Gas-Phase Tautomerism in the Triazoles and Tetrazoles: A Study by Photoelectron Spectroscopy and ab Initio Molecular Orbital Calculations

Michael H. Palmer, Isobel Simpson, and J. Ross Wheeler
Department of Chemistry, University of Edinburgh, Edinburgh, Scotland

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The photoelectron spectra of the tautomeric 1,2,3,- and 1,2,4-triazole and 1,2,3,4-tetrazole systems have been compared with the corresponding N-methyl derivatives. The dominant tautomers in the gas phase have been identified as 2H-1,2,3-triazole, 1H-1,2,4-triazole and 2H-tetrazole.

Full optimisation of the equilibrium geometry by ab initio molecular orbital methods leads to the same conclusions, for relative stability of the tautomers in each of the triazoles, but the calculations wrongly predict the tetrazole tautomerism.

Introduction

In a previous study [1] one of us reported the gas phase He(I) photoelectron spectra for the aza derivatives of pyrrole (1a), derived by progressive substitution of ≧CH by ≧N, namely pyrazole (2a), imidazole (3a), 1,2,3-triazole (4a), 1,2,4-triazole (5a) and tetrazole (6a). The spectra obtained in the latter three cases relate to tautomeric mixtures, namely 4a⇋7a, 5a⇋8a, 6a⇋9a, and it had been assumed that the tautomer present in the gas phase would be the same as in the solid state or solution, there being no evidence to the contrary; thus we assigned the spectra on the basis of 4a, 5a and 6a rather than 7a, 8a or 9a, respectively [2, 3, 4].

Two pieces of information have subsequently made us reconsider this topic. The dominant tautomer present in the (gas-phase) microwave spectrum of 1,2,3-triazole is now thought to be the 2H-form (7a), previously not identified because of its very low dipole moment (relative to 4a) [5]. Secondly, as part of an investigation of nuclear quadrupole coupling using large basis sets [6], we unexpectedly found that assigned geometries for some of the un-observed tautomers (7a, 8a, 9a) led to energies very similar to those using known structures for the other compounds (e.g. 4a und 5a); optimisation could lead to a reversal of assignment for the thermodynamically most stable tautomer.

Reprint requests to Dr. M. H. Palmer, Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland.

In the present paper we report (a) a comparison of the photoelectron spectra of the tautomeric mixtures with the corresponding N-methyl compounds of each type, e.g. 1,2,3-triazole with 4b and 7b; (b) ab initio calculations of the optimum geometry for each tautomeric form, with a view to determining the calculated equilibrium ratio from the energy difference (Figure 1).

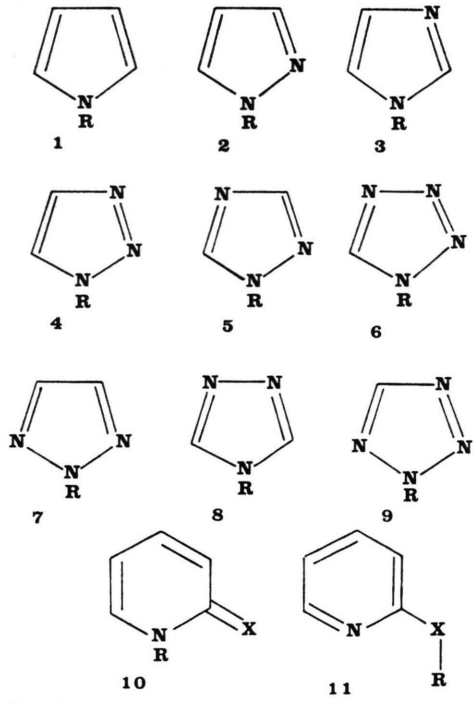

Fig. 1. Molecular structures. **1–9**: (a) R=H, (b) R=Me; **10, 11**: (a) R=H, X=O, (b) R=H, X=S, (c) R=Me, X=O, (d) R=Me, X=S.

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Methods

(*a*) *The Photoelectron Spectra*

These were obtained from the previous samples [6] on a Perkin Elmer PS16 Spectrometer, modified by incorporation of a Helectros hollow cathode lamp and Vacuum Science Workshop power supply. A Varian C1024 signal averaging device was used to repetitively scan and increase signal-to-noise for some of the compounds, which have comparatively low vapour pressure at normal temperatures, but which require to be drawn into the spectrometer from an external reservoir. Calibration was by means of $Xe/Ar/N_2$ mixtures (IP's 12.13, 15.75 and 18.6 eV, respectively) and He^+ self-ionisation (26.2 eV).

