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THE MOLECULAR ENERGY LEVELS OF THE AZINES. AB INITIO CALCULATIONS AND THE CORRELATION WITH PHOTOELECTRON SPECTROSCOPY

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Photoelectron spectroscopy has rapidly become the major method for investigation of molecular energy levels;[1] line assignments are generally made on the basis of chemical intuition or semiempirical molecular orbital calculations. Thus for the azines two groups of workers[2,3] have arrived at different conclusions. The present work used minimal basis set (cf. Reference 4) non-empirical calculations and leads to firm conclusions, both for the known and unknown azines. The total energies and binding energies (Table 1) show that the binding energy decreases as the value of n increases in $C_{6-n}H_{6-n}N_n$, but that 1,2,3-triazine, and 1,2,3,4- and 1,2,3,5-tetrazines should be stable in contrast to pentazine or hexazine.

Table 1

Molecule	Total Energy (a.u.)	Binding Energy[a] (kcal/mole)
Pyridine	-245.76489	-597.5
Pyrazine[b]	-261.559	-444.9
Pyridazine	-261.68003	-438.9
Pyrimidine	-261.67872	-438.0
1,2,3-Triazine	-277.59443	-279.8
1,2,4-Triazine	-277.61161	-290.6
1,3,5-Triazine	-277.54134	-246.5
1,2,3,4-Tetrazine	-293.51233	-122.6
1,2,3,5-Tetrazine	-293.54386	-142.4
1,2,4,5-Tetrazine	-293.47477	- 99.31
Pentazine	-309.39321	+ 57.4
Hexazine	-325.28963	+227.6

a) Binding Energy = Molecular Energy - Σ Atom Energies.

b) Data from Reference 5b, which used a similar basis set, is included for completeness.

The corresponding molecular orbital energies, correlated with the known experimental ionisation potentials via Koopmans' Theorem, lead to the linear relationship $IP_{lbs} = 0.785\ IP_{calc} + 0.33eV$ shown graphically in Figure 1 (the standard deviations in slope and intercept and the overall standard deviation are 0.01, 0.2 and 0.54 eV respectively); the line is effectively identical to that found for the azoles.[4] The usual semiempirical methods lead to the following results (method, slope, intercept, standard deviation in slope, standard deviation in intercept, overall standard deviation):-

(a) CNDO-2, 0.546, 3.71, 0.015, 0.34, 1.03;
(b) INDO, 0.504, 4.98, 0.022, 0.52, 1.69;
(c) Extended Huckel Method[2] 1.359, -7.49, 0.037, 0.651, 1.05. It is clear that the scatter is much worse in these methods than in the LCGO calculations. Furthermore graphical presentation of these results shows that the major groupings of the experimental spectra are only reproduced well by the non-empirical calculations (Figure 2).

For pyridine, the present work (as in previous calculations[5a,6]) gives the I.P. order $1a_2$ $2b_1$ $11a_1$ in contrast to the order from the earlier assignments.[2,3] Our ordering agrees almost completely with Lindholm's[2] Extended Huckel calculations for pyrimidine, pyridazine, 1,3,5-triazine and 1,2,4,5-tetrazine, and contrast with those of Heilbronner et al.[3]

Although the symmetry of the molecules $C_{6-n}H_{6-n}N_n$ n = 0-6 varies from D_{6h} through C_{2v} to C_s, all of the molecules show pseudo D_{6h} (e.g. C_6H_6) symmetry, in that the orbitals can be classified on the basis of their eigenvectors into the D_{6h} types. This leads to the correlation diagram (Figure 3), and allows an explanation of the apparently anomalous "lone pair" orbital

