Electronic Structure of Substituted Diphenylmethylcarbenium Ions. A Proton Magnetic Resonance and MO–INDO Study

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Abstract: Methyl proton chemical shifts of para-monosubstituted and para,para′-disubstituted diphenylmethylcarbenium ions are reported. Brown, Swain–Lupton, and Taft treatments demonstrate the prime importance of π charge at the positive trigonal carbon in the shielding. MO–INDO electronic structure more accurately shows that chemical shifts are mainly caused by both π electron density changes at the carbenium carbons and σ electron density changes at the hydrogen. Because of a strong π-electron donation by the OCH_3 group, INDO calculation fails for the *p*-methoxy monosubstituted ion whereas it runs well for the *p,p′*-dimethoxy disubstituted ion. "Saturation" of electronic effects in some polysubstituted ion is explained by the existence of a concerted π-inductive-mesomeric interaction of substituents. Experimental facts as well as the semiempirical MO–INDO approach provide strong evidence that all the ions have a single two-bladed propeller conformation, whatever the para substituent.

The question of the structure and reactivity of arylcarbenium ions is of prime importance in organic chemistry because many reactions involve such cations as key intermediates (e.g., electrophilic additions on aryl ethylenic compounds).[1] The experimental and theoretical interest is reflected as well by the numerous thermodynamic, kinetic, or spectroscopic measurements as by the various LCAO–SCF–MO investigations. Because these species contain an electron-deficient (positively charged) carbon atom, they are likely to be more sensitive to the electronic effects of substituents than corresponding neutral molecules and may therefore provide a useful basis for studying substituent effects. Much information in this field may be obtained by NMR spectroscopy and semiempirical all-valence electron calculations.

In a carbon-13 magnetic resonance (^{13}C NMR) study of substituted styryl and cumyl cations, Olah and co-workers[2a–c] observe that carbon chemical shifts are linearly related to Brown σ^+ constants; they also prove the nonconstancy of the α-methyl effect on electronic densities in phenylcarbenium ions[2d] and discuss the reliability of ^{13}C chemical shifts at the various carbons as a reflection of charge distributions in these ions.[2e] Ray, Kurland, and Colter[3] have also shown the importance of charge delocalization in the carbenium center shielding of trisubstituted trityl cations: substituent effects on carbon screenings are also expressed in terms of σ^+ constants while all the carbon chemical shifts of the unsubstituted species are well correlated with CNDO/2 charges; the authors still question the validity of an additivity relation for electronic effects on carbon chemical shifts. Taft and McKeever[4a] have noticed that ^{19}F screenings of *p*-fluorotrityl-substituent cations are proportional to stabilization energies of these ions; later, in a systematic investigation of fluorine shielding of conjugated systems, Dayal, Ehrenson, and Taft[4b] conclude that substituent constants $\sigma_R{}^+$ must be used to estimate π electronic delocalization in carbenium ions. Few proton magnetic resonance (^1H NMR) papers on aryl carbenium ions have been published; up to date studies in this field are limited to some experimental results on substituted styryl[3b] and cumyl[3c,5a] cations without an attempt at quantitative interpretation of the observed trends. Very recently, Farnum[5b] reviewed the charge density–NMR chemical shift correlations in organic ions with great emphasis on the difference between proton and carbon chemical shifts; among these, electrostatic field (particularly the E^2 term), ring current, and magnetic anisotropy contributions in hydrogen shielding are pointed out.

The present paper sets out to (i) report on some results obtained for a series of mono- and disubstituted diarylmethylcarbenium ions and compare them with literature data, (ii) analyze methyl proton substituent chemical shifts (SCS)[6] with usual substituent constants and interpret them with the help of INDO σ charge on the hydrogen and π charge on the positive trigonal carbon, and (iii) propose a qualitative explanation for the failure of INDO predictions of charge delocalization in the *p*-methoxydiphenylmethylcarbenium ion and for the nonadditivity observed in the SCS of the *p,p′*-dimethoxydiphenylmethylcarbenium ion.

Experimental Section

The samples of carbenium ions were prepared in situ by introduction of about 20 mg of diphenyl-1,1-ethylene in 0.3 ml of purified and dried SO_2 contained in a NMR tube at −50 °C; 0.1 ml of freshly distilled FSO_3H was slowly and carefully added with a few drops of CH_2Cl_2 for internal standard and locking signal. The spectra of this solution (about 0.25 mol/l. concentration in carbenium ion) was then recorded at −30 °C on a JEOL JNM-C-60 HL spectrometer in the internal lock mode; chemical shifts were measured with a frequency counter at ±0.1 Hz. No dilution effect and no temperature dependence in the range −20 to −60 °C were noticed. Data in Table I are the average of three distinct measurements and are given within ±0.006 ppm.

Results and Computing Conditions

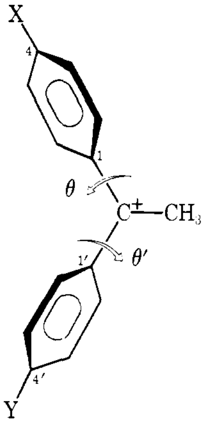
The chemical shifts δ for the methyl protons and the corresponding SCS $\Delta\delta$ of the para-substituted diphenylmethylcarbenium ions **1** and the para-substituted phenyl-*p′*-methoxyphenylmethylcarbenium ions **2** are reported in Table I. The resonances of phenyl groups were not considered as they are outside the scope of the present work.

