247. Enamines. III. A Theoretical and Photoelectron Spectroscopic Study of the Molecular and Electronic Structures of Aziridine Enamines

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Summary

The photoelectron (PE.) spectra of *N*-vinylaziridine (**1**) and some methyl and ethyl substituted derivatives are discussed in the light of quantum-chemical model calculations using the PRDDO SCF method. All aziridine enamines are found to exist as equilibrium mixtures of variable compositions, with an enamine-type conformation (I) generally as the major and a *trans*-bisected form (II) as the minor component.

In the course of our photoelectron (PE.) spectroscopic and quantum-chemical studies of aliphatic enamines [1], we have investigated aziridine enamines. Among simple secondary amines, aziridine is the least basic [2] and the least nucleophilic [3] owing to a structurally and electronically enforced [4] high pyramidality at the N-atom [5] with concomitant stabilization of the lone electron pair [6]. A high degree of N-pyramidality persists even if the N-atom can engage in π-conjugation with a strong electron acceptor such as a carbonyl or a nitro group, as shown by X-ray structure analyses of *N*-acylaziridine [7], *N*-nitroaziridine [8], and aziridinone [9] derivatives. The low π-donor capacity of the aziridino group is further documented by chemical and spectroscopic evidence [4] [10-13]. *N*-Alkenyl aziridines are thus of particular interest as a class of enamines with anticipated minimal amine-double bond interaction.

The PE. spectrum of the simplest aziridine enamine, *N*-vinylaziridine (**1**), shows a series of prominent IP. bands *(Fig. 1)*, the first two of which can be assigned to ionizations from (n, π)-dominant enamine orbitals. This assignment is supported by quantum-chemical predictions on the basis of *Koopmans'* theorem [14] using the PRDDO SCF method [15] as well as by a correlation of the ionization potentials of **1** with those of the constituents aziridine and ethylene *(Fig. 2)*.

Aziridine has four ionization potentials (IP.) below 14 eV [6] [16]. The first is well separated from the other three and can be safely assigned to n-type ionization. The next two IP. are due to ionizations from *Walsh*-type orbitals [17], denoted as w_S (5 a') and w_A (3 a'') in *Fig. 2*. There is some controversy regarding the correct order of the corresponding ionic states. Whereas PRDDO and *ab initio* SCF methods at various

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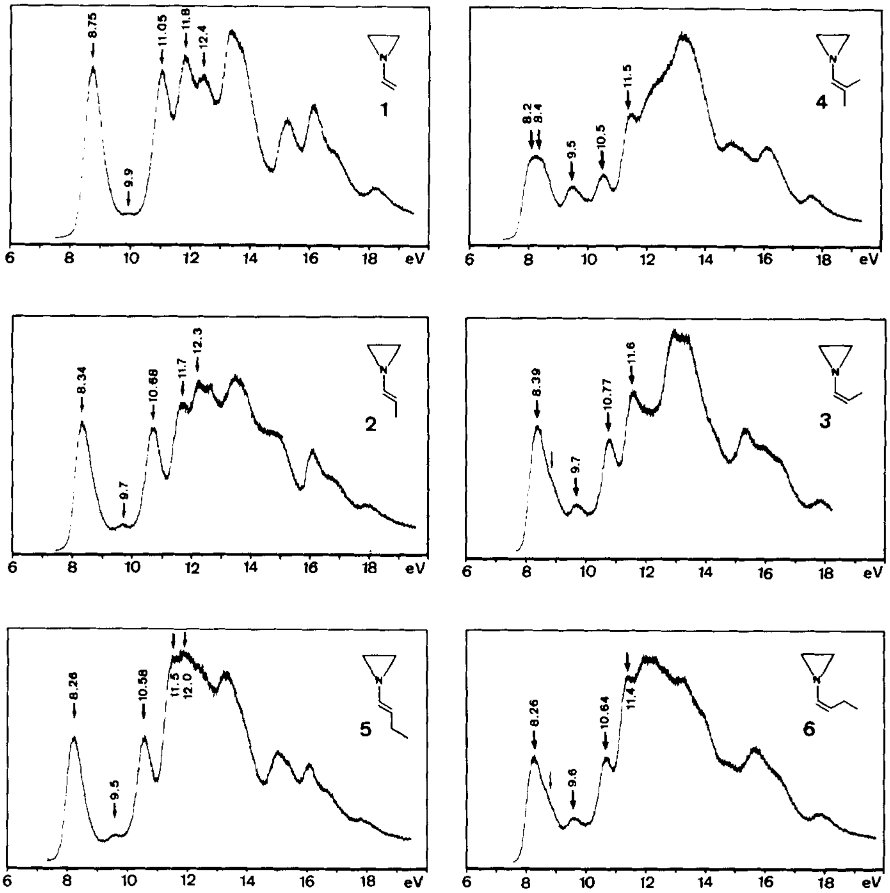

