Molecular Energy Levels of Azines; *ab initio* Calculations and Correlation with Photoelectron Spectroscopy

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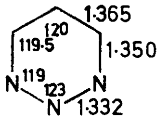
Non-empirical calculations using a standard gaussian atomic orbital basis (LCGO) have been carried out for known and unknown azines. The wavefunctions show pseudo D_{6h} symmetry and have been correlated with those of benzene; this correlation has been used to interpret the combinations of ' lone pair ' orbitals that occur. In the case of the tetrazines the splitting of the lone pair levels leads to extensive overlap with the CH region of energy so that mixing occurs and 1,2,4,5-tetrazine shows five orbitals which can be described as ' lone pair orbitals '. The orbital energy ordering is effectively identical with that obtained from recent double ζ calculations on a few of the molecules; these energies correlate well with photoelectron spectra and obey the relationship $IP_{obs} = 0{\cdot}790IP_{calc}$. Correlations using CNDO/2, INDO, and the Extended Huckel Method (EHM) are less satisfactory both in grouping of the orbitals and absolute energies. The LCGO band assignments are generally in good agreement with those made by Lindholm *et al.* based upon the EHM. The thermodynamic stability of the azines with respect to fragmentation is discussed; the difference in energies between the classical alternating bond lengths and the observed ones for selected examples are in the region 6—10 kcal mol^{-1}.

We have previously reported *ab initio* calculations of the energy levels of azoles,[1] and five-membered ring heterocycles containing one oxygen, sulphur, or phosphorus atom, and have given a preliminary account of similar calculations on azines.[2] Throughout this work we have used the same basis set on the grounds that this is more likely to disclose trends in computed properties. The gaussian set is a ' best atom ' basis † of seven *s*-type and three *p*-type gaussian functions for carbon and nitrogen, with three *s*-type for hydrogen. With the exception of pyrazine where a very similar calculation was reported previously,[3] we have obtained wavefunctions for all the monocyclic molecules $C_mH_mN_{6-m}$ where $m = 0$—6. All the computations were made using the experimental geometry if known,[4-9] while those of the other compounds (1)—(6) were based upon values from the known compounds. Very recently *ab initio* calculations of the wavefunctions of seven of the thirteen possible monocyclic molecules of type $C_mH_mN_{6-m}$ were reported; [10] these calculations used an identical gaussian set to the present ones, but the orbitals were split into a double ζ basis and σ-polarisation functions were introduced on the hydrogen atoms.



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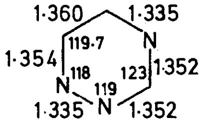

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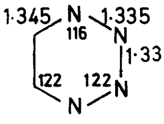

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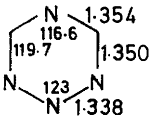

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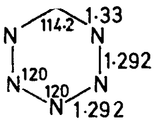

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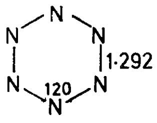

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Other than the intrinsic interest in the azines as a series of probably varying aromatic character, the present work indicates which of the unknown azines should be capable of existence, investigates the extent of perturbation introduced by the nitrogen atoms, and assists in the assignment of the recently reported photoelectron spectra, where conflicting assignments have been made.[11-15]

RESULTS

The molecular orbital and total energies are given in Table 1, while a comparison of the former with the experimental ionisation potentials through Koopmans theorem is shown in Figure 1. The correct number of groupings of ionisation potentials for each molecule are obtained. We note that comparison of our orbitals with those of Almlof *et al.*[10] leads to *only two* reassignments of order [pyrimidine (a_2 and $1b_1$)] in 75 calculated levels and that further discussion of the assignments of experimental IP values is unnecessary.‡ In Figure 2 we record a typical

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† A best atom set is defined as that set of functions of chosen size which best optimises the atom energy. For the atoms in this set of molecules the total energies obtained are H(^1S) −0·4970, C(^3P) −37·6104, and N(^4S) −54·2754 a.u. which may be compared with the Hartree–Fock limiting values of −0·5000, −37·6886, and −54·4009 a.u. respectively.

‡ A further factor supporting this proposal is that in each diazine spectrum there is at least one peak near 16 eV (experimental) that has much lower intensity than adjacent peaks. The cross-section of 2*s* electrons is much lower than that of 2*p* electrons under He(I) irradiation, and the low intensity of the line is therefore consistent with high 2*s* character. We assign this peak and the corresponding peak in benzene to $2b_{1u}$; in the latter this is the alternating CH bonding level in which the carbon contribution is equally split between $2s_C$ and $2p_{RC}$ orbitals.

