanes, which involve two different halogen atoms in a molecule. The preferential downfield contact shift was observed for C_2 in 1-bromo-2-iodoethane or in 1-chloro-2-bromoethane, as expected. The results for allyl and benzyl halides are given in Table IV.

Table V. DTBN-Induced ^{13}C Contact Shifts for Haloethylenes (ppm)[a]

Haloethylene	α	β
$C^\alpha Cl_2{=}C^\beta H_2$	−0.14	−0.74
$C^\alpha Cl_2{=}C^\beta HCl$	−0.44	−2.72
$C^\alpha Cl_2{=}C^\beta Cl_2$	−0.64	−0.64
C_6H_5—$C^\alpha H{=}C^\beta HBr$	−0.28	−1.33

[a] Measured at [DTBN] = 3.0 × 10^{-4} M.

(B) **Halogenated Ethylenes.** The ^{13}C contact shift data for some chlorinated ethylenes are given in Table V. The ^{13}C contact shift for C_1 increases as the number of substituted chlorine atoms is increased. However, quite a large downfield ^{13}C contact shift for C_2 in trichloroethylene as compared with 1,1-dichloroethylene could be due to the CH-DTBN hydrogen bond strengthened by the geminal chlorine atoms substituted at C_1. The features of ^{13}C contact shifts for β-bromostyrene were similar to those for trichloroethylene.

(C) **Halobenzenes.** We have observed DTBN-induced ^{13}C contact shifts for monohalobenzenes dissolved in 50 mol % benzene solution except for fluorobenzene; neat liquid was used to observe DTBN-induced ^{13}C contact shifts for fluorobenzene. Table VI summarizes the observed ^{13}C contact shifts for various monohalobenzenes. For comparison, we also list the relative values of ^{13}C contact shifts with respect to that for meta carbon (C_m), and these results are given in parentheses. For the substituted carbon (C_j), DTBN-induced downfield ^{13}C contact shifts were decreased in the order of I > Br > Cl > F, as expected. In fluoro- and chlorobenzenes upfield contact shifts were observed for the substituted carbons, although downfield contact shifts were experienced in bromo- and iodobenzenes.

We have also examined DANO-induced ^{13}C contact shifts with the aim to elucidate the origin of abnormal upfield shifts encountered for halobenzenes. These ^{13}C contact shifts were observed in chloroform solutions because of limited solubility of DANO radical in a benzene solvent. Table VI contains the observed contact shifts and their relative values with respect to those for C_m given in parentheses, which is to be compared with the results of DTBN-induced shifts. The downfield ^{13}C contact shifts for C_j induced by DANO decreased in the order of I > Br > Cl > F, as in the case for DTBN. However, upfield contact shifts were encountered for C_j of fluoro-, chloro-, and bromobenzenes. In addition, it should be noted that the decrease of DANO-induced ^{13}C contact shifts for C_j along the series of C_6H_5I, C_6H_5Br, C_6H_5Cl, and C_6H_5F are more rapid than the corresponding behavior for DTBN-induced shifts, and the DANO-induced downfield contact shifts of C_0 are smaller than DTBN-induced shifts.

(D) **Stable Free Radical Induced ^1H Contact Shifts.** We have also observed ^1H contact shifts induced by DTBN and galvinoxyl radicals, which are expected to provide additional insight into the intrinsic nature of the interaction between halogenated molecules and stable free radicals. The results of ^1H contact

Table IV. DTBN-Induced ^{13}C Contact Shifts for Allyl and Benzyl Halide (ppm)[a]

	Cl			Br		
Halide	α	β	γ	α	β	γ
$C^\gamma H_2{=}C^\beta H$—$C^\alpha H_2$—X	−1.08	−0.11	−0.42	−1.10	−0.12	−0.41
C_6H_5—$C^\alpha H_2$—X	−0.81	+0.13		−1.00	+0.12	

[a] Measured at [DTBN] = 3.0 × 10^{-4} M.

