Tetrahedron Letters,Vol.26,No.5,pp 315-318,1985
Printed in Great Britain

0040-4039/85 $3.00 + .00

INDUCTIVITY AND CHARGE DISPERSAL IN QUINUCLIDINIUM AND BICYCLO[2.2.2]OCTYL-1-CATIONS

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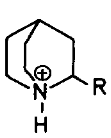
Abstract: The pK_a of 2-, 3- and 4-substituted quinuclidinium perchlorates and the solvolysis rates of the corresponding bicyclo[2.2.2]octyl-1-p-nitrobenzenesulfonates reveal the dispersal of charge in ammonium ions and carbocations.

Recent studies[1] have shown that the solvolysis rates (log k) of several substituted bi- and tricyclic arylsulfonates correlate well with inductive substituent constants σ_I^q according to the equation $\log k = \rho_I \sigma_I^q + \log k_o$. Since σ_I^q values were derived from the pK_a of 4-substituted quinuclidinium perchlorates 3[2], it followed that the relative ionization rates of the compounds are controlled by the inductive effects of the substituents[1]. On the other hand the reaction constants ρ_I varied widely with structure, even when distances through space and through bonds were practically the same. It was therefore concluded, that inductivity, as measured by ρ_I, is a directional property of the whole molecule and that the latter is anisotropic to the transmission of polar effects. When inductivity was high, as in the solvolysis of 6-exo-substituted 2-exo-norbornyl tosylates 4 ($\rho_I = -2.0$)[3], substitution occurred with complete retention of configuration. When inductivity was low, as in the solvolysis of 4-substituted 2-adamantyl brosylates 5 ($\rho_I = -0.82$)[4], substitution took place with retention and inversion. It was therefore concluded that in carbenium ions through space induction involves graded bridging, i.e. partial bonding between the cationic center and neighboring carbon atoms[1,5], as illustrated in the ion pair 6 from 4.



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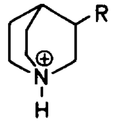

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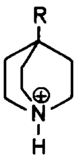

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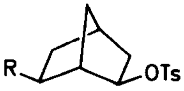

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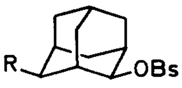

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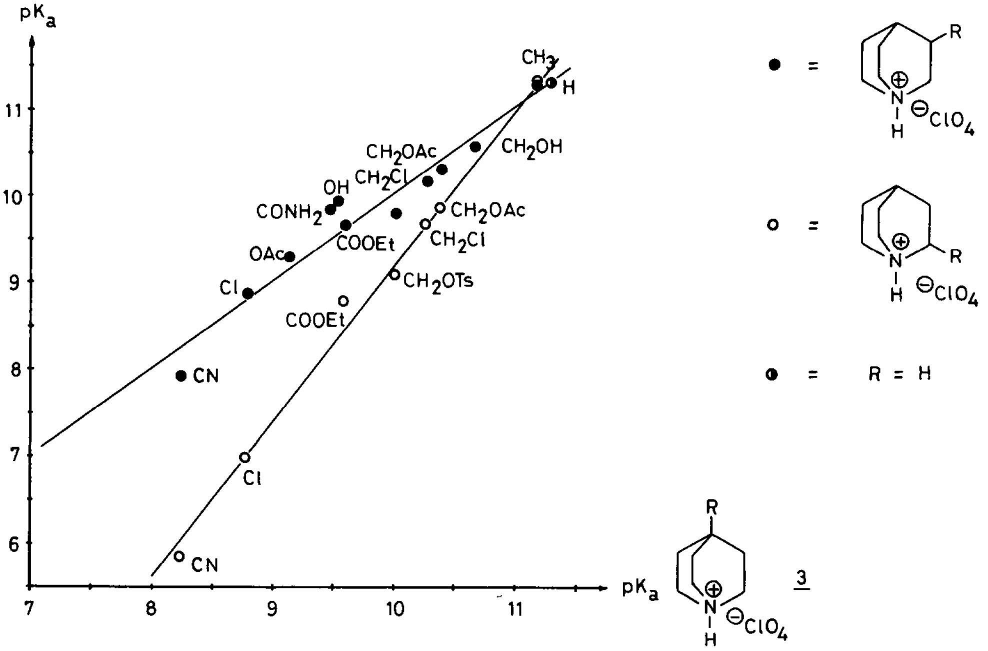


Figure 1. Plots of pK_a for 1 and 2 against pK_a for 3 at 25.0°.

