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THE MOLECULAR ENERGY LEVELS OF THE AZOLES: A STUDY BY PHOTOELECTRON SPECTROSCOPY AND AB INITIO MOLECULAR ORBITAL CALCULATIONS

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Abstract—HeI photoelectron spectroscopy and *ab initio* calculations have been applied to the azoles, providing sets of energy levels that correlate well with each other in the upper valence shell region. Observed IPs are assigned to the three π- and to the five σ-levels that involve (principally) valence shell *p* orbitals. The observed vibration structure is not particularly informative as an aid to assignment since both π- and σ-levels give some bands with vibration structure. The calculations provide in addition to eigenvalues (energy levels) a set of eigenvectors, permitting analysis of the bonding characteristics of the levels, and trends apparent within the series.

The photoelectron spectrum of pyrrole has been reported by several authors;[1-3] while there is general agreement on the assignment of the two isolated bands at lowest ionisation potential (IP) to two of the π-levels, there has been no completely convincing assignment to either the third π- or the σ-levels. Lindholm[3] has arrived at a spectroscopically parameterized set of calculated energy levels for pyrrole (SPINDO) which fits the observed spectra well; our non-empirical calculations (containing no adjustable parameter beyond those necessary to specify the atom involved) suggest that this is fortuitous, since some band assignments are incorrect. One of us[2] has attempted to perform these assignments by comparison of pyrrole with furan and 1,2,5-oxadiazole, and with *ab initio* molecular orbital calculations, but the results were not entirely satisfactory. The present work attempts to extend and clarify knowledge of pyrrole (**1**) by similar calculations for the azoles (**2**–**6**) and by HeI photoelectron spectroscopy. Spectra for pyrrole and pyrazole (**3**) agree with those previously published, but interpretations differ in several significant points; no data on the remaining azoles have been published to date.

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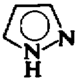

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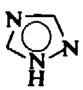

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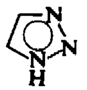

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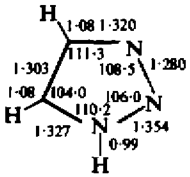

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INSTRUMENTAL PROCEDURES

Photoelectron spectra of gas phase samples were recorded using a Perkin Elmer PS16 spectrometer. The instrument resolution was approximately 30 meV for bands near 10 eV. Pyrrole was admitted through a volatile sample manifold, the pressure being controlled by a needlevalve; the samples **2**–**6** were introduced *via* a direct insertion probe in the temperature range 25–75°, the lowest temperature to give a satisfactory spectrum being used. The energy scale was calibrated by means of the sharp peaks arising from water (12·62 eV) and argon (15·75, 15·93 eV). The samples were either commercial materials or prepared by standard procedures; for high resolution gas phase infra-red spectra (Perkin Elmer 225), pyrrole was purified by distillation and by low temperature fractional crystallisation. Raman spectra were recorded on a Cary 83 spectrometer with 4880 Å (Ar^+) excitation.

CALCULATIONS

In order to provide comparability with earlier work on heteroaromatic compounds, the *ab initio* calculations used a best-atom* minimal basis set consisting of seven s-type and three p-type (for each p_x, p_y, p_z) gaussian functions

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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 $H(^1S) - 0{\cdot}4970$ au, $C(^3P) - 37{\cdot}6104$ au, $N(^4S) - 54{\cdot}2754$ au, which may be compared with the Hartree-Fock limiting values of $-0{\cdot}5000$, $-37{\cdot}6886$, $-54{\cdot}4009$ au respectively.[5]

for carbon and nitrogen and three of s-type for hydrogen. The functions were contracted to 1s (five functions) 2s (two functions) and 2p (three functions) for carbon and nitrogen and one for hydrogen. The calculations were performed using the programme IBMOL-4 on IBM360/195, 360/50 and 370/155 computers; initially delocalised molecular orbitals were obtained, which show the degree of localisation of the 2s levels (see below). The basis integrals were then converted, by Coulson's method,[4] to hybrid orbitals about the ring atom centres, with orbitals pointing along each bond, or bisecting the exterior angle for lone pairs. Bond orbitals were obtained by taking linear combinations of the hybrid orbitals or hybrid and hydrogen 1s orbitals as appropriate in the symmetry transformation part of the programme. This transformation has no effect upon the total energies, eigenvalues or density matrix. The eigenvalues are shown in Table 3 and in graphical form in Fig. 1.

In these calculations the recent microwave structure for pyrrole[6] was used, while imidazole (**2**),[7] pyrazole (**3**)[8] and 1,2,4-triazole (**4**)[9] and tetrazole (**6**)[10] were represented by their crystal structures or the 5-amino derivative in the last case. The 1,2,3-triazole geometry was based upon general experience of lengths in heterocyclic molecules and is shown above (**5a**).

