

pound are such that the carbonyl rearrangement process is 20 times faster than the ring process. This indicates that even though the motion of the ring can itself average the carbonyls, there is an independent mechanism which does so. This type of independence has been observed before in  $C_8H_8Fe(CO)_3$ ,<sup>14</sup>  $C_7H_8Fe_2(CO)_6$ ,<sup>29</sup> and  $C_7H_8M(CO)_3$  where  $M = Mo$  and  $Cr$ .<sup>30</sup>

**Extension to Other Cases.** The explanation proposed above for the behavior of the molecules **2** suggests where to look for other cases of random exchange *via* a symmetrical, "piano stool" type intermediate configuration. The principle involved implies that in any case where the metal is attached to a relatively large ring (seven-, eight-, or nine-membered, but probably not six-membered) so as to employ all but one pair of  $\pi$ -electrons, the random shift process may be more facile than the 1,2-shift process. Specific examples which we have commenced to investigate are those containing  $C_7H_7$  rings, such as  $C_7H_7Fe(CO)_3$ ,<sup>31</sup> and the recently reported  $C_8H_8Fe$  (norbornadiene).<sup>32</sup> Compounds with  $C_7H_7$  rings are of special interest because it can easily be shown that for this case all of the 1,*n*-shift processes, namely, 1,2, 1,3, and 1,4, there will be selective line broadening. Should a uniform pattern of broadening be observed, the occurrence of random shifts will be indicated in a completely unequivocal way, without need for any argument such as the one used in the present case to reject 1,3-shifts.

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## Photoelectron Spectra of Some Cyclic Di- and Polyamines. Lone Pair-Lone Pair Interaction in 1,3- and 1,4-Diamines

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**Abstract:** Nitrogen "lone pair" ionization potentials measured by photoelectron spectroscopy are reported for four bicyclic and four monocyclic 1,3- and 1,4-diamines and for examples of bridgehead di-, tri-, and tetraazaadamantanes. Assignments of the ionizations to symmetric and antisymmetric lone pair orbital combinations based on extended Hückel calculations are consistent with observed vibrational structure in the few cases where such structure was observed. The magnitude of through-space and through-bond contributions to the observed splittings and the possible utility of photoelectron spectroscopy for conformational analysis of 1,3- and 1,4-diamines (not very promising due to a lack of large enough splitting differences between lone pair axial-equatorial and equatorial-equatorial conformers in six-ring systems, causing drastic overlapping of the spectra) are discussed.

Hoffmann has discussed the general importance of through-space and through-bond orbital interactions<sup>1</sup> and several applications of these concepts. One of the nicest examples of such interactions occurs in 1,4-diazabicyclo[2.2.2]octane (Dabco, **1**). The nitrogen lone pair orbitals



have a through space interaction which tends to place  $n_-$  higher in energy than  $n_+$ . Through bond interaction of  $n_+$  with other orbitals (most importantly the symmetrical  $\sigma_{CC}$  orbital depicted as  $\sigma_+$  which can be perfectly aligned for maximum lone pair- $\sigma_{CC}$  overlap) preferentially raises the energy of the (now mixed but still principally)  $n_+$  orbital. Extended Hückel calculations<sup>2</sup> predicted that  $n_+$  would actually be 1.57 eV higher in energy than  $n_-$  (MINDO/2 calculations gave a 1.36-eV splitting).<sup>3</sup> This prediction was

**Table I.** PES Spectra of Some Cyclic Di- and Polyamines

Compd	IP <sub>1</sub> , eV <sup>a</sup>	IP <sub>2</sub> , eV <sup>a</sup>	Δ, eV <sup>b</sup>	Assignment <sup>c</sup>
1	7.61	9.68	2.07	n <sub>+</sub> > n <sub>-</sub>
2	7.43	8.65	1.22	n <sub>+</sub> > n <sub>-</sub>
3	8.89	9.64	0.75	n <sub>-</sub> > n <sub>+</sub>
4	7.75	8.78	1.03	n <sub>-</sub> > n <sub>+</sub>
5	7.46	8.55	1.09	n <sub>-</sub> > n <sub>+</sub>
6	8.08	9.90	1.82	E <sub>2</sub> > A <sub>1</sub>
7	8.53			T <sub>2</sub>
8	8.98	9.53	0.55	n <sub>-</sub> > n <sub>+</sub>
9	8.77			n <sub>+</sub> > n <sub>-</sub>
10	8.11	8.51	0.40	
11	8.03	8.41	0.41	