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TABLE 1

Calculated molecular orbital energies (eV)

	Pyridine[a]		Pyridazine[a]		Pyrimidine[a]		1,3,5-Triazine[a]		1,2,4-Triazine[a]		1,2,3-Triazine[a]
a_1	−426·37	a_1	−427·70	a_1	−427·07	e'	−427·79	a'	−428·36	a_1	−428·84
	−311·96		−312·35		−313·04		−313·90		−428·09		−428·21
	−311·40		−311·95		−312·60		−35·8		−427·59		−313·15
	−311·27		−38·8		−311·72		−27·4		−313·48		−312·40
	−35·85		−32·5		−38·0		−19·05		−313·12		−40·46
	−31·51		−25·4		−31·5		−13·50		−312·78		−33·14
	−24·95		−21·9		−25·7	a_1	−427·73		−39·74		−27·00
	−21·04		−20·9		−21·8		−313·88		−36·00		−21·88
	−19·11		−17·9		−19·5		−40·3		−32·89		−19·18
	−17·21		−14·7		−17·8		−23·0		−27·42		−16·91
	−12·46	b_2	−427·73		−14·2		−16·9		−26·27		−12·46
b_2	−311·96		−312·36	b_2	−427·07	a_2'	−22·2		−21·78	b_2	−429·25
	−311·28		−311·94		−312·60	a_2''	−19·3		−21·38		−313·16
	−30·18		−32·1		−34·5	e''	−14·4		−19·77		−35·13
	−24·61		−26·2		−26·1				−18·51		−26·70
	−19·70		−19·3		−20·7				−15·41		−21·44
	−18·24		−18·1		−18·05				−14·58		−18·65
	−15·91		−12·1		−12·75				−12·00		−13·14
b_1	−16·79	b_1	−17·8	b_1	−17·9			a''	−18·61	b_1	−18·67
	−12·42		−13·25		−12·9				−14·13		−13·73
a_2	−12·12	a_2	−12·85	a_2	−13·4				−13·45	a_2	−13·89

	1,2,4,5-Tetrazine[a]		1,2,3,4-Tetrazine[a]		1,2,3,5-Tetrazine[a]		Pentazine[a]		Hexazine[a]
a_{1g}	−429·23	a_1	−429·46	a_1	−429·50	a_1	−430·67	a_{1g}	−431·69
	−314·15		−429·13		−428·66		−430·49		−46·60
	− 41·8		−313·72		−428·04		−429·60		−22·57
	−27·7		−41·99		−314·17		−315·35		
	−22·3		−34·81		−41·26		−44·47	e_{2g}	−431·75
	−15·45		−28·36		−36·47		−37·80		−31·65
b_{2u}	−429·25		−22·39		−28·32		−29·40		−13·52
	−314·16		−22·02		−22·17		−22·72		
	−34·7		−17·67		−17·95		−19·70	e_{1u}	−431·72
	−21·1		−12·68		−15·81		−16·19		−41·09
	−15·7				−12·35		−13·96		−18·29
b_{3u}	−429·23	b_2	−429·49	b_2	−428·69	b_2	−430·68	b_{1u}	−431·76
	−38·7		−429·13		−314·22		−429·60		−17·32
	−22·7		−313·72		−35·70		−39·52	b_{2n}	−25·12
	−16·9		−37·54		−27·29		−30·08	a_{2u}	−22·34
b_{1g}	−29·5		−27·82		−22·02		−23·73	e_{1g}	−17·14
	−12·35		−19·85		−19·02		−17·30		
b_{1u}	−19·8		−16·78		−13·71		−12·25		
b_{3g}	−14·45		−13·36						
b_{2g}	−15·35	b_1	−19·58	b_1	−19·29	b_1	−21·02		
			−14·41		−14·37		−15·64		
		a_2	−14·93	a_2	−14·57	a_2	−16·05		

[a] The total energies (and binding energies) for each of these molecules are as follows: pyridine −245·7649 a.u. (−597·5 kcal mol^{-1}); pyridazine −261·6800 (−438·9); pyrimidine −261·6787 (−438·0); 1,3,5-triazine −277·5413 (−246·5); 1,2,4-triazine −277·6116 (−290·6); 1,2,3-triazine −277·5944 (−279·8); 1,2,4,5-tetrazine −293·4748 (−99·31); 1,2,3,5-tetrazine −293·5439 (−142·4); 1,2,3,4-tetrazine −293·5123 (−122·6); pentazine −309·3932 (+57·4); hexazine −325·3896 (+227·6).

comparison of the energy levels from various semi-empirical methods with the LCGO and experimental levels.

A least squares fit of the present minimal basis set (MB) and double ζ basis (DZ) calculations, symmetry by symmetry, leads to the orbital energy linear relationship DZ = 0·983MB − 1·6 eV with an average scatter of 0·3 eV. Thus it is clear that as far as orbital energy is concerned the results are effectively identical.* On the assumption that the calculated (MB and DZ) ordering is correct, the least squares fit for each of the two sets of data with the experimental IP values (data from Tables 3 and 5 of ref. 10) are (i) MB $\mathrm{IP}_{\mathrm{expt}} = 0{\cdot}785\mathrm{IP}_{\mathrm{calc}} + 0{\cdot}334$ eV with a standard deviation in slope and intercept of 0·01 and 0·20 eV respectively; (ii) DZ $\mathrm{IP}_{\mathrm{expt}} = 0{\cdot}760\mathrm{IP}_{\mathrm{calc}} + 2{\cdot}711$ eV with standard deviations as above of 0·01 and 0·23 eV respectively. The MB data are shown in Figure 3, and the scatter from molecule to molecule is effectively constant. In contrast the DZ data shows an increasing scatter from the least-squares fit line as the number of nitrogen atoms in the ring increases; thus for the latter calculations the number of points outside one standard

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* The effect of basis set on the orbital ordering is not important in furan and pyrrole,[3,16] thiophen,[17,18] pyrazine,[3b,19,20] or benzene[21] and we feel that the present LCGO ordering is substantially correct. Possible minor changes could be to interchange $1b_{2u}$ and $2b_{1u}$ in benzene and rearrangements in the group $1a_2$, $2b_1$ and $11a_1$ in pyridine, *etc.* The justification of the use of minimal basis sets of the present size in *initial* non-empirical calculations follows directly from these observations.

