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THE LONE-PAIR ORBITALS OF TRIAZIRIDINE

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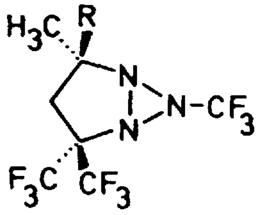
ABSTRACT

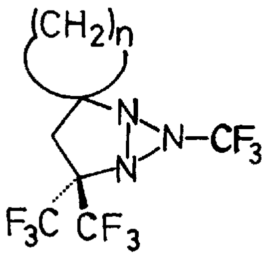
The PE spectra of four stable bicyclic triaziridines with trifluoromethyl, methyl, phenyl, spirocyclopentane and spirocyclohexane substituents are measured. From a comparison of these experimental data with MNDO calculations the energies and the interactions of the nitrogen lone-pair orbitals were obtained. The trifluoromethyl group may be reliably simulated by a fluorine atom. The ionization potentials are unexpectedly high and so are the cyclovoltammetric anodic potentials. The MNDO valence electron densities are in agreement with the comparatively small differences in the chemical shifts of the differently substituted nitrogens of the triaziridine rings.

One of the interesting aspects of triaziridines is the fact that they contain three lone-pairs of electrons in a three-membered ring. Whereas the alkoxycarbonyl and alkyl substituted triaziridines[1] turned out to be too unstable for PE measurements the stable triaziridine derivatives **1** and **2**[2], as well as **3** and **4**[2] are well suited for the investigation of the electronic structure of the triaziridine ring by means of PE spectroscopy in order to gain some information about the interaction of its lone-pair electrons. In this paper we report the PE spectra of **1** through **4** and the results of MNDO calculations which were carried out in order to estimate the influence of the various groups in these highly substituted compounds.



R = Ph: **1**

R = CH_3: **2**



n = 4: **3**

n = 5: **4**

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* After submission of our paper a report on the PE spectra of 3 *cis*-fixed triaziridines appeared: R. Gleiter, C. Sigwart, H. Irngartinger, S. Giries, W. Marterer, O. Klingler and H. Prinzbach *Tetrahedron Lett.* **29**, 185 (1988).

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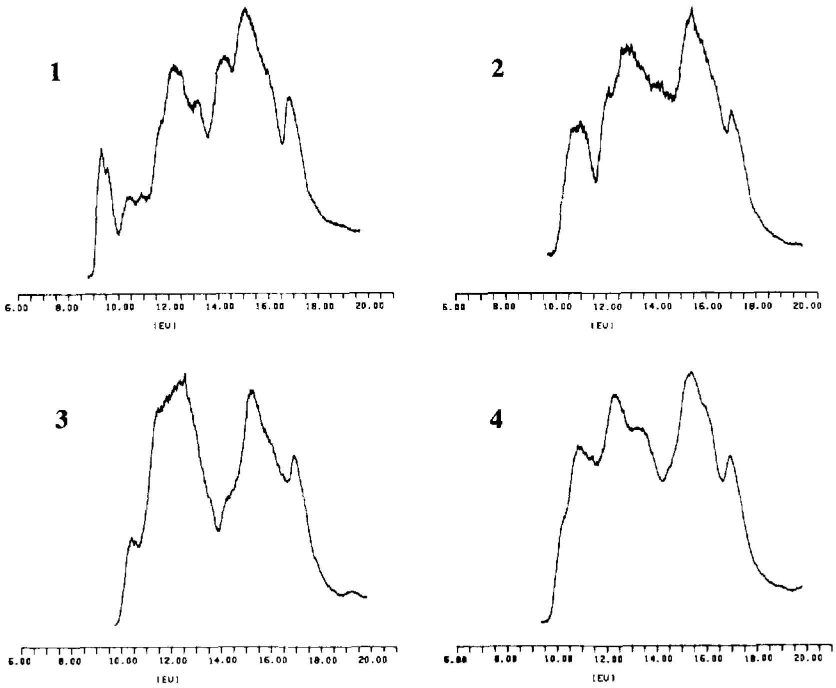


