Conformational Analysis of Saturated Heterocycles. Part 94.[1a] Applications of Photoelectron Spectroscopy to Molecular Properties. Part 3.[1b] Photoelectron Spectroscopic Studies of Some 1-Oxa-3,4-diaza-, 1-Thia-3,4-diaza-, 1,2,4-Triaza-, and 1,2,4,5-Tetra-aza-cyclohexanes

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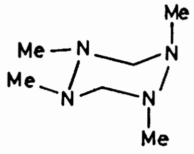
2-Oxa-4a,8a-diazadecalin (2) shows bands of the predominant αα and a minor εα form. 1,2,4-Trimethyl-1,2,4-triaza- (3) and 3,4-dimethyl-1-thia-3,4-diaza-cyclohexane (4) probably exist in the αεα and εα conformations, respectively. These conclusions are in good agreement with those from solution measurements, as are those for four 1,2,4,5-tetra-azacyclohexanes.

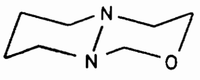
PHOTOELECTRON spectroscopy (p.e.s.) is an efficient technique for the study of molecules containing vicinal free lone pairs, and has clarified the conformational equilibria of many acyclic and cyclic derivatives of hydrazine.[2-4] The correlations between the splitting $\Delta(n^- - n^+)$ of the ionization potentials and the dihedral angle of the lone pairs allows, without ambiguity, differentiation of the interaction between axial–axial (αα) † lone pairs from that between equatorial–axial (εα) and/or equatorial–equatorial (εε) lone pairs. The distinction between the last two can be subtle because of the similar dihedral angles.

We now report on the conformational analysis by p.e.s. of six-membered heterocycles containing a hydrazine fragment and one or two additional heteroatoms. 1,2,4,5-Tetramethyl-1,2,4,5-tetra-azacyclohexane (1) is the only such compound previously examined:[3] ionization potentials at 7.90 and 10.37 (ΔE 2.47) and 8.45 and 9.00 eV (ΔE 0.55 eV) were interpreted in favour of a conformation with the lone pairs of the nitrogen atoms in an ααεε conformation. Results from ^{1}H[6] and ^{13}C n.m.r.[7] studies indicate that in solution also the ααεε conformation is predominant for *sym*-tetramethyltetra-azacyclohexane (1).



aaee — (1)

1,2,4-*Triheterocyclohexane Systems*.—Vertical ionization potentials for 2-oxa-4a,8a-diazadecalin (2), 1,2,4-trimethyl-1,2,4-triaza- (3), and 3,4-dimethyl-1-thia-3,4-diaza-cyclohexane (4) are reported in Table 1 (*cf.* Figures 1a—c).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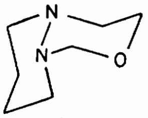
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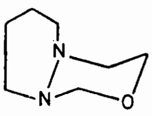
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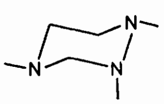
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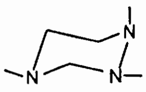
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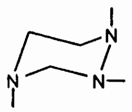
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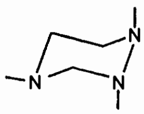
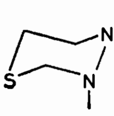
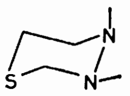

(3αεε)


(4εα)


(4αε)

2-Oxa-4a,8a-diazadecalin (2) shows two intense bands at 8.04 and 9.82 eV (ΔE 1.78 eV) together with a broad band of low intensity at 9.02 eV. The doublet with 1.8 eV splitting is assigned to the predominant form (2αα) containing vicinal αα lone pairs (*cf.* $\Delta E = 2.47$ eV for αα pairs in 1,2,4,5-tetramethyl-1,2,4,5-tetra-azacyclohexane[3]). The weak broad absorption at 9.02 eV indicates a minor conformer with vicinal εα lone pairs present in the vapour phase, either (2εα) or (2αε). Previous ^{1}H n.m.r. results[8] demonstrated that, for solutions, (2εα) coexisted with the major (2αα) form. Furthermore, ^{1}H[9] and ^{13}C n.m.r.[10] studies on 3,4-dimethyl-1-oxa-3,4-diazacyclohexane (5) have shown the major