All-valence-electron INDO calculations were performed on an IBM/370/168 computer using the standard program of Pople and co-workers[7] which was modified for the introduction of atom coordinates from bond lengths, bond angles, and dihedral angles. Standard bond lengths and angles as recommended in ref 7a, p 111, were used. In their CNDO/2 calculations on phenylcarbenium and onium, Olah, Westerman, and Forsyth[2e] also preferred such an approach to an arbitrary adjustment in individual geometries. The C_1–C_α and $C_{1'}$–C_α bond lengths were varied as a function of the two aryl twist angles θ and θ' in respect to the nodal plane of the empty 2p orbital of the carbenium center (Table II); for the C_α–C_β bond, we chose 1.52 Å. OCH_3 and NO_2 substituents were located in the phenyl plane; $\angle C_1C_\alpha C_\beta$, $\angle C_{1'}C_\alpha C_\beta$, $\angle C_4OCH_3$, and $\angle C_4NO$ angles were fixed at the standard value of 120°. For mono- and dichloro-substituted carbenium ions **1**, no

Table I. Chemical Shifts, δ, and SCS Values, $\Delta\delta$, for Methyl Protons of Diarylmethylcarbenium Ions[a]

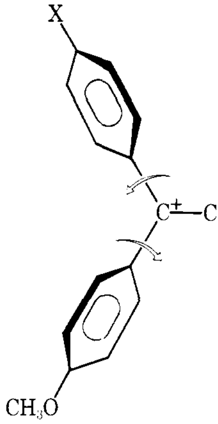
	Ions **1a**		Ions **1b**		Ions **2**	
X	δ	$\Delta\delta$	δ	$\Delta\delta$	δ	$\Delta\delta$
OCH_3	−1.938	−0.361	−1.990	−0.413	−1.990	−0.052
CH_3	−1.665	−0.088	−1.745	−0.168	−1.947	−0.009
F	−1.620	−0.043	−1.653	−0.076		
Cl	−1.603	−0.026	−1.637	−0.060		
H	−1.577	0	−1.577	0	−1.938	0
CF_3	−1.467	0.110	−1.300	0.277		
NO_2	−1.372	0.205			−1.927	0.011

[a] Low-field values in ppm from internal CH_2Cl_2 (δ) and from the unsubstituted ion ($\Delta\delta$).



1a, Y = H; X = OCH_3, CH_3, F, Cl, H, CF_3, NO_2

b, Y = X = OCH_3, CH_3, F, Cl, H, CF_3



2, X = OCH_3, CH_3, H, NO_2

Table II. INDO Conformational Analysis of Diphenylmethylcarbenium Ions[a]

X	θ, deg	C_1-C_α, Å	Y	θ', deg	$C_{1'}$-C_α, Å	Electronic energy,[b] kcal/mol
H	60	1.50	H	0	1.46	2.06
H	47	1.49	H	17	1.47	0.51
H	34	1.48	H	34	1.48	0
NO_2	60	1.50	H	0	1.46	0.27
NO_2	34	1.48	H	34	1.48	0
OCH_3	60	1.50	OCH_3	0	1.46	2.32
OCH_3	34	1.48	OCH_3	34	1.48	0

[a] To allow for a decrease in π conjugation between the aryls and the positive trigonal carbon when the twist angles θ or θ' increase, the C_1-C_α and $C_{1'}$-C_α bonds were varied as indicated in the table; for the symmetrically twisted conformation, these two bonds were taken as 1.48 Å long as in the theoretical study of diaryl-1,1-ethylenes: C. Favini and M. Simonetta, *Theor. Chim. Acta*, **1**, 294 (1963); G. Casalone and M. Simonetta, *J. Chem. Soc. B*, 1180 (1971). [b] From the symmetrically twisted conformation.

Table III. INDO Charge Densities on C_α and C_β Carbons and on Methyl Protons for Diphenylmethylcarbenium Ions **1**[a]

X	Y	$q_{C_\alpha}{}^{\pi}$	$q_{C_\alpha}{}^{\sigma+\pi}$	q_{C_β}	q_H	Σq^{π} [b]
OCH_3	H	0.5297	3.7397	4.0086	0.9511	13.3216
CH_3	H	0.5165	3.7333	4.0097	0.9492	13.2587
F	H	0.5156	3.7301	4.0108	0.9477	13.2997
H	H	0.5063	3.7280	4.0111	0.9473	13.2468
CF_3	H	0.5018	3.7254	4.0120	0.9447	13.2490
NO_2	H	0.5002	3.7242	4.0120	0.9545	13.2551
OCH_3	OCH_3	0.5483	3.7471	4.0067	0.9545	13.3934
CH_3	CH_3	0.5254	3.7364	4.0087	0.9510	13.2698
F	F	0.5244	3.7330	4.0106	0.9480	13.3517
CF_3	CF_3	0.4965	3.7224	4.0131	0.9420	13.2505

[a] Symmetrical two-bladed propeller conformation assumed with $\theta' = \theta' = 34°$ and C_1-C_α = $C_{1'}$-C_α = 1.48 Å. [b] Total π charge on carbons in the diphenylmethylcarbenium substrate.

calculation was carried out since the INDO program is not yet available for chlorine.[7] Geometry of the ions was determined by an INDO conformational analysis of the unsubstituted, the *p*-nitro substituted, and the *p,p'*-dimethoxy-substituted diphenylmethylcarbenium ions; results are reported in Table II. Charge densities for the propeller conformation ($\theta = \theta' = 34°$) of ions **1** are collected in Table III.

