Synthesis of Highly Dipolar Betaines: Pyridinium Azolates

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Theoretical calculations have been carried out and experimental dipole moments measured for several pyridinium azolate inner salts; depending on the substituent on the pyridinium ring the compounds are either planar, almost freely rotating molecules, or are hindered with the rings perpendicular to each other, and in all cases the dipole moments are very large (10—18 Debye).

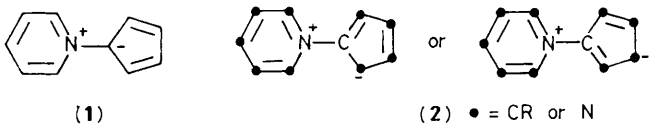
In the authoritative review on heterocyclic mesomeric betaines, Ollis, Stanforth, and Ramsden[1] give as an example of compounds isoconjugated with odd non-alternant hydrocarbon anions, the *N*-ylide (**1**). To this class belongs a rather neglected family of compounds, the inner salts of azinium azolates (**2**). The first example (**3**) of such structures was described by Boyd in 1966,[2] by the reaction between 2-chlorobenzimidazole and pyridine. Other pyridinium benzimidazolates have been prepared by Postovskii *et al.*[3] and by Dorofeenko *et al.*,[4] who also prepared the pyridinium tetrazolate (**4**).

We have carried out MNDO calculations[5] on the series of azinium azolate inner salts including (**3**) and (**5**)—(**10**) with complete optimization of geometry. The torsion angle θ beween the rings was allowed to vary between 0 and 90° to give the resulting calculated properties in Table 1.

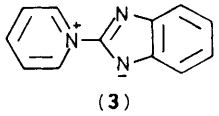
Unsubstituted pyridinium salts appear to be planar, (**3**), (**5**), (**9**), (**10**), or somewhat twisted, (**7**), (owing to the presence of 4-H), with low activation energies for rotation around the central bond. In contrast, the 2,4,6-trimethylpyridinium derivatives (**6**) and (**8**) have perpendicular rings, with highly destabilized planar transition states. In (**6**) and (**8**) there is little interaction between the rings, charges are localized, the central C–N bond has a high single bond character (Wiberg index ~0.9), and their dipole moment values are unusual, having the largest values known for organic molecules excluding polymers (natural or synthetic).

In order to verify the above predictions we have synthesized the eight betaines (**3**), (**4**), and (**11**)—(**16**) of the pyridinium azolate class.

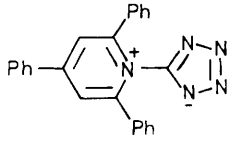
In the first step *N*-azolylpyridinium salts were prepared by two standard procedures: reaction of an activated chloroazole with pyridine (chlorohydrates of *N*-azolylpyridinium) and reaction of an aminoazole with triphenylpyridinium tetrafluoroborate (tetrafluoroborates of *N*-azolyl-2,4,6-triphenylpyridinium). In the second step the acidic *N*H proton was removed by different techniques, the best procedure being the use of a strong base anion exchange resin (OH^- form). Overall yields were >50% in all cases, and the



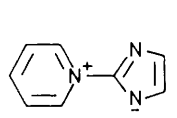
(**1**) (**2**) • = CR or N



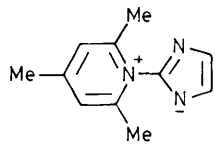
(**3**)



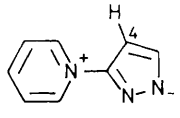
(**4**)



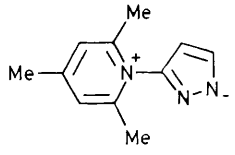
(**5**)



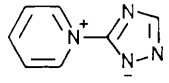
(**6**)



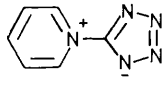
(**7**)



(**8**)



(**9**)

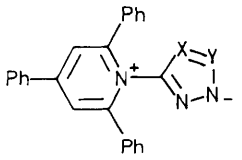


(**10**)

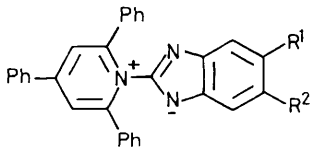
Table 1. MNDO calculations on azinium azolate inner salts; variations with change in torsion angle θ.

		$\theta_{min.}$		$\theta = 0°$		$\theta = 90°$	
Compound	$\theta_{min.}$	ΔH_f[a]	μ[b]	ΔH_f[a]	μ[b]	ΔH_f[a]	μ[b]
(**3**)	0°	135.69	11.6			138.37	12.67
(**5**)	0°	113.92	8.19			118.25	10.49
(**6**)	90°	102.59	10.15	128.48	7.66		
(**7**)	37.5°	127.11	11.72	127.81	11.23	128.40	12.85
(**8**)	90°	112.75	12.52	196.25	10.57		
(**9**)	0°	123.04	11.19			125.35	12.44
(**10**)	0°	140.77	13.84			142.00	14.64

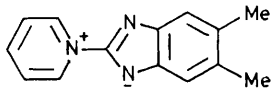
[a] In kcal/mol; 1 cal = 4.184 J. [b] In Debye; 1 Debye = 3.34×10^{-30} C m.



(**11**) X = CH, Y = CMe
(**12**) X = N, Y = CH



(**13**) $R^1 = R^2 = H$
(**14**) $R^1 = R^2 = Me$
(**15**) $R^1 = COPh$, $R^2 = H$



(**16**)

compounds were characterized by their ^1H and ^{13}C n.m.r. and fast-atom bombardment mass spectra.

The experimental dipole moments of the anhydrous betaines (**13**), (**14**), (**3**), and (**16**) were determined in dioxane. The planar betaines (**3**) and (**16**) are strongly associated when ω (w/w) >0.0002, and their dipole moments tend to 0 when the concentration increases, indicating a head-to-tail association to form a non-polar dimer. The non-planar betaines (**13**) and (**14**) do not associate. Dipole moment values extrapolated to infinite dilution are: (**13**) 13.08, (**14**) 18.70, (**3**) 10.33, and (**16**) 13.52 Debye. The calculated value for (**3**) (Table 1) was 11.06 Debye, which lends credence to our calculations (the other betaines whose dipole moments were determined are too large for us to carry out MNDO calculations).

We thank Professor J. L. Aubagnac, Université des Sciences et Techniques du Languedoc, Montpellier, France, for mass spectra.

Received, 16th December 1985; Com. 1767

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