Figure 1. PE spectra of the triaziridine derivatives **1**–**4**

RESULTS

In Figure 1 the PE spectra of **1**–**4** are given; the relevant ionization potentials are summarized in Table 1. From the spectra it is seen that no bands are hidden by the ionizations from the phenyl group of **1** at 9·30 and 9·55 eV, so that all I.P.'s of the triaziridine ring must be higher than 10·4 eV. In all spectra two I.P.'s are discernible between 10 and 11 eV, that can be

Table 1. Vertical ionization potentials (eV) of triaziridine derivatives **1**–**4** (mean values out of 3 measurements)

1	**2**	**3**	**4**	character
9·30				π (Ph)
9·55				π (Ph)
10·42	10·65	10·43	10·41	n_A
10·88	10·95	11·0	10·98	n_S
11·7		11·5	11·4	
12·3	12·1	12·4	12·4	
13·1	13·0	13·4	13·3	
14·25	14·1	14·2	14·4	
15·1	15·4	15·3	15·4	
16·0	16·2	15·9	16·0	
16·9	17·0	17·0	17·0	

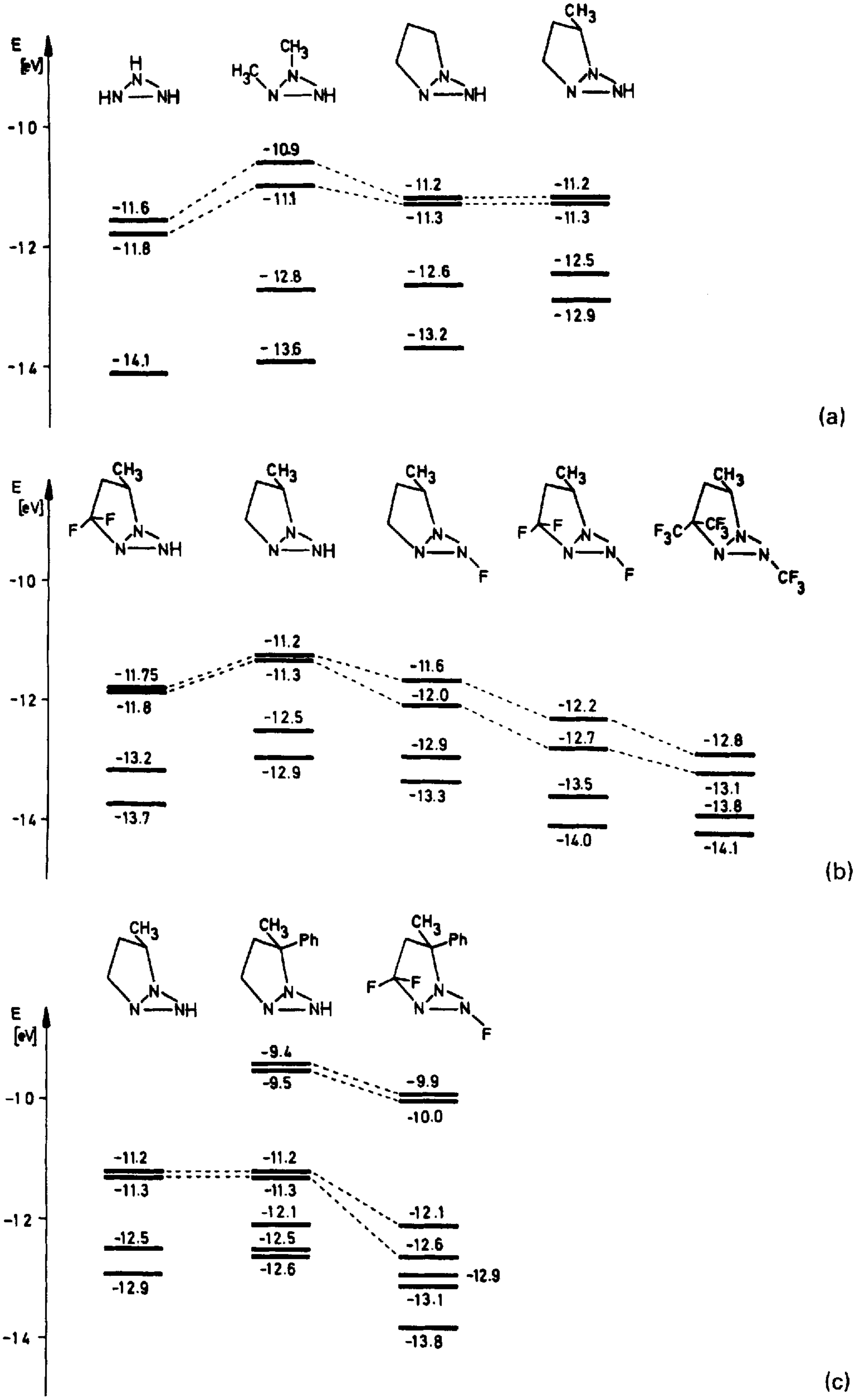
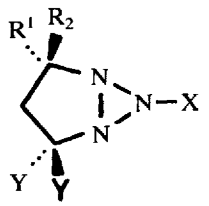
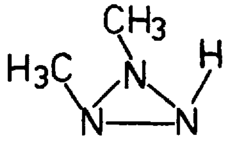


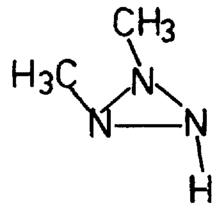
Figure 2. MNDO calculated energies of the highest occupied orbitals of triaziridine derivatives demonstrating the effect of (a) alkyl substituents at the triaziridine, (b) F and CF_3 substituents at the bicyclic triaziridine and (c) the phenyl group in compound **1**

Table 2. Heats of formation ΔH_f in kcal/mol from MNDO calculations of bicyclic triaziridines and monocyclic dimethyltriaziridine with optimized geometries

		X=H Y=H	X=H Y=F	X=F Y=H	X=F Y=F	X=CF$_3$ Y=CF$_3$
	$R_1 = R_2 = H$	+64·2	--	--	--	--
	$R_1 = CH_3$, $R_2 = H$	+60·1	−33·8	46·7	−44·4	−365·9[a]
	$R_1 = CH_3$, $R_2 = Ph$	+103·4	--	--	−1·0	--



84·0



70·4

[a] $\Delta H_{N-F} - \Delta H_{N-CF_3} = -150$ kcal/mol.
$\Delta H_{C-F} = \Delta H_{C-CF_3} = -103{\cdot}6$ kcal/mol.

assigned to lone-pair ionizations of the triaziridine ring. It has however to be stated that these bands are relatively broad — probably caused by the presence of diastereomeric mixtures (**1**) and conformational flexibility. In **3** and **4** these bands are already overlapped by strong σ-ionizations from the cycloalkane rings. The general appearance of the spectra and the location of the peak maxima are rather similar for **1** – **4** (Table 1). However, no attempt was made to assign the I.P.'s above 11 eV to molecular orbitals or ionic states.

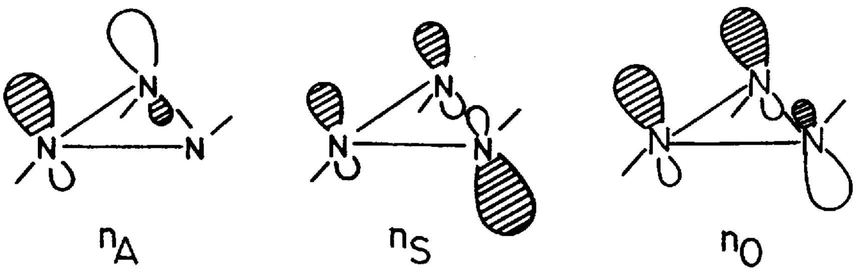
The results of the MNDO calculations[3] are collected in Table 2 and Figure 2. The heats of formation ΔH_f in Table 2 show that the *cis*-dimethyl substituted *cis*, *cis*-triaziridine with all three lone-pairs on the same side of the plane containing the three nitrogens is less stable by *ca.* 14 kcal/mol than the *cis*, *trans*-isomer. This is in good agreement with *ab initio* results for the parent compound.[4] Therefore, a *cis*-arrangement of all three lone-pairs is to be expected only if the triaziridine is sterically fixed by incorporation into an appropriate ring system.[5] This is not the case for the compounds studied in this paper, which are all assumed to be *cis*, *trans*-triaziridines for steric and electronic reasons. From the orbital correlation diagram in Figure 2a it is seen that alkyl substituents destabilize the triaziridine orbitals and that the effect of the trimethylene bridge in the bicyclic compounds is slightly smaller than that of two methyl groups. The effect of the methyl group in α-position of the bicyclic compound is only marginal.

