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246. Enamines. II. A Theoretical and Photoelectron Spectroscopic Study of the Molecular and Electronic Structures of Aliphatic Enamines

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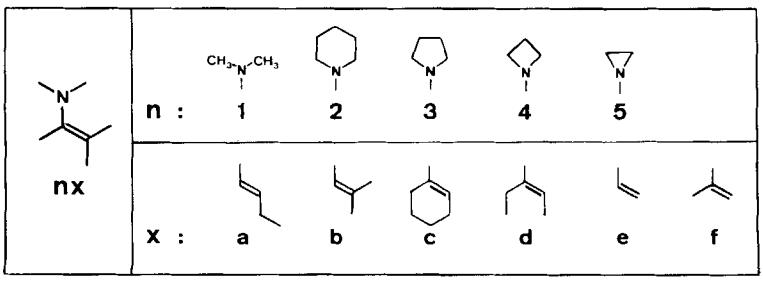
Summary

Comparison of PE. spectroscopic data for four series of enamines (including azetidine and some aziridine derivatives) for studying the influence of amine-ring size on electronic structure show the pyrrolidino group to exhibit the strongest amine/double bond coupling in sterically unconstrained enamines. However, the azetidino group accommodates best steric congestion due to dialkyl substitution at the β-position of the enamine unit. Quantum-chemical calculations of equilibrium structures and energy profiles for amine rotations in model enamines by the PRDDO SCF method agree satisfactorily with experimental results. Notable exceptions are pyrrolidine derivatives for which PRDDO overestimates the amount of N-pyramidality.

Recent experimental and theoretical work suggests that aliphatic enamines as well as vinylamine itself prefer non-planar equilibrium structures [1–3]. In order to investigate the molecular and electronic structures of alkyl substituted enamines further, we have performed a photoelectron (PE.) spectroscopic study on simple alkyl substituted enamines as well as extended quantum-chemical structure calculations [4] [5] using the PRDDO SCF approximation [6]. We report here our results for the enamines listed in the *Scheme*. The series **1a–5a** represents sterically unconstrained enamines that can be used to probe the influence of amine ring size on electronic structure. Comparison with **1b–5b** reveals the effect of steric con-

Scheme



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gestion within the enamine unit due to dialkyl substitution at the β-carbon atom. Comparisons with series **1c–4c** and **1d–4d** assess the influence of, respectively, cyclic and acyclic alkyl substituents in α-position.