Table VI. DTBN-Induced ^{13}C Contact Shifts for Monohalobenzenes (C_6H_5–X) (ppm)[a]

X	Radical	C_j	C_o	C_m	C_p
F	DTBN[b]	+0.14 (−0.38)	−0.40 (+1.08)	−0.37 (+1.00)	−0.32 (+0.86)
	DANO[c]	+0.20 (−0.51)	−0.25 (+0.64)	−0.39 (+1.00)	−0.34 (+0.87)
Cl	DTBN[d]	+0.07 (−0.20)	−0.28 (+0.80)	−0.35 (+1.00)	−0.33 (+0.94)
	DANO[c]	+0.16 (−0.44)	−0.22 (+0.61)	−0.36 (+1.00)	−0.31 (+0.86)
Br	DTBN[d]	−0.09 (+0.25)	−0.29 (+0.81)	−0.36 (+1.00)	−0.31 (+0.86)
	DANO[c]	+0.01 (−0.03)	−0.21 (+0.55)	−0.38 (+1.00)	−0.31 (+0.82)
I	DTBN[d]	−0.61 (+1.97)	−0.22 (+0.71)	−0.31 (+1.00)	−0.28 (+0.90)
	DANO[c]	−0.63 (+1.70)	−0.18 (+0.49)	−0.37 (+1.00)	−0.28 (+0.26)

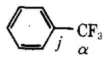
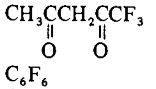
[a] Measured at [radical] = 3.0 × 10^{-4} M. The relative ratios to meta-carbon shift were given in parentheses. [b] Measured in neat liquid sample. [c] Measured in 50 M % $CDCl_3$ solution. [d] Measured in 50 M % benzene solution.

Table VII. DTBN- and Galvinoxyl-Induced ^1H Contact Shifts for Alkyl Halides (Hz)[a]

		X =		
Halide	Radical	Cl	Br	I
CH_2X_2	Galvinoxyl	−7.2	−11.7	−19.1
	DTBN	+159.9	+154.5	*b*
CHX_3	Galvinoxyl	−6.8	−16.8	*c*
	DTBN	+879.0	+811.2	*c*
CH_3CH_2X	Galvinoxyl	*b*	−5.1	−8.7
	DTBN	*b*	+14.0	+15.4

[a] Measured at [DTBN] = 3.0 × 10^{-4} M. [b] Not measured. [c] A chemical reaction occurred with DTBN.

Table VIII. DTBN-Induced ^{13}C Contact Shifts for Fluorinated Molecules

Fluorinated molecule	^{13}C contact shift, ppm[a]
	(α) +0.82 (*j*) +0.62
 $CH_3\underset{O}{\underset{\parallel}{C}}CH_2\underset{O}{\underset{\parallel}{C}}CF_3$	+0.63
C_6F_6	+0.85
C_6H_5–F	+0.30
p-$CH_3C_6H_4$–F	+0.25

[a] Measured at [DTBN] = 3.0 × 10^{-4} M.

shifts are summarized in Table VII. The DTBN-induced ^1H contact shifts for some of the halogenated molecules listed in this table have already been reported elsewhere.[5] This table shows that DTBN induces upfield ^1H contact shifts for halomethanes and ethyl halides, which are interpreted in terms of hydrogen bonding involved in these systems.[5] In contrast to this, galvinoxyl induced downfield ^1H contact shifts, although the magnitudes of the contact shifts were smaller than the DTBN-induced contact shifts. Furthermore, the magnitudes of galvinoxyl-induced ^1H downfield contact shifts increased in the order of Cl < Br < I and also increased with the number of halogen substituents, as has been encountered for DTBN-induced downfield ^{13}C contact shifts for halogenated molecules.

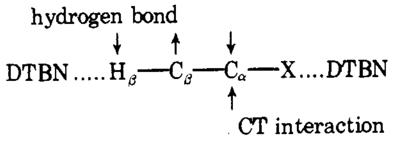
(E) ^{13}C Contact Shifts for Fluorinated Molecules. The ^{13}C contact shifts for fluorinated carbons in benzo trifluoride and 1,1,1-trifluoroacetylacetone and for the substituted carbons of fluorobenzene derivatives were found to be upfield shifts, while upfield ^{13}C contact shifts were not observed for aliphatic chloride, bromide and iodide. These results are listed in Table VIII. The magnitude of the contact shift for the α carbon in benzo trifluoride was larger than that of the substituted carbon of the phenyl ring, implying that the upfield shifts observed for fluorinated molecules could be induced by specific interaction between the fluorine atom and the nitroxide radical.

Discussion

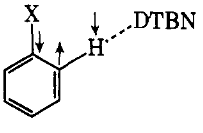
(A) The Feature of Halide–Stable Free Radical Interaction. As was previously envisioned,[6] the magnitude of DTBN-induced downfield ^{13}C contact shifts for the carbon connected directly with the halogen atom in various aliphatic and aromatic halides follows generally the trend of I > Br > Cl > F established for halomethanes. This trend allowed us to expect[6] that an electron donor–acceptor interaction between nitroxide and halogen atom is relatively important, since the C–I bond would serve as the electron accepting site in this interacting system. This trend of ^{13}C downfield contact shifts is generally experienced for a series of halogenated molecules such as halomethanes, alkyl halides, allyl halides, benzyl halides, and halobenzenes (Tables I–VI). We do not mention here any more experimental details of these downfield ^{13}C contact shifts, since they have been stated in our previous work.[6] The above feature of DTBN-induced downfield ^{13}C contact shifts was interpreted in terms of the electron donor–acceptor type of interaction where the C–X bond serves as the electron accepting site toward the DTBN radical.

