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Deuterium Isotope Effects on Aromatic Carbon-13 Chemical Shifts. II. Dependence of One- and Two-bond Isotope Shifts on Electron Densities of Substituted Benzenes

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One- and two-bond deuterium isotope effects ($^1\Delta$ and $^2\Delta$) on ^{13}C chemical shifts of substituted benzenes are reported. The one-bond effects are correlated with the π-electron densities on the observed carbons, and the two-bond effects are correlated with the σ-electron densities on the observed carbons. There are no correlations between $^1\Delta$ and $^2\Delta$. $^1\Delta$s reflect the direct change on going from a C–H bond to a C–D bond, but $^2\Delta$s reflect their indirect effect.

Deuterium isotope effects on ^{13}C chemical shifts are useful parameters for structural studies.[1] They are correlated with several physicochemical parameters. For example, long-range isotope shifts in deuteriomethylated compounds were described as the change of the hyperconjugational effect from CH_3 to CD_3.[2,3,4] For carbocations, Servis et al. described their isotope shifts as an isotopic perturbation of their canonical structures.[5] However, the origins of the isotope shifts have not yet been clarified. MO calculations, which assume the different average bond lengths for the C–H and the C–D bonds, can establish the sign of $^1\Delta$, but can not represent that of $^2\Delta$.[6,7] Further studies are necessary. We have shown that two-bond isotope shifts for the substituted phenols are correlated with the SCS values of the substituents of ^{13}C NMR.[8] In this study, about 40 one-bond isotope shifts ($^1\Delta$) are presented and discussed. $^1\Delta$ of the para-positioned carbons are correlated with their π-electron densities, while two bond isotope shifts ($^2\Delta$) are correlated with σ-electron densities on the observed carbons. These facts suggest that the origins, which contribute to $^1\Delta$, will be different from those of $^2\Delta$.

Experimental

The samples were selected for substituted phenols, anisoles, and anilines. Deuterium-labeled compounds were prepared with acid- or base-catalyzed proton–deuteron exchange-reactions of the selected substituted benzenes. Details were given in our previous report.[8] In the measurement of $^1\Delta$, broad signals were observed due to the quadrupole effect of the adjacent deuterium whose resolution was increased by measuring the spectra at a rather high temperature (80 °C). An example of our measurements is given in Fig. 1. As shown in Fig. 1, the line width at 80 °C is about half of that measured at 22 °C. Linear regression calculations of the experimental data were carried out on an NEC PC9801VX personal computer using a BASIC program.

Results and Discussion

Thirty-nine one-bond isotope shifts ($^1\Delta$) of twenty substituted benzenes were determined, which were ranged from 217 to 318 ppb. Two-bond isotope shifts ($^2\Delta$) were observed in seventy-six different sites, most of which have been reported previously.[8] The values observed ranged from 29 to 138 ppb. The data are given in Tables 1 and 2. The data observed for the unsubstituted benzene (283 and 111 ppb[9]) can be used as references for these substituted benzenes. The $^2\Delta$ values observed are smaller than that of benzene except for one which is observed for C_3 of 3-iodophenol. In the cases of $^1\Delta$, both larger and smaller values are observed for substituted benzenes as compared with

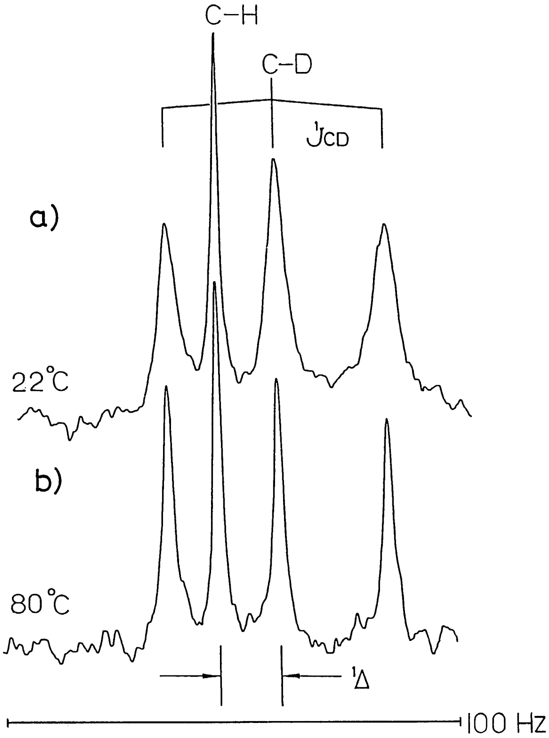

Fig. 1. ^{13}C NMR signals of C_2 or C_6 atoms of the products obtained from the proton–deuteron exchange reaction of 4-methylphenol in a neat liquid mixture. a) At 22 °C and b) at 80 °C.