Discussion

1. General Remarks and Comparison with Literature Data. Examination of SCS in Table I shows a strong influence of substituents and, generally, an additivity of the effects in poly-substituted derivatives **1b**, but an apparent "saturation" of structural influences occurs when a methoxy group substitutes a phenyl (ions **1b**, Y = X = OCH_3 and ions **2**). In order to explain these facts which are probably related to the charge delocalization, a comparison of our data with literature results on other arylcarbenium ions must be very powerful. We have thus attempted correlations between SCS of five ions **1a** (X = OCH_3, CH_3, F, H, and CF_3) and corresponding SCS of respectively (i) methyl protons (eq 1), (ii) methyne protons (eq 2), and (iii) ^{13}C carbenium carbons (eq 3) of styryl cations reported by Olah et al.[2b,c]

$$\Delta\delta(\mathbf{1a}) = 0.489\Delta\delta_{CH_3}(\text{styryl}) \qquad r = 0.996,\ \text{sd} = 0.015^8 \quad (1)$$

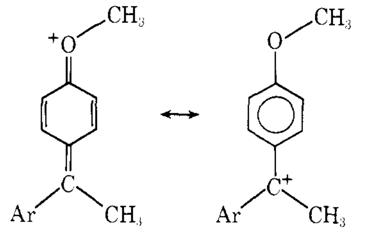
$$\Delta\delta(\mathbf{1a}) = 0.228\Delta\delta_{CH}(\text{styryl}) \qquad r = 0.998,\ \text{sd} = 0.002 \quad (2)$$

$$\Delta\delta(\mathbf{1a}) = 0.097\Delta\delta_{^{13}C^+}(\text{styryl}) \qquad r = 0.991,\ \text{sd} = 0.024 \quad (3)$$

Equation 1 is very instructive with regard to the stereochemistry of ions **1**. Assuming a planar and substituent-independent conformation for all the styryl cations, correlation 1 means that the preferred conformation of ions **1a** is also independent of the aromatic substituents X; consequently, this is so for all ions **1** and **2**. Moreover, the slope of relation 1 reflects a strong decrease in susceptibility to electronic effects in ions **1a** with respect to styryl cations. This reduction may have two distinct reasons. First, positive charge delocalization into the unsubstituted aromatic ring for ions **1** decreases the sensitivity to the first ring substituent effects. Second, and this is certainly the main reason, it is evident that a planar conformation for ions need not be considered; indeed, a completely coplanar model ($\theta = \theta' = 0°$) would force the ortho hydrogens of adjacent rings to within 0.6 Å of each other, a value well below the normal van der Waals distance of about 2.2 Å; to overcome the steric repulsions, the phenyl groups must rotate out of the nodal plane of the carbenium center, but the extent of rotation would be expected to be minimal, consistent with a maximum delocalization of the positive charge. Further INDO conformational analysis (vide infra) will show that all the ions **1** are shaped like a two-bladed propeller with $\theta = \theta' = 34°$. Similar trends are also observed in ^{13}C NMR of cumyl cations[2c] and ^{19}F NMR of fluorophenyl carbenium ions.[4]

Few NMR results on disubstituted arylcarbenium ions have been published so that comparison with SCS in ions **1b** and **2** is very difficult. Nevertheless, SCS in cations **1b** show the same particularities as ^{19}F shieldings in disubstituted *p*-fluorotrityl cations:[4a] in the two families, nonadditivity of methoxy effects on chemical shifts of dimethoxy-disubstituted arylcarbenium ion is clearly evident; in addition, it must be noticed that, in fluorotrityl cations, this phenomenon is increased with a greater π electronic donation, i.e., more marked with $N(CH_3)_2$ than with OMe.[4] Similar facts can also be observed from ^{13}C shieldings in symmetrical trisubstituted trityl cations.[3]

