Photoelectron Spectra of Alkyldiaziridines

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HeI photoelectron (PES) spectra have been obtained for six trisubstituted and three tetrasubstituted diaziridines: 1,3,3-trimethyldiaziridine (**1**), 1-isopropyl-3,3-dimethyldiaziridine (**2**), 1-methylspiro-[diaziridine-3,1′-cyclopentane] (**3**), 1-benzyl-3,3-dimethyldiaziridine (**4**), 3-benzyl-1,3-dimethyldiaziridine (**5**), 3,3-dibenzyl-1-methyldiaziridine (**6**), tetramethyldiaziridine (**7** or Me-**1**), 1-benzyl-2,3,3-trimethyldiaziridine (**8** or Me-**4**) and 3-benzyl-1,2,3-trimethyldiaziridine (**9** or Me-**5**). Analysis provided information about the outer valence electronic structures and geometric conformations. The observed splitting of the n+ and n− ionization events indicates that all compounds exist in *trans* configurations; the lone pair–lone pair dihedral angle is $100 \leq \theta/\text{deg} \leq 110$; and θ decreases with substitution. The centre of gravity of the two lone-pair ionizations remains fairly constant at $E = 9.5(9.15)$ eV for trialkyl (tetraalkyl) substitution. *N*-Alkylation has a much greater effect on the electronic structure of diaziridine than does *C*-alkylation. The additional phenyl group of benzyl substituents and the *p*-methoxyphenyl group of 1-(*p*-methoxybenzyl)-3,3-dimethyldiaziridine (**10**) exert negligible influences. The 1,3-trisubstituted diaziridine **10** decomposes thermally to form NH_3, a reaction described previously only for 3,3-dialkyl- and 1,2,3-trialkyl-diaziridines.

Diaziridines occupy a unique position among the three-membered heterocyclics. Although the parent, unsubstituted diaziridine molecule is unstable and its properties uncertain, its alkyl derivatives are very well known. Our interests in diaziridines relate to their conformations in the gas phase and in solution, the mechanisms of nitrogen inversion, interactions of the two nitrogen lone-pair orbitals, and general electronic structures. Photoelectron (PE) spectroscopy provides some answers to these questions.

The degree to which the interaction of neighbouring lone pairs influences the PE spectra of saturated organic molecules has been studied, especially in connection with molecular gas-phase conformations.[1] Cyclic molecules might seem to be advantageous for such studies because of a reduction of conformational freedom; unfortunately, cyclization introduces strain energies which are *a priori* unknown. Diaziridines are simple examples of such cyclic molecules and, in principle, they can occur in both *cis* and *trans* forms. However, the simple alkyl derivatives, which also possess this freedom, have been observed only in *trans* configurations. The *cis* configurations, apparently, can only be realized by preparing rigid bicyclic compounds.[2,3]

Gas-phase structure determinations of diaziridines are quite scarce.[4] Such quantum chemical calculations as exist refer only to semiempirical or small basis set *ab initio* levels.[5–11] Only a few reports of PE spectra of diaziridines are available.[10–13]

The PE spectra of several trialkyl- and tetraalkyl-diaziridines are reported here. The substituents are methyl or isopropyl groups, the divalent pentamethylene chain, benzyl or *p*-methoxybenzyl groups. These substitutions have been used to study the effects of alkylation, the influence of substituent crowding, and benzene ring conjugation, as mediated by a methylene link, on conformation and electronic structure. The experimental quantities of interest were (*i*) the vertical ionization energies $E_{i,v}$ of the low-energy PE band systems, (*ii*) the energy difference or splitting Δ of the two nitrogen lone pair PE bands, (*iii*) the centre of gravity energy E_{av} of the same two PE bands. Comparisons with the PE spectra of toluene and *p*-methoxytoluene were used to facilitate π-ionization assignments within the confines of a composite molecule method.

