Deuterium Isotope Effects on Aromatic C-13 NMR Chemical Shifts. IV. Can the Isotope Shifts Be Correlated with Bond Lengths?

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The deuterium isotope effects on the ^{13}C NMR chemical shifts of the ring carbons of aromatic heterocycles were investigated. One-bond shifts are correlated with the C–H bond lengths calculated by the MNDO MO method. Two-bond shifts are dependent on the nature of the observed sites. On the other hand, three-bond shifts are controlled by the hetero atoms existing in the pathway.

The deuterium isotope effects on the ^{13}C chemical shifts ($^n\Delta$, where n is the number of intervening bonds) are useful parameters for structural studies.[1] Although they are correlated with several physicochemical parameters, the origin of $^n\Delta$ is still unclear. They are therefore currently being intensively discussed. We have shown an additivity of substituent effects on the isotope shifts and dependence of the isotope shifts on the electron densities for two systems of substituted benzenes and pyridines, respectively.[2–4] Further, the dependence of one-bond shifts ($^1\Delta$) on the C–H bond lengths was presented for mono-substituted methanes.[5] In this paper we report on the dependence of the $^1\Delta$ on C–H bond lengths in unsubstituted aromatic compounds. The data are discussed from the standpoint of the vibrational model on the basis of different contributions of anharmonicity for shorter and longer C–H bonds. In addition, the dependence of $^2\Delta$ on the C–C bond lengths and the irregular behavior of $^3\Delta$ in heteroaromatic rings are discussed.

Experimental

The samples treated were pyridine, pyridine *N*-oxide, pyridazine, quinoline, quinoline *N*-oxide, isoquinoline, furan, thiophene, benzo[*b*]thiophene, cyclopentadienylsodium, purine, and imidazole. Deuterium-labeled compounds were prepared mostly with acid- or base-catalyzed H/D exchange reactions of the starting materials in an autoclave or thermostated air oven. Furan-2-*d* was prepared by decarboxylation of the corresponding 2-carboxylic acid-*d*. Pyridine-4-*d* and pyridine-3,5-d_2 were prepared by a previously reported method.[6] Cyclopentadienylsodium was prepared from dicyclopentadiene by the method described in Ref. 7. Dicyclopentadiene-*d* was obtained by quenching the above-mentioned compound with D_2O. The method given in Ref. 7 was repeatedly applied; a mixture of H- and D-cyclopentadienylsodium was then prepared. ^{13}C NMR measurements were carried out using a Varian XL-200 (50.3 MHz) or UNITY-400 (100.6 MHz) FT-NMR spectrometer at about 22 °C. Details concerning the measurements were described previously.[2] Examples of the ^{13}C NMR spectra are shown in Figs. 1 and 2. The MNDO MO calculations were carried out by using the MOPAC program (J. J. P. Stewart, *QCPE Bull.*, 3, 43 (1983)) at the Computer Center, Institute for Moleculer Science at Okazaki, or by using an NEC PC-9801 RA 32-bit personal computer with "PASOCON MOPAC/386" program, which is based on the MOPAC (V3.1 QCPE No. 516) by Toray Systems Center. Gas-phase FT-IR spectra were measured within an error of 4 cm^{-1} by using a Hewlett Packard on-line GC-IR-MS system (Models 5890II Gas Chromatograph, 5965B FT-IR detector, and 5971A mass-selective detector). Samples were introduced into the FT-IR and MS system at the same time. Their deuterated sites and ratios were confirmed by ^{13}C NMR and mass spectra.

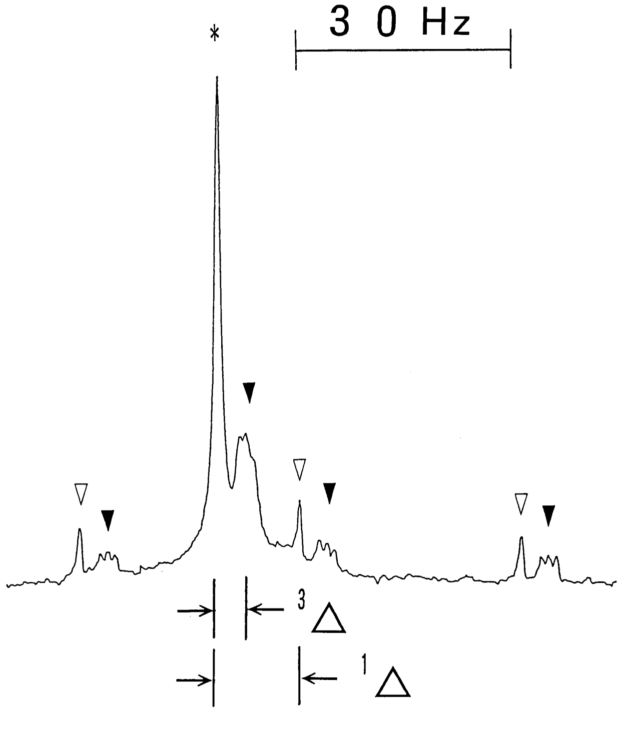


Fig. 1. ^{13}C NMR spectra of a mixture of furan (★), furan-2-*d* (▽), and furan-2,5-d_2 (▼). The trace shows C_2 and C_5 signals. $^1\Delta$ and $^3\Delta$ can be observed with CD couplings.