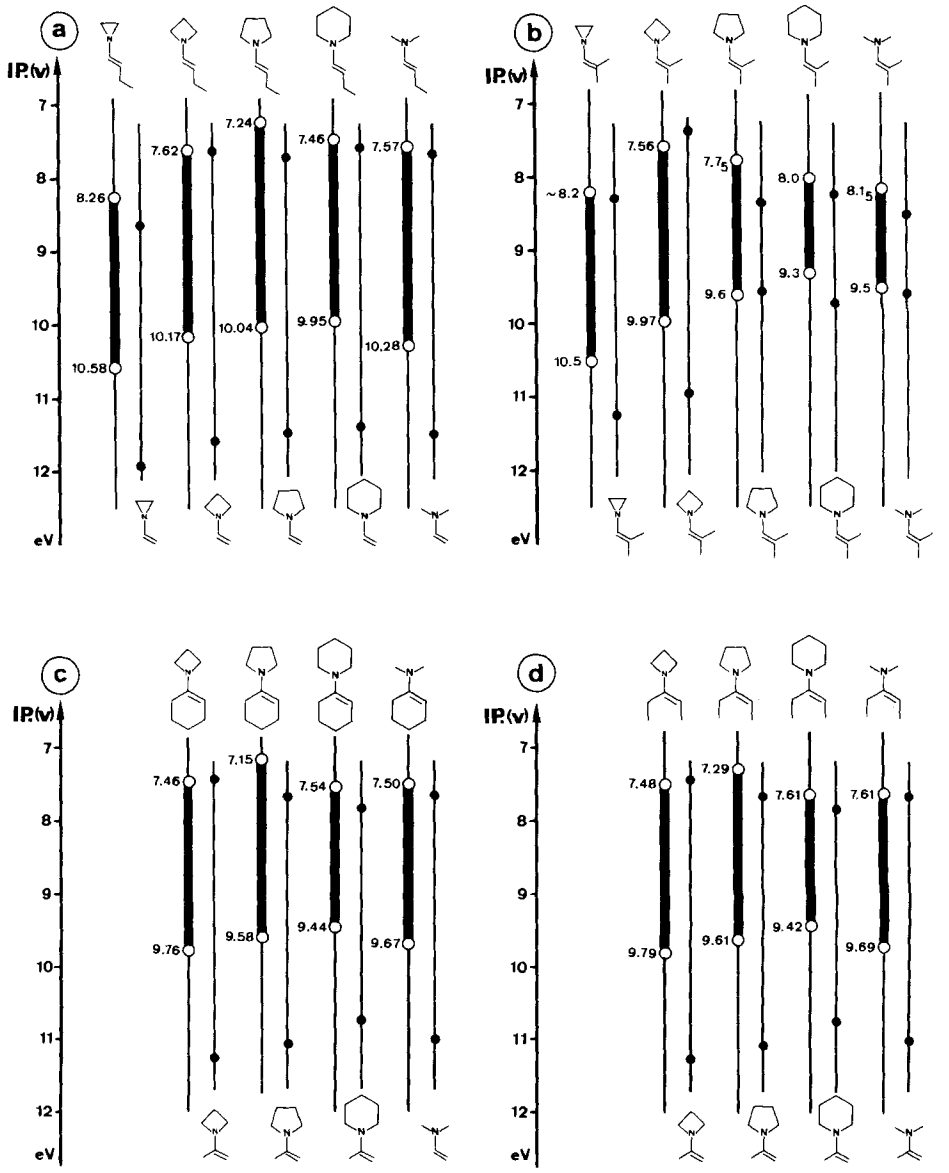

Figure 1. *Correlation diagrams for the first two vertical ionization potentials* (open circles) *of enamines* **1a–5a** (part a), **1b–5b** (part b), **1c–4c** (part c), **1d–4d** (part d), *and of the negative PRDDO SCF orbital energies* (filled circles) *for the highest occupied and subjacent MO of enamines* **1e–5e** (part a), **1b–5b** (part b), **1f–4f** (parts c and d)

PE. spectroscopic data for compounds **1c**–**3c**, **2b** and **3b** have already appeared [7–11]. Apart from a noted discrepancy [11], the reported values for individual ionization potentials (IP.) scatter within ranges of 0.05–0.1 eV. Our own results, which are included in *Figure 1* for internal consistency, agree with these data within the same error limits. There is one conflict, however, regarding the second IP. of **3b**. While our value supports that given earlier by *Colonna et al.* [8] (IP.(2)= 9.53 eV) it disagrees with that reported later [10] (IP.(2)=8.97 eV) and cited in [11]. The latter value is fairly close to the first IP. of pyrrolidine (~8.8 eV [12]). In our experience, spurious amounts of ketone and amine, formed by unintentional enamine hydrolysis, cannot be avoided even under careful operating conditions and must be pumped from the samples before spectra of pure enamines can be obtained.

