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An *ab initio* Study of Some Heterocyclic 6π-Carbenes

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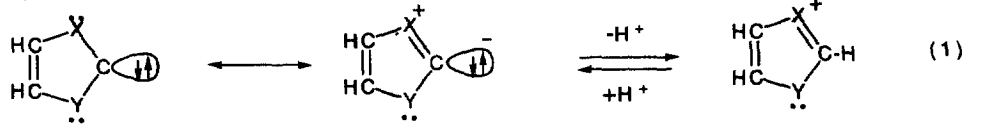
Abstract: *Ab initio* calculations on a series of 6π-electron heterocyclic ring systems containing O, N, and S atoms provided evidence for aromatic stabilization ranging from 7.6 to 25.5 kcal/mol. The most highly stabilized system was the imidazolyl carbene which had an aromatic stabilization energy comparable to furan and pyrrole. Proton affinity data was consistent with literature pKa measurements of the conjugate acids.

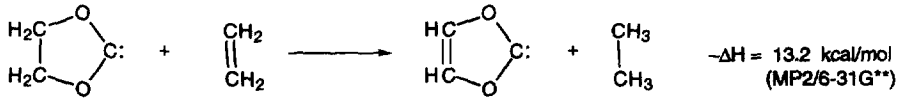
Conjugate bases **1**↔**2** (X=NR,Y=S) of heterocyclic five-membered ring onium salts **3** have been implicated as important reaction intermediates since the early work of Breslow[1] on the mechanism of thiazolium salt-catalyzed benzoin condensation. These bases were generally portrayed as ylides **2** (X=NR, Y=S), representations which stressed their nucleophilic behavior toward carbonyl groups and other electrophilic centers. Wanzlick, and later workers characterized the analogous diaza systems (**1**, X=NR, Y=NR) as nucleophilic carbenes.[2,3] There has been a surge of activity[4,5,6] in this area which includes isolation and X-ray



(1)

1 **2** **3**

crystallographic determinations of stable imidazol-2-ylidenes,[2a] synthetic and mechanistic studies on tetrathiofulvalenes, pKa measurements of onium salts, and studies involving silicon and germanium analogs. Our interest in cyclic carbenes developed from earlier *ab initio* studies on the properties of cyclic dioxocarbenes **4** and **5**.[7] Calculations revealed that the saturated carbene **4** can decompose with loss of carbon dioxide *via* a synchronous low energy pathway (~ 7.1 kcal/mol). Similar calculations on the unsaturated analog gave rise to a much higher barrier (~25 kcal/mol). The isodesmic comparison[8] shown in equation 2 provided evidence that system **5** has "aromatic" character, presumably the result of delocalization of the cyclic 6π-electron system.



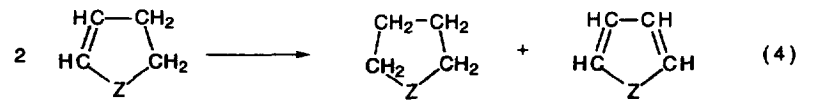
(2)

4 **5**

These results stimulated our interest in an effort to initiate a more general investigation of the energetics and properties of analogs containing combinations of O, S, and N atoms. Our primary objectives were to (a) evaluate the aromaticity[9,10] of these moieties, (b) investigate the nucleophilic properties associated with the anionic/carbenic center, and (c) provide structural information on these molecules in light of their chemistry.

The first objective was to be met by utilizing isodesmic reactions[8] illustrated in equation 3. It was felt that the reliability of the earlier comparison (eq. 2) would be improved if the reference molecules were more

similar in structure. We describe below the use of these comparisons to evaluate the Aromatic Stabilization Energies (ASE = $-\Delta H_{eq.3,4}$) of the following X, Y systems: O, O; O, NH; NH, NH; NH, S; and S, S. As a test of the methodology, we included two well-known aromatic systems in this analysis, namely, furan (Z=O) and pyrrole (Z=NH) (equation 4).



Since much of the chemistry of the carbenes/ylides in question is based on their formation *via* deprotonation reactions of onium salts **3** (cf. eq. 1), we also calculated proton affinities (PA) for each of these carbenes, defined as $-\Delta H$ for the protonation reaction shown in equation 1.[11]

Computations. All geometry optimization and frequency calculations were done analytically at the MP2(FC)/6-31G** level using the default convergence criteria in the Gaussian92 suite.[12] Normal coordinate analyses confirmed that each of the final structures was an energy minimum (no negative frequencies).

