The Relative Electron-Donating Ability of Substituents, Determined in 2,6-Disubstituted Pyrylium Cations

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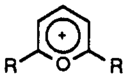
The carbon-13 NMR spectra of a series of 2,6-disubstituted pyrylium compounds have been investigated. The chemical shift of C(4) is a measure of the charge density in that position of the ring. The variation of the chemical shift with the change of substituent is determined by the ability of substituents to delocalize the positive charge from C(4), an effect which for substituents at C(2) and C(6) is free from any other shielding or deshielding effects. The electron-donating ability of substituents vary in the order: H < *i*-Pr < Me < p-ClC$_6$H$_4$ < p-FC$_6$H$_4$ ≤ Ph ≪ 2-thienyl ≤ *c*-Pr ≤ p-MeOC$_6$H$_4$. The ordering of alkyl groups indicates that C–H hyperconjugation is stronger than C–C hyperconjugation. For the aryl substituents the chemical shifts are correlated linearly with the partial rate factor (log (p_f)) for the protiodesilylation of the parent arenes. The ability of cyclopropyl to delocalize the positive charge is similar to that of 2-thienyl and *p*-anisyl.

Introduction

The ability of various substituents to delocalize the positive charge from an electron-deficient center has been the subject of many studies.[1] The extensive investigations and the variety of methods and models employed were in good measure due to the conflicting results that various approaches gave in comparing the electron-donating ability of the cyclopropyl and phenyl substituents. A summary and discussion has been published.[2] Thus, pK_{R^+} measurements[3] and differences in solvolytic reactivities of para-substituted *tert*-cumyl chlorides[4] indicated that the electron-releasing ability varies in the order c-Pr > Ph > Me > H. Subsequently, determination of carbon-13 chemical shifts of the sp^2 carbon in carbocations $RR'C^+X$ showed an upfield trend in the order X = Me < c-Pr < Ph.[5] The same ordering of chemical shifts for carbons carrying cyclopropyl and phenyl substituents was observed in trisubstituted cyclopropenyl cations.[6] Based on an established correlation between carbon chemical shifts and the density of π-electrons at an individual position in cyclic, delocalized systems,[7] it was concluded that the upfield shift can be translated in a decrease in charge density and, therefore, that the electron-donating ability increases in the order Me < c-Pr < Ph.[5]

Inconsistencies in the ^{13}C chemical shifts data have been pointed out, however.[8] It had been known also that substituents bonded directly to a carbon atom (α-substituents), or separated by two bonds from the carbon atom (β-substituents) induce a change in chemical shift of the latter even in the absence of charge.[9] Chemical shift comparisons can, therefore, offer valid information about electron density (excess or deficit) only if the structural differences do not include a change of α- or β-substituents. Other workers have argued that carbon-13 chemical shifts reflect trends of charge density only when hybridization and substitution are invariant.[10] The published comparisons of substituents in carbocations[5] did not satisfy this requirement.[11]

It occurred to us that 2,6-disubstituted pyrylium cations (**1**) represent appropriate models for such a study. In the ring of **1** the charge is manifested in positions 2, 4, and 6, and an increase in the electron-donating ability of substituents R, bonded to C(2) and C(6), diminishes the amount of positive charge at C(4).[12] Because the structural perturbations are operated at least three bonds away from C(4) the chemical shift change of the latter reflects the variation in its charge density free of other substituent effects.



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2, R = H; **3**, R = *i*-Pr; **4**, R = Me; **5**, R = p-ClC$_6$H$_4$; **6**, p-FC$_6$H$_4$; **7**, R = Ph; **8**, R = 2-thienyl; **9**, R = c-Pr; **10**, R = p-MeOC$_6$H$_4$.