Figure 1. *He(Ia) PE. spectra of aziridine enamines* **1-6** (IP. values refer to average IP. band maxima from five Ar/Xe-calibrated spectra)

levels [6] [18-20] place the w_A orbital above the w_S orbital, albeit by small margins for certain structural models, a reversed state ordering is obtained from calculations with inclusion of electron correlation [21], thus indicating a potential failure of *Koopmans'* approximation. However, knowledge of the true level ordering is not essential for the low-energy part of the IP. correlation diagram of *Figure 2*. In the most stable PRDDO-calculated equilibrium conformation of **1** [1], the bisecting plane of the aziridine ring is almost perpendicular to the C=C–N plane so that the double-bond π-orbital interacts predominantly with the aziridine n and w_S-orbitals. This leads to an upshift and downshift of, respectively, the n and w_S-orbitals, and to a slight stabilization of the π-level due to predominant bonding n-orbital admixture. The aziridine w_A-orbital, on the other hand, interacts almost exclusively with σ-levels of the ethylene unit. This interaction picture thus confirms the above assignments of the first two IP. for **1**.

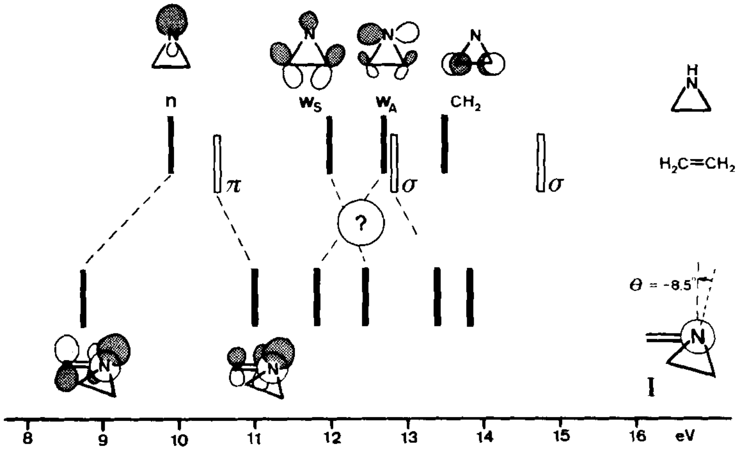

Figure 2. *Qualitative IP. correlation diagram for aziridine* (level ordering according to [21]), *ethylene, and* N-*vinylaziridine* (**1**) *with orbital typification*

Comparison of the PE. spectra of **1**-**4** reveals pronounced spectral changes upon methyl substitution at the terminal C-atom of the enamine unit. While IP.(1) and IP.(2) are shifted to lower values by approximately equal amounts (0.3-0.4 eV for the first and 0.1-0.2 eV for the second methyl group[1])), two new bands appear, one centered between IP.(1) and IP.(2), the other on the high-energy tail of IP.(1). Spectral superposition with appropriately shifted energy scales *(Fig. 3)* suggests that the new bands grow at the expense of the former two. Interestingly, a small, but distinct hump between the first two IP. bands is also detected in the PE. spectrum of **1**[2]). These observations are most easily interpreted in terms of equilibrium mixtures of variable conformer compositions with a gradual growth of the minor component in going from **1** to **4**. For *N*-vinylaziridine (**1**), the equilibrium is shifted far towards the conformer with substantial (n, π)-coupling. For the β-dimethyl substituted derivative **4**, it is almost balanced between this and a new conformer with a small ΔIP.(1,2) gap.