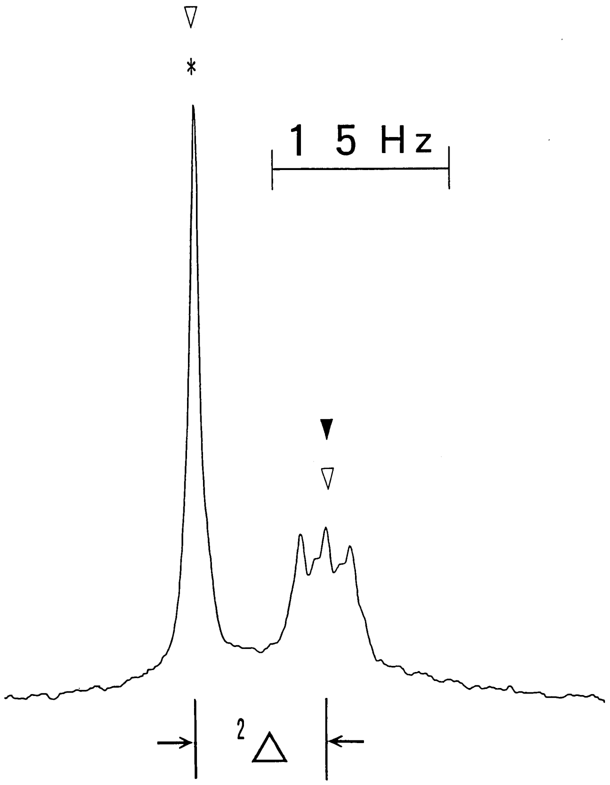


Fig. 2. ^{13}C NMR spectra of a mixture of furan (★), furan-2-*d* (▽), and furan-2,5-d_2 (▼). The trace shows C_3 and C_4 signals. $^{2}\Delta$ can be observed with CD coupling.

Results and Discussion

One- and two-bond isotope shifts ($^{1}\Delta$ and $^{2}\Delta$) of heteroaromatic compounds are shown in Tables 1 and 2. Furthermore, the characteristic large three-bond shifts ($^{3}\Delta$) were observed in five-membered heteroaromatic compounds, as given in Table 3, for the cases of D–C–X–^{13}C (where X is a hetero atom). Several $^{1}\Delta$ and $^{2}\Delta$ values of polynuclear aromatic compounds were cited from Refs. 8 to 11. All of the observed $^{1}\Delta$, $^{2}\Delta$, and $^{3}\Delta$ were toward the higher field. The values given in Tables 1, 2, and 3 should therefore be negative in the conventional manner. However, the signs are neglected in the Tables.

One-bond shifts ($^{1}\Delta$) ranged from 191 to 373 ppb; $^{2}\Delta$ ranged from 51 to 213 ppb; $^{3}\Delta$ of the five-membered ring carbons (D–C–X–^{13}C) ranged from 28 to 101 ppb. The largest and smallest $^{1}\Delta$ were observed in the tropylium ion and in imidazole, respectively. It has been reported that $^{1}\Delta$ is dependent upon the hybridization of the carbon atom.[12] Since all of the carbon atoms studied in this work are sp^{2}-hybridized, hybridization cannot become a main controlling factor of the change in $^{1}\Delta$. The observed $^{1}\Delta$ spreads over a wide range of 182 ppb; this range extends beyond that observed by a hybridization change from ethane to ethylene and acetylene[12] (sp^{3}, 284.0; sp^{2}, 273.6; and sp, 226.7 ppb). Accordingly, in the present system $^{1}\Delta$ is considered to be controlled by other factors, except for hybridization. The $^{2}\Delta$ observed in the carbons neighboring the heteroatoms were

Table 1. One-Bond Deuterium Isotope Shifts ($^{1}\Delta$) of Aromatic Compounds in ppb[a] and C–H Bond Lengths ($r_{\mathrm{C-H}}$) in Å Optimized by the MNDO MO Calculation