(*b*) *Ab Initio Electronic Structure Calculations*

These proceded in stages as follows: — (i) a minimal basis (7s3p/3s; MB) for (C, N/H) was used for a full gradients procedure search for the lowest energy structure. This is a different procedure to that adopted in our recent paper on 9-membered ring heterocycles [7] where the method involved gradients of total energy with respect to cartezian coordinate followed by up-dating of a Hessian matrix; the new method, using the HONDO program [8, 9], uses a gradient procedure based upon derivatives of the integrals over the gaussian basis [9]. The program was implemented on an ICL 2972 computer; optimisation was started from an assigned geometry [6] and cycled until the energy had converged to 0.00001 a.u. (1 a.u. = 2626 kJ mol^{-1}) and the bond lengths and angles to 0.001 Å and 0.01° respectively. A recent example of the power of this method using our basis for nitrogen is for S_4N_2 [10] where a crystal structure has recently been reported [11]; the two structures are nearly identical. (ii) At the end of the optimisation phase the calculations were extended to a double zeta (DZ) basis [6, 12] at the previously computed equilibrium geometry. This was to confirm that (a) no major change in either orbital ordering had occurred in the region of interest to the present photoelectron spectra, and (b) to check that the electric field gradients (c.f. [6]) (EFG) were not markedly effected by the geometry optimisation. These are discussed below (and elsewhere for the EFG), but we note that energy differences between tautomers must ideally be determined at the equilibrium geometry, and hence refer to the minimal basis calculations in the present work.

Results and Discussion

(*a*) *The Final Equilibrium Geometries*

The final equilibrium (computed) geometries for each tautomeric pair are shown in Fig. 2, and the total energies in Table 1. Both MB and DZ bases predict the 2H-tautomer to be more stable than the 1H- for 1,2,3-triazole, in agreement with the microwave data [5]. The ratio is predicted to be (2H/1H) 1.68 from the MB calculations, while the less rigorous value from the DZ ones is 586; the two values thus bracket the experimental estimate (~ 100). To date 4H-1,2,4-triazole has not been detected experimentally, and the present calculations suggest that the 1H-isomer is more stable than the 4H by 11.3 kJ mol^{-1} (MB), (or 21.4 kJ · mol^{-1} from the DZ calculations). These lead to equilibrium constants of 93 and 5300 respectively, the former being more rigorous. The results for the

Table 1. Total Energies in the Optimisation Process (a.u.).

	Starting Geometry		Final Geometry	
	Minimal Basis	Double Zeta Basis	Minimal Basis	Double Zeta Basis
1H-1,2,3-Triazole (4a)	— 240.0154	— 240.6370	— 240.0659	— 240.6571
2H-1,2,3-Triazole (5a)	— 240.0227	— 240.6644	— 240.0679	— 240.6631
Energy difference (2H-1H) (kJ mol^{-1})	— 19.2	— 72.0	— 1.3	— 15.9
1H-1,2,4-Triazole (6a)	— 240.0618	— 240.6909	— 240.0834	— 240.6871
4H-1,2,4-Triazole (7a)	— 240.0669	— 240.6773	— 240.0791	— 240.6789
Energy difference (4H-1H) (kJ mol^{-1})	— 13.4	+ 35.7	+ 11.3	+ 21.4
1H-Tetrazole (8a)	— 255.9109	— 256.6034	— 255.9708	— 256.6169
2H-Tetrazole (9a)	— 255.8959	— 256.6182	— 255.9697	— 256.6166
Energy difference (2H-1H) (kJ mol^{-1})	+ 39.4	— 38.9	+ 3.0	+ 0.70

