the benzyl alcohol. Since the ketone rapidly polymerizes, the alcohol should be oxidized and the product ketone **7** distilled and used immediately.

(9) The general ethylation–reduction procedure used was the same as is described in the Experimental Section for compound **8**, except that ethyllithium was generated in situ, from freshly distilled ethyl bromide and excess lithium, in ether. Yield of **15:** 98% (isolated).

(10) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, pp 55–127.

(11) (a) W. R. Woolfenden and D. M. Grant, *J. Am. Chem. Soc.*, **88**, 1496 (1966); (b) D. M. Grant and B. V. Cheney, *ibid.*, **89**, 5315 (1967).

(12) Reference 10, p 98.

(13) Reference 10, p 58.

(14) G. A. Olah, P. W. Westerman, and J. Nishimura, *J. Am. Chem. Soc.*, **96**, 5348 (1974).

(15) J. I. Kroschwitz, M. Winokur, H. J. Reich, and J. D. Roberts, *J. Am. Chem. Soc.*, **91**, 5928 (1969).

(16) W. B. Jennings, *Chem. Rev.*, **75**, 307 (1975).

(17) The ir spectra were determined with a Beckman Model IR-10 infrared recording spectrophotometer. The ^{1}H NMR spectra were determined at 60 MHz with a Varian Associates Model T-60 NMR spectrometer or with a Hitachi Perkin-Elmer Model R-24A NMR spectrometer, and at 100 MHz with a JEOL Model JNM-PS-FT-100 fast Fourier transform NMR spectrometer. The chemical shift values are expressed in δ values (parts per million) relative to a Me$_4$Si internal standard. ^{1}H NMR samples were run with and without Me$_4$Si. The mass spectra were determined with an AEI Model MS-30 mass spectrometer (70 eV) to which was interfaced a Pye Unicam Model 104 gas chromatograph.

(18) The ammonium chloride is most conveniently introduced by attaching a glass bulb tube filled with the salt to a side arm by means of tygon tubing. When the ammonium chloride is to be added, the bulb is raised and tapped gently to smoothly introduce the quenching agent. Should this step start to become violent, the addition and sometimes even the vigorous stirring should be momentarily stopped to avoid an eruption.

The Electronic Effect of Substituted Methyl Groups. A Carbon-13 Nuclear Magnetic Resonance Study

William Adcock*[1] and B. D. Gupta

School of Physical Sciences, Flinders University, Bedford Park, S.A. Australia

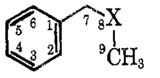
William Kitching

Department of Chemistry, University of Queensland, Brisbane, Australia

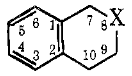
Received November 12, 1975

The ^{13}C NMR spectra of a large number of stereochemically well-defined model compounds possessing heteroatoms have been obtained and assigned. An analysis of the data provided the following conclusions: (1) hyperconjugative π-polarization is an important component of the net electronic effect of –CH$_2$X groups in the neutral ground state; (2) polar field effects play an important role in determining aryl ^{13}C chemical shifts; and (3) the γ shielding effect of second-row heteroatoms is a very general phenomenon.

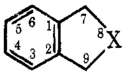
In order to assess the relative importance of the possible modes of action of substituents in unsaturated systems (polar and π-electron effects) it is necessary to study a series of stereochemically well-defined model systems in which the capacity for the transmission of the electronic effects may be varied systematically. Recently, ^{19}F NMR studies[2,3] have shown that model systems **1**, **2**, and **3** are of value in this regard



1



2



3

since here the CX σ bond is constrained to a varying degree to the nodal plane of the adjacent π system, thus allowing the possible assessment of the relative importance of polar (field-inductive and σ-inductive), π-inductive (inductomesomeric), and mesomeric or resonance (hyperconjugation) effects of substituted methyl groups (vide infra).

In an earlier paper[4] we described a ^{13}C chemical shift study of systems **1**, **2**, and **3** [where X = Si(CH$_3$)$_2$] which helped to confirm our previous conclusions[2] regarding the importance of metallohyperconjugation in the neutral ground state. Here we report an extension of our ^{13}C NMR studies of these systems to situations where X is an electronegative element or group (NH, NCH$_3$, CO, O, CF$_2$, S, and SO$_2$). The basic objectives in this investigation were threefold. Firstly, we wanted to substantiate our recent proposals[3] regarding the electronic behavior of –CH$_2$X substituents where X is electronegative: namely, that hyperconjugative electron withdrawal involving the CX σ bond is an important mode of interaction of these groups in the neutral ground state. Secondly, we wanted to examine the effect of pure polar contributions (field-inductive or electrostatic-field effects) on aryl ^{13}C chemical shifts. Previously, this has been prevented because of the difficulty of separating polar and π-electron effects in unsaturated systems where the substituent (X) is directly attached to the substrate, as well as a lack of suitable model compounds with well-defined stereochemistry.

Finally, we wished to assess further the generality of a phenomenon recently reported by Eliel and co-workers.[5] Their ^{13}C NMR studies of a series of model alicyclic systems indicate that a carbon atom located anti or gauche to a second-row heteroatom in the γ position generally resonates at a significantly higher field than an analogous nucleus anti or gauche to a methyl or methylene group, or to a third-row heteroatom. Furthermore, it was also observed that the incremental upfield shift for the anti carbon was generally greater than that for the gauche carbon. A ^{13}C NMR study of systems **2** and **3** should indicate whether this effect can also be transmitted to aromatic carbon centers which are γ disposed to an externally located heteroatom.

Experimental Section

^{13}C Spectra. A Bruker Scientific, Inc. WH-90 Fourier transform spectrometer operating at 22.625 MHz was used to record the spectra. All samples were prepared in deuteriochloroform (0.5–1.0 M) with Me$_4$Si as an internal reference.

Chemicals. Most of the compounds were known and thus were synthesized by well-established literature procedures: 1-phenylpropan-2-one,[6] benzyldimethylamine,[7] benzyl methyl sulfide,[8] benzyl methyl sulfone,[8] 2-indanone,[9] 1,3-dihydroisobenzofuran,[10] 1,3-dihydroisoindole,[11] *N*-methyl-1,3-dihydroisoindole,[11] 1,3-dihydrobenzo[*c*]thiophene,[12] 1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide,[12] 2-tetralone,[13] 1,2,3,4-tetrahydroisoquinoline[14] (and *N*-methyl derivative[15]), isochroman,[16] and isothiochroman.[17] The latter compound was oxidized to 1,2,3,4-tetrahydro-2-thionaphthalene 2,3-dioxide (mp 164–165 °C) utilizing the procedure outlined for 1,3-dihydrobenzo[*c*]thiophene.[12] Geminal difluoro derivatives of systems **1**, **2**, and **3** (X = CF_2) were synthesized from the corresponding ketones employing diethylaminosulfur trifluoride as the fluorinating agent.[18] Except for 6- or 7-fluoro-2-methyl-1,2,3,4-tetrahydroisoquinoline, all the necessary aryl fluorine analogues of **1**, **2**, and **3** were available from other studies.[3,6,18] 6-Fluoro-2-butyl-1,2,3,4-tetrahydroisoquinoline was prepared from 4-fluoro-*o*-2-bromoethylbenzyl bromide and *n*-butylamine in acetone as described previously for the *N*-methyl analogue.[3] The *n*-butyl derivative was employed rather than the methyl analogue because it was easier to prepare in good yields.