Compound	Observed carbon	Solvent	$^{1}\Delta$	$r_{\mathrm{C-H}}$	No.[e]
Pyridine	C-2	D_2O	327	1.095	1
	C-4	Neat	296	1.090	2
Pyridine *N*-oxide	C-2	0.1wt% NaOH–D_2O	268	1.092	3
	C-4	10wt% NaOH–D_2O	252	1.089	4
Quinoline	C-2	Methanol-*d*	336	1.096	5
Quinoline *N*-oxide	C-2	5wt% NaOH–D_2O	269	1.093	6
Isoquinoline	C-1	Methanol-*d*	361	1.097	7
Pyridazine	C-3	5wt% NaOH–D_2O	314	1.093	8
	C-4		296	1.089	9
Cyclopentadienylsodium		THF	219	1.083	10
Furan	C-2	Neat	225	1.084	11
Thiophene	C-2	Neat	194	1.079	12
Benzo[*b*]thiophene	C-2	$CDCl_3$	219	1.082	13
	C-3		242[d]	1.084	14
Purine	C-8	D_2O	237	1.087	15
Imidazole	C-2	D_2O	191	1.085	16
Benzene		Acetone-d_6	283[8]	1.090	17
Naphthalene[c]	C-1	$CHCl_3$	310[9]	1.091	18
	C-2		280[9]	1.091	19
Phenanthrene[c]	C-9	$CHCl_3$	310[9]	1.092	20
Benzo[*c*]phenanthrene[c]	C-2	$CHCl_3$	270[9]	1.091	21
Azulene	C-2	Acetone-d_6	246[10]	1.082	22
	C-6		332[10]	1.098	23
Tropylium ion[b]		CD_3CN	373[11]	1.100	24

a) Errors are estimated to be within 5 ppb. b) The values were based on the assumption of a negligible $^{4}\Delta$ as described by Forsyth (see Ref. 1-b). c) These values were reported only to the nearest 10 ppb, so are considerably less accurate than the others. d) With a larger error (15 ppb). e) The numbers are referred to those in Fig. 4.

Table 2. Two-Bond Deuterium Isotope Shifts ($^{2}\Delta$) of Aromatic Compounds in ppb[a]

Compound	Observed carbon and D-site		Solvent	$^{2}\Delta$	$r_{\mathrm{C-C}}$	No.[f]
Pyridine	C-2	From 3-D	Neat	59[e]	1.411	1
	C-3	From 2-D	Neat	129	1.411	2
	C-3	From 4-D	Neat	106	1.404	3
Pyridine *N*-oxide	C-3	From 2-D	0.1wt% NaOH–D_2O	129	1.400	4
	C-3	From 4-D	10wt% NaOH–D_2O	106	1.404	5
Quinoline	C-3	From 2-D	Methanol-*d*	124	1.436	6
Quinoline *N*-oxide	C-3	From 2-D	1wt% NaOH–D_2O	117	1.420	7
Isoquinoline	C-9	From 1-D	Methanol-*d*	109	1.445	8
Pyridazine	C-3	From 4-D	5wt% NaOH–D_2O	51	1.411	9
	C-4	From 5-D		105	1.401	10
Cyclopentadienylsodium			THF	127	1.418	11
Furan	C-3	From 2-D	Neat	213	1.390	12
Thiophene	C-3	From 2-D	Neat	148	1.368	13
Benzo[*b*]thiophen	C-2	From 3-D	$CDCl_3$	94	1.367	14
	C-3	From 2-D		146	1.367	15
	C-3a	From 3-D		69	1.462	16
Benzene[d]			Acetone-d_6	111	1.407	17
Naphthalene[c,d]	C-2	From 1-D	$CHCl_3$	120	1.383	18
	C-8a	From 1-D		120	1.400	19
	C-1	From 2-D	$CHCl_3$	120	1.383	20
	C-3	From 2-D		80	1.427	21
Phenanthrene[c,d]	C-10	From 9-D	$CHCl_3$	120	1.365	22
	C-8a	From 9-D		70	1.451	23
Benzo[*c*]phenanthrene[c,d]	C-1	From 2-D	$CHCl_3$	110	1.389	24
	C-3	From 2-D		100	1.416	25
Azulene[d]	C-1	From 2-D	Acetone-d_6	108	1.412	26
	C-5	From 6-D		96	1.400	27
Tropylium ion[b,d]			CD_3CN	98	1.406	28

a) Errors are estimated to be within 5 ppb. b) The values were based on the assumption of a negligible $^{4}\Delta$ as described by Forsyth (see Ref. 1-b). c) These values were reported only to the nearest 10 ppb, so are considerably less accurate than the others. d) Same references with Table 1. e) A value obtained from pyridine 3,5-d_2. Thus, it is based on an assumption of a negligible $^{4}\Delta$ (an effect of 5-D on C-2). f) The numbers are referred to those in Fig. 5.

Table 3. Three-Bond Deuterium Isotope Shifts ($^{3}\Delta$) of Five-Membered Aromatic Compounds in ppb[a]

Compound	Observed carbon and D-site		Solvent	$^{3}\Delta$
Cyclopentadienylsodium			THF	28
Imidazole	C-4,5	From 2-D	D_2O	41
Furan	C-2	From 5-D	Neat	76
	C-3	From 5-D	Neat	c)
Thiophene	C-2	From 5-D	Neat	101
	C-3	From 5-D	Neat	c)
Benzo[*b*]thiophene	C-7a	From 2-D	$CDCl_3$	40[b]

a) Errors are estimated to be within 3 ppb. b) With a larger error (10 ppb). c) It is evaluated to be smaller than 20 ppb from its line width.

smaller than the others. Although $^{3}\Delta$ were not observed since they are very small, only for heteroaromatic five-membered compounds could $^{3}\Delta$ be observed as measurable shifts in a pathway (D–C–X–^{13}C).