TABLE 1

Vertical ionisation potentials (eV) for 2-oxa-4a,8a-diazadecalin (2), 1,2,4-trimethyl-1,2,4-triaza- (3), and 3,4-dimethyl-1-thia-3,4-diazacyclohexane (4)

Compd.	$I_v n^-$	$I_v n^+$	$I_v n^+$	E(ev)	I_x
(2)	8.04	9.02	9.82	*ca.* 1.80	10.32
(3)	8.10		9.08	0.98	8.30
(4)	8.18		9.13	0. 95	8.52

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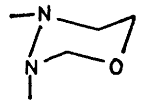
† The terms α and ε, as adopted by Nelsen,[5] refer to lone pair orientations whereas *a* and *e* refer to substituent orientations.

conformer in this case to be (5εα). Hence it is probable that the minor form observed in the gas phase for (2) is (2εα).



(5εα)

1,2,4-Trimethyl-1,2,4-triaza- (3) and 3,4-dimethyl-1-thia-3,4-diaza-cyclohexane (4) both show doublets split by *ca.* 1 eV (Table 1) corresponding either to adjacent αε or εε lone pairs. For the triazacyclohexane (3) four such conformations may be envisaged: (3αεα), (3ααε), (3εαε), and (3αεε). Of these conformers, (3αεε) and (3εαε) may be neglected, containing as they do two axial substituents, thus leaving (3αεα) and (3ααε) for consideration. The splitting of 1 eV is larger than expected (ΔE *ca.* 0.65—0.7 eV) for unperturbed vicinal αε lone pairs: the 1,2-interaction is evidently augmented by 1,3- and/or 1,4-interactions. The 1,3-interactions expected for the (3αεα) and (3εαε) forms are *ca.* 0.4 eV as found by Nelsen in 1,3-diazacyclohexanes.[5] 1,3-Interaction between equatorial lone pairs (3εεα) is estimated to be 1 eV. 1,4-Interaction [5] is negligible if the lone pairs are αα or εα but *ca.* 0.8 eV for the pairs εε. Thus from the experimental data it would appear that the 1,3-(εε) and 1,4-interactions (αα, εα, and εε) may be neglected and we therefore propose that in the vapour phase (3) exists preferentially as conformer (3αεα) (εα 1,2-splitting of *ca.* 0.65 eV augmented by an αε 1,3-interaction of *ca.* 0.4 eV), a result in accord with the conclusions of solution studies.[11]

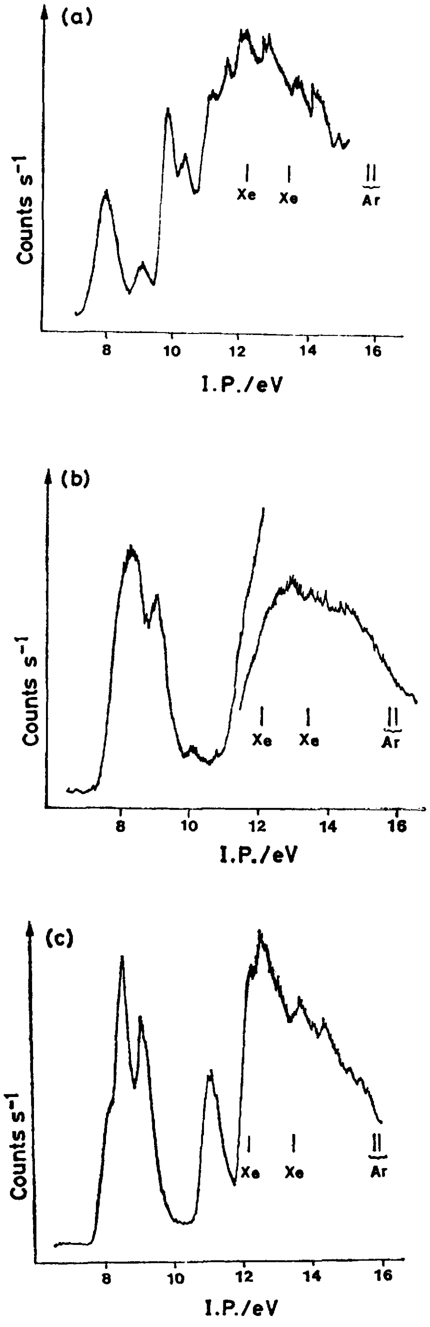
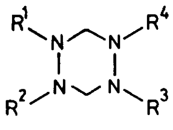