Results and Discussion

The compounds investigated were the unsubstituted pyrylium perchlorate (**2**), the 2,6-diisopropyl- (**3**), 2,6-dimethyl- (**4**), 2,6-bis(*p*-chlorophenyl)- (**5**), 2,6-bis(*p*-fluorophenyl)- (**6**), 2,6-diphenyl- (**7**), 2,6-bis(2-thienyl)- (**8**), 2,6-dicyclopropyl- (**9**), and 2,6-bis(*p*-methoxyphenyl)pyrylium perchlorate (**10**). The carbon-13 NMR spectra of **2** and **7** had been published;[13] we recorded the spectra of the other compounds, and redetermined the spectrum of **7**, for comparison with the previous work.[13] Compounds **3–10** were obtained as described in the Experimental Section. Their carbon NMR spectra are presented in Table I.

The lack of correlation of chemical shifts with charge densities for the substituted ring carbons is immediately

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Table I. ^{13}C NMR Spectral Data of Pyrylium Perchlorates[a]

		chemical shifts[b]			
compd	R	C(2),(6)	C(3),(5)	C(4)	other carbons[c]
2[d]	H	169.12	127.54	161.01	-
3	*i*-Pr	189.35	122.05	160.16	36.59 (α-CH), 20.48(Me)
4	Me	182.93	124.32	159.39	22.17 (Me)
5	p-ClC$_6$H$_4$	174.08	120.44	158.68	127.87 (ipso), 131.25 (*o*), 132.66 (*m*), 146.19 (*p*)
6	p-FC$_6$H$_4$	173.81	119.80[e]	158.35	125.92 (ipso), 132.99 (*o*), 119.37 (*m*),[e] 169.97 (*p*)[f]
7	Ph[g]	175.08	120.01	158.23	129.51 (ipso), 130.02 (*o*), 132.03 (*m*), 138.25 (*p*)
8	2-thienyl	168.24	117.13	155.76	133.25 (2′), 141.28 (3′), 132.66 (4′), 137.45 (5′)
9	c-Pr	185.77	119.92	155.69	18.54 (α-CH), 17.17 (CH$_2$)
10	p-MeOC$_6$H$_4$	173.30	117.27[e]	155.57	122.68 (ipso), 132.36 (*o*), 117.79 (*m*),[e] 168.19 (*p*) 57.16 (MeO)

[a] In 4:1 (v:v) trifluoroacetic acid–CD$_2$Cl$_2$ (ref 13). [b] From CD$_2$Cl$_2$ taken as δ 53.80; off-resonance decoupling was used for compounds **9** and **10**. [c] Chemical shifts for the substituted phenyl carbons were assigned by assuming that a para substituent X introduced in **7** would alter the chemical shifts of the phenyl group in the same way as for the transformation of PhH into PhX. In the case of **8**, the changes produced in thiophene by introduction of electron-withdrawing substituents (ref 9, p 256) and the differences between the benzene resonances in PhH and **7** were used to ascertain chemical shifts for the thiophene carbons. [d] The values from ref 13 were corrected by subtracting 0.2 ppm, as established for **7**. [e] Assignments might be reversed. [f] J(C–F) = 265 Hz. [g] The literature values (ref 13): 175.29, 120.23, 158.44, 129.74, 130.20, 132.23, and 138.39 (from internal TMS) are consistently downfield by about 0.2 ppm.

apparent. Thus, C(2) and C(6) resonate at higher field in the parent compound **2** than in all substituted compounds, **3–10**, even though it is well established that the electron deficiency is the highest in **2**.[12] The greater (lower field) chemical shifts for **3–10** reflect, therefore, the normal deshielding effects of substituents, rather than the variation in electron density and positive charge.[9,14]

The comparison of chemical shifts for C(4), on the other hand, shows clearly that the amount of positive charge in that position decreases from **2** through **10**. The data are consistent with the expectations in showing that the alkyl groups, exemplified here by methyl and isopropyl, have a definite character of electron donors relative to hydrogen. A comparison of the alkyl groups shows that methyl ($\Delta\delta$ −1.62 ppm) delocalizes the positive charge better than isopropyl ($\Delta\delta$ −0.85). The alkyl groups are thus ranked in the Baker–Nathan order,[15] a finding which indicates that C–H hyperconjugation is stronger than C–C hyperconjugation. The α- and β-substituent effects make the carbon chemical shifts of simple carbocations[16] unsuitable for making such a comparison. We find the same ordering as revealed by the solvolysis rates of *p*-alkyl-substituted benzhydryl[17] and cumyl[18] chlorides.