However, previous work on the parent substituted 1,1-diphenylethylenes[9] has shown a strict additivity on SCS of vinyl protons so that "saturation" in π electronic effects appears as a particular characteristic of ions in which a strong donor substituent can conjugate with the vacant 2p orbital of the carbenium center;[10,11] for example, such a property has also been observed in solvolysis of benzhydryl chlorides,[12] bromination of 1,1-diarylethylenes[13] and polysubstituted benzenes,[14] stability of trityl cations,[4a,11,15] arylxanthylcarbenium,[15] and triphenylcyclopropenium[15] ions, and heat of formation and ionization potential of methyl cations.[16] Thus, *p*-methoxy-substituted derivatives are certainly better described by a quinoidal oxonium ion (a) rather than by a benzenoidal carbenium ion (b), the largest fraction of positive charge being onto the methoxy group, but, it must be remembered that (a) and (b) are only a convenient shorthand form for portraying electronic delocalization and that neither the quinoid (a) nor the benzenoidal (b) structure can exclude the other.[11] From this resonance theory point of view, additivity of multiple substituent effects in ion **1b**, X ≠ OCH_3, can be understood while structure (a) explains both "exaltation" on SCS of ions **1b**, X = OCH_3, and "saturation" on SCS of ions **1b**, X = OCH_3, and **2**, the sensitivity of methyl proton chemical shifts to the X substituent electronic effects in these cations will be different from that of other ions **1** because drastic structural changes occur when going from one set to the other.



a b

The above considerations and the linear relations 1–3 clearly prove that electronic charge at the positive trigonal carbon is the most important contribution to the shielding of methyl protons of ions **1** and **2**. Thus, quantitative interpretation of SCS in terms of π electronic density changes on the carbenium center can be investigated.

2. Relation between SCS and Substituent Constants. Substituent effects on charge delocalization in cations **1a** may be expressed by Brown σ^+ parameters since these constants were defined in solvolysis of substituted cumyl chlorides, a reaction which has a highly electron-deficient, carbenium ionlike transition state. Equation 4 represents the correlation of $\Delta\delta(\mathbf{1a})$ vs. $\sigma_p{}^+$ for the seven monosubstituted diphenylcarbenium ions **1a**:

$$\Delta\delta(\mathbf{1a}) = 0.308\sigma_p{}^+ \qquad r = 0.961, \text{sd} = 0.043 \qquad (4)$$

From this relationship, it is clear that resonance interactions between carbenium center and substituent contribute mainly to delocalization of positive charge. However, correlation 4 is not statistically very good. Furthermore, close examination of SCS in Table I indicates that chlorine acts on methyl proton as a repelling substituent although it is expected to attract because of its $\sigma_p{}^+$ parameter; other NMR data on arylethylenic compounds and on aryl carbenium ions[3-5,17,18] reveal that chlorine acts both as a repelling and as an attracting substituent. But it must be remembered that, from a strictly resonance point of view, chlorine is a well-donor substituent according to Swain–Lupton[17] *R* or Taft[18] $\sigma_R{}^0$, σ_R, $\sigma_R{}^+$, and $\sigma_R{}^-$ constants. Godfrey[19] has resolved this apparent discrepancy by assuming that chlorine exerts a secondary field effect which does not disturb π electronic distribution, but only affects the energy of the electrons.

A two-parameter treatment is then expected to give better results since the hypothesis of equal susceptibility of SCS to field and resonance effects is not generally valid.[17,18] The Swain–Lupton or the Taft treatments may be retained for they both achieve maximum separation between field and resonance contributions. We have compared them (eq 5 and 6, respectively), the $\sigma_R{}^+$ constants being used in the latter as recommended by Taft in the study of carbenium ions.[4b,18]

$$\Delta\delta(\mathbf{1a}) = 0.102F + 0.578R \qquad r = 0.936, \text{sd} = 0.056 \quad (5)$$

$$\Delta\delta(\mathbf{1a}) = 0.215\sigma_I + 0.367\sigma_R{}^+ \qquad r = 0.981, \text{sd} = 0.030 \quad (6)$$

Correlation 6 is statistically better than correlation 5; "percent resonance" % *R* is greater in (5) than in (6), 78% when calculated with statistical weights defined in ref 17 instead of 63%. Taft treatment underestimates the sensitivity to π electronic effects of the carbenium center positive charge since it is well established that σ electronic effects (i.e., field and inductive) are unimportant;[2-5,17,18] the Swain–Lupton correlation 5 thus seems to give a more realistic picture of the susceptibility to charge delocalization by resonance interaction between the substituent and the positive trigonal carbon.

From the previous discussion, it is clear that such correlations as 5 or 6 cannot be extended to the disubstituted ions **1b** and **2**; the point corresponding to the dimethoxy ion does not fit the regression lines of (5) or (6). Nonadditivity of the two methoxy effects in the ion **1b**, X = Y = OCH_3, cannot be explained on the single ground of substituent constants *F* and *R* or σ_I and $\sigma_R{}^+$. Because of this "saturation" and of the important structural changes caused by one methoxy group, analysis of the whole SCS on ions **1** and **2** by a single Hammett-type or dual substituent parameter-type approach is therefore irrelevant; however, SCS on ions **2** can be independently investigated, but insufficient data on cations **2** preclude more detailed examination.

The Swain–Lupton or Taft treatments improve the correlation quality and show the reality of distinct field and resonance effects; they have nearly the same merits although the adequacy of a single resonance parameter set to describe π electronic effects is not realistic and some controversy may exist about the best choice of resonance constants.[17,18] Nevertheless, the physical meaning of the weighting factors is not yet clear as pointed out by Miller and co-workers.[20]

These deficiencies of the Brown, Swain–Lupton, and Taft approaches have prompted us to search for a semiempirical interpretation of chemical shielding of methyl protons in ions **1** with the help of their MO-INDO electronic structure.

