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Relation of ^{13}C NMR Shifts to the Effect of Methyl Substitution on Electronic Charge Distribution at Trigonal Carbons[1]

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Abstract: The effect of the substitution of methyl for hydrogen on the electronic charge distribution at the carbon undergoing substitution (C_α) is discussed in relation to the deshielding of C_α observed in ^{13}C NMR spectra. In particular, the effect of methyl substitution at trigonal carbons in carbocations is examined by considering the electron populations predicted by a variety of molecular orbital methods for the series of simple alkyl cations: methyl, ethyl, isopropyl, and *tert*-butyl. Also, the ^{13}C NMR spectra of a series of *p*-methyl-substituted benzene derivatives, including *p*-tolylcarbenium ions and related onium ions, were determined in order to study the possible constancy of the effect of methyl substitution on ^{13}C chemical shifts, i.e., the validity of the additivity relationship for substituent-induced chemical shifts (SCS). The SCS data are consistent with an interpretation supported by molecular orbital calculations in which the methyl group has a negative inductive effect that increases in magnitude as the extent of electron donation from methyl increases via hyperconjugation.

The traditional view of the electronic effect of the methyl group is that the methyl substituent is electron releasing (i.e., electron donor) compared with hydrogen, by both inductive and hyperconjugative mechanisms, when attached to an sp^2 hybridized carbon.[3] This view is in large part derived from consideration of methyl substituent effects in aromatic systems and from the energetic stabilization provided by methyl substitution at a trigonal carbon in carbocations and in electron-deficient transition states. The effects of substituents on carbenium ion stabilities are frequently attributed to the capability of the attached groups to disperse or neutralize the positive charge by electron donation to the positive center. Thus it is disturbing to find that several molecular orbital treatments of such simple ions as the *tert*-butyl and isopropyl cations indicate that the central carbon atom actually becomes more positive upon substitution of methyl for hydrogen.[4-10] Some recent experimental work which also indicates that a methyl group is not necessarily electron donating has been reviewed by Sebastian.[11]

^{13}C NMR studies are an integral part of the evidence concerning the electronic effect of the methyl group. Substitution of a methyl group for hydrogen consistently produces a deshielding of the α carbon in the ^{13}C NMR spectrum. The deshielding α effect of a methyl group has been attributed to a reduction in electron density at the α carbon in alkanes,[12] ketones,[13] and carbenium ions.[14] Although the dependence of ^{13}C chemical shifts on electron density is a well-recognized phenomenon, the importance of other factors governing chemical shifts is not well understood, and the use of the α effect of the methyl group as evidence for inductive electron withdrawal has been questioned on the basis of this uncertainty.[15] In regard to this question, the deshielding effect of α-methyl substitution is usually small and fairly regular at a variety of trigonal carbon atoms (ethene to propene, $\Delta\delta_{^{13}\mathrm{C}}$ 7.8 ppm;[16] benzene to toluene, $\Delta\delta_{^{13}\mathrm{C}}$ 8.9 ppm;[17] formic acid to acetic, $\Delta\delta_{^{13}\mathrm{C}}$ 10.9 ppm;[18] acetaldehyde to acetone, $\Delta\delta_{^{13}\mathrm{C}}$ 5.5 ppm;[19] isopropyl cation to *tert*-butyl cation, $\Delta\delta_{^{13}\mathrm{C}}$ 10.4 ppm),[14] which raises the possibility of a constant neighboring-group effect of the methyl group that is unrelated to a charge effect.

In this paper, we examine the problem of the relation of ^{13}C chemical shifts to the effect of methyl substitution on electronic charge distributions, with particular emphasis on improving our understanding of the methyl-group effect on charge distribution in carbocations. The emphasis of our work was directed toward clarifying the meaning of ^{13}C shifts in terms of hyperconjugative (resonance), polarizing, and inductive influences of the methyl group. In order that problems of interpretation be kept to a minimum, only methyl substitution at trigonal carbons bonded to carbon and hydrogen will be considered.