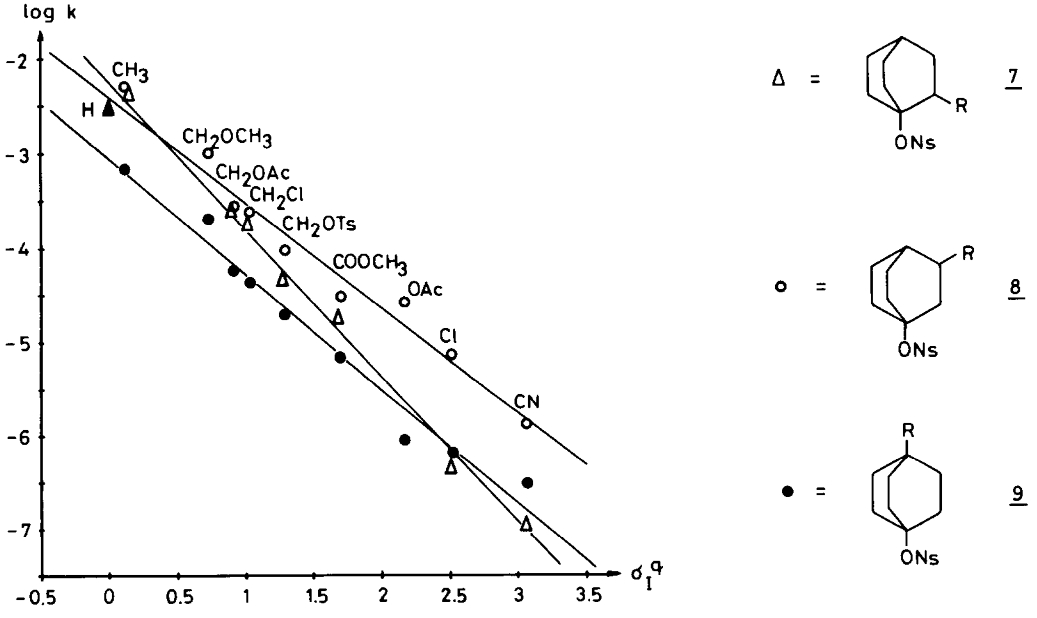
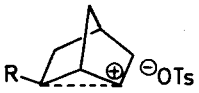


Figure 2. Plots of log k for the series 7, 8 and 9 in 80% (v/v) ethanol at 70.0°.



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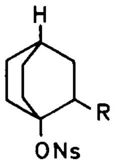

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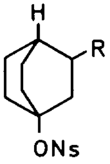

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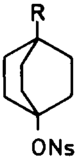

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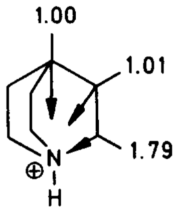
In contrast, bridging of tri- or tetravalent nitrogen in amines and ammonium ions by neighboring C-atoms is unlikely, due to the octett rule. It was therefore of interest to compare the inductivities of the 2-, 3- and 4-substituted quinuclidinium ions 1, 2 and 3, as measured by their pK_a, with the inductivities of correspondingly substituted bicyclo[2.2.2]octyl p-nitrobenzenesulfonates (nisylates) 7, 8 and 9, as derived from solvolysis rates. In these models the substituents serve as probes for charge transfer to neighboring C-atoms.

As the plots in Figure 1 show, the pK_a of the series 1 and 2 correlate well with the known[2] pK_a of the series 3 [6]. Whereas ρ_I for 3 is one by definition[2], ρ_I for 1 and 2 are 1.79 and 1.01, respectively. It follows then that inductivity at C3, and hence at the equivalent C5 and C8, is practically the same as at the equidistant C4. As expected, inductivity is much higher at C2, and hence at C6 and C7, where the through bond component of the total inductive effect coincides with the direct effect. This is illustrated by the arrows in 10 (drawn in one ethano bridge only). The fact that inductivity is not significantly higher at C3 than at C4 suggests that the through bond component does not contribute appreciably to the direct effect of C3.



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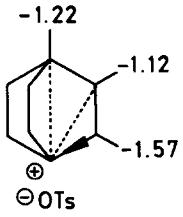

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The plots in Figure 2 show that log k for all three series of nisylates 7, 8 and 9 correlate well with the substituent constants σ_I^q of R except log k for the unsubstituted nisylate (R = H) which is accelerated by a factor of ca. 3.5 with respect to the regression line for the series 9. The ρ_I values of -1.57, -1.12 and -1.22 for 7, 8 and 9, respectively, indicate that inductivity is again highest at C2, C6 and C7. Surprisingly, inductivity is apparently slightly lower at C3, C5 and C8 than at the equidistant C4 in 11. Nevertheless, the 3-substituted nisylates 8 all react faster than the 4-substituted series 9, probably due to the constant presence of a hydrogen atom at C4[7]. A possible reason for the slightly higher inductivity of the series 9, as compared to the series 8, is that propellane-like bridging between C1 and C4 generates less strain than bridging between C1 and C3 (see formula 11). In the carbocation 11 inductivity at C3 and C4 is distinctly higher than in the ammonium cations 10. The reverse obtains for inductivity at C2, probably due to the presence of the anion in the transition state leading to 11.

The fact that the pK_a of the quinuclidines 1, 2 and 3 as well as log k for the nisylates 7, 8 and 9 correlate linearly with one another and with σ_I^q points to the common nature of induction in these structures. It can be described as a general drift of electron density towards the cationic center, either directly through the cage or through the bonds to the nearest neighbors.

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2. C.A. Grob, M.G. Schlageter and B. Schaub, Helv. Chim. Acta 63, 57 (1980).
3. W. Fischer, C.A. Grob, R. Hanreich, G. von Sprecher and A. Waldner, Helv. Chim. Acta 64, 2298 (1981).
4. Ph. D. thesis of Gerhard Wittwer, Basel 1982.
5. C.A. Grob and P. Sawlewicz, Tetrahedron Letters 25, 2973 (1984).
6. The pK_a of 2-substituted quinuclidinium perchlorates 1, in which R equals CH_2OH, $CONH_2$ and CH_3O, tend to be too high because of hydrogen bonding of ^+N-H.
7. Rate enhancements are commonly observed when electrofugal substituents, such as COO^-, $CONH_2$ and CH_2OH, are present at the rear of the C-X bond undergoing cleavage in the transition state, as in 4 and 9; but these accelerations are usually smaller for hydrogen[8].
8. C.A. Grob and B. Schaub, Helv. Chim. Acta 65, 1720 (1982).

(Received in Germany 12 October 1984)