In contrast to these downfield contact shifts, upfield ^{13}C contact shifts were observed in some halogenated molecules such as *tert*-butyl halides and halobenzene derivatives. Such an upfield contact shift prompted us to explore further the features of the interaction between halogenated molecules and stable free radical.

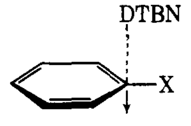
Table II[14] shows that ^{13}C contact shifts of α carbons decrease in the order of Et-X > *i*-Pr-X > *t*-Bu-X as the number of methyl groups increases. It is reasonable to conclude that this result may be due to the decrease in direct CX–DTBN interaction which is hindered by the increased bulkiness of alkyl groups. In the case of *t*-Bu-X, slightly upfield shifts were found for α carbons. Apparently the steric hindrance caused by the bulky *t*-Bu group is enough to prevent direct CX–DTBN interaction. Subsequently the dominant factor responsible for the upfield shifts may be a hydrogen bond between the β hydrogen (hydrogen atom of the methyl group) and nitroxide radical. It is well established that the CH–DTBN hydrogen bond induces negative spin density on the β-hydrogen atom, then propagates along the σ bond and induces positive and negative spin densities on the β- and α-carbon atoms, respectively. This negative spin density on α-carbon atom is relatively large as compared with positive spin density induced by the direct halogen-nitroxide interaction. Thus the upfield contact shifts observed for *tert*-butyl halides are accounted for by this negative spin density resulting from the hydrogen bonding at the β-hydrogen atom. Such an effect of steric hindrance was encountered for the hydrogen-bonding interaction between proton donor and nitroxide radical,[5] and this will be discussed elsewhere.



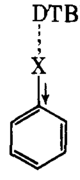
Abnormal upfield shifts were also observed for halobenzene/nitroxide radical systems, where there is no steric hindrance which prevents the direct halogen-nitroxide interaction. These upfield shifts are exemplified in Table VI. The upfield shifts were observed for C_j's in fluoro- and chlorobenzenes, while downfield contact shifts were observed for bromo- and iodobenzenes. It is generally seen that the downfield contact shifts for C_j decrease in the order of I > Br > Cl > F. These upfield and downfield ^{13}C contact shifts for C_j lead us to explore the mode of the interaction between halide and nitroxide and the mechanism of spin transfer in this bimolecular system. Three different types of possible interactions may lead to the upfield ^{13}C contact shifts for C_j: the hydrogen bonding interaction at the ortho hydrogen atom (I), the π-stacking interaction (II),[7] and possibly the halogen/nitroxide direct interaction (III). In this respect, some insight into the mode of interaction might be obtained by a comparison of ^{13}C contact shifts for halobenzenes induced by different types of stable free radicals. Our photoelectron spectroscopic studies[15] of stable free radicals have disclosed that the first ionization potentials of DTBN (7.2 eV)[15a] and DANO (7.1 eV)[15b] are very close. It is therefore likely that this small difference in the ionization potentials could not be responsible for substantial difference in the observed ^{13}C contact shifts induced by these two nitroxide radicals. The difference in the structures of these two nitroxides could be rather responsible for different features of ^{13}C contact shifts. DANO is reported to be planar[16] while nonplanar for DTBN. The DANO-induced upfield shifts for C_j (see Table VI) are larger than the corresponding DTBN-induced shifts. Nevertheless DTBN induces greater downfield ^{13}C contact shifts for the ortho carbon than does DANO. Supposing that these greater DANO-induced upfield shifts for C_j are caused by hydrogen bonding at the ortho proton, the greater downfield shifts could be expected for the ortho carbon (C_o). However, the observed DANO-induced contact shifts for ortho carbons were smaller than DTBN-induced shifts, implying that hydrogen bonding interaction may not be important. Particularly in the hexafluorobenzene/DTBN system which has no proton available for hydrogen bonding, a slightly upfield ^{13}C contact shift was observed. Therefore, the hydrogen bonding interaction (I) contributes little to the upfield contact shift for C_j. The π-stacking interaction (II) in which the nitroxide radicals attack directly over the π orbital of benzene derivatives may also induce an upfield contact shift for C_j.[7] In the simple cases of haloethylenes, however, downfield ^{13}C contact shifts were induced by DTBN (Table V). On this basis the π-stacking interaction is not responsible for the upfield contact shifts of C_j. Furthermore, the ^{13}C contact shifts of C_α for benzo trifluoride were larger than that of C_j, which suggests that this interaction is less important for the halide/nitroxide system.



