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A PHOTOELECTRON STUDY (HeI, HeII) OF THE TAUTOMERIC EQUILIBRIUM OF CHLORO- AND BROMO-1,2,4-TRIAZOLES[1]

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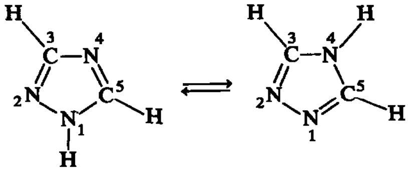
Abstract—Photoelectron spectroscopy (HeI, HeII) and quantum mechanical calculations (STO-3G) were used to analyze the electronic structure of tautomers of 1,2,4-triazole and its halogenated derivatives.

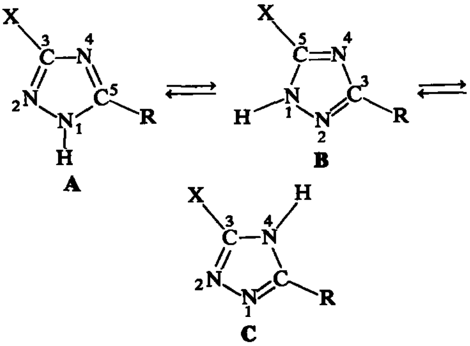
The photoelectron spectra of the title compounds compared to those of fixed structure models demonstrated that 3-chloro and 5-bromo-1,2,4-(1H)-triazole exist in the vapor phase.

The tautomeric equilibrium of 1,2,4-triazole, which can exist in the 1H and 4H forms, has been studied with X-ray crystallography,[2,3] microwave spectroscopy,[4,5] electron diffraction,[6] mass spectroscopy,[7] NMR[8,9] and PE spectroscopy.[10] The predominant existence of the dissymetrical 1H form in the solid, liquid and vapor phases has been demonstrated by all these methods. These conclusions are in agreement with the theoretical calculations performed a decade ago.[11]



1H FORM   4H FORM

The halogen derivatives of 1,2,4-triazole have been the object of far fewer studies. To our knowledge, only three techniques, quadrupole nuclear resonance,[12] dipole measurements[13] and mass spectrometry[14,15] have been applied, in order to determine the preferential form in tautomeric equilibrium (X = Cl or Br; R = H or Me).



The conclusions reached differ as a function of the technique employed, *i.e.* according to the physical state of the compounds. Thus, 5-chloro 1,2,4(1H)-triazole (form **B**) has been observed in the crystalline state,[12] whereas it appears that form **A** is predominant in solution,[13] regardless of the halogen. Finally, there is general agreement that a mixture of forms **A** and **B** exists in the vapor phase.[14,15] Nevertheless, the results of the latter research seems to indicate that chlorine is preferentially in position 3 (form **A**)[15a] and that bromine is preferentially in position 5 (form **B**).[15b]

We have reinvestigated this tautomeric equilibrium in the vapor phase with photoelectron spectroscopy, a technique found to be particularly well adapted to this type of study.[10,16,17] We utilized the conventional procedure, consisting of an analysis of the spectra of fixed forms followed by their comparison with those of the free forms in order to deduce the structure of the latter.

In order to facilitate the analysis of these spectra, we will initially present the electronic structure of 1,2,4-triazole in its two possible forms, 1H and 4H.

Electronic structure of 1,2,4-*triazole*

The electronic structure of 1,2,4-triazole (Fig. 1) has been previously studied by Cradock *et al.*[18] In agreement with these authors and with the *ab-initio* STO-3G minimal base calculation[19] shown in Table 1, we attribute the first broad band comprising three partially overlapping bands to the ionization of two π electrons (10.6 eV and 11.05 eV) and of one n electron (10.7 eV). The fourth band is thus associated with the ionization of an n electron (12.15 eV).