For the evaluation of the electronic effect of phenyl and other aryl groups one must take into account that the extent of conjugative interaction is a function of the relative orientation of the phenyl ring and the electron-deficient center. The deviation from coplanarity[19] affects the conjugation in biphenyl derivatives and influences the effect of a *p*-phenyl group upon the solvolysis rates of 1-phenylethyl[20] and cumyl[21] chlorides. The steric repulsion identified in the ^{13}C NMR spectra of ring -substituted 1,1-diphenylethyl cations,[22] which exists between ortho hydrogens in two aromatic rings and between ortho hydrogens and the third ligand (hydrogen or methyl) at the carbocationic center, certainly affected the electron delocalization measured by the ^{19}F chemical shift in 1-(*p*-fluorophenyl)-1-phenylethyl cation[23] and in 1-(6-fluoro-2-naphthyl)-1-phenylethyl cation,[24] or by the rotational barrier in the 4-methoxydiphenylmethyl cation,[25] employed by previous workers for the evaluation of the relative electron donating ability of cyclopropyl and phenyl. This problem was specifically addressed in the study of the solvolysis of substituted cumyl chlorides, in which the examination of 2-(2-fluorenyl)-2-chloropropane indicated that deviation from coplanarity in the 4-phenylcumyl chloride reduced the rate by a factor of 6.6 at 25 °C.[26]

It has been known that steric interactions are not additive; instead a "telescopic effect", by which the second interacting group has a larger (in many cases much larger) effect than the first, is observed.[27] The phenyl ring in the 2,6-diphenylpyrylium cation (**7**) and its derivatives interacts with only one ortho hydrogen in the pyrylium ring. Therefore, the steric hindrance that can bring about a deviation from coplanarity must be definitely smaller than in the *p*-phenylcumyl system and should not impair significantly the conjugative interaction between the two rings.[28] The variation of chemical shift of C(4) with substituent in **4** and **7** relative to **2** shows that phenyl ($\Delta\delta$ −2.78) is a significantly better donor than methyl ($\Delta\delta$ −1.62).

The data in Table I indicate also that the relative ability to stabilize positive charge of the aryl groups investigated varies in the order: p-ClC$_6$H$_4$ ($\Delta\delta$ −2.33) < p-FC$_6$H$_4$ ($\Delta\delta$ −2.66) ≤ Ph ($\Delta\delta$ −2.78) ≪ 2-thienyl ($\Delta\delta$ −5.25) < p-MeOC$_6$H$_4$ ($\Delta\delta$ −5.44). The halogen-bearing phenyl groups are somewhat poorer electron donors than phenyl, whereas thienyl is a very strong donor, approaching the *p*-anisyl in this respect.

If the aryl substituent and the pyrylium ring interact mostly by resonance, then the decrease in positive charge

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(14) Similarly, C(4) of the pyrylium ring in 2,6-di-*tert*-butyl-4-phenylpyrylium cation resonates at higher field than the same carbon in the cations carrying either a *p*-nitro or a *p*-methoxy substituent, whereas for C(2) and C(6) the chemical shift order is *p*-OMe < H < *p*-NO$_2$: Cerichelli, G.; Doddi, G.; Ercolani, G. *Gazz. Chim. Ital.* **1988**, *118*, 291.

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measured by $\Delta\delta$ should be related to the π-electron availability (or density) in the aryl substituent at the position of attachment to the pyrylium ring. With due allowance for the inherent differences between "static" and "dynamic" (or reacting) systems,[5] the same π-electron availability determines the reactivity of the given position in an electrophilic aromatic substitution of the parent arene.[4a] It was, therefore, interesting to find that the $\Delta\delta$ values measured by us correlate linearly with the partial rate factors in the protiodesilylation reaction of the para positions of chlorobenzene, fluorobenzene, and anisole[4a] and the α-position of thiophene.[29,30] The correlation $\Delta\delta = m \log (p_f)$ for five points (including benzene) had a slope $m = -0.73$ and a correlation coefficient $r = 0.99$.