Figure 2b shows that CF$_3$ groups at the nitrogen and at the α-carbon stabilize the triaziridine orbitals considerably and that this stabilization can be simulated to a very good approximation with F atoms instead of CF$_3$ groups as substituents, as may be confirmed from the heats of formation given in Table 2. This reduces the complexity of the calculations considerably. From the data in Figure 2b and Table 2 it is also seen that for X,Y = F the electronegative substituents in α-position are more important for the heat of formation whereas the orbital energies are affected equally by substituents in both positions. Finally Figure 2c shows that the phenyl group hardly affects the orbital energies of the bicyclic system, whereas electronegative substituents at the nitrogen and at the α-carbon again strongly stabilize all orbitals.

From the numerical results it is to be expected that the stabilizing effect of the CF_3 groups in **1**–**4** more or less compensates the destabilizing effect of the alkyl part of the molecule so that apart from the π orbitals of the phenyl group in **1**(9·30 and 9·55 eV) the first two ionization potentials of these compounds are characteristic for the triaziridine moiety.

DISCUSSION

The calculated heats of formation in Table 2 prove quite clearly the effect of electron withdrawing substituents like the CF_3 group in **1**–**4** on the stability of the triaziridine ring. Thus it is not surprising that a triaziridine containing only methyl and 1,8-naphthyl substituents, which could be obtained by biphotonic laser photolysis at 10–85 K, proved unstable and reacted quantitatively to the corresponding azimine even at 150 K.[6]



The unexpectedly high ionization potentials of the triaziridine ring correspond to the two highest occupied orbitals n_A and n_S which are degenerate in the *cis*, *cis*-isomer of the parent molecule. The calculated energies of these orbitals in **1** and **2** are between −12 and −12·8 eV whereas the lowest ionization potentials which could be assigned to these orbitals are 10·42 and 10·88 eV for **1** and 10·65 and 10·95 eV for **2**, respectively. This discrepancy could be due to the fact that the MNDO method may not be well suited for small ring compounds. But the good agreement between the MNDO orbital energies for the unsubstituted triaziridine ($\varepsilon(n_A) = -11{\cdot}6$ and $\varepsilon(n_S) = -11{\cdot}8$ eV) with the *ab initio* values [4] ($\varepsilon(n_A) = -11{\cdot}8$ and $\varepsilon(n_S) = -11{\cdot}2$ eV) rather suggests, that similar linear deviations from Koopmans approximation[7] are to be expected for *ab initio* and for MNDO calculations. From the empirical relation for *ab initio* orbital energies[8] and from the results for ionizations from nitrogen lone-pairs in lactams[9] the triaziridine ionization potentials estimated from MNDO orbital energies are expected to be too high by something like 10% or 1 eV.

From the MNDO calculations the energy gap between the lone-pair combinations n_A and n_S and the Walsh orbitals ω_A and ω_S is expected to be of the order of 2·5 eV. The interaction between these two types of orbitals is therefore smaller than in the case of the triphosphoranes,[10] although it is by no means negligible, as may be seen from LCAO coefficients of the order of 0·15–0·25 for the out-of-plane contributions to the Walsh orbitals. The ionizations corresponding to these orbitals are obscured beneath the σ ionizations starting at 11·5 eV in the PE spectra of **1**–**4**. The totally symmetric combination n_O of the three lone-pair orbitals is expected to give rise to a much higher ionization potential, as may be estimated from the MNDO orbital energy $\varepsilon(n_O) = -17{\cdot}6$ or $-15{\cdot}9$ eV (both MO's show large contributions of the n_O-orbital) for dimethyl triaziridine. As no unique assignment of a PE band to an ionization from this orbital is available it is not possible to obtain from the PE spectra a reliable estimate of the interaction between the lone-pairs. Since the three-orbital six-electron interaction is repulsive, the *cis*, *trans*-isomer with reduced 1,2- and 1,3-interactions is expected to be more stable in agreement with the SCF results.

