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RELATIVE BASE STRENGTHS FROM CNDO-2 CALCULATIONS

By

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The base strengths of aromatic nitrogen heterocycles can be related to the energy of protonation of the bases if the entropies of protonation are assumed to be constant or proportional to the energies of protonation. Thus,

$$pK_a \propto - \Delta E$$

where K_a is the acid constant of the conjugate acid of the base and ΔE is the energy of protonation. If the pi approximation is made,

$$\Delta E = \Delta E_\sigma + \Delta E_\pi + \Delta E_R + \Delta E_{ST} + \Delta E_S$$

where ΔE_σ is the energy change of localized bonds upon protonation, ΔE_π the pi protonation energy, ΔE_R the change in internuclear repulsion, ΔE_{ST} the change in non-bonding interactions, and ΔE_S the change in solvation energy (1). In treating aromatic systems, it is common practice to neglect all the terms in ΔE except ΔE_π, on the grounds that they will be essentially constant for all the bases of a given series. Recently, it was shown that Pariser, Parr, Pople protonation energies failed to order the base strengths of diazoles and of triazoles respectively unless the two-center Coulomb core integrals were drastically altered (2). However, these alterations in the integrals led to uneven pi charge distributions (2) and unreasonably large pi dipole moments (3). These observations, together with conclusions drawn from Pariser, Parr, Pople calculations of base strengths of pyridine, quinoline, isoquinoline, and acridine (1,4), cast doubt upon the validity of pi protonation energy as a criterion for base strength. Unlike pi electron calculations, the CNDO-2 method (5) utilizes all valence electrons, permitting calculation of the total valence electronic energy ($E_e = E_\sigma + E_\pi$) and the total molecular energy ($E_T = E_e + E_R$). It is of considerable interest to ascertain if ΔE_e and/or ΔE_T can serve as indices of the base strengths of nitrogen heterocycles. To this end, we have made CNDO-2 calculations on diazoles and triazoles and their conjugate acids in order to compare various calculated properties with pK_a values. Since the detailed geometries of the unprotonated and protonated forms of the diazoles and triazoles are not known, we assumed both forms to be regular pentagons with sides of 1.38 A, C - H distances were taken to be 1.084 A, and N - H distances to be 1.00 A (6). The calculations were carried out on the CDC 6400 computer using a program obtained from the Quantum Chemistry Program Exchange (QCPE 91).

According to the Longuet-Higgins approximation (6)

$$\Delta E_{\pi} \propto q_{\pi}^{N}$$

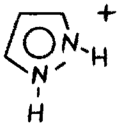
where q_{π}^{N} is the pi charge on the pyridine-type nitrogen atom of the heterocyclic base. These pi charges, calculable from the nitrogen $p\pi$ eigenvector elements, therefore provide a relative measure of the pi protonation energies. Table I gives the pi charges of the pyridine-type nitrogen atoms, the total valence electronic protonation energy (ΔE_e), and the total molecular protonation energy (ΔE_T). All tautomeric forms of the molecular and cationic forms of the triazoles were considered.

Examination of Table I reveals the following main points. First, ΔE_T values correlate with the pK_a values of pyrazole and imidazole, and also with pK_a values of the triazoles. However, neither ΔE_T nor ΔE_e nor q_{π}^{N} correlate with pK_a values of diazoles and triazoles considered together. This result may be attributable to large differences in the entropies of protonation of the diazoles and triazoles, respectively. Second, ΔE_e values do not indicate the relative basicities of the triazoles unequivocally, whereas q_{π}^{N} values fail to predict correctly the order of the base strengths of pyrazole and imidazole. Third, E_T values predict that the 1,2,4,1H- and 1,2,4,4H- triazole tautomers are equally stable, but that 1,2,3,1H-triazole is more stable than 1,2,3,2H- triazole. Similarly, the stable protonated triazoles are predicted to be (VI) and (X), with the protons maximally separated. Therefore, (V) → (VI), (IX) → (X), and (XI) → (X) are indicated to be the most likely protonation steps. In summary, it appears that the total molecular protonation energy (ΔE_T) is a more reliable index of base strength than either ΔE_e or q_{π}^{N} (and hence ΔE_{π}) for the bases of this study. This research is currently being extended to other five member, six member, and larger heterocyclic bases, which we plan to report in full later.

TABLE I

CNDO-2 PROPERTIES AND BASE STRENGTHS OF DIAZOLES AND TRIAZOLES

I.



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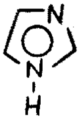

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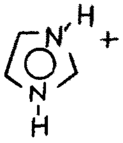

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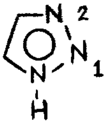

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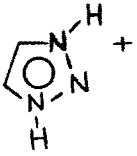

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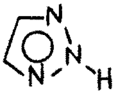

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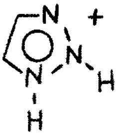

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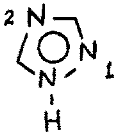

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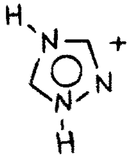
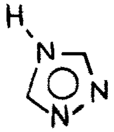


X.



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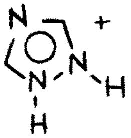

XII.

Molecule	q_{π}^{N}	E_e [b]	E_T [b]	$-\Delta E_e$	$-\Delta E_T$	pK_a [a]
Pyrazole (I)	1.273	-131.4434	-47.6017	7.047	0.299	2.47
Pyrazolinium ion (II)		-138.4902	-47.9010			
Imidazole (III)	1.052	-131.3362	-47.5647	7.326	0.544	6.95
Imidazolinium ion (IV)		-138.6624	-48.1088			
1,2,3,1H-Triazole (V)	0.902(1) 1.091(2)	-135.5264	-51.5473	7.300	0.517	
1,2,3,1H,3H-Triazolinium ion (VI)		-142.8263	-52.0643			
1,2,3,1H-Triazole (V)				7.420	0.503	1.17
1,2,3,1H,2H-Triazolinium ion (VIII)		-142.9466	-52.0503			
1,2,3,2H-Triazole (VII)	1.176	-135.5256	-51.5404	7.421	0.510	
1,2,3,1H,2H-Triazolinium ion (VIII)		-142.9466	-52.0503			
1,2,4,1H-Triazole (IX)	1.270(1) 1.203(2)	-135.3325	-51.4174	7.358	0.532	
1,2,4,1H,4H-Triazolinium ion (X)		-142.6910	-51.9492			
1,2,4,1H-Triazole (IX)				7.432	0.521	2.30
1,2,4,1H,2H-Triazolinium ion (XII)		-142.7648	-51.9384			
1,2,4,4H-Triazole (XI)	1.160	-135.3266	-51.4176	7.364	0.532	
1,2,4,1H,4H-Triazolinium ion (X)		-142.6910	-51.9492			

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b. Atomic units

Acknowledgements

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