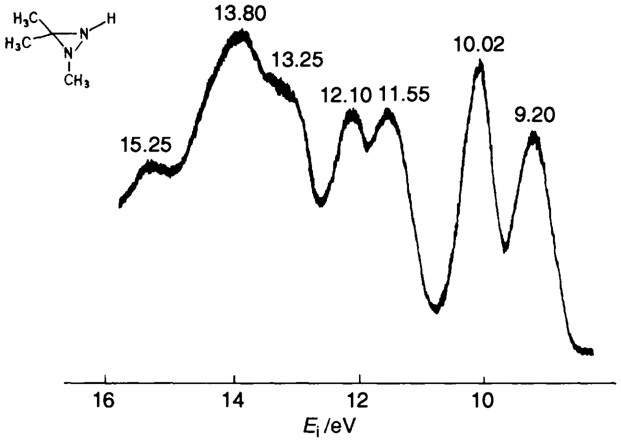

Fig. 1 HeI PE spectrum of 1,3,3-trimethyldiaziridine[12]

Experimental

The preparation of all compounds **1**,[1b,14] **2**,[4] **3**,[15,16] **4–6**,[16] **7**,[1b,17] **8–10**[18] has been described. Low-resolution HeI PE spectra (30 meV FWHM) of compounds **2–10** were recorded on a Vacuum Generators UV-G3 instrument.[19] The PE spectrum of **1** (Fig. 1) had been recorded earlier[12] on a PS-18 instrument.

Results

The HeI PE spectra of compounds **2–10** are given in Figs. 2(*a*)–(*i*), respectively. The vertical ionization energies, $E_{i,v}$ are