The $r_{\mathrm{C-H}}$'s and $r_{\mathrm{C-C}}$'s given in Tables 1 and 2 were obtained from the optimized geometries calculated using the MNDO MO method.[13] In the present system they varied from 1.079 to 1.100 and from 1.365 to 1.462 Å, as given in Tables 1 and 2.

To evaluate the performance of the MNDO MO method, the C–D stretching frequencies ($\nu_{\mathrm{C-D}}$) in the IR spectra of several compounds were measured. Since $\nu_{\mathrm{C-H}}$ depends on $r_{\mathrm{C-H}}$[14] it is possible to estimate the "relative" errors of $r_{\mathrm{C-H}}$ by comparing $\nu_{\mathrm{C-H}}$ with $r_{\mathrm{C-H}}$. $\nu_{\mathrm{C-H}}$ can be related to $\nu_{\mathrm{C-D}}$ by using the following simple equation with a consideration of the mass difference between H and D:[15]

$$\nu_{\mathrm{C-H}} = (13/7)^{1/2}\,\nu_{\mathrm{C-D}}. \qquad (1)$$

Since aromatic compounds have many C–H bonds, their IR spectra in a $\nu_{\mathrm{C-H}}$ region are highly complicated. It is considered that use of the "isolated" frequency ($\nu_{\mathrm{C-H}}^{\mathrm{is}}$) seems to be most suitable for any discussion due to the

Table 5. $\nu_{\text{C-D}}$ and $\nu_{\text{C-H}}$ (Calculated) of Several Partially Deuterated Aromatic Compounds

Compound	Site	$\nu_{\text{C-D}}$[a]	$\nu_{\text{C-H}}$ (calcd)[b]
Furan	C-3	—	3137[c]
Benzo(*b*)thiophene	C-2	2291	3122
	C-3	2291	3122
Pyridine	C-2	2260	3080
	C-3	2279	3106
	C-4	2276	3102
Quinoline	C-2	2260	3080
Isoquinoline	C-1	2246[d]	3061
Pyridazine	C-3	—	3070[e]
Benzene	C-1	2284[f]	3113

a) In cm^{-1}. b) $\nu_{\text{C-H}}$ (calcd) were obtained by Eq. 1 in cm^{-1}. c) Averaged $\nu_{\text{C-H}}$ (3144 and 3130) observed in 2,5-d_2 compound. d) Averaged for two nonequivalent C–D frequencies (2240 and 2251). e) Averaged $\nu_{\text{C-H}}$ (3076 and 3063) observed for 4,5-d_2 compound. f) Obtained from hexadeuterobenzene.

independence of $\nu_{\text{C-H}}{}^{\text{is}}$ from any other motion. However, $\nu_{\text{C-H}}{}^{\text{is}}$ is difficult to determine. To solve this problem, partial deuterium labeling techniques were used. A partially deuterated molecule in the gas-phase usually gives a single C–D stretching band ($\nu_{\text{C-D}}$). Such a $\nu_{\text{C-D}}$ is shown in Table 5. Since the $\nu_{\text{C-D}}$ region usually gives a few peaks, the coupling of $\nu_{\text{C-D}}$ to other motions is minimal. This $\nu_{\text{C-D}}$ can therefore be considered as being an "isolated" frequency ($\nu_{\text{C-D}}{}^{\text{is}}$). Thus, $\nu_{\text{C-H}}{}^{\text{is}}$ was evaluated by using $\nu_{\text{C-D}}{}^{\text{is}}$ from Eq. 1 (Table 5). There is a good linear correlation between $\nu_{\text{C-H}}{}^{\text{is}}$ and $r_{\text{C-H}}$.[16] Therefore, $r_{\text{C-H}}$ optimized by the MNDO MO method has an accuracy that is sufficient to discuss the C–H bond lengths.[13]

One-Bond Shift, $^1\Delta$: Theoretical studies of the isotope effect on the NMR chemical shifts have focused on the way in which vibrational changes due to isotopic substitution affect the nuclear shieldings. Batiz-Hernandez and Bernheim explained the effect in terms of slight changes in the bond lengths and angles associated with the lower zero-point vibrational energy in an anharmonic potential well when a heavier isotope is attached.[17a] Servis and Shue stated, "Although the energy surface for the deuterated and nondeuterated materials should exactly coincide, small changes in the bond lengths and bond angles, which result from averaging over a vibrational motion in an anharmonic potential well, can be expected to occur."[17b] Thus, the lower zero-point vibrational energy of a C–D bond leads to a reduced bond length and an effectively greater electron density at the carbon. Hansen also stated the same theory in his review.[1e] The isotope effect on nuclear shielding occurs in most cases because the lower vibrational energy of the heavier isotopomer and the anharmonicity of potential curve result in a shorter average internuclear separation of the isotopomer. A shorter bond length leads to higher shielding and, hence, to a shift in the NMR resonance position to lower frequency for the heavier isotopomer.