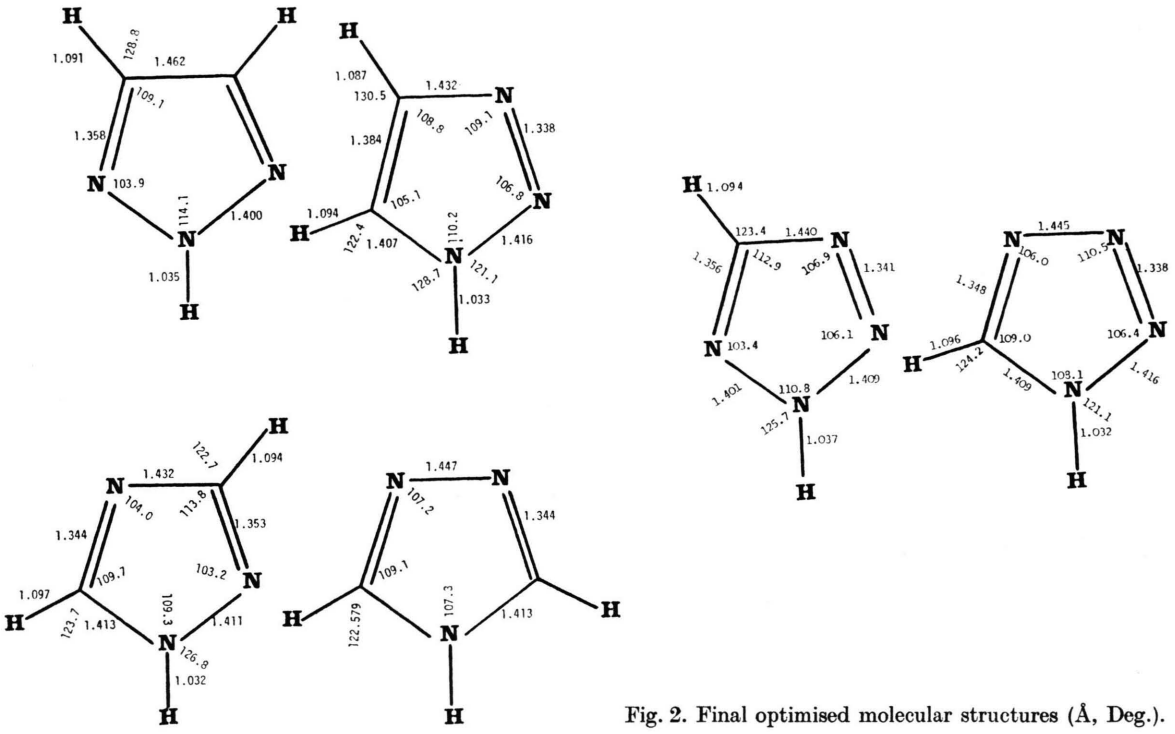

Fig. 2. Final optimised molecular structures (Å, Deg.).

tetrazoles are more nearly equal, with the 1H-isomer being preferred by 3.0 kJ mol^{-1} (MB) and 0.7 kJ mol^{-1} (DZ), leading to equilibrium constants of 3.3 and 1.3, respectively; this is in agreement with previous solution and crystal data [4], but not with the new spectral information below.

(*b*) *Assignment of the Dominant Tautomers from the Photoelectron Spectra*

Provided substitution of NH by NMe does not lead to a major change in spectrum, it should be possible to assign the NH-compound spectra of the mixture to a particular tautomer; this has been done previously for the pyridinone-hydroxypyridine systems (10a—d, 11a—d) [13]; previous studies of the pyroles (1a, b) and imidazoles (3a, b), where no tautomerism is possible [14] have shown the low binding region to be very similar for the NH and NMe compounds.

Replacement of an NH-delocalised bonding orbital by NMe leads to the introduction of three new valence shell orbitals of $(A_1 + E)$ symmetry, in the local C_{3v} framework. In aromatics, the E levels are split into E_σ and E_π, and are near 14 eV in toluene and related compounds [15]. The A_1 Me level has high $2s_C$ character and lies near 21 eV in such compounds. Thus all these group orbitals lie outside the present region of interest. It is convenient [1] to divide the spectra into regions A, B, C ... (low to high binding); the region of primary interest in the present work is Region A, containing most of the π- and lone pair levels [1]; it extends from about 8—10 eV for pyrrole (1a), with progressive shift to higher binding energy on aza-substitution, to 10—13 eV for tetrazole. Comparison of the spectra of 1a, b—3a, b shows there is a general shift to lower binding energy in the N-methyl compounds [14]; this is attributable in part to electron donation from the Me group, and in part from antisymmetric combinations of ring and Me group levels.