<sup>a</sup> Vertical ionization potentials (peak maxima for gaussians used to fit the data). <sup>b</sup> Δ = IP<sub>2</sub> - IP<sub>1</sub>. <sup>c</sup> See text for justification.

**Table II.** Results of Extended Hückel Calculations on Cyclic Di- and Polyamines, eV

Compd	Molecular symmetry	-E <sub>1</sub> (orb sym)	-E <sub>2</sub> (orb sym)	Δ = E <sub>1</sub> - E <sub>2</sub>
1	D <sub>3h</sub>	10.133 (A <sub>1</sub> ', n <sub>+</sub> )	12.089 (A <sub>2</sub> '', n <sub>-</sub> )	1.956
2	C <sub>s</sub>	10.462 (A', n <sub>+</sub> )	11.194 (A'', n <sub>-</sub> )	0.732
3	C <sub>s</sub>	10.740 (A'', n <sub>-</sub> )	10.938 (A', n <sub>+</sub> )	0.198
5'	C <sub>2v</sub>	10.604 (B <sub>2</sub> , n <sub>-</sub> )	11.066 (A <sub>1</sub> , n <sub>+</sub> )	0.462
6'	C <sub>2v</sub>	10.721 (E)	11.533 (A <sub>1</sub> )	0.812
7	T <sub>d</sub>	10.890 (T <sub>2</sub> )	12.857 (A <sub>1</sub> )	1.967
8A (εε)	C <sub>2h</sub>	10.493 (A <sub>g</sub> , n <sub>+</sub> )	12.147 (B <sub>u</sub> , n <sub>-</sub> )	1.654
8B (εα)	C <sub>s</sub>	10.970 (A', n <sub>-</sub> )	11.446 (A', n <sub>+</sub> )	0.476
8C (αα)	C <sub>2h</sub>	11.206 (A <sub>g</sub> , n <sub>+</sub> )	11.374 (B <sub>u</sub> , n <sub>-</sub> )	0.168
10'D (αα)	C <sub>s</sub>	11.081 (A', n <sub>+</sub> )	11.554 (A'', n <sub>-</sub> )	0.473
10'E (αε)		11.244 (n <sub>+</sub> )	11.301 (n <sub>-</sub> )	0.058
10'F (εε)	C <sub>s</sub>	10.999 (A'', n <sub>-</sub> )	11.589 (A', n <sub>+</sub> )	0.590

strikingly verified by the PES work of Heilbronner and co-workers, who observed an n<sub>+</sub>-n<sub>-</sub> splitting of 2.13 eV<sup>4a</sup> and showed that the n<sub>+</sub> orbital was in fact the highest in energy from the vibrational structure observed in the PES bands.<sup>4b</sup>