Table 1 also shows the four highest occupied molecular orbitals of 1,2,4-(4H)-triazole. According to these data, the similarity of the π systems of the two tautomers is obvious. The plane of symmetry of the 4H form is practically in the 1H form,

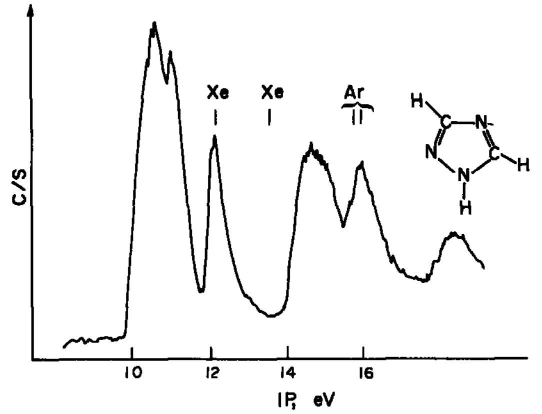


Fig. 1. Photoelectron spectrum (HeI) of 1,2,4-(1H)-triazole.

thus defining an antisymmetrical π_3 orbital which is less stable than two symmetrical π_2 and π_1 orbitals. This order is found in all 5-membered heterocyclic rings with C_{2v} symmetry, such as pyrrole, furan, phosphole, thiophene and selenophene[21,26]. This pseudo-symmetry appears less clearly in thiazole.[27]

The primary difference in the electronic structure of these two tautomers is thus not in the π system, but rather in the σ system; more precisely in the order of energy of the anti-bonding and bonding combinations of the two atomic n orbitals of the imino nitrogens. These two combinations, which are partially mixed with the other σ orbitals of the molecule (Table 1), have a greater splitting in the 1H form (1.94 eV calculated and 1.45 eV experimental) than in the 4H form (1.64 eV). This may be considered surprising if we compare this result to that found for six-membered rings, such as pyrimidine and pyridazine,[28] in which the splitting is greater when both lone pairs are in 1,2 position (pyridazine: 2.3 eV) than when they are in 1,3 position (pyrimidine: 1.50 eV). This difference, which is due primarily to a through-space interaction (lesser in the case of pyrimidine), thus appears to be attenuated in 5-membered rings. Furthermore, although the anti-symmetrical combination of the 4H form is calculated to be slightly less stable than that of the 1H form (−9.22 eV *vs* −9.26 eV), the inversion of the order of splitting between 5- and 6-membered rings arises from the pronounced destabilization of the bonding combination in the 4H form (−10.86 eV *vs* −11.20 eV). According to localization results performed with the STO–3G calculations,[29,30] this seems to be due to a greater interaction (reinforced by symmetry) of this n^+_{NN} combination with the σ orbitals of the ring, particularly with the σ_{NN} orbital, and to a less effective participation of 2s orbitals, resulting from a slight change in geometric structure.

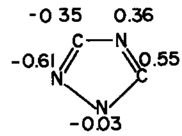
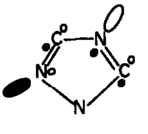
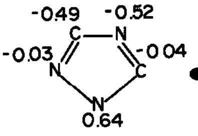
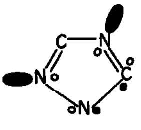
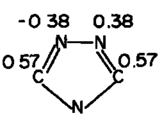
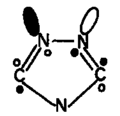
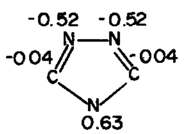
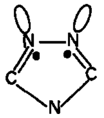
As we will see below, this theoretical analysis is in good agreement with the experimental results.

*Electronic structure of chloro- and bromo-*1,2,4-*triazoles*

A. *Fixed models*. The experimental ionization potentials of the chlorine and bromine derivatives of the 1H and 4H forms of N-methyl-1,2,4-triazole are shown in Tables 2 and 3.

The assignment of non-bonding electron ionization bands of electrons localized on the halogen atoms (n^σ_X and n^π_X) is based primarily on two experimental criteria: the profile and intensity of these spectral bands. In most cases, these bands are indeed fine and intense; however, in certain cases a broadening of the bands reflects the existence of strong interactions between these and other molecular orbitals of the system. It thus becomes useful to compare the spectra recorded with irradiations of two different energies, such as HeI (21.21 eV) and HeII (40.81 eV). Indeed, the intensity of the electron ionization bands corresponding to atoms of the third and fourth periods decrease significantly in the HeI/HeII transition in relations to the bands assigned to the ionization of electrons

Table 1. Ionization potentials (eV) of (1H) and (4H) forms of 1,2,4-triazole and associated O.M. The theoretical values are calculated by a STO-3G program[19], assuming the validity of Koopmans' theorem[20].

