The Substituent Effect of the Bromomethyl Group. A Carbon-13 Magnetic Resonance Study

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The natural abundance carbon-13 NMR spectra of benzyl bromide, 1- and 2-bromomethylnaphthalenes, 6-methyl-2-bromomethylnaphthalene, 4-bromomethylbiphenyl, and 9-bromomethylanthracene have been obtained and assigned. At each carbon position chemical shift differences ($\Delta\delta$) for the structural change $ArCH_3 \rightarrow ArCH_2Br$ have been tabulated, and for formally conjugated positions significant downfield shifts occur. The magnitudes of $\Delta\delta$ are very dependent on the aryl group and disposition, and correlate with theoretical measures of the *change* in π-charge density for $ArCH_3 \rightarrow ArCH_2^+$. This deshielding is considered to be associated with removal of π charge by C–Br hyperconjugative electron withdrawal, and parallels trends previously established by ^{19}F NMR measurements. This removal of π charge is not inconsistent with predominant (ortho, para) electrophilic substitution in benzyl halides if in the transition state rotation in $-CH_2X$ occurs to promote C–H hyperconjugative electron release, but necessarily impeding C–Br electron withdrawal.

The substituent effects of halogenated methyl groups are of much current interest, and a variety of approaches have been employed to assess them. Regarding electrophilic aromatic substitution, Ridd and co-workers[2] established that the $-CH_2Cl$ group had a definite ortho–para directing effect in nitration, and very recently Symons[3] regarded this as evidence for electron release *from* the carbon–halogen bond

$$\overset{\delta+}{-CH_2}-\overset{\delta-}{X}$$

despite the indicated polarization. The greater acidifying effect of $-CH_2X$ when para compared with meta on benzoic acid has been attributed by Exner to a π-inductive mechanism.[4] Studies[5] of electron-density distributions (in the ground state) in bromomethylaromatics by ^{19}F chemical shifts, and related computational work,[5,6] have indicated quite strongly that such groups are hyperconjugatively electron withdrawing, involving interaction of aryl-ring MO's with the polarized

$$\overset{\delta+}{C}-\overset{\delta-}{X}$$

σ-bonding MO. Additional ^{19}F SCS[7a] data have been provided for a wide range of bicyclic systems, incorporating the benzylic C–X fragment[7b] (where X is appreciably more electronegative than carbon) in such a manner that C–X hyperconjugation was essentially impossible. As monitored by ^{19}F SCS, electron withdrawal was substantially reduced, but residual polar components still operated. Some earlier NQR (chlorine) results[8] were in line with the above conclusions.

In closely related series of aromatic compounds, ^{13}C chemical shifts have provided important insight into π-electron distributions, and such shifts correlate well with other measures of substituent–substrate interactions.[9–12] While in some respects complementing ^{19}F SCS, ^{13}C SCS provides simultaneous measures of perturbations at all carbons in the system, and provided care is exercised, therefore unveils a more detailed canvas. In view of our disinclination[7] to accept the proposal of Symons[3] regarding the mode of behavior of $-CH_2X$ (X = halogen), we deemed it essential to provide another measure of this substituent effect and to attempt to correlate the results with an established quantum mechanical description.

Experimental Section

Compounds. Toluene, 1- and 2-methylnaphthalenes, 2,6-dimethylnaphthalene, 4-methylbiphenyl, and 9-methylanthracene were commercially available, and samples utilized were of high purity as judged by vapor phase chromatography and ^1H and ^{13}C NMR spectra.

o-Deuteriotoluene was obtained by treating the Grignard reagent from *o*-bromotoluene with D_2O in the standard way. The mass spectrum indicated 85% D.

4-Deuterio-1-methylnaphthalene was obtained by quenching the lithio derivative (*n*-butyllithium) from 4-bromo-1-methylnaphthalene with D_2O (80% D by mass spectrum).

Arylmethyl Bromides. Method 1. To 0.1 mol of the appropriate methylaromatic in dry CCl_4 (100 ml) was added *N*-bromosuccinimide (18.5 g) and a little benzoyl peroxide. The mixture was refluxed, and the progress of the bromination monitored by ^1H NMR spectroscopy (appearance of CH_2Br resonance at ca. δ 4.5) so that formation of dibromide ($-CHBr_2$) (ca. δ 6.6) was not significant. The cooled reaction mixture (0 °C) was filtered (to remove succinimide), and then washed with cold dilute NaOH solution and cold water (100 ml). The CCl_4 solution was separated, dried (Na_2SO_4), and then evaporated under reduced pressure. The arylmethyl bromide was either distilled or recrystallized for purification purposes.

***o*-Deuteriobenzyl bromide** was obtained in 76% yield (method 1).

1-Bromomethylnaphthalene (method 1) was furnished in 62% yield and two recrystallizations from hexane yielded material with mp 55–56 °C (lit.[14] 55–56 °C) showing ^1H NMR absorptions (CCl_4) at δ 4.71 (2 H, CH_2Br) and 7.2–8.0 (Ar).

4-Deuterio-1-bromomethylnaphthalene (method 1), % D ~ 80% (mass spectrum).