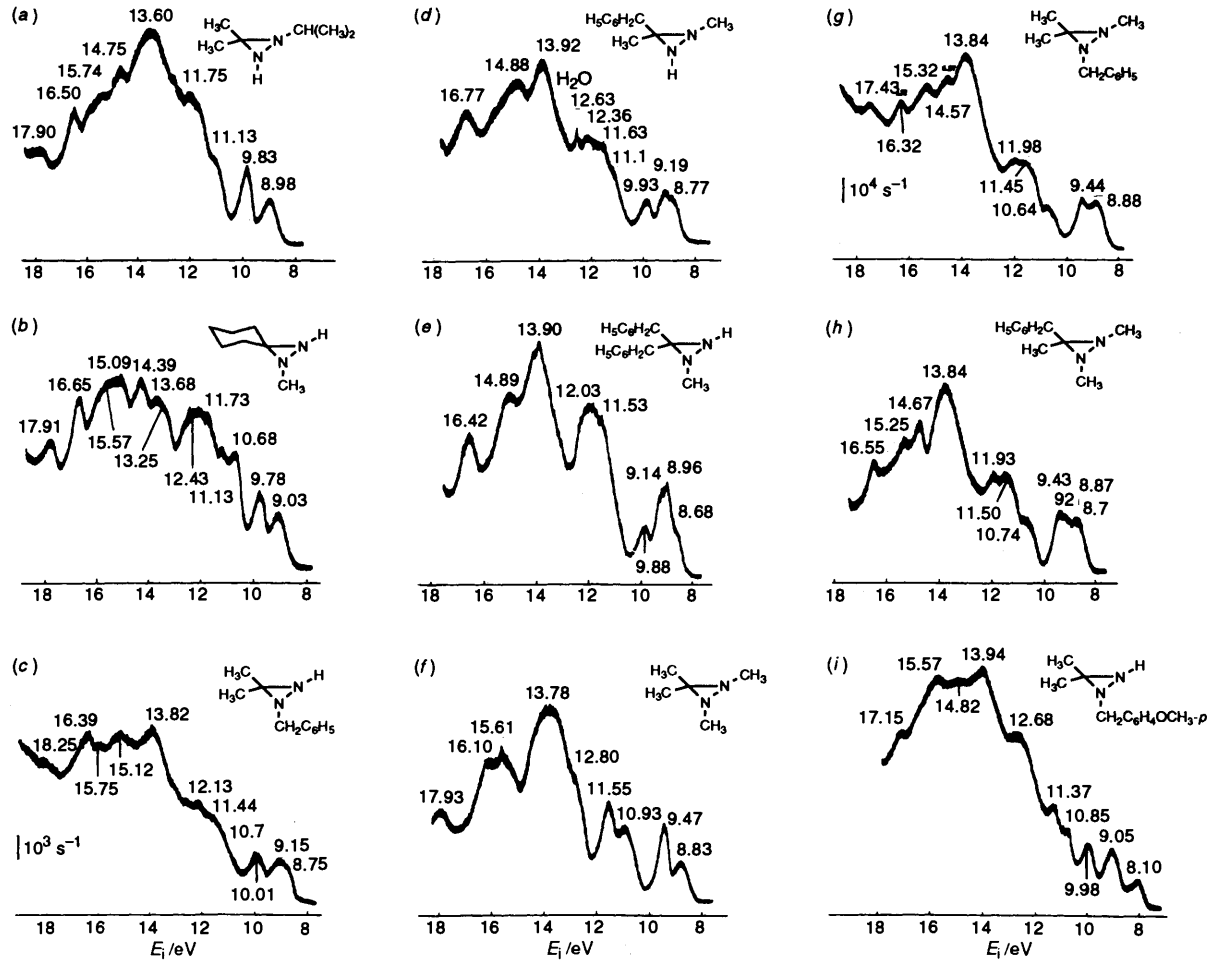

Fig. 2 HeI PE spectra of diaziridines **2**–**10** [(*a*)–(*i*), respectively]

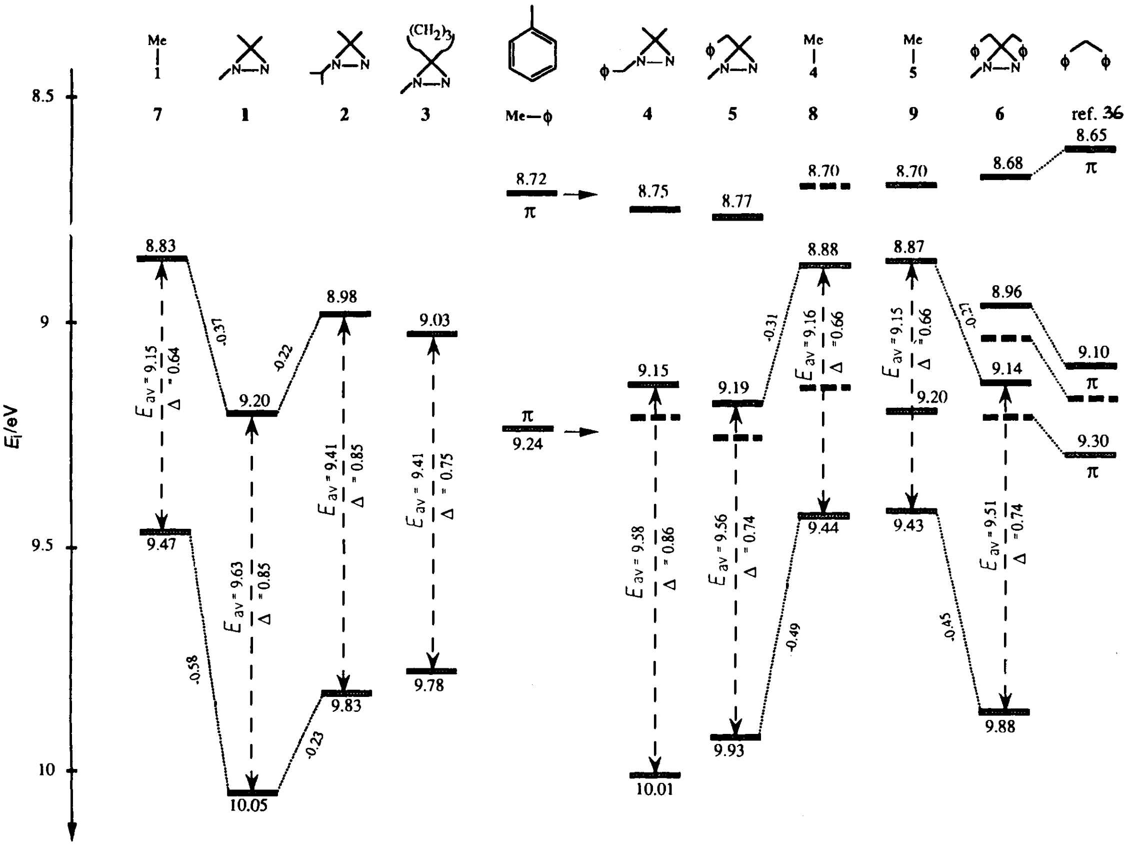

Fig. 3 Correlation diagram of vertical ionization energies for compounds **1**–**10** using results for toluene (Me-φ) and diphenylmethane (φCH_2φ).[37] The splitting (Δ) and centre of gravity (E_{av}) of the two nitrogen lone-pair ionizations are shown. The broken horizontal lines identify ionisation events (or MOs) whose energies could not be determined with precision or whose presence was inferred.

indicated on the band heads. Correlation diagrams for the nitrogen lone pair and phenyl π-ionizations are given in Figs. 3 and 4. The average of the lone-pair ionizations E_{av} and their splitting Δ are also given in these figures. Poorly resolved band systems, ones which appear either as shoulders on, or asymmetries of, other PE bands are denoted by broken lines. The location of such poorly resolved features may also be deduced from band shape and band intensity considerations, and by correlations with related molecules for which PE assignments are definitive.