The PE spectroscopic and MO theoretical results are in good agreement with other properties of compounds **1** and **2**. The high ionization potential indicative for the low availability of all lone-pair electrons correlates well with the cyclovoltammetric anodic potentials which are higher than expected for compounds with N—N single bonds: whereas for **1** due to the phenyl groups a concentration dependent peak potential of 2·78–2·66 V is obtained in the range of 12 to 0·8 mmol/l, there are no deviations from the blank trace for **2** in the same range of concentration up to the limit of ~3 V. In order to judge whether this might be caused by strange effects of the trifluoromethyl groups we measured the first two peak potentials of 6,6-dimethyl-4,4,8,8-tetrakis(trifluoromethyl)-1,5-diazabicyclo[3.3.0]oct-2-ene[11] and found the quite reasonable values of 1.26 and 1.73 V for this compound. Thus, the unusually high oxidation potential is inherent to the triaziridine ring.

As expected, the ^{15}N-NMR chemical shifts (see Experimental) show comparatively small differences ($\Delta\delta$ = 30–50 ppm) for the alkyl and the CF_3 substituted nitrogens which is in agreement with the MNDO values of 5·07, 5·06 and 5·19 calculated for the valence electron density at the nitrogens in the CF_3 substituted compound of Figure 2b as compared to 5·13 at all three nitrogens in the unsubstituted bicyclic system of Figure 2a. This again confirms the fact that the CF_3 groups, although very effective in stabilizing the triaziridine ring, leave the highest ionization potentials and the populations of the lone-pair orbitals nearly unperturbed, as their influence is compensated by the alkyl part of the molecule.

EXPERIMENTAL

The PE spectra were recorded in the region of 6–21 eV using a Leybold–Heraeus UPG 200 spectrometer with He–I excitation (21·21 eV). The calibration of the energy scale was performed with an Ar–Xe mixture. The accuracy of ionization potentials is ±0·03 eV for sharp peaks. ^{15}N-NMR spectra were recorded on a Bruker WP400 spectrometer after addition of $Cr(acac)_3$ with the external standard nitromethane (δ = +380·23 δ = 0 for liquid ammonia). Cyclovoltammograms were recorded with a Potentioscan Wenking POS 73 in acetonitril at Pt vs. SCE with 0·10 mol/l Bu_4NClO_4 as supporting electrolyte with a scan rate of 200 mV/s. MNDO calculations were performed by using the MNDOC version of QCPE 438 for Perkin-Elmer 3242 (double precision) by Walter Thiel, with geometry optimization but taking into account symmetry equivalences wherever applicable.

1 (two diastereomers 1:1) :^{13}C-NMR ($CDCl_3$, 100MHz): δ = 144·2, 129·1 (2C), 128·1, 125·1 (2C), 123·2–122·1 ($3CF_3$, q), 79·9 (septet, J = 25 Hz), 77·0, 37·7, 30·2 and 142·8, 128·9 (2C), 127·9, 125·0(2C), 123·2–122·1 ($3CF_3$, q,J = 25 Hz), 79·9 (septet, J = 25 Hz), 76·0, 37·2, 29·7 ppm; ^{15}N-NMR ($CDCl_3$, 40·6 MHz):δ = 171·7, 156·2, 126·4 (q, J = 20 Hz) and 167·3, 154·7, 122·0 ppm (q, J = 20 Hz).

2 ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 122·3 (q, J = 284 Hz), 121·8 (q, J = 285 Hz), 121·7 (q, J = 271 Hz), 80·0 (septet, J = 27 Hz), 70·7, 38·7, 26·5, 26·1 ppm; ^{15}N-NMR ($CDCl_3$, 40·6 MHz): δ = 173·3, 158·3 (septet, J = 6 Hz), 124·8 ppm (q, J = 20Hz).

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