Benzyl ethyl ether, *n*-propylbenzene, indan, and tetralin were commercially available.

Results

Since our recent ^{13}C NMR studies of various phenyl derivatives,[4,19] particularly benzocycloalkenes,[20] demonstrated convincingly that fluorine substitution is an effective and relatively simple strategy for ^{13}C spectral assignments in such systems, and since all the necessary fluorine analogues of **1**, **2**, and **3** were available from previous investigations,[3,6,18,21] we adopted this approach in order to unambiguously assign the aromatic region of the ^{13}C spectra of systems **1**, **2**, and **3**.

Fluorine substitution in the phenyl ring manifests itself in two important ways. Firstly, there is observed a characteristic regular pattern of ^{13}C–^{19}F coupling constants in the aromatic region of the proton-decoupled spectrum, ^1J ($\simeq$245 Hz) $\gg$ ^2J ($\simeq$18–20 Hz) > ^3J ($\simeq$6–9 Hz) > ^4J ($\simeq$1.5–4 Hz). In addition, coupling is generally observed ($^4J_{^{13}C-^{19}F} \simeq 2$ Hz) to any meta disposed external carbon center which is in a preferred "zigzag" array. A consideration of these data, together with signal intensities and the observed chemical shift patterns previously reported[4,20] for 5-fluoroindan and 6-fluorotetralin, leads to the assignments listed in Table I for the aromatic carbons of the various fluorine derivatives of **1**, **2**, and **3**. The assignments listed (Table I) for the aliphatic carbons were relatively straightforward for most of the compounds, being based essentially on the known α and β effects of the various elements or substituent groupings.[22] However, it should be noted that for many of the bicyclic derivatives (6, 8, 12, 16, and 19–22) the expected coupling ($^4J_{^{13}C-^{19}F}$) to the meta disposed external carbon center, which would have immediately identified that particular carbon, was not resolved. Thus, the listed assignments for C_7 and C_9 (entries 6, 8, and 12) and C_7 and C_{10} (entries 19 and 20) could possibly be reversed. Unfortunately, the α and β shifts of sulfur[5,22] are such that the chemical shifts of C_7 and C_{10} in entries 19 and 20 are fairly similar. Incomplete spectra are listed for entries 9, 13, and 18 because of the limited amounts of these compounds which remained from our previous investigations.[3,18,21] No concerted effort was made to observe the remaining carbon resonances since they were not crucial for assigning the spectra of the unfluorinated analogues.

Secondly, fluorine substitution induces a regular and pronounced effect on the ^{13}C chemical shifts which is an added benefit with regard to the use of fluorine as an assignment strategy. The carbon bearing fluorine is quite deshielded (by >30 ppm), whereas carbons ortho to fluorine experience quite large upfield shifts ($\simeq$14 ppm). Carbons para to fluorine are also shielded by a lesser amount ($\simeq$5 ppm) whereas meta carbons appear to be always deshielded (1–2 ppm). A consideration of this information, together with the data listed in Table I, leads to the assignments tabulated in Table II for systems **1**, **2**, and **3**. The assignments for the asterisked carbons are insecure and could possibly be reversed. It is of interest to note that although the aromatic carbons for entries 18–22 could be readily assigned on the data from one appropriately substituted fluorine derivative, two such derivatives were required for the confident assignments listed for entries 23 and 24. Here many of the aromatic carbons absorb over a narrower range.

The spectra for **2** and **3** where X = $Si(CH_3)_2$, which have been previously reported (measured as concentrated solutions in cyclohexane at 15.18 MHz),[4] were reexamined in DCl_3 (0.5 M) as solvent and are also listed in Table II (entries 16 and 25).

Discussion

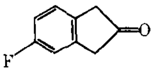
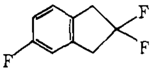
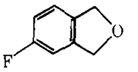
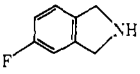
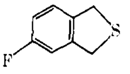
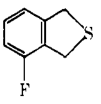
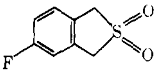
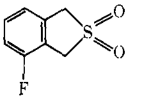
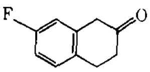
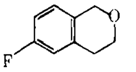
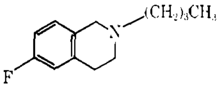
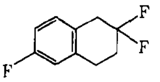
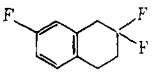
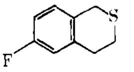
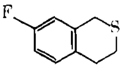
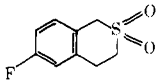
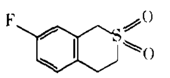
It is well known that a manifold of factors determine the magnitude of carbon chemical shifts.[22,23,24] However, by confining comparisons of chemical shifts to a closely related series of compounds and, at the same time, to those carbons reasonably remote from the site of substitution such that steric, neighboring group, and bond order effects are not important, the ^{13}C nucleus can be employed as a sensitive and reliable monitor of charge density fluctuations. This fact is clearly exemplified by a number of successful empirical and theoretical correlations which have clearly established that para (or C_4) ^{13}C SCS[27] of monosubstituted benzenes accurately reflect the charge density at that position.[24–26] Recent studies have shown that this close relationship between ^{13}C SCS and charge density is also strongly adhered to at para (or C_4) sites remote from the substituent in disubstituted benzenes.[19] However, various attempted correlations of meta (or C_3, C_5) carbon chemical shifts, which absorb over a narrow range and appear to be only marginally influenced by the electronic effect of a substituent, are much less satisfactory.[24–26] Although meta carbon chemical shifts are of limited value, they do assist in substantiating mesomeric phenomena, particularly for weak polar substituents,[28] since it is generally observed that any substituent exercising a significant resonance component clearly effects a chemical shift differential between the meta and para carbon sites.

Thus, in the present context of trying to assess the relative importance of hyperconjugation (σ–π interactions involving the CX σ bond) vs. π-inductive effects of $-CH_2X$ groups from the ^{13}C chemical shifts of **1**, **2**, and **3**, as well as the significance of polar field effects on aryl carbon chemical shifts, the relevant carbon centers are C_4 and $C_{3,5}$ in **1**, C_4 and C_5 in **2**, and $C_{4,5}$ in **3**. Since our recent ^{13}C NMR studies of benzocycloalkenes[20] indicated clearly that the $C_{4,5}$ chemical shifts in these systems are not very sensitive to ring size effects, we were confident that effects related to strain should not cloud the interpretation of the C_4 and C_5 chemical shifts of **2** and **3** for most of the substituents (X). However, our previous studies[4] of **2** and **3**, where X is a large third-row element [$Si(CH_3)_2$], suggested the possibility that structural factors may complicate the interpretation of the chemical shifts in terms of pure electronic phenomena where X = S or SO_2 in **2** and **3**. We shall return to this point below.