hydrogen bond (I)



π-stacking interaction (II)



CT interaction (III)

It follows from the above discussion that the upfield and downfield contact shifts for C_j in halobenzenes are caused by specific interactions between the halogen atom and the nitroxide radical. In addition, the greater values of upfield contact shifts for C_j's in halobenzenes induced by the planar DANO radical compared with the nonplanar DTBN radical may suggest that nitroxide radical attacks the halogen atom from the vertical axis to the C-X bond in a stacking mode and this interaction could be responsible for the particular upfield contact shifts.

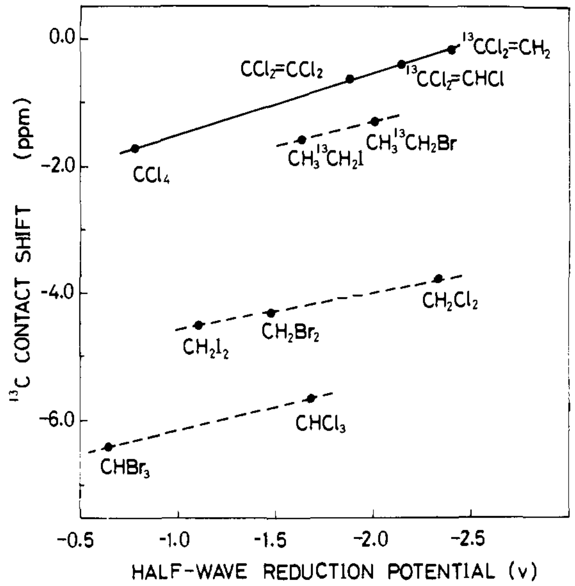
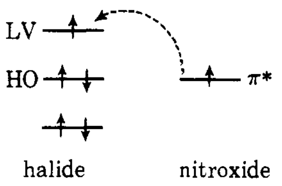


Figure 1. The linear relation between the DTBN-induced ^{13}C contact shifts and the polarographic half-wave reduction potentials.

(B) Linear Relation between DTBN-Induced ^{13}C Contact Shifts and Half-Wave Reduction Potentials. In the previous section, we indicated the CT interaction could be responsible for the observed DTBN-induced ^{13}C contact shifts. However, since there is no direct evidence for the CT character in the interaction of halide/nitroxide bimolecular systems, it will be of interest to correlate the observed ^{13}C contact shifts to other physical properties, which may provide additional evidence for the CT interaction. We found a correlation between DTBN-induced ^{13}C contact shifts and polarographic half-wave reduction potentials for various aliphatic halogenated molecules (Figure 1). A linear relation is obtained for each group of the related molecules.[17] Inspection of Figure 1 shows that the smaller the half-wave reduction potential, the greater the DTBN-induced ^{13}C contact shifts for the carbons bonded directly to the halogen atom, and all the contact shifts for the carbon without hydrogen atoms are related linearly to the reduction potentials. It is well documented[18,19] that the polarographic half-wave reduction potential is correlated to the energy of the lowest unoccupied molecular orbital. On this basis, the lowest unoccupied orbital of halogenated molecules plays an important role in producing ^{13}C contact shifts. This linear relation strongly suggests that the odd electron on the highest occupied orbital of nitroxide radical transfers directly onto the lowest unoccupied orbital of halides. This mechanism may correspond to the electron donor-acceptor (or charge transfer) interaction. It is, therefore, likely that positive spin densities are induced on both carbon and halogen atoms by nitroxide through this CT interaction, which accounts for the trend in the observed ^{13}C contact shifts for halogenated molecules in the order of I > Br > Cl > F.



Reinspection of Figure 1 reveals that the broken lines for ^{13}C contact shifts of the carbons bonded to both halogen and hydrogen atoms in CH_2X_2 and CHX_3 are underset to the full line for those bonded to the carbon without hydrogen atoms. This implies that there could be an additional effect for observed ^{13}C contact shift due to hydrogen bonding. This effect may correspond to the trend of ^{13}C contact shifts for halomethanes, $C\mathit{H}Cl_3 > C\mathit{Br}Cl_3 > C\mathit{Cl}Cl_3$. So it should be noted that DTBN-induced upfield ^{1}H contact shifts for halomethanes imply the involvement of the XCH-DTBN hydrogen bond as well as the HCX-DTBN CT interaction which is detected by downfield ^{13}C contact shifts. On the other hand, the downfield ^{1}H contact shifts were observed for the halomethane/galvinoxyl system. These downfield shifts are probably due to the charge transfer interaction and the hydrogen bonding interaction is less important in this system, probably because the HCX-galvinoxyl charge transfer type interaction could be preferred to the XCH-galvinoxyl hydrogen bonding due to steric constraint of the bulky galvinoxyl radical.

