# The Torsional Barrier around the Phenyl–C$^+$ Bond in Phenylcarbenium Ions

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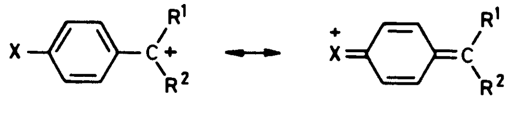
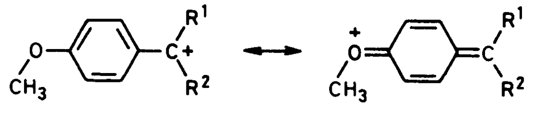
The barrier to rotation around the phenyl–carbenium carbon bond in a series of carbenium ions $R^1R^2C^+Ph$ (with $R^1$ and/or $R^2$ = H, $CH_3$, cyclopropyl, and $C_6H_4X$) has been measured by complete line-shape analysis of the n.m.r. spectra or by the spin saturation transfer method. $\Delta G^\ddagger$ Values range from 36 to 78 kJ mol$^{-1}$. The results are discussed in terms of steric and electronic contributions and the relationship of the $^{13}C$ chemical shift of the carbenium centre with the $\sigma_{C^+}$ values of the *para*-substituent is analysed.

Species containing an electron-deficient carbon atom are more sensitive to the electronic effects of substituents than neutral molecules and provide useful models for studying substituent effects. Since the pioneering work of Olah and his group [1] in the spectroscopic observation of long-lived stable ions dramatic progress has been made in this field both by theoretical calculations and by n.m.r. spectroscopy. $^{13}C$ Chemical shifts have been widely used for measuring of charge delocalization.[2] The measurement of substituent chemical shifts (s.c.s.) has shown that the electron transfer from the substituents to the carbenium centre depends on the nature of the other groups at this centre which modify the electron demand.[3] The measurement of torsional barriers has also proven useful for the estimation of substituent effects.[4]

The existence of a barrier to rotation around the phenyl-C$^+$ bond in the phenylcarbenium ions (Ia and b) has been recognized quite early from the magnetic non-equivalence of the *ortho*- and *meta*-nuclei at low temperature.[5] However, until now only one value for the activation energy has been published in the case of the cyclopropyl(methyl)phenyl cation ($\Delta G^\ddagger$ 36 kJ mol$^{-1}$).[6]



(Ia) (Ib)



(IIa) (IIb)

In the *p*-methoxyphenyl(dialkyl)carbenium ions (IIa and b) there is a second barrier to rotation, *i.e.* around the phenyl-oxygen bond, and we have recently shown that the measurement of this barrier was a good probe for the estimation of the electron demand on the carbenium centre enabling us to compare the electron-releasing ability of H, Me, Ph, and cyclopropyl.[7]

Due to the strong π-electron donation of the *p*-MeO group, the canonical form (IIb) is important and consequently the barrier around the phenyl-C$^+$ bond will be quite high in these ions. Whereas the barrier around the phenyl-oxygen bond can be related directly to the electron demand of the carbenium centre depending on the electron-releasing ability of the substituents, the barrier around the phenyl-C$^+$ bond also depends on the steric requirement of the substituents on the carbenium centre. For this reason we felt it of interest to study this barrier in a number of easily available ions.

## Results and Discussion

For the measurement of the rotational barriers either by complete line-shape analysis (LSA) or by spin saturation transfer (SST) the n.m.r. technique can only be used when the ions show non-equivalent nuclei under slow exchange conditions. This unfortunately excludes the study of the barrier around the phenyl–carbenium bond in all ions in which $R^1 = R^2$, including the *p*-methoxyphenyl ions, as the barrier around the phenyl-oxygen bond is much lower than the barrier to be measured. On the other hand some secondary ions ($R^1,R^2$ = H, Me and H, cyclopropyl) are too short-lived even at low temperature to allow a barrier measurement by the n.m.r. technique.

In Table 1 we have collected all the free-energy data of the rotational barrier in the phenylcarbenium ions. Figure 1 shows as an example the spectra of ion (2) during spin transfer measurements.

