

The Substituent-induced Carbon-13 Chemical Shifts in the 2-Substituted Fluorenes.

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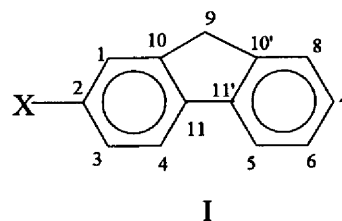
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Abstract

The carbon-13 NMR chemical shifts for thirteen 2-substituted fluorenes have been measured in chloroform-*d* at 100 MHz. The substituent induced chemical shifts (SCS) for C_{11'} showed an inversed trend where as SCS for C₇ exhibited normal trend in the sense of the substituent electronic effect. These phenomena are as good as those observed for the SCS of the corresponding carbons of the 4-substituted biphenyls. The π electrons of the remote benzene ring were polarized by the charge of the substituted phenyl moiety.

It is well known that the substituent-induced chemical shifts of the ring carbons of *m*- and *p*-substituted benzenes are predicted by the substituent electronic effect and related to the Hammett substituent constants and to the carbon electron-densities. The direction of the ¹³C chemical shifts of side-chain bearing the π -electrons, however, exhibits a different trend. SCS for C α of *p*-substituted styrenes,¹⁾ *p*-substituted phenylethyne,²⁾ and *p*-substituted phenylacetonitriles^{3,4,5)} shows an inverse trend (i. e. electron-attracting groups such as NO₂ lead a high field shift), while SCS(C β) shows a normal trend. The most important interaction causing such SCS trends is a partial π -polarization of the multiple bond.^{6,7)} The direct resonance perturbation through *p*-phenylene is small because of the unstable cumulate character of the polarized canonical form. E. M. Schulman and co-workers determined ¹³C chemical shifts of 4-substituted biphenyls and found that SCS (C_{1'}) showed an inverse trend, due to the π polarization of the remote benzene ring to the substituent.⁸⁾ In this paper, we report the ¹³C-SCS of the 2-substituted fluorenes (I) which have a coplanar structure.

The obtained ¹³C-SCS of I are summarized in Table 1. An inspection of the Table 1



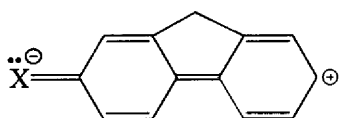
reveals that the SCS for the carbons of the XPh group is similar to the substituted benzenes. It is interesting that the C_{11'}-SCS exhibits an inverse trend for the electron-attracting groups with resonance. This trend is not expected by the ionic canonical form II. C₇ showed a normal trend for both the electron-attracting groups and the electron-donating groups. These results are as good as the SCS of the corresponding position of the 4-substituted biphenyls which is an twisting molecule in solution. It is evident that the π -electron framework of the remote ring from the substituent suffers the polarization induced by the charge in the XPh moiety in the 2-substituted fluorenes as shown by the scheme IV where as the two benzene rings take a coplanar structure as mentioned above and accept more easily the contribution of the resonance effect than the twisted 2-substituted biphenyls do. The electron-donating groups by resonance such as the methoxyl group

Table 1. The carbon-13 substituent induced chemical shifts of 2-substituted fluorenes measured in chloroform-*d* .^a

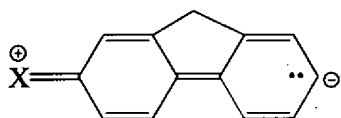
Subst.	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	C _{10'}	C ₁₁	C _{11'}
H	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	124.98 ^b	126.67 ^b	126.67 ^b	119.84 ^b	119.84 ^b	126.67 ^b	126.67 ^b	124.98 ^b	36.89 ^b	143.18 ^b	143.18 ^b	141.68 ^b	141.68 ^b
NH ₂	-13.23	19.04	-12.75	0.74	-1.32	-0.09	-1.65	-0.29	-0.13	1.92	-1.09	-8.75	0.53
OH	-12.78	28.26	-12.61	0.83	-0.83	0.05	-1.03	-0.14	-0.04	2.17	-0.59	-6.73	-0.15
CH ₃ O	-14.40	32.59	-13.73	0.67	-0.79	0.05	-1.10	-0.15	0.12	1.88	-0.51	-6.92	-0.01
NHCOCH ₃	-7.98	11.38	-7.95	-0.39	0.16	0.04	-0.40	-0.06	0.06	1.06	-0.06	-4.98	-0.45
Br	3.22	-6.24	3.17	1.22	0.06	0.24	0.42	0.03	-0.18	1.98	1.57	-1.03	-1.02
COOH	2.76	8.92	1.34	1.02	-0.21	-1.43	0.38	-0.05	-0.03	1.32	0.10	4.74	-1.22
CHO	0.77	8.35	2.98	1.20	0.20	0.43	1.67	0.26	-0.13	1.44	0.44	6.14	-1.48
CH ₃ CO	-0.16	8.85	0.96	0.93	-0.31	0.31	1.26	0.17	-0.12	1.24	0.02	4.62	-1.30
COOCH ₃	1.34	2.10	2.00	1.00	-0.23	0.42	1.30	0.31	0.00	1.24	-0.03	4.66	-1.00
CO ₂ C ₂ H ₅	1.19	2.21	1.97	0.90	-0.35	0.31	1.17	0.22	-0.08	1.15	-0.16	4.47	-1.04
CN	3.56	-17.09	4.43	1.06	0.45	0.57	1.85	0.26	-0.20	0.65	0.38	4.46	-1.86
NO ₂	-4.63	20.02	-3.60	1.39	-0.10	0.67	2.11	0.34	-0.03	1.55	0.65	6.28	-2.32

a: Positive values represent downfield shifts.