(C) Interpretation of the Upfield ^{13}C Contact Shifts for Fluorinated Molecules.[20] In order to get further insight into the intrinsic nature of the interaction between nitroxide radical and halogenated molecules, we have observed DTBN-induced ^{19}F and ^{13}C contact shifts for various aliphatic and aromatic fluorinated molecules, such as benzo trifluoride, 1,1,1-trifluoroacetylacetone and fluorobenzene.[20] All of these fluorine nuclei exhibited downfield contact shifts,[20] while upfield contact shifts were observed for the carbons bonded directly to fluorine atom in these molecules. These general features of ^{19}F and ^{13}C contact shifts for fluorinated molecules may allow us to expect some specific interaction between the fluorine atom and the nitroxide radical. The similar alternating DTBN-induced contact shifts were encountered for phosphorus and α carbon in some phosphine derivatives.[20] Preferential downfield ^{31}P contact shift and substantial upfield ^{13}C contact shift for the substituted carbon (C_j) in triphenylphosphine, for example, appear to be quite similar to the case of fluorobenzene. It is tempting to suggest that the lone pair electrons of the fluorine or phosphorus atom may serve as an electron donor to DTBN which might act as an electron acceptor. The residual positive spin density of F or P induced by the direct interaction between the F or P atom with DTBN may be distributed to the adjacent carbon atom by the spin polarization mechanism.[20] It is therefore likely that all of the three types of interaction I-III could be responsible for observed DTBN-induced upfield contact shifts for the substituted carbon (C_j) in fluorinated benzenes.

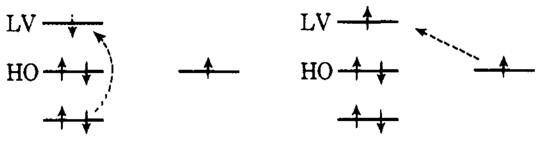
(D) Molecular Orbital Studies on the Mechanism of Intermolecular Spin Transfer Through CT Interaction between Nitroxide and Halogenated Molecules. In order to substantiate theoretically the CT nature of the CX-DTBN interaction and to elucidate the mechanism of intermolecular electron spin transfer, we have performed molecular orbital calculations of the nitroxide/halomethane bimolecular systems. In the previous preliminary study,[6] we reported the unrestricted Hartree-Fock (UHF)-SCF-MO (INDO method) calculations of spin density on the halide molecule induced by the interaction with dimethyl nitroxide (DMNO). Here we wish to present more detailed results on this calculation and to analyze the mechanism of electron spin transmission through the halide-nitroxide interaction. Bond lengths and bond angles of DMNO used for MO calculation and details of the method of INDO calculations were presented in the previous paper.[6] The geometries of the bimolecular system adopted here for MO calculations are σ and π types as depicted in Figure 2. In the σ and π models, the C-X bond is directed to the DMNO oxygen (or nitrogen) atom. For these models we obtain spin densities and stabilization energies. In Figure 3 are depicted the variation of stabilization energies for the CH_3X/DMNO system with varying intermolecular distance between the nitrogen or oxygen atom and the halogen atom. The results are summarized in Table IX. The π model appears to be responsible for the observed trend of the ^{13}C contact shifts.[6] Before discussing the results, it should be noted that the UHF wave function is not, in principle, an eigenfunction of $\langle s^2 \rangle$. However, in our calculation, the UHF values of $\langle s^2 \rangle$ for three models of the CH_3X/DMNO bimolecular system are very close to $\frac{3}{4}$, implying that UHF results for these interacting systems are not unreasonable when we discuss the CT stabilization energy ΔE.

Table IX. Values of Molecular Properties of Complexes between CH_3X and DMNO from INDO Calculations at the Calculated Equilibrium Intermolecular Distance

Halomethane	Complex model	R, Å	$-\Delta E$,[a] kcal/mol	Calcd spin density[b] $\rho_X(2s)$	$\rho_C(2s)$	$\rho_H(1s)$
CH_3F	π(O)	1.5	20.3	+0.037	+0.018	−0.002
	π(N)	1.75	2.77	+0.006	+0.003	−0.000
	σ(120°)	1.5	4.79	−0.003	−0.003	+0.000
CH_3Cl	π(O)	1.5	4.82	+0.041	+0.025	−0.002
	π(N)	2.1	0.44	+0.001	+0.001	−0.000
	σ(120°)	1.75	0.77	−0.001	−0.001	+0.000

[a] $\Delta E = E - E_\infty$, the energy of stabilization. [b] Spin density on CH_3X.