(a) *Comparison between the Barrier around the Phenyl–Oxygen Bond with the Barrier around the Phenyl–Carbenium Bond.*—The measurement of both barriers in the same cation could only be achieved for ions (2)—(4). Ion (1) decomposed rapidly at −40 °C, a temperature much too low for the measurement of a barrier roughly estimated as more than 80 kJ mol$^{-1}$ (see discussion below). For ions (5)—(7) the barrier around the C–O bond is too low to be measured under our experimental conditions, but an estimated value could be obtained from the correlations of $\Delta G^\ddagger_{(OMe)}$ *versus* the $^{13}C$ chemical shift of C(4).

From the early work of Olah *et al.*[5] it was known that the barrier around the phenyl–oxygen bond was lower than the barrier around the phenyl-C$^+$ bond. This can easily be rationalized on the basis of the electronic transmission effects. In the dialkyl(alkoxy)carbenium ions the barrier around the $C^+$–OR bond is estimated at *ca.* 75—80 kJ mol$^{-1}$;[7] the intercalation of the phenyl group in the $C^+$–O bond lowers the barrier around the C–O bond [ion (1)] to 44 kJ mol$^{-1}$, roughly by half.

In ion (4) in which there is very little steric hindrance we also observed that $\Delta G^\ddagger_{(Ph\text{-}C^+)} \simeq 2\Delta G^\ddagger_{(Ph\text{-}O)}$. If electronic effects are the only important parameter, the height of the two barriers should stay in the same proportionality for all ions. Comparison of our results for ions (1)—(7) shows that this is not the case.

**Table 1.** Free-energy data of the rotational barriers in phenylcarbenium ions $p\text{-}XC_6H_4\overset{+}{C}R^1R^2$

| Ion | X | $R^1$ | $R^2$ | $\Delta G^{\ddagger}_{(Ph\text{-}C^+)}$ [a] | Method | $\Delta G^{\ddagger}$(other) [a] |
|---|---|---|---|---|---|---|
| (1) | MeO | H | Me | *b* | LSA | 44.4 [c,d] |
| (2) | MeO | H | Ph | 67.8 [h] | SST | 37.2 [c,d] |
| (3) | MeO | Me | Ph | 49.8 [h] | SST | 29.8 [c,d] |
| (4) | MeO | Me | Cyclopropyl | 49.0 [h] | LSA | 25.5 [c,d] |
| (5) | MeO | OH | H | 78.0 [f] | LSA | 28 [c,e] |
| (6) | MeO | OH | Me | 61.4 [f] | LSA | 23 [c,e] |
| (7) | MeO | OH | Et | 61.3 [f] | LSA | |
| (8) | Me | H | Ph | 54.8 [h] | SST | 40.6 [g,h] |
| (9) | Me | OH | H | 67.4 [f] | LSA | |
| (10) | Me | OH | Me | 54.2 [f] | LSA | |
| (11) | Me | OH | Et | 49.3 [f] | LSA | |
| (12) | H | H | Ph | 46.0 [h] | SST | 46.0 [g,h] |
| (13) | H | Me | Cyclopropyl | 36.0 [i] | LSA | |
| (14) | H | OH | H | 61.3 [f] | LSA | |
| (15) | H | OH | Me | 48.1 [f] | LSA | |
| (16) | H | OH | Et | 43.2 [f] | LSA | |

[a] In kJ $mol^{-1}$. [b] Ion decomposes. [c] Methoxy-group rotation. [d] Ref. 7. [e] Extrapolated from the correlation of $\Delta G^{\ddagger}_{(OMe)}$ = f [δC(4)]. [f] Ref. 4. [g] Barrier around the $C^+$–C(1′) bond. [h] This work. [i] Ref. 6.

Whereas the replacement of the cyclopropyl group on the carbenium centre in ion (4) by a phenyl group [ion (3)] increases the barrier around the C–O bond by *ca.* 4 kJ $mol^{-1}$, in agreement with the corresponding decrease in charge delocalization,[7] the barrier around the C–$C^+$ bond changes by only 0.8 kJ $mol^{-1}$. This difference has to be ascribed to the steric interaction between the two phenyl rings, which forbids coplanarity and destabilizes the ground state in ion (3). It is known that in diphenylcarbenium ions the molecule adopts a propeller-shaped twisted conformation to overcome steric repulsion, but also that the twist angle will be a minimum to favour the positive charge delocalization into the ring. The resonance energy, as a function of $\cos^2\theta$, does not vary significantly for smaller values of θ [see (III)].