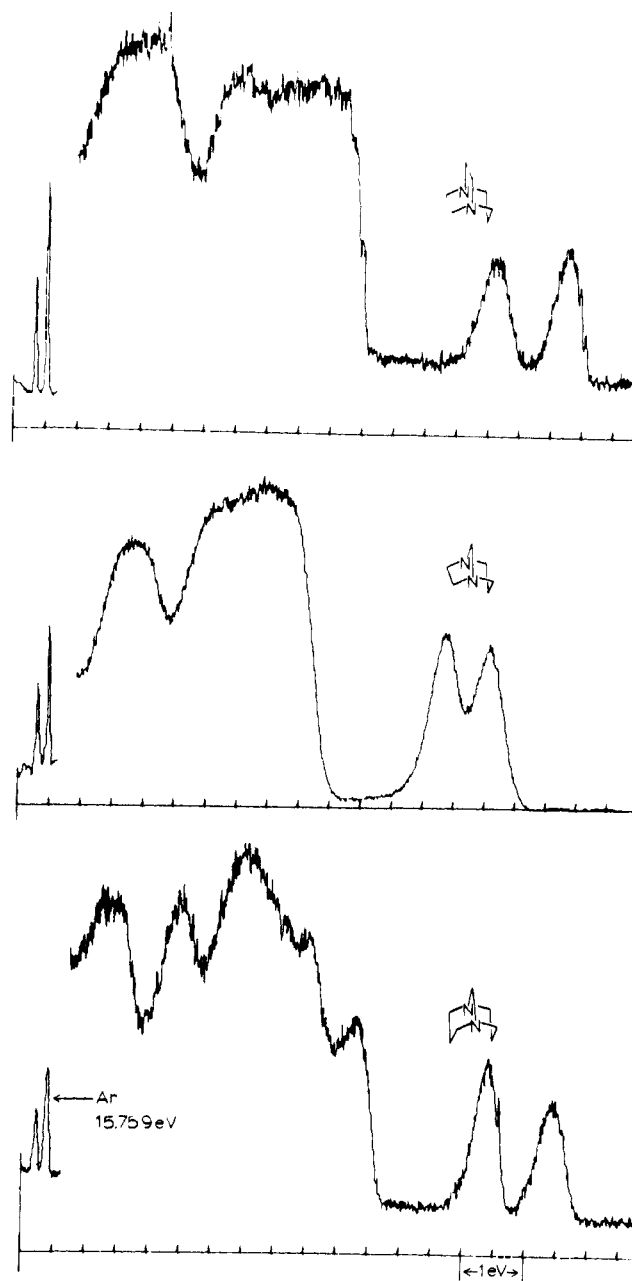
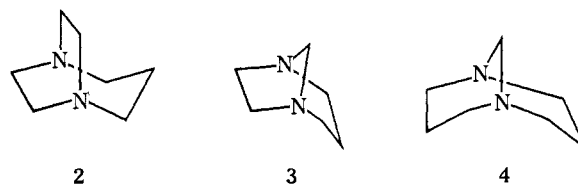
The amount of "through-bond" mixing should clearly be dependent upon alignment of the C-C bonds with the lone pair axes, which might lead to different PES spectra for different conformers, in a manner similar to that demonstrated for hydrazines,<sup>5</sup> where the lone pair-lone pair splitting is very dependent upon the lone pair-lone pair dihedral angle (a "through-space" effect). To evaluate "through-space" and "through-bond" contributions to the observed lone pair-lone pair splittings experimentally, we have determined the PES spectra for several cyclic compounds containing 1,3 and 1,4 nitrogens.

## Results and Discussion

The peak positions observed for the compounds examined in this work appear in Table I. Our data for Dabco (**1**) agree well with that of Heilbronner and coworkers,<sup>4</sup> whose vertical IP values of 7.52 and 9.65 eV differ from those we observed by 90 and 30 meV, respectively. An adiabatic (initial rise) value of 8.26 eV was reported by Dewar and Worley<sup>6</sup> for **7**. Although "very small" splittings have been reported for **8** and **9**,<sup>7</sup> no ionization potentials were given. Extended Hückel (EH) calculations, using arbitrary "standard" geometries, were carried out for several of the compounds. These results are summarized in Table II.

### Bridgehead Bicyclic Diamines 1-4

In this series of compounds, the aligned NCH<sub>2</sub>CH<sub>2</sub>N groupings of Dabco which are responsible for the large through-bond interaction observed<sup>4</sup> are successively removed, and the splittings observed are 2.07, 1.22, 0.75, and 1.03 eV, respectively (for **1-4**). The spectra of **2-4** are shown in Figure 1. For 1,5-diazabicyclo[3.2.2]nonane (**2**),

