Tetrahedron Letters,Vol.30,No.21,pp 2727-2730,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

SUBSTITUENT EFFECTS ON THE STABILITY OF CARBODICATIONS

Winn Peebles and Richard M. Pagni*

Department of Chemistry, University of
Tennessee, Knoxville, TN 37996-1600 USA

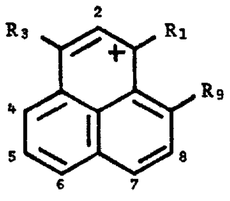
Robert C. Haddon

AT and T Bell Laboratories, Murray Hill, NJ 07974 USA

Summary: Disubstituted phenalenyl cations undergo deuterium exchange in CF_3SO_3D by a mechanism that involves protonation of the ring to form carbodications. The effect of a variety of substituents on this process is reported.

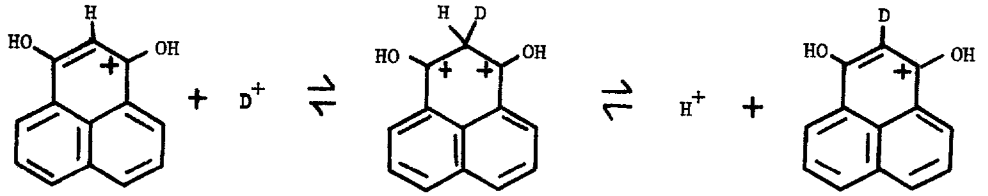
There is considerable current research devoted to the synthesis, chemistry and physical properties of carbodications, both in solution and in the gas phase.[1] Because these species are expected to be less stable than the corresponding singly charged counterparts, it would be useful to know how substitutents stabilize or destabilize dications. There is, of course, a vast literature on how substituents affect the stability of carbocations. Will substituents affect the stability of carbodications in the same way? It is the purpose of this communication to provide a partial answer to this question.

Phenalenyl cations (**I**) are ideal species for probing this question because many of them are known to yield carbodications when protonated by strong acids such as CF_3SO_3H and FSO_3H/SbF_5.[2] Furthermore, a variety of substituents can be placed at various positions on the phenalenyl ring. Prior work, for example, has shown unequivocally that certain hydroxyl-substituted phenalenyl cations such as **Ia** form dications in strong acid. Although several dications were observed directly by ^1H nmr spectroscopy in 1:1 $FSO_3H:SbF_5$, the reaction is most easily and profitably followed by deuterum exchange in the weaker CF_3SO_3D (eq.1). The following results were obtained by this method,[2] and are in line with the qualitative expectations on how hydroxyl groups should stabilize one unit of positive change, as well as molecular orbital calculations.



I

	Positional Selectivity	Relative Reactivity
a. $R_1 = R_3 = OH$, $R_9 = H$	H-2>H-5/8	
b. $R_1 = R_9 = OH$, $R_3 = H$	H-2/8~H-5	**Ia>Ib>Ic>Id**
c. $R_1 = OH$, $R_3=R_9=H$	H-2>>H-5, H-8	
d. $R_1 = R_2 = R_3=H$	No Exchange	



(1)

The new exchange reactions were run on dilute solutions (circa 0.025 M; > 500 - fold excess of acid) of the new substrates, which contain amino, hydroxyl and sulfur-containing substituents, to insure that the processes are essentially irreversible, pseudo-first-order reactions. The reactions were followed by in situ 200 MHz ^1H nmr spectroscopy.[3] All the phenalenyl cations reported in **Table 1** contain substituents at the 1 and 9 positions of the ring. For comparison purposes the exchange reaction of 1,9-dihydroxyphenalenyl cation (**Ib**) was repeated under the present reaction conditions.

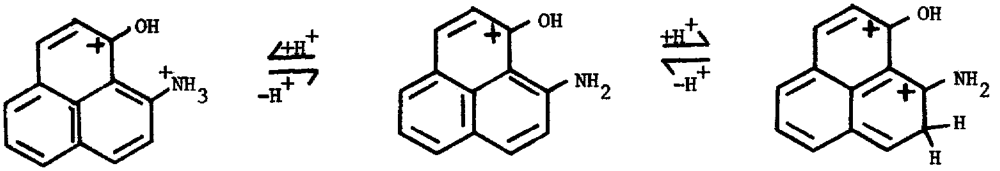
Table 1. Half-lives of Exchange of Phenalenyl Cations in CF_3SO_3D at 60°.[a]

	Substituents[b]		$\tau_{\frac{1}{2}}$ (Days) at			Total $\tau_{\frac{1}{2}}$ (Days)
Substrate	R_1	R_9	H-2	H-5	H-8	(H-2,H-5 + H-8)
Ie	$NHCH_3$	$NHCH_3$	0.07	0.3	0.07	0.03
If	NH_2	NH_2	0.3	0.7	0.3	0.12
Ig	OH	NH_2	6.5	2.0	0.3	0.25
Ib	OH	OH	1.3	4.0	1.3	0.56
Ih	OH	SH	2.5	15	6.0	1.6
Ii	-S-S-[c]		7.0	No Exchange	7.0	3.5

a) Because of the competing, reversible protonation of the nitrogen on **Ie-g**, $\tau_{\frac{1}{2}}$ (obs) has been corrected to obtain the desired $\tau_{\frac{1}{2}}$ associated with ring protonation. b) R_3=H in all cases. c) Exchange also occurs at H-4 and H-6 with $\tau_{\frac{1}{2}} = 7.2$ days at each position.