Table 1. One-Bond Deuterium Isotope Effects ($^{1}\Delta$) on ^{13}C Chemical Shifts of Substituted Benzenes in ppb[a]

Substituent	Solvent	Observed carbon			
		C_2	C_3	C_4	C_6
1-OH	Neat	262		269	262
1-OH, 3-D	$CDCl_3$		272		
1-OH, 3-NH_3	0.10 wt% NaOH–D_2O	257		260	239
1,3-$(OH)_2$	0.10 wt% NaOH–D_2O	251		247	247
1-OH, 3-OMe	Neat	275		283	254
1-OH, 4-OMe	Neat	263	285		263
1-OH, 3-*t*-Bu	Neat	b)		280	b)
1-OH, 4-*t*-Bu	1,4-Dioxane	274			274
1-OH, 3,5-*t*-Bu_2	1,4-Dioxane	269		295	269
1-OH, 3-Me	Neat	287		285	258
1-OH, 4-Me	Neat	262			262
1-OH, 3-Cl	Neat	264		264	250
1-OH, 4-Cl	Neat	255			255
1-OH, 3,5-Cl_2	Neat	257		267	257
1-OH, 3-I	Neat	314		305	260
1-OH, 3-F	1.0 wt% NaOH–D_2O	217[c]		218[c]	251[c]
1-NH_2	Neat	278		259	278
1-OMe, 3-Me	Neat	318		293	296
1-Me	$CDCl_3$		280[d]	276[e]	
1-*t*-Bu	Acetone-d_6			278[e]	

a) Errors are estimated to be within 4 ppb. b) Signal is not available because lines overlapped. c) With large uncertainty. d) Ref. 9. e) Ref. 12.

Table 2. Two-Bond Deuterium Isotope Effects ($^{2}\Delta$) on ^{13}C Chemical Shifts of Phenols in ppb[a]

Substituent	Solvent	Observed carbon		
		C_1	C_3	C_5
3-I	Neat	48	138	111
4-I	$CDCl_3$	—	82	82
3-F	Neat	46	29	102

a) Errors are estimated to be within 5 ppb.

that of the unsubstituted benzene. Especially large values are obtained for 3-iodophenol. While, very small values are obtained for 3-fluorophenol. The observed isotope effects are different for iodine and fluorine which belong to the same column in the periodic table. Therefore, the effects can correlate simply to the electronegativity of the substituent.

On the other hand, it has been reported that $^{1}\Delta$ is dependent upon hybridization of the carbon atom.[10] Since all of the carbon atoms studied in this articles are in the sp^2 hybridization, the hybridization can not become a controlling factor of the $^{1}\Delta$ change, because the $^{1}\Delta$ observed spread over a wide range of 100 ppb. This range is nearly equal to a hybridization change from cyclohexane (sp^3: 418 ppb) to benzene (sp^2: 283 ppb).[11] Accordingly the $^{1}\Delta$ is considered to be controlled by factors other than hybridization.

Statistical Determination of SIS of $^{1}\Delta$. The method used in our previous report was applied to the analyses of the observed $^{1}\Delta$s. The contributions of various substituents to the one-bond isotope shifts were determined by linear regression analyses using an additivity equation similar to that used previously,[8]

$$^{1}\Delta = {}^{1}B_0 + n_i{}^{1}a + n_o{}^{1}b + n_m{}^{1}c + n_p{}^{1}d, \qquad (1)$$

where $^{1}B_0$ is $^{1}\Delta$ of unsubstituted benzene(cited as 283 ppd[9]). The SIS(Subsituent Isotope Shilft) parameters (^{1}a, ^{1}b, ^{1}c, and ^{1}d) are the contributions from ipso, ortho, meta, and para-positioned substituents, respectively. It is necessary that the SIS parameters determined for $^{1}\Delta$ must be differentiated from those previously determined for $^{2}\Delta$'s. For this purpose, we propose here that the SIS parameters of $^{n}\Delta$ can conveniently be represented as ^{n}a and ^{n}b, where n_i, n_o, n_m, or n_p is a weight factor for each substituent parameter. Details of the calculations were described in our previous report.[8]