The parent systems employed for computing the ^{13}C SCS[27] of the relevant carbon centers in 1, 2, and 3 are *n*-propylbenzene (**1**, where X = CH_2), tetralin (**2**, where X = CH_2), and indan (**3**, where X = CH_2), respectively. It is then assumed, as a first approximation, that these ^{13}C SCS are reasonable monitors of the electronic behavior of the CX σ bond. This postulate is based essentially on two reasonable assumptions: (1) that the effects of CH and CC hyperconjugation are indistinguishable in the ground states of neutral molecules;[29] and (2) that the extent to which CH_2 can undergo hyperconjugative electron release from its CH bonds is the same for similar groups (X) in each particular system.

Before considering the relative ^{13}C SCS of these various carbon centers (listed in Table III), it is pertinent to discuss the structural features inherent in these model systems which allow a definitive decision to be made on the involvement of the CX σ bond in the electronic behavior of a $-CH_2X$ substituent. From an examination of Dreiding molecular models

Table I. Carbon-13 Assignments[a,b] of Fluorine-Substituted Derivatives of Systems 1, 2, and 3

Registry no.	Entry	Compd	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
459-03-0	1	p-FC$_6$H$_4$-CH$_2$C(=O)CH$_3$	130.4 (3.7)	131.2 (8.5)	115.5 (22)	162.0 (244.1)	115.5 (22)	131.2 (8.5)	49.7	205.9	29.2	
58325-14-7	2	p-FC$_6$H$_4$CH$_2$CF$_2$CH$_3$	129.8 (broad)	132.1 (8.8)	115.5 (20.6)	162.6 (245.6)	115.5 (20.6)	132.1 (8.8)	43.8 (26.5)	123.5 (239.7)	22.8 (27.9)	
702-11-4	3	p-FC$_6$H$_4$CH$_2$N(CH$_3$)$_2$	134.9 (broad)	130.5 (8.6)	115.0 (22)	162.1 (245.5)	115.0 (22)	130.5 (8.6)	63.6		45.2	
7116-50-9	4	p-FC$_6$H$_4$CH$_2$OCH$_3$	134.1 (broad)	129.6 (8.6)	115.3 (22)	162.5 (244.5)	115.3 (22)	129.6 (8.6)	74.0		58.0	
5925-83-7	5	p-FC$_6$H$_4$CH$_2$SO$_2$CH$_3$	124.1 (broad)	132.5 (7.3)	116.1 (22)	163.2 (250.2)	116.1 (22)	132.5 (7.3)	60.2		39.1	
57584-69-7	6		133.5 (broad)	139.9 (8.8)	112.3 (22.1)	162.3 (245.6)	114.6 (22.1)	126.4 (7.5)	43.4	214.3	44.3 (broad)	
57584-73-3	7		133.3 (broad)	139.8 (10.3)	112.1 (23.5)	162.8 (244.1)	114.8 (22.1)	126.2 (8.8)	41.8 (25.0)	131.5 (250)	42.1 (26.5)	
57584-70-0	8		134.8 (broad)	141.7 (10.3)	108.4 (23.6)	162.9 (244.1)	114.4 (23.5)	122.2 (8.8)	73.1		73.4	
57584-71-1	9				109.7 (22.0)		114.0 (23.5)	123.4 (10.3)				
55831-05-5	10		136.1 (broad)	142.9 (7.4)	111.5 (22.1)	162.1 (245.6)	113.8 (22.1)	125.5 (8.8)	37.1		37.8 (2.9)	
58325-15-8	11		144.4 (7.3)	127.7 (18.3)	159.1 (246.6)	113.1 (20.7)	128.8 (7.3)	120.2 (3.6)	38.2		33.9	
55831-03-3	12		127.2 (broad)	133.4 (8.8)	113.3 (22.1)	162.6 (248.6)	116.3 (23.5)	127.9 (8.8)	56.3		57.0 (broad)	
58325-16-9	13					115.3 (19.5)	130.5 (7.3)	121.7 (3.6)	56.9 (2.4)		53.0	
29419-15-6	14		135.5 (7.9)	132.4 (3.1)	129.0 (7.9)	113.5 (21.4)	161.7 (248.8)	114.9 (22.0)	44.8 (1.20)	209.2	38.1	27.7
50396-63-9	15		130.6 (3.1)	135.4 (7.3)	115.3 (20.8)	161.5 (244.1)	113.2 (22.0)	125.9 (7.9)	67.7		65.0	28.5 (1.2)
58325-17-0	16[c]		130.7 (broad)	136.5 (6.1)	114.8 (19.5)	161.5 (245.5)	112.7 (22)	127.9 (8.6)	58.3		55.8	29.4
57584-67-5	17		127.6 (broad)	136.4 (8.8)	115.0 (22.1)	161.8 (244.1)	113.8 (22.1)	130.6 (8.4)	37.5 (27.2)	123.1 (239.7)	30.8 (25.0)	27.1 (5.9)
57584-68-6	18				130.0 (8.8)	114.0 (20.7)		115.4 (22.1)	38.1 (27.2)		31.1 (25.0)	26.3 (5.9)
50396-75-3	19		130.8 (≃2.0)	138.9 (7.4)	115.8 (22.1)	161.5 (245.6)	112.9 (22.1)	129.1 (8.8)	28.7		25.9	30.6
50396-76-4	20		136.9 (7.4)	132.4 (2.9)	130.6 (8.8)	113.4 (20.6)	161.0 (245.6)	114.3 (20.6)	29.2		26.5	29.7
50396-79-7	21		124.5 (≃2.0)	135.7 (7.4)	115.9 (22.1)	162.6 (248.6)	114.8 (22.1)	131.7 (8.8)	54.4		49.3	28.4
50396-80-0	22		130.8 (7.4)	129.3 (2.9)	130.8 (7.4)	115.7 (20.6)	161.7 (245.6)	116.6 (22.1)	54.6		49.7	28.4

[a] Chemical shifts referenced to Me$_4$Si (± 0.1 ppm). Positive values indicate decreased shielding relative to Me$_4$Si. [b] Values in parentheses are $^{13}C-^{19}F$ couplings in hertz. The carbon numbering system is as shown on the structural formulas in the introduction. This system is for convenience only and bears no relation to the numbering system employed for the systematic naming of these compounds. [c] Chemical shifts for the *N*-butyl group are as follows. $-CH_2{}^aCH_2{}^bCH_2{}^cCH_3{}^d$: a, 50.6; b, 29.4; c, 20.8; d, 14.1.