2-Bromomethylnaphthalene (method 1) was obtained as a white solid, mp 54 °C (lit.[15] 54–55 °C), after two recrystallizations from hexane: ^1H NMR (CCl_4) δ 4.46 (CH_2Br) and 7.2–7.7 (Ar).

6-Methyl-2-bromomethylnaphthalene was obtained from 2,6-dimethylnaphthalene using method 1, in 67% overall yield. The crude material was recrystallized twice from hexane to provide a white solid: mp 89–90 °C (lit.[14] 90 °C); ^1H NMR (CCl_4) δ 2.51 (CH_3), 4.63 (CH_2Br), 7.2–7.8 (Ar).

4-Bromomethylbiphenyl was obtained in 52% yield from 4-methylbiphenyl (method 1). After two recrystallizations from ethanol, a white, crystalline solid of mp 84–85 °C was obtained: ^1H NMR (CCl_4) δ 4.48 (CH_2Br), 7.4–7.6 (Ar).

Anal. Calcd for $C_{13}H_{11}Br$: C, 63.18; H, 4.46. Found: C, 63.01; H, 4.41.

9-Bromomethylanthracene (Method 2). To triphenylphosphine (2.8 g, 0.108 mol) in dry CH_3CN (20 ml) was added slowly bromine (1.6 g, 0.01 mol) until a faint persistence of the orange

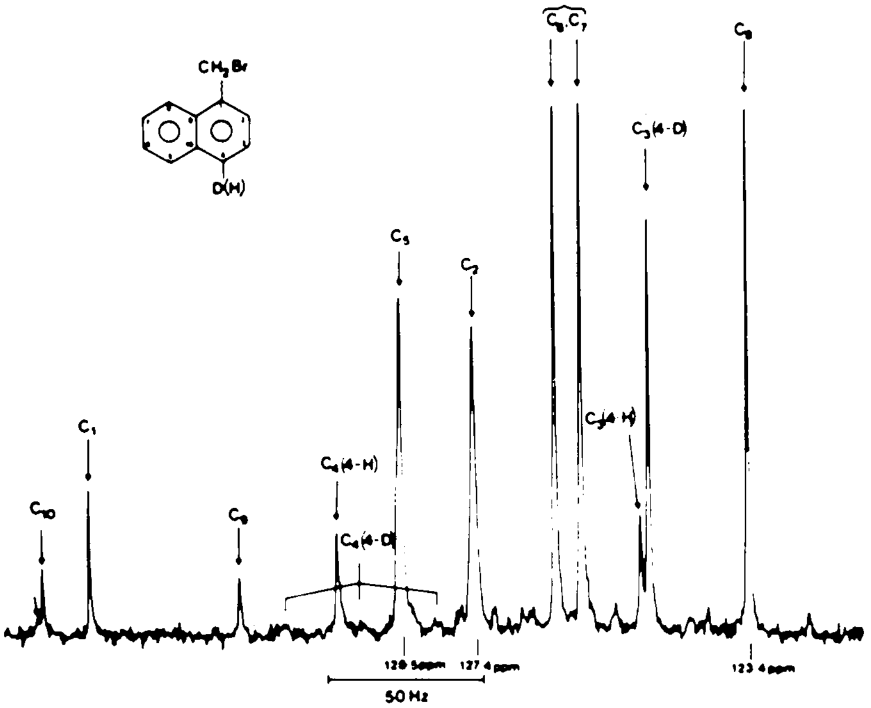


Figure 1. Proton decoupled ^{13}C spectrum (22.63 MHz) of 4-deuterio-1-naphthylmethyl bromide ($CDCl_3$ solvent). The deuterium isotope effect on the chemical shifts of C_4 and C_3 is apparent and results from incomplete 4-deuteration. The broadened signals correspond to C_2, C_5, and C_9 (compare with C_{10}) which are vicinal to 4-D, and experience $^{13}C-^{2}H$ coupling of ca. 1 Hz. A full listing of chemical shifts is given in Table I. (Methylene carbon resonance omitted.)

color. 9-Hydroxymethylanthracene (2.08 g, 0.01 mol) was added slowly (as a solid) and after about 1.0 g of the alcohol had been added, the solution became quite clear and a yellow solid then precipitated. The remainder of the alcohol was added, and the solution was stirred for an additional 1 h. The flask was cooled (0 °C) and the yellow solid was filtered and recrystallized from chloroform. The overall yield was 86%: mp 147–148 °C; ^{1}H NMR ($CDCl_3$) δ 5.46 (CH_2Br), 7.5 (H_2, H_3, H_6, H_7), 8.0 (H_4, H_5), 8.3 (H_1, H_8), and 8.4 (H_{10}).

Anal. Calcd for $C_{15}H_{11}Br$: C, 66.45; H, 4.06. Found: C, 66.47; H, 4.13.