1,2,3-Triazole

It is apparent that the spectrum of the tautomeric mixture (Fig. 3) is much more similar to that of the 2-methyl- (7b) than the 1-methyl tautomer (4b); the width and placing of the IP's is such that it is not possible to say whether the minor compo-

Table 2. Orbital Energies (eV).

Pyrrole (1a)	Pyrazole (2a)	Imidazole (3a)	1H-1,2,3-triazole (4a)
− 8.211 a_2	− 9.678 a″(π)	− 9.020 a″	− 10.212 a″
− 9.579 b_1	− 10.248 a″	− 11.065 a″	− 11.782 a′(LP_N^-)
− 14.453 a_1	− 12.456 (LP_N) a′(σ)	− 11.758 a′(LP_N)	− 11.941 a″
− 14.920 b_2	− 15.624 a′	− 15.724 a′	− 13.873 a′(LP_N^+)
− 15.630 b_1	− 16.200 a′	− 16.586 a″	− 17.297 a′
− 15.942 b_2	− 16.803 a″	− 16.646 a′	− 17.807 a′
− 16.307 a_1	− 16.904 a′	− 16.778 a′	− 18.033 a″
− 20.181 a_1	− 20.466 a′	− 20.942 a′	− 21.330 a′
− 20.979 b_2	− 22.033 a′	− 21.991 a′	− 23.612 a′
− 21.794 a_1	− 22.686 a′	− 22.879 a′	− 23.649 a′
− 26.825 b_2	− 29.113 a′	− 27.857 a′	− 30.335 a′
− 28.647 a_1	− 30.339 a′	− 32.236 a′	− 33.499 a′
− 35.576 a_1	− 38.155 a′	− 37.204 a′	− 40.557 a′

1H-1,2,4-triazole (5a)	(C_2V) 2H-1,2,3-triazole (6a)	(C_2V) 4H-1,2,4-triazole (7a)	2H-tetrazole (8a)	1H-tetrazole (9a)
− 10.728 a″	− 10.885 a_2	− 10.783 a_2	− 11.990 a″	− 11.809 a″
− 11.841 a″	− 11.181 b_1	− 11.474 b_1	− 12.720 a″	− 12.636 a′(LP_N)
− 12.173 a′(LP_N^-)	− 12.868 b_2(LP_N^-)	− 12.394 a_1(LP_N^+)	− 12.880 a′(LP_N)	− 13.077 a″
− 13.616 a′(LP_N^+)	− 13.741 a_1(LP_N^+)	− 12.558 b_2(LP_N^-)	− 13.545 a′(LP_N)	− 13.319 a′(LP_N)
− 16.687 a′	− 17.035 b_2	− 17.001 a_1	− 15.686 a′(LP_N)	− 15.443 a′(LP_N)
− 17.651 a″	− 17.323 a_1	− 17.310 b_1	− 18.366 a′	− 19.185 a″
− 18.072 a′	− 17.491 b_1	− 17.645 b_2	− 19.025 a″	− 19.458 a′
− 21.364 a′	− 20.335 a_1	− 21.762 a_1	− 21.460 a′	− 21.945 a′
− 22.654 a′	− 22.719 b_2	− 22.997 a_1	− 24.082 a′	− 24.929 a′
− 24.159 a′	− 23.437 a_1	− 23.677 b_2	− 25.585 a′	− 25.404 a′
− 31.081 a′	− 30.320 a_1	− 30.867 b_2	− 33.39 a′	− 33.568 a′
− 33.479 a′	− 32.911 b_2	− 32.968 a_1	− 34.98 a′	− 35.273 a′
− 39.392 a′	− 39.413 a_1	− 38.242 a_1	− 42.239 a′	− 42.497 a′