CORRELATION OF EXPERIMENTAL WITH CALCULATED VALUES

In all cases the inner valency shell orbitals up to 9a′ in **2** to **6** are predominantly 2s-type as can be seen from the eigenvector matrix in delocalised orbitals. The orbitals 9a′ to 11a′ are largely sp^2 hybridised bonding orbitals from the ring atoms to each other or to the hydrogen atoms. The orbitals above 11a′ in **2** to **6** are dominated by two types of bonding: (a) solely p-orbital contributions to ring bonding and/or CH and NH bonding; (b) lone pair orbitals from 15a′ downwards. The last type, effectively sp^2 hybrid orbitals, occur in symmetric and antisymmetric combinations (14a′ and 15a′) for the triazoles, while 1,2,3,4-tetrazole shows three lone pair levels in the form of a pseudo C_3 rotation group with A_1 (13a′) and E type orbitals (14a′ and 15a′). These generalisations are amplified below but they enable us to correlate the experimental and theoretical data in two ways: (a) by direct use of Koopmans' theorem and the assumption of a linear correlation, but better by (b) using the calculated values to estimate the experimental band intensity. Thus the cross section for HeI (584 Å) stimulated emission of electrons in 2p levels is greater than that for 2s electrons; this means that the π- and other outer valency shell orbitals rich in p-orbital character (11a′) etc. should be stronger than the "lone pair" and inner valency shell orbitals which have higher s-orbital character.

The observed spectra up to about 20 eV may be separated into three distinct regions (A, B and C), Figs 3, 4 and Table 2. Region A, which extends from 8–10 eV in pyrrole, moves to higher binding energy as nitrogen atoms are substituted for CH groups, and is at 10–14 eV in tetrazole. It contains two or three more or less separated bands, some or all of which show resolved vibrational structure. Region B begins some 2 eV to higher binding energy than region A for each molecule, and contains a set of strong overlapping bands with no resolvable fine structure. It extends over about 3 eV for pyrrole, reducing gradually to about 1·5 eV for tetrazole. Region C consists of a single band of moderate intensity and no vibrational structure, with vertical I.P. 17·5–18 eV and with a downward trend from pyrrole to tetrazole. Lindholm[3,11] has observed a group [Region (D)] of bands in the range 19–26 eV for HeII irradiated cyclopentadiene, pyrrole, furan and thiophene.[11] Those of this group which are accessible to HeI are much weaker to HeI than to HeII excitation, and it is plausible on cross-section grounds, and indeed on the grounds of the calculations reported here, to assign five σ(a′) levels to the 2s orbitals in this region D. For the molecules with one or two nitrogen atoms there is comparatively little delocalisation of $2s_N$ with $2s_C$, $2p_C$ or $2p_N$; this can be understood in terms of the free atom orbital energies which in the Hartree Fock limit are $2s_N$ (^4S) 25·72, $2s_O$ (^3P) 19·20, $2p_N$ (^4S) 15·44, and $2p_C$ (^3P) 11·79 eV, respectively.[5] For

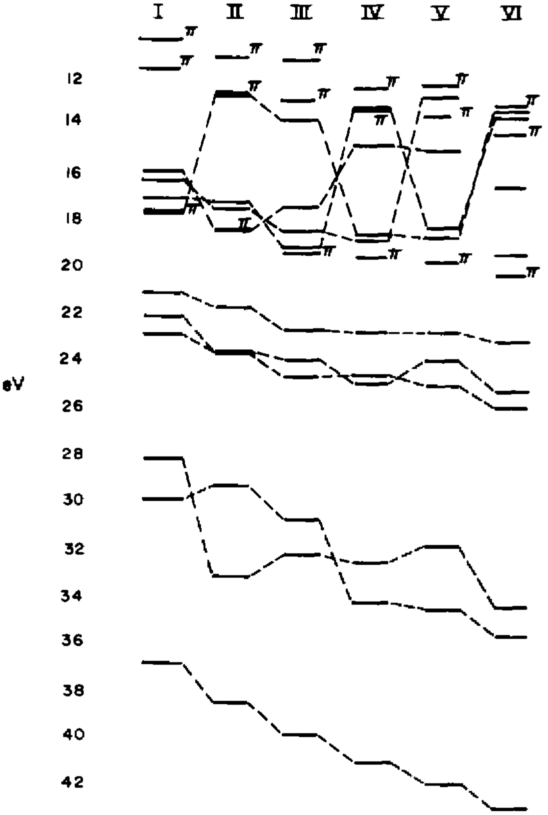


Fig 1. Correlation diagram for theoretical energy levels in the azoles **1** to **6**.