FIGURE 1 Photoelectron spectra of: a, 2-oxa-4a,8a-diazadecalin (2); b, 1,2,4-trimethyl-1,2,4-triazacyclohexane (3); c, 3,4-dimethyl-1-thia-3,4-diazacyclohexane (4)

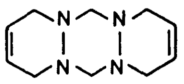
For the thiadiazacyclohexane (4) experimental data to estimate 1,3- and 1,4-interactions are lacking. However the similar p.e.s. observed for (3) and (4) may suggest that (4εα) is the preferred conformer; only a theoretical evaluation on the nature and importance of the 1,3 and 1,4 S–N interaction will permit definite resolution. A ^{13}C dynamic n.m.r. [11a,12] study of (4) showed that (4εα) is predominant with *ca.* 5% (4αε) at −120 °C.

1,2,4,5-*Tetra-azacyclohexanes*.—We report also the p.e.s. of four 1,2,4,5-tetra-azacyclohexane derivatives: 1,4-dibenzyl-2,5-dimethyl- (6), *sym*-tetrabenzyl- (7), *trans*-1,2,3,4,5,6-hexamethyl-1,2,4,5-tetra-azacyclohexane (9), and the tricyclic derivative (8). The ionization potentials for these and for *sym*-tetramethyl-1,2,4,5-tetra-azacyclohexane (1) are reported in Table 2.

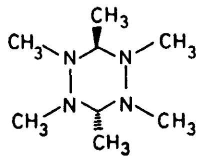


(6) $R^1 = R^3 = CH_2Ph$, $R^2 = R^4 = Me$

(7) $R^1 = R^2 = R^3 = R^4 = CH_2Ph$



(8)



(9)

The benzyl groups in (6) and (7) and the ethylene bonds for (8) give broad intense bands at *ca.* 9 eV.[4] The other ionization potentials derive from the nitrogen lone pairs. For (6) and (8), doublets at 7.71 and 10.22 and 7.73 and 10.0 eV, respectively (ΔE *ca.* 2.2—2.4 eV,

TABLE 2

Vertical ionisation potentials (eV) for 1,2,4,5-tetramethyl- (1), 1,4-dibenzyl-2,5-dimethyl- (6), 1,2,4,5-tetrabenzyl- (7), and *trans*-1,2,3,4,5,6-hexamethyl-1,2,4,5-tetra-azacyclohexane (9), and 6*H*,13*H*-1,4,8,11-tetrahydrobis-(pyridazino[1,2-*a*:1′,2′-*d*]-s-tetrazine) (8)

Compound	I_vn	I_vn	$I_vn + I_v\pi_{Ph}$ (6), (7) or $I_v\pi_{C=C}$ (8)	I_vn	I_vn
(1)	7.90	8.45	9.00		10.37
(6)	7.71	8.34	9.02—9.16		10.22
(7)	7.44	8.09	9.07		
(8)	7.73	8.32	9.16—9.40		10
(9)	7.63	8.09	8.75	9.43	10.03

Figure 2a) demonstrate the presence of vicinal αα lone pairs: similar evidence and conclusions have been published for (1).[3] We believe that bands at 8.34 and 8.32 eV, respectively, for (6) and (8) are associated with the broad intense bands at *ca.* 9 eV in both these compounds. This splitting of *ca.* 0.7 eV corresponds either to an εε lone-pair orientation which has been proposed for (1) or to αε lone-pair orientation only compatible for (3). In fact, εε for (6) and αε for (8) seem likely; however, for (6) three and for (8) two conformers with εε or αε lone pairs need be considered (Scheme), and an unequivocal conclusion cannot be reached. From ^1H and ^{13}C n.m.r. data [7] it has been concluded that (6) exists as ααεε (65%) and αεαε (35%) forms, and (8) as αααε (66%), αεαε (20%), and αααα (13%).

