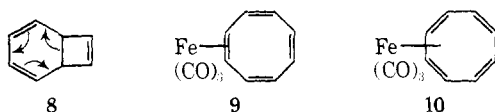


the same conditions the half-lives for the thermal ring opening are approximately 16 hr and 3 weeks, respectively. The metal atoms are clearly assisting the ring opening process, especially since the slow step in the metal reactions may well be the initial loss of CO.

The data provide for the first time experimental evidence supporting the hypothesis that cyclobutene-metal complexes, in which the metal is bound to the olefin, can undergo facile, disrotatory, concerted ring opening of the ligand to yield butadiene-metal complexes; in the absence of any experimental evidence to the contrary, we consider that this provides a satisfactory explanation of the analogous silver ion catalyzed reactions mentioned above.

A further point of interest concerns the pronounced stability of the bicyclooctatriene complexes **2** and **6** compared to bicyclooctatriene **8** itself. Whereas the latter system readily converts to cyclooctatetraene at 0° (half-life 14 min),<sup>10</sup> complex **2**, on the other hand, shows no sign of rearrangement to cyclooctatetraene-Fe(CO)<sub>3</sub> upon heating for 10 hr in refluxing hexane. We attribute this to the fact that the isomerization of the free ligand presumably proceeds *via* a Cope type rearrangement as indicated in formula **8**.<sup>11</sup> A similar type of rearrangement of the ligand in complex **2** would lead to the *dihaptocyclooctatetraene*-Fe(CO)<sub>3</sub> complex (**9**) in which the inert gas structure about iron is now lost. The isomerization which would lead directly to *tetrahaptocyclooctatetraene*-Fe(CO)<sub>3</sub> (**10**), with the



inert gas structure about iron maintained, would involve disrotatory ring opening of the four-membered ring in the complex **2** and this is of course "forbidden," the metal atom not now being in a position to render it an "allowed" process.

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the reactions leading to the complexes **2** and **6** are based on data points obtained for initial low conversions.

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## Photoelectron Spectroscopic Study of Cyclic Amines. The Relation between Ionization Potentials, Basicities, and s Character of the Nitrogen Lone Pair Electrons

Sir:

Photoelectron spectroscopy (PES) has recently been proved to be potentially useful for structural studies of organic molecules.<sup>1</sup> Much attention has been paid to the studies of electronic interactions such as  $\pi, \pi$ ,  $n, \pi$ , and  $n, n$  interactions in a molecule.<sup>2</sup> However, there has been no report on the systematic PES studies of amines with attention to the ionization potentials (IP) of the lone pair electrons.<sup>3</sup> Here we wish to report the relation between IP's, basicities, and the hybridized nature of lone pair electrons for cyclic amines. We are concerned with the effect of the ring size on the physicochemical properties of cyclic amines with much attention to the IP's of the lone pair electrons as a probe for elucidation of the intrinsic nature of cyclic molecules. We have studied here the PES of three- to seven-membered cyclic amines. The measured vertical ionization potentials (IP's) are shown in Table I. All of the first

Table I. Vertical Ionization Potentials (eV) for Cyclic Amines<sup>a</sup>

| Compound | R = H       | R = CH <sub>3</sub> |
|----------|-------------|---------------------|
|          | 9.85, 11.90 |                     |
|          | 9.57        |                     |
|          | 9.29, 11.07 | 8.68, 10.58         |
|          | 9.04, 11.50 |                     |
|          | 8.77, 11.49 | 8.41, 11.19         |
|          | 8.64, 10.75 | 8.29, 10.59         |
|          | 8.41, 10.85 | 8.29, 10.68         |

<sup>a</sup> He(I) photoelectron spectra were recorded on a JASCO PE-1 spectrometer. Vertical IP values are accurate to  $\pm 0.02$  eV.

IP's of these amines are readily assigned to the ionizations from lone pair orbitals. A remarkable feature of this table is that the values of the IP's of lone pair electrons in N-H derivatives fall in the order of increasing ring size, *i.e.*, aziridine > azetidine > pyrrolidine > piperidine > hexamethylenimine. The similar trend in IP is also the case for *N*-methyl homologs, *i.e.*, *N*-methylpyrrolidine > *N*-methylpiperidine  $\approx$  *N*-methylhexamethylenimine, although the data for three- and four-membered imines are lacking. It is, there-

(1) For example, (a) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, New York, N. Y., 1970; (b) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

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(3) Though Gallegos, *et al.*, reported 9.94, 9.1, and 9.0 eV for the IP's of aziridine, azetidine, and pyrrolidine, respectively, by using electron impact spectroscopy, these data seem to contain considerable experimental error: E. Gallegos and R. W. Kiser, *J. Phys. Chem.*, **65**, 1177 (1961); **66**, 136 (1962).

fore, tempting to suggest that this is because of changes in the overall hybridization of the nitrogen atom as the ring size is increased, *i.e.*, a change of the lone pair orbital from an  $sp^2$  hybrid (in aziridine) toward an  $sp^3$  orbital. It is well established<sup>4</sup> that in cycloalkanes the  $s$  character of the carbon-hydrogen bond increases with decreasing ring size. This may allow us to expect that in cyclic amines the  $s$  character of the lone pair electrons increases with decreasing ring size and the IP of the nitrogen lone pair will reflect this hybridized nature. To examine the relation between the IP's and the  $s$  character of lone pair electrons in cyclic amine, we plotted in Figure 1 the first IP's of cyclic amines against the values of the directly bonded  $^{13}\text{C}$ - $^1\text{H}$  nuclear spin coupling constants<sup>4a</sup> of the corresponding cycloalkanes. This figure shows that the IP's of lone pair electrons are well correlated linearly with their  $s$  character.<sup>5</sup>