Table II. Carbon-13 Assignments[a,b] of Systems 1, 2, and 3

Registry no.	Entry	Compd	Carbons									
			C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
103-65-1	1	$PhCH_2CH_2CH_3$	142.7	128.3*	128.5*	125.7	128.5*	128.3*	38.2	24.7	13.9	
103-79-7	2	$PhCH_2C(=O)CH_3$	134.5	129.5	128.7	126.9	128.7	129.5	50.7	205.8	29.1	
58325-18-1	3[c]	$PhCH_2CF_2CH_3$	134.1	130.5	128.7	127.5	128.7	130.5	44.5	123.7	22.8	
			(4.4)						(26.5)	(238.2)	(28.0)	
103-83-3	4	$PhCH_2N(CH_3)_2$	139.0	129.0	128.2	127.0	128.2	129.0	64.4		45.3	
539-30-0	5	$PhCH_2OCH_2CH_3$	138.8	127.6	128.3	127.4	128.3	127.6	72.7		65.7	15.2
766-92-7	6	$PhCH_2SCH_3$	138.3	128.8*	128.3*	126.8	128.3*	128.8*	38.2		14.7	
3112-90-1	7	$PhCH_2SO_2CH_3$	128.4	130.6	129.1	129.1	129.1	130.6	61.2		39.1	
496-11-7	8	3, X = CH_2	144.1	144.1	124.4	126.0	126.0	124.4	32.9	25.4	32.9	
496-12-8	9	3, X = NH	141.9	141.9	122.1	126.4	126.4	122.1	52.9		52.9	
3474-87-1	10	3, X = NCH_3	140.8	140.8	122.0	126.5	126.5	122.0	60.9		60.9	42.1
615-13-4	11	3, X = C=O	137.8	137.8	124.8	127.2	127.2	124.8	43.8	214.5	43.8	
54265-06-4	12	3, X = CF_2	137.8	137.8	124.9	127.6	127.6	124.9	42.8	131.5	42.8	
			(4.4)	(4.4)					(26.5)	(250)	(26.5)	
496-14-0	13	3, X = O	139.4	139.4	121.0	127.2	127.2	121.0	73.5		73.5	
2471-92-3	14	3, X = S	140.4	140.4	124.6	126.6	126.6	124.6	38.0		38.0	
2471-91-2	15	3, X = SO_2	131.5	131.5	126.1	128.9	128.9	126.1	57.0		57.0	
2474-87-6	16[d]	3, X = $Si(CH_3)_2$	142.2	142.2	129.2	125.6	125.6	129.2	21.3		21.3	
119-64-2	17	2, X = CH_2	137.1	137.1	129.1	125.4	125.4	129.1	29.5	23.3	23.3	29.5
530-93-8	18	2, X = C=O	133.0	136.3	127.7	126.3*	126.2*	127.0	44.4	209.2	37.5	27.8
58325-19-2	19	2, X = CF_2	132.1	134.2	128.6	126.7*	126.5*	129.2	38.1	123.1	31.1	27.0
			(broad)						(27)	(239.7)	(25)	(5.9)
91-21-4	20	2, X = NH	136.1	134.8	129.2	125.8*	125.6*	126.1	48.2		43.8	29.1
1612-65-3	21[e]	2, X = NCH_3	136.0	134.8	128.5	125.9*	125.4*	126.3	57.9		52.8	29.2
493-05-0	22	2, X = O	135.0	133.2	128.8	126.3*	125.9*	124.3	67.8		65.2	28.3
4426-75-9	23	2, X = S	135.0	136.7	129.1	126.7	126.1	127.6	29.1*		26.3	30.4*
18436-01-6	24	2, X = SO_2	129.0	133.5	129.0*	128.7*	127.7	130.0	55.1		49.9	28.0
5136-93-6	25[d]	2, X = $Si(CH_3)_2$	138.2	141.7	129.5	124.9	126.3	127.9	20.9		11.7	29.6

[a] Chemical shifts referenced to Me_4Si (±0.1 ppm). Positive values indicate decreased shielding relative to Me_4Si. Asterisked assignments could be reversed. [b] The carbon numbering system is as shown on the structural formulas in the introduction. [c] Values in parentheses are $^{13}C-^{19}F$ couplings in hertz. [d] Chemical shift for $Si(CH_3)_2$, −2.4 ppm (16) and −2.1 ppm (25). [e] Chemical shift for NCH_3, 46.0 ppm.

Table III. ^{13}C Substituent Chemical Shifts (SCS)[a]

Substituent X	System				
	1[b]		2[c]		3[d]
	$C_{3,5}$	C_4	C_4	C_5	$C_{4,5}$
CO	+0.2	+1.2	+0.9	+0.8	+1.2
CF_2	+0.2	+1.8	+1.3	+1.1	+1.6
NH			+0.4	+0.2	+0.4
NCH_3	−0.3	+1.3	+0.5	+0.0	+0.5
O	−0.2	+1.7	+0.9	+0.5	+1.2
S	−0.2	+1.1	+1.3	+0.7	+0.6
SO_2	+0.6	+3.4	+3.3	+2.3	+2.9

[a] Positive values imply a downfield shift relative to the appropriate standard. [b] Relative to C_3 (or C_5) and C_4 in *n*-propylbenzene. [c] Relative to C_4, C_5 in tetralin. [d] Relative to C_4, C_5 in indan.

it is readily seen that the geometries of the bicyclic systems **2** and **3** are considerably more constrained than those of the monocyclic analogues **1** in which the $-CH_2X$ group can be assumed to undergo free rotation. In system **2**, where X = CH_2, CO, CF_2, NH, NCH_3, or O, the alicyclic ring is conformationally mobile, there being two freely interconvertible conformations in which the dihedral angle (θ) (angle between the C_1C_7X plane and the plane of the aromatic ring) is $\simeq$25 ± 5° for CH_2, CF_2, NH, or NCH_3; $\simeq$15 ± 5° for O; and $\simeq$0° for CO. However, where X = S or SO_2 the models cannot be maintained in a half-chair-like conformation but prefer a rigid half-boat arrangement in which the dihedral angle (θ) is approximately 65 ± 5°. A consequence of the half-boat arrangement is that the benzylic hydrogens are eclipsed with H_3 and H_6 whereas they are staggered in the half-chair. This leads to "perilike" nonbonding interactions which appear to have a significant influence on the chemical shifts of remote carbon positions (vide infra). It is important to note that our previous deductions[2,4] from Dreiding models regarding the half-boat conformation of **2**, where X = $Si(CH_3)_2$, have subsequently been vindicated by x-ray crystallographic studies.[30]

For system **3**, the models indicate essentially a coplanar situation where the CX σ bond lies in the nodal plane of the adjacent π system, i.e., the dihedral angle (θ) is zero. Interestingly, recent structural studies[31] on **3**, where X = $SiPh_2$, indicate the possibility of substantial deviations ($\simeq$30°) away from coplanarity of the C_7XC_9 plane with respect to the aromatic ring.