Results

To approach the problem of the effect of methyl substitution on charge distribution in carbocations, we first examined the electron populations predicted by a variety of mo-

Table I. Excess Charge Densities at Carbenium Ion Centers

	2pπ (C^+) charge				Total (C^+) charge			
Molecular orbital method	CH_3^+	$CH_3CH_2^+$	$(CH_3)_2CH^+$	$(CH_3)_3C^+$	CH_3^+	$CH_3CH_2^+$	$(CH_3)_2CH^+$	$(CH_3)_3C^+$
Ab initio								
STO-3G Pople[a]	1.000	0.888	0.814	0.766	0.225	0.249	0.283	0.328
Allen[b]	1.000				−0.545	−0.339		
Wolfsberg[c]						0.195		
Semiempirical								
Extended Hückel[d]					0.609	0.571	0.611	0.692
ASMO SCF[e]	1.000	0.850	0.704	0.607	0.261	0.339	0.362	0.382
CNDO-modified[f]	1.000	0.862			0.214	0.225	0.250	0.273
NDDO[g]						0.294	0.309	
CNDO/2 (Pople)[h,i]	1.000	0.786	0.689	0.631	0.439	0.369	0.349	0.338
CNDO/2 (Wiberg I)[h,j]	1.000	0.798	0.708	0.655	0.442	0.376	0.356	0.345
CNDO/2 (Wiberg II)[h,k]	1.000	0.783	0.695	0.645	0.328	0.302	0.327	0.360
INDO[h,l]	1.000	0.773	0.675	0.617	0.546	0.437	0.392	0.360
MINDO/2[h,m]	1.000	0.815	0.741	0.702	0.601	0.435	0.345	0.273

[a] Reference 10. [b] Reference 9. [c] L. J. Massa, S. Ehrenson, M. Wolfsberg, and C. A. Frishberg, *Chem. Phys. Lett.*, **11**, 196 (1971). [d] Reference 4. [e] Reference 5. [f] References 7 and 8. [g] Reference 6. [h] Calculations performed for this study. [i] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966). [j] K. B. Wiberg, *J. Am. Chem. Soc.*, **90**, 59 (1968): β_H, 10.0; β_C, 17.5; $I(1s)$, 7.176; $I(2s)$, 10.3; $I(2p)$, 6.3. [k] Same as Wiberg I, except: $I(2s)$, 11.0; and $I(2p)$, 7.4. [l] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967). [m] M. J. S. Dewar and E. Haselbach, *J. Am. Chem. Soc.*, **92**, 590 (1970).

lecular orbital methods for the series of simple alkyl cations: methyl, ethyl, isopropyl, and *tert*-butyl. The calculated 2pπ and total charge densities for the carbenium ion centers are presented in Table I. The table summarizes the available literature data on the subject and includes the results of INDO, MINDO/2, and CNDO/2 (with three different parameter sets) calculations performed for this study. In the presently performed calculations, geometries were defined by the use of standard bond lengths and angles.[20] Rotational conformations of the methyl groups were chosen so as to minimize steric interactions.

In order to study and to determine the possible constancy of the effect of methyl substitution on ^{13}C chemical shifts, i.e., the validity of the additivity relationship for substituent-induced chemical shifts (SCS), the ^{13}C NMR spectra of a series of para-substituted toluene derivatives, including *p*-tolylcarbenium ions and related onium ions, were determined. ^{13}C chemical-shift data for para-substituted toluenes are given in Table II. ^{13}C spectra of several of these derivatives had been reported in earlier studies,[21] but the results had been obtained by several methods of varying reliability. All of the chemical shifts presented in Table II are from spectra obtained by the pulsed Fourier transform method on a Varian XL-100 or a modified Varian HA-100 spectrometer. The spectra of the uncharged toluenes were measured using ~25% solutions in CCl_4, which should make the results comparable to the results obtained by Nelson, Levy, and Cargioli for monosubstituted benzenes in CCl_4.[17] The spectra of the cationic species were measured using solutions prepared in the same manner as the corresponding cationic monosubstituted benzenes,[22] which should also facilitate direct comparison of results.