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deviation is C_6H_6, 2; C_5H_5N, 3; 1,2-$C_4H_4N_2$, 6; 1,3-$C_4H_4N_2$, 3; 1,4-$C_4H_4N_2$, 3; 1,3,5-$C_3H_3N_3$, 8; 1,2,4,5-$C_2H_2N_2$, 6 (with three points greater than two standard deviations from the line). The most obvious effect here is not an inadequate geometry of the higher azines (this point is also discussed below), because the same geometries were used in the present work.

For the semi-empirical calculations, the *best* least squares fit that can be obtained with the experimental levels is to assume that the ordering given by *each* of the methods is *correct*: of course not all of the methods and the LCGO calculations can be correct simultaneously. Thus the least squares fits for 77 points (benzene was omitted from these correlations) are as follows: (i) CNDO/2, $\mathrm{IP}_{\mathrm{expt}} = 0\cdot546\mathrm{IP}_{\mathrm{calc}} + 3\cdot710$ eV, with a standard deviation in the slope of 0·015 and intercept of 0·342 eV; (ii) INDO, $\mathrm{IP}_{\mathrm{expt}} = 0\cdot504\mathrm{IP}_{\mathrm{calc}} + 4\cdot987$ eV, with a standard deviation in the slope of 0·022 and intercept of 0·522 eV; (iii) EHM, $\mathrm{IP}_{\mathrm{expt}} = 1\cdot359\mathrm{IP}_{\mathrm{calc}} - 7\cdot485$ eV, with the standard deviation in the slope of 0·037 and intercept of 0·651 eV; (v) MIEHM [22] (including benzene, as in the LGGO correlations of 92 points) $\mathrm{IP}_{\mathrm{expt}} = 0\cdot596\mathrm{IP}_{\mathrm{calc}} + 5\cdot02$ eV, with the standard deviation in the slope of 0·023 and intercept of 1·573 eV. The average scatter of the points from the lines is: LCGO: 0·540 (MB), 0·466 (DZ); CNDO/2: 1·026; EHM: 1·05; MIEHM: 1·37; INDO: 1·69. The marked difference in slope between the EHM and other methods is immediately apparent; this arises from the choice of parameters giving results that are numerically similar to experiment in the 12—16 eV region, but considerably different at both ends of the observed region of energy. Furthermore, the orbital energies are very severely cramped in the outer valency shell; assignments are thus more uncertain, and even the primary groupings are difficult to define in some cases. The CNDO/2 and INDO procedures grossly exaggerate the spread of energy levels and are effectively identical in orbital ordering in most cases. One obvious feature of the latter methods is the shift of the strongly bonding π-orbital of nominal $1a_{2u}$ type to very high binding energy compared with the LCGO calculations; this is responsible for the major cross-overs in the orbital correlation diagram. It seems likely that this effect is due to the omission of the core

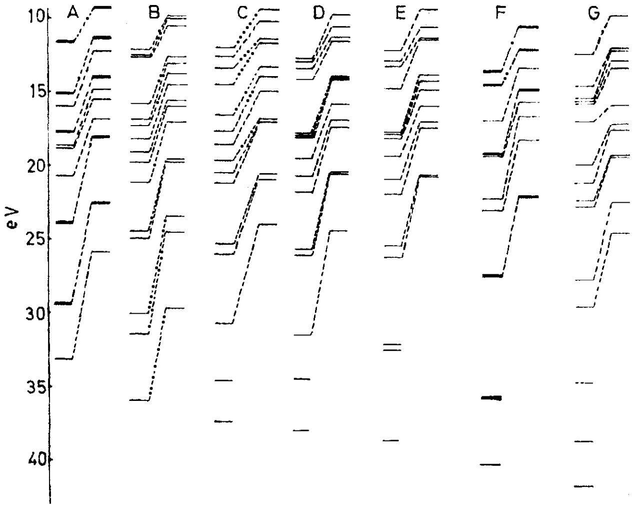

FIGURE 1 Correlation diagram of experimental and theoretical (LCGO–MB) ionisation potentials: A, C_6H_6; B, C_5H_5N; C, 1,4-$C_4H_4N_2$; D, 1,3-$C_4H_4N_2$; E, 1,2-$C_4H_4N_2$; F, 1,3,5-$C_3H_3N_3$; G, 1,2,4,5-$C_2H_2N_4$