Important consequences follow from this systematic variation of the geometrical relationship between the CX σ bond and the adjacent aromatic ring within model systems **1**, **2**, and **3**. First, if hyperconjugation is important, and if we neglect electrostatic-field effects, then according to the specific stereoelectronic requirements of this mechanism[29,32] (an approximate cosine dependence on the appropriate dihedral angle, $\cos 90° - \theta$) the relative magnitude of this interaction as monitored by the ^{13}C SCS should be C_4 (system **1**) > C_4 (system **2**) > $C_{4,5}$ (system **3**) where X = CO, CF_2, NH, NCH_3, or O. However, where X = S or SO_2, the order of ^{13}C SCS could be somewhat perturbed (**1** $\simeq$ **2** > **3** or **2** > **1** > **3**), depending on the magnitude of the effective dihedral angle in the monocyclic analogue **1**. In addition, if hyperconjugation is significant then a chemical shift differential should be observed between C_4 and $C_{3,5}$ in system **1**, and C_4 and C_5 in system **2**. This should be particularly pronounced in the latter system where $\cos 90° - \theta$ is significant (X = S or SO_2), and marginally so where X = CF_2, NH, NCH_3, or O.

If, on the other hand, the π-inductive effect[29] (no angular dependence) is more important than hyperconjugation in effecting π-polarization of the adjacent aromatic ring, then the electrical effect of the CX σ bond should be similar in all systems for a particular substituent, i.e., in terms of the relevant ^{13}C SCS, C_4 (system 1) $\simeq$ C_4 (system 2) $\simeq$ $C_{4,5}$ (system 3). However, since the π-inductive effect is indistinguishable from mesomeric phenomena in the way it polarizes a π system,[29] a chemical shift differential should still be observed between C_4 and $C_{3,5}$ in system 1, and C_4 and C_5 in system 2, as mentioned above for hyperconjugation.

Second, since the CX σ bonds lie in the plane of the ring system in system 3, σ–π conjugation should play no role here in determining the chemical shifts. Hence, perturbations of the chemical shift at $C_{4,5}$ can only be induced by a significant electrostatic-field or π-inductive effect. According to recent proposals,[33] the effect of an electric field emanating from a polar substituent (dipole or pole) on aryl ^{13}C chemical shifts can be interpreted on the basis of *nonlocalized* polarization (the π-inductive effect is a localized polarizing phenomenon) of the adjacent π-electron system such that significant electron density variations only occur at the terminal carbon centers. Since the π electrons should be polarized toward a positive charge, the polar field effect from electronegative elements or groups (X) will decrease the electron density at C_4 in system 1, C_4 and C_5 in system 2, and $C_{4,5}$ in system 3, and thus lead to more positive ^{13}C SCS at these remote probe sites. Intuitively, one would also expect that this π-polarization phenomenon should be dependent on the component of the electric field in the plane of the aromatic ring and, therefore, be most pronounced when the lines of force emanating from a dipolar group are constrained to operate in the plane of the aromatic ring, i.e., as in system 3. An examination of molecular models indicates that in system 2 the dipole or group moments for the strong polar substituents (excluding X = N or S) lie in a plane which makes a distinct angle (ϕ) with the plane containing the aromatic ring: for X = CO or CF_2, $\phi \simeq 40 \pm 5°$; and for X = SO_2, $\phi \simeq 65 \pm 5°$. Only where X = O in system 2 does the plane containing the dipole almost coincide with the molecular plane ($\phi \simeq 15 \pm 5°$). Thus, a distinction between polar field and π-inductive effects can be made on the following basis. If the electrostatic-field effect predominates (neglecting hyperconjugation) then the relative magnitude of the ^{13}C SCS should be $C_{4,5}$ (system 3; $\cos \phi = 1$) > C_4 and C_5 (system 2; $\cos \phi = 0.766$) where X = CO or CF_2; $C_{4,5}$ (system 3; $\cos \phi = 1$) $\simeq$ C_4 and C_5 (system 2; $\cos \phi = 0.966$) where X = O; and $C_{4,5}$ (system 3; $\cos \phi = 1$) $\gg$ C_4 and C_5 (system 2; $\cos \phi = 0.423$) where X = SO_2.

If, on the other hand, the π-inductive effect is more important, then the ^{13}C SCS of C_5 in system 2 should be small for all the groups and the magnitude of the C_4 SCS in all the systems, which should parallel the polarity of the CX σ bond, will be similar for a particular substituent.

Since the direction and magnitude of the resultant dipole in system 1 depends upon the various rotamer populations in an unknown way, the data from this system are of little value for defining unambiguously polar field effects. However, it should be noted that if hyperconjugation is highly significant then the relative magnitude of the C_4 SCS for 1 and 3 should be 1 $\gg$ 3. This should be particularly pronounced for weak polar groups (X = N or S).

We have already mentioned that the size of X markedly influences the geometry of system 2 and, according to our previous ^{13}C NMR studies on 2 where X = $Si(CH_3)_2$, the ^{13}C SCS at remote sites in this system. Thus, it is informative at this stage to reevaluate the ^{13}C SCS data from 2 (and 3), where X = $Si(CH_3)_2$, in the light of recent structural studies[30,31] on these systems as well as the now-established importance of metallohyperconjugation in the ground state of neutral molecules.[19] This should provide a firm basis for interpreting the data from system 2 where X = S or SO_2 and thus allow the data for these groups to be discussed within the general framework. Based on tetralin and indan as the parent systems, the ^{13}C SCS (ppm) for C_4 and C_5 in 2 (entry 25, Table II) and $C_{4,5}$ in 3 (entry 16, Table II) are −0.5, +0.9, and −0.4, respectively. Two aspects of this data deserve notice with regard to the validity of these systems as models for investigating electronic phenomena. First, the SCS at C_5 in 2 implies fairly *strong electron withdrawal by the CSi σ bond, a result which* is clearly contrary in magnitude and direction to expectations based on the established weak polar character of this bond[19b,34] (a value of ca. *zero* was expected). Second, the hyperconjugative effect of the C–Si bond, as monitored by the C_4 SCS, is approximately the same in both systems yet a simple cosine dependence of the σ–π interaction implies that the interaction in 2 should be approximately 2.6 times that in 3.[35] We believe that these anomalous results are a manifestation of structural factors due to "perilike" nonbonding interactions (vide supra) in the half-boat form of 2 which do not occur in the parent system (tetralin).