Chemical-shift assignments were made primarily by analogy with chemical-shift data for monosubstituted benzenes. Assignments were aided by running both completely proton decoupled spectra and off-resonance decoupled spectra, which allowed differentiation of carbons based on the number of attached hydrogens. Results for NH_2, OCH_3, OH, CH_3, $COCH_3$, and NO_2 substituted toluenes were in agreement with literature data on the ordering of carbon resonances although differing somewhat in numerical values.[21]

Discussion

Comparison of MO Methods. Several studies have shown that polarization of the electron distribution in π bonds is a more important effect than actual charge transfer from the methyl substituent, especially in electronically neutral systems.[20,23-28] Hoffmann has reported a detailed analysis of the methyl polarization effect in terms of perturbation theory.[28] However, since for the purposes of analysis we would like to individually isolate the polarization, hyperconjugative, and inductive effects, at this point we will consider only the theoretical results for methyl, ethyl, isopropyl, and *tert*-butyl cations. Besides being the most simple representatives of alkyl substituted carbenium ions, they are well suited for our purposes since polarization of the electron distribution in the π system can be neglected, because the π system consists of only one carbon, the carbenium center. In these carbenium systems, the magnitude of hyperconjugative electron donation is measured by the charge density in the carbon 2pπ orbital. The charge density in the σ-bond system is measured at C_α by subtracting the 2pπ-charge density from the total charge density on C_α. Changes produced in the σ-charge density by methyl substitution can be equated to the inductive effect.

Table I summarizes the results of charge-density calculations for the four carbocations from literature sources and from calculations performed for this study. It is clear that the numerical values differ greatly among the various methods. In some of the calculations, the total charge on the central carbon becomes more positive with increasing methyl substitution, indicating that the overall effect of a methyl group is electron withdrawing, while some of the popular semiempirical all-valence-electron methods, CNDO/2 (Pople), INDO, and MINDO/2, predict that the overall effect of methyl substitution is electron release to the carbenium center. The extended Hückel method and a CNDO/2 method (Wiberg II parameterization) show a decrease in positive charge on going from methyl to ethyl, but an increase in positive charge between ethyl and isopropyl and between isopropyl and *tert*-butyl.

Despite great discrepancies among the methods in the numerical values for the total carbon charges, all methods show hyperconjugative electron donation from methyl groups to the central carbon 2pπ orbital. In each method, the amount of π-electron donation per methyl group decreases with successive methyl substitutions, the expected result of decreasing demand for charge stabilization by resonance. Furthermore, *all methods except MINDO/2 show inductive withdrawal in the σ framework by methyl relative to hydrogen.* For instance, in the CNDO/2 method (Pople parameterization), the 2pπ charge is reduced by 0.369 electrons from 1.000 for methyl cation to 0.631 for

Table II. ^{13}C Chemical Shifts[a] of 4-Substituted Toluenes,[b] and Deviations from SCS Additivity Relationship[c]