NMR Spectra. ^{13}C spectra were obtained using a Bruker HX-90 spectrometer operating in the FT mode, and chemical shifts are relative to internal Me_4Si and accurate to ±0.05 ppm. Concentration effects on these ^{13}C shifts at the 10–20% concentration level were very small for tertiary carbons (i.e., CH) and were disregarded. ^{1}H NMR spectra were recorded on an MH-100 instrument for CCl_4 or $CDCl_3$ solutions with internal Me_4Si. Measurements of relaxation times (T_1) were conducted as previously described.[16]

Results and Discussion

^{13}C Shifts. A. Methylaromatics. The chemical shifts of all carbons in the parent methylaromatics are tabulated in Table I. For toluene, the assignments are secure,[17,18] and in the case of 1-methylnaphthalene the only doubt involves C_6 and C_7,[19-21] but possible reversal of these shifts does not alter any conclusions. The assignments for 2-methylnaphthalene and 2,6-dimethylnaphthalene have been reported by two groups,[20,21] but our chemical shifts agree closely with those reported by Wilson and Stothers,[21] who also employed dilute solutions in $CDCl_3$. For 4-methylbiphenyl, the key 4 carbon was readily assigned by its relative intensity, while the other assignments were based on additivity considerations and agree with those already published.[22] The latter published data[22] were based on detailed statistical and parameterized analyses of substituent effects for a range of 4-substituted biphenyls. The assignments for 9-methylanthracene were based upon signal intensities, substituent effects, and chemical shifts and agree with those recently published[23] for enriched 9-methyl-*9*-^{13}C-anthracene.

B. Bromomethylaromatics. Assignments for the bromomethylaromatics are located also in Table I to facilitate comparisons with the methyl series. For benzyl bromide and 1-naphthylmethyl bromide, tactical deuteration (ortho and position 4, respectively) and consideration[19] of deuterium isotope effects on chemical shifts and $^{13}C-^{2}H$ coupling, led to the recorded assignments. The only possible ambiguity concerns C_6 and C_7 in the 1-naphthylmethyl bromide. A fully proton-coupled spectrum[19a] (67.8 MHz) of 1-naphthylmethyl bromide provided assignments absolutely consistent with those deduced from effects of deuterium substitution at the 4 position. "Multiplet patterns" due to long-range vicinal coupling (C–C–C–**H**) differ for carbons in different ring positions (Figures 1 and 2). C_3, assigned on the basis of a high-field 4-deuterium-induced shift in 4-deuterio-1-naphthylmethyl bromide, should appear as a sharp doublet in the ^{1}H-coupled spectrum, because C_3 is forbidden structurally from experiencing vicinal ^{1}H coupling. C_8, previously assigned at highest field on the basis of a substantial δ effect, appears as a doublet of doublets, with vicinal coupling to H_6. C_6 and C_7, expected to have very similar chemical shifts, appear as overlapping doublets of doublets, as anticipated for β carbons in such a benzo fragment. C_4, previously assigned by direct deuteration, experiences two different vicinal H couplings (H_2, H_5) and hence has a "pseudotriplet" appearance, in each component of the overall doublet (i.e., one-bond coupling). C_5, somewhat broadened in the (^{1}H decoupled) spectrum of the 4-deuterio compound, now displays a "broadened" doublet of doublets due to coupling to H_7 and H_4. H_2, previously assigned on the basis of braodening (vicinal ^{2}H coupling) in the 4-deuterio analogue, would be anticipated to exhibit considerable fine structure in each half of the (one-bond) doublet, as vicinal couplings to H_4 and $-CH_2Br$ are possible. This anticipation is realized in the form of "quartets" for C_2. The three quaternary carbons are not well resolved and these assignments in Table I are tentative. Nevertheless, the least coupled carbon would be C_1, and this agrees with the features of Figure 1. It is clear that proton-

Table I. Carbon-13 Assignments[a] for Methyl-and Bromomethylaromatics

Registry no.	Compd[b]	Carbon[b,c] 1	2	3	4	5(1')	6(2')	7(3')	8(4')	9	10	Other
108-88-3	Toluene	137.6	129.1	128.3	125.4	128.3	129.1					21.5
100-39-0	Benzyl bromide	137.9	129.1	128.8	128.4	128.8	129.1					33.1
	Δδ[e]	+0.3	-0.0	+0.5	+3.0	+0.5	-0.0					11.6
90-12-0	1-Methylnaphthalene	134.2	126.6	125.5	126.6	128.6	125.4	125.7	124.1	132.7	133.6	19.3
3163-27-7	1-Bromomethylnaphthalene	132.0	127.4	125.0	129.3	128.5	125.8	126.2	123.4	130.8	133.7	31.5
	Δδ[e]	-2.2	+0.8	-0.5	+2.7	-0.1	+0.4	+0.5	-0.7	-1.9	+0.1	12.2
91-57-6	2-Methylnaphthalene	126.9	135.4	128.0	127.3	127.8	125.0	125.9	127.6	133.6	131.8	21.6
939-26-4	2-Bromomethylnaphthalene	126.3	134.9	127.8	127.6	127.5	126.6	126.2	128.6	133.0	132.9	33.9
	Δδ[e]	-0.6	-0.5	+0.3	-0.3	-0.3	+1.6	+0.3	+1.0	-0.6	+1.1	+12.3
581-42-0	2,6-Dimethylnaphthalene	126.6	134.3	128.1	127.0	126.6	134.3	128.1	127.0	132.1	132.1	21.5
52988-15-5	6-Methyl-2-bromomethylnaphthalene[d]	126.7 (126.2)	134.2 (134.1)	127.7 (127.9)	127.6 (127.6)	126.7 (126.6)	136.2 (136.2)	128.6 (128.5)	128.0 (128.0)	131.4 (131.2)	133.4 (133.1)	34.0, 21.6
	Δδ[e]	+0.1	-0.1	-0.4	+0.6	+0.1	+1.9	+0.5	+1.0	-0.7	+1.3	+12.5

