Ground State *vs.* Transition State Substituent Effects on Reactions of Aziridinium Salts

DeLanson R. Crist*, Saleh A. Turujman [1a] and Joseph A. Hashmall [1b]

Department of Chemistry, Georgetown University,
Washington, DC 20057

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The possibility that the similarity of Hammett ρ values for several very different reactions of 2-arylaziridinium salts is due to ground state effects was investigated by MO methods and ESCA. Minimum energy structures of *p*-nitrophenyl-, phenyl-, and *p*-methoxyphenyl-substituted ions, however, have the same C_2-N bond lengths. This result shows that substituent effects are primarily a transition state phenomenon, even in the three-membered ring heterocycles. In agreement, the ground state does not have significant amino carbocation character based on similar charge distributions of 2-phenyl-*N,N*-dimethylaziridinium ion and *N,N,N*-trimethylbenzylammonium ion as well as the same nitrogen 1s binding energies by ESCA studies on corresponding salts.

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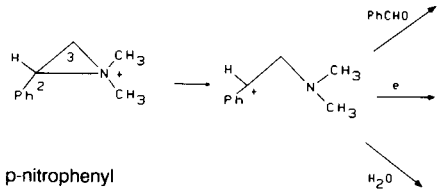
Three-membered ring heterocycles are important for theoretical reasons [2] as well as for their ring-opening reactions [3]. In the case of 2-arylaziridinium salts some of these appear to be independent of nucleophile, as shown by cycloaddition of benzaldehyde [4] with zero order in benzaldehyde ($\rho = -1.25$) and electrochemical reduction [5] with an abnormal substituent effect ($\rho = -1.45$). Since hydrolysis [6] had a similar ρ of -1.2, it seems reasonable to represent these very different reactions with a common intermediate (Scheme 1).

Scheme 1



1a p-nitrophenyl
b phenyl
c p-methoxyphenyl

Hoffmann has shown that protonation of aziridines provides an electron-withdrawing moiety that weakens the ring C-N bond [7]. However, by perturbation theory one can see that an electron-withdrawing group on a ring *carbon* should strengthen the ring C-N bond in aziridinium ions and electron-donating groups weaken that bond. The common substituent effect noted above may thus represent a ground state phenomenon: electron-donating groups on a 2-phenylaziridinium ion may destabilize the ground state which therefore has longer C_2-N bonds and more amino carbocation character. We now report MO calculations and ESCA results to test this possibility.

Optimum C_2-N bond lengths for **1a-c** were determined by calculating heats of formation by MINDO/2 [8] for various distances keeping other angles (except C_2C_3N) the same. As indicated by the minima in Figure 1, this length, 1.525 Å, does not depend on the substituent. Also, Mulliken overlap populations between C_2-N are essentially the same (0.471 ± 0.002) for these derivatives. Although the *absolute values* of equilibrium separations and populations may differ somewhat from these calculated ones, the fact that they do not change with substituent is significant. Neither result provides any evidence for ground state destabilization by electron-donating groups.

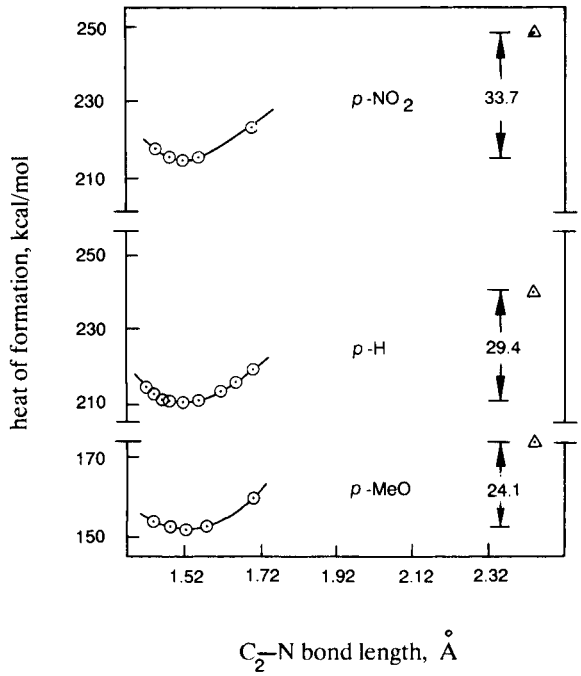
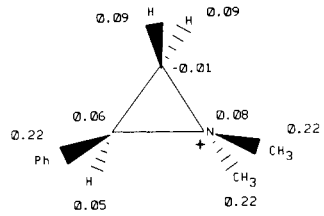


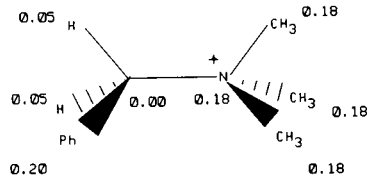
Figure 1. Variation of heats of formation of 2-arylaziridinium ions **1** with change of C_2-N bondlength (⊙) and ΔH_f for open amino carbocations **3** (△), with $\Delta\Delta H_f$ for the change **1** to **3** indicated.

Calculated charge densities can indicate the extent of amino carbocation character in the ground state. As indicated in Scheme 2 positive charge densities in **1b** resem-

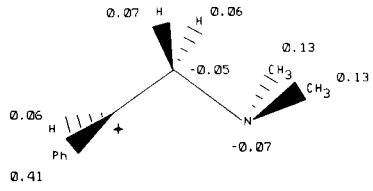
Scheme 2



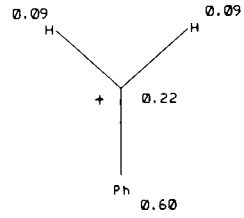
1 b



2



3



4

ble much more closely those for benzylammonium ion **2** than carbocations **3** and **4**. For example, charges on C_2 are small for **1b** and **2** (*ca.* +0.03) and significantly larger for **3** and **4** (*ca.* +0.24). Also, phenyl carries much more positive charge in the carbocations. On this basis **1** has little aminocarbocation character in the ground state.