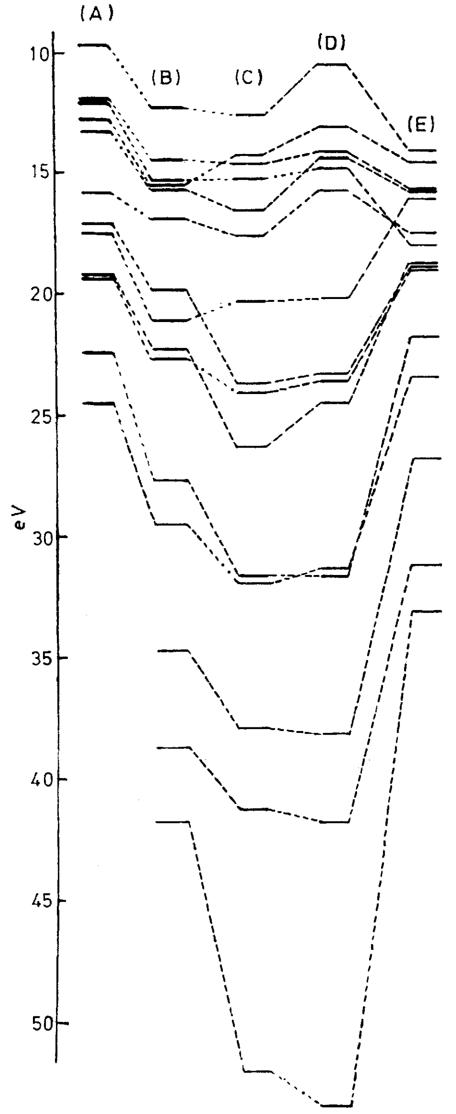

FIGURE 2 Correlation of experimental (A), LCGO–MB (B), CNDO/2 (C), INDO (D), and EHM (E) orbital energies in 1,2,4,5-tetrazine

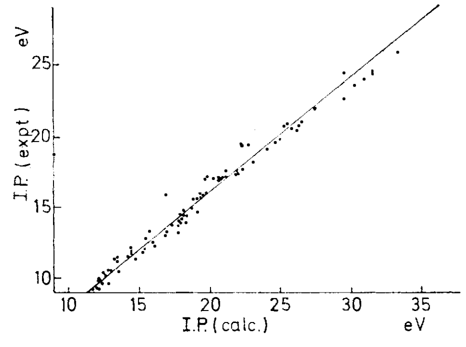

FIGURE 3 Correlation of experimental and theoretical (LCGO–MB) ionisation potentials

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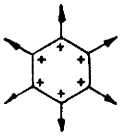
[22] E. Clementi, ' Tables of Atomic Functions,' Supplement to IBM Journal of Research and Development, 1965, vol. 9, p. 2.

levels and the reduction of the nuclear atomic numbers, so that the innermost σ- and π-levels become effectively pseudo-core levels.

DISCUSSION

Molecular Symmetry Orbitals.—The molecules $C_mH_mN_{6-m}$ vary in molecular point group, such that the only theoretically required similarity of the molecular wave functions is the σ–π separation, the highest common element of symmetry. However, a study of the eigenvectors for each of the molecules, with regard to sign rather than magnitude, and position of nodal planes, shows that the latter in particular have an apparent D_{6h} symmetry for all the series $C_mH_mN_{6-m}$. Thus all the molecular orbitals can be assigned to one of the types (7)—(13), with ± representing the sign of the atomic orbital in the wave-function of either the 1*s*, 2*s*, or 2*p* orbitals seen, for example, from above the molecular plane. The arrows represent either the radial ($2p_R$) or tangential 2*p* orbital ($2p_T$) which transform according to D_{6h}; the arrow head is taken here to represent conventionally the positive end of the 2*p* orbital. The C_{2v} molecules can be divided into two types, A, where the point group symmetry axis passes through the nuclear centres (C_5H_5N; 1,3-$C_4H_4N_2$; 1,2,3-$C_3H_3N_3$; 1,2,3,5-$C_2H_2N_4$ and CHN_5), and B, where it passes through bond midpoints (1,2-$C_4H_4N_2$; 1,2,3,4-$C_2H_2N_4$).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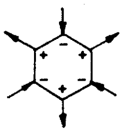
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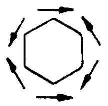
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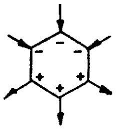
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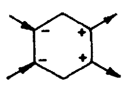
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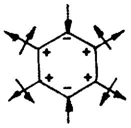
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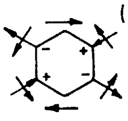
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Each molecule contains 42 electrons in 21 doubly occupied molecular orbitals in the ground state; these are divided between the benzenoid orbital types as follows: three each of a_{1g} (7), $e_{1u\text{A}}$ (10), $e_{1u\text{B}}$ (11), $e_{2g\text{A}}$ (12), $e_{2g\text{B}}$ (13), two of b_{1u} (8) and one of each of b_{2u} (9), a_{2u} (7), $e_{1g\text{A}}$ (12), and $e_{1g\text{B}}$ (13). The core levels (1*s* electrons) account for one each of the species (7), (8), and (10)—(13).

Correlation of the Theoretical Energy Levels.—To avoid undue repetition we now present some of the conclusions arising from detailed analysis of the effect of aza-substitution on the orbital energies. Although there is a shift to higher binding energy as the number of nitrogen atoms increases, we observe that the introduction of a nitrogen atom in $C_mH_mN_{6-m}$ can have a large, medium, or small perturbation upon any orbital energy in $C_{m-1}H_{m-1}N_{7-m}$.

The small perturbation occurs when a nitrogen atom is introduced on a nodal plane in an orbital; there is in general a non-zero transverse (tangential) $2p_T$ component at the nitrogen atom and these orbitals interact with the antisymmetric 2*s* or 2*p* orbitals on the adjacent centres, and thus can lead to an energy perturbation. For the inner valency shell orbitals of largely $2s_N$ or $2s_C$ character the tangential $2p_T$ components are small so that the effect is particularly small, and is *ca.* 0·6 eV per nitrogen atom introduced in the $2e_{1u\text{B}}$ (11) and $2e_{2g\text{B}}$ (13) orbitals.