The experimentally observed values given in Tables 1 and 2, and Table 1 of Ref. 8 are used to evaluate the SIS parameters for each substituent. The SIS parameters obtained for nine substituents are given in Table 3. $^{1}B_0$ can be calculated from the regression analyses using the experimental $^{1}\Delta$ values at 80 °C. The calculated $^{1}B_0$ (283.4 ppb) is consistent with the observed value (283 ppb[9]) at room temperature. Therefore, the temperature effect for $^{1}\Delta$ seems to be negligibly small. The observed one-bond isotope shifts can be well-expressed by Eq. 1 using the SIS values of $^{1}\Delta$, with an RMS error of 3.0 ppb and a correlation coefficient of 0.995. The present SIS's of $^{1}\Delta$ for the CH_3 group are consistent with those reported by Berger and Diehl.[9] The values for the para-substituents, namely ^{1}d's are also consistent with those

Table 3. Statistical Parameters for Eq. 1

Substituent	SIS ($^1\Delta$)[a]			SIS ($^2\Delta$)[b]			
	^1b	^1c	^1d	^2a	^2b	^2c	^2d
H	0	0	0	0	0	0	0
F	−47.8	—	−14.0	−78.5	—	−2.9	—
OH	−18.5	−12.3	−17.8	−64.7	−3.0	−3.5	0
OMe	14.7	−2.0	−10.9	−60.2	−6.5	2.7	0
NO_2	—	—	—	−46.5	−3.5	−1.4	0
NH_2	−6.4	—	−25.2	−44.5	—	−3.4	—
t-Bu	14.1	9.0	−7.8	−41.5	−6.8	−6.9	0
Me	20.4	−3.2	−5.5	−22.7	−4.1	0.2	0
Me[c]	23.7	−0.9	−7.4	−26.4	−5.5	0	0
Cl	0.5	−10.0	−11.7	−19.7	−9.5	0.7	0
I	44.2	—	−5.0	30.5	−25.5	2.6	0
	$^1B_0=283.4$			$^2B_0=111$ (const.)			

a) RMS error=3.0 ppb. Linear correlation coefficient between experimental and calculated data=0.995. Standard deviation=2.1 ppb. b) RMS error=4.3 ppb. Linear correlation coefficient between experimental and calculated data=0.992. c) Ref. 9.

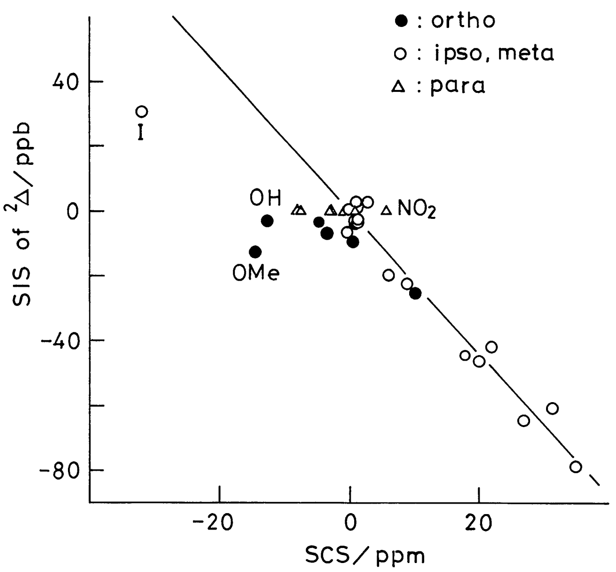

Fig. 2. Correlation between the SIS and SCS values of the ^{13}C NMR determined for substituted benzenes. A correlated straight line is expressed as SIS(ppb)= −2.18 SCS(ppm)−0.181 with $r=0.982$ and the standard deviation of 5.3 ppb when only white circles are used except for a point of ipso-positioned I.

reported by Berger and Diehl.[12)] No correlation exists between the SIS's of $^1\Delta$s and $^2\Delta$s.

The origins of the isotope shifts were partly attributed to the different vibrations based on a change from the C–H bond to the C–D bond.[1a,13)] As already reported,[8)] SIS's of $^2\Delta$ are strongly correlated with the SCS values of the carbons, as shown in Fig. 2. Both the SIS's and the SCS's are linearly correlated with each other at ipso and meta positions. A correlated straight line is given in Fig. 2. The deviation of the data points given by black-filled circles and triangles are downward from the straight line except for that of the para position of an NO_2 group. They give shielding effects to the ^{13}C chemical shifts except for the NO_2 group.[10)] The deviation which appeared in Fig. 2 can be explained by assumig no contribution from the resonance effects of the substituents. For, while the SCS values are affected by the resonance effects of the substituents, the SIS values are not affected by them.