In order to elucidate the nature of CX-DMNO CT interaction, we have studied the mechanism of electron spin transmission from DMNO radical to the halogenated molecules by UHF-MO calculations. According to Nakatsuji et al.[21] it is possible to separate the spin density obtained by the UHF method into contributions which arise from spin polarization (SP) and spin delocalization (SD) mechanisms. Here SP and SD mechanisms correspond to electron spin transfer caused by electron configurations depicted below. The UHF wave function for the doublet state is contaminated by a small amount of contribution from higher multiplet states which can be eliminated by the annihilation method. The restricted HF (RHF) wave function, which produces only the SD mechanism of spin delocalization, is obtained from the UHF wave function by annihilation. For the doublet state, the following equation is applied



spin polarization (SP)   spin delocalization (SD)

$$\rho_{SD} = \tfrac{3}{2}(\rho_{UHF} - \rho_{aa})$$

$$\rho_{SD} = (\rho_{UHF} - \rho_{SP})$$

where ρ_{SP} denotes the SP contribution to the spin density calculated by the UHF method, ρ_{UHF} is the UHF spin density, and ρ_{aa} is the spin density after annihilation. With the aid of these equations, we estimated the SP and SD contribution to UHF spin densities induced on the halogenated molecules by the CT interaction with the DMNO radical. These results given in Table X, which contains ρ_{UHF}, ρ_{SP}, and ρ_{SD} and their contributions for halogen and carbon atoms in various bi-

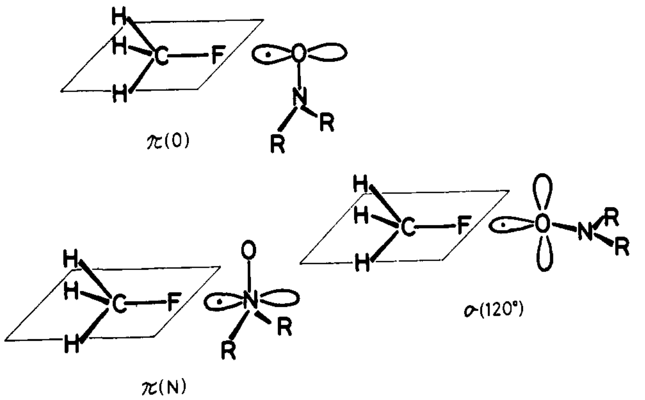


Figure 2. MO calculated models of the CH_3X/nitroxide bimolecular system.

Table X. A Breakdown into SP and SD Components of the Spin Densities Calculated for CH_3X–DMNO Bimolecular Systems[a]

Halomethane	Complex model	Component	Calcd spin density			
			$\rho_X(2s)$	$\rho_X(2p)$	$\rho_C(2s)$	$\rho_C(2p)$
CH_3F	π(O)	Total	+0.0369	−0.0362	+0.0176	+0.0736
		SP	+0.0010 (3)	−0.0502 (68)	+0.0067 (38)	+0.0327 (44)
		SD	+0.0359 (97)	+0.0239 (32)	+0.0109 (62)	+0.0409 (56)
CH_3Cl	π(O)	Total	+0.0407	−0.0932	+0.0249	+0.1088
		SP	+0.0037 (9)	−0.1047 (90)	+0.0154 (62)	+0.0700 (64)
		SD	+0.0370 (91)	+0.0115 (10)	+0.0095 (38)	+0.0388 (36)

[a] Percents of SP and SD components to total spin density are given in parentheses.

Table XI. A Breakdown into SP and SD Components of the Spin Densities Calculated for Proton Donor–DMNO Bimolecular Systems[a]

Proton donor (X–H)	Component	Calcd spin density	
		$\rho_H(1s)$	$\rho_X(2s)$
CH_3OH	Total	−0.0154	−0.0010
(O–H)	SP	−0.0157 (98)	−0.0018 (70)
	SD	+0.0003 (2)	+0.0008 (3)
$(CH_3)_2NH$	Total	−0.0173	−0.0001
(N–H)	SP	−0.0173 (100)	−0.0001 (100)
	SD	+0.0000 (0)	+0.0000 (0)
$HC{\equiv}CH$	Total	−0.0102	+0.0081
(C–H)	SP	−0.0105 (96)	+0.0012 (13)
	SD	+0.0003 (4)	+0.0069 (87)

[a] Percents of SP and SD components to total spin density are given in parentheses.