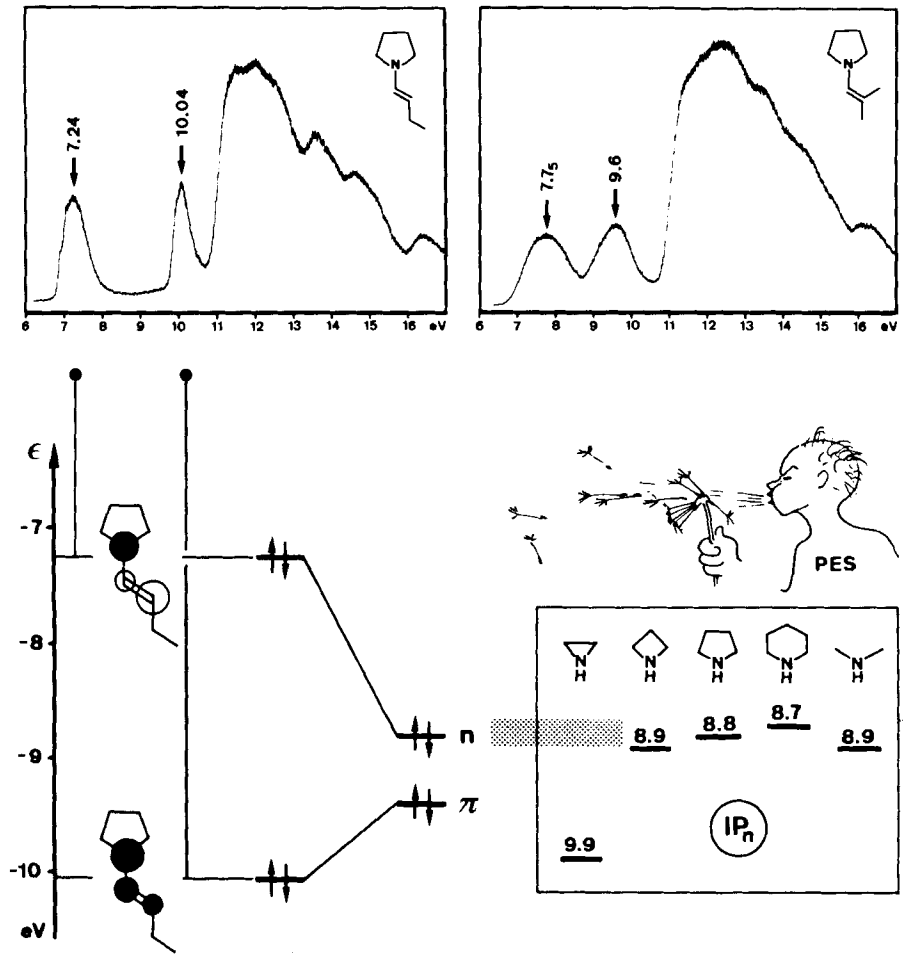

Figure 2. *He(Ia) PE. spectra of enamines* **3a** (top left) *and* **3b** (top right); *qualitative* (n,π)*-level interaction diagram* (bottom)

With the exception of aziridine derivatives **5a, b**, all enamines of the *Scheme* exhibit two prominent IP. bands in the PE. spectral region of 7–11 eV. This is shown in *Figure 2* for the typical cases **3a** and **3b**. The two bands are well separated from the remaining, strongly overlapping bands at higher energies and can be safely assigned to ionizations from (n, π)-dominated enamine orbitals. A correlation of these two ionization potentials for dimethylamine, piperidine, pyrrolidine, and azetidine enamines is of interest since the free amines possess very similar n-type IP. (*Fig. 2*, bottom) [12–14]. Thus, for a series with common olefin components, the band separation ΔIP.(1,2) can be taken as a rough measure of the relative amount of interaction between an amino group and the double bond unit. The detailed orbital interaction picture may be quite complex, though, for non-planar enamine groups. Substantial σ-admixtures are noted even in conformations favoring strong interactions between the nitrogen lone pair orbital and the double bond π-system. Whatever the mechanism that produces the final energy gap between the two highest occupied orbitals, PRDDO SCF model calculations support the expectation that, independently of the degree of N-pyramidality, this energy gap, and hence ΔIP.(1,2), reaches a maximum for conformations in which the bisecting plane of the amino group is nearly orthogonal to the C=C–N plane, hence (n, p_π)-overlap is maximum.

The correlation of the first two ionization potentials of **1a–5a** is displayed in *Figure 1a*. In this series of sterically unconstrained enamines, the pyrrolidine derivative stands out with the largest amine-double bond interaction, thus documenting once more the prominent donating power of the pyrrolidino group in enamines as compared to other secondary amine components [11] [15–18]. Interestingly, the four-membered azetidine and the six-membered piperidine ring show virtually equal amine-double bond interactions, whereas the dimethylamino group

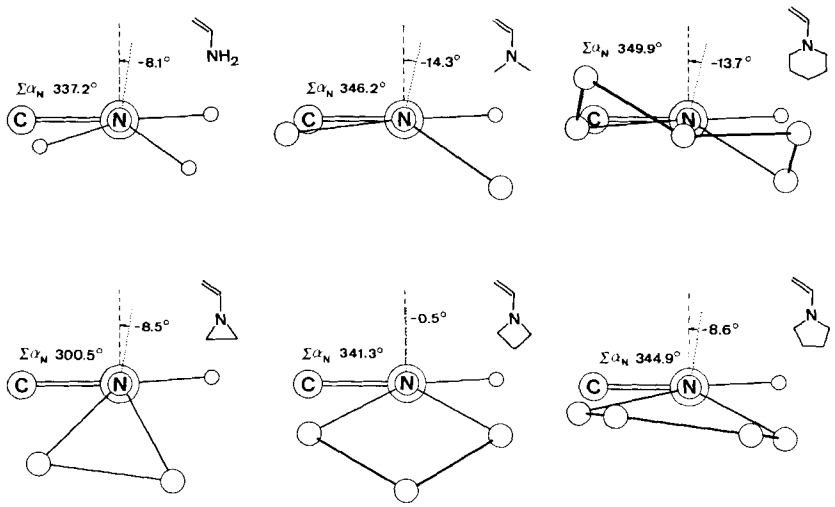

Figure 3. Newman *projections along the N, C-bond, amine rotation angles, and sums of bond angles at the N-atom for PRDDO calculated equilibrium structures of vinylamine* [2] *and enamines* **1e–5e**