It is well documented that the actual manifestation of the electron-donating ability is determined by the extent of electron demand from a deficient center.[31] Thus, the para position of fluorobenzene is less reactive than benzene in protiodesilylation or nitration, but more reactive in bromination.[4a] Likewise, the 2-position of thiophene[32] is less reactive than the para position of anisole[33] in bromination in acetic acid, but more reactive in protiodesilylation.[4a,29] Such inversions occur, however, only for groups of similar electron-donating ability; after all, the $\Delta\delta$ value for p-fluorophenyl is only by 0.12 ppm less negative than the value for benzne, which may well be not significant. Unless there is no electron demand (positive charge) one can surely expect that the 2-thienyl or p-anisyl substituents be better electron donors than the phenyl group.

Our results allow also a better evaluation of the cyclopropyl as an electron donor by comparison with the aryl substituents. Cation **9** exhibits a $\Delta\delta$ value for C(4) of −5.32, which is between those of **8** and **10**. Cyclopropyl is, therfore, similar with 2-thienyl and p-anisyl, and much more powerful than phenyl. Our findings are in better agreement with the conclusions based on solvolysis rates[4,8] than with the conclusions based on NMR studies of simple carbocations.[5]

Experimental Section

Pyrylium Perchlorates. Compounds **3** and **5–10** were prepared by the perchloric acid catalyzed reaction of methyl ketones, R-CO-Me, with triethyl orthoformate, followed by concentration of the reaction mixture and precipitation with ether, and then purification from acetone–ether.[34] All perchlorates melt with decomposition. 2,6-Diisopropylpyrylium perchlorate (**3**), 35% yield, mp 144–7 °C (lit.[34] mp 146 °C). 2,6-Diphenylpyrylium perchlorate (**7**), 46% yield, mp 225–7 °C (lit.[35] mp 230 °C). 2,6-Bis(p-chlorophenyl)pyrylium perchlorate (**5**), 20% yield of product with mp 280–3 °C, unchanged after purification (lit.[34] mp 279 °C). 2,6-Bis(p-fluorophenyl)pyrylium perchlorate (**6**), 19% yield; a second crop of 23% was obtained by adding a large quantity of ether to the first filtrate. The pure product melted at 284 °C (lit.[34] mp 176 °C). The protium NMR agreed fully with the literature report.[34] 2,6-Bis(p-methoxyphenyl)pyrylium perchlorate (**10**), 86% yield of product melting at 250–3 °C. After purification, mp 264–7 °C (lit.[36] mp 275–6 °C). 2,6-Bis(2-thienyl)pyrylium perchlorate (**8**), 32% yield of product melting at 133–5 °C. The melting point was raised to 204–6 °C by purification from acetone–ether. Two more purifications from $HClO_4$-containing acetic acid–ether raised the mp to 205–209 °C (lit.[37] mp 209–10 °C). 2,6-Dicyclopropylpyrylium perchlorate (**9**), 11% yield, mp 134–7 °C (lit.[34] mp 139 °C).

2,6-Dimethylpyrylium perchlorate (**4**) was obtained by hydride transfer from 2,6-heptanedione[38] to triphenylmethyl perchlorate. We found, however, that purification by precipitation from acetone with a mixture of ether and petroleum ether[39] is unreliable, because two liquid layers tend to separate. Instead, precipitation with a large excess of diethyl ether was employed successfully in this work. The yield of pure product was 36%, mp 126–8 °C (lit.[39] mp 124–6 °C).

NMR Spectra. An IBM NR250 NMR instrument, operating at 62.896 MHz for ^{13}C was employed. The spectra were run in an 80:20 (v:v) mixture of trifluoroacetic acid and deuteriomethylene chloride as solvent,[13] at 20 °C. Chemical shifts were measured from the center line of the deuterated solvent, taken as δ 53.80.

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Registry No. **2**, 2567-32-0; **3**, 91220-49-4; **4**, 31436-85-8; **5**, 55666-00-7; **6**, 91220-56-3; **7**, 3558-68-7; **8**, 54827-55-3; **9**, 91220-51-8; **10**, 21172-76-9.

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