1-methyl-1,2,4-triazole (5b)	2-methyl-1,2,3-triazole (6b)	4-methyl-1,2,4-triazole (7b)	2-methyltetrazole (8b)	1-methyltetrazole (9b)
− 10.390 a″	− 10.281 a″	− 10.604 a″	− 11.718 a″	− 11.585 a″
− 11.281 a″	− 11.027 a″	− 10.878 a″	− 12.007 a″	− 12.322 a″
− 11.928 a′(LP_N^-)	− 12.724 a′(LP_N^-)	− 12.190 a′(LP_N^+)	− 12.572 a′(LP_N)	− 12.344 a′(LP_N)
− 13.346 a′(LP_N^+)	− 13.603 a′(LP_N^+)	− 12.320 a′(LP_N^-)	− 13.309 a′(LP_N)	− 13.074 a′(LP_N)
− 15.813 a″	− 15.441 a′	− 15.698 a″	− 15.398 a′(LP_N)	− 15.128 a′(LP_N)
− 16.008 a′	− 15.480 a″	− 16.370 a′	− 16.329 a′	− 16.835 a″
− 16.594 a′	− 16.557 a′	− 16.501 a′	− 16.506 a″	− 17.027 a′
− 17.183 a′	− 17.310 a′	− 17.782 a′	− 17.923 a′	− 18.743 a′
− 18.375 a″ Me(e)	− 18.267 a″ Me(e)	− 18.456 a″ Me(e)	− 19.415 a″ Me(e)	− 19.656 a″ Me(e)
− 20.072 a′	− 19.612 a′	− 19.810 a′	− 20.246 a′	− 20.851 a′
− 22.647 a″	− 22.125 a′	− 21.988 a′	− 23.682 a′	− 23.655 a′
− 22.844 a″	− 22.752 a′	− 23.744 a′	− 24.058 a′	− 25.210 a′
− 26.817 a′ Me(a)	− 26.372 a′ Me(a)	− 27.181 a′ Me(a)	− 28.329 a′ Me(a)	− 28.394 a′ Me(a)
− 31.306 a′	− 31.211 a′	− 30.683 a′	− 33.403 a′	− 33.381 a′
− 33.463 a′	− 32.754 a′	− 33.225 a′	− 34.978 a′	− 35.516 a′
− 39.228 a′	− 39.377 a′	− 38.116 a′	− 42.009 a′	− 42.270 a′
− 307.577 a′	− 307.093 a′	− 308.093 a′	− 308.081 a′	− 308.437 a′
− 307.697 a′	− 307.122 a′	− 308.478 a′	− 308.113 a′	− 308.594 a′
− 308.321 a′	− 307.421 a″	− 308.478 a′	− 425.058 a′	− 424.806 a′
− 423.491 a′	− 425.486 a′	− 424.685 a′	− 425.661 a′	− 426.073 a′
− 425.141 a′	− 425.487 a′	− 424.696 a′	− 426.837 a′	− 426.506 a′
− 426.149 a′	− 426.651 a′	− 425.786 a′	− 427.514 a′	− 426.999 a′

Table 2. (continued).

1-methylpyrrole[a] (1b)	1-methylpyrrole[b] (1b)	1-methylpyrazole (2b)	1-methylimidazole (3b)	1-methyl-1,2,3-triazole (4b)
— 8.106 a″	— 8.099 a′	— 9.559 a″	— 8.858 a″	— 10.031 a″
— 9.158 a″	— 9.152 a′	— 9.796 a″	— 10.529 a″	— 11.329 a″
— 14.286 a″	— 14.306 a′	— 12.377 a′(LP_N)	— 11.550 a′(LP_N)	— 11.533 a′(LP_N^-)
— 14.360 a′	— 14.324 a″	— 14.184 a″	— 15.159 a″	— 13.683 a′(LP_N^+)
— 14.402 a′	— 14.406 a″	— 15.057 a′	— 15.345 a′	— 16.031 a″
— 15.504 a′	— 15.497 a″	— 15.662 a′	— 15.871 a′	— 16.103 a′
— 15.517 a′	— 15.522 a″	— 16.125 a′	— 16.071 a′	— 17.129 a′
— 16.469 a′	— 16.469 a″	— 16.695 a′	— 17.018 a′	— 17.655 a′
— 17.318 a″ Me(e)	— 17.319 a′ Me(e)	— 17.465 a″ Me(e)	— 17.879 a″ Me(e)	— 18.788 a″ Me(e)
— 19.378 a′	— 19.377 a″	— 19.785 a′	— 19.735 a′	— 20.298 a′
— 20.429 a′	— 20 424 a″	— 21.138 a′	— 21.445 a′	— 22.274 a′
— 21.103 a′	— 21.100 a″	— 22.209 a′	— 22.092 a′	— 23.622 a′
— 25.558 a′ Me(a)	— 25.559 a″	— 25.744 a′ Me(a)	— 26.548 a′ Me(a)	— 27.611 a′
— 26.767 a′	— 26.762 a″	— 29.243 a′	— 27.978 a′	— 30.166 a′
— 29.353 a′	— 29.351 a″	— 30.766 a′	— 32.486 a′	— 33.901 a′
— 35.664 a′	— 35.661 a″	— 38.166 a′	— 37.147 a′	— 40.419 a′
— 305.257 a′	— 305.243 a″	— 305.829 a′	— 306.255 a′	— 306.687 a′
— 305.286 a′	— 305.284 a″	— 306.552 a′	— 306.872 a′	— 307.216 a′
— 306.428 a′	— 306.376 a″	— 307.296 a′	— 307.643 a′	— 307.974 a′
— 306.428 a′	— 306.463 a″	— 307.560 a′	— 307.676 a′	— 424.531 a′
— 307.224 a′	— 307.234 a″	— 424.434 a′	— 423.307 a′	— 425.766 a′
— 424.698 a′	— 424.694 a″	— 425.744 a′	— 425.281 a′	— 426.359 a′