4-Substituent	C_1	$C_{2,6}$	$C_{3,5}$	C_4	Additional shifts
NH_2	127.5 (−0.1)	130.3 (0.2)	115.9 (0.8)	145.0 (1.4)	CH_3, 21.3
OCH_3	129.7 (0.0)	130.3 (0.1)	114.3 (0.3)	158.3 (1.3)	CH_3, 21.2; OCH_3, 55.3
OH	130.6 (0.5)	130.8 (0.2)	116.0 (0.3)	153.2 (0.7)	CH_3, 21.1
CH_3	134.6 (0.1)	129.3 (0.2)	129.3 (0.2)	134.6 (0.1)	CH_3, 21.7
Cl	136.3 (0.8)	130.9 (0.4)	128.8 (0.0)	131.9 (0.1)	CH_3, 21.5
H[d]	137.4 (0.0)	129.2 (0.0)	128.4 (0.0)	125.6 (0.0)	
CN	144.0 (2.7)	130.6 (0.8)	132.5 (0.5)	110.4 (0.2)	CH_3, 22.5; CN, 119.0
$COCH_3$	143.6 (2.0)	129.7 (0.5)	129.0 (0.5)	135.5 (0.8)	CH_3, 22.1; $\mathit{C}OCH_3$, 196.0; $CO\mathit{C}H_3$, 26.7
CHO	145.3 (2.4)	130.2 (0.4)	130.2 (0.5)	135.2 (1.0)	CH_3, 22.5; CHO, 191.0
NO_2	146.3[e] (3.1)	130.3 (0.2)	123.8 (0.2)	146.7[e] (1.1)	CH_3, 21.9
CNH^+	153.9 (4.7)	131.2 (0.0)	136.2 (0.0)	95.8 (−0.9)	CH_3, 21.8; CNH, 108.5
N_2^+[f]	157.1 (3.7)	133.8 (−1.1)	133.0 (−1.4)	109.1 (−2.8)	CH_3, 22.7
$C(OH)CH_3^+$[g]	160.6 (6.5)	131.8 (0.1)	138.7 (0.3) 133.1 (0.2)	126.5 (0.4)	CH_3, 22.7; $\mathit{C}(OH)CH_3$, 216.0; $C(OH)\mathit{C}H_3$, 24.2
NO_2H^+	164.6 (9.0)	133.2 (0.3)	129.5 (0.7)	138.5 (−0.4)	CH_3, 23.1
$CHOH^+$[g]	165.9 (8.1)	133.1 (0.6) 132.5 (0.0)	146.2 (0.2) 133.8 (0.2)	126.0 (0.5)	CH_3, 23.5; CHOH, 200.3
CO^+[h]	166.3 (8.0)	133.5 (−0.1)	140.3 (−0.9)	82.8 (−2.0)	CH_3, 24.5; CO, 156.5
$C(CH_3)_2^+$	174.4 (9.6)	133.5 (−0.5)	141.5 (−0.8)	137.7 (0.6)	CH_3, 24.4; C_α, 242.8; $C(\mathit{C}H_3)_2$, 30.9
$CHCH_3^+$	181.8 (11.3)	134.7 (0.2) 134.4 (−0.1)	153.5 (−1.5) 142.4 (−1.1)	139.6 (1.0)	CH_3, 25.8; $\mathit{C}HCH_3$, 218.3; $CH\mathit{C}H_3$, 25.0

[a] δ_C, ppm from Me_4Si. [b] See Experimental Section for details of solution preparation. [c] $\delta_{^{13}C}$ (obsd) − $\delta_{^{13}C}$ (pred); positive deviations indicate greater deshielding than predicted. [d] Reference 17. [e] Interchangeable values. [f] G. A. Olah and J. Grant, *J. Am. Chem. Soc.*, in press. [g] Partial results in ref 22. [h] G. A. Olah and P. W. Westerman, *J. Am. Chem. Soc.*, **95**, 3706 (1973).