The different spectral characteristics of the tetrabenzyl compound (7) and the hexamethyl derivative (9) compared with those for (6) and (8) indicate different predominant conformers. For (7) the absence of absorption in the 10 eV region eliminates the ααεε and the αααα

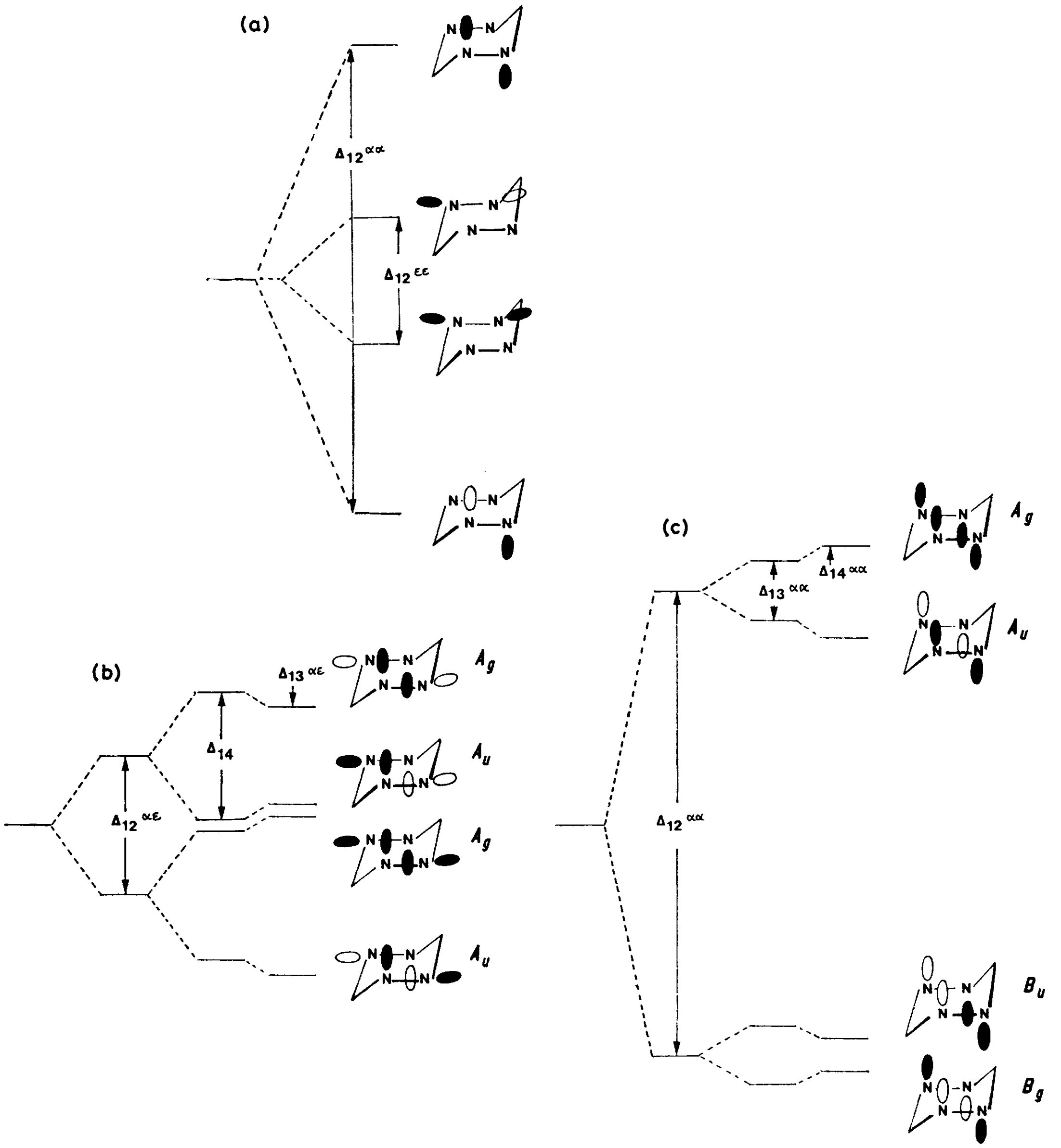
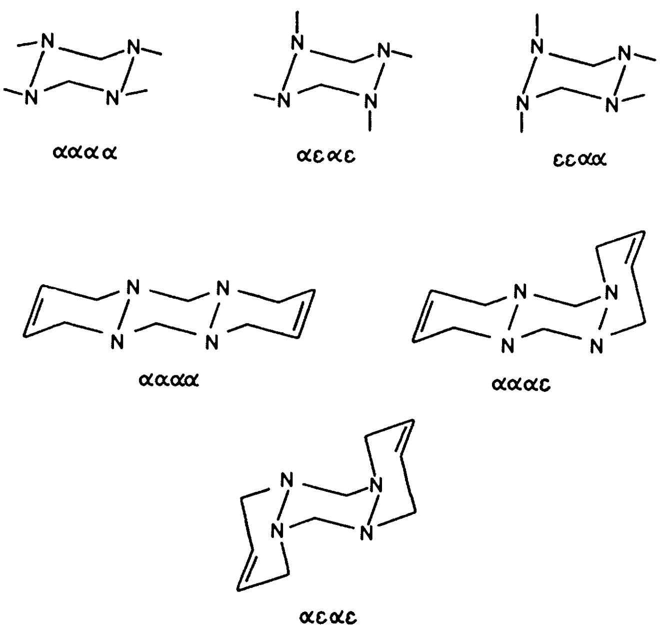