is intermediate between the pyrrolidino and the piperidino groups. The sequence pyrrolidine > dimethylamine > piperidine is gratifyingly consistent with the ranking obtained by detailed analyses of ^{1}H- and ^{13}C-NMR. spectral data of related enamines [18]. The aziridine derivative **5a**, which is included here for completeness, would have to be placed last on the basis of the ΔIP.(1,2) criterion. However, a direct comparison with the other members of the series is not possible owing to the disparity in IP.(1) of the free amines *(Fig. 2)*. Nevertheless, the substantial increase of both IP.(1) and IP.(2) in going from **2a** or **4a** to **5a** is a PE. spectroscopic correlate of the marked inertness of *N*-vinyl aziridines. Whereas *N*-vinyl derivatives of secondary amines polymerize rapidly in free form or in dilute solution at RT. [4] [17] [18], *N*-vinyl aziridines are easily handled even at elevated temperatures [4].

To gain insight into the molecular structures of sterically unconstrained enamines, we performed PRDDO SCF calculations on *N*-vinyl amines. In order to keep computational costs at a justifiable level, the amine components were premodelled by geometry optimizations of the free amines under C_s symmetry constraints (envelope and chair conformations, respectively, for pyrrolidine and piperidine), keeping all C,H-bond lengths fixed. The *N*-vinyl group was then attached using parameters obtained for the unsubstituted vinylamine [2], and the enamine structures so obtained were relaxed by partial geometry optimizations under the constraints of local C_s symmetries for the amino and vinyl groups[1]).

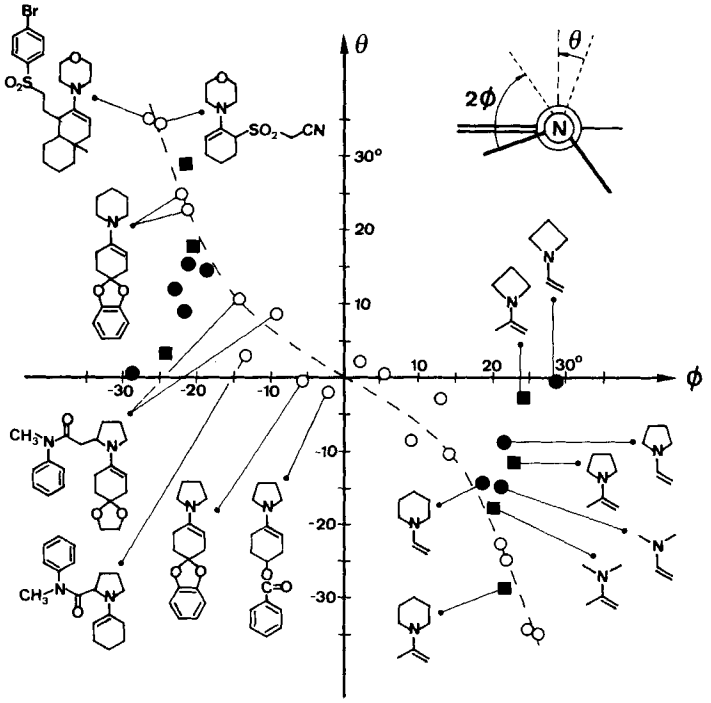

Figure 4. *Scatter plot for amine inversion and rotation parameters, ϕ and θ, from experimental* [3] (open circles) *and PRDDO optimized enamine structures* (filled symbols)

[1]) Full computational details are given in [4]. Copies of this Ph. D. thesis may be requested from *K. M.*

The equilibrium structures calculated for the model enamines **1e–5e** are very similar to that of the unsubstituted vinylamine [2] *(Fig. 3)*. In each case the configuration at the N-atom is pyramidal with average bond angles at the N-atom somewhat larger than in vinylamine, except for the aziridine derivative as anticipated. Pyramidalization at the N-atom is coupled with a torsion about the enamine C,N-bond so that the N,C-bond *syn* to the C,C double bond moves less out of the C=C–N plane than the other N,C-bond. A notable exception is **4e**, where the four-membered azetidine ring remains almost perfectly aligned for maximum (n, p_π)-overlap. The planar vinyl group is tilted by a small amount ($\sim$3–4°) with respect to the C=C–N plane. This produces a slight pyramidality at the central C-atom of the enamine unit in opposite direction to the N-atom in agreement with experimental observation [3].

The PRDDO results are displayed in the amine inversion-rotation diagram of *Figure 4* together with experimental points obtained from X-ray structure analyses by the groups of *Dunitz & Eschenmoser* [3]. On first sight, the theoretical predictions for dimethylamine, piperidine, and pyrrolidine enamines fit satisfactorily into the experimental scatter plot, which documents a strong coupling between the inversion and rotation motions of the amino group in aliphatic enamines. The azetidine and aziridine cases are more exceptional in that a substantial pyramidalization at the N-atom appears to go without much torsion about the C,N-bond. Interestingly, however, a higher-energy *trans*-bisected conformation with complete decoupling of the N-lone-pair orbital from the double bond π-system is also available to the aziridine derivative [19].

There is one disturbing discrepancy between theory and experiment. The X-ray structural results [3] clearly show the N-atom to be less pyramidal in pyrrolidine enamines than in corresponding piperidine enamines, whereas PRDDO predicts the opposite. One reason for this apparent failure may lie in the local C_s symmetry constraint imposed on the pyrrolidino group in **3a**. This constraint has no justification other than to keep computational costs on an acceptable level. A complete PRDDO geometry optimization on **3a** is presently unfeasible. However, structure optimizations on pyrrolidine itself suggest that N-pyramidality is not much affected by the imposition of symmetry constraints [20]. Juxtaposition of IP.(1) and IP.(2) values for **1a–5a** with negative orbital energies of the highest and subjacent occupied MO for the calculated equilibrium structures of **1e–5e** *(Fig. 1a)* reveals a satisfactory correlation between respective quantities except for the pyrrolidine derivative, for which the computed energy gap is too small. Since this gap would increase upon a decrease in N-pyramidality, we are led to agree with the inference [3] that a major factor contributing to the prominent donating power of the pyrrolidino group in enamines is due to its ability to engage a less pyramidal N-site into π-conjugation, and have to accept the failure of the PRDDO model to provide an adequate description of the pyrrolidine unit at least as far as relative N-pyramidality is concerned.

The PE. spectra of enamines **1b–5b** differ markedly from those of **1a–5a**. This is seen in *Figure 2* by comparison of the PE. spectra of enamines **3a** and **3b**. For **3b** the two IP. bands in the 7–11 eV region appear as broad, overlapping bands. The gap ΔIP.(1,2) is considerably reduced owing to shifts of IP.(1) to higher and IP.(2)

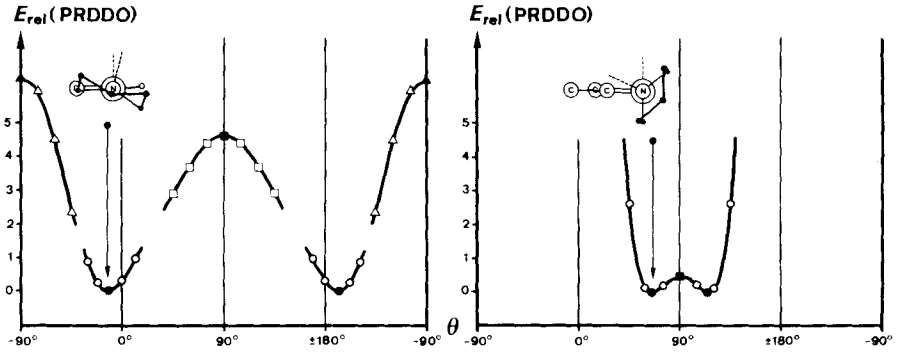

Figure 5. *Energy profiles for internal rotations in enamines* **2a** (left) *and* **2b** (right). Filled symbols refer to partially optimized structures, open symbols to structures obtained by rigid rotations of the piperidine ring; relative energies in kcal/mol.

to lower energies. These spectral differences, which are also observed for enamine pairs **1a/1b** and **2a/2b**, are strong indicators of a substantial torsion of the enamine units and concomitant partial uncoupling of the amine and double bond units in **1b–3b** due to dimethyl substitution at the β-position. The torsional deformation induced by steric congestion, for which there is independent chemical and spectroscopic evidence [15], is well reflected by PRDDO model calculations. *Figure 5* shows rotation energy profiles for **2e** and **2b**, obtained by partial geometry optimizations for equilibrium and bisected[2]) conformations, followed by rigid rotations of the amino group. Similar energy profiles are obtained for enamines **1e**, **1b** and **3e**, **3b**. For the sterically unconstrained enamines **1e–3e**, PRDDO predicts pronounced double-well potentials with minima around $\theta \sim -10°$ and $-170°$ and torsional barriers in the ranges of 4–6 kcal/mol and 6–8 kcal/mol for transitions *via trans*-bisected ($\theta = 90°$) and *cis*-bisected ($\theta = -90°$) forms, respectively. The barrier heights are comparable to those calculated for vinylamine [2]. By contrast, the sterically demanding isobutenyl group restricts low-energy forms of **1b–3b** to narrow regions around $50° \lesssim \theta \lesssim 130°$, with shallow minima near $\theta \sim 70°$ and 110° and small torsional barriers for transitions *via trans*-bisected forms. Although we believe that PRDDO exaggerates the amount of enamine torsion due to steric crowding [19], experimental corroboration for the potential ease of torsional deformation of enamines comes from X-ray structural studies of piperazine bis-enamines [21]. The molecular structure of a bis(3-methyl-2-buten-2-yl) derivative, retrieved from the Cambridge Crystallographic Data Base[3]), is reproduced in *Figure 6* together with the computed equilibrium structure of **2b**. There is a striking similarity between the two enamine units. In fact, a torsional angle $\theta = -56.5°$ is derived from the data in [21] as compared to $\theta \sim -65°$ calculated for **2b**.

An interesting case is provided by the azetidine derivative **4b**. Comparison of the relevant portions of the PE. spectra of **4a** and **4b** *(Fig. 7)* reveals relatively little change upon substitution of the butenyl by the isobutenyl group. The shapes of both

[2]) Structure optimizations with C_s molecular symmetry enforced.

[3]) Access to a copy of this data base at the computing center of ETHZ is gratefully acknowledged.

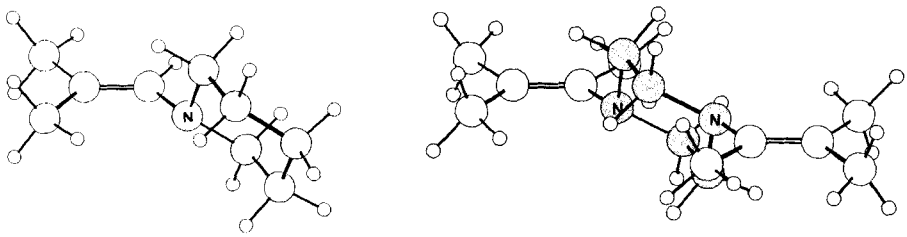

Figure 6. *Comparison of the PRDDO optimized structure of* **2b** (left) *with the experimental structure* [21] *of 1,4-bis(2-methyl-2-buten-2-yl)piperazine* (right)

IP. bands remain comparatively narrow, although some broadening is apparent. Both IP.(1) and IP.(2) are shifted slightly to lower energies so that ΔIP.(1,2) is only marginally reduced. PRDDO calculations for **4b** predict an equilibrium conformation (*Fig. 7*, bottom) with rather modest torsional deformation of the enamine unit. Thus, azetidine stands out among simple secondary amines as a lucky compromise, the four-membered ring being small enough to accomodate steric crowding in β-dialkyl substituted enamines, but not too small (like aziridine [19]) to loose most of its donating ability in π-type conjugation. The azetidine enamine **4b** indeed