All the exchange reactions proceeded in a straight forward fashion including the amino-substituted ions (eq.2), where protonation of the nitrogen occurred competitively with ring protonation.[5] For all ions the observed exchange rates reflect the exchange that is occurring in the singly charged phenalenyl cations. The results in **Table 1**, which are reported as half-lives of exchange ($\tau_{\frac{1}{2}}$, days) at the individual sites, as well as half-lives for the total incorporation of deuterium at those sites, are in qualitative agreement with those expected based on the known electron-releasing, cation-stabilizing capabilities of the substituents.[6,7]

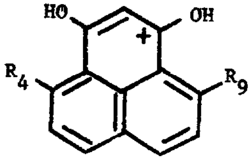
Amino and methylamino groups accelerate the rate of exchange and sulfur-containing substituents decelerate the rate of hydrogen-deuterium exchange on the phenalenyl ring when compared to hydroxyl groups, but in no case is the effect dramatic. Furthermore, except for ion **Ii**, exchange only occurs at H-2, H-5 and H-8, which is consistent with a protanation-deprotanation mechanism similar to the one shown in eq.1. Ion **Ii**, which reacts much more slowly than any other ion in **Table 1**, also exchanges, unexpectedly, at H-4 and H-6. Undoubtedly in relatively unreactive ions such as **Ii**, other mechanisms of exchange become competitive. This had previously been noted for the highly unreactive 1,2-dihydroxyphenalenyl cation.[2d]



(2)

The regiochemistry of the exchange is also interesting. In most cases, exchange occurs at the sites closest to the substituents (H-2, H-8 vs. H-5). In unsymmetrical examples (**Ig**, R_1=OH, R_9=NH_2; **Ih**, R_1=OH, R_9=SH) the site closest to the more activating substituent - NH_2 in the first case and OH in the second - exchanges more rapidly. This had previously been observed for ion Ic (R_1=OH, R_9=H) and most dramatically for 1,3-dihydroxyphenalenyl cation (Ia) where exchange at H-2, the site between the two substituents, is very fast.[2d]

Although groups such as NH_2 and $NHCH_3$ accelerate the rate of exchange by several-fold when compared to OH and SH, the position of substitution is much more significant in determining the rate of exchange than the nature of the substituent. For example, 1,9-dihydroxyphenalenyl cation (**Ib**) has a half-life of exchange of 0.56 days at 60° in CF_3SO_3D, whereas 1,3-dihydroxyphenalenyl cation (**Ia**) has a half-life of exchange of 90 seconds at 20° (primary at H-2), a rate difference of greater than 80,000.[8] Even more dramatic is the behavior of the tetrasubstituted 4,9-dimethoxy-1,3-dihydroxyphenalenyl cation (**Ij**). The ^1H nmr spectrum of this ion in CF_3SO_3H at ambient temperature shows H-2 to be significantly broadened because H-2 is undergoing rapid exchange with protons in the acid.[9] Estimates suggest that the half-life of exchange for H-2 in this ion is less than 0.02 seconds, a 4500-fold increase in rate when compared to the same site in **Ia**.



		Half-life of Exchange at	
		H-2	H-5
Ia	R_4=R_9=H	90 sec (20°)	18 days (60°)
Ij	R_4=R_9=OCH_3	<.02 sec (20°)	105 min (20°)

These results clearly show that electron-releasing substituents stabilize phenalenyl carbodications, but the stabilizing influence is modest. Far more important in determining carbodication stability is where the substituents are located on the ring. The number of substituents also plays a significant role in determining carbodication stability.

Acknowledgment: We wish to thank the National Science Foundation for funds to purchase the NMR spectrometer used in this work.

References and Notes

1. (a) Prakash, G.K.S.; Rawdah, T.N.; Olah, G.A. Angew. Chem. Int. Ed. Engl. 1983, **22**, 390; (b) Pagni, R.M. Tetrahedron 1984, **40**, 4161; (c) Koch, W.; Maquin, F.; Stahl, D.; Schwarz, H. Chimia 1985, **39**, 376.
2. (a) Pagni, R.M.; Smith, R.J. J. Am. Chem. Soc. 1979, **101**, 506; (b) Smith, R.J.; Pagni, R.M. ibid. 1979, **101**, 4769; (c) Pagni, R.M.; Smith, R.J.; Moore, T.; Burnett, M.N. Israel J. Chem. 1980, **20**, 308; (d) Smith, R.J.; Moore Miller, T.; Pagni, R.M. J. Org. Chem. 1982, **47**, 4181.
3. NMR peak assignments for the new cations were unambiguously made on the basis of splitting patterns, extensive spin dicoupling experiments, charge density considerations, and comparison to the nmr spectra of known phenalenyl cations.[4]
4. Reference 2 and citations therein.
5. Solodar', S.L.; Kochkin, V.A. J. Org. Chem. (USSR), 1982, **18**, 1096.
6. Jones, R.A.Y. "Physical and Mechanistic Organic Chemistry;" 2nd ed.; Cambridge University Press: Cambridge, U.K., 1984; p.65.
7. The best measure of the substituent effect would be the pK_a's of the ring-protonated dications, and they are not available. As with unchanged substrates such as benzene, rates of reaction are used instead.
8. This assumes a rate difference of 16 between 20° and 60°.
9. The only other example where exchange can be detected directly by ^1H nmr spectroscopy in CF_3SO_3H at ambient temperature is tris(2,6-dimethoxyphenyl)methyl cation, where the exchange is even faster than in **Ij**.[2a,d]

(Received in USA 29 November 1988)