A comparison of ions (2) and (3) shows 18 kJ $mol^{-1}$ difference in $\Delta G^{\ddagger}_{(PH\text{-}C^+)}$ and only 7.2 kJ $mol^{-1}$ difference in $\Delta G^{\ddagger}_{(Ph\text{-}O)}$. In this case the large difference noticed for the barrier around the phenyl–carbenium carbon bond is due to two complementary effects: the increase in electron demand when $CH_3$ in ion (3) is replaced by H in ion (2) as well as the steric strain relief obtained in the same way. In the secondary diphenylcarbenium ions, strain relief between the two phenyl groups can be obtained by a widening of the phenyl–$C^+$–phenyl angle which results in a smaller value for θ. This is confirmed by an *X*-ray study of 3,3′-dibromobenzophenone[8] ($C\hat{C}C$ 126°, θ 24°).

Comparison between ions (2) and (5) gives another illustration of the difference in the barriers around the phenyl–oxygen and the phenyl–$C^+$ bonds. In the course of our acidity measurements of superacid solutions[9] we have used both ions as indicators and found that ion (2) was half-protonated at $H_0$ − 21.5 whereas for ion (5) half-protonation was already achieved at $H_0$ − 19.5. These $pK_{BH^+}$ values are a direct measure of the availability of the oxygen lone-pair which is related to the electron demand on the carbenium centre and can also be measured by the barrier height around the phenyl–oxygen bond [respectively 37 for ion (2) and 28 kJ $mol^{-1}$ for ion (5)]. In the former ion $\Delta G^{\ddagger}_{(Ph\text{-}O)} \simeq 1/2\ \Delta G^{\ddagger}_{(Ph\text{-}C^+)}$ whereas in the latter $\Delta G^{\ddagger}_{(Ph\text{-}O)} \simeq 1/3\ \Delta G^{\ddagger}_{(Ph\text{-}C^+)}$. This shows the importance of the steric strain even in secondary diphenylcarbenium ions and again we notice that the barrier around the phenyl–oxygen bond can be well related to the electron demand on the carbenium centre whereas the barrier around the phenyl–carbenium bond is very much more sensitive to the steric effects and cannot easily be related to the charge delocalization on $C^+$ only.

(b) *The* para-*Substituent Effect on the Torsional Barrier around the Phenyl–Carbenium Bond.*—Since Hammett's work on the ionisation rates of *p*-substituted benzoic acids[10] many free energy relationships have been developed involving *p*-substituent effects. As a probe for π-electron delocalization Hammett plots have been applied to various n.m.r. data such as $^{19}F$ and $^{13}C$ chemical shifts and it is well known that the free energy of activation of a torsional barrier correlates well with the $\sigma_p^+$ constants. This relationship has been tested by us previously on a large number of *p*-substituted benzaldehydes, acetophenones, and their conjugate acids.[4]

In all the phenylcarbenium cations investigated here we found a good correlation between the electron-releasing ability of the *p*-substituent (expressed as $\sigma_p^+$) and the height of the torsional barrier. The resulting relationships are collected in Figure 2. The slopes of the lines measure the sensitivity of the barrier on the *p*-substituent effect and are a good indication of the electron demand on the carbenium centre. The slopes are very similar for all systems investigated with the exception of the diphenylmethyl cations. This indicates that the electron demand on $C^+$ is much higher in this case than predicted on the basis of the electron-releasing ability of a phenyl group. For unsymmetrically substituted diphenylcarbenium ions the propeller shape is probably not symmetrical and the deviation from planarity is related to the electron-releasing ability of the *p*-substituent.