Registry no.	Compd[b]	1	2	3	4	5(1')	6(2')	7(3')	8(4')	9	10	11/14	12/13	Other
779-02-2	9-Methylanthracene	124.5	125.0	124.5	128.2	128.2	124.5	125.0	124.5	129.7	125.2	131.2	129.9	13.5
2417-77-8	9-Bromomethylanthracene	123.5	126.7	125.4	129.2	129.2	125.4	126.7	123.5	129.2	129.2	131.5	127.7	26.8
	Δδ[e]	-1.0	+1.7	+0.9	+1.0	+1.0	+0.9	+1.7	-1.0	-0.5	+4.0	+0.3	-2.2	+13.3
644-08-6	4-Methylbiphenyl	138.5	127.0	129.5	136.8	141.4	127.0	128.7	127.0					21.0
2567-29-5	4-Bromomethylbiphenyl	140.3	129.7	127.4	136.7	141.8	127.0	128.7	127.4					33.1
	Δδ[e]	+1.8	+2.7	-2.1	-0.1	+0.4	0	0	+0.4					+13.1

[a] Chemical shifts in parts per million downfield from Me_4Si. [b] IUPAC numbering adopted. [c] Numbering in parentheses applied to biphenyl system only. [d] Calculated values in parentheses. [e] The uncertainty in δ values is ±0.1 so the uncertainty in Δδ is ±0.2.

Table II. Calculated Changes in Charge Density (Δq) for $ArCH_3 \rightarrow ArCH_2^+$

System	Method	Carbon position[a] α	1	2	3	4	5(1')	6(2')	7(3')	8(4')	9	10	11	12	13	14
Benzyl	HMO	0.571	0.0	0.143	0.0	0.143	0.0	0.143								
	SCF-II	0.499	-0.076	0.142	0.035	0.222	0.035	0.142								
α-Naphthyl	HMO	0.450	0.0	0.200	0.0	0.200	0.050	0.0	0.05	0.0	0.050	0.0				
	SCF-II	0.381	-0.064	0.205	-0.009	0.263	0.092	0.046	0.133	-0.012	0.014	-0.049				
β-Naphthyl	HMO	0.522	0.232	0.0	0.058	0.0	0.0	0.058	0.0	0.058	0.0	0.058				
	SCF-II	0.440	0.227	-0.061	0.034	0.060	0.016	0.133	0.050	0.062	-0.036	0.074				
	SCF-II[b]	0.403	0.242	-0.064	0.046	0.047	0.010	0.148	0.048	0.064	-0.040	0.100				
4-Biphenylyl	HMO	0.512	0.0	0.128	0.0	0.128	0.0	0.032	0.0	0.032						
	SCF-II	0.437	-0.071	0.131	0.012	0.214	-0.080	0.037	0.027	0.086						
9-Anthrylmethyl	HMO	0.284	0.0	0.071	0.0	0.071	0.071	0.0	0.071	0.0	0.0	0.284	0.0	0.071	0.071	0.0
	SCF-II	0.270	-0.010	0.138	0.033	0.090	0.090	0.033	0.138	-0.010	-0.056	0.304	-0.065	0.056	-0.056	-0.065

[a] IUPAC numbering adopted. Numbering in parentheses refers to biphenyl system only. For naphthyl systems $C_{10} = C_4a$ and $C_9 = C_8a$. [b] Self-consistent in bond lengths.