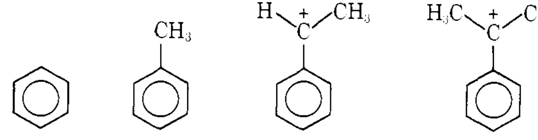
tert-butyl cation, while the total charge is reduced by only 0.101 electron; this means the σ charge on C_α gains in positive charge by 0.268 units. In MINDO/2, methyl is electron withdrawing in the initial substitution at the methyl cation but becomes slightly electron donating in substitutions to form the isopropyl and *tert*-butyl cations. Clearly, in most methods, the effect of methyl substitution on the total charge at C_α is a question of the balance between hyperconjugative electron donation to the vacant $2p\pi$ orbital and electron withdrawal in the σ-bond system. Another important feature common to all methods except MINDO/2 is that, while electron donation to the $2p\pi$ orbital per methyl group decreases with successive methyl substitution, inductive electron withdrawal per methyl group also decreases with successive methyl substitution. As noted above, in the MINDO/2 method, electron withdrawal per methyl group "decreases" to the point of reversing and becoming electron donation with successive substitutions. In other words, *σ-electron withdrawal by methyl increases as hyperconjugative electron donation to the π system increases.* A strongly hyperconjugating methyl is a stronger inductive withdrawing group.

While all of the computational methods show the same trends for the effect of methyl substitution on the $2p\pi$ charge at C_α, the widely varying results in Table I make it difficult to draw meaningful conclusions about the magnitude of the methyl inductive effect, although most methods agree on its direction. For the present purposes, most of the difficulties associated with the population analyses can be avoided by using only the π-charge results. Then, for a *hypothetical* molecular property which is linearly dependent only upon atomic charge density, any systematic deviations from a correlation with π-charge densities could be attributed to the σ-framework charge.

The ^{13}C chemical shift is a property which is known to be related to charge densities, but the best correlations with charges have been observed for trigonally hybridized carbons where the differences in total charges are controlled primarily by differences in π-charge densities, i.e., in situations such as the para carbons of monosubstituted benzenes[29] and the carbons in monocyclic aromatic ring systems.[30] For these systems, even the most simple π-approximation MO methods successfully reproduce the shielding trends. Several approaches have been devised for the theoretical estimation of ^{13}C chemical shifts, and most of these are based on charge densities, as well as other calculated or assumed quantities such as excitation energies and bond orders.[31] As would be expected, the success of these methods is highly dependent on the MO method used.[32] Thus, while it is probable that the chemical shifts of trigonally hybridized carbons are related to other molecular properties in addition to atomic-charge densities, we feel that, in this case, the best approach is to use π charges and attribute any systematic deviations from a correlation with π charges to either charges in the σ system or possibly other influences on the chemical shift. This approach at least allows π-charge effects to be separated out and thereby simplifies the interpretation of shielding differences.

Nonconstancy of α-Methyl SCS. Before discussing the ^{13}C evidence relevant to the problem of the methyl inductive effect, it is important to point out that ^{13}C chemical-shift data support the concepts of π-system polarization by the methyl group and hyperconjugative electron release from methyl under conditions of electron demand. The para-carbon shifts of monosubstituted benzenes can be used to support these points, especially since charge-density differences appear to be the only significant influence on such shifts. The para carbon in toluene shows a slight upfield shift (2.9 ppm) from the benzene shift, consistent with the molecular orbital picture of some π polarization and, less significant, charge transfer which results in a slight gain in electron density at the para position of toluene relative to benzene. Hyperconjugative charge transfer is suggested in comparing the para-carbon shifts of the phenylmethyl- and phenyldimethylcarbenium ions (α-styryl and *tert*-cumyl cations).[22] These para shifts differ by a larger amount (5.7 ppm), indicating greater methyl hyperconjugative electron donation in the electron-deficient system.[33]

The increased contribution of hyperconjugation in electron-deficient situations, where there is a high demand for