The large and medium perturbations occur when the nitrogen atom is introduced in non-nodal positions either at the centre of the wave or adjacent to the nodal position. Thus for benzene the orbital coefficients at various positions (i) of $e_{1u\text{A}}$ (10) can be arbitrarily assigned as (i) = (1) 1·0, (2) 2·0, (3) 1·0, (4) −1·0, (5) −2·0, (6) −1·0 (unnormalised) for any 1*s*, 2*s*, or $2p_R$ orbital. Thus for this ring numbering the wave function has maximum amplitude at positions 2 and 5; introduction of nitrogen atoms at these positions leads to a large effect, since the electron-attracting property of the nitrogen atom supports the waves' natural tendency; the effect is seen to be 2·5 eV or more in most cases. For the other benzenoid orbitals, a_{1g} (7), b_{1u} (8), b_{2u} (9), and $e_{1g\text{A}}$ (12), all the orbital coefficients are equal, so that introduction of a nitrogen atom has only a medium effect (1·2 eV approximately).

Core Levels.—The core levels of N_{1s} and C_{1s} are heavily localised (eigenvectors >0·98) and show fairly monotonic shifts to higher binding energy as the number of nitrogen atoms increase across the series. The largest separations (1·4 eV) of the N_{1s} *and* C_{1s} levels occur in a pair of molecules of similar type, *e.g.* 1,2,3,5-tetrazine and pyrimidine where N and CH are effectively interchanged. Other pairs of molecules related in this way, and showing the same splits of C_{1s} *and* N_{1s} levels are pyridazine and 1,2,3,4-tetrazine (0·4 eV), 1,2,3-triazine (0·7 eV) and 1,2,4-triazine (0·4 eV). If this type of correlation could be extended to other series of molecules it would enable quite accurate prediction of the theoretical separation energies of core electrons. The experimental separations are likely to be smaller than the calculated ones, but gas-phase spectra would be necessary for significant comparisons.

π-Electron Energy Levels.—Although the $1e_{1g}$ benzene level is split in all the azines except hexazine and 1,3,5-triazine, the split is <2 eV in all cases; if a mean value of these pairs is taken then the $1e_{1g}$ and $1a_{2u}$ aza-analogues behave similarly. Furthermore these π-levels vary in an almost superimposable manner with the σ-aza-analogues of $3a_{1g}$, $2e_{2g}$, and $1b_{2u}$. In all these cases there is a largely monotonic shift to higher binding energy as the number of nitrogen atoms in the ring increases

Inner Valency Shell Orbitals $2a_{1g}$, $2e_{1g}$, *and* $2e_{2u}$ *and their Aza-analogues.*—The orbitals cover the range 7—11σ and are largely $2s_N$ and $2s_C$ in character. There are no nodes in 7σ ($2a_{1g}$ type) so that this is stabilised by all atoms in the ring; although the eigenvectors are larger at N than C in this series it is wrong to consider these as solely $2s_N$ levels; thus there is a progressive energy shift from benzene to hexazine and although the largest jump (2·8 eV) lies between benzene and pyridine, the separation of the free atom orbital energies is 6·52 eV in the Hartree–Fock limit,[22] so that considerable delocalisation is implied on energetic as well as eigenvector grounds.

The pseudo $2e_{1u}$ pair of orbitals, non-degenerate in all except benzene, 1,3,5-triazine, and hexazine, show similar energetic shifts from molecule to molecule as above if the mean value is taken, although pyridazine is an exception to this. This last point and the apparently capricious separation of the levels varying from 0·4 eV in pyridazine to 4·0 eV in 1,2,4,5-tetrazine can be explained in terms of the large and medium perturbations described above. Similar considerations apply to the variations of the $2e_{2g}$ levels with nitrogen substitution; the medium effect of a nitrogen atom is *ca.* $1{\cdot}2 \pm 0{\cdot}3$ eV, and the small effect in $2e_{2g\mathrm{B}}$ is *ca.* 0·6 eV. The substantially higher binding energy of $2b_{1g}$ (D_{2h}) in 1,2,4,5-tetrazine (an $2e_{2g\mathrm{B}}$ orbital) arises from the fact that this molecule is exceptional among the nearby molecules in having all four nitrogen atoms off the nodal planes and hence has a higher $2s_\mathrm{N}$ character than the other ones.

The entirely tangential orbitals of pseudo $1b_{2u}$ character show variations in energy with structure very similar to $2a_{1g}$ except that the binding energy rise per nitrogen atom is less. This is a natural consequence of the difference in orbital energies between $2s_\mathrm{N}$ and $2s_\mathrm{C}$ being 6·5 eV while that for $2p_\mathrm{N}$ and $2p_\mathrm{C}$ is 3·6 eV.