Our interpretation is supported by PRDDO-based conformational analyses. *Figure 4* displays computed energy profiles for rigid rotations of the aziridino group in **1**-**4** for various geometry-optimized structures[3]). For *N*-vinylaziridine (**1**), PRDDO predicts three stable conformations, separated by comparatively small barriers. The most stable conformer is **I** with considerable (n, π)-coupling. This result, which is consistent with our PE. spectroscopic observations, contradicts an earlier INDO SCF study [26] favoring a *trans*-bisected form. Of the two higher-

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[1]) Similar shifts are observed for methyl substituted ethylenes [22] and butadienes [23]; for a review see [24].

[2]) The sample purity was >99.5% by GC. analysis both before and after PE. spectroscopic measurements. The PE. spectral appearance remained unchanged during > 10 h of continued measurements.

[3]) Structure optimizations were performed under the constraints of *(i)* fixed C,H-bond lengths, *(ii)* local C_s symmetries for the aziridine and double bond units, *(iii)* tetrahedral methyl groups. Full computational details are given in [25]. Copies of this Ph. D. thesis may be requested from *K. M.*

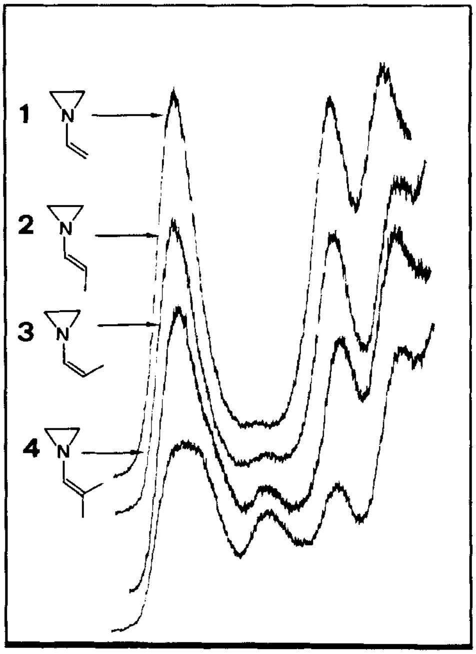

Figure 3. *Superposition of PE. spectra of enamines* **1-4** (energy scales are shifted to compensate for systematic IP. changes due to methyl substitution; see text)

energy conformers, the *trans*-bisected form **II** lies energetically close enough to **I** so that it may be populated sufficiently to be experimentally detectable. In conformation **II** the double bond π-system is completely uncoupled from the aziridine n- and w_S-orbitals, but mixes with the *Walsh*-type orbital w_A. This leads, within the PRDDO model, to almost degenerate n- and π-dominant MO for **II**, which are located right in-between the two (n, π)-dominant MO of conformer **I**. This is precisely what is observed in the PE. spectrum of **1**.

Our conjecture of a conformational equilibrium for *N*-vinylaziridine (**1**) calls for comparisons with the closely related cases of vinyl- and formyl-cyclopropane. Gaseous formylcyclopropane is known to exist predominantly as a mixture of *trans*- and *cis*-bisected forms (corresponding to conformations **II** and **III**) [27], in which there are optimum π-type donor-acceptor interactions between the cyclopropyl and the carbonyl groups. Substitution of the carbonyl by the less electronegative vinyl group allows a *gauche* form (corresponding to conformation **I**) to compete effectively with a *trans*-bisected form, the *gauche/trans* ratio being approximately 1:3 [28] to 1:7 [29] for vinylcyclopropane in the gas phase. Replacement of the cyclopropyl methine unit by a N-atom then shifts the equilibrium towards the *gauche* form as a result of increased stabilization of conformer **I** by enamine-type conjugative interactions and decreased stabilization of conformer **II** due to the reduced donating power of the three-membered ring system *via* (w_A, π)-type interactions. The PRDDO-guided PE. spectroscopic identification of a conformational