As given in Fig. 3, SIS's of $^2\Delta$ can be well-correlated with the change of σ-electron densities on the observed carbons. The electron densities were cited from two reports in which they were calculated by the CNDO/2 method.[14,15)] The correlation suggests that $^2\Delta$ are induced by transmitting a shielding change of the α-carbon. That is to say, $^2\Delta$ are interpreted as a result of increased inductive electron release. Osten et al. called this mechanism "a secondary shielding change with a primary bond length change".[16)] One of the SIS's, ^1d can be well-correlated with change of π-electron densities, as shown in Fig. 4. The correlated straight line has a positive slope. This is opposite in sign to the case of $^2\Delta$. Therefore, the higher the π-electron density is, the smaller is the $^1\Delta$. If the C–H bond is already polarized by electron release of the substituent,[9)] SIS's of $^1\Delta$ will have negative values consistent with those presented in Table 3.

Conclusion

One-bond isotope shifts for the substituted benzenes are represented additively by three parameters assigned to each substituent. Among the three parameters, ^1d's are correlated with π-electron densities on the observed carbons with positive slope. On the other hand, SIS's of $^2\Delta$ for the subsituted benzenes are correlated with the σ-electron densities on the observed carbons with negative slope. There are no correlation between $^1\Delta$ and $^2\Delta$. $^1\Delta$ on the benzene ring carbons are dominated by the π-polarization effects originated by the substituents on the observed carbons. $^2\Delta$ are interpreted as a result of increased inductive electron release by the

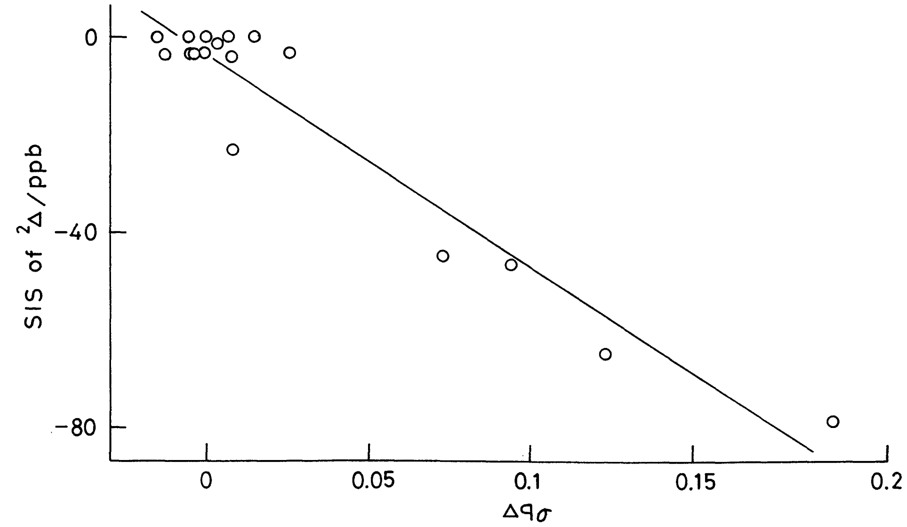

Fig. 3. Correlation between SIS($^{2}\Delta$) and $\Delta q_{\sigma}=q_{\sigma}-q_{\sigma}(C_6H_6)$ for substituted benzenes. A correlated straight line is expressed as SIS($^{2}\Delta$)$=-427\Delta q_{\sigma}-4.35$ with $r=0.966$ and the standard deviation of 6.8 ppb.

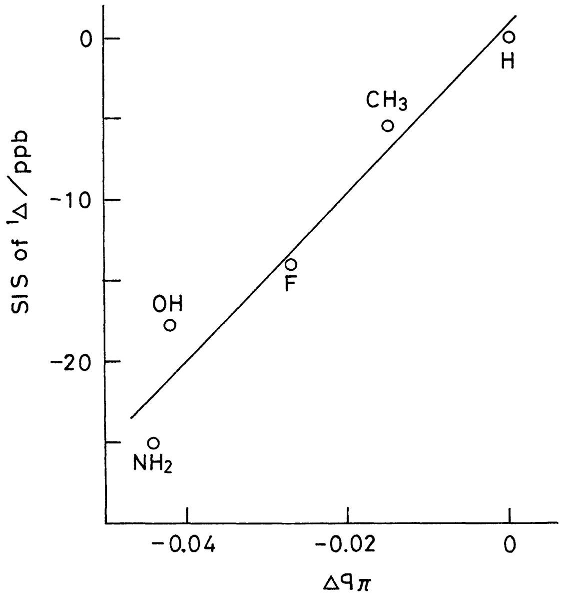

Fig. 4. Correlations between SIS($^{1}\Delta$) and $\Delta q_{\pi}=q_{\pi}-q_{\pi}(C_6H_6)$ for substituted benzenes. A correlated straight line is expressed as SIS($^{1}\Delta$)$=517\Delta q_{\pi}+0.796$ with $r=0.967$ and the standard deviation of 2.9 ppb.

α-carbon (C–D bond carbon).

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