The hydroxy(phenyl)carbenium ions (protonated benzaldehydes, acetophenones, and propiophenones) have been shown to be planar or quasiplanar[11] and the replacement on the carbenium centre of the hydrogen in benzaldehydes by a methyl or an ethyl group decreases the slope somewhat as the electron demand is decreased. The same behaviour is observed for the cyclopropyl(methyl)arenium ion series, the cyclopropyl ring adopting an *s-trans* conformation which gives a maximum orbital overlap with the $C^+$ vacant orbital and the least strained conformation (IV).[6]

In the diphenylmethyl ion series, the variation of the electron demand at the $C^+$ centre affects the energy of activation for the barrier around the two phenyl–$C^+$ bonds as can be seen from

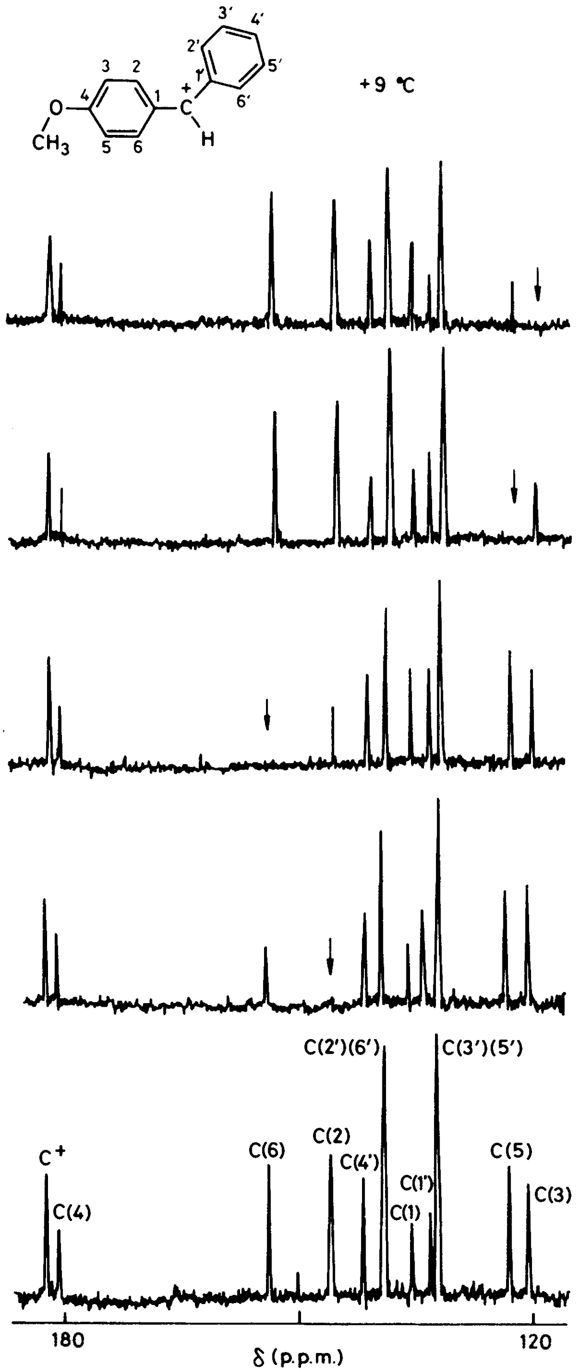
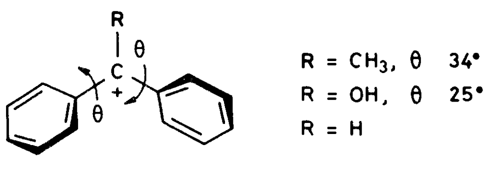
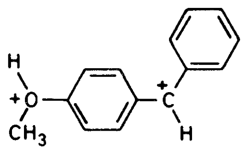


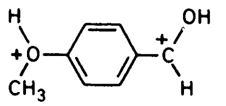
**Figure 1.** $^{13}$C N.m.r. spectra of cation (2) at +9 °C: (a) without saturation of any of the carbon atoms; (b) with saturation of C(2); (c) with saturation of C(6); (d) with saturation of C(5); (e) with saturation of C(3)



(III)



(2H+)



(5H+)