**Figure 1.** Photoelectron spectra of **2-4**.

a vibrational spacing of about 0.09 eV (*ca.* 730 cm<sup>-1</sup>) was observed in the first ionization peak (IP<sub>1</sub>). This splitting is near the 765-815 cm<sup>-1</sup> splitting of **1**<sup>4b</sup> (for which we observed a splitting of 0.10 eV, about 800 cm<sup>-1</sup>). This suggests a similar vibrational mode (principally involving ethylene bridge C-C stretch) and hence the same type of orbital symmetry for the first ionization peaks of **1** and **2**, both n<sub>+</sub>. This is not unreasonable on qualitative grounds since only one of the three aligned ethylene bridges raising n<sub>+</sub> above n<sub>-</sub> was removed, and the nitrogen-nitrogen distance has been increased, reducing the magnitude of any through-space splitting. The n<sub>+</sub> < n<sub>-</sub> ordering was also that

given by the EH calculation (Table II), leaving little doubt that the assignment given in Table I is correct.

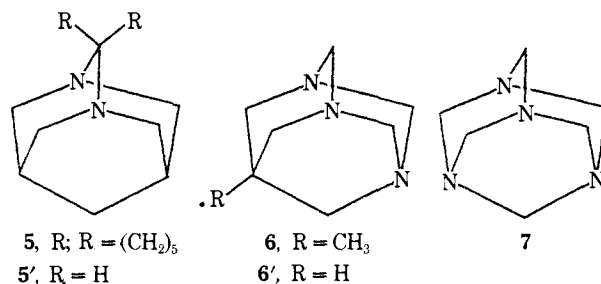
Although no vibrational structure was observed in either  $IP_1$  or  $IP_2$  for 1,5-diazabicyclo[3.2.1]octane (**3**), since a second  $n_+$ -raising aligned C-C interaction has been removed, and the N-N distance substantially decreased, raising the through space interaction, it seemed likely on qualitative grounds that a reversal of  $n_+$  and  $n_-$  had occurred, and that **3** should be assigned  $n_- > n_+$ . This was the result of an EH calculation, although the 0.75-eV splitting observed was substantially larger than the calculated one of 0.20 eV. In 1,5-diazabicyclo[3.3.1]nonane (**4**), no  $NCH_2CH_2N$  bridges remain, leaving an unambiguous qualitative prediction that  $n_- > n_+$ . Although C-C bonds are present in **4**, the lone pair-N-C dihedral angle is quite large, ensuring poor overlap and consequently a rather small interaction. Furthermore,  $\sigma_{CC}$  combinations involving both  $n_+$  and  $n_-$  symmetry should be of rather similar energy, predicting (small) raising of both  $n_+$  and  $n_-$  in energy. Our EH calculation (performed on diazadamantane (**5'**)), gave a smaller calculated splitting ( $n_- > n_+$ , 0.46 eV) than the observed value (1.03 eV). The calculation underestimates the through-space  $NCH_2N$  interaction, further substantiating the assignment made for **3**; both **3** and **4** have  $n_- > n_+$ .

The observed splittings for **1-4** should reflect changes in through-bond and through-space lone pair-lone pair interactions as a function of the geometry of these molecules. A quantitative analysis seems precluded since the lone pair-N-C-C dihedral angle is not accurately known for any of these compounds. Although we have followed previous workers<sup>1,4</sup> in using the fully eclipsed  $D_{3h}$  model for **1** in our calculation, it is not clear that it really exists in this eclipsed form, and not in the  $D_3$  torsionally twisted form; experimental evidence on this point in vapor, solution, or solid phases is lacking. Force field calculations for both bicyclo[2.2.2]octane and bicyclo[3.2.2]nonane indicate that virtually no energy is lost by a modest torsional twist;  $\Delta E$  is less than 0.3 kcal/mol for  $\pm 10$  and  $\pm 15^\circ$  twists, respectively.<sup>8</sup> Since both **1** and **2** have an additional interaction in the eclipsed conformation caused by maximized  $n, \sigma_{CC}$  interactions, one might predict these systems to have some torsional twist. Dewar and Wasson<sup>3</sup> have argued that the through-space interaction in **1** is small since the calculated splitting only changed by 0.05 eV when this interaction was artificially "turned off" in performing a MINDO/2 calculation. If the through-space ( $E(N,N)$ ) interaction of **1** is taken as -0.1 to 0, the through-bond interaction,  $E(NC-CN)$ , is 0.69-0.72 eV per ethylene unit (assuming additivity). For **2**, one obtains  $E(NC-CN) = 0.61-0.65$  eV, possibly suggesting a larger dihedral angle. Comparing **3** and **4**,  $E(NC-CN)$  for the ethylene unit of **3** is only 0.28 plus  $\Delta E(N,N)$  for **3** and **4**. From models, the lone pair-N-C-C dihedral angle is clearly less favorable for **3** than for **1** or **2**.