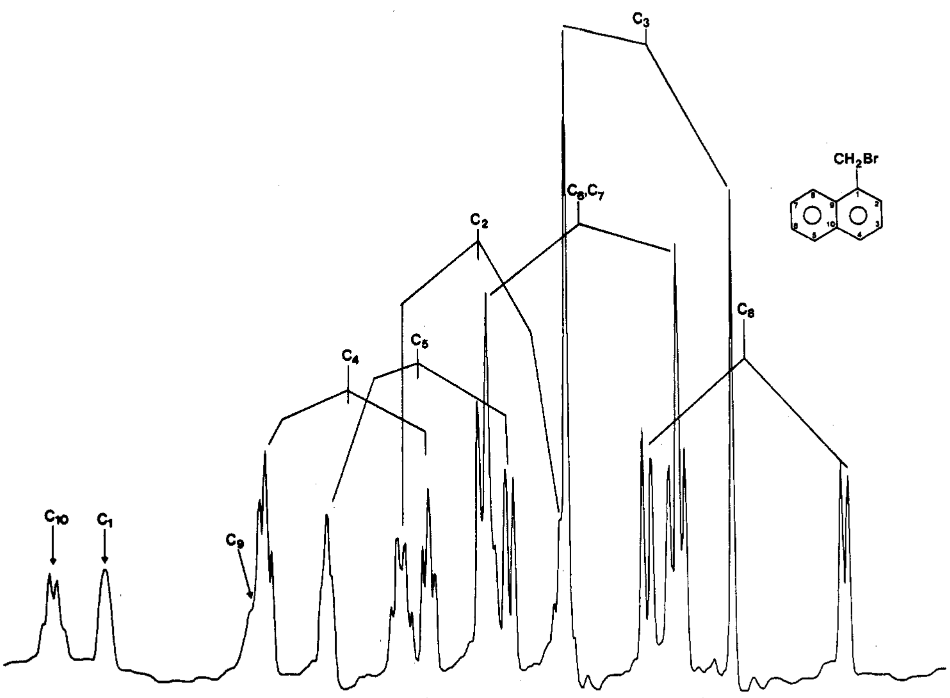


Figure 2. Proton *coupled* spectrum of 1-naphthylmethyl bromide at 67.89 MHz ($CDCl_3$ solvent) illustrating the characteristic coupling patterns. Assignments are as marked and correspond with those in Figure 1. The low-field half of the C_4 doublet is superimposed on a quaternary carbon resonance. (Methylene carbon resonance omitted.)

coupled spectra provide an additional and powerful approach for assignments in substituted naphthalenes, and complement the effects of specific deuterium substitution.

For 2-alkyl substituted naphthenes additivity effects on ^{13}C shifts have been established.[20,21] The procedure then was to assign as reasonably as possible the spectrum of 2-bromomethylnaphthalene and, knowing the effect of 2-methyl substitution at all positions in naphthalene, to calculate the signal positions for 6-methyl-2-bromomethylnaphthalene, using the chosen assignments for the 2-bromomethyl compound. These assignments were then adjusted until the calculated and observed signals for the 6-methyl-2-bromomethyl compound harmonized. No deviation greater than 0.5 ppm occurred, and except for two positions, deviations were 0.2 ppm or less. No other combinations could afford such impressive consistency, and we regard the assignments for these systems as established. The 4′ carbon in 4-bromomethylbiphenyl was identified by its relative intensity compared with other tertiary (protonated carbons). The effects of the $-CH_2Br$ group at ring positions in benzyl bromide were applied to the directly attached ring in the biphenyl compound. Additivity considerations of phenyl and $-CH_2Br$ substitution on benzene shifts then led to the indicated allocations. For 9-bromomethylanthracene, C_{10} was identified by its intensity (22.6 and 67.8 MHz spectra) relative to other tertiary carbons. Other assignments were based essentially on compressional and chemical shift arguments, and, while in all probability correct, cannot be regarded as definitely established. Our main concern in this system was with C_{10}.

Quaternary carbons in all systems were identified by their characteristically lower intensities and longer relaxation times and in some cases, quite positively assigned by deuterium effects on the spectra and substituent chemical shifts. The CH_3 and $-CH_2Br$ signals were the only ones at higher field.

An assessment of the substituent effect of $-CH_2Br$ requires comparison with the corresponding methylaromatic, and the chemical shift changes ($\Delta\delta$) for all carbons in these systems, associated with the structural change $ArCH_3 \rightarrow ArCH_2Br$, are tabulated in Table I. For purposes of analysis, data pertaining to ortho-type positions are rejected since steric and compressional effects at these sites may mask any bona fide electronic effect. The data in Table I show quite definitely the deshielding effect of CH_2Br (vs. CH_3) at conjugative unencumbered positions[24] and in view of available evidence[9-12] relating ^{13}C shift and π-charge density, $\Delta\delta$ is logically associated with removal of such charge density by the C–Br bond. A very striking aspect of the data in Table I is the variation in $\Delta\delta$ with the nature of the aryl group in $ArCH_2Br$.

The Theoretical Model. The above dependence of $\Delta\delta$ on the aryl system in $ArCH_2Br$, and previous information[7] indicating a strong stereoelectronic dependence of C–X substituent effects generally, pointed to a σ–π or hyperconjugative mode[25] of π-charge removal by $-CH_2Br$. Therefore it seemed attractive to examine the $\Delta\delta$ trends with Ar in the framework of a conjugative model. Considering that the hyperconjugative effect is due to interaction of aryl ring MO's with the (polarized) C–Br σ-bonding MO, a very simplified approach would be to use $ArCH_2^+$ as the model, and obtain a measure of the transmission of mesomeric effects between ring positions and CH_2. The ^{13}C shift differences ($\Delta\delta$) are taken as a reflection of π-charge levels in the immediate region of the carbon atom.

π-Charge Densities in $ArCH_2^+$. A. HMO Technique. The special properties of the NBMO of odd alternate hydrocarbon systems $ArCH_2$ allow ready calculation of the NBMO coefficients (a_{0i}) at the more numerous "starred" set of atoms.[26,27] In an odd alternant cation, the charge density is $(1 - a_{0i}^2)$, a_{0i} being the NBMO coefficient of atom i.[27] In Figure 3 the quantity $\Delta\delta$ is plotted against the change in charge density (Δq), a_{0i}^2. The data for the 6-methyl-2-naphthyl system (Table I) have not been plotted, but the trends in $\Delta\delta$ for C_6, C_8, and C_{10} (and other positions) closely parallel those for the parent 2-naphthyl sys-

