May, 1982] © 1982 *The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, ***55***, *1665—1666 (1982)* 1665

^{13}C and ^{19}F Chemical Shifts Induced by C–H···Base Hydrogen Bonding. Particular Polarizations of C–Halogen and C=C Bonds

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(Received September 21, 1981)

Synopsis. The ^{13}C and ^{19}F chemical shifts induced by C–H···Base hydrogen bonding were measured for dichlorofluoromethane, chloroform, pentachloroethane, and trichloroethylene. These chemical shifts were shown to be linear using the β scale of hydrogen-bond acceptor basicities proposed by Kamlet and Taft. The analysis of the linear solvation energy relationships reveals that the particular polarizations of the C–halogen and C=C bonds play an important role in the C–H···Base hydrogen-bond formation.

The participation of C–H groups of haloforms in hydrogen bonding has been recognized for a long time.[1)] The C–H hydrogen bonds with bases (C–H···Base hydrogen bonds) have been extensively investigated by means of IR and ^{1}H NMR spectroscopies. However, comparatively little attention has been paid to the chemical shifts of other nuclei.

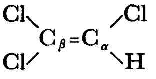
Here, we wish to report on the ^{13}C and ^{19}F chemical shifts of haloforms and related compounds induced by the C–H···Base hydrogen bonding. The mode and mechanism of the inductive electronic effects will be discussed on the basis of the linear solvation energy relationships between the observed chemical shifts and the β scale of the hydrogen-bond acceptor basicities.

Results and Discussion

The ^{13}C chemical shifts of **1**—**4** and the ^{19}F chemical shifts of **1** were measured in a variety of solvents which can act as proton acceptors (Table 1). The β scale for the solvents listed in Table 1 is the measure of the hydrogen-bond acceptor basicities recently proposed by Kamlet and Taft.[2)] Both the ^{13}C and ^{19}F chemical shifts are very sensitive to the change in solvent. In order to clarify the origin of the solvent shifts observed, the concept of the linear solvation energy relationship (LSER)[3)] is applied to these chemical-shift data. Then, a good LSER is obtained for each compound [$\delta(\text{ppm}) = (\text{slope})\beta + (\text{intercept})$].[4)] Table 2 summarizes the magnitudes and signs of the slopes for these LSER's. The success of the LSER means that both the ^{13}C and ^{19}F chemical shifts are mainly controlled by the strength of the C–H···Base hydrogen bonds. Since the corresponding fully halogenated compounds were used as internal references, other solvent effects should be largely canceled out.[5)]

$Cl_2FC\text{-}H$ $Cl_3C\text{-}H$ $Cl_3C_\beta\text{-}C_\alpha Cl_2\text{-}H$

1 **2** **3**



$\mathrm{Cl_2C_\beta{=}C_\alpha(Cl)H}$

4

An inspection of the chemical-shift data (Table 1) shows that the C–H···Base hydrogen-bond formations induce downfield shifts of the C_α–(H) atoms of **1**—**4**. This observation is consistent with those of Morishima *et al.*[6)] and Lichter and Roberts.[7)] However, no definite information about the behavior of halogen atoms and carbon atoms other than C_α in such hydrogen bonding has yet been established.

As is shown in Table 2, the magnitudes and signs of the slopes for the LSER's are characteristic of each carbon atom of each compound. The slope is related to the sensitivity to the inductive electronic effects, and the (+) and (−) signs of the slopes should correspond to the positive and negative charge densities induced on the carbon (or the fluorine) atom respectively. Therefore, the magnitudes and signs of the slopes serve as a probe for studying the mode and mechanism of the transmission of the inductive electronic effects.

For **1**, it should be noted that the sign (+) of the slope for the carbon atom is opposed to that (−) for the fluorine atom, thus suggesting the existence of the $\overset{+}{C}\text{–}\overset{-}{F}$ bond polarization. According to a recent theoretical study on hydrogen bonds,[8)] the C–H···Base hydrogen bond is well represented by this electrostatic model:

$$\underset{(1)}{C\text{–}H\cdots \text{Base}} \longleftrightarrow \underset{(2)}{\overset{-}{C}\!:\ \overset{+}{H}\!:\ \text{Base}}$$

The observed ^{13}C downfield shifts seem to be incon-

TABLE 1. ^{13}C CHEMICAL SHIFTS[a)] OF **1**—**4** AND ^{19}F CHEMICAL SHIFTS[a)] OF **1** IN VARIOUS SOLVENTS

Solvent β Scale		Anisole 0.247	Dioxane 0.368	Acetone 0.499	Cyclohexanone 0.534	DMF 0.710	DMSO 0.752	HMPA[b)] 0.990
1	^{13}C	−13.59	−13.01	−12.75	−12.89	−11.98	−11.95	−11.28
	^{19}F	−80.35	−80.55	−80.70	−80.81	−80.84	−81.07	−80.93
2	^{13}C	−19.39	−18.45	−17.90	−17.50	−16.95	−16.40	−15.36
3	^{13}C(α)	−17.13	−16.80	−16.25	−16.10	−15.49	−15.91	−15.54
	^{13}C(β)	+2.86	+3.26	+3.68	+3.90	+4.08	+4.08	+4.51
4	^{13}C(α)	−3.66	−3.30	−2.70	−2.50	−2.07	−1.71	−0.36
	^{13}C(β)	+2.80	+2.43	+2.48	+2.62	+2.19	+1.88	+1.16

a) The (+) and (−) signs indicate the downfield and upfield shifts from the internal reference respectively. b) Hexamethylphosphoric triamide.