Results. The calculated ASEs found for furan (20.3 kcal/mol) and pyrrole (25.5 kcal/mol) support the claim that this methodology provides reasonable estimations of aromaticity. These results are consistent with those of other calculations and with known experimental behavior.[9,10] The calculated ASEs (Table) for the carbene/ylide systems range from 7.65-21.2 kcal/mol in the following ordering for **1** (X,Y): O,O < NH,O, ~S,S < NH,S < furan < NH,NH < pyrrole. The proton affinity calculations (Table) gave rise to the following basicity order for the reaction **1** (X,Y) -> **3**: O,O < NH,O, ~S,S < NH,S < NH,NH.[13]

FIGURE 1. Carbene Symmetry and Geometry: MP2(FC)/6-31G**

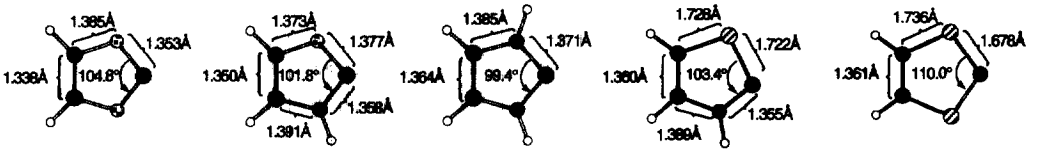


FIGURE 2. Cation Symmetry and Geometry: MP2(FC)/6-31G**

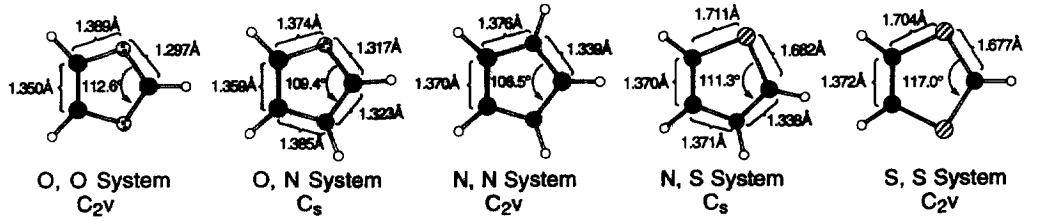


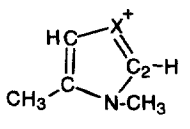
TABLE Aromatic Stabilization Energies (ASE), Proton Affinities (PA) and Charges at C_2 for 1

A-B System	ΔH^a eq. 3	ΔZPE^a eq. 3	ASE^a	Charge[b] at C_2 Mulliken	NPA[c]	PA^a
O, O	-8.06	0.41	7.65	0.253	0.622	228.2
O, N	-13.76	0.64	13.12	0.174	0.254	247.2
N, N	-22.41	1.22	21.19	0.098	0.073	262.1
N, S	-18.54	0.91	17.63	-0.134	-0.252	254.7
S, S	-14.06	0.59	13.47	-0.414	-0.707	247.7

[a] kcal/mol. [b] based on MP2 density. [c] Natural population analysis.

Discussion. The question of aromaticity in these carbenes is one of degree. Our results are consistent with variable π-delocalization as reflected in calculated ASEs. Other criteria, e.g., charge densities and geometry are less easily associated with aromaticity because of the difficulty in evaluating the effects of variable electronegativities and atomic sizes on structure. The calculated charge on C_2 is a case in point. While the imidazolyl carbene has the largest ASE, it has the smallest charge on C_2. To the extent that resonance structures of the type shown in eq. 1 are important one expects a build-up of negative charge. The calculated charges at C_2 are consistent with a changing balance between π-donation and electron withdrawal through the σ-network. The calculations of Arduengo, *et al.* on the imidazolyl carbene indicate that π-overlap between C_2 and the nitrogen lone pairs is negligible[3a] yet we find a substantial ASE for this system. This discrepancy is puzzling and may indicate that even a small amount of π-donation can lead to significant lowering in energy.

Other aspects of the calculations that are noteworthy are related to recent measurements of exchange rates and pKa's of onium salts. Haake and co-workers[4b] measured the following pKa's and relative bimolecular rates of OD^- catalyzed hydrogen exchange at C_2:



pKa		Exchange krel		Proton Affinity
X = O:	~12	X = O:	$10^{5.5}$	X = O: 247
X = S:	~14	X = S:	$10^{3.5}$	X = S: 255
X= NCH_3:	~17	X= NCH_3:	1	X= NH: 262

Our calculated proton affinities are consistent with the pKa measurements, *i.e.* the diaza carbene is the strongest base and the imidazolium salt is the weakest acid. Haake and co-workers suggested that these trends were unexpected on the basis of $J(^{13}C_2\text{-H})$ data which attributed nearly equal acidity to the C_2-H protons of thiazolium and imidazolium systems. As a result, they proposed that the thiazolium ylide "probably has considerably greater stability than the imidazolium ylide". Our data do not confirm this proposal, but we do agree on the relative acidity data. Since $J(^{13}C_2\text{-H})$ couplings depend solely on the electronic distribution in the onium salts, one should not expect a consistent correlation with acidity. It should also be noted that basicity does not correlate with the calculated negative charge on C_2 (cf. Table). On the other hand, our results emphasize the dependence of acidity on the relative stability of both the carbene and the onium salts. The same factors that are involved in stabilization of the carbenes are involved in stabilizing the cations.

We also examined the calculated geometric features of these systems (Figure 1) to probe for any trends that would indicate onset of aromaticity.[14] With one exception, bond length changes follow a monotonous pattern. For example, the X-C_2-Y angle increases by 4.2-5° on introduction of the double bond into the saturated carbene. The X-C_2 (Y-C_2) bond lengths increase on introduction of a double bond by 0.015-0.03 Å

except in the thiazole system in which the S-C_2 bond decreases by 0.007 Å. Comparing the unsaturated carbenes to the conjugate acids, the X-C_2 (Y-C_2) bond lengths uniformly decrease by 0.01-0.06 Å.

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