#### Azadamantanes 5-7

The observed PES splitting of **5** is very similar to that of **4**, although the six-membered rings are substantially flattened in **4**,<sup>9</sup> suggesting that the "through-space" N-N interaction dominates nearly completely, as expected. A vibrational progression with a frequency of about 970  $cm^{-1}$  was observed for  $IP_2$  of **5**.

The spectrum of the triazaadamantane **6** showed only two peaks in the region expected for "lone pair" ionizations. This is expected since this  $C_{3v}$  molecule should have a doubly degenerate set of E orbitals occurring above the  $A_1$  orbital in energy because of through-space interactions. The 1.82-eV observed splitting was over twice as large as the



EH calculated one of 0.81 eV (for **6'**), again pointing out the underestimation of the through-space 1,3 nitrogen interaction in the EH calculations performed. A fairly distinct vibrational series corresponding to *ca.* 970- $cm^{-1}$  splitting was observed in  $IP_2$ , and the  $IP_1$  peak was somewhat larger than  $IP_2$ , as expected since  $IP_1$  is doubly degenerate.

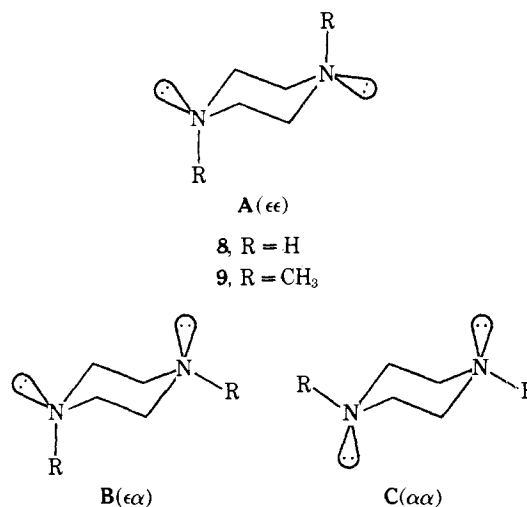
Tetraazaadamantane (**7**) showed only a single ionization peak, well separated from the  $\sigma$  bond onset. From the  $T_d$  symmetry, a triply degenerate  $T_2$  level should occur above the  $A_1$  level, and since the EH calculation gave a 1.97-eV separation (probably a factor of 2 smaller than expected experimentally), it is not surprising that the  $A_1$  lone pair ionization was buried in the sigma levels. Dewar and Worley<sup>6</sup> have pointed out that **7** is only 1 eV less difficult to ionize than adamantane itself, indicating a high degree of localization of the nitrogen lone pair orbitals. The ease of electrochemical oxidation of **5-7** parallels their PES ionization potentials.<sup>9</sup>

Complex fine structure was observed in  $IP_1$  of **7**, the most well-defined series appearing to have splittings of about 1130 and 650  $cm^{-1}$ . Although the vibrational frequencies of both adamantane<sup>10</sup> and **7**<sup>11</sup> have been assigned, vibrational states of different symmetries have frequencies close enough to make interpretation of assignments based upon these frequencies tenuous at best. We feel the peak assignments for **5-7** must rest on other arguments, although the vibrational structure observed is not inconsistent with the assignments given.<sup>19</sup>

#### Conformational Analysis of 1,3- and 1,4-Diamines

Since both through-space and through-bond interactions are geometry dependent, one might expect the PES spectra observed to be able to distinguish conformers. To access the likelihood of PES being useful for conformational analysis of 1,3- and 1,4-diamines, as we believe it certainly is for hydrazines (1,2-diamines),<sup>5</sup> we have run PES spectra of two piperazines and two hexahydropyrimidines.