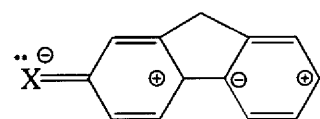
b: The values are chemical shifts from TMS.



II



III



IV

do not afford a remarkable influence to the C_{11'}-SCS but to the C₇-SCS. Thus, the electron-donating groups do not cause the polarization for the π -framework of the second ring. It appears that the resonance effect contributes to the C₇-SCS as shown in II and III.

It is well established that the contribution of the polar effect of the X to ¹³C-SCS is strictly

analyzed by the application of the linear substituent free energy (LSFE) equation presented by Yukawa and Tsuno.⁹⁾

$$\text{SCS} = \rho_i \sigma_i + \rho_{\pi}^+ \sigma_{\pi}^+ + \rho_{\pi}^- \sigma_{\pi}^-$$

Here, σ_i is the inductive substituent constant; σ_{π}^+ and σ_{π}^- are substituent constants which measure the capability of substituents to either donate or withdraw electrons by resonance effect, respectively. The results of an LSFE analysis carried out for the C_{11'}-SCS and C₇-SCS are as follows. The bromo-substituent was excluded since the SCS for halogen substituents were larger than those expected from the usually observed electronic effect.

$$\text{SCS}(C_{11}') = -3.3\sigma_i - 4.03\sigma_{\pi}^-, \quad r = 0.991,^{10)} \quad s = 0.087^{11)}$$

(Subst: CHO, CH₃CO, CO₂CH₃, CO₂C₂H₅, CN, and NO₂)

An excellent correlation ($r = 0.991$) was obtained for this carbon. The ρ_i and ρ_{π}^- values are negative and the absolute values are larger than those observed for the C α -SCS of *p*-substituted styrenes (2.22 and 1.81 respectively).¹²⁾ Thus, six π electrons of the second ring of the 2-substituted fluorenes are strongly polarized relative to the double bonding of the *p*-substituted styrenes.

$$\text{SCS}(C_7) = 1.77\sigma_i + 4.24\sigma_{\pi}^+ + 3.74\sigma_{\pi}^- - 0.03, \quad r = 0.998, \quad s = 0.117$$

(subst: H, OH, CH₃, NH₂, CHO, CH₃CO, CO₂CH₃, CO₂C₂H₅, CN, and NO₂).

The r values of 0.998 and the positive values of ρ_i , ρ_{π}^+ , and ρ_{π}^- for this carbon revealed that the correlation was an excellent one and the resonance effect contributed to the SCS for the most remote site as shown in scheme II and III.

The SCS for the C_5 , C_6 , and C_8 are small and a remarkable trend from the substituent was not found.

2-substituted fluorenes were obtained commercially except for the ethoxycarbonyl derivative (mp 77°C) which was prepared by the ethanolysis of the corresponding chloride, itself obtained by the chlorination of the fluorene-2-carboxylic acid using thionyl chloride. The carbon-13 nuclear magnetic resonance spectra were recorded on a JEOL Lambda 400 spectrometer at 100 MHz in chloroform- d at 27°C. The identifications of the spectra were made by the ^1H - ^{13}C two dimensional spectra. The typical ^{13}C NMR measurement was carried out under following conditions: concentration of the sample, 10% (W/V); tube bore, 5 mm; pulse length, 6.00 μs ; pulse delay, 1.79 μs ; number of data points, 32768; spectral width, 27100; digital resolution, 0.83 Hz; number of

scans, 2000.

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【要旨】 2-置換フルオレンの炭素-13核磁気共鳴スペクトルにおける置換基効果: 2-置換フルオレンの炭素-13核磁気共鳴(NMR)スペクトルを測定し、2-位の置換基による化学シフト(SCS)を決定した。 C_{11} -SCSはニトロ基に代表される電子求引性共鳴基により高磁場シフトした(逆置換基効果)。一方 C_7 -SCSは低磁場シフト(通常の置換基効果)したことから、第2のベンゼン環(置換基から遠い方)の π 電子が強く分極していることが明らかになった。電子供給共鳴基による C_{11} への効果は小さいが、 C_7 に対しては明らかに高磁場シフトすることから、この炭素に対しては C_{11} (1-置換ベンゼンの p -位に相当)と同様に共鳴効果も寄与していることが実証された。