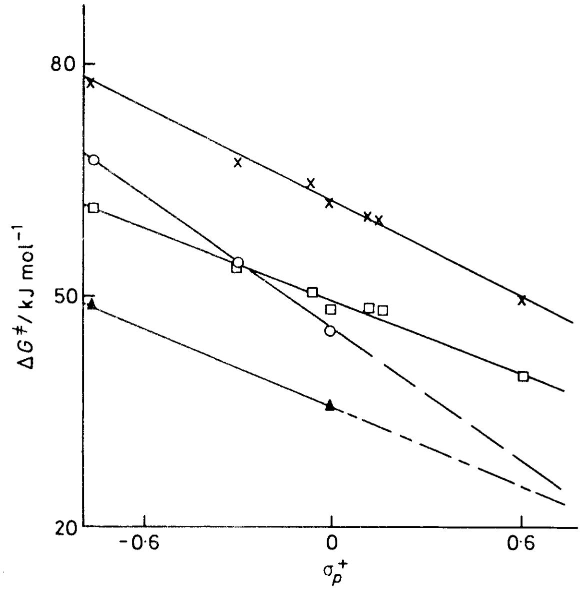
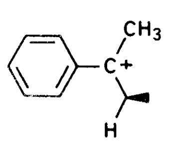


**Figure 2.** Correlations of the free energy of activation $\Delta G^{\ddagger}$ of the torsional barrier around the phenyl–C$^+$ bond in *p*-substituted phenylcarbenium ions *versus* the $\sigma_p{}^+$ constants: × R$^1$ = H, R$^2$ = OH; □ R$^1$ = Me, R$^2$ = OH; ▲ R$^1$ = Me, R$^2$ = cyclopropyl; ○ R$^1$ = H, R$^2$ = Ph



(IV)

our n.m.r. data on the *p*-tolyl(phenyl) ion (8) and the unsubstituted diphenylmethyl ion (12). The temperature-dependent $^{13}$C spectra of ion (8) are shown in Figure 3.

At −96 °C rotation around both the C$^+$–C(1) and the C$^+$–C(1′) bond are frozen out as shown by the non-equivalence of C(2),C(6) (Δδ 6.8 p.p.m.), C(3),C(5) (Δδ 0.8 p.p.m.), and C(2′),C(6′) (Δδ 4.9 p.p.m.). C(3′) and C(5′) are not separated even at −100 °C. When the temperature is raised the signals at C(2′) and C(6′) coalesce, and the rotation around the C$^+$–C(1′) bond appears as unrestricted on the n.m.r. time scale at −46 °C. The signals for C(2),C(6) and C(3),C(5) remain unchanged, showing that at this temperature rotation around the C$^+$–C(1) bond is still frozen out. As line broadening starts only at temperatures above −20 °C, the rate of rotation around this bond was measured by the spin saturation transfer method. The values found for the two barriers are $\Delta G^{\ddagger}_{\mathrm{C^+-C(1')}}$ 40.6 and $\Delta G^{\ddagger}_{\mathrm{C^+-C(1)}}$ 54.8 kJ mol$^{-1}$. Ion (8) is the only case among the unsymmetrical carbenium ions studied here for which both barriers could be measured: in the *p*-methoxyphenylcarbenium ions the electron demand from the carbenium centre towards the second phenyl group is very weak and the barrier around the C$^+$–C(1′) bond was too low to be measured under our experimental conditions.

The diphenylmethyl cation has the two phenyl groups twisted equally out of the plane of C$^+$. The symmetry will be

