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AN ORIGIN FOR NONEQUIVALENCY OF CARBONS CONSTITUTING ROTATIONAL AXES IN ^{13}C NMR SPECTRA: A CASE OF ROTAMERIC 9-(o-ALKYLPHENYL)FLUORENES

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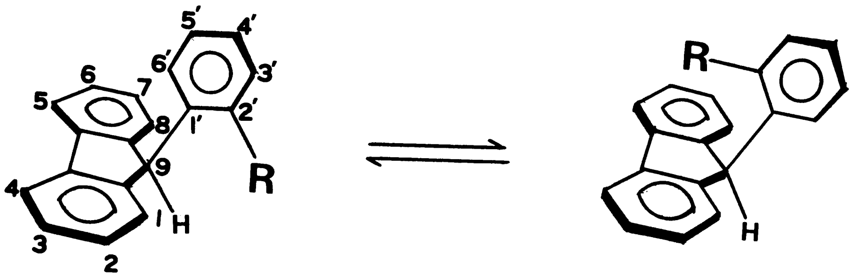
The difference in chemical shifts of 9-C in ap and sp forms of 9-(o-alkylphenyl)fluorenes increases as the size of the alkyl groups increases. The change in the difference is correlated with $^{1}J_{CH}$ and is discussed on the ground of bond angle deformation.

Although there have been scattered literatures1) which report nonequivalence of tetrahedral carbons constituting the rotational axes in ^{13}C NMR spectroscopy, none discusses thoroughly the origin for the nonequivalency. Chemical shifts of carbons in nuclear magnetic resonance may be determined, in principle, by the electron density, geometry of the extending bonds, and magnetic anisotropy of atoms or groups in proximity. Since the first factor is not dominant if we discuss the chemical shifts of nuclei in rotational isomers, the remaining two should play important roles. We wish to report a finding which clearly indicates that geometry of four bonds extending from a carbon has some role in determining the chemical shifts of carbons of 9-(o-alkylphenyl)fluorenes in ^{13}C NMR spectroscopy.



sp

ap

9-(o-Alkylphenyl)fluorenes were prepared by the Grignard reaction of 9-fluorenone with arylmagnesium halides followed by reduction with hydriodic acid.$^{2)}$ Although these compounds generally exist as a mixture of ap and sp forms on the NMR time scale,$^{3)}$ the ap form of (2-tert-butylphenyl)fluorene had to be prepared by protonation of the corresponding fluorenide anion because of its unfavorable steric conditions. The ap form of the tert-butyl compound was found to isomerize to the sp form gradually at 0°C: in the equilibrium state, it was not possible to detect any of the ap form at room temperature. Assignment of the conformation is straightforward if one considers the structural features of the conformers. The ap form possesses the alkyl group in 2'-position of the 9-aryl over the fluorene ring whereas the proton in 6'-position is located within the plane of the fluorene ring. Thus a combination of a high alkyl and a low 6'-H signal must be the feature of ^{1}H NMR spectra of the ap form. The oposite is expected for the sp form. The assigned structure and ^{1}H NMR data are listed in Table 1 together with some ^{13}C NMR data.

Assignement of ^{13}C NMR signals can be performed by taking the populations determined by ^{1}H NMR spectra into account, although the aromatic region was too complicated to assign. From the data shown in Table 1, we can point out a few characteristics.

9-C's give two distinct signals corresponding to sp and ap forms. The bulkier is the alkyl group, the larger is the difference in the chemical shift of the two 9-C signals. The increasing size of the alkyl group decreases the ^{13}C-^{1}H coupling constants of the 9-C of the ap form. Since the magnitude of ^{13}C-^{1}H coupling constant is correlated to s-character of the C-H bonding orbital,$^{4)}$ the decrease can be taken as an indication of the increase in p-character of the C-H bonding orbital. This may be caused by widening any of the C-C-C angles at 9-C but bending of the C_9-C_{ar} bond outwards from the fluorene ring will be most reasonable: such deformation will relieve severe steric strain caused by the alkyl group and the fluorene ring. Thus a most probable reason for the splitting of the carbon signal

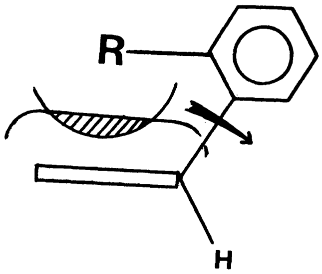


Table 1 NMR Spectral Data of Rotameric 9-(o-Alkylphenyl)-fluorenes in $CDCl_3$ (δ from TMS)a)

Alkyl Group		^{1}H NMRb)			^{13}C NMRc)			
		CH_3	9-H	6'-H	CH_3	9-C	Other Aliphatic C	$^1J_{CH}$ of 9-C (Hz)
CH_3	sp	2.63	5.30	6.38	20.33	49.79		127.6
	ap	1.13	4.90	——d)	18.28	55.96		125.1
$(CH_3)_2CH$	sp	1.46	5.42	6.33	24.39	48.90	29.42	127.6
	ap	0.47	4.87	——d)	23.13	56.33	28.04	122.7
$(CH_3)_3C$	sp	1.72	6.85	6.22	32.55	50.97	35.54	127.2
	ap	0.71	5.19	——d)	31.94	59.66	36.61	115.4

a) Temperature was 0°C for the methyl compound and was -50°C for the ap form of the t-butyl compound. Others were obtained at room temperature.

b) Obtained with a Hitachi R 20B spectrometer.

c) Obtained with a JEOL FX-60 spectrometer.

d) Hidden by other aromatic proton signals at δ 7.6 ∿ 8.0.

is the change in hybridization of orbitals due to the steric effect. Appearance of the 9-C signals of ap forms at a lower field relative to those of the sp supports this interpretation: increasing the bond angle should lead to a low field shift as is seen in the change from sp^3 to sp^2 carbons.

Another point which deserves comment is the difference in chemical shifts of the methyl carbons of alkyl groups in 2'-position of the aryl group: the signals of ap forms consistently appear at higher magnetic fields than those of sp forms. The results may be attributed to the ring current effect of the benzene ring of the fluorene group. The fact that the differences become smaller by going from methyl to isopropyl and then to t-butyl may be taken as a reflection of the averaged distance of the carbon from the benzene ring. Although the ring current effect on the ^{13}C NMR spectrum is evident in macrocyclic aromatic systems,5) it is of minor importance in benzene derivatives under normal conditions.6) The data presented here suggest that the ring current effect in ^{13}C NMR spectra can be seen to a small extent even in benzene derivatives if a carbon is compressed closely enough to a benzene ring.

References and Note

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