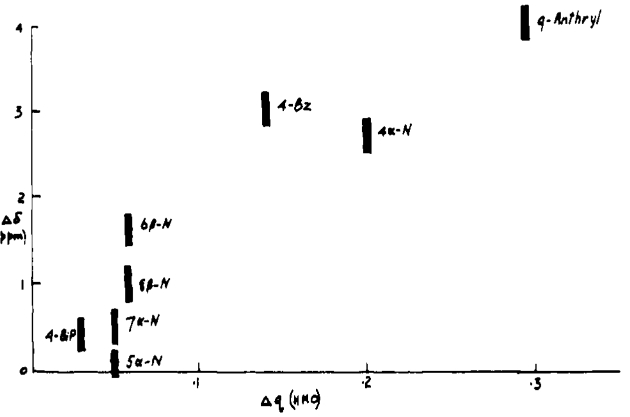


Figure 3. Plot of carbon-13 chemical shift changes (Δδ) for the change $ArCH_3 \rightarrow ArCH_2Br$ at the indicated ring positions against the HMO-derived changes in π-charge density (Δq) at those sites. The heights of rectangular "points" correspond to uncertainties (±0.2 ppm) in Δδ. Statistical treatment of the data (omitting 4-biphenyl, 5α- and 7α-naphthyl data) yields a correlation coefficient of 0.93, significant at the 95% level. Inclusion of the 4-biphenyl datum yields $r^2 = 0.94$, significant at the 99% level. The best straight line in the latter circumstance has an intercept of 0.44 (Y axis) and passes through X = 0.20, Y = 3.05.

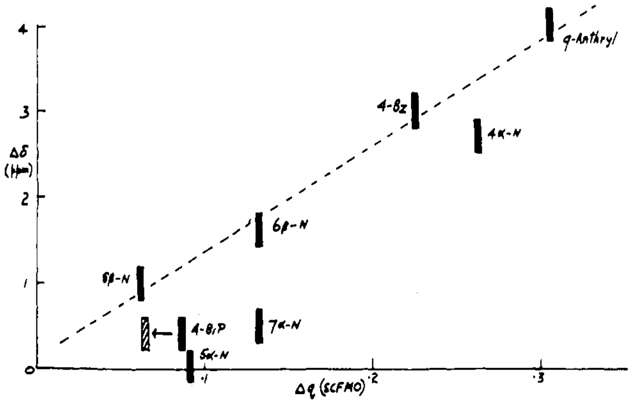
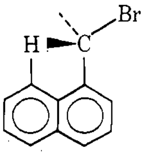


Figure 4. Plot of carbon-13 chemical shift changes (Δδ) for the change $ArCH_3 \rightarrow ArCH_2Br$ at the indicated ring positions against the SCF-π derived changes in π-charge density (Δq) at those sites. The heights of rectangular "points" correspond to uncertainties (±0.2 ppm) in Δδ. The hatched rectangle for 4-biphenyl corresponds to Δq = 0.065 calculated for an interannular angle of θ = 45°. Statistical treatment of the data (including the "hatched" 4-biphenyl datum but omitting 5α- and 7α-naphthyl data) yields a correlation coefficient $r^2 = 0.96$, significant at the 99% level. The best straight line has an intercept Y = 0.11 and passes through X = 0.20, Y = 2.46. Treatment of all data (in Figure 4) (eight observations) yields $r^2 = 0.92$, again within the 99% level. The intercept is now Y = 0.67, and the best line passes through X = 0.2, Y = 2.26.

tem. Data for quaternary carbons have not been employed as we and others[21,28] have noted that these carbons are far more sensitive to concentration and bond-order changes. In these circumstances, the prudent course seemed to be to confine attention to tertiary carbons but it should be noted that Δδ values for quaternary carbons (Table II) are not glaringly out of line with $a_{0i}{}^2$. The data for positions 2 and 4 in anthracene are not plotted owing to the unproven nature of these assignments.[29]

The general dependence of Δδ on $a_{0i}{}^2$ (in Figure 3) is immediately apparent, and, considering the gross nature of this treatment, constitutes impressive evidence for a conjugative mode of electron withdrawal by the C–Br bond. Several pieces of data are somewhat poorly correlated, particularly the points 7α-naphthyl, 4-biphenyl, and 5α-naphthyl. We shall see that these deviations have a most convincing explanation or agreement with other experiment, that strengthens the general conclusion.

The Δδ values for 4-benzyl and 4α-naphthyl are of interest, as although all treatments of conjugative interactions in these positions show 4α-naphthyl to be superior,[30] the Δδ values are, within error (±0.2 in Δδ), identical (2.7 and 3.0 ppm). The explanation in part may involve the regulating action of the peri hydrogen (at position 8) on the conformational populations of the $-CH_2Br$ system in the α-naphthyl case. That conformation drawn below (A) may be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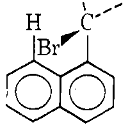
B