Discussion

The assignment of the two lowest energy PE bands of **1**–**3** as the nitrogen lone-pair ionizations, n+ and n−, is straightforward. The same holds for **7**. In hydrazines, both noncyclic and cyclic, it was shown that the energy difference $\Delta = [E_i(n+) - E_i(n-)]$ of the first two ionization energies is controlled by the dihedral angle θ between the axes of the two nitrogen lone-pair orbitals.[10–13,17,20–33] These lone pair orbitals interact[34] to form two MOs of which the symmetric (n+) combination should be bonding (and, hence, of higher E_i) at $\theta < 90°$, whereas the antisymmetric (n−) MO should be of higher E_i for $\theta > 90°$. Empirical relations developed by Rademacher *et al.*[13,21–24] and by Nelsen *et al.*[25–31] permit the determination of θ from the observed Δ. Some of these relationships are also functionally dependent on the average energy E_{av}, and on the ring size; others are not. However, regardless of the functional dependence or of the manner in which the parameters are determined, there is reasonable coherence in the set of derived θ. Despite this, Shustov *et al.*[10] and Denisenko *et al.*[11] assert that the pyramidality of nitrogen is a crucial parameter and that it should not be neglected.

The Δ-values of 0.85, 0.85 and 0.75 eV for **1**–**3**, respectively, confirm the expected *trans*-configuration for these compounds and suggest that $\theta \approx 110°$. Replacement of the *N*-methyl by an *N*-isopropyl group lowers the lone-pair ionization energies by about −0.22 eV (Figs. 1, 2 and 3). Extension of the double alkylation at C by three additional CH_2 groups (*i.e.*, replacement of the two methyl groups of **2** by a six-membered ring as in **3**) produces almost the same effect on **1** as does the *N*-isopropyl substitution leading to **2**. Additional *N*-alkylation, as shown for **7**, **8** and **9** in Figs. 2(*f*)–(*h*) and Fig. 3, destabilizes both lone-pair levels (*i.e.*, lowers E_{av}) and reduces Δ. Thus, n+ is affected less than n− in **7**, the shifts being −0.37 and −0.58 eV, respectively. Finally, all three tetrasubstituted diaziridines show remarkable constancy of $E_i(n+)$, $E_i(n-)$, E_{av} and Δ. The corresponding θ values should be somewhat greater than 100°.

The presence of a phenyl ring in compounds **4**, **5**, **8** and **9** introduces two additional π-ionizations into the low-energy PE region. The assignment of these $E_i(\pi)$ is facilitated by comparison with toluene,[35] Me-φ. Indeed, the two $E_i(\pi)$ of toluene are almost energetically coincident with the π-levels of a benzyl substituent in the diaziridines, regardless of the position of benzyl substitution. This observation accords with the predictions of a composite molecule method,[36] and it simplifies the determination of the energies of the two lone-pair bands, as is illustrated in Fig. 3.

As in diphenylmethane (φCH_2φ)[37] and diphenylethane,[38] the lowest-energy π-MOs of the two benzyl groups interact to produce a set of four π-MOs, one of which is of low energy and three of which form a compact group of three at somewhat higher energies. This situation is illustrated on the extreme right of Fig. 3. Indeed, even when the two phenyl groups are separated by more than one carbon atom, as in **6**, the same behaviour is observed (Fig. 3). Such a ready identification of the $E_i(\pi)$ events, makes the assignment of the $E_i(n+)$ and $E_i(n-)$ events relatively easy. Thus, E_{av} and Δ for **6** are found to be 9.51 eV and 0.74 eV, respectively. Such assignments for **9**, **5** and **6** lead one to conclude that the effect of *C*-alkylation (*i.e.*, the additional benzyl) is negligible whereas that of *N*-alkylation (*i.e.*, the additional methyl) is substantial in destabilizing the n+ and n− MOs (−0.27 eV and −0.45 eV, respectively) and reducing Δ (Δ = 0.66 eV).