[a] All methyl "H's" out of plane of molecule. [b] All methyl "H's'$_2$ in plane of molecule.

nent is present in small amounts or below the detection limit for the technique (say 0.1%). The dominance of the 2H-tautomer is, however, consistent with recent microwave studies [5] and the computed relative energies of the present study.

1,2,4-Triazole

The spectrum of the 4-methyl isomer (8b) Fig. 4 is markedly different in the low binding Region A when compared with either the 1-methyl compound (5b) or the tautomeric mixture; we conclude that the latter is almost entirely in the 1H-form (5a) in the vapour phase, and thus is the same in solution and solid state measurements made to date. This is consistent with the high difference in computed energy between 5a and 8a.

Tetrazole

The assignment for tetrazole shows the 2H-tautomer (9a) to be dominant; the almost complete absence of the 1H-form (6a) can be assumed from the absence of a broad band near 12.8 eV which occurs in the 1-Me spectrum. The presence of marked vibrational structure on the tautomer spectrum and that of the 2-methyl compound (9b) is very evident (Figure 5).

Conclusions

The present results confirm the earlier suggestions that the most stable tautomer for 1,2,3-triazole in the gas phase is the 2H-one (4a), and that photoelectron spectroscopy can be used to differentiate between tautomers in cases of this type. 1,2,4-Triazole appears to be in the 1H-form under all conditions so far investigated, and the calculations suggest that this is likely to be true for most circumstances. In contrast, the energy difference between the tautomers of tetrazole is clearly small, and either tautomer can be anticipated, depending upon conditions. The 2H-tautomer is dominant in the gas phase at low pressures. It seems probably that the assumption of particular tautomeric structures for the vapour phase based upon solution or crystal data is likely to be hazardous, since further examples in the hydroxypyridine-pyridinone (**10**—**11**) systems have led to be the same conclusion [13]. Relative energies based upon arbitrary choices of geometry seem particularly suspect, and the failure of the present ab initio minimal calculations for tetrazole make the use of even more restricted basis sets, such as in semiempirical calculations even less reliable.