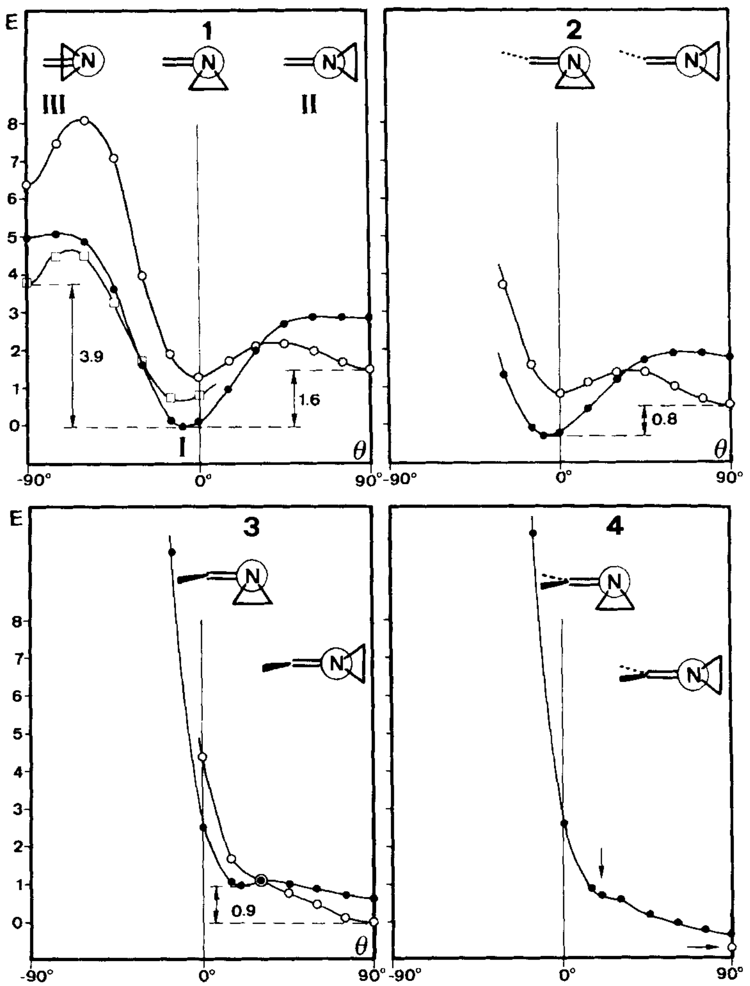

Figure 4. *PRDDO energy profiles for internal rotations in aziridine enamines* **1–4**, *obtained by rigid rotations of the aziridine unit in the optimized conformer I* (filled circles), *the optimized* trans-*bisected form II* (open circles), *and the* cis-*bisected form III* (open squares). Relative energies in kcal/mol.

equilibrium for *N*-vinylaziridine (**1**) is thus consistent with what is known about closely related cyclopropane derivatives.

The slight, but distinct shift of the equilibrium in going from **1** to **2** is qualitatively well reproduced by the PRDDO-calculated reduction of the energy gap between conformations of type **I** and **II** *(Fig. 4)*. It reflects a reduced electron-accepting power of the 1-propenyl group as compared to the vinyl group, *i.e.*, a reduced enamine-type conjugative stabilization in **2** relative to **1**.