3. Separation of the Different Contributions to SCS and Influence of the Carbenium π Electronic Density. Since Pople's work,[21] it is well known that the screening σ_A of a nucleus A in a molecule results from the summation of many distinct contributions:

$$\sigma_A = \sigma_d + \sigma_p + \sigma_M + \sigma_E + \sigma_R + \sigma_S \qquad (7)$$

σ_d is associated with the A electrons moving freely around the nucleus A in a spherical symmetry s state and represents the diamagnetic Lamb term. σ_p is a local correction due to the nonspherical electronic distribution around A and involves the mixing of ground and excited states; for a hydrogen, the absence of low-lying atomic p orbitals made this paramagnetic term very small so that it can be neglected. σ_M is the contribution to the screening of A by the atomic currents induced in atoms other than A; it is then related to their magnetic anisotropy. σ_E represents an electric field effect on the shielding of A by the internal dipole moment and charges on carbons in the molecule. σ_R stands for an interatomic contribution and is related to the current produced by electrons which are delocalized in the rings of the molecule. σ_S represents all the contributions of the solvent to the screening of A.

Such a decomposition obviously involves a significant error in σ_A and any attempt to obtain the absolute screening of a given nucleus is fallacious. However, in studies of proton SCS, eq 7 may be rewritten as (8) where the $\Delta\delta_i$ ($= -10^6\Delta\sigma_i$) are the variations of the different contributions from the unsubstituted ion to the substituted one.

$$-10^6\Delta\sigma = \Delta\delta \simeq \Delta\delta_d + \Delta\delta_M + \Delta\delta_E + \Delta\delta_R + \Delta\delta_S \quad (8)$$

Evaluation of each term in (8) requires a precise knowledge of the stereochemistry of ions **1**. We have previously demonstrated that steric hindrance between ortho protons of vicinal rings prevents a completely planar model. In principle, geometry of the para-substituted diarylmethylcarbenium ions should be determined by the minimization of the total molecular energy with respect to the two angular parameters θ and θ'. However, such a long conformational analysis does not appear indispensable here. Indeed, in a previous work on the parent diphenyl-1,1-ethylenes,[9] we have pointed out that minimum energy conformation is made up of a two-bladed-propeller conformation, whatever the para substituent: the two rings are rotated out of the central trigonal plane by an angle of 34° and in the same direction, the ortho protons above and below this plane are distant from about 2.6 Å, and the two rings form an angle of about 60°.[9] In view of the stereochemical analogy between diarylmethylcarbenium ions and diaryl-1,1-ethylenes, the relief of steric interactions in ions **1** can be expected to require the same angle of 60° between the two aryls. Thus, we have only to compare total electronic energies of conformations which satisfy this steric condition. On the other hand, relations 1 to 4 have proved the independence between substituent electronic power and geometry of ions **1a**. Calculations may then be carried out only on the unsubstituted ion, on a monosubstituted ion **1a**, and on a disubstituted ion **1b**. Several quantum chemical methods may be used for such a theoretical conformational analysis; literature comparisons between them reveals that the MO-INDO method on carbocations gives results as good as ab initio STO-3G calculations.[22-24] We have thus retained the MO-INDO method. Results for diphenylmethyl-, *p*-nitrodiphenylmethyl-, and bis(*p*-methoxyphenyl)methylcarbenium ions are collected in Table II.

Potential minima are found for $\theta = \theta' = 34°$, whatever the para substituent, as expected from the above discussion. Conformations of diarylmethylcarbenium ions are similar with this of the parent olefins.[9]

We may then attempt an estimation of the different contributions of methyl proton SCS of ions **1** in this propeller conformation (eq 8). But, it must be recalled that the diamagnetic component $\Delta\delta_d$ gives the most important part of this shielding, other terms being only slight corrections. Theoretical calculations reveal that $\Delta\delta_d$ depends upon quantum chemistry indices such as electronic charge and bond order, whatever the various molecular wave functions retained;[21,25-27] unfortunately, distinct expressions were obtained by the authors. In this work, we will use an empirical approach to $\Delta\delta_d$ from the MO-INDO electronic structures of ions **1**: first, from the calculated secondary contributions to SCS (i.e., $\Delta\delta_M$, $\Delta\delta_E$, $\Delta\delta_R$, and $\Delta\delta_S$), we will reach an approximate value of the $\Delta\delta_d$ terms; second, we will attempt to explain these "experimental diamagnetic contributions" $\Delta\delta_d$ by INDO charge on the carbenium center and methyl protons.

For low concentrations of carbocations in inert SO_2, $\Delta\delta_S$ is only made up of an electrostatic reaction field.[28] From our previous studies on arylethylenic compounds,[9,29] we may expect it to be very small; thus, we have disregarded it.