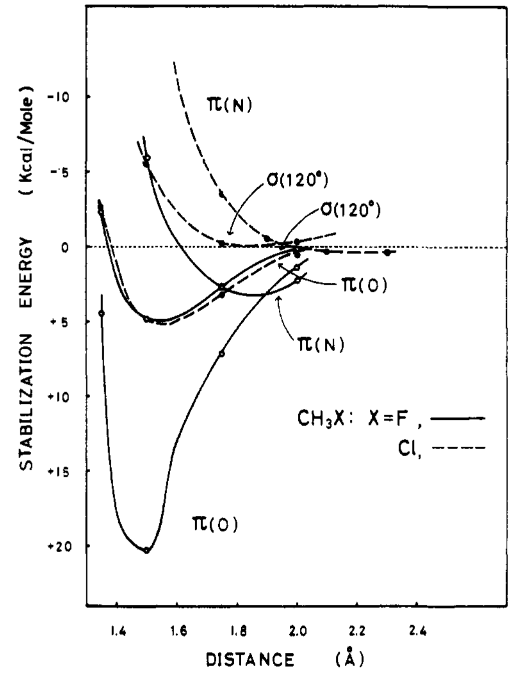


Figure 3. *R* dependence of the stabilization energies in CH_3X/DMNO systems.

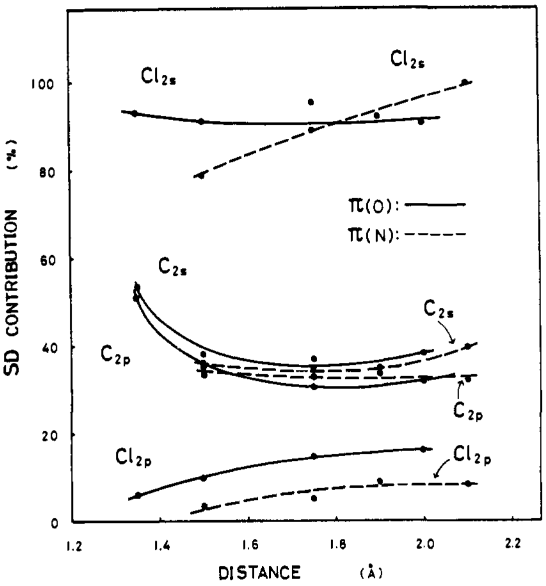


Figure 4. *R* dependence of the SP and SD components of the spin densities calculated for CH_3X/DMNO systems.

Table XII. The Relative Change of Atomic and Total Charges and C–X Bond Orders from the Charge-Density Matrix from the INDO Wave Function for Complexes of CH_3X with DMNO[a]

Halomethane	Complex model	Δq_N[b]	Δq_O[b]	Δq_C[b]	Δq_X[b]	$\Delta p_{CX}(p-\sigma)$[c]	$\Delta p_{CX}(s-s)$[c]	Δq[d]
CH_3F	π(O)	+0.058	−0.065	−0.003	−0.054	−0.053	−0.026	−0.031
	π(N)	−0.055	+0.037	+0.031	−0.019	−0.029	−0.019	+0.011
	σ(120°)	+0.011	−0.060	+0.085	−0.063	−0.295	−0.045	+0.047
CH_3Cl	π(O)	+0.045	−0.042	+0.053	−0.077	−0.059	−0.027	−0.026
	π(N)	−0.015	+0.005	+0.004	−0.001	−0.005	−0.003	+0.002
	σ(120°)	+0.005	−0.025	+0.026	−0.027	−0.238	−0.014	+0.013

[a] Values are given at the calculated equilibrium intermolecular distance. The numbers in the table are the numbers of valence-shell electrons on the atom. [b] Δq_N, Δq_O, Δq_C, and Δq_X denote the change in charge densities on the nitrogen, oxygen, carbon, and halogen atoms in DMNO and CH_3X, respectively. The plus and minus sign mean the increase and decrease in electron densities. [c] $\Delta p_{CX}(p-\sigma)$ and $\Delta p_{CX}(s-s)$ mean the change in the total p–σ and s–s bond orders for the C–X bond in CH_3X. The plus and minus signs mean the increase and decrease in the bond order. [d] Δq denotes the change in the total charge density on the CH_3X molecule.

molecular models, show that the $\pi(\mathrm{O})$ and $\pi(\mathrm{N})$ models are responsible for the observed ^{13}C downfield contact shifts for carbons bonded directly to the halogen atoms. In addition, the SD contribution is essential for the induced halogen 2s spin density. Figure 4 shows how the SD contribution varies with the CH_3Cl-DMNO intermolecular distance (R) for the three models. Inspection of this figure reveals that there is no marked R dependence of SD contribution for each model.