favored as it most effectively alleviates nonbonded 8H–Br interactions, but this geometry prohibits (hyperconjugative) σ C–Br-π mixing, which is pronoted, however, in B. More extensive studies of these effects are proceeding. These effects on properties of other α-naphthyl and related systems have been well documented.[31,32] Since A represents an energy well for rotation about C_1–CH_2 bond, it seemed that evidence for an exalted population of this conformer might result from T_1 (relaxation time) measurements of the methylene carbon. Such an experiment would be definitive if the rate of overall molecular reorientation was less than the rate of $-CH_2Br$ group rotation for benzyl bromide but faster in the 1-naphthyl derivatives.[33] Direct comparison of $-CH_2Br$ T_1 values in the two cases is not valid because the overall molecular microdynamics are different. However, it should be possible to compare T_1 $(-CH_2Br)/T_1$ (backbone) in the two cases to indicate any differences in CH_2Br group rotation. When this is done we conclude that in both cases the rate of CH_2Br rotation is slower than that of overall reorientation. This result is to be compared with other T_1 studies on CH_3 group rotation where the internal motion of the CH_3 group is important.[34] We conclude that, in general, the rotation of CH_2Br is much slower, probably the consequence of a larger moment of inertia.

For 1-naphthylmethyl bromide, ^{13}C spectra were recorded at 323 K (50 °C) and 223 K (−50 °C), in the expectation that conformation A would experience significant population changes, with attendant variations in the ^{13}C chemical shifts.[35] Over this temperature range, however, the changes were very modest indeed,[36] and not reliably interpreted.[37] The barrier to CH_2Br rotation seems to be low and would require study at much lower temperatures. Here, however, the problems of aggregation and molecular ordering could be most distressing.[38]

As indicated above, the point for 5α-naphthyl appears to be disturbingly misbehaved, particularly since both HMO and SCFMO calculations place significant charge density in odd AH systems at this site. However, for this disposition in naphthalene, experiment is well ahead of theory since the evidence (both NMR and reactivity studies) is overwhelming that any conjugation here is trifling. For example, Schreiber and Byers[39] demonstrated that whereas 1-chloromethyl-4-methoxynaphthalene solvolyzes 38 × 10^4 times faster than 1-chloromethylnaphthalene, 1-bromomethyl-5-methoxynaphthalene solvolyzes only *2.4* times as fast as 1-bromomethylnaphthalene. More recently, in an extensive assessment of ^{19}F SCS in naphthyl systems, Adcock and co-workers[40] reported that replacement of the hydrogens in NH_2 by CH_3 groups in 1-fluoro-5-aminonaphthalene produced a negligible effect, confirming the absence of 1,5 mesomerism.[41] Hence this lack of correlation in Figure 3 for 5α-naphthyl is in fact consoling and additional support that $-CH_2Br$ is mimicking the behavior of other authentic conjugating substituents.[42] Deviations for 7α-naphthyl and to a lesser extent 8β-naphthyl are also apparent. Regarding the biphenyl system, the lack of correlation was anticipated, since the value of $a_{0i}{}^2$ (Δq) is based on an assumed planar molecule, which is certainly incorrect for the liquid phase.[5] Other assumptions regarding geometry, e.g., interannular bond length, and a general overestimation of mesomerism to the second ring, also contribute.

B. SCFMO Approach. While the foregoing HMO-based treatment provides a convincing analysis to the problem, it was considered desirable to obtain π charges by a more rigorous SCFMO approach, with particular hope that some of the deviant data may be "rescued". A program was already available[43] which assigns the exocyclic C–C bond the fully conjugated benzene bond length of 1.39 Å, and which treats all C–C lengths as such. In the biphenyl case, a planar geometry was assumed and the interannular bond was assigned a length of 1.39 Å. This procedure has had impressive success[44,45] in correlating other spectral parameters and details of the method can be found elsewhere.[27,46] In Figure 4, the quantities $\Delta\delta$ correlate exceptionally well with the SCFMO π-charge densities (Δq), except for 4α-, 7α-, and 5α-naphthyl and 4-biphenyl. Cogent reasons for these deviations have been presented (vide infra), but it is apparent that the 5α disposition in naphthalene cannot be regarded as a "conjugated" position, and more refined calculations are required to reproduce experimental facts in the second ring of α-naphthyl systems. The situation is that inter-ring communication for some dispositions, notably 5α, is far less than available calculations indicate. Treatment[40] of substituent behavior by the DSP approach[47] (Dual Substituent Parameter) at various positions provides the following sensitivity factors for resonance: 4α, −31.42; 6β, −12.54; 7α, −4.43; 8β, −4.71; and 5α, +0.096. These parameters correspond generally with π charges (or mesomeric transmission factors) listed in Table II, except for 7α and 5α, which we have noted are poorly correlated in Figures 3 and 4.[49] Reduction in the value of $a_{0i}{}^2$ for 4-biphenyl to a more realistic value,[48] e.g., 0.065, indicates acceptable behavior for this system. A somewhat interesting conclusion from Figure 4 is that any component of $\Delta\delta$, other than the hyperconjugative one, must be quite small as the best correlation line passes very close to the origin.

The HMO and SCF π charges employed are located in Table II.

Previously, the demonstration was made[5] that the ^{19}F NMR substituent chemical shifts for bromomethyl substituted flurorayl systems correlated handsomely with the π-charge densities in the benzyl, α- and β-naphthyl, and 4-biphenyl systems. In view of the general correspondence between ^{13}C and ^{19}F SCS in aryl systems in situations of strong conjugation, e.g., 4α, 6β,[40] it is reassuring that in the present cases this type of dependence is also observed.