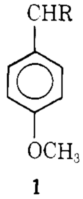
128.5 125.6 161.6 155.9

resonance stabilization of a positive charge, is important. The change in total charge at an α carbon upon substitution by methyl should reflect the balance among the hyperconjugative, polarizing, and inductive effects of a methyl group. If the demand for hyperconjugative stabilization is increased by creating more electron-deficient systems, it would be remarkable if the balance of effects remained the same so that the change in charge at C_α was always constant. Thus, if ^{13}C shifts were related to the total charge, it would not be expected that the α-methyl SCS would remain the same either. However, in contrast to this expectation of a varying α-methyl SCS, it is widely accepted that chemical shifts for multisubstituted benzenes can be predicted on the basis of the additivity of the SCS determined from the corresponding monosubstituted benzenes.[21a,c,34] The implication of an additivity relationship is that the α-methyl SCS will be constant in substituted benzenes. Therefore, we reexamined the validity of the additivity relationship for para-substituted toluenes to determine if in fact the α-methyl SCS is constant. For this purpose, the ^{13}C chemical-shift data for para-substituted toluenes presented in Table II include data for substituents of carbocationic and onium ion nature which have a much higher demand for positive-charge stabilization than in any previously reported study.

If the additivity relationship is valid, the chemical shifts in Table II should be predictable from adding the methyl SCS values for each ring position, determined by comparing toluene and benzene chemical shifts with the corresponding chemical shifts of the monosubstituted benzenes: $\delta_{CH_3PhX}(pred) = \delta_{PhX} + SCS$. The methyl SCS values determined from the benzene shift of δ 128.5 and the toluene shifts given in Table II are, in ppm: α SCS, 8.9; ortho SCS, 0.7; meta SCS, -0.1; and para SCS, -2.9.[34c] The reference chemical shifts of monosubstituted benzenes were those found by Nelson, Levy, and Cargioli[17] for uncharged benzenes and Olah, Westerman, and Forsyth[22] for the cationic derivatives. The deviations from the additivity relationship, $\delta_{CH_3PhX}(obsd) - \delta_{CH_3PhX}(pred)$, are given in parentheses in Table II.

Table II clearly demonstrates that the α-methyl SCS is not constant. There is a clear and systematic deviation from the additivity relationship. As the charge at C_1 increases (C_1 is less shielded), the deshielding produced by methyl substitution at C_1 also increases. Thus, methyl deshields C_1 by 8.9 ppm in toluene relative to benzene and by 20.2 ppm in the (*p*-methylphenyl)methylcarbenium ion relative to the phenylmethylcarbenium ion. Chemical shifts at the other ring positions show only small, irregular deviations from the additivity relationship.

Other examples can be cited in which substitution of methyl for hydrogen at a position of high positive-charge concentration results in greater deshielding than is typical of electronically neutral systems. Substitution of methyl for hydrogen at C_α in the *p*-methoxyphenylcarbenium ion (**1**, R = H) results in a deshielding of ~30 ppm for the C_α resonance.[35] Substitution by methyl in the dibenzocycloheptadienyl cation (**2**, R = H) deshields C_α by ~23 ppm.[36] Methyl substitution deshields C_α by ~25 ppm in the ethylenebenzenium ion (**3**, R = H).[37] The obvious exception to this trend is the carbenium center in the isopropyl cation which is deshielded upon methyl substitution only by an amount (10.4 ppm) comparable to uncharged systems, despite the expectation of a highly electron-deficient carbenium center due to the lack of π delocalization of the charge.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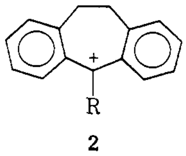
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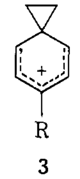
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The reason for the exceptionally low α-methyl SCS for the isopropyl cation compared with cations with more extended π systems is explained by considering π-charge distributions. Hyperconjugative electron donation to the carbenium ion center decreases the $2p\pi$-charge density significantly in the simple alkyl cations (see Table I), which is a shielding influence on C_α. In nearly all of the species with more extended π systems, molecular orbital calculations[38] indicate that the π-electron density is polarized away from C_α by methyl substitution, an expected deshielding influence on C_α. Also, in the simple alkyl cations, the gain in electron density in the π system from hyperconjugation is localized at the α carbon; in more extended π systems, the gain in electron density from hyperconjugative electron donation is spread out over several carbons. When these π-electron effects on the chemical shifts are subtracted from the observed SCS, the substitution of methyl for C_α-H in the isopropyl cation has one of the larger deshielding effects.[38]