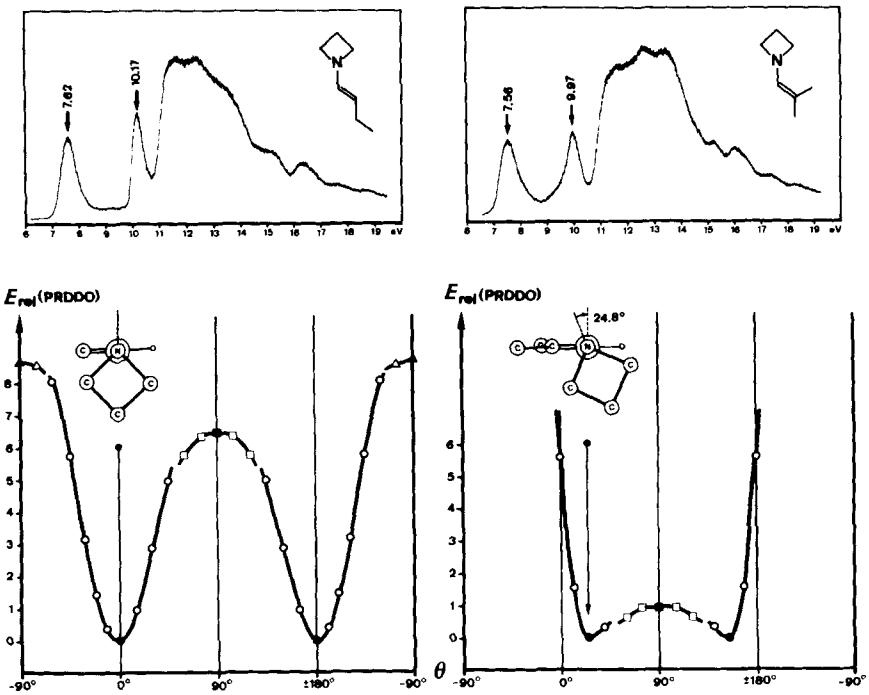

Figure 7. *PE. spectra of enamines* **4a** (top left) *and* **4b** (top right). *Energy profiles for internal rotation about the enamine C,N-bond* (filled symbols refer to partially optimized structures, open symbols to structures obtained by rigid rotations of the azetidine group). Relative energies in kcal/mol.

shows the largest ΔIP.(1,2) gap, hence strongest amine-double bond coupling, among the isobutenyl derivatives **1b–5b** *(Fig. 1b)*. While a systematic study of the scope and limitation of azetidine enamines in preparative organic chemistry remains is still lacking, our PE. spectroscopic evidence of their exclusive properties is consistent with earlier conclusions based on chemical and UV. spectroscopic observations for pyrrolidine and azetidine enamines of α-tetralone derivatives [22].

The PE. spectra of enamines **1c–4c** and **1d–4d** show all the characteristic features that have been discussed already for the series of sterically unconstrained enamines **1a–4a**. This is nicely borne out by comparisons of respective IP. correlations in *Figure 1* (parts *a, c, d*). Introduction of an alkyl substituent at the central C-atom of the enamine unit produces shifts of about 0 ± 0.15 eV for IP.(1) and 0.5 ± 0.1 eV for IP.(2), resulting in consistently reduced ΔIP.(1,2) gaps. These shifts can be rationalized, at least qualitatively, in terms of perturbational arguments, *viz.*, different hyperconjugative destabilizations of the π-type enamine orbitals. Hence, the reductions in ΔIP.(1,2) values do not primarily reflect on increased torsional deformations of the enamine units. Indeed, apart from shifts in absolute IP. values, the three correlations for IP.(1), and likewise for IP.(2), are almost superimposable on each other. PRDDO model calculations for *n*-isopropenyl amines **1f–4f** support the view that introduction of small alkyl substituents at the central C-atom does not critically affect the structure of the enamine unit. As can be seen from the amine inversion-rotation diagram of *Figure 4*, the calculated positions of enamines **1e**, **3e** and **4e** are close to those of the corresponding *N*-vinyl derivatives. For the piperidine enamine **2e**, PRDDO predicts a somewhat more pronounced torsional deformation in excellent agreement with X-ray structural data [3]. However, this result may be fortuitous in view of the persisting discrepancy between the calculated and experimental structures for corresponding pyrrolidine enamines.

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Experimental Part

He(Iα) PE. spectra were recorded on a *Perkin-Elmer* PS-18 photoelectron spectrometer using an Ar/Xe mixture for *in situ* calibration. Reported ionization potentials are average IP. band maxima positions from 5 spectra, obtained after pumping a sample for at least 1 h to constancy of spectral appearance. Reproducibility was well within ± 0.02 eV for narrow and ± 0.03 eV for broad bands.

Enamines **nx** *(Scheme)* were prepared by known procedures (see *Table*) and purified by preparative GC. All samples had a purity of $> 97\%$ by GC. analysis and were handled under an inert atmosphere in NaOH-pretreated glassware. Full experimental details are given in [4].

Spectroscopic data for azetidine enamines **4a**, **4b**, **4d**. – Enamine **4a**. UV. (cyclohexane): 229 (3.8). – IR. (CCl_4): 3035*w*, 3005*m*, 2965*vs*, 2935*s*, 2926*s*, 2880*m*, 2855*s*, 1728*vw*, 1658*vs*, 1487*vw*, 1467*vw*, 1460*vw*, 1450*vw*, 1415*vw*, 1378*vw*, 1357*vw*, 1321*m*, 1312*m*, 1290*m*, 1260*w*, 1241*w*, 1198*w*, 1150*vw*, 1131*w*, 1112*vw*, 1062*w*, 987*vw*, 945*m*, 912*vw*. – ^{1}H-NMR. (C_6D_6): 0.99 (*t*, $J = 7$ Hz, 3 H); 1.66–2.16 (*m*, 4 H); 3.29 (*m*, 4 H); 4.20 (*d*×*t*, $J = 14$ and 7 Hz, 1 H); 5.76 (*d*, $J = 14$ Hz, 1 H); spurious signals at 3.48 (*t*, $J = 7$ Hz) and 5.47 (*d*, $J = 7$ Hz) due to the presence of the (*Z*)-isomer.