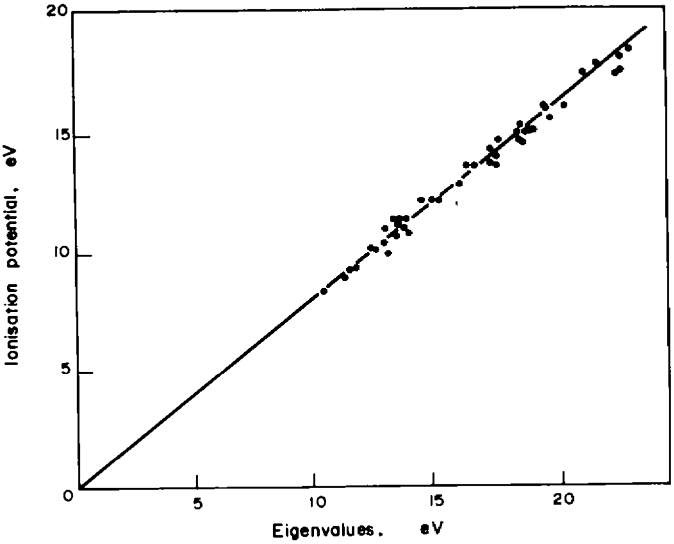


Fig 2. Correlation of observed ionisation potential and eigenvalues.

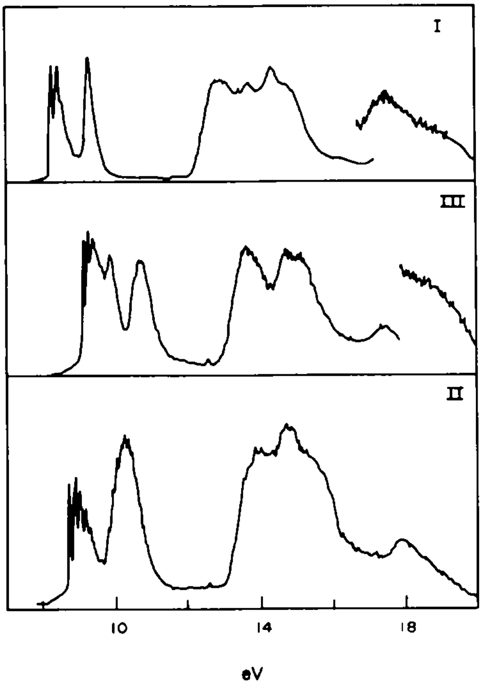


Fig 3. HeI photoelectron spectra of pyrrole (1), imidazole (2) and pyrazole (3).

molecules with three nitrogen atoms, splitting of the atomic $2s_N$ levels on molecule formation leads to the overlap of $2s_N$ and $2s_C$ levels and hence very delocalised orbitals; this is clearly observed in the 6a′–8a′ levels of 1,2,3-triazole. We may thus conclude that eight valency shell orbitals, five σ(a′) and three π(a″), remain to be assigned in the present investigation. In practice we observe 5, 6 or 7 bands

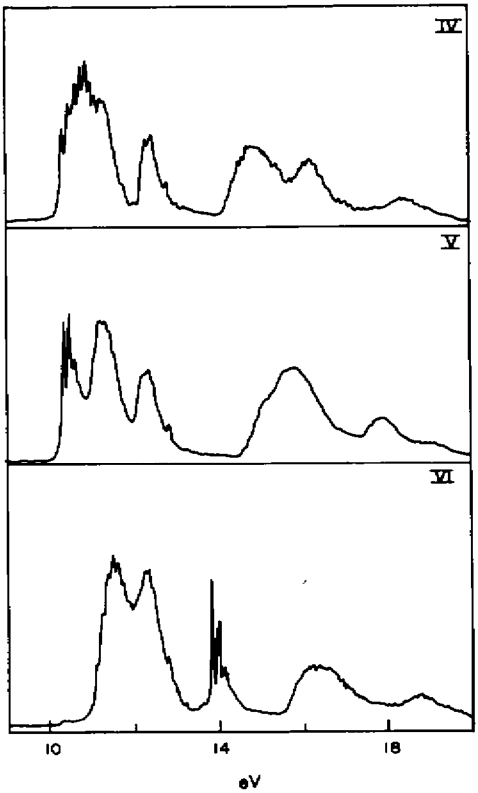


Fig 4. HeI photoelectron spectra of 1,2,4-triazole (4), 1,2,3-triazole (5) and 1,2,3,4-tetrazole (6).

so that some overlapping is occurring. Our calculations confirm the anticipated effect of substitution of CH by N in the ring, transforming one σ-level from largely $\geqq$C—H bonding to $\geqq$N: lone pair character. The binding energy of the orbital in this substitution will thus be markedly decreased, while the reverse tendency should occur with the other orbitals owing to the general effect that an increase in nuclear attraction leads to a lowering of the eigenvalues. These effects are found to occur; while pyrrole has two clearly separated bands in Region A, pyrazole has three and 1,2,4-triazole has four (two of which overlap considerably). Region B correspondingly shrinks in width and overall intensity, while Region C is unaffected except for the expected shift to higher binding energy.