It is also tempting to expect some relation between the IP of amines and their basicity. It was reported<sup>6</sup> that in aqueous solution the basicity of cyclic amines falls in the order: azetidione ( $pK_a = 11.29$ ) > pyrrolidone (11.27) > piperidone (11.22) > hexamethylenimine (11.07) > aziridine (8.04). It is apparent that these basicities do not parallel the IP values for cyclic amines; the basicity of azetidione appears to be too strong for its IP value. Recently, Bowers, *et al.*,<sup>7</sup> have determined the relative basicity of cyclic amines in the vapor phase using icr (ion cyclotron resonance) spectroscopy;<sup>8</sup> the basicity falls in the order, piperidine > pyrrolidone > azetidione. Here the basicities correspond well to the trend of IP's in cyclic amines.<sup>9</sup> Therefore, the abnormal feature of the relative basicities of cyclic amines could be attributed to the solvent effect.<sup>10,11</sup> It is also to be noted in Table I that the values of the IP's decrease on going from secondary to tertiary amines. This trend does not parallel the relative strength of basicity.<sup>6,12,13</sup> This could be also attributable to a solvent effect involved in basicity in solution.<sup>10,11</sup>

From the above results and discussion it may be reasonable to conclude the IP values of cyclic amines could be used as a measure of the basicity and the hybridized nature of their lone pair electrons. Similar studies for bicyclic amines are now in progress.

(4) (a) J. J. Burke and P. C. Lauterbur, *J. Amer. Chem. Soc.*, **86**, 1870 (1964); (b) A. Streitwieser, Jr., R. A. Caldwell, and W. R. Young, *ibid.*, **91**, 529 (1969).

(5) This relationship would be acceptable, if we assume that the C-N-C bond angle in cyclic amines is not so different from the C-C-C angle in the corresponding cycloalkanes. This is because the C-C-C angle is directly related to the  $J_{\text{C-H}}$  value, a measure of  $s$  character of the C-H bond: C. S. Foote, *Tetrahedron Lett.*, 579 (1963); K. Mislow, *ibid.*, 1415 (1964).

(6) S. Searles, M. Tamres, F. Block, and L. A. Quarterman, *J. Amer. Chem. Soc.*, **78**, 4917 (1956); H. K. Hall, *J. Phys. Chem.*, **60**, 63 (1956).

(7) M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, Jr., *J. Amer. Chem. Soc.*, **93**, 4314 (1971).

(8) The gas-phase basicity of amines has also been extensively studied by others (see ref 10-13).

(9) The gas-phase basicities of aliphatic amines determined by icr have been related to the N-H bond dissociation energies and the IP's of amines (see ref 11).

(10) E. M. Arnett, F. M. Jones, III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 4724 (1972).

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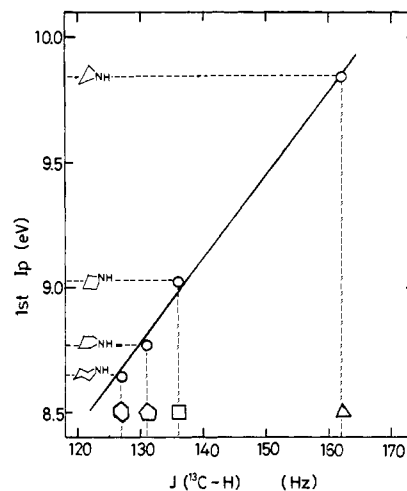


Figure 1. A plot of first IP's against  $J_{\text{C-H}}$  in cycloalkanes.

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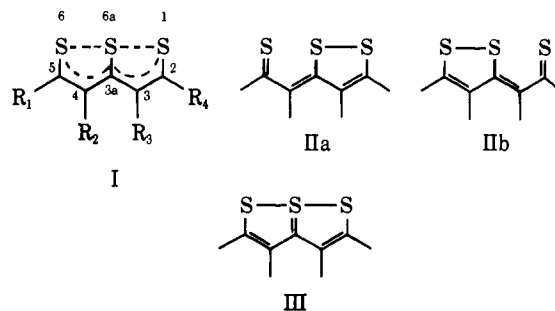
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### Molecular Structure of 1,6,6a-Trithia(6a- $S^{IV}$ )pentalene

Sir:

The trithiapentalenes (I) are substances of unusual composition having aromatic properties. The crystal structures of several of these substances have been investigated by X-ray diffraction with the following important results. In the symmetrically substituted 2,5-



dimethyl compound<sup>1</sup> the distances  $S_6-S_{6a}$  and  $S_1-S_{6a}$  are equal in length at 2.36 Å, which is about 0.32 Å longer than the sum of the covalent single bond radii, implying important contributions from resonance structures IIa and IIb involving single-bond no-bond resonance. Although the equality of the S-S bonds in this compound has been verified by a reinvestigation,<sup>2</sup> these bonds do not appear to be equal in the 2,5-di-

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