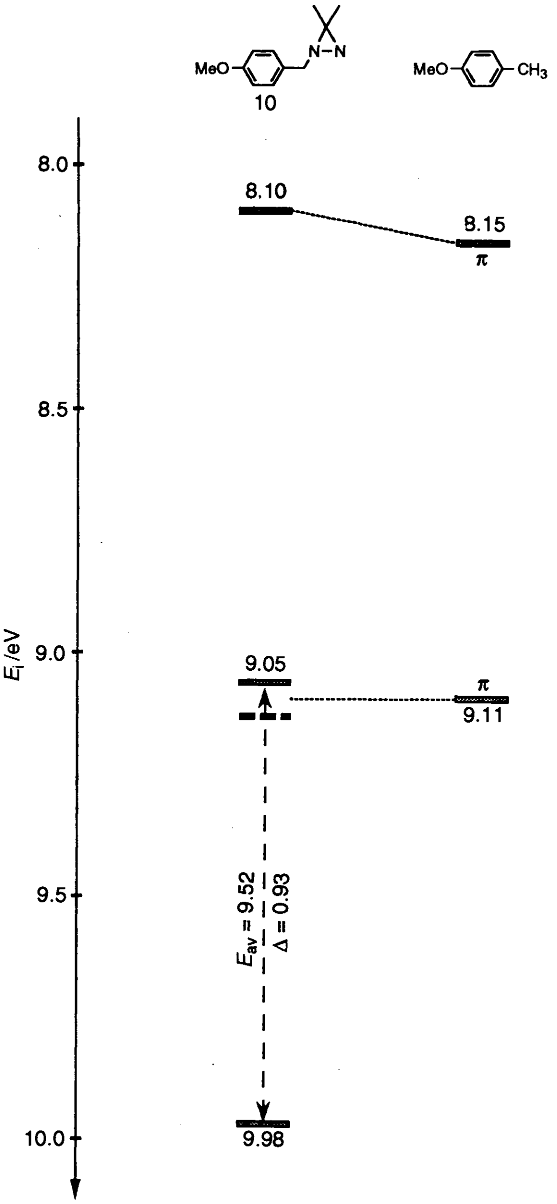

Fig. 4 Correlation diagram of vertical ionization energies for **10** and *p*-methoxytoluene[39] indicating the splitting (Δ) and centre of gravity (E_{av}) of the two nitrogen lone-pair ionizations

The PE spectrum of **10** is shown in Fig. 2(*i*). The PE spectrum is easily assigned by comparison with that of *p*-methoxytoluene[39] (Fig. 4). As for benzyl substitution, the π-levels of **10** are shifted only slightly relative to those of *p*-methoxytoluene. The 9.05 eV band system in **10** is unresolved but evidently contains both the n+ and π-ionizations. Since the n− level occurs at 9.98 eV, E_{av} and Δ values for **10** are 9.52 eV and 0.93 eV, respectively; and θ is somewhat greater than 110°. The fine structure of the 10.85 eV band of **10** is due to ammonia. It is known that 3,3-dialkyldiaziridines and 1,2,3-trialkyldiazidines may decompose thermally and yield NH_3 as a product.[15b,40] Our observations indicate that such a reaction also occurs in 1,3,3-trialkyldiaziridine.

Conclusions

This investigation of trialkyl- and tetraalkyl-diaziridines **1–10** is concerned with the assignment of nitrogen lone-pair ionizations. All the compounds are shown to exist in *trans*-configurations, the estimated lone pair–lone pair angles ranging between 100° and 110°. In the trialkyl compounds, the mean value of the lone-pair ionizations is $E_{av} = 9.5$ eV and is fairly constant; for the tetraalkyl compounds, $E_{av} = 9.15$ eV. *N*-Alkyl substitution has a much stronger effect than *C*-alkyl substitution on the lone-pair ionization energies. Phenyl or substituted phenyl rings, as parts of the alkyl substituents, appear to have negligible influence on the lone-pair levels of diaziridines; thus the hyperconjugative interaction of the phenyl and three-membered ring, which might be presumed to proceed through methylene linkage, is important.

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