The assignment of this single level in Region C to $7a_1$ in pyrrole and $11a'$ in the azoles is a key step in the overall assignment. It is based upon the observation that it is well separated from the other bands, has moderately high intensity and hence largely p-orbital character; the calculations show that a band is expected to occur in this region which derives largely from p-orbital components from the ring atoms towards the hydrogens of the α-positions with respect to the NH group. The seven outstanding bands in regions A and B combined can then be divided on experimental intensity and calculated groupings to be in the following ratios (A:B): pyrrole, 2:5; diazoles, 3:4; triazoles, 4:3; tetrazole, 5:2. Region A contains $2\pi + (n-1)\sigma$ levels, where n is the number of ring nitrogen atoms. The calculations suggest that in all the compounds studied, the $1a_2(3a'')$ π-level is the least strongly bound; assigning the first band in each spectrum to this level and the band near 18 eV to $7a_1$ ($11a'$) suggested that the ratio of observed IP to calculated eigenvalue was consistently about 0·81. The whole set of 48 points were then plotted as a graph of observed IP against calculated eigenvalue (Fig 2), using the intensity ratios of the regions A and B and assuming that the calculated orbital ordering was correct. The two sets of data correlate well, the best straight line having a slope of $0{\cdot}799 \pm 0{\cdot}023$, while the maximum deviation from the line is 0·6 eV and the standard deviation is 0·4 eV. Bearing in mind the uncertainties in the geometries used for some of the molecules and the limited size of basis set, this is an excellent correlation and justifies the assumption that the ordering of the energy levels is correctly calculated. The third π level ($1a''$; $1b_1$ for pyrrole) may be assigned to the *high* IP end of region B, as suggested by the calculations, rather than to the low IP end, as assigned by Lindholm for pyrrole. No distinct band appears for this level in any of the compounds in the present study.

Vibrational structure

As mentioned earlier, only bands in region A (upper π and N lone pair levels) show vibrational structure. We find two modes excited in the first band of pyrrole, and these have frequencies of $1020 \pm 40\ \mathrm{cm}^{-1}$ and $1370 \pm 40\ \mathrm{cm}^{-1}$; we assign these two modes to the skeletal stretching frequencies of A_1 symmetry which are at 1148 cm^{-1} and 1472 cm^{-1} in the ground state molecule, thus suggesting a reduction of about 10% in the frequencies for the ion. Lindholm,[12] using H Lyman α (1215 Å) excitation and higher resolution, observed four vibrational modes for this band, two of which correspond with our modes. However, we do not agree with his assignments of these bands to those at 1017 cm^{-1} and 1387 cm^{-1} in the free molecule, since it seems unlikely that removal of a bonding electron would leave the molecular vibrational frequencies essentially unchanged. Furthermore it is clear that both the published assignment[13] of the vibrational spectrum of pyrrole and Lindholm's reassignment are incorrect, since the line at 1387 cm^{-1} appears only in the spectrum of *liquid* pyrrole and not in its gas phase spectrum.

Imidazole, 1,2,4-triazole and 1,2,3,4-tetrazole also give bands containing two vibrational modes, which again appear singly and in combination; in the last case all of the combinations up to $3a + 2b$ (where a and b are the apparent fundamentals) occur. The magnitudes of the two fundamentals, which are given in Table 2 are similar to those found in pyrrole, and we feel it is likely that they may be assigned to the two most symmetric skeletal stretching modes in each case.

In 1,2,3-triazole, as in the second band of pyrrole, only one vibrational mode appears to be excited, though a short progression appears. In pyrazole a more complex pattern appears with three or possibly four modes excited. The lowest frequency, of 660 cm^{-1}, does not correlate well with the A_1 frequencies of pyrrole, the lowest of which is at 882 cm^{-1}. We propose that an in-plane deformation mode may be involved, but in the absence of a complete assignment of the vibrational spectrum of pyrazole, this remains to be confirmed. The third band of tetrazole shows two fundamentals, and is the only band in this set of molecules to be assigned solely to a nitrogen lone pair in-plane level. The higher frequency mode has an energy (1470 cm^{-1}) very close to that expected for an unaltered skeletal stretching vibration, found for instance at 1472 cm^{-1} in the pyrrole ground state molecule.