It is of interest to compare the present results with those for the XH-DMNO hydrogen bonding interaction;[2] see Table XI. In the hydrogen bonding interaction,[2] the negative spin density is induced dominantly by the SP mechanism on the X-H hydrogen 1s orbital as has been qualitatively discussed in our early work.[2c] On the other hand, the SD mechanism plays an essential role in the CT interaction of the halide/nitroxide bimolecular system. This SD mechanism corresponds to the charge transfer interaction between the halide and the nitroxide radical.

We then wish to discuss this charge transfer interaction as a model of halogen abstraction reaction by organic free radicals. It then appears to be interesting to discuss the magnitude of electron transfer Δq or change in the C-X bond order Δp for halomethanes induced by the interaction with DMNO. These results are summarized in Table XII. The direction of electron transfer is different between three models. The whole molecule of halomethane gains electron density from the DMNO radical for the $\pi(\mathrm{N})$ model and loses for the $\pi(\mathrm{O})$ model (see Table XII). Therefore, the direction of electron transfer, cannot be predicted alternatively by these simple models. However, it should be pointed out again that $\pi(\mathrm{O})$ and $\pi(\mathrm{N})$ models may be responsible for the observed contact shifts. The discussion on the mode of electron transfer will be performed in the next paper.

In addition, the electron density of the carbon atom in CH_3X (Δq) is increased in going from free to interacting systems and the corresponding values of Δq_{O} and Δq_{N} for the nitroxide radical are decreased. These calculated data show that the carbon atom of CH_3X is slightly negative and the interacting site of the nitroxide radical has a slightly positive character in the CH_3X/nitroxide bimolecular systems. This charge distribution of the CH_3X-nitroxide complex

$$\mathrm{C\text{-}X^{\delta-}\cdots DMNO^{\delta+}}$$

appears to be related to the transition state in the halogen abstraction reaction proposed by Danen et al.[22]

$$\mathrm{R\text{-}I + \cdot Rad \rightarrow [R^{\delta-}\cdots I\cdots Rad^{\delta+}] \rightarrow \cdot R + I\text{-}Rad}$$

Concluding Remarks

The present study on the ^{13}C and ^{1}H contact shifts of halogenated molecules induced by the nitroxide and galvinoxyl radicals and INDO-MO calculations for these bimolecular systems may lead to the following conclusions.

(1) Measurements of contact shifts reveal the specific features of the weak interaction between halogenated molecules and stable free radicals. Direct halogen-nitroxide interactions appear important and the CT interaction may be responsible for the observed downfield contact shifts for the carbon bonded directly to the halogen atom. In addition, halogenated molecules are expected to serve as the electron acceptors for the nitroxide radical. This conclusion is supported by the linear correlation between ^{13}C contact shifts and corresponding half-wave reduction potentials.

(2) Spin delocalization (SD) is important for the spin appearing mechanism of the spin density induced on halogen and carbon s atomic orbitals, in contrast to the spin polarization (SP) for the hydrogen bonding system.

Acknowledgment. The authors are grateful to Dr. H. Nakatsuji for making his computer program available to us in this work.

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(17) It appears that a true correlation in Figure 1 should probably not require separation of the organohalides into groups. However, in this study we are concerned with the observed ^{13}C contact shifts which are not the limiting shifts obtained by taking into account the equilibrium constants. In addition to the CT interaction, steric and hydrogen bonding effects may be involved in the origin of the observed ^{13}C contact shifts. The features of these interactions may be different for a series of halogenated molecules. The complicated modes of halide-nitroxide radical interaction stated above may be responsible for the finding of separation into four groups.

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(19) The failure of the single linear plot of Figure 1 may also be due to the following. Half-wave reduction potentials are related to the energies of the lowest vacant orbitals only for chemically and electrochemically reversible reductions. Since reduction of the organohalides in Figure 1 is followed by rapid decomposition, the reduction potentials are shifted to varying extents. Therefore, the linear relation in Figure 1 may *reflect* the CT nature of the halide-nitroxide system. The authors are grateful to a referee for this point.

(20) Details of ^{19}F and ^{31}P contact shift studies on electron donor-acceptor interactions between stable free radicals and lone pair electrons will appear in a forthcoming paper (I. Morishima, T. Inubushi, and T. Yonezawa, submitted for publication).

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