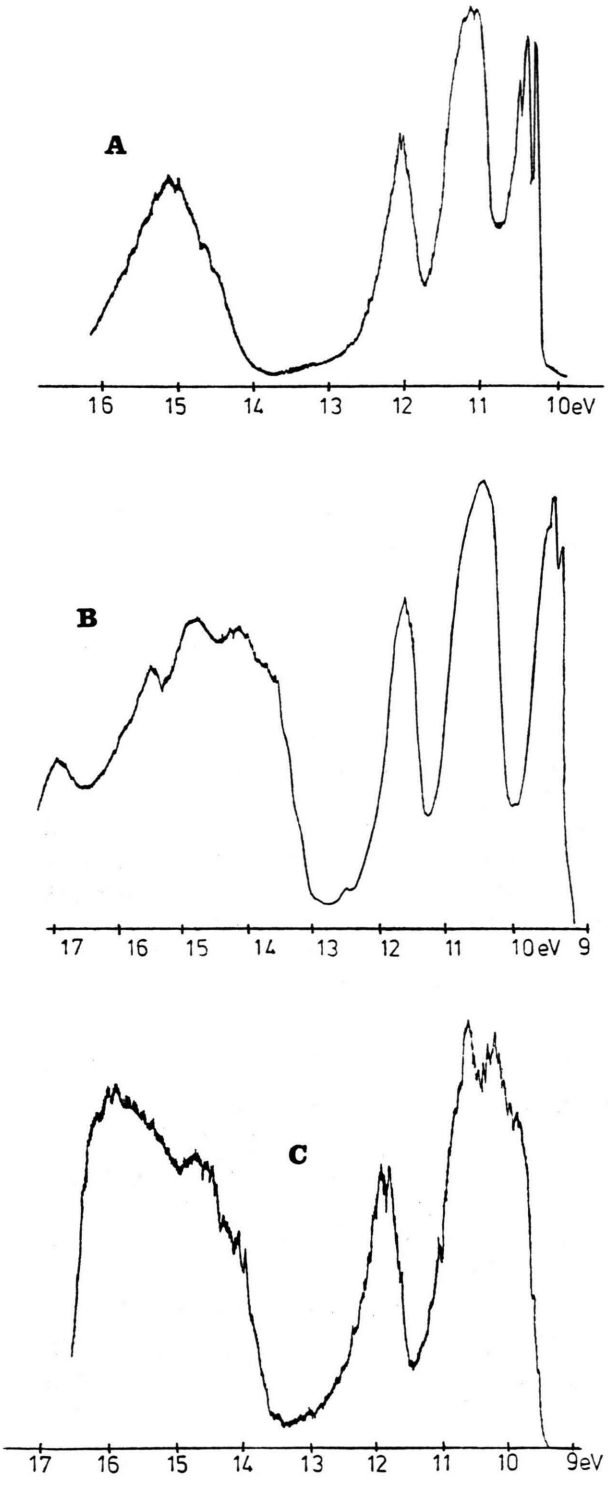

Fig. 3. Photoelectron spectra (HeI) of 1,2,3-Triazole (A) and its 1- and 2-Methyl compounds (C & B, respectively).

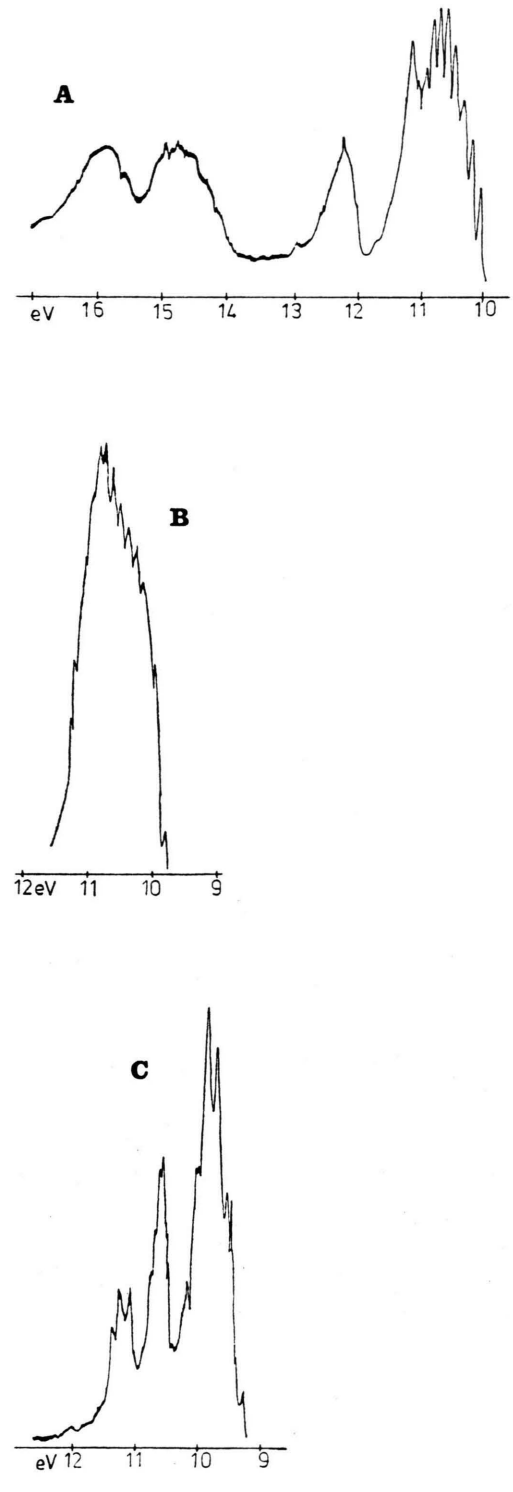

Fig. 4. Photoelectron spectra (HeI) of 1,2,4-Triazole (A) and its 1- and 4-Methyl compounds (B and C, respectively).