Detailed description of the molecular orbitals

(i) *Core levels.* The orbitals $1a'$ to $5a'$ (2 to 6) and $1a_1$ to $3a_1$ with $1b_2$ and $2b_2$ (pyrrole, 1) are highly localised 1s levels (eigenvectors about 0·98). The nitrogen atom attached to hydrogen (N_1 in all cases) has the highest binding energy while a nitrogen atom in the α-(2,5-) positions is more strongly bound than one in the β-(3,4-) positions. The carbon 1s levels move smoothly to higher binding energy as more nitrogen atoms are incorporated into the rings. The separation of the levels calculated here (Table 3) is likely to be larger than experiment, and this can be largely explained by the limited size of

Table 1. Vertical ionisation potentials (eV) and assigned energy levels

1		2		3		4		5		6		Regions
8·23	$1a_2$	8·78	3a″	9·15	3a″	10·0	3a″	10·06		11·3	3a″ 15a′ 14a′	A
9·22	$2b_1$	10·3	2a″ 15a′	9·88	2a″	10·56	15a′		15a′ 2a″			
				10·7	15a′	11·1	2a″	10·9				
						12·15	14a′	12·1	14a′	12·1	2a″	
12·85	$9a_1$									13·63	13a′	
13·65	$6b_2$	13·7	14a′	13·6	14a′ 13a′							
14·3	$5b_2$	14·0	13a′			14·6	13a′	15·0	13a′ 12a′			
14·7	$8a_1$ $1b_1$	14·7	1a″	14·7	1a″	15·1	12a′			16·1	12a′ 1a′	B
		15·3	12a′	15·1	12a′	16·0	1a′	15·6	1a″			
17·5	$7a_1$	17·9	11a′	17·5	11a′	18·2	11a′	17·6	11a′	18·5	11a′	C

Table 2. Vibration frequencies excited in spectra of azoles 1–6

Azole	1		2		3	4			5		6		Suggested assignment
Band	1	2	1	2	1	1	2	3	1	2	1	3	
					82 (660)								In-plane deformation?
	126 (1020)	125 (1010)	120 (970)	100 (810)	112 (900)	130 (1050)	130 (1050)	110 (900)	131 (1060)	120 (970)	100 (810)	123 (1000)	"Breathing" vibration
	170 (1370)		163 (1320)	140 (1130)	130 (1050)	147 (1190)					145 (1170)	182 (1470)	Symetric skeletal stretch

Note. These figures represent a plausible choice of fundamentals in each case sufficient to explain the observed patterns, which include up to 12 peaks. In each case all observed peaks can be explained as combinations of the fundamentals listed. The units are meV (values in cm^{-1} in brackets).

the basis set. Gas phase measurements would be necessary for comparison since the molecules form hydrogen bonded polymers in the solid state.

The molecules **1–6** are aza-analogues of the cyclopentadienyl anion (D_{5h} symmetry), but of lower symmetry (C_{2v} for **1**, C_s for the others **2–6**). The splitting of the cyclopentadienyl anion e_1' and e_2' levels in the series **1–6** is comparatively small being typically 0·6 and 0·4 eV respectively in the orbitals $6a_1/4b_2$ and $8a_1/5b_2$ for pyrrole, 9a′–12a′ for **2–6**. However, attempts to correlate the orbitals of the azoles **2–6** directly back to the cyclopentadienyl anion by the use of radial and tangential orbitals in D_{5h} are unsuccessful; an analysis based upon the C_{2v} system of pyrrole is much more successful and is shown in Fig 1. Thus there is an apparent C_2 axis for each molecule and the linear combinations of bond orbitals are either symmetric or antisymmetric with respect to this axis; of course the correlation is only in sign of the wave function and not in the magnitudes of the eigenvectors. For example the "lone pair" orbitals in the triazoles 14a′ and 15a′, are linear combinations of approximately sp^2 hybrid orbitals centred at the tertiary nitrogens (N_A, N_B) and are of form $N_A \pm N_B$. The interaction energy in the 1,2,3-isomer is greater (2·3 eV) than in the 1,2,4-isomer (1·6 eV) owing to the closer proximity in the former case. Similarly for tetrazole (Table 4) there is a pseudo A_1 ($N_A+N_B+N_C$) type (13a′) and E ($2N_A-N_B-N_C$, N_B-N_C) types (14a′, 15a′). This dominance of the outmost σ-orbitals of the azoles by the nitrogen atoms both in the eigenvectors and the siting of the "C_2 axis" is apparent in the inner valency shell also. The NH σ-bond is not evident among the largely 2s levels, thus the position of the C_2 axis is determined purely by the siting of the nitrogen atoms rather than whether they are formally ⩾N or >NH: as an example we cite (Table 5) the orbitals 6a′ to 8a′ for pyrazole which is largely $2s_N+2s_C$ and conform to the A_1+E of the cyclopentadienyl anion, or $4a_1+5a_1+3b_2$ for pyrrole. The only example in this group 6a′ to 8a′ where the nodal position is not determined purely by symmetry with respect to the siting of the nitrogen atoms is in 1,2,3-triazole, where the division is into bonding regions CC + NN (8a′) and CN + CN N (7a′) rather than 2CN (8a′) and CC + NNN (7a′). The two separately strongly NN bonding regions obtained are evidently more favourable than the NNN system. The large split in the pseudo degenerate pair is much larger for 1,2,3-triazole (2·71 eV) and imidazole

Table 3.1. Pyrrole (1)

Eigenvalue (eV)	Principal character	Centres/bond orbitals
a_1		
−427·9	1s	N
−311·0	1s	C_α^+
−309·8	1s	C_β^+
−36·95	2s	$N^+, (C_\alpha + C_\beta)^+$
−30·01	2s	$C_\beta^+, -N$
−22·93	2s	$C_\alpha N^+$
−21·29	$2p_{C\alpha\beta}, 1s_H$	$C_\alpha H^+, C_\beta C_\beta$
−17·68	$2p_{C\alpha\beta}, 2p_N, 1s_H$	$NH, C_\alpha C_\beta^+$
−16·02	$2p_{C\beta}, 1s_H$	$C_\beta H^+, C_\beta C_\beta$
b_2		
−311·0	1s	C_α^+
−309·8	1s	C_β^-
−28·27	$2s_{C\alpha\beta}, 2p_N$	$C_\alpha C_\beta^- + C_\alpha N^-$
−22·23	$2s_{C\beta}, 2p_{yC\alpha}, 2p_{xN}$	$C_\alpha C_\beta^- - C_\alpha N^-$
−17·31	$2p_{xC}, 1s_H$	$C_\alpha H^-$
−16·37	$2p_{xC}, 2p_{yC\beta}, 1s_H$	$C_\beta H^-, C_\alpha C_\beta^-$
b_1		
−17·69	$2p_{zCN}$ ("A")	$N + C_\alpha C_\beta^+$
−11·65	$2p_{zCN}$ ("E")	$-N, C_\beta C_\beta$
a_2		
−10·34	$2p_{zC}$ ("E")	$C_\alpha C^-$

Table 3.2. Imidazole (2)

Eigenvalue (eV)	Principal character	Centres/bond orbitals
a'		
−428·3	1s	N_1
−425·5	1s	N_3
−312·1	1s	C_2
−311·5	1s	C_5
−310·9	1s	C_4
−38·69	$2s_{N,C}$ ("A")	N, C
−33·31	$2s_{N,C}$ ("E")	$C_5N_1 - C_4N_3$
−29·39	$2s_{N,C}$ ("E")	$C_4C_5, N_3C_2N_1H$
−23·79	$2s_{N,C}, 2p_{N,C}, 1s_H$	NH, CN
−23·71	$2s_{N,C}, 2p_{N,C}, 1s_H$	$C_4H - C_5H$
−21·84	$2s_{N,C}, 2p_{N,C}, 1s_H$	$C_2H + C_5H$
−18·59	$2p_{N,C}, 1s_H$	C_4C_5, NH
−17·60	$2p_{N,C}, 1s_H$	$C_2N_1C_5, C_2H - C_5H$
−17·33	$sp^2, 1s_H$	$C_2H - C_4H, C_2N_3C_4$
−12·83	sp^2	N_3
a''		
−18·57	$2p_z$ ("A")	N, C
−12·71	$2p_z$ ("E")	CN^-
−11·17	$2p_z$ ("E")	CC, NCN

Table 3.3. Pyrazole (3)

Eigenvalue (eV)	Principal character	Centres/bond orbitals
a'		
−429·7	1s	N_1
−426·9	1s	N_2
−312·2	1s	C_5
−311·5	1s	C_3
−310·6	1s	C_4
−39·95	2s ("A")	N, C
−32·32	2s ("E")	$N_1C_5 - N_2C_3$
−30·81	2s ("E")	$C_3C_4C_5 - N_1N_2$
−24·77	$2p, 1s_H$	$NH + C_3H$
−24·07	$2p, 1s_H$	$C_3H + C_5H - C_4H$
−22·79	$2p, 1s_H$	$C_5N_1, C_4H + C_5H$
−19·24	$2p, 1s_H$	$NH - C_3H$
−18·59	$2p, 1s_H$	$C_4H - C_5H$
−17·58	$2p, 1s_H$	$C_4C_5 - C_3C_4$
−13·84	sp^2	N_2
a''		
−19·15	$2p_z$ ("A")	N_1, C
−13·01	$2p_z$ ("E")	$N_2C_3C_4 - N_1C_5$
−11·32	$2p_z$ ("E")	$N_1N_2 - C_2C_3$