Conclusions

The ^{13}C results reported here show conclusively that the deshielding produced by α-methyl groups cannot be attributed to a constant neighboring-group effect. The general trend observed in Table II is that the deshielding α-effect of the methyl group increases as methyl hyperconjugation becomes more important because of increased π charge at C_α. A strongly hyperconjugating methyl has a greater deshielding effect on C_α, after π-charge effects have been accounted for, than a methyl in an electronically neutral system where hyperconjugation is unimportant. By treating ^{13}C chemical shifts as a hypothetical property dependent only upon total atomic-charge density, we have shown that the data are consistent with an interpretation based on charge distributions in which the methyl group has a negative inductive effect in the σ-bond framework that increases in magnitude as the extent of electron donation from methyl to the π system increases via hyperconjugation. This interpretation based on charge distributions is supported by the trends observed in several different types of molecular orbital calculation on simple alkyl cations.

Other factors besides charge may also be involved in the α-methyl SCS. In the Karplus-Pople theory of chemical shifts,[31a] the substitution of methyl for hydrogen increases the sum of the mobile bond orders at C_α, thereby producing a paramagnetic deshielding effect.[32a,39] If the bonding from methyl to C_α increases as the charge at C_α increases, it is expected that the bond-order contribution to deshielding will increase. Similarly, it is conceivable that the methyl group could have a local effect of lowering the relevant excitation energies at C_α,[40] which in the Karplus-Pople formalism would also result in paramagnetic deshielding. These contributions to the α-methyl SCS cannot be discounted, although the use of the Karplus-Pople theory has sometimes given less satisfactory results than correlations with charge calculations alone. Another postulated factor is a neighboring-group diamagnetic *shielding* of about 30 ppm produced by replacement of carbon for hydrogen in methyl substitution.[41] If this shielding factor is included, it is obvious that the deshielding influences on C_α must be substantial to result in the overall downfield shift caused by methyl substitution.

While it is evident that the ^{13}C NMR results presented here are relevant to the question of the methyl inductive effect, its quantitative determination cannot be given at the present stage of development of ^{13}C chemical-shift theory or until more reliable methods are developed for calculating charge distributions in good models of these systems. It is important to note that our discussion has centered around the details of charge distributions and not the effect of methyl substitution on energies. Even when the molecular orbital calculations predict a gain in positive charge at a carbenium center upon substitution by methyl, the calculated energies show that both hyperconjugative electron donation *and* other electron redistributions are stabilizing influences.[7-9]

Experimental Section

Sample Preparation and ^{13}C NMR Spectra. All of the neutral para-substituted toluenes were obtained from standard commercial sources and were used without further purification. The ^{13}C NMR spectra were measured from solutions of about 25% by volume of the substituted toluene in CCl_4. Spectra of some of the cationic toluene derivatives had been measured in earlier studies in these laboratories, as noted in Table II. Protonation of 4-nitrotoluene and 4-methylbenzonitrile with 1:1 SbF_5–FSO_3H in SO_2ClF at −80° gave solutions of $4\text{-}CH_3C_6H_4NO_2H^+$ and $4\text{-}CH_3C_6H_4CNH^+$, respectively; ^{13}C NMR spectra were recorded at −60°. Ionization of 1-*p*-methylphenylethyl alcohol and 2-*p*-methylphenyl-2-propanol gave solutions of $4\text{-}CH_3C_6H_4CHCH_3{}^+$ and $4\text{-}CH_3C_6H_4C(CH_3)_2{}^+$, respectively, as previously described;[42] ^{13}C NMR spectra were measured at −80°.

The ^{13}C NMR spectra were obtained on Varian Associates Model XL-100 and HA-100 spectrometers operated in the pulsed Fourier transform mode. Details of the instrumentation and methods have been described elsewhere.[43] External (capillary) tetramethylsilane was used as a reference.

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References and Notes

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