If we assume that this structural factor affects the chemical shifts equally at the C_4 and C_5 probe sites, then the most realistic measure of the σ–π interaction of the CSi σ bond in system 2 is the difference between the ^{13}C SCS at C_4 and C_5, i.e., −1.40 ppm. Based on a simple cosine dependence,[35] the maximum effect of the $-CH_2Si(CH_3)_3$ group in the phenyl ring in terms of a ^{13}C SCS is then computed to be −1.75 ppm. The experimental value[4] of −1.50 ppm is in excellent agreement with this prediction given that the relevant effective dihedral angle in benzyltrimethylsilane is ca. 30° (based on the value determined for benzyltrimethylstannane from carbon–tin coupling constants[19]). The calculated value for 3, where X = $Si(CH_3)_2$, is −0.5 ppm, which is also in excellent agreement with the experimental result (−0.4 ppm). Thus, it is clear from this analysis that although the ^{13}C SCS at C_4 and C_5 in the half-boat arrangement of 2 may be unreliable monitors of electrical phenomena in an absolute sense, their difference provides a sound measure of hyperconjugative interactions. Since similar structural factors will perturb the chemical shifts at C_4 and C_5 in system 2 when X = S or SO_2, then based on the relatively weak polar character of the CS σ bond, the fact that the dipole moment is considerably out of plane of the aromatic ring ($\phi = 65 \pm 5°$) and the chemical shift at C_5 for silatetralin (entry 25, Table II), the ^{13}C SCS at C_5 in 2 where X = S should be approximately zero. It follows then that a correction factor of −0.7 ppm *should be applied to the* ^{13}C SCS *for* C_4 *and* C_5 in system 2 where X = S or SO_2 (Table III) in order to provide approximate values that can be validly compared with the other groups.

Examination of the data listed in Table III indicates quite clearly that the ^{13}C SCS of the appropriate carbon centers for a large variety of groups (X) in 1, 2, and 3 provide a distinct pattern consistent only in terms of angular dependent electronic mechanisms.[36] It can be seen that in general the electron-withdrawing ability of the CX σ bond in the various systems is in the order C_4 (system 1) > $C_{4,5}$ (system 3) > C_4 (system 2) and $C_{4,5}$ (system 3) > C_5 (system 2). Furthermore, the differential between C_4 and C_5 in 2 is most significant when the dihedral angle is substantial (X = S or SO_2). Based on our proposed criteria (vide supra), we believe that only combined significant hyperconjugative and polar field effects can account for these observations. However, it is important to stress that since our arguments are based on geometries deduced from molecular models it is impossible to estimate accurately the relative magnitude of the inherent hyperconjugative abilities of the various CX bonds. The qualitative order deduced from the data in Table III is S ~ SO_2 ~ N > O > CF_2 > CO, which is in line with predictions from the ^{19}F NMR studies.[3,18,21] The importance of similar hyperconjugative interactions in several other connections has been described elsewhere.[3,37]

Unfortunately, it is not possible to distinguish from NMR experiments such as those described here whether the σ–π interactions involve charge redistribution with associated charge transfer.

Perhaps the most important aspect of the data in Table III is the pronounced influence of polar field effects on aryl ^{13}C chemical shifts. Note the significant SCS for the very polar groups (CO, CF_2, O, and SO_2) in system **3** where structural factors should preclude hyperconjugative interactions.[38] This was somewhat surprising since in most discussions of aryl ^{13}C SCS (remote carbon sites) it is tacitly assumed that mesomeric phenomena are overwhelmingly more important than field effects. Apart from the fact that no suitable studies had been performed on well-defined model systems, this situation seems to have arisen essentially from two well-established correlations:[22–25] (1) para ^{13}C SCS (monosubstituted benzenes) correlate better with σ_p^+ (66% resonance) than σ_p (53% resonance); and (2) para ^{13}C SCS (monosubstituted benzenes) correlate as well with CNDO/2 calculated π-charge densities as they do with total charge densities. More recently, an empirical analysis by Schulman et al.[39] has led to the conclusion that mesomeric effects are 41 times greater than field effects in their effect on aromatic ^{13}C chemical shifts.

An approximate estimate of the relative importance of field vs. mesomeric effects on aryl ^{13}C chemical shifts can be obtained from the ^{13}C SCS for system **3** where X = CF_2 (+1.6 ppm; Table III) and the para SCS (+3.2 ppm; CCl_4)[25] for the CF_3 substituent in trifluoromethylbenzene. If we make the very reasonable assumption that the SCS of the former is a minimum value for the electric field contribution to the total electronic effect by the latter substituent at the para position in trifluoromethylbenzene, then by utilizing the σ_I and $\sigma_R{}^0$ values for the CF_3 substituent (0.45 and 0.08, respectively)[40] it can be readily shown that mesomeric effects are approximately five times greater than field effects in their effect on aromatic ^{13}C chemical shifts. Interestingly, a correlative analysis by the Taft dual substituent parameter (DSP) equation of para ^{13}C SCS derived from monosubstituted benzenes leads to a similar conclusion.[41]

Two final features of the data listed in Table III, which reflect on the way polar field effects perturb the ^{13}C chemical shifts of remote aromatic carbon sites,[42] are worthy of note. First, it can be seen that the formally meta C_5 position in system **2** is significantly more affected by the electric field of the strong polar substituents than the meta position in system **1**. This confirms that only the chemical shifts of the terminal carbon positions of the aromatic ring are markedly effected by electric field induced π-polarization. Second, it is clear from the larger $C_{4,5}$ SCS in system **3** compared to C_5 (and C_4) in **2** (particularly for X = SO_2) that electric field induced π-polarization is more efficient when the lines of force emanating from the dipole (or pole) are constrained to operate in the plane of the aromatic ring.

The shielding effects of carbon nuclei oriented anti (or syn) to the γ heteroatoms in systems **2** and **3** are given in Table IV. It should be noted that whereas the γ effects of NH, NCH_3, O, and S are referenced with respect to methylene, O in CO and F in CF_2 are referenced with respect to hydrogen. However, since the γ effect of methylene should be small in the configurations described here, all the values can be considered referenced to a common standard, hydrogen. A careful scrutiny of Dreiding molecular models indicates that the anti coplanar arrangement is well defined in system **3** where X = NH, NCH_3, O, CO, or S. Although there are minor deviations away from exact coplanarity where X = NH, NH_3, O, or CO in system **2** for the anti (and syn) arrangement, coplanarity is completely destroyed where X = S since here the fused ring adopts a half-boat configuration. Where X = CF_2, both fluorines are out of plane by approximately 50° in the anti arrangement of **3**, but in system **2**, the quasi-equatorial fluorine is almost coplanar for the anti arrangement and roughly so for the syn.