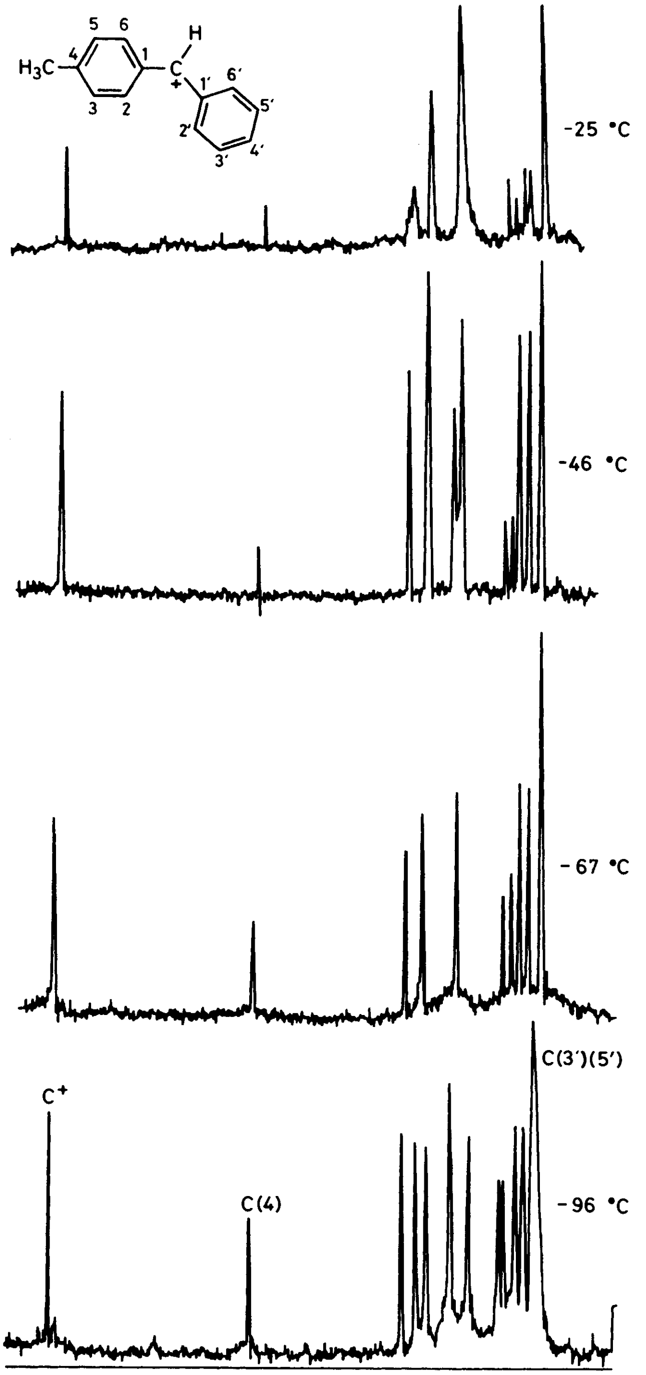


**Figure 3.** The temperature-dependent $^{13}C$ n.m.r. spectra of ion (8)

destroyed by replacing the *p*-hydrogen atom on one phenyl by an electron-donating substituent, causing the substituted ring to become more coplanar with the trigonal cationic carbon due to the increased delocalization of the ring electrons. This will lower the electron demand on the other phenyl ring which in turn will be forced further out of the plane. The increased electron demand at $C^+$ will thus enhance further the torsional barrier around the $C^+$–C(1) bond. This explains the greater sensitivity of this barrier to *p*-substitution.

(c) $^{13}C$ *Chemical Shift Correlation.*—The advantages of $^{13}C$ n.m.r. spectroscopy as a tool to study structure and charge delocalization in carbenium ions have been amply demonstrated. Combined with the method of increasing electron demand originally developed by Winstein *et al.*,[12] $^{13}C$ n.m.r. has been used both by Olah and Brown to investigate π participation in stable long-lived ions. On the other hand, we have shown recently that selected $^{13}C$ chemical shifts were extremely useful for the estimation of rotational barriers in ions with a precision of a few kJ mol$^{-1}$ compared with the experimental values. For this reason we have tried here to use $^{13}C$ chemical shifts for the study of the *para*-substituent effect on the carbenium centre chemical shift in phenylcarbenium ions (including the symmetrical ions for which the barrier cannot be measured).

In Table 2 we have collected the $^{13}C$ chemical shifts of $C^+$ in various series of *p*-substituted arylcarbenium ions and the correlations with the $\sigma_{C^+}$ values recently developed by Brown *et al.*[13] It has often been shown that the $C^+$ chemical shift in stable ions does not show a decent correlation either with the calculated charge density on this carbon or with the $\sigma^+$ values in the phenylcarbenium series. For this reason Brown and Kelly have calculated $\sigma_{C^+}$ parameters based on $^{13}C$ chemical shift measurements in aryl cations. These constants revealed excellent correlations against the $C^+$ shifts for a large number of aryl(dialkyl) carbocations. We thought it of interest to take the opportunity to check the correlations of these $\sigma_{C^+}$ values with the $^{13}C$ chemical shifts of diversely substituted aryl cations.

Table 2 shows that the correlations are excellent in all cases where the substituent $R^1$,$R^2$ is either alkyl and/or hydroxy ($r > 0.991$). However, when $R^1$,$R^2$ is either phenyl or cyclopropyl the correlation becomes fair or even poor ($R^1$ = Ph, $R^2$ = cyclopropyl). By plotting the correlation lines we tried to understand why the correlation coefficients were so poor and we noticed that in all the poorly correlating cases the *p*-$CF_3$ point was the main cause for deviation.