TABLE 2. MAGNITUDES AND SIGNS OF SLOPES IN LINEAR SOLVATION ENERGY RELATIONSHIPS

	1		**2**	**3**		**4**	
	^{13}C	^{19}F	^{13}C	^{13}C(α)	^{13}C(β)	^{13}C(α)	^{13}C(β)
Slope	+3.21	−1.11	+5.41	+2.32	+2.31	+4.46	−2.40
r[a]	0.988	0.872	0.994	0.953	0.965	0.988	0.930

a) Correlation coefficient.

sistent with the structure (2) having a localization of electrons on the carbon atom. Lichter and Roberts[7] reported that the ^{13}C downfield shifts for chloroform hydrogen-bonded with bases are attributable to the change in the average distance of bonding electrons in the C–H bond of chloroform. Here, we wish to propose a new concept of bond polarizations to explain the electronic structure in the hydrogen-bonded systems. The electronic structure of **1** can be explained by assuming that the localized electrons on the carbon atom are transmitted through the $\overset{+}{\mathrm{C}}\text{–}\overset{-}{\mathrm{F}}$ bond polarization onto the fluorine atom, thus resulting in the ^{13}C downfield and ^{19}F upfield chemical shifts. Furthermore, the holding of the LSER shows that the degree of the $\overset{+}{\mathrm{C}}\text{–}\overset{-}{\mathrm{F}}$ bond polarization increases with the increase in the strength of the hydrogen bonding.

Similar ^{13}C downfield shifts are observed for **2**; they can also be interpreted in terms of the $\overset{+}{\mathrm{C}}\text{–}\overset{-}{\mathrm{Cl}}$ bond polarization. However, the magnitude of the slope for **2** is larger than that for **1**. This experimental result can be nicely explained by the fact that the longitudinal polarizability[9] of the C–Cl bond (3.2×10^{-24} cm^3) is larger than that of the C–F bond (1.2×10^{-24} cm^3); hence, the carbon atom of **2** becomes more positive than does that of **1**.

For **3**, both the C_α and C_β atoms show the positive sign arising from the $\overset{+}{\mathrm{C}}\text{–}\overset{-}{\mathrm{Cl}}$ bond polarization. The small slope for the C_α atom is attributable to the smaller polarizability of the C–C bond (0.99×10^{-24} cm^3).[9] On the other hand, the slope for the C_β atom is larger than that which might be predicted from a simple attenuate transmission mode of the inductive effects in the C_α–C_β saturated bond. However, the polarization effect of three C–Cl bonds reinforces the positive charge on the C_β atom; this makes the magnitude of the slope larger than expected.

In the system containing the C_α=C_β bond, **4**, the sign of the slope for the C_α atom is opposite to that for the C_β atom. This sign alternation can be attributed to the polarization of the $\overset{+}{\mathrm{C}}_\alpha\text{=}\overset{-}{\mathrm{C}}_\beta$ bond, because the C=C bond is significantly more polarizable (2.8×10^{-24} cm^3)[9] than the C–C bond. At the same time, the $\overset{+}{\mathrm{C}}_\beta\text{–}\overset{-}{\mathrm{Cl}}$ bond polarization should be considered; it will partially reduce the negative charge induced on the C_β atom. In fact, this idea agrees well with the experimental result.

Experimental

The ^{13}C spectra were obtained under proton-decoupled conditions in the pulse FT mode at 25.03 MHz (45° pulse width of 10 μs; 8 K data points; resolution of 0.06 ppm) with a JEOL PS-100 spectrometer. The ^{19}F spectra were measured with the same spectrometer operating at 94.10 MHz in the frequency sweep mode with an external lock. The ^{13}C and ^{19}F chemical shifts of **1**, **2** and **3**, and **4** were determined with reference to internal $CFCl_3$, CCl_4, and Cl_2C=CCl_2 respectively. The concentration of the sample was *ca.* 1.5 M.[10]

The authors are indebted to Dr. T. Satokawa of Daikin Industry Co., Ltd, for a gift of dichlorofluoromethane.

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3) Recently, Kamlet and Taft have reported a number of successful applications of LSER's to the problems of solvent effects in organic chemistry; *e.g.*, R. W. Taft, J. M. Abboud, and M. J. Kamlet, *J. Am. Chem. Soc.*, **103**, 1080 (1981).

4) These ^{1}H chemical shifts also show rough correlations in the LSER's. The deviations from the correlations are attributable to the solvent anisotropy.

5) In fact, the lack of any correlation between our chemical-shift data and the solvent parameter, $(\varepsilon-1)/(\varepsilon+1)$, indicates that the reaction field effect is not a major contribution to the origin of the solvent shift.

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10) At this concentration, the solute-solute interaction may occur. The slope in the LSER increases slightly with the decrease in the solute concentration, but the trend is almost the same.