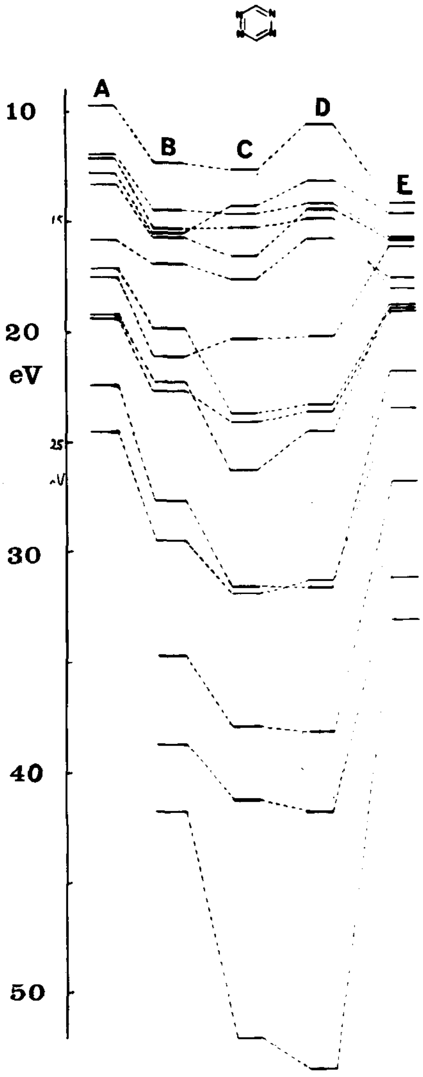

Fig. 2. Correlation of Experimental (A), LCGO (B), CNDO-2 (C), INDO (D), EHM (E) Orbital Energies for 1,2,4,5-Tetrazine.

combinations which are calculated for some of the molecules. The filling of the σ-orbitals from low to high binding energy is in the same order as benzene namely $3e_{2g}$, $3e_{1u}$, $2b_{1u}$. Thus if the lone pair orbitals at centre i are given by N_i, with the corresponding D_{6h} orbital in brackets, then for 1,2,4-triazine the calculated combinations are 18a' ($N_1-N_2+N_4$) (e_{2g}), 17a' ($N_2 + N_4$) (e_{2g}), 16a' ($N_1 - N_4$) (e_{1u}); 1,2,3,4-tetrazine has $9a_1$ and $10a_1$ ($N_2 + N_3$) (e_{1u} and e_{2g} respectively), $8b_2$ ($N_2 - N_3$) (e_{2g}), and $7b_2$ ($N_1 - N_4$) (e_{1u}); 1,2,3,5-tetrazine has 11a' ($N_1 + N_3$) - ($N_2 + N_5$) (e_{2g}), 10a' ($N_2 - N_5$) (b_{1u}), 9a' ($N_1 + N_2 + N_3 - N_5$) (e_{1u}), $7b_2$ ($N_1 - N_3$) (e_{2g}). Combinations for the remaining azines can be interpreted in similar terms.