Table IV. Electrostatic, $\Delta\delta_E$, Magnetic, $\Delta\delta_M$, and Diamagnetic, $\Delta\delta_d$, Contributions of Methyl Proton SCS for Ions **1**[a]

	Ions **1a**			Ions **1b**		
X	$\Delta\delta_E$	$\Delta\delta_M$	$\Delta\delta_d$	$\Delta\delta_E$	$\Delta\delta_M$	$\Delta\delta_d$
OCH_3	0.017		−0.378	0.034		−0.447
CH_3	−0.003	0.012	−0.097	−0.006	0.024	−0.186
F	0.030	0.007	−0.080	0.060	0.014	−0.150
Cl	0.028	0.012	−0.006	0.056	0.024	−0.140
H	0	0	0	0	0	0
CF_3	0.020	0.010	0.080	0.040	0.020	0.217
NO_2	0.050	−0.007	0.162	0.100	−0.014	

[a] Low-field values from the unsubstituted ion.

For organic ions, the $\Delta\delta_E$ term consists of two distinct contributions: (i) a polarization of the C–H bonding electrons by the C–X electrostatic dipole field,[9,29] and (ii) an effect proportional to the variation of the square of the field (the E^2 correction) generated at the proton by charge density located at the carbenium center.[5] However, the full-scale variation of this charge in ion **1** (from **1a**, X = NO_2, to **1b**, X = Y = OCH_3) is only about 0.025 electron (cf. Table III) so that the E^2 correction for SCS, calculated by means of formula 5 of ref 5b, does not exceed 0.013 ppm, an extremely negligible value; we have disregarded this contribution to SCS in ions **1**, $\Delta\delta_E$ being then limited to the first polarization effect.

Free rotation of the methyl protons about the $C_\alpha{}^+$–C_β bond complicates precise calculation of the $\Delta\delta_R$, $\Delta\delta_E$, and $\Delta\delta_M$ terms. However, bearing in mind that these corrections are small, we can assume that the average position of the methyl protons is along the $C_\alpha{}^+$–C_β axis at a distance of 1.09 cos (70.5°) = 0.36 Å from the C_β carbon. All the $\Delta\delta_R$, $\Delta\delta_E$, and $\Delta\delta_M$ evaluations on ions **1** were then led for a proton located at this point.

Ring anisotropy contribution $\Delta\delta_R$ depends upon the charge transfer between the substituent(s) and the two aryl rings and appears as a diamagnetic shift of the methyl proton; for example, if we suppose a 0.15 π-electron transfer, the Pople's dipole model[30] gives a diamagnetic shift of about 0.007 ppm at the average methyl proton location. Table III shows that this π-electron transfer is unimportant within the range of studied substituents so that the ring anisotropy corrections can be neglected for the whole ions **1**.

Electrostatic $\Delta\delta_E$ and magnetic $\Delta\delta_M$ contributions were respectively estimated by the usual Buckingham–Musher and MacConnell expressions as in previous works.[9,29] The C-X dipole moments and magnetic susceptibilities were also those previously retained.[9,29] Results of the calculations at the average methyl proton position are collected in Table IV.

It is evident from Table III that substituents strongly influence charge densities on C_α carbons and methyl protons whereas C_β carbon remains almost insensitive (variation of about 10^{-3} electron within the range of substituents). In addition, MO calculations indicate that substituent-induced changes on the carbenium center are dominated by changes in electron density despite the non-negligible and reverse changes in σ population. Now this π population measures the electronic interaction of the empty 2p orbital at the positive carbon with (i) the substituent 2p orbitals (conjugation) and with (ii) vicinal C–H bonds (hyperconjugation). Because of this hyperconjugation and perhaps also of a through space influence of this π density on the proton location, diamagnetic contribution $\Delta\delta_d$ to SCS of ions **1** should be mainly reflected by the variations $\Delta q_{C^+}{}^{\pi}$ in electron density from the unsubstituted ion to the substituted one. An attempt to correlate $\Delta\delta_d$ and $\Delta q_{C^+}{}^{\pi}$ gives eq 9.

$$\Delta\delta_d(\mathbf{1}) = -12.73\Delta q_{C^+}{}^{\pi} \quad r = 0.964, \text{sd} = 0.053 \quad (9)$$

The point corresponding to the *p*-methoxydiphenylcarbenium ion clearly deviates from the regression line of (9); at the opposite, $\sigma_{OCH_3}{}^+$ seems to accurately picture the ability of the methoxy substituent to release π electrons into the empty 2p orbital at the positive carbon (see relation 4). Conversely, the dimethoxy-substituted ion **1b**, X = Y = OCH_3, falls on the regression line of (9) whereas it does not fit eq 4 because of the nonadditivity of the two methoxy electronic effects.

The reasons for such an apparent discrepancy between the Brown-type and the MO–INDO approaches require a detailed discussion.

4. Failure of MO–INDO Calculation and "Saturation" of Electronic Effects in Some Substituted Ions. The π-electron transfer from the methoxy group to the empty 2p orbital at the carbenium center is certainly better approximated by the valence bond structure (a) than by the benzenoidal form (b). Evidently, this π-electron migration is accurately pictured by the $\sigma_{OCH_3}{}^+$ empirical parameter since, in the definition reaction of the Brown set, the π-electron transfer from the methoxy group is very important; now it is well known that this is the main reason for the large difference between Hammett σ_{OCH_3} and Brown $\sigma_{OCH_3}{}^+$ constants.