Table IV. γ Shielding Effects (ppm)[a] of Heteroatoms in Systems 2 and 3

Substituent X	System 2 Anti	System 2 Syn	System 3 Anti
NH	-3.0^b	-2.3^d	-2.3^f
NCH_3	-2.8^b	-2.3^d	-2.4^f
O	-4.8^b	-3.9^d	-3.4^f
S	-1.5^b	-0.4^d	$+0.2^f$
CO	-4.1^c	-1.7^e	-6.3^g
CF_2	-5.0^c	-2.5^e	-6.3^g

[a] Negative values imply an upfield shift relative to the appropriate standard. [b] Relative to C_6 in tetralin. [c] Relative to C_1 in tetralin. [d] Relative to C_2 in tetralin. [e] Relative to C_{10} in tetralin. [f] Relative to $C_{3,6}$ in indan. [g] Relative to $C_{1,2}$ in indan.

Inspection of the data in Table IV clearly reveals that second-row heteroatoms (N, O, F) in systems **2** and **3** cause significant upfield shifts in the resonance of anti- and syn-coplanar carbon nuclei, the effect being more pronounced for the anti than the syn conformational array. Furthermore, the anti γ effect of a third-row element (S) is almost negligible (X = S; system **3**). These observations are clearly in line with the recent observations reported by Eliel and co-workers[5] from a ^{13}C NMR study of a large number of alicyclic derivatives. Thus, the generality of this phenomenon has clearly been extended since all the anti carbon centers in **2** and **3** are part of an adjacent aromatic framework, i.e., sp^2 hybridized carbon centers. The larger anti effects observed in **3** for O in CO and F in CF_2 as compared to the same effects in **2** is not surprising since the chemical shifts of the C_1 and C_2 carbon centers in the former system are expected to be more sensitive[20b] (hybridization effects) to the nature of X in the smaller fused ring. Further, the significantly smaller anti effect for O in **3** as compared to **2** could be a consequence of complicating strain effects in the former system.[29b]

Although we do not wish to rehash in detail on the possible origin of the shielding γ anti effect, since this has been adequately discussed by the previous workers,[5] we would like to comment briefly on the favored proposal, namely, direct hyperconjugative transfer of charge from the free-electron pairs on the heteroatom to the trans γ atom. Eliel et al.[5] failed to point out that CNDO/2 calculations[43] indicate that the donation of the free electrons on a heteroatom by this mechanism in a σ-bonded framework go preferentially to the β and not the γ position, the latter being positively charged. In valence bond terminology, a no-bond resonance structure can be drawn to represent this. More recently, experimental evidence has been presented[44] which appears to support the computational result. Unfortunately, the myriad effects determining the chemical shifts of carbon sites proximate to substituents[22,23,24] preclude any disentanglement of the hyperconjugative mechanism at the β position by ^{13}C NMR. Thus, although we believe that hyperconjugative transfer of charge is likely to be important in an indirect way (relay of charge from the β to the γ position), other mechanisms must also be contributing (field effects[5] and 1,3-back-lobe interactions[5]) which are impossible to specify in any sort of quantitative and predictable way. Interestingly, the anti γ effect for O in SO_2 (system **3**), where a very polar $^+S–O^-$ bond is involved, is −8.9 ppm (referenced with respect to $C_{1,2}$ in system **3** where X = S).

Acknowledgments. We thank the University of Adelaide and Monash University for the use of their NMR facilities and are grateful to Dr. D. Doddrell (Griffith University) for assistance with the recording of some of the ^{13}C NMR spectra.