In general, the trends in Table III can be rationalized on the basis that ^{13}C and ^{19}F SCS incorporate a different blend of mesomeric and field effects, with the latter more important for ^{19}F SCS. For example, the increase in the ^{19}F SCS on proceeding from 4-benzyl to 4α-naphthyl (Table III) is in all probability due to an increase in the π-polarization component of the field effect which apparently compensates for any reduction in C–Br hyperconjugation. The ^{13}C probe, on the other hand, being less influenced by field effects, more effectively reflects the reduction in C–Br hyperconjugation.

Table III. ^{19}F and ^{13}C SCS for Arylmethyl Bromides

Disposition	^{19}F SCS	^{13}C SCS
4-Benzyl	5.07	3.0
4α-Naphthyl	5.60	2.7
6β-Naphthyl	2.48	1.6
4,4′-Biphenyl	0.89	0.4

If $-CH_2Br$ is conjugatively electron withdrawing, how then can we rationalize greatly preferred ortho-para electrophilic substitution in benzyl halides?[2] The answer lies in the potentially multicomponent nature of the overall CH_2X substituent effect:[7] (a) hyperconjugative electron withdrawal by the C–halogen σ bond; (b) hyperconjugative electron release by C–H σ bonds; and (c) electron withdrawal by an inductive field effect. (For an essentially noncharged polar system this latter effect is minor). Depending on the confirmation of CH_2X with respect to the ring, it is clear that either a or b could be dominant. In aromatic electrophilic substitution which appreciable charge development, rotation about the C–C bond generates an arrangement favoring C–H electron release, but essentially prohibiting C–X electron withdrawal. In the neutral ground state, however, it seems reasonable that the conformation favoring C–Br electron withdrawal will be favored. Careful vibrational spectroscopic studies of arylmethyl halides could prove illuminating in this regard.

The change $ArCH_3 \rightarrow ArCH_2Br$ results in downfield shifts of ca. 12–13 ppm for C_α, somewhat less than the normal "α" effect of bromine substitution (~20 ppm) in saturated alkyl systems.[50] A rehybridization effect, $sp^3 \rightarrow sp^2$, with charge deficiency[51] may be partly responsible, but other "special" effects may also contribute. The $\Delta\delta$ values for ipso carbons are irregular and small, and "special" influences of various sorts would need to be considered, in addition to π-charge variations.

While we believe that the present data pertaining to the ground-state behavior of CH_2Br groups are most persuasive, final justification must await ^{13}C chemical shifts particularly for α- and β-naphthylmethyl cations. Our analysis would predict (a) a feeble interaction at C_5 in the α cation and (b) an essentially linear correlation between our $\Delta\delta$ values for $ArCH_2Br$ (vs. $ArCH_3$) and $\Delta\delta$ for $ArCH_2{}^+$ vs. $ArCH_3$. Further studies of conformationally constrained arylmethyl systems are in progress.

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Registry No.—*N*-Bromosuccinimide, 128-08-5; 9-hydroxymethylanthracene, 1468-95-7.

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(42) There is evidence (ref 40) that in the case of ^{19}F shielding in the 5α-naphthyl system, field effects and steric crowding may contribute to the overall ^{19}F SCS. These would be less important for ^{13}C SCS.

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(49) We at first suspected that the assumptions regarding bond lengths in the naphthyl framework may have been partly to blame for the overestimation of mesomerism to the second ring. A calculation with self-consistency in bond lengths was not enlightening, and if anything, aggravated the situation. More thorough (and expensive) calculations are required.

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Evidence for Free-Radical Reductive Dehalogenation in Reaction of Zinc and Acid with 1-Perfluoroalkyl-2-iodoalkanes and with 1-Perfluoroalkyl-2-iodoalkenes[1]

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Reductive dehalogenation of 7-perfluorobutyl-6-iodo-1-heptene by either tri-*n*-butyltin hydride or zinc and acid gave partial cyclization to *cis*- and *trans*-1-methyl-2-(perfluorobutyl)methylcyclopentane, and at a rate consistent with previously studied free-radical cyclizations. Cyclization was slower for 8-perfluorobutyl-7-iodo-1-octene, while 6-perfluorobutyl-5-iodo-1-hexene gave only unrearranged product. Reductive dehalogenation of 1-perfluoropropyl-2-iodo-1-hexene was not stereospecific but inversion of the intermediate vinyl radicals occurred. Free-radical addition of perfluoropropyl iodide to 1-heptyne did not give internal hydrogen transfer and cyclization as had been observed for analogous reaction of CCl_4 or of $HCCl_3$.

The purpose of this research was (1) to synthesize iodine-free perfluoroalkyl-substituted alkanes and alkenes of various types; (2) to compare the behavior of a homologous series of 1-perfluoroalkyl-2-iodo terminal alkenes and of 1-perfluoroalkyl-2-iodo-1-alkenes during dissolving metal reduction, in which free radicals might be involved; and (3) to compare reductive dehalogenation of tri-*n*-butyltin hydride with that given by zinc and acid in this series of compounds.[2]

It is important to recognize that in most chemical reactions the perfluoroalkyl group retains its integrity, as a result of the high C–F bond strength. Rearrangement, loss of