Outer Valency Shell Orbitals. CH *Bonding and Lone Pair Levels.*—The principal CH bonding levels in benzene are $3e_{2g}$, $3e_{1u}$, $2b_{1u}$, and $3a_{1g}$ although $3e_{2g}$ has *ca.* 50% tangential orbital character in benzene * itself. Replacement of $>$CH in benzene by $\geqslant$N: removes a CH bonding level and introduces a 'lone pair' level, characterised by very high coefficients of $2s_\mathrm{N}$ and $(2p_\mathrm{R})_\mathrm{N}$ in the molecular orbital. These orbitals clearly cannot be termed non-bonding since the first ionisation potential of any azine is >9 eV. Although the total populations in pyridine, pyrazine, and other molecules based upon a Mulliken population analysis show that the nitrogen atoms are overall effectively sp^2 hybridised, in the 'lone pair' orbitals the proportion of $2s$ to $2p$ varies sharply from molecule to molecule. Furthermore in the diazines (where the nitrogen atoms are labelled N_i and N_j) the two 'lone pair' levels ($\mathrm{N}_i \pm \mathrm{N}_j$) have quite different character, as has been noticed previously for pyrazine,[35] both in $2s:2p$ orbital population ratios and also in the extent of delocalisation. If the 'lone pair' orbitals were strictly localised on nitrogen then the distinction between $3e_{2g}$ and $3e_{1u}$ would disappear in several cases; for example $3e_{1u\mathrm{A}}$ (10) and $3e_{2g\mathrm{A}}$ (12) would both be the symmetric lone pair combination for pyrimidine. Thus the residual amounts of CH bonding character have enabled us to complete the correlation diagram Figure 4 without this loss of distinction between symmetry species. In Table 2 we record the calculated lone pair combinations together with their assignment in terms of benzene-like orbitals; in all cases it is clear that the orbitals have been filled in the order $3e_{2g} > 3e_{1u} > 2b_{1u} > 3a_{1g}$ and this is consistent with the orbital energies in benzene.

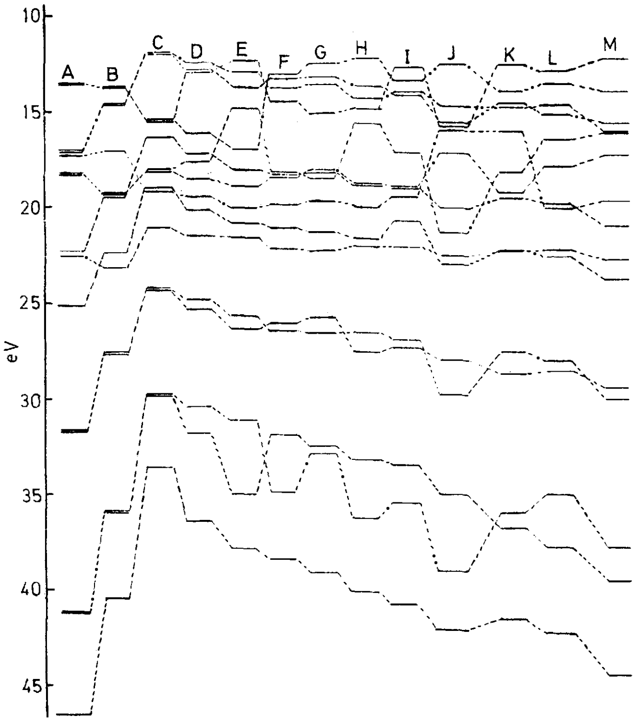

FIGURE 4 Correlation of the azine orbital energy levels with those of benzene: A, N_6; B, 1,3,5-$C_3H_3N_3$; C, C_6H_6; D, C_5H_5N; E, 1,4-$C_4H_4N_2$; F, 1,3-$C_4H_4N_2$; G, 1,2-$C_4H_4N_2$; H, 1,2,4-$C_3H_3N_3$; I, 1,2,3-$C_3H_3N_3$; J, 1,2,4,5-$C_2H_2N_4$; K, 1,2,3,5-$C_2H_2N_4$; L, 1,2,3,4-$C_2H_2N_4$; M, CHN_5

The most obvious feature in the lone pair orbitals of the diazines is that the antisymmetric combination lies to higher binding energy than the symmetric combination in pyrazine, but this order is reversed in the other two diazines. For pyrazine the $e_{2g\mathrm{B}}$ and $e_{1u\mathrm{B}}$ orbitals are nodal at the nitrogen atoms and hence cannot be lone pair orbitals; however, the lone pair combinations are satisfied by $e_{2g\mathrm{A}}$ and $e_{1u\mathrm{A}}$ and since e_{2g} lies to lower binding energy in benzene than e_{1u}, and aza-substitution is likely to have a similar effect in the two cases, the order of the lone pair orbitals is interpretable. For both pyrimidine and pyridazine the lowest binding energy benzene-like molecular orbitals available for the lone pairs are $e_{2g\mathrm{A}}$ and $e_{2g\mathrm{B}}$, *i.e.* a degenerate pair. In both molecules $e_{2g\mathrm{B}}$ has a node between the nitrogen

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* It has been suggested that the calculated order of binding energy in benzene $2b_{1u} < 3a_{1g}$ is incorrect, since the high concentration of $2s_\mathrm{C}$ character in the former (50%) is inconsistent with a CH bonding level above $3a_{1g}$ which is largely $1s_\mathrm{H}$ with $2p_\mathrm{R}$.[23] This point is not of immediate importance to the present discussion, but it is worth noting that the overlap integral between optimal $2s_\mathrm{C}$ and $1s_\mathrm{H}$ orbitals (0·60) in fact is greater than for $(2p_\mathrm{R})_\mathrm{C}$ with $1s_\mathrm{H}$ (0·50) at normal CH bond lengths.