References and Notes

(1) Author to whom correspondence should be addressed at the School of Physical Sciences, Flinders University, Bedford Park, S.A. 5042, Australia.
(2) W. Adcock, S. Q. A. Rizvi, and W. Kitching, *J. Am. Chem. Soc.*, **94,** 3657 (1972).
(3) W. Adcock, M. J. S. Dewar, and B. D. Gupta, *J. Am. Chem. Soc.*, **95,** 7353 (1973).
(4) S. Q. A. Rizvi, B. D. Gupta, W. Adcock, D. Doddrell, and W. Kitching, *J. Organomet. Chem.*, **63,** 67 (1973).
(5) E. L. Eliel, W. F. Bailey, L. D. Kopp, R. L. Miller, D. M. Grant, R. Bertrand, K. A. Christensen, D. K. Dalling, M. W. Duch, E. Wenkert, F. M. Schell, and D. W. Cochran, *J. Am. Chem. Soc.*, **97,** 322 (1975), and references cited therein.
(6) W. Adcock, P. D. Bettess, and S. Q. A. Rizvi, *Aust. J. Chem.*, **23,** 1921 (1970).
(7) E. L. Eliel, T. N. Ferdinand, and M. C. Hermann, *J. Org. Chem.*, **19,** 1963 (1954), and references cited therein.
(8) T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 69 (1932).
(9) J. E. Horan and R. W. Schiessler, *Org. Synth.*, **41,** 53 (1961).
(10) J. Entel, C. H. Ruof, and H. C. Howard, *J. Am. Chem. Soc.*, **74,** 443 (1952).
(11) J. Bornstein and J. E. Shields, *Org. Synth.*, **47,** 110 (1967); **48,** 65 (1968); and references cited therein.
(12) J. A. Oliver and P. A. Ongley, *Chem. Ind. (London)*, 1024 (1965).
(13) A. Rosowski, J. Battaglia, K. K. N. Chen, and E. J. Modest, *J. Org. Chem.*, **33,** 4288 (1968).
(14) N. H. Cromwell and D. J. Cram, *J. Am. Chem. Soc.*, **65,** 305 (1943).
(15) E. Wedekind and R. Oechslen, *Ber.*, **34,** 3987 (1901).
(16) S. Siegel and S. Coburn, *J. Am. Chem. Soc.*, **73,** 5494 (1951).
(17) F. G. Holliman and F. G. Mann, *J. Chem. Soc.*, 37 (1945).
(18) Details will be published elsewhere: W. Adcock, B. D. Gupta, and T. C. Khor, *Aust. J. Chem.*, to be published.
(19) (a) W. Adcock, B. D. Gupta, W. Kitching, D. Doddrell, and M. Geckle, *J. Am. Chem. Soc.*, **96,** 7360 (1974); (b) W. Adcock, B. D. Gupta, W. Kitching, and D. Doddrell, *J. Organomet. Chem.*, **102,** 297 (1975).
(20) (a) W. Adcock, B. D. Gupta, T. C. Khor, D. Doddrell, D. Jordan, and W. Kitching, *J. Am. Chem. Soc.*, **96,** 1595 (1974); (b) W. Adcock, B. D. Gupta, T. C. Khor, D. Doddrell, and W. Kitching, *J. Org. Chem.*, accepted for publication.
(21) W. Adcock and B. D. Gupta, *J. Am. Chem. Soc.*, **97,** 6871 (1975).
(22) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972.
(23) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972.
(24) G. J. Martin, M. L. Martin, and S. Odiot, *Org. Magn. Reson.*, **7,** 2 (1975).
(25) G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Am. Chem. Soc.*, **94,** 3089 (1972), and references cited therein.
(26) G. A. Olah, P. W. Westerman, and D. A. Forsyth, *J. Am. Chem. Soc.*, **97,** 3419 (1975), and references cited therein.
(27) Defined as the difference (ppm) between the ^{13}C chemical shift of the uubstituted compound and that of the appropriate carbon in the parent hydrocarbon. Positive signs imply deshielding, negative signs shielding.
(28) (a) C. D. Schoeffer, Jr., and J. J. Zuckermann, *J. Organomet. Chem.*, **55,** 97 (1973); (b) D. Doddrell, K. G. Lewis, C. E. Mulquiney, W. Adcock, W. Kitching, and M. Bullpitt, *Aust. J. Chem.*, **27,** 417 (1974); (c) M. Bullpitt, unpublished work.
(29) M. J. S. Dewar, "Hyperconjugation", Ronald Press, New York, N.Y., 1962.
(30) (a) P. J. P. Vidal, J. Lapasset, and J. Falgueirettes, *Acta Crystallogr., Sect. B*, **28,** 3137 (1972); (b) P. J. P. Vidal and J. Falgueirettes, *ibid.*, **29,** 2833 (1973).
(31) P. J. P. Vidal and J. Falgueirettes, *Acta Crystallogr., Sect. B*, **29,** 263 (1973).
(32) σ–π conjugation should be most favored when the CCX plane is orthogonal to the ring and vanishes when the C–X bond lies in the plane of the ring; see (a) R. S. Mulliken, *J. Chem. Phys.*, **7,** 339 (1939); R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Am. Chem. Soc.*, **63,** 41 (1941); (b) M. J. S. Dewar, *ibid.*, **74,** 3345 (1952). The resonance integral β^θ is given approximately by $\beta^\theta \simeq \beta^0 \cos\theta$, where θ is the angle of twist.
(33) (a) G. K. Hamer, I. R. Peat, and W. F. Reynolds, *Can. J. Chem.*, **51,** 897 (1973); (b) W. F. Reynolds, I. R. Peat, M. H. Freedman, and J. R. Lyerla, *ibid.*, **51,** 1857 (1973); (c) D. A. Dawson and W. F. Reynolds, *ibid.*, **53,** 373 (1975); (d) J. G. Batchelor, J. H. Prestegard, R. J. Cushley, and S. R. Lipsky, *J. Am. Chem. Soc.*, **95,** 6358 (1973), and references cited therein; (e) J. G. Batchelor, *ibid.*, **97,** 3410 (1975), and references cited therein.
(34) (a) W. Hanstein, H. J. Berwin, and J. G. Traylor, *J. Am. Chem. Soc.*, **92,** 7476 (1970), and references cited therein; (b) C. G. Pitt, *J. Organomet. Chem.*, **61,** 49 (1973).
(35) The appropriate dihedral angles for **2** and **3**, where X = Si(CH$_3$)$_2$, are ca. 40 and 70°, respectively (see ref 2, 4, 30, and 31).
(36) The overall ^{13}C SCS pattern is very similar to the ^{19}F SCS results previously observed utilizing the fluorine nucleus at the relevant carbon sites (see ref 3, 18, and 21). Although there is no exact linear correspondence between the ^{13}C and ^{19}F SCS, this was not unexpected since the determining balance between mesomeric and polar field effects of each substituent for both probes are quite different. Plots of the data indicate quite reasonable linear correspondence between the ^{13}C SCS of C$_4$ (system **1**), C$_4$ (system **2**), and C$_{4,5}$ (system **3**) and the corresponding fluorine data.
(37) (a) It is of interest to note that according to the ^{13}C SCS (C$_4$) in system **1** [or para ^{19}F SCS in system **1** (ref 2 and 3)] the electron-withdrawing effect of the weak polar CN σ bond (X = NCH$_3$, Table III) is similar in magnitude but opposite in sign to the electronic effect of the weak polar CSi σ bond (X = Si(CH$_3$)$_2$ which is now accepted as being due to hyperconjugative electron donation. (b) M. Bullpitt, W. Kitching, D. Doddrell, and W. Adcock, *J. Org. Chem.*, accepted for publication. (c) P. Beltrame, P. L. Beltrame, P. Caramella, G. Cellerino, and R. Fantechi, *Tetrahedron Lett.*, 3543 (1975).
(38) (a) The relative magnitude of the C$_{4,5}$ SCS in system **3** are approximately in accord with expectations based on dipole moment values (ref 38b and 38c) for the various polar bonds in some simple system: tetramethylenesulfone (4.7 D); tetrahydrofuran (1.7 D); difluoromethane (1.93 D); formaldehyde (2.17 D); dimethylamine (1.03 D). (b) "Handbook of Chemistry and Physics", 54th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1973. (c) A. L. McClellan, "Tables of Experimental Dipole Moments", W. H. Freeman, San Francisco, Calif., 1963.
(39) E. M. Schulman, K. A. Christensen, D. M. Grant, and C. Walling, *J. Org. Chem.*, **39,** 2686 (1974).
(40) S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Prog. Phys. Org. Chem.*, **10,** 1 (1973).
(41) S. K. Dayal and R. W. Taft, *J. Am. Chem. Soc.*, **95,** 5595 (1973).
(42) (a) Although attempts to quantitatively estimate electric field shifts have been presented (ref 22, 33d, 33e, and 42b), we have adopted a purely qualitative approach to our data since the limits of expectation for electric field calculations are not good (approximately a factor of 2–3). The main difficulty lies in estimating the variation of the field effect with distance since the distance dependence of electric fields within molecules may not be simple. Further, the effective dielectric constant term also presents severe problems. (b) G. W. Buchanan and T. Durst, *Tetrahedron Lett.*, 1683 (1975), and references cited therein.
(43) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89,** 4253 (1967).
(44) S. A. Holmes and T. D. Thomas, *J. Am. Chem. Soc.*, **97,** 2337 (1975).

The Palladium(II)-Catalyzed Olefin Carbonylation Reaction. IV. Carbon-13 Nuclear Magnetic Resonance Analysis of the Reaction Products

D. E. James[1] and J. K. Stille*

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242

Received August 15, 1975

Carbon-13 NMR spectra of the acyclic and alicyclic diester and β-methoxy ester products from the palladium(II)-catalyzed olefin carbonylation reaction are reported. Substituent effects were derived for the carbons of an alkyl chain containing two carbomethoxyl functions which demonstrate the importance of the steric environment on carbon-13 chemical shifts.

Carbon-13 nuclear magnetic resonance spectrometry (^{13}C NMR) is one of the most powerful techniques available for the study of the structure of organic molecules. This usefulness is based, in part, on empirical correlations of carbon-13 shieldings and molecular structure.[2,3] In general, the effects of various substituents on the ^{13}C shieldings of neighboring carbons are found to be additive within families of compounds. Consequently, the positions of ^{13}C absorptions for related compounds may often be predicted with good precision in a wide variety of systems and can be valuable for signal assignments in the analysis of complex spectra.