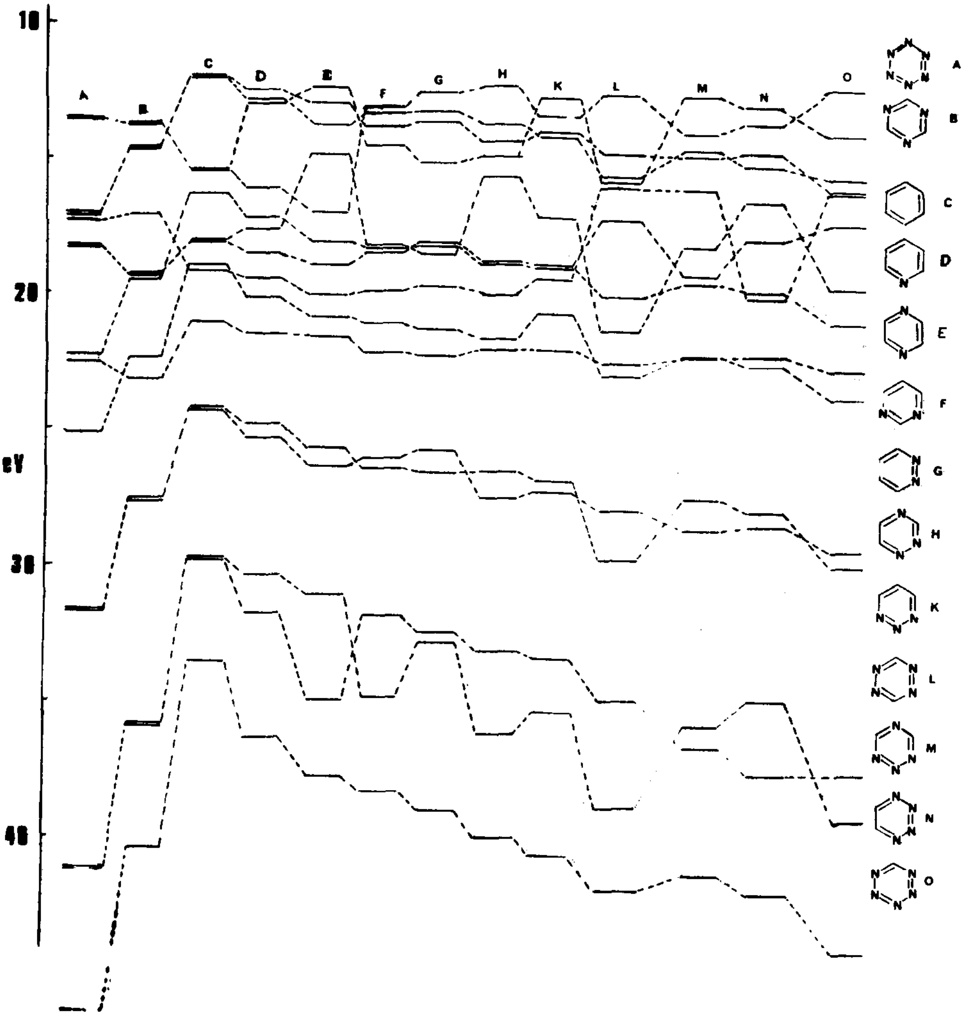

Fig. 3 Correlation of Theoretical (LCGO) Orbital Energies in the Azines.

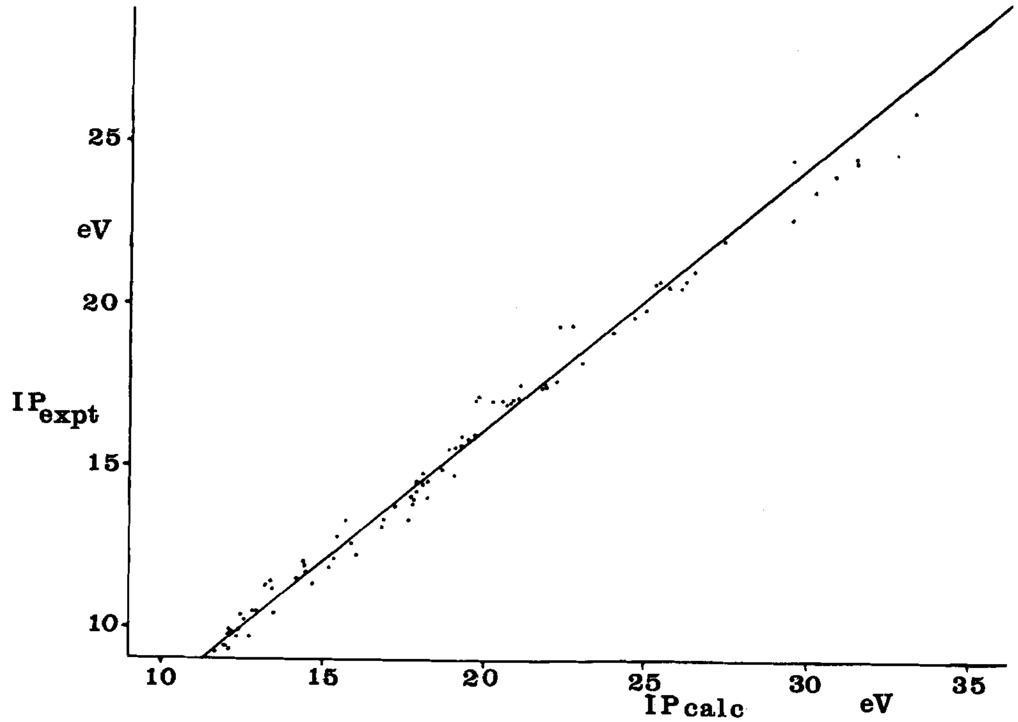

Fig. 1 Least Squares plot of Orbital Energies as Ionisation Potentials.

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