Table 3.4. 1,2,4-Triazole (4)

Eigenvalue (eV)	Principal character	Centres/bond orbitals
a′		
−429·5	1s	N_1
−427·5	1s	N_2
−426·2	1s	N_4
−313·1	1s	C_5
−312·1	1s	C_3
−41·13	2s ("A")	$N_1+N_2+N_3, C_3+C_5$
−34·40	2s ("E")	$N_1N_2-C_5N_4C_3$
−32·73	2s ("E")	$C_5N_1-C_3N_2$
−25·07	2s 2p $1s_H$	$C_5H+N_1N_2+C_3N_4$
−24·68	2s 2p $1s_H$	C_3H+NH
−22·90	2s 2p $1s_H$	$C_5H+N_1C_5N_1$
−19·02	2p	$N_2C_3N_4$
−18·76	2p	C_3H+CN
−14·92	sp^2	N_2+N_4
−13·34	sp^2	N_2-N_4
a″		
−19·72	$2p_z$ ("A")	$N_1+N_2+N_4+C_3+C_5$
−13·42	$2p_z$ ("E")	$N_1-C_3N_4$
−12·50	$2p_z$ ("E")	$C_3N_2-N_4C_5$

Table 3.5. 1,2,3-Triazole (5)

Eigenvalue (eV)	Principal character	Centres/bond orbitals
a′		
−429·4	1s	N_1
−428·2	1s	N_2
−427·0	1s	N_3
−312·5	1s	C_5
−311·5	1s	C_4
−42·03	2s ("A")	$N_1+N_2+N_3$
−34·69	2s	N_1-N_3
−31·98	2s	$N_2-(C_4+C_5)$
−25·18	2s 2p $1s_H$	NH, N_3C_4, C_4C_5
−24·09	2s 2p $1s_H$	$NN+CN, C_4H-C_5H$
−22·85	2p $1s_H$	CN, C_4H+C_5H
−18·85	2p $1s_H$	$C_4C_5, NH-C_5H$
−18·47	2p $1s_H$	C_4H, CN
−15·16	sp^2	N_3+N_2
−12·81	sp^2	N_3-N_2
a″		
−19·90	$2p_z$	$N_1+N_2+N_3+C_4+C_5$
−13·71	$2p_z$	$N_3C_4-N_1C_5$
−12·35	$2p_z$	$(N_1+N_2+N_3)-(C_4+C_5)$

Table 3.6. 1,2,3,4-1H-Tetrazole (6)

Eigenvalue (eV)	Principal character	Centres/bond orbitals
a′		
−429·7	1s	N_1
−429·0	1s	N_2
−428·0	1s	N_3
−427·0	1s	N
−313·8	1s	C_5
−43·09	2s ("A")	$N_1+N_2+N_3+N_4, C_5$
−35·80	2s ("E")	$N_2+N_3-2N_4$
−34·55	2s ("E")	$N_1+N_2-(N_3+C_5)$
−26·08	2s 2p $1s_H$	NH
−25·35	2s 2p $1s_H$	$N_1N_2+C_5H$
−23·26	2s 2p $1s_H$	C_5H+CN
−19·56	2p	$N_1N_2N_3N_4$
−16·70	sp^2 ("A")	$N_2+N_3+N_4$
−13·73	sp^2 ("E")	N_2-N_4
−13·50	sp^2 ("E")	$2N_3-N_2-N_4$
a″		
−20·46	$2p_z$ ("A")	$N_1+N_2+N_3+N_4+C_5$
−14·47	$2p_z$ ("E")	$N_1C_5-N_2N_3N_4$
	$2p_z$ ("E")	$N_1N_2-C_5N_4$

Table 4. Tetrazole lone pair orbitals

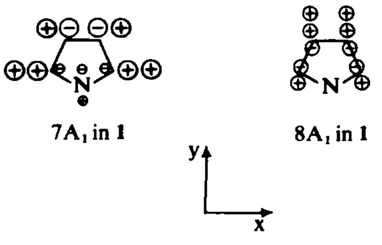
15a′	$-0{\cdot}822\,N_3+0{\cdot}444\,N_4+0{\cdot}424\,N_2$	"E"
14a′	$-0{\cdot}763\,N_4+0{\cdot}576\,N_2$	"E"
13a′	$-0{\cdot}455\,N_3-0{\cdot}382\,N_4-0{\cdot}629\,N_2$	"A"