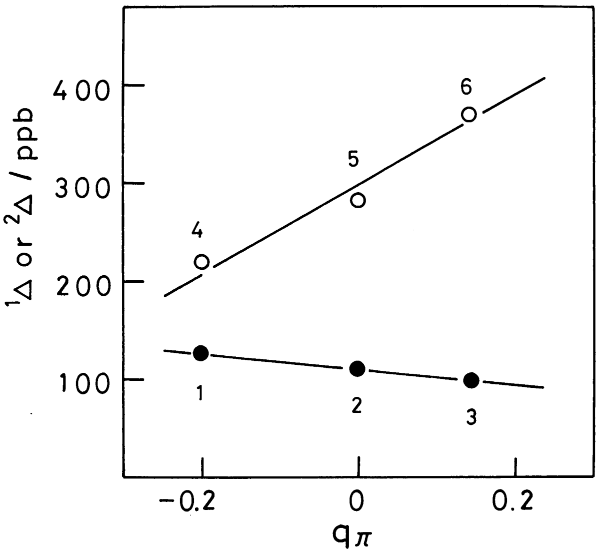


Fig. 3. Correlations between the π-electron densities (abscissa) and $^1\Delta$ (○) or $^2\Delta$ (●) (ordinate in ppb) in cyclopentadienyl anion (1,4), benzene (2,5), and tropylium cation (3,6).

On the other hand, it is known that $^1\Delta$ gives a linear correlation with the chemical shifts of the observed carbons.[2,3,4,18] In this work, however, there is no correlation between the $^1\Delta$ and δ_c. The reason for this can be attributed to the system treated. We have reported on linear correlations between the $^1\Delta$ and π-electron densities for substituted benzenes[2,3] and 3-substituted pyridines,[4] respectively. However, in the present system there is no correlation between $^1\Delta$ and π-electron densities. We therefore believe that there is a correlation between $^1\Delta$ and the chemical shifts, or electron densities, only within limited systems. The $^1\Delta$ of cyclopentadienyl anion ($C_5H_4D^-$), benzene (C_6H_5D), and tropylium cation ($C_7H_6D^+$), which are typical aromatic compounds, show a good linear correlation with the π-charge densities (q_π) of the observed carbons, as follows (Fig. 3):

$$^1\Delta = 441\, q_\pi + 300. \tag{2}$$

On the other hand, q_π also shows a linear correlation with $r_{\text{C-H}}$ (Eq. 3) for the above three aromatic compounds:

$$r_{\text{C-H}} = 0.0486\, q_\pi + 1.09. \tag{3}$$

Namely, this correlation suggests from Eq. 2 that a correlation also exists between $^1\Delta$ and $r_{\text{C-H}}$. In this paper we discuss the dependence of $^1\Delta$ on the C–H bond lengths in unsubstituted aromatic compounds. Figure 4 shows a linear correlation between $^1\Delta$ and the C–H bond lengths of 24 observed carbons. The equation of the least-square line is

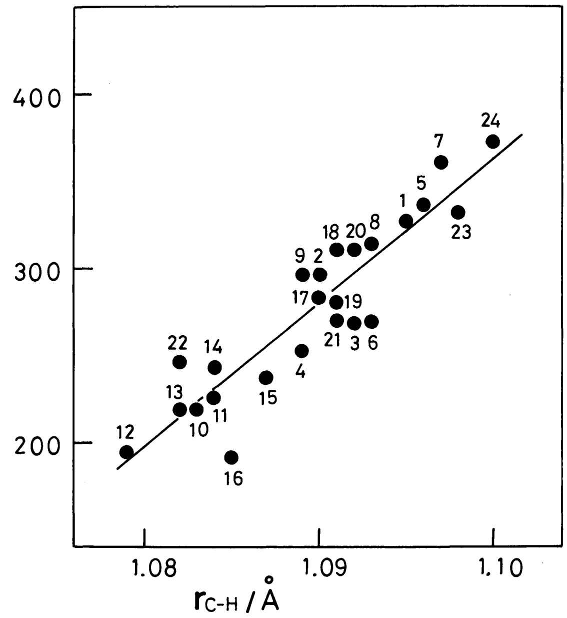


Fig. 4. Correlation between $^{1}\Delta$ (ordinate in ppb) and $r_{\mathrm{C-H}}$ (abscissa in Å) for aromatic compounds with $r=0.917$ and a standard deviation of 21 ppb.