In agreement with this result, substituent effects on calculated heats of formation for **1** are nearly the same as those for **2**. This can be seen from the Table 1 values of $\Delta\Delta H_f$, defined as the difference between heats of formation of substituted and unsubstituted ions. For a *p*-nitro group these values in kcal/mol are *ca.* 3.7 for ammonium ions **1** and **2**, but 7.9 and 12.2 for carbocations **3** [9] and **4**, respectively. Parallel results were obtained for ions with the *p*-methoxy group.

ESCA spectra confirm the conclusion based on MO calculations that there is no significant amino carbocation character to the ground state of **1**. The nitrogen 1s binding energy of 1,1-dimethyl-2-phenylaziridinium fluorosulfonate is 402.2 ± 0.2 eV which is within experimental error of the value for benzyl-*N,N,N*-trimethylammonium fluorosulfonate (402.5 ± 0.2 eV). The direction of the difference can be explained by the slightly larger charge on nitrogen of **2** (+0.18) compared to **1** (+0.08).

Table 1

Calculated Heats of Formation of *p*-Substituted Phenyl Ions

Ion	*p*-NO_2		H	*p*-OCH_3	
	ΔH_f	$\Delta\Delta H_f$[a]	ΔH_f	ΔH_f	$\Delta\Delta H_f$[a]
1	214.8	3.6	211.2	152.3	-58.9
2	205.4	3.8	201.6	143.3	-58.3
3	248.5	7.9	240.6	176.4	-64.2
4	240.6	12.2	228.4	160.2	-68.2

[a] Substituent effect on heat of formation, defined as $\Delta H_f^X - \Delta H_f^H$.

The origin of faster rates for electron-donating groups of reactions of 2-arylaziridinium salts thus appears to lie in transition state effects. Values of $\Delta\Delta H_f$ in Table 1 support this conclusion. Since the transition state would be expected to resemble open amino carbocations, ΔH_f values of **3** are plotted in Figure 1 where it can be seen that formation of these species is indeed favored for electron-donating groups ($\Delta\Delta H_f$ of 24.1 kcal/mol for *p*-OMe *vs.* 33.7 kcal/mol for *p*-NO_2). The fact that this difference is due mostly to transition state effects can be seen by the following comparisons. Substituting *p*-methoxy for H stabilizes the ground state **1** by 211.2-152.3 or 58.9 kcal/mol. However, this substitution stabilizes amino carbocation **3** by 240.6-176.4 or 64.2 kcal/mol. A *p*-methoxy group therefore stabilizes a species similar to the transition state more than the ground state by 64.2-58.9 or 5.3 kcal/mol. In a similar way it can be shown that a *p*-nitro group destabilizes a species similar to the transition state more than the ground state by 4.3 kcal/mol.

EXPERIMENTAL

MO Calculations.

MINDO/2 heats of formation for 1,1,2-trimethylaziridinium ion were minimized by MINSIM2 [10]. The initial geometry was based on the corresponding heavy atom coordinates of *trans*-13,13-dimethyl-13-azoniabicyclo[10.1.0]tridecane iodide whose X-ray structure has been determined [11] and on standard tables [12] of bond lengths and angles for the C_2-methyl group as well as

for other groups below. In all cases 0.1 Å was added [8] to literature C-H bond lengths. Ring bond lengths and internal angles were optimized and the resulting geometry used for initial values of later structures. Use of the C_2-Me bond length for the C_2-C_{aryl} length was justified by energy minimization of that length for **1a**. Data for **1** are for a phenyl rotation angle corresponding to an energy minimum.

Lengthening of C_2-N (Figure 1) was done keeping all other bond lengths and angles constant (except the expanding C_2C_3N angle). For amino carbocation **3**, the C_2C_3N angle was set at 109.5°, the benzylic C_2 carbon planar, and the N-C_3 and C_2-C_3 lengths optimized by MINSIM2 (for the 2-methyl derivative). All other dimensions were those of **1**.

The geometry of **2** was based on trimethylethylammonium ion. After MINSIM2 optimization of all bonds and angles associated with the CH_2 group, phenyl was substituted for CH_3 of ethyl for final coordinates. Data for **2** are for a phenyl rotation angle corresponding to an energy minimum. The same procedure was followed for **4**.

ESCA Study.

The 1,1-dimethyl-2-phenylaziridinium fluorosulfonate [13] and *N,N,N*-trimethylbenzylammonium fluorosulfonate [2] salts were made as previously described. Samples were deposited on graphite holders from concentrated methylene chloride solutions. XPES spectra were run at 0° for the aziridinium salt, where no decomposition or presence of impurity was noted, and at a probe temperature (40-50°) for the benzylammonium salt, which was hygroscopic and showed slight decomposition during the spectral run. The 1s peak of F and 2p peak of S (both of the counterion) were used as internal standards for the desired N 1s peaks. Binding energies in eV for the F 1s, S 2p, and N 1s electrons are as follows:

ammonium salt:	687.0, 169.4, 402.5 eV, respectively
aziridinium salt:	687.0, 169.2, 402.2 eV, respectively.

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[9] Similar charge density and substituent effects on ΔH_f were found for a planar benzyl carbocation with the C_{3v} axis of trimethylamine perpendicular to this plane and at a distance of 2.44 Å from the benzylic carbon, the same distance as between C_2 and N in **3**.

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