FIGURE 2 Interactions between the nitrogen lone-pair orbitals for 1,2,4,5-tetra-alkyl-1,2,4,5-tetra-azacyclohexanes: a, for conformation ααεε; b, for conformation αεαε; c, for conformation αααα



SCHEME

conformations. For the αεαε form (C_i symmetry) experimental values for the 1,2-, 1,3-, and 1,4-interactions allow qualitative estimates of the expected splitting (Figure 2b); the αε 1,2-interaction is *ca.* 0.65 eV, the εε 1,4-interaction is similar (*ca.* 0.8 eV) and the 1,3-interaction is weak (*ca.* 0.4 eV). The p.e.s. should therefore show three bands, the second and third I.P. being very similar. This is observed for (7), the fourth I.P. being under that due to the benzyl groups. Therefore in accordance with the solution results, we propose that the predominant conformer for *sym*-tetrabenzyl-1,2,4,5-tetra-azacyclohexane (7) is αεαε.

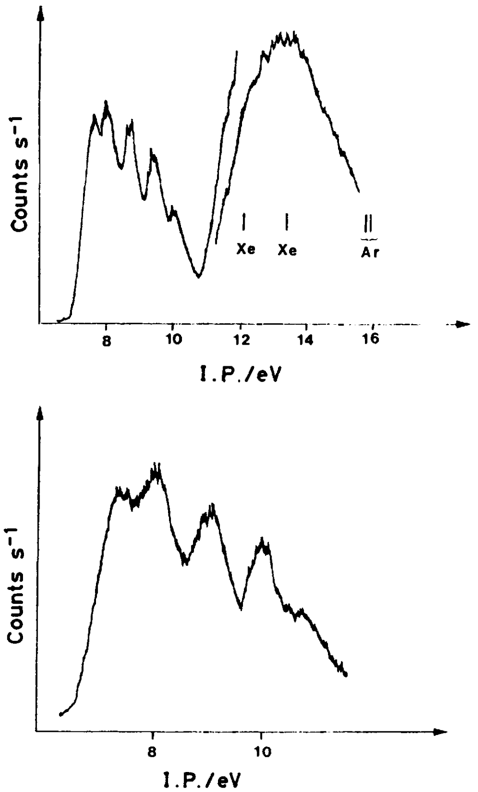
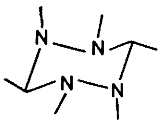
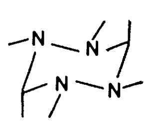