Three chair conformations, **A**, **B**, and **C** are conceivable



as possibilities for piperazines **8** and **9**. Since the most important structural feature for the PES spectrum is whether the lone pairs are axial or equatorial, we have also designated this for conformations A–C, using  $\alpha$  for axial lone pair and  $\epsilon$  for equatorial, to avoid confusion of lone pair and alkyl group configuration. One expects a sizable through-bond interaction for A( $\epsilon\epsilon$ ), leading to  $n_+ > n_-$ , smaller through-bond interaction for B and C, and the largest through-space interaction for B( $\alpha\epsilon$ ). We could observe no splitting in the PES spectrum of **9**, which is consistent with the assignment of the diequatorial *N*-methyl conformation 9C( $\alpha\alpha$ ) made on the basis of its solution nmr spectrum<sup>12a</sup> and microwave spectrum.<sup>12b</sup> In contrast, **8** showed a modest splitting of 0.55 eV, suggesting that the conformations of **8** and **9** might be different. The EH calculations for 8A–C given in Table II allow observation of peaks assignable to A to be ruled out for either **8** or **9**. They also suggest that **8** exists at least partially as 8B( $\alpha\epsilon$ ) in the vapor phase. Although the monoaza analog piperidine has often been claimed to exist predominantly as the axial  $\alpha$ H conformer,<sup>13a</sup> recent dipole moment studies by Jones, Katritzky, and coworkers<sup>13b</sup> indicate that the equatorial NH conformer predominates ( $\Delta G^\circ = 0.4 \pm 0.2$ ). We probably observe a superposition of the 8B and 8C spectra, but overlap is so serious we cannot estimate the relative amounts.

Hexahydropyrimidines **10** and **11** were run because con-

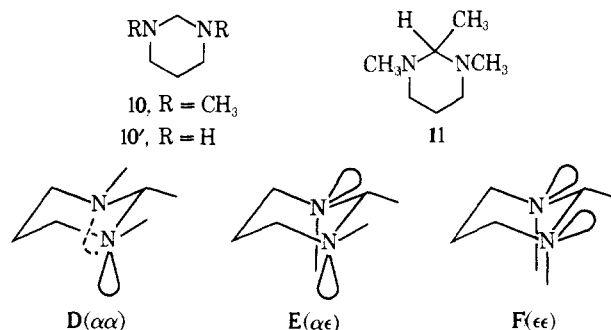


Figure 2. Sizes of lone pair-lone pair splittings in 1,3- and 1,4-diamines.

lows presentation of the experimentally measured splittings given in Figure 2. These splittings should be compared with the similar presentation given by Hoffmann for  $sp^2$  hybrids on carbon.<sup>1</sup>

### Experimental Section

The preparation of the compounds employed has been described elsewhere.<sup>14</sup> All samples were purified by vpc (**2–4**, **8–11**) or vacuum sublimation (**1**, **5–7**) before use.

**PES Spectra.** A Varian IEE-15 spectrometer, with a flowing helium discharge lamp source (predominant emission line 584 Å) was employed; typical resolution was 22 meV at 30,000 counts/sec on the argon 15.759-eV line; spectra were calibrated vs. internal argon. Spectra of inert gas mixtures and methyl iodide indicated a maximum error in peak position relative to argon of about 40 meV over the IP range employed in this work. All reported ionization potentials are vertical IP values, measured at the maxima of gaussians used to fit the data, using the program GFIT, written by D. Lichtenberger, University of Wisconsin.