The correlation data in parentheses in Table 2 show that if the $CF_3$ group is left out, *all* correlations are >0.992. The $\sigma_{C^+}$ value for $CF_3$ (0.79) cannot be questionned as the fit is excellent when $R^1$,$R^2$ = alkyl. This deviation from linearity in the case of electron-demanding groups like $CF_3$ was noticed earlier by Farnum *et al.*[14] in the case of 1-aryl-1-phenylethyl cations. We agree with their conclusion that " their ' extra-ordinary ' behaviour can be interpreted in terms of reasonable changes in structure for the cations with the more electron-demanding aryl groups: for the 1-aryl-1-phenylethyl cations, a change from a planar aryl carbocation to a twisted aryl carbocation ".

The slope of the correlation line $\rho_{C^+}$ is an excellent indicator of the sensitivity of the carbenium centre to the substituent. We notice here that for the various systems having similar structural features the slope is indeed characteristic. It is steepest for the dialkyl(phenyl)carbenium ions with a value of *ca.* −17 depending on the inductive contribution of the alkyl groups. This value is in the range of those already published by Brown *et al.*

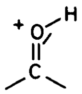
For the alkyl(phenyl)- and alkyl(cyclopropyl)phenylcarbenium ions the slope is much smaller ($\rho_{C^+}$ *ca.* 8.4—10.3) as can be predicted on the basis of the decreased electron demand. When $R^1$ and $R^2$ are phenyl or cyclopropyl the slope is *ca.* 6.1—7.5. Considering the values obtained with R = phenyl and cyclopropyl we must admit that the precision on $\sigma_{C^+}$ is probably not good enough to differentiate the relative ability of these two groups to delocalize the positive charge.

For all the hydroxy(aryl)carbenium ions the slope is very weak (3.4—5.3). This is in agreement with the protonated carbonyl structure (Va) of the hydroxycarbenium ions as a predominant contribution to the resonance form as shown recently by the $^{17}O$ n.m.r. studies by Olah *et al.*[15]

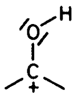
**Table 2.** $^{13}C$ Chemical shifts (p.p.m.)[a] and correlations with $\sigma_{C}+$ constants for $XC_6H_4\overset{+}{C}R^1R^2$

| | | X | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $R^1$ | $R^2$ | H | MeO | Me | F | Cl | Br | $CF_3$ | *i* | $\rho_{C}+$ | *r* | Standard deviation |
| H | Me | 229.8 | 196.3 | 219.1 | 223.4 | 225.7 | 226.1 | 244.1 | 230.1<br>(229.7) | 16.8<br>(16.5) | 0.999<br>(0.999) | 0.54<br>(0.36) |
| H | Cyclopropyl | 226.3 | 208.6 | 221.6 | 222.2 | 223.2 | 223.6 | 225.9 | 224.2<br>(225.8) | 6.6<br>(8.4) | 0.937<br>(0.992) | 2.29<br>(0.89) |
| H | Ph | 199.8 | 183.5 | 196.1 | 197.1 | 197.8 | 198.1 | 202.2 | 199.0<br>(200.1) | 6.9<br>(8.0) | 0.971<br>(0.993) | 1.56<br>(0.79) |
| H | OH | 204.4 | 193.5 | 200.3 | | 202.8 | 203.5 | | 204.3<br>(204.3) | 5.4<br>(5.4) | 0.998<br>(0.998) | 0.29<br>(0.29) |
| Me | Me | 255.7 | 225.4 | 243.6 | 248.4 | 251.4 | 252.3 | 270.0 | 255.7<br>(254.8) | 15.7<br>(14.8) | 0.995<br>(0.997) | 1.38<br>(0.87) |
| Me | Cyclopropyl | 246.2 | 227.1 | 241.9 | 243.2 | 244.8 | 245.3 | 250.0 | 245.9<br>(247.1) | 8.4<br>(9.7) | 0.977<br>(0.994) | 1.72<br>(0.82) |
| Me | Ph | 227.6 | 207.3 | 222.1 | 223.8 | 224.7 | | 231.8 | 226.6<br>(227.7) | 8.9<br>(10.0) | 0.987<br>(0.996) | 1.49<br>(0.73) |
| Me | OH | 219.5 | 209.0 | 216.7 | 217.6 | 219.0 | 219.5 | 223.5 | 219.8<br>(220.1) | 5.2<br>(5.4) | 0.995<br>(0.995) | 0.48<br>(0.43) |
| Cyclopropyl | Et | 251.6 | 231.0 | 246.1 | 247.8 | 249.4 | 250.6 | 254.8 | 250.7<br>(252.1) | 8.8<br>(10.3) | 0.975<br>(0.998) | 1.89<br>(0.60) |
| Cyclopropyl | Cyclopropyl | 261.0 | 248.7 | 257.0 | 258.0 | 259.8 | 260.0 | 264.6 | 260.7<br>(261.0) | 5.8<br>(6.1) | 0.996<br>(0.998) | 0.49<br>0.32 |
| Cyclopropyl | Ph | 235.0 | 219.8 | 231.5 | 232.5 | 233.4 | 233.5 | 235.2 | 233.9<br>(235.4) | 5.9<br>(7.5) | 0.936<br>(0.994) | 2.06<br>(0.69) |
| Et | OH | 223.3 | 213.3 | 219.9 | 220.6 | 222.2 | 222.7 | | 223.2<br>(223.2) | 5.0<br>(5.0) | 0.991<br>(0.995) | 0.995<br>(0.31) |
| Ph | OH | 208.7 | 201.5 | 206.5 | 206.7 | 207.4 | 207.7 | 209.3 | 208.0<br>(208.4) | 2.9<br>(3.4) | 0.972<br>(0.994) | 0.66<br>(0.31) |