It is then tempting to assert that the semiempirical MO–INDO method fails in describing the π-electron transfer from the methoxy group to the diphenylmethylcarbenium substrate in the ion **1a**, X = OCH_3, and consequently the electronic structure of the latter. Indeed, the reliability of the INDO approach with some substituted aryl cations was also questioned by Evleth and Horowitz.[24] They showed that the effect of the strong π-electron-donating substituent NH_2 cannot be predicted in the filled shell singlet state of the *p*-aminophenyl cation, but looks like the π delocalization calculated in the lowest triplet state of this ion.[24] They concluded that INDO calculations are inadequate to study ions which are substituted by a strong π-electron-releasing group.

The main reason which may be invoked to explain this failure of the INDO method is the parameterization of some integrals since Jaffé[31] has demonstrated that an unreparameterized form of CNDO–INDO calculation does not give good estimates of spectroscopic transition energies. For example, in the standard version of the INDO program, bonding parameters are calibrated to give the best possible overall agreement between INDO and nonempirical SCF calculations for some diatomic molecules; these bonding parameters are then assumed to depend only upon the nature of the two-bonded atoms, whatever the orbitals and the compounds.[7a] Such a drastic assumption is very questionable. In view of the present results, we believe that the π-resonance integral of the C_4–OCH_3 bond is not suitable to reflect the important π-electron transfer from the methoxy to the substrate in the *p*-methoxydiphenylmethylcarbenium ion. It is also possible that C_1–C_α bonding parameters and oxygen valence-state ionization potentials are not accurately calibrated for CNDO–INDO calculations on this ion.

On the contrary, the INDO method runs well for the *p,p′*-dimethoxydiphenylmethylcarbenium ion. From the above analysis, this requires a slight π-electron transfer by each of the two methoxy groups. Then standard parameterization, particularly for bonding parameters, can give a good fit between INDO electronic structure and experimental charge delocalization in this ion. Conversely, this decrease in π-electron donation by each of the two methoxy groups explains the nonadditivity of the $\sigma_{OCH_3}{}^+$ parameters in the Brown-type eq 4. But why is there such a reduction in π-electron migration from each of the OCH_3 substituents to the empty 2p orbital of the positive carbon?

This striking phenomenon can be readily accommodated by the Mulliken[32] and Godfrey[19] concepts of concerted π-inductive-mesomeric action. Indeed, physical organic chemists and theoretical chemists now recognize that the electron-releasing power of a group such a methoxy must be divided into two distinct effects, i.e., a charge transfer (or mesomeric) by which π electrons are removed from a filled 2p orbital of the substituent to the conjugated π system and a π-inductive effect which only redistributes π electrons without any net transfer from the substituent.[33] Mulliken[32] and Godfrey[19] assume that, in polysubstituted compounds, the amount of π-electron donation by a group such as a methoxy depends on the π-inductive effect of all the other substituents; for example, it decreases when the π-inductive effect of all the other groups increases.

That such a concerted π-inductive-mesomeric interaction exists has already been proved in two elegant and independent works by Taft and co-workers[4a,34] and by Rakshys, McKinley, and Freedman.[35] McKeever and Taft[34a] have shown that π-donor effects of *p*-OCH_3 and *p*-$N(CH_3)_2$ on the stabilization energies of triphenylmethyl anions are essentially identical while "saturation" is clearly evident from the electronic effects of several NO_2 groups; conversely, stabilization effects by π-electron-donating groups occur in polysubstituted trityl cations.[4a,34b] On the other hand, Freedman and co-workers[35] have demonstrated that the rotational barrier about the N-aryl bond of the para′-substituted *p*-dimethylaminotrityl cation is substituent dependent and is directly related to π delocalization; the observation that the barrier is increased by donor groups unambiguously confirms that the π bond order of the N-aryl and, consequently, the π-electron transfer from the $N(CH_3)_2$ group depend on the electronic power of the other substituents. This last demonstration also casts some doubt on the validity of the standard parameterization of bonding parameters for INDO calculations on such ions. Very recently, similar observations about the rotational barrier in protonated benzaldehydes and acetophenones were reported by Olah and co-workers.[2e]

The present work provides another experimental proof of the validity of the Mulliken–Godfrey concepts. In the *p,p′*-dimethoxy-substituted ion **1b**, the strong π donor inductive effect of a methoxy opposes an appreciable π-electron migration from the second methoxy toward the 2p positive carbon orbital and vice versa; the overall effect is a significant reduction in electron transfer from each of the methoxy groups in respect to that taking place in the *p*-monomethoxy-substituted ion **1a**. On the contrary, CH_3, F, Cl, and CF_3 groups whose π-mesomeric interactions with the carbenium center are small mainly exert a π-inductive effect on the charge delocalization in ions **1**. Additivity of electronic effects of CH_3, F, Cl, and CF_3 groups and nonadditivity of effects of OMe groups on the diamagnetic term $\Delta\delta_d(\mathbf{1})$ are then clearly interpreted by this concerted π-inductive charge-transfer action. It can also be noticed that this theory explains the relative inefficiency of substituents on methyl proton chemical shifts of ions **2** and, generally, "saturation" of electronic effects on different strongly polar species such as cations and anions.