**MO Calculations.** We employed EXTHUC (Quantum Chemistry Program Exchange, Indiana University, No. 64), modified for use on the Univac 1108 computer by J.M.B., for the extended Hückel calculations. The coordinates used were based on the standard geometrical models as described by Pople and Beveridge;<sup>17</sup> bond lengths employed were N–N, 1.45 Å; C–N, 1.47; C–C, 1.54; N–H, 1.01; C–H, 1.09. The heavy-atom positions were obtained from the use of Dreiding models and adjusted for the above bond lengths, and hydrogens were attached using an HCH angle of  $109^\circ 28''$ , in the plane bisecting the X–C–Y plane using program MIRAGE, obtained from Joseph C. Calabrese, University of Wisconsin. The EH parameterization used was modified from that described by Hoffmann and Lipscomb<sup>18</sup> to give a better fit to the observed PES data for **1**; we used Coulomb integrals:  $C_{2s} = 22.5$ ,  $C_{2p} = -11.8$ ,  $N_{2s} = -24.5$ ,  $N_{2p} = -12.0$  eV;  $H_{ij} = 0.5k(H_{ii} + H_{jj})S_{ij}$  with  $k = 2.0$ . Slater exponents:  $C = 1.625$ ,  $N = 1.950$ ,  $H = 1.000$  eV.

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siderable conformational work has been done in solution. General agreement has been reached using nmr and dipole moments that, although both conformations D and E are present in substantial amounts, 10D and 11E predominate.<sup>14–16</sup> The lone pair regions of the PES spectra of **10** and **11** were nearly identical except for an 80-meV shift to lower IP for the trimethyl compound **11**. If the solution conformational mixtures are also present in the vapor phase, PES does not distinguish conformation D( $\alpha\alpha$ ) from E( $\alpha\epsilon$ ). The EH calculations on 10'D–F suggest substantially different splittings for D and E, but since the 1,3-nitrogen  $\epsilon\epsilon$  through space interaction is about 0.5 eV too low (see calculated and observed spectra of **4** and **5**), it would not surprise us greatly if E( $\alpha\epsilon$ ) showed a detectable splitting instead of the 58-meV splitting calculated. Other explanations are clearly possible: **10** and **11** might be present so predominantly as either conformation D or E in the vapor phase that only one was seen, or either D or E could have small splitting but lie under one of the peaks for the other conformation (although a substantial difference in size of the two peaks was not observed). In any event, PES is not a powerful tool for conformational analysis of hexahydropyrimidines, although the  $\epsilon\epsilon$  conformation E is distinguishable from the  $\alpha\alpha$  and  $\alpha\epsilon$  conformations, as is indicated from the spectra of the bicyclic compounds.

### Conclusions

This work measured lone pair-lone pair splittings for 1,3- and 1,4-diamines in various geometric arrangements and al-

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(19) NOTE ADDED IN PROOF. T. Sasaki, S. Eguchi, T. Kiriya, and Y. Sakito, *J. Chem. Soc., Chem. Commun.*, 725 (1974), have recently reported the PES of three bridgehead diphenyl analogs of **5**, R,R = H,H; R,R = O; and R,R = H,OH. Their assignment and the  $n_{-},n_{+}$  splitting of 1.06 eV for diphenyl **5**, R,R = H,H, agree well with ours for **5**, R,R = (CH<sub>2</sub>)<sub>5</sub>. For our work on the first two compounds, see the Ph.D. Thesis of J.M.B.