Such an electronic factor is operating similarly in **3** and even more strongly in **4**. Steric congestion due to the presence of a methyl group *cis* to the aziridine ring further destabilizes conformations of type **I** in **3** and **4**. Non-bonded repulsions appear to be grossly overestimated by the PRDDO model. Geometry optimizations for **3** lead to a flat energy minimum for a twisted conformation of type **I**, separated by a small barrier from the more stable *trans*-bisected form **II**. For isobutenylaziridine (**4**) only one minimum corresponding to form **II**, but no minimum corresponding to a conformer of type **I** can be located on the energy hypersurface. Neither a reversal of the conformational equilibrium in going from **2** to **3** nor an exclusive existence of **4** in the *trans*-bisected form, as predicted by PRDDO, are confirmed by experiment. However, such failures concern quantitative rather than qualitative aspects. On a qualitative level, the quantum-chemical prediction of a continuously shifted *gauche/trans* conformational equilibrium along the series **1**–**4** meets well with our experimental observations.

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Experimental Part

He(I*a*) PE. spectra were recorded as described in [1]. All aziridine enamines were prepared according to known procedures [30] [31] and purified to > 99% purity by GC. Full experimental details are given in [25].

Spectroscopic data of aziridine enamines. – *1-Vinylaziridine* (**1**). UV. (cyclohexane): 209 (4.4). – IR. (CCl_4): 3105*w*, 3078*s*, 2990*vs*, 2932*w*, 2898*w*, 1724*vw*, 1688*w*, 1622*vs*, 1557*vw*, 1472*s*, 1447*w*, 1402*s*, 1311*vs*, 1278*vs*, 1160*s*, 1115*s*, 1079*m*, 1016*w*, 972*vs*, 855*vs*, 818*m*, 737*s*, 705*m*. – ^1H-NMR. ($CDCl_3$): 1.78 (*s*, 4 H); 4.42 (*d*, *J* = 8 Hz, 1 H); 4.49 (*d*, *J* = 15 Hz, 1 H); 6.34(*d*×*d*, *J* = 15 and 8 Hz, 1 H). – MS. (200°): 70 (3), 69 (51, M^+), 68 (18), 54 (6), 43 (7), 42 (58), 41 (100), 40 (14), 39 (14), 28 (27), 27 (22), 26 (9), 18 (5), 16 (11).

(E)-*1-Propenylaziridine* (**2**). – UV. (cyclohexane): 212 (2.9). – IR. (CCl_4): 3055*m*, 3020*m*, 2980*s*, 2950*m*, 2925*m*, 2910*m*, 2870*m*, 2850*w*, 2730*w*, 1722*vw*, 1657*s*, 1465*w*, 1445*w*, 1435*w*, 1378*w*, 1303*vs*, 1272*m*, 1157*m*, 1115*vw*, 1099*vw*, 1085*w*, 1047*vs*, 940*vs*, 852*vw*. – ^1H-NMR. ($CDCl_3$): 1.55 (*d*×*d*, *J* = 7 and 1 Hz, 3 H); 1.68 (br. *s*, 4 H); 5.00 (*d*×*qa*, *J* = 13 and 7 Hz, 1 H); 5.91 (*d*×*qa*, *J* = 13 and 1 Hz, 1 H). – MS. (200°): 84 (5), 83 (83, M^+), 82 (38), 68 (16), 67 (6), 56 (13), 55 (100), 54 (28), 53 (8), 52 (6), 43 (14), 42 (65), 41 (97), 40 (8), 39 (48), 38 (6), 29 (35), 28 (75), 27 (44), 26 (21).

(Z)-*1-Propenylaziridine* (**3**). – UV. (cyclohexane): 214 (3.8). – IR. ($CHCl_3$): 3055*m*, 3020*m*, 2980*vs*, 2935*s*, 2905*s*, 2850*s*, 1646*vs*, 1445*w*, 1395*vs*, 1360*s*, 1288*vs*, 1157*m*, 1107*m*, 1097*vw*, 1080*vw*, 1002*vs*, 916*vw*, 854*vw*, 822*vw*. – ^1H-NMR. ($CDCl_3$): 1.72 (*d*×*d*, *J* = 7 and 2 Hz, 3 H); 1.80 (br. *s*, 4 H); 4.88 (*d*×*qa*, *J* = 8 and 7 Hz, 1 H); 5.67 (*d*×*qa*, *J* = 8 and 2 Hz, 1 H). – MS. (200°): 84 (4), 83 (63, M^+), 82 (31), 68 (17), 67 (7), 56 (12), 55 (69), 54 (24), 53 (7), 52 (6), 43 (10), 42 (47), 41 (72), 40 (8), 38 (6), 32 (23), 29 (23), 28 (100), 27 (17).