[a] Values taken from refs. 3, 5, 8. [b] Correlations in parentheses are without the $CF_3$ group.



(Va)



(Vb)

## Experimental

*Synthesis of Precursors.*—Diphenylmethanol was commercially available. *p*-Tolyl(phenyl)methanol was prepared by standard Grignard synthesis starting from *p*-bromoanisole and *p*-tolualdehyde. The preparation of the other compounds has been described earlier.[7]

*Preparation of Ions.*—All the carbenium ions were generated in an apparatus as described by Ahlberg *et al.*[16] Precursor (20—40 mg) was dissolved in $CD_2Cl_2$ (*ca.* 100 mg) and added at −110 °C, with efficient mixing, to a solution of $HSO_3F$–$SO_2ClF$–$CF_2ClH$ (1 : 1 : 1 v/v/v) (0.4 ml). The yellow to red-brown solutions are fairly stable at temperatures below −40 °C, except those containing the methoxyphenyl(cyclopropyl)carbenium ion which decomposed rapidly at the temperature where the spin transfer experiment should be performed.

For the spin saturation transfer measurements on *p*-methoxyphenyl(phenyl)carbenium ion at +7.5 °C, the alcohol (80 mg) was dissolved at low temperature in pure $FSO_3H$ (0.4 ml). The yellow solution showed no change even after several hours at room temperature.

*Spectroscopy.*—$^{13}C$ N.m.r. spectra were recorded on a JEOL FX100 Fourier transform spectrometer equipped with a 5 mm variable-temperature $^1H$–$^{13}C$ dual probe, external lithium lock, quadrature phase detection, and a multi-irradiation unit. $CD_2Cl_2$ (δ 53.8) and/or $CHF_2Cl$ (δ 110.3, 98.6 p.p.m.) were used as internal standards.

*Spin saturation transfer experiments.* The method used has been described earlier,[17] and was used here essentially when the thermal instability of the ions limited the temperature interval necessary for complete line-shape analysis. Typical spectrometer settings were: spectral width 6 kHz, 8K data points, pulse flip angle of 90°, pulse repetition time $>5T_1$. The spin–lattice relaxation times $T_1$ were obtained with the inversion-recovery method (pulse sequence 180, π, 90). The analysis of the spectra was made off-line through a non-linear least-squares fitting procedure.

*Complete line-shape analysis.* Spectra at least eight different temperatures were recorded for each ion. Rate constants were obtained with the $DNMR_2$ program[18] on the UNIVAC 1100 system at the Laboratoire de Calcul de Strasbourg-Cronenbourg.

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