## Stereochemistry of Olefinic Cyclization and Solvolytic Displacement at Vinyl Carbon

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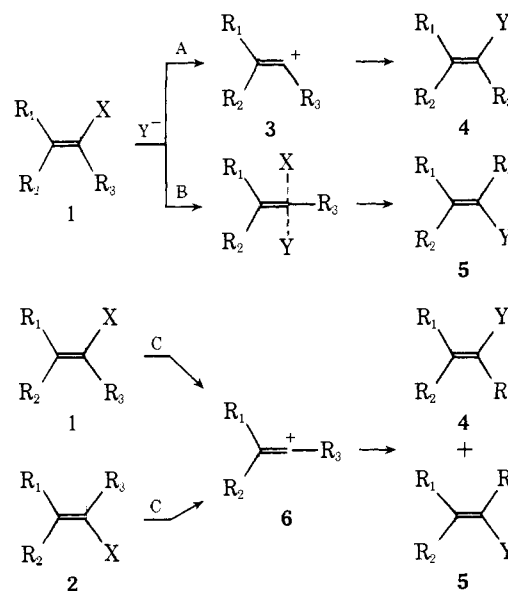
**Abstract:** In order to determine the stereochemistry of solvolytic displacement and intramolecular nucleophilic substitution by a remote double bond at a vinyl center, the synthesis and solvolysis in trifluoroethanol of (*Z*)- and (*E*)-3-methyl-2,6-heptadien-2-yl trifluoromethanesulfonates (**9Z** and **9E**) and (*Z*)- and (*E*)-3-methyl-2-hepten-2-yl trifluoromethanesulfonates (**30Z** and **30E**) were undertaken. In the case of **9Z** and **9E**, in addition to 3-methyl-1,2,6-heptatriene and the products of solvolytic displacement, four cyclized trifluoroethyl ether products were formed. These four products were also generated in the trifluoroethanolysis of 1,2-dimethyl-1-cyclohexen-4-yl tosylate. Net inversion of stereochemistry was observed in both the solvolytic displacement and cyclization processes in the vinyl triflates. Solvolysis of **30Z** and **30E** also resulted in net single inversion of the vinyl trifluoroethyl ether products. These results are explained in terms of competitive attack on the initially formed ion pairs and on free vinyl cation intermediates.

The stereochemistry of solvolytic displacement at a saturated ( $sp^3$ ) carbon center has been the subject of extensive research over the past 4 decades. One of the more important tools in the demonstration of the importance of the  $S_N1$  mechanism<sup>3a</sup> in many of these displacements has been the use of optically active substrates whose absolute configuration could be correlated with the configurations of the solvolytic products. In the solvolyses of optically active substrates which would be expected to lead to highly stabilized carbonium ions on ionization, the observation of racemic products provided striking confirmation of the predictions of the simple  $S_N1$  mechanism.<sup>3</sup> However, the reactions of substrates leading to less stable carbonium ions have played an even more important role in the evolution of a more detailed understanding of the ionization process. The observation of significant amounts of inversion at the carbon center in the solvolyses of these substrates prompted the elaboration of the  $S_N1$  mechanism to include such features as solvent participation and ion pair formation.<sup>3b,c</sup>

The expectation that comparable experiments might provide valuable insight into the nature of solvolytic displacement at a vinyl ( $sp^2$ ) center has only recently begun to be realized. Undoubtedly, this delay in the investigation of vinyl systems was due in large part to the presumed inaccessibility of dicoordinated carbonium ions (vinyl cations) under reasonable solvolytic conditions. However, beginning with the demonstration of Grob and Cseh in 1964 that certain  $\alpha$ -bromostyrenes solvolyze *via* vinyl cations in 80% aqueous ethanol at 100°,<sup>4</sup> a convincing body of evidence has been presented to show that vinyl cations can be generated under relatively mild conditions from a variety of precursors.<sup>5</sup> The  $S_N1$  nature of these processes has been established quite conclusively.<sup>5,6</sup>

The planar nature of the ethylenic system of course rules out the use of chirality as a tool in the investigation of the displacement stereochemistry at a vinyl center. Instead, the relationships of the leaving group and the displacing nucleophile to the remote substituents on the double bond must be

Scheme I



employed. Scheme I depicts the three extreme possibilities for the stereochemical outcome of displacement at a vinyl center. Retention of configuration, shown as path A, could presumably arise by the formation and trapping of a configurationally stable bent vinyl cation **3** (or, alternatively, by participation of a migrating R<sub>2</sub>, leading to a bridged ion). Direct backside participation by the nucleophile or backside attack on an ion pair formed by the initial ionization of **1** would lead to the inverted product **5** (path B). The stereochemical randomization shown in path C would result from the intermediacy of either a linear vinyl cation (**6**) or a rapidly equilibrating pair of bent vinyl cations. The observation of the same ratio of products **4** and **5** from either starting isomer becomes the vinyl equivalent of the racemization process observed at tetrahedral centers.