FIGURE 3 Photoelectron spectrum of *trans*-1,2,3,4,5,6-hexamethyl-1,2,4,5-tetra-azacyclohexane (9)

The spectrum for hexamethyltetra-azacyclohexane (9) is complex with five bands (Figure 3), implying the presence of at least two conformers with superpositions of some I.P. Three relatively intense bands are observed at 8.09, 8.75, and 9.73 eV. The first I.P. appears at 7.63 eV as a shoulder on the 8.09 band, whereas the last band at 10.03 eV is broad and less intense. Because the intensities of the three bands at 8.09, 8.75, and 9.43 eV are similar, the logical conclusion is that these are due to a predominant form αεαε as deduced for (7). The splittings observed of 0.65 eV correspond to the superposition of vicinal interactions of about 0.65 eV with that from 1,4-interaction of the same importance.

Besides this form, the presence of two bands at 7.63 and 10.03 eV indicates the existence of a conformation with vicinal αα lone pairs. ^{13}C n.m.r. results [13] have suggested (9αααα) as a minor conformer in solution: we have examined the p.e.s. splittings with this possibility in mind. The different interactions are illustrated qualitatively in Figure 2c: a major αα 1,2-interaction, an αα 1,3-interaction with an arbitrary experimental value (assumed to be weak), and a weak αα 1,4-interaction. From this diagram, if the I.P. at 7.63 and 8.09 eV are associated with the ionization corresponding to the molecular orbitals of symmetry A_g and A_u, then the broad band at 10.03 eV is associated with ionizations of electrons in orbitals B_u and B_g. This conclusion appears to be coherent with the intensities of the different bands in the p.e.s. of (9), notably the somewhat greater intensity of the band at 8.09 eV than the one at 8.75 eV: (9αααα) is thus a strong possibility for the minor I.P. in the p.e.s. of (9).


(9αεαε)


(9αααα)

Analysis of the p.e.s. of compounds (6)—(9) allows definite assignment of the predominant conformer. The existence of a minor conformer (9αααα) awaits confirmation by a rigorous theoretical analysis of the various interactions.

EXPERIMENTAL

2-Oxa-4a,8a-diazadecalin [8] [b.p. 86 °C at 15 mmHg (characterised by n.m.r. and mass spectroscopy)], 1,2,4-trimethyl-1,2,4-triazacyclohexane [b.p. 49 °C at 20 mmHg (lit.,[11b] 49 °C at 20 mmHg)], 3,4-dimethyl-1-thia-3,4-diazacyclohexane [b.p. 65 °C at 20 mmHg (lit.,[12] 65 °C at 20 mmHg)], 1,4-dibenzyl-2,5-dimethyl- [m.p. 70—71 °C (lit.,[7] 70—71 °C)], *sym*-tetrabenzyl- [m.p. 160 °C (lit.,[7] 160—161 °C)], and *trans*-1,2,3,4,5,6-hexamethyl-1,2,4,5-tetra-azacyclohexane [m.p. 32 °C (lit.,[13] 32 °C)], and 6*H*,13*H*-1,4,8,11-

tetrahydrobis(pyridazino[1,2-*a*:1′,2′-*d*]-*s*-tetrazine) [m.p. 151 °C (lit.,[7] 151 °C)] were prepared following literature methods.

Photoelectron spectra were recorded on a Perkin-Elmer PS 18 spectrometer with He^{I} source (584 Å). They were calibrated by using the $^{2}P_{\frac{1}{2}}$ and $^{2}P_{\frac{3}{2}}$ doublets of argon (15.755 and 15.93 eV) and of xenon (12.13 and 13.43 eV). The ionisation potentials recorded are accurate to within 20 meV with the exception of superimposed peaks.

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