Hence, interpretation of diamagnetic contributions $\Delta\delta(\mathbf{1})$ of ions **1** from their INDO electronic structure requires the exclusion of the *p*-monomethoxy-substituted ion; eq 9 is thus slightly modified into (9′) which obviously has better statistical indices.

$$\Delta\delta_d(\mathbf{1}) = -11.88\Delta q_{C^+}{}^{\pi} \quad r = 0.985, \text{sd} = 0.033 \quad (9')$$

The slope amplitude of this linear relation is very unusual. Literature data show that SCS of aromatic protons are directly proportional to changes in the π-electron densities at the bonded carbon atoms with generally a proportionality factor of about -10 ppm/electron so that the greater sensitivity of methyl protons is, of course, a surprising point. Other results on cations reveal also a lack of quantitative agreement with this value of -11.88 ppm/electron. From a qualitative approach in cyclobutenyl cations[36] and benzenonium ions,[37] it is concluded that methyl proton chemical shifts are linearly related to localized charge on adjacent trigonal carbon atoms and constants of -3.30 and -4.75 ppm/electron are respectively proposed. A slope of -3.5 ppm/electron is found again in an empirical MO-ω calculation on substituted pyrylium salts by Boyd and Balaban,[38] whereas Farnum[5b] proposed -2.33 after calculation from the Buckingham–Musher expression. Several reasons may be invoked for this large scatter in sensitivity to electronic charges. First, in the empirical works on aromatic cations,[36,37] the assumption of a repartition of positive charge on the ring trigonal carbons alone is approximate; other carbon atoms and also hydrogen atoms certainly carry a large fraction of positive charge as expected from all-valence-electron calculations. Secondary interactions such as ring or magnetic contributions and field effects may be other causes of differences in slopes. Second, it is now well established from theoretical studies on stabilization of carbenium ions by methyl groups that an α-methyl on a cation is a σ acceptor by inductive action and a π donor by hyperconjugative interaction;[39,40] on the other hand, Olah and Forsyth,[2d] after a pertinent comparison of the various SCF–MO methods, conclude that these two effects depend on the total charge at the carbenium center and exhibit parallel variations. Thus, σ electron density on methyl protons will also be sensitive to para and para′ substituents whereas charge on methyl carbons will roughly remain constant.

5. General Semiempirical Expression of the Diamagnetic Contribution to SCS. Table III clearly shows this trend: while π population $q_{C^+}{}^{\pi}$ is largely increased by a strong π-donating substituent, the slighter increase in total charge $q_{C^+}{}^{\sigma+\pi}$ indicates a greater σ-inductive effect of methyl. Such an observation means that SCS on methyl protons of ions **1** must depend upon both π charge on positive carbon and σ charge on methyl proton. An attempt to interpret all the diamagnetic contributions $\Delta\delta(\mathbf{1})$ for ions **1**, except that for the monomethoxy ion, in terms of both $\Delta q_{C^+}{}^{\pi}$ and Δq_H by a least-squares treatment gives eq 10.

$$\Delta\delta(\mathbf{1}) = -7.23\Delta q_{C^+}{}^{\pi} - 22.33\Delta q_H \qquad (10)$$

$$r = 0.996,\ \mathrm{sd} = 0.017$$

Relation 10 not only improves the quality of the fit but also gives a more significant picture of physical reality. Sensitivity of SCS diamagnetic contribution to charges in σ-electron density on methyl protons is in fairly good agreement with values of -21.4 to -26.6 ppm/electron σ which are usually retained by researchers.[25-28] Moreover, a susceptibility to π-electron density variations at the carbenium center of -7.23 ppm/electron is also more realistic since it will be unreasonable to suppose a sensitivity greater than for an aromatic proton. The remaining large differences with literature results[5,36-38] may be due to stronger hyperconjugative interaction of the methyl group in open carbenium ions than in cyclic cations. Lastly, an important through-space π polarization cannot be definitively excluded.

Conclusion

Proton magnetic studies of diphenylmethylcarbenium ions show that methyl proton chemical shifts mainly reflect the positive charge density at the carbenium carbon; diamagnetic contribution to shielding can be expressed as a linear combination of π-electron density at the positive carbon and σ-electron density at the methyl hydrogen.

It is pointed out that strong π-electron donation by a methoxy group at the carbenium empty 2p orbital cannot be obtained by the semiempirical MO–INDO method in its standard version. On the contrary, "saturation" of electronic effects in the *p,p′*-dimethoxy-disubstituted diphenylcarbenium ion is accurately predicted by the all-valence-electron calculation. A concerted π-inductive-mesomeric interaction between substituents in polysubstituted ions is invoked to explain such an observation.

INDO conformational analysis and comparison with literature data also demonstrate that geometry of substituted diphenylmethylcarbenium ions is made up of a two-bladed propeller, whatever the para substituent; the two vicinal rings are twisted in the same direction from the same angle of 34° in order to relieve steric hindrance between ortho protons.

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