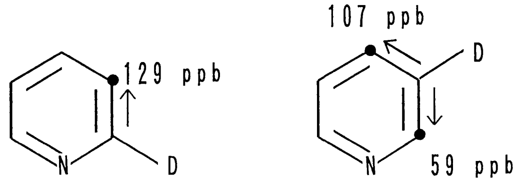
$$^{1}\Delta\ (\mathrm{ppb}) = 8378\, r_{\mathrm{C-H}}(\text{Å}) - 8853\ (r=0.917,\ \mathrm{S.D.}=21\ \mathrm{ppb}). \tag{4}$$

Thus, the slope of the line is about 8.4 ppm/ Å. The sign of the slope is positive. That is to say, a shorter (i.e. stronger) C–H bond of the observed carbon will produce a smaller $^{1}\Delta$. This fact strongly suggests that Jameson's assumption is reasonable. Recently, Jameson and Osten have established theoretical aspects of the isotope effects on nuclear shielding in diatomic molecules.[1c,19,20] In articles they used the following assumption: Assuming that the potential is less anharmonic for shorter and stronger bonds, the presumably smaller fractional bond shortening upon replacement of hydrogen by deuterium should then result in a diminished isotope shift.[19,20] Günther et al. tentatively interpreted their $^{1}\Delta$ by using this assumption for a shorter C–H bond, such as that in acetylene.[12] Such a treatment can be applied to the case of the observed carbon's hybridization change. For example, in the system of ethane, ethylene, and acetylene, the correlated straight line between $^{1}\Delta$ and the C–H bond lengths[9,21] does exist. Since $r_{\mathrm{C-H}}$ depends on carbon hybridization for the above three compounds, there is a correlation according to

$$^{1}\Delta\ (\mathrm{ppb}) = 1673\, r_{\mathrm{C-H}}(\text{Å}) - 1544\ (r=0.997,\ \mathrm{S.D.}=3.4\ \mathrm{ppb}). \tag{5}$$

However, the slope of Eq. 5 is about five-times smaller than that of 4.

Two-Bond Shift, $^{2}\Delta$: The origins of $^{2}\Delta$ are considered to be as follows. $^{2}\Delta$ is induced by transmitting a shielding change of the D-labelled carbon.[3,12] Jameson and Osten called this mechanism "a secondary shielding change with a primary bond length change".[1c,24] The shielding change of the D-labelled carbon is $^{1}\Delta$.



Scheme 1.

We can thus consider that $^{1}\Delta$ induces $^{2}\Delta$. However, $^{2}\Delta$ shows no correlation with $^{1}\Delta$. On the other hand, $^{2}\Delta$ is correlated with the ^{13}C chemical shifts and electron densities of the $^{2}\Delta$-observed carbons.[2-4] Therefore, $^{2}\Delta$ is controlled by the electron densities on the $^{2}\Delta$-observed carbon. For example, as shown in Scheme 1, pyridine-3-*d* gave two different $^{2}\Delta$ at C_2 and C_4, respectively. Pyridine-3-*d* or -2-*d* also shows different $^{2}\Delta$ at C_2 or C_3 in which the same pathway is contained. From these results the nature of the $^{2}\Delta$-observed sites is important for $^{2}\Delta$.

In a series of three typical aromatics ($C_5H_4D^-$, C_6H_5D, $C_7H_6D^+$), a linear correlation between $^{2}\Delta$ and q_π in the $^{2}\Delta$-observed carbons is found (Fig. 3). The two slopes for $^{1}\Delta$ and $^{2}\Delta$ in Fig. 3 are opposite in sign. When q_π is higher, $^{1}\Delta$ becomes smaller. On the other hand, $^{2}\Delta$ becomes larger. They can be interpreted as follows. A higher q_π produces a shorter $r_{\mathrm{C-H}}$. Thus, $^{1}\Delta$ becomes smaller. A higher q_π increases the transmittance of any shielding change. Thus, $^{2}\Delta$ becomes larger. Sardella et al. have reported on a correlation between $^{2}\Delta$ and the carbon–carbon bond length ($r_{\mathrm{C-C}}$) in several neutral π-systems.[25] $r_{\mathrm{C-C}}$ in a neutral π-system can be correlated with the bond order. The bond order is a function of the electron densities. The electron densities of the pathways are therefore important for $^{2}\Delta$, even though no correlation between $^{2}\Delta$ and $r_{\mathrm{C-C}}$ was found in the present heteroaromatic system,[26] which is quite different from that shown by Sardella et al.[25] (Fig. 5) The reason must therefore be attributed to the hetero atoms in the aromatic rings. When heteroatoms exist, the electron density changes in the system are larger than those in hydrocarbons. Therefore, large $^{2}\Delta$ changes were observed in aromatic heterocycles. For example, a very large $^{2}\Delta$ (213 ppb) was observed in the C_3 of furan. This is very close to $^{1}\Delta$ in the C_2 of furan (225 ppb). It is a typical example in which $^{2}\Delta$ is of the same order as $^{1}\Delta$. It must be noted that such a large $^{2}\Delta$ is observed in heteroaromatic compounds.