Enamine **4b**. UV. (cyclohexane): 240 (3.8). – IR. (CCl_4): 2990*s*, 2955*vs*, 2910*vs*, 2870*vs*, 2840*vs*, 2730*w*, 1754*vw*, 1734*vw*, 1675*s*, 1480*w*, 1445*m*, 1383*w*, 1375*s*, 1346*w*, 1305*vs*, 1270*s*, 1244*vs*, 1236*vs*,

Table. *Registry numbers of enamines* **nx** (Scheme), *procedures (A–F)*[a]) *used for their preparation, and references to spectroscopic data*

x	1	2	3	4	5
a	14548-12-0	7182-10-7	13937-89-8	–	–
	F [30] [31]	A [32]	A [32]	D, this work	E [19]
b	6906-32-7	673-33-6	2403-57-8	–	–
	A [33]	B [18] [25] [34]	B [18] [25] [35]	D, this work	E [19]
c	13815-46-8	2981-10-4	1125-99-1	7326-44-5	
	C [30] [37]	C [30] [35] [38] [39]	C [30] [34] [39]	C [38] [40]	
d	32317-47-8	21086-43-1	13750-57-7	–	
	C [36]	C [36]	C [17] [36]	C, this work	

[a]) Methods A [23], B [24] [25], C [26], D [27], E [28], F [29].

1222*s*, 1182*w*, 1118*vw*, 1106*vw*, 1056*m*, 980*w*, 955*w*, 937*vw*, 898*vw*, 830*w*. – ^{1}H-NMR. (C_6D_6): 1.62 (br. *s*, 6 H); 1.82 (*m*, 2 H); 3.45 (*t*×*m*, $J \approx 7$ Hz, 4 H); 5.52 (*m*, 1 H). – MS. (200°): 112 (6), 111 (60, M^+), 110 (5), 108 (5), 96 (10), 94 (5), 83 (32), 82 (100), 80 (5), 69 (5), 68 (56), 67 (6), 56 (9), 55 (21), 54 (10), 53 (7), 43 (7), 42 (30), 41 (43), 40 (6), 39 (22), 29 (12), 28 (12), 27 (16).

Enamine **4d**. UV. (cyclohexane): 226 (3.9). – IR. ($CHCl_3$): 3040*vw*, 2970*vs*, 2935*vs*, 2920*vs*, 2855*vs*, 2735*vw*, 1712*w*, 1649*vs*, 1488*w*, 1467*s*, 1380*s*, 1366*s*, 1305*vs*, 1265*m*, 1140*m*, 1115*m*, 1070*m*, 1050*w*, 986*m*, 950*w*, 910*vw*, 660*vw*. – ^{1}H-NMR. (C_6D_6): 1.03 (*t*, $J=7$ Hz, 3 H); 1.66 (*d*, $J=7$ Hz, 3 H); 1.73 (*m*, 2 H); 1.95 (*qa*, $J=7$ Hz, 2 H); 3.29 (*t*×*m*, $J \approx 7$ Hz, 4 H); 4.05 (*qa*, $J=7$ Hz, 1 H); spurious signals at 3.61 and 3.92–4.2 are assigned to the presence the (*Z*)-isomer. – ^{13}C-NMR. (C_6D_6): 12.2, 13.4 (2 *qa*, 2 CH_3); 16.5 (*t*, CH_2); 19.5 (*t*, CH_2); 51.2 (*t*, 2 CH_2); 90.7 (*d*, CH); 150.4 (*s*); spurious signals at 13.9, 17.8, 25.9, 53.8, 91.8 due to the presence of the (*Z*)-isomer. – MS. (200°): 126 (30), 125 (100, M^+), 124 (47), 110 (14), 98 (8), 97 (52), 96 (85), 95 (7), 87 (8), 86 (37), 82 (13), 75 (m*), 73.5 (m*), 70 (16), 69 (63), 68 (36), 67 (10), 58 (7), 57 (79), 56 (44), 55 (23), 54 (15), 53 (8), 43 (6), 42 (26), 41 (48), 40 (5), 39 (17), 30 (9), 29 (56), 28 (19), 27 (25), 26 (5).

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