[23] A. W. Potts, W. C. Price, D. G. Streets, and T. A. Williams, *Faraday Discuss. Chem. Soc.*, 1972, **54**, 168.

atoms so that they are unlikely to perturb the energy level as strongly as in the e_{2gA} series; thus the latter (the symmetric combination) are expected to lie to higher binding energy.

Several apparently anomalous lone pair combinations are explained similarly; thus in 1,2,4-triazine the symmetric combination ($N_1 + N_2 + N_4$) can only occur with $3a_{1g}$ whose binding energy is too high to be capable of supporting a lone pair combination of three nitrogen atoms. The same argument applies with 1,2,3,5-tetrazine where the $2b_{1u}$ analogue (N_2—N_5) replaces the symmetric $3a_{1g}$ type. It is interesting to note that both 1,2,4-triazine and 1,2,3,5-tetrazine behave like combinations of pyrazine and pyrimidine; the lack of pyridazine character in the former is repeated in 1,2,3,4-tetrazine in part, for it behaves like a combination of pyrazine and one pyridazine unit rather than two of the latter. This has been achieved by having two lone pair orbitals of similar character, largely $N_2 + N_3$, of symmetry e_{2gA} and e_{1uB}. They are non-degenerate owing to the small amount of ($-N_1 - N_4$) character in the former and different levels of CH content.

TABLE 2

Lone pair orbitals observed from the azines and their benzene equivalent symmetry orbitals

Pyridine $11a_1\ N_1\ (e_{2gA})$	Pyrazine $a_g\ N_1 + N_4\ (e_{2gA})$ $b_{2u}N_1 - N_4\ (e_{1uA})$	Pyrimidine $7b_2\ N_1 - N_3\ (e_{2gB})$ $11a_1\ N_1 + N_3\ (e_{2uA})$	Pyridazine $8b_2\ N_1 - N_2\ (e_{2gB})$ $10a_1\ N_1 + N_2\ (e_{2uA})$
1,2,3-Triazine $11a_1\ N_1 - N_2 + N_3\ (e_{2gA})$ $7b_2\ N_1 - N_3\ (e_{2gB})$ $10a_1\ N_1 + N_2 + N_3\ (e_{1uA})$	1,2,4-Triazine $18a'\ N_1 - N_2 + N_4\ (e_{2gB})$ $17a'\ N_2 + N_4\ (e_{2gA})$ $16a'\ N_1 - N_4\ (e_{1uB})$	1,3,5-Triazine $6e'\ 2N_1 - N_3 - N_5$ $N_3 - N_5$ $(e_{2gA,B})$ $5a_1'\ N_1 + N_3 + N_5$ $(2b_{1u})$	1,2,4,5-Tetrazine $3b_{1g}\ N_1 + N_4 + (N_2 - N_5)\ (e_{2gB})$ $6a_g\ (N_1 + N_2 + N_4 + N_5) - (C_3H + C_6H)\ (e_{2gA})$ $5b_{2u}\ (N_1 + N_5) - (N_2 + N_4)\ (e_{1uA})$ $4b_{3u}\ (N_1 + N_2) - (N_4 + N_5)\ (e_{1uB})$ $5a_g\ (N_1 + N_2 + N_4 + N_5) + (C_3H + C_6H)\ (a_{1g})$
1,2,3,4-Tetrazine $10a_1\ N_2 + N_3\ (e_{2gA})$ $8b_2\ N_2 - N_3\ (e_{2gB})$ $7b_2\ N_1 - N_4\ (e_{u1A})$ $9a_1\ N_2 + N_3\ (e_{1uB})$	1,2,3,5-Tetrazine $11a_1\ (N_1 + N_3) - (N_2 + N_5)\ (e_{2gA})$ $7b_2\ N_2 - N_3\ (e_{2gB})$ $10a_1\ N_2 - N_5\ (b_{1u})$ $9a_1\ (N_1 + N_2 + N_3) - N_5\ (e_{1uA})$	Pentazine $11a_1\ N_3\ (e_{2gA})$ $10a_1\ (N_1 + N_5) - (N_2 + N_4)\ (b_{1u})$ $7b_1\ (N_1 + N_4) - (N_2 + N_5)\ (e_{2gB})$ $6b_2\ (N_1 + N_2) - (N_4 + N_5)\ (e_{1uB})$	

The interaction between the lone pairs and the CH levels (which are of similar symmetry) is particularly obvious with 1,2,4,5-tetrazine where there are five levels high in lone pair character; of these $5a_g$ and $6a_g(D_{2h})$, separated by 6·8 eV, are the symmetric and antisymmetric combinations of ($N_1 + N_2 + N_4 + N_5$) with the symmetric ($C_3H + C_6H$) grouping. Although the effect is less marked, the symmetric lone pair combination ($N_1 + N_3 + N_5$) of 1,3,5-triazine shows similar evidence of interaction with the symmetric CH levels since the two orbitals $5a_1'$ (largely lone pair as described above) and $4a_1'$ (largely CH) are separated by *ca.* 6 eV, this and the separation in 1,2,4,5-tetrazine are the largest single separations of orbitals of the same symmetry in the outer-valency shell of the azines.