Three-Bond Shift, $^{3}\Delta$: The origin of $^{3}\Delta$ is considered to be as follows.[4] The shielding change on the $^{2}\Delta$-observed carbon is transmitted to the observed $^{3}\Delta$ carbon. Thus, $^{3}\Delta$ originates from the transmitted shielding change of the $^{2}\Delta$-observed carbon. This

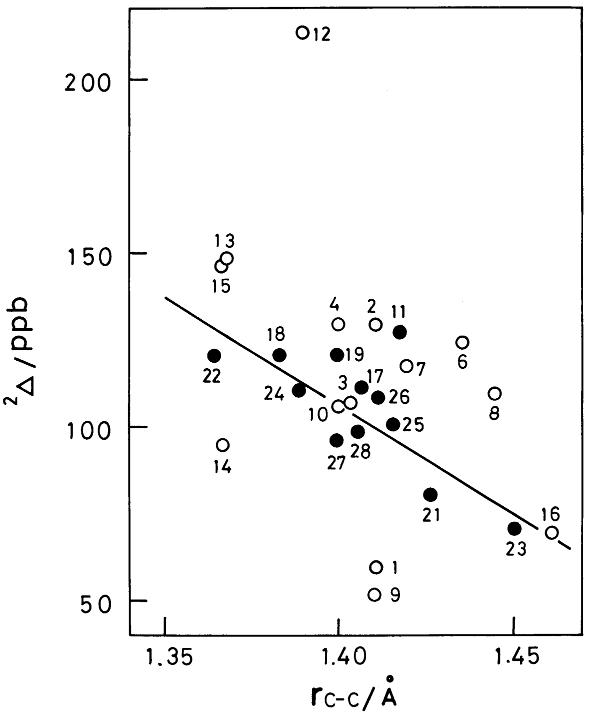


Fig. 5. Plot between $^2\Delta$ (ordinate in ppb) and $r_{\text{C-C}}$ (abscissa in Å) for aromatic compounds. The white points indicate hetero aromatics. The black points indicate a linear correlation with $r=0.875$ (excepted for $C_5H_4D^-$).

mechanism is similar to that of $^2\Delta$. The transmitted shielding change of $^3\Delta$ is expected to be smaller than that of $^2\Delta$. Therefore, $^3\Delta$ is always smaller than $^2\Delta$ and is often not observed. In the present experimental system, $^3\Delta$ is not usually observed, except for the case of five-membered heteroaromatic compounds such as furan, imidazole, thiophene, benzo[*b*]thiophene. $^3\Delta$ in furan and thiophene are of the same order as that compared with $^2\Delta$. The cyclopentadienyl anion, which has no heteroatom, gives a small $^3\Delta$ (28 ppb). On the other hand, in thiophene-5-*d*, although C_2 has a large $^3\Delta$, C_3 has a small $^3\Delta$. The same is true for furan-5-*d*. From these experimental results, a condition which can provide a large $^3\Delta$ is that a hetero atom (X) exists in a three-bond pathway (D–C–X–^{13}C).

To clarify the mechanism of $^3\Delta$, some aliphatic compounds were investigated. Three compounds, CD_3–X–Bu^n (X=CH_2, O, S), were selected. The $^3\Delta$ observed in this series are listed in Table 4. The order of $^3\Delta$ in this series is S>O>CH_2. Thus, $^3\Delta$ increases when a heteroatom, for example S or O, exists in its pathway. In the presence of heteroatoms, S and O, the values in Table 3 are twice as large as those in Table 4. It therefore must be noted that the presence of π-electrons in the systems is important, since they are effective regarding transmission over a long distance.

Another point is that heteroatoms have high electron densities. Two factors can therefore be considered for $^3\Delta$. First, the site two bonds apart from deuterium (namely heteroatom itself) has a high electon density. As a result, the transmitted shielding changes through the site should increase. Second, the site three bonds apart from deuterium (namely $^3\Delta$-observed carbon) has a low electron density. As a result, the transmittance to the site should decrease. Since the three-bond pathway has two positive and negative factors, $^3\Delta$ cannot be simply correlated with the electronegativities of the heteroatoms.

Table 4. One, Two, Three, and Four-Bond Deuterium Isotope Shifts of Several Aliphatic Compounds in ppb[a)]

Compound	$^1\Delta$	$^2\Delta$	$^3\Delta$	$^4\Delta$
CH_2D-CH_2-Bu$^{n\,\text{b)}}$	300.7	87.7	28.2	−5.6[d)]
CD_3-O-Bu$^{n\,\text{c)}}$	301	—	39	−4[d)]
CD_3-S-Bu$^{n\,\text{c)}}$	249	—	50	−12[d)]

a) Errors are estimated to be within 3 ppb. Measured for neat solution. b) Ref. 12. c) Per one deuteron atom. Synthesized by the Williamson's method using CD_3I. d) Deshielding shift.