Table 5. 2s Levels in pyrazole

8a′	$0{\cdot}213\,N_1+0{\cdot}331\,N_2-0{\cdot}165\,C_3-0{\cdot}398\,C_4-0{\cdot}305\,C_5$	"E"
7a′	$0{\cdot}424\,N_1+0{\cdot}369\,N_2-0{\cdot}353\,C_3+0{\cdot}245\,C_5$	"E"
6a	$0{\cdot}500\,N_1+0{\cdot}358\,N_2+0{\cdot}132\,C_3+0{\cdot}096\,C_4+0{\cdot}168\,C_5$	A

(3·92 eV) than for the other compounds (1·6 eV). That in imidazole may also be a consequence of the absence of NN bonds.

The centre group of valency shell σ-orbitals contains the main XH bonding levels, together with CN and CC bonding. Again the pseudo "A_1+E" system occurs, but the separation of the pseudo "E" type orbitals is more variable. The orbitals 9A′ to 13A′ ($6a_1$ to $8a_1$, $4b_2$ and $5b_2$ for pyrrole) are strongly influenced by the NH position and contain nodes through the NH (along the y-axis) or across the ring at right angles to it; the principal orbitals are correspondingly largely $(2p_y\pm 2s)_{N,C}\pm 1s_H$ and $(2p_x\pm 2s)_{N,C}\pm 1s_H$, and it is convenient to refer to this as *longitudinal* and *transverse polarisation* of the *orbitals* respectively. This does not infer polarisation in the sense of molecular charge separation as in a dipole moment, since as in pyrrole (Fig 5) transverse polarisation (for example $7a_1$) leads to a zero dipole moment vector component in the x-direction. There is some vestigial character of the radial and tangential character of the E orbitals of the cyclopentadienyl anion in $7a_1$ and $8a_1$ of pyrrole respectively, but this is still less evident in the other azoles, such that it is better to regard these as $C_\beta C_\beta+C_\alpha H^+$ and $C_\alpha C_\beta^\ddagger+C_\beta H^+$ bonding respectively where the superscript sign + indicates symmetric (a_1) or − sign an antisymmetric (b_2) combination (see Table 3.1). All of these orbitals contain $1s_H$ together with s and p character from the ring atoms. The longitudinal or transverse polarisation allows a direct correlation with the orbitals of pyrrole. Thus $6a_1$ in pyrrole ($NH+C_\beta H^+$) correlated with 9a′ in all azoles (except 1,2,4-triazole where it is 10a′) which are all longitudinally polarised and consist of NH with C_3H in 3 and 4 for example; similarly $8a_1$ in pyrrole ($C_\beta C_\beta+C_\alpha H^+$) correlates with those 11a′ orbitals with largely transverse CH components—C_5H with less C_4H in 3 and 5, C_2H+C_5H (2), C_5H in 4 and 6. Further considerations of this type lead to the complete correlation diagram shown in Fig 1. The complication is in the cases of accicental degeneracy where it is apparent that both orbitals have mixed character; this is the case with 9a′ and 10a; and 13a′ and 14a′ in imidazole and 12a′ and 13a′ in 1,2,3-triazoles. Finally the orbitals 12a′–15a′ in tetrazole cannot really be correlated directly with the same group of orbitals in the other molecules; this is especially true for the symmetric lone pair combination 13a′ and the immediately lower orbital 12a′.



$7A_1$ in 1 $8A_1$ in 1

Fig 5. Transverse ($7A_1$) and longitudinal ($8A_1$) polarisation of orbitals in pyrrole.

The π orbitals similarly correlate well with the A_1+E π-levels of cyclopentadienyl (D_{5h}); the separation of the two levels at lower IP ($1b_1$ and $1a_2$ for pyrrole, 2a″ and 3a″ for the others) is almost invariant (1·5±0·3 eV) throughout the set. The most strongly bound π-level is a totally symmetric combination of p_z orbitals in each case, while the others have a single node each, passing through NH or perpendicular to it respectively.

CONCLUSIONS

Leaving aside the question of whether Koopmans' theorem has validity here or elsewhere, or what form of relationship should hold between eigenvalue and photoelectron energy levels, we observe that a linear relationship between these two variables holds over the first seven observed levels and has the form $(IP)_{\text{expu}} = 0{\cdot}799\ (IP)_{\text{calc}}$.

The lone pair levels are heavily localised on nitrogen, but occur as linear combinations where more than one lone pair exists. The other molecular orbitals of the valency shell are heavily delocalised but their principal components determined by the calculations assist in the correlation through the use of relative intensity, and the known different cross sections to 2s and 2p electrons.

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