Molecular Total Energies.—Using the definition, binding energy (BE) = $E_{\text{mol}} - \Sigma E_{\text{atoms}}$ shows that all the azines except pentazine and hexazine are stable relative to atomisation; furthermore when the equation $(\text{BE})_{\text{exp}} = 0{\cdot}814(\text{BE})_{\text{calc}} - 708$ kcal mol^{-1}, established from the known heats of formation of certain azines is used we conclude that even pentazine and hexazine should be capable of existence, with 'experimental' binding energies of —660·3 and —521·7 kcal mol^{-1} respectively. However, a more realistic decomposition pathway for the azines is fragmentation to acetylene, hydrogen cyanide, or nitrogen; the question of whether this will occur depends upon (a) the transition state barrier to such a fragmentation and (b) the total energy of the azine ring relative to that of the sum of the fragments. The energy of the transition states for such processes are difficult to evaluate precisely, but an indication can be obtained from the energy of the appropriate Kekulé structures, where bond compression and extension along the co-ordinate for fragmentation has occurred. Based upon bond lengths C=C, C–C, C=N, C–N, N=N, N–N of 1·334, 1·485, 1·270, 1·445, 1·240, and 1·319 Å [24] we have calculated the total energy (E_{mol} in a.u.) of the Kekulé forms of benzene (14)

TABLE 3

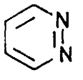
Fragmentary decomposition stabilities (kcal mol^{-1})

Molecule	No. of HCCH [a]	No. of HCN [b]	No. of N_2 [c]	$E_{\text{mol}} - E_{\text{atoms}}$
Benzene	3	0	0	−315·9
Pyridine	2	1	0	—215·1
Pyridazine	2	0	1	−162·6
Pyridazine	1	2	0	−112·1
Pyrimidine	1	2	0	−111·3
Pyrazine [d]	1	2	0	−33·2
1,2,3-Triazine	1	1	1	−59·1
1,2,4-Triazine	1	1	1	−69·9
1,2,4-Triazine	0	3	0	−19·41
1,3,5-Triazine	0	3	0	+24·69
1,2,3,4-Tetrazine	1	0	2	−8·3
1,2,3,4-Tetrazine	0	2	1	+42·22
1,2,3,5-Tetrazine	0	2	1	+22·43
1,2,4,5-Tetrazine	0	2	1	+65·78
Pentazine	0	1	2	+116·29
Hexazine	0	0	3	+180·61

[a] Total energy = −76·447566 a.u. [b] Total energy = −92·526893 a.u. [c] Total energy = −108·52582 a.u. [d] Clementi's pyrazine and above fragments.

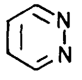
(14)

E_{mol} -229·83580



(15)

E_{mol} -261·67028



(16)

E_{mol} -261·66702 (a.u.)

and the two pyridazine species (15) and (16). The compression + extension energies are 6·5 (1), 6·1, and 8·2 kcal mol^{-1}.

We have not pursued this method throughout the azines owing to the difficulties in determining an adequate geometry for all the systems, where small variations could be important with small energy differences. Direct calculation of the resonance energy is not possible by our present procedure since we have no method of avoiding an interaction between the classical double bonds.

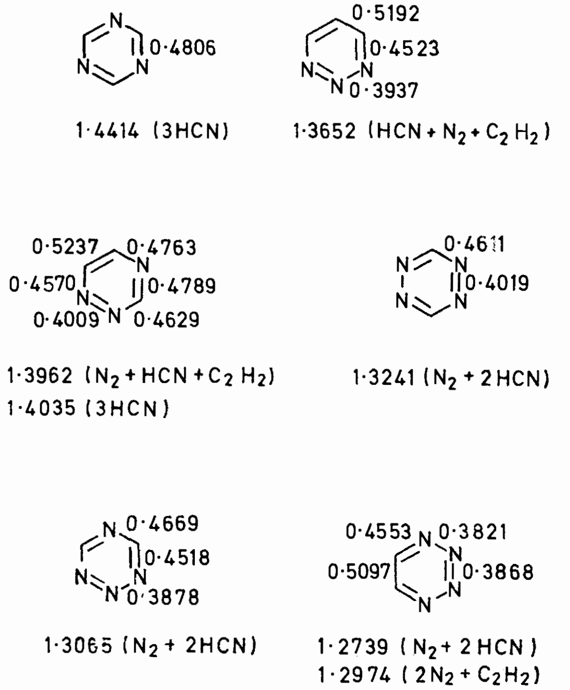


FIGURE 5 Overlap populations and fragmentation paths

Another approach to estimating the energy barrier to fragmentation is to consider the total overlap population (Figure 5) lost during the competing fragmentation processes, using the basis that overlap populations are related to bond strength. On both these bases it seems probable that only 1,2,3-triazine of the unknown molecules will prove to be stable. It is worth noting that 1,3,5-triazine which is thermodynamically unstable with respect to decomposition to hydrogen cyanide has the highest overlap population to be broken for fragmentation to occur; 1,3,5-triazines are usually made by the reverse to this fragmentation path, but only at high temperatures and pressures.[25] 1,2,4,5-Tetrazine is stable at normal temperatures, but is highly reactive, undergoing Diels–Alder-type additions across the 3,6-bonds. In thermal retro-Diels–Alder reactions these products readily liberate nitrogen rather than regenerate the tetrazine.

[3/2517 *Received*, 10*th December*, 1973]

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[24] M. J. S. Dewar and G. J. Gleicher, *J. Chem. Phys.*, 1966, **44**, 759.

[25] M. H. Palmer, 'The Structure and Reactions of Heterocyclic Compounds,' Arnold, London, 1967, pp. 94 and 102.