Conclusion

One-bond isotope shifts on the ^{13}C NMR chemical shifts for aromatic heterocycles reflect the C–H bond lengths calculated by the MNDO MO method. Two-bond shifts depend on the nature of the observed sites. On the other hand, three-bond shifts are controlled by their pathways.

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References

1) For recent reviews see, a) P. E. Hansen, *Annu. Rep. NMR Spectrosc.*, **15**, (1983) 105; b) D. A. Forsyth, "Isotope in Organic Chemistry," ed by E. Buncel and C. C. Lee, Elsevier, New York (1984), Vol. 6, Chap. 1, p. 1; c) C. J. Jameson and H. J. Osten, *Annu. Rep. NMR Spectrosc.*, **17**, (1985) 1; d) S. Berger, "Isotope Effects in NMR Spectroscopy," ed by H. Günther, Springer, Berlin (1990), Vol. 22, p. 1; e) P. E. Hansen, *Prog. Nucl. Magn. Reson. Spectrosc.*, **20**, 207 (1988).

2) Y. Nakashima, A. Yoshino, and K. Takahashi, *Bull. Chem. Soc. Jpn.*, **62**, 1401 (1989).

3) Y. Nakashima, H. Nakane, S. Ban, and K. Takahashi, *Bull. Chem. Soc. Jpn.*, **63**, 2025 (1990).

4) Y. Nakashima, S. Ban, S. Itoh, and K. Takahashi, *Bull. Chem. Soc. Jpn.*, **64**, 3694 (1991).

5) Y. Nakashima and K. Takahashi, *Bull. Chem. Soc. Jpn.*, **64**, 3166 (1991).

6) G. Miyajima, K. Takahashi, and H. Sugiyama, *Org. Magn. Reson.*, **6**, 181 (1974).

7) "Advances in Organometallic Chemistry," ed by F. G. A. Stone and Robert West, Academic Press, New York (1964), Vol. 2, p. 365.

8) S. Berger and B. W. K. Diehl, *Magn. Reson. Chem.*, **24**, 1073 (1986).

9) R. H. Martin, J. Moriau, and N. Defay, *Tetrahedron,* **30**, 179 (1974).

10) S. Berger and H. Künzer, *Tetrahedron,* **39**(8), 1327 (1983).

11) H. Günther, H. Seel, and M. E. Günther, *Org. Magn. Reson.,* **11**, 97 (1978).

12) J. R. Wesener, D. Moskau, and H. Günther, *J. Am. Chem. Soc.,* **107**, 7307 (1985).

13) Mean "absolute" errors for optimized sp^2 C–H bond lengths were stated as 0.006 Å in Ref. 22. However, relative errors for analogous compounds such as those in this report will be smaller. For example, we obtained a good linear correlation between $\nu_{\text{C-D}}$ on IR and optimized C–H bond length for aromatic compounds.[16] Since there is a good correlation between $\nu_{\text{C-H}}$ and C–H bond lengths,[5,14] it is strongly supported that "relative" errors for optimized C–H bond lengths by the MNDO MO method will be small (ca. 0.003 Å).

14) D. C. Mckean, J. L. Duncan, and L. Batt, *Spectrochim. Acta, Part A,* **29**, 1037 (1973).

15) K. Nakanishi, P. H. Solomon, and N. Furutachi, "Infrared Absorption Spectroscopy," 17th ed, Nankodo, Tokyo (1978), p. 66.

16) A linear correlation coefficient=0.936, S.D.=0.0023 Å (N=10).

17) a) H. Batiz-Hernandez and R. A. Bernheim, *Prog. Nucl. Magn. Reson. Spectrosc.,* **3**, 63 (1967); b) K. L. Servis and F.-F. Shue, *J. Am. Chem. Soc.,* **102**, 7233 (1980).

18) S. Berger and B. W. K. Diehl, *Tetrahedron Lett.,* **28**, 1243 (1987).

19) C. J. Jameson, *J. Chem. Phys.,* **66**, 4983 (1977).

20) C. J. Jameson and H. J. Osten, *J. Chem. Phys.,* **81**, 4293 (1984).

21) $^1\Delta$ were cited from Ref. 12. C–H bond lengths were cited from Ref. 23 as below; ethane 1.094, ethylene 1.085, acetylene 1.059 Å.

22) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.,* **99**, 4907 (1977).

23) L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," the Chemical Society Special Publication No. 18, The Chemical Society, London (1965).

24) H. J. Osten, C. J. Jameson, and N. C. Craig, *J. Chem. Phys.,* **83**, 5434 (1985).

25) D. J. Sardella and Alyaa Emad El-Din, *Magn. Reson. Chem.,* **27**, 253 (1989).

26) In our experimental system, the linear correlation coefficient (r) is 0.454. When the data points for heteroaromatics and $C_5H_4D^-$ are excepted, r increases to 0.875 (N=12).