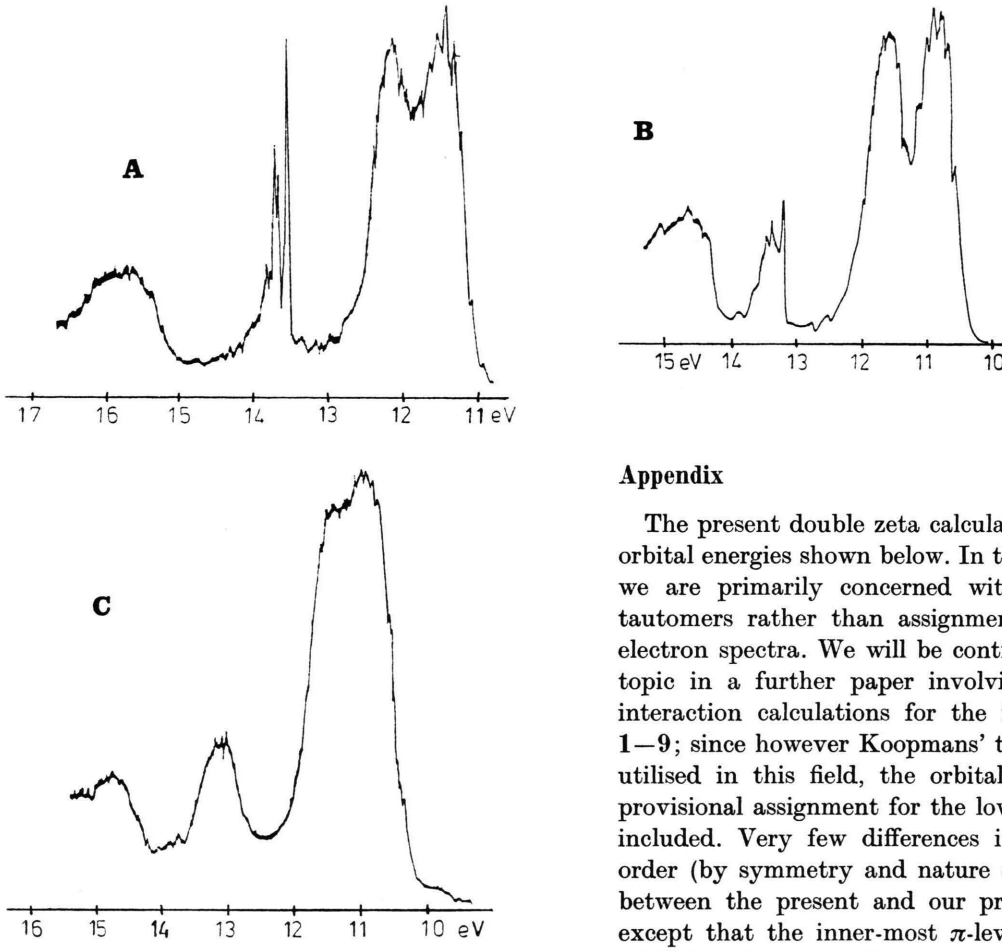

Fig. 5. Photoelectron spectra (HeI) of Tetrazole (A) and its 1- and 2-Methyl compounds (C and B, respectively).

Appendix

The present double zeta calculations yielded the orbital energies shown below. In this present paper we are primarily concerned with the gas-phase tautomers rather than assignment of the photoelectron spectra. We will be continuing this latter topic in a further paper involving configuration interaction calculations for the ionised states of **1**—**9**; since however Koopmans' theorem is widely utilised in this field, the orbital energies give a provisional assignment for the lower IP's, and are included. Very few differences in the calculated order (by symmetry and nature of orbital) occur between the present and our previous work [1], except that the inner-most π-level is often more shifted to lower binding energy relative to some σ-levels on going from MB to DZ.

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