1-(2-Methylpropenyl)aziridine (**4**). – UV. (cyclohexane): 209 (3.7). – IR. (CCl_4): 3670*vw*, 3050*s*, 3020*m*, 2990*vs*, 2955*vs*, 2920*vs*, 2905*s*, 2875*s*, 2850*s*, 2730*vw*, 2160*vw*, 1732*vw*, 1683*m*, 1672*s*, 1580*vw*, 1466*m*, 1448*s*, 1376*vs*, 1337*s*, 1283*vs*, 1218*vw*, 1160*vs*, 1092*s*, 1071*vs*, 1026*w*, 1003*s*, 980*w*, 956*w*, 866*s*. – ^1H-NMR. ($CDCl_3$): 1.58 (*d*, *J* ≈ 1 Hz, 3 H); 1.75 (br. *s*, 4 H); 1.72 (*d*, *J* ≈ 1 Hz, 3 H); 5.31 (*m*, 1 H). – MS. (200°): 98 (7), 97 (100, M^+), 96 (64), 94 (5), 82 (56), 81 (16), 80 (7), 69 (23), 68 (16), 67 (13), 56 (8), 55 (74), 54 (14), 53 (14), 52 (5), 43 (13), 42 (61), 41 (92), 40 (12), 39 (37), 38 (6), 30 (6), 29 (25), 28 (41), 27 (31), 26 (7).

(E)-*1-(1-Butenyl)aziridine* (**5**). UV. (cyclohexane): 212 (4.1). – IR. (CCl_4): 3060*s*, 3027*s*, 2985*vs*, 2960*vs*, 2925*s*, 2890*s*, 2875*s*, 2850*m*, 1768*vw*, 1714*vw*, 1654*vs*, 1468*s*, 1576*w*, 1342*m*, 1315*s*, 1296*vs*, 1164*vs*, 1140*w*, 1096*w*, 1056*vs*. 1004*m*, 950*vs*, 916*w*. – ^1H-NMR. ($CDCl_3$): 0.92 (*t*, *J* = 7 Hz, 3 H); 1.69 (br. *s*, 4 H); 1.93 (*m*, 2 H); 5.05 (*d*×*t*, *J* = 14 and 7 Hz, 1 H); 5.92 (*d*×*t*, *J* = 14 and 1 Hz, 1 H). – MS. (200°): 98 (5), 97 (69, M^+), 96 (8), 82 (63), 80 (5), 69 (27), 68 (25), 67 (14), 56 (5), 55 (35), 54 (12), 53 (8), 43 (16), 42 (67), 41 (100), 40 (6), 39 (23), 29 (15), 28 (33), 27 (21), 26 (5).

(Z)-1-(1-Butenyl)aziridine (**6**). - UV. (cyclohexane): 214 (4.0). - IR. (CCl_4): 3055*m*, 3015*m*, 2980*s*, 2960*vs*, 2925*s*, 2885*m*, 2870*m*, 1745*vw*, 1644*s*, 1460*m*, 1400*vs*, 1374*vw*, 1298*vs*, 1226*vw*, 1164*m*, 1156*w*, 1126*vw*, 1104*vw*, 1086*vw*, 1072*w*, 1027*m*, 994*m*, 898*vw*. - MS. (200°): 98 (5), 97 (66, M^+), 96 (11), 83 (5), 82 (7), 81 (5), 80 (5), 70 (5), 69 (30), 68 (29), 67 (17), 56 (7), 55 (39), 54 (16), 43 (17), 42 (70), 41 (100), 40 (8), 39 (26), 30 (7), 29 (20), 28 (43), 27 (28), 26 (5).

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