				
	π_3	n^-_{NN}	π_2	n^+_{NN}
calc	8.29	9.26	9.64	11.20
exp	10.6	10.7	11.05	12.15
				
	π_3	n^-_{NN}	π_2	n^+_{NN}
calc	8.22	9.22	9.83	10.86

localized on second period atoms.[31] These intensity changes, previously studied and utilized for the assignment of certain spectra,[32,35] are particularly evident when the bands overlap little or not at all. This is the case in the spectra shown in Figs. 2, 3, and 6.

Since the identification of bands associated with halogen lone pairs is relatively certain, we assign the other bands by analyzing their evolution in the spectra of the different tautomeric forms and by comparing this evolution to the calculated results in Table 1 (Tables 2 and 3).

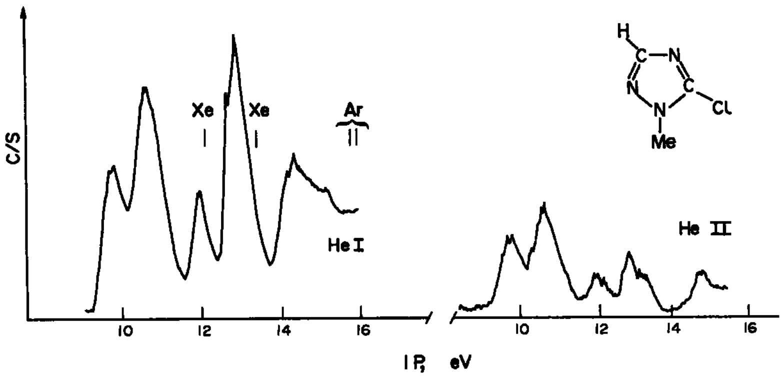


Fig. 2. Photoelectron spectrum (HeI, HeII) of 1-methyl 5-chloro 1,2,4-(1H)-triazole.

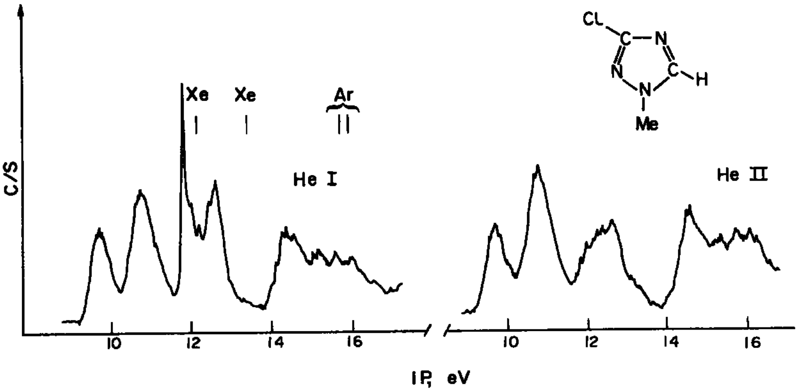


Fig. 3. Photoelectron spectrum (HeI, HeII) of 1-methyl 3-chloro 1,2,4-(1H)-triazole.

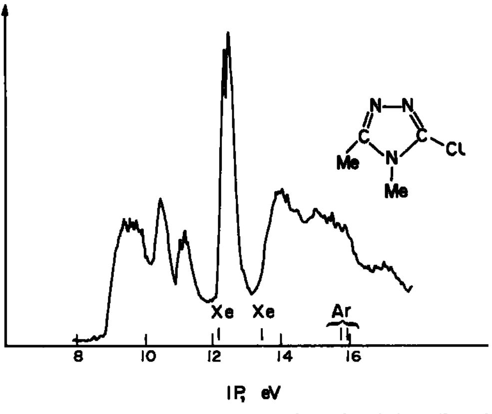


Fig. 4. Photoelectron spectrum (HeII) of 3,4-dimethyl 5-chloro 1,2,4-(4H)-triazole.

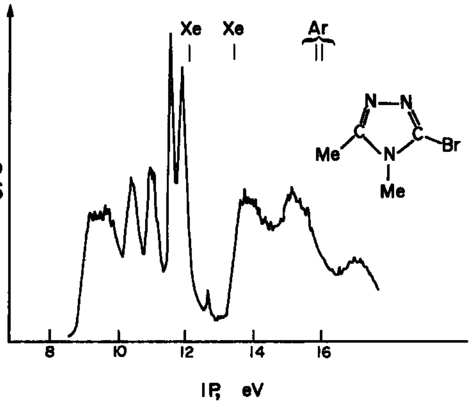


Fig. 5. Photoelectron spectrum (HeII) of 3,4-dimethyl 5-bromo 1,2,4-(4H)-triazole.

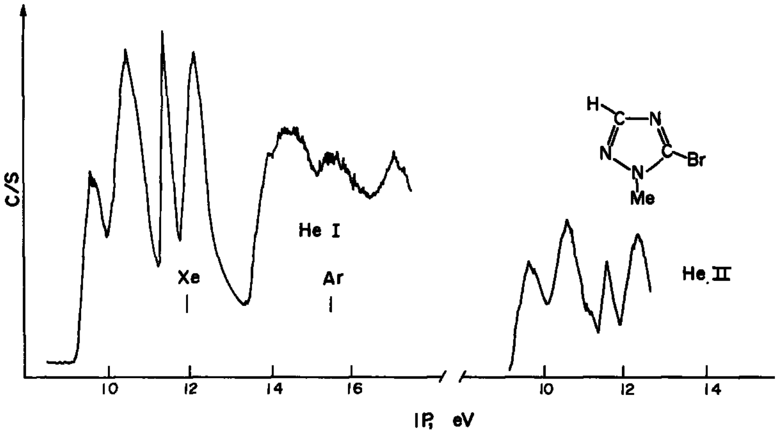


Fig. 6. Photoelectron spectrum (HeI, HeII) of 1-methyl 5-bromo 1,2,4-(1H)-triazole.

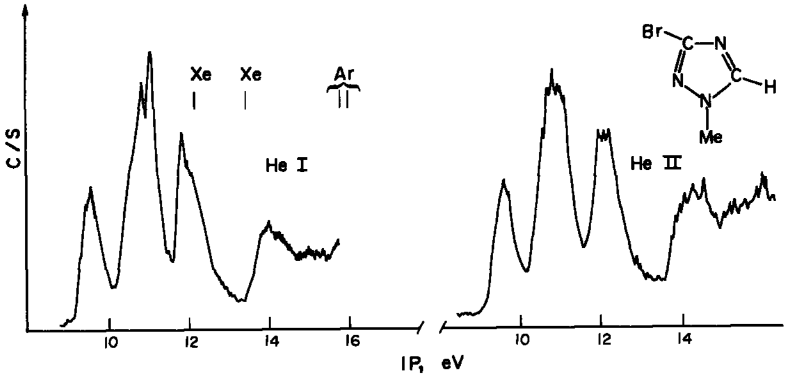


Fig. 7. Photoelectron spectrum (HeI, HeII) of 1-methyl 3-bromo 1,2,4-(1H)-triazole.

We will first discuss compounds B and C, corresponding to an α-halogenation of the pyrrole nitrogen of the 1H and 4H forms of 1,2,4-triazole, and will then analyze the differences found between the two tautomeric 1H forms (**A** and **B**).

In agreement with the theoretical results in Table 1, the assignments proposed in Tables 2 and 3 account for a practically identical π structure of the 1H (**B**) and 4H (**C**) forms. In addition, this assignment emphasizes the destabilization of the combinations n_{NN}^- and n_{NN}^+ of the non-bonding atomic orbitals of the imino nitrogens in 4H, regardless of the halogen. This destabilization, apparently more pronounced for the n_{NN}^- combination than that indicated for non-substituted molecules by the STO-3G calculation, may be explained by the form of this orbital. These calculations indeed show that the n_{NN}^- orbital exhibits a greater localization on the carbon atoms in the 4H than in the 1H. This localization increases the overlap of this orbital with n_X^σ and thus its initial destabilization. In the case of the n_{NN}^+ orbital, the differentiation of the order of energy between forms **B** and **C** is particularly well seen.

In summary, the comparison of the spectra of the halogen derivatives of the 1H (**B**) and 4H (**C**) forms of 1,2,4-triazole indicates the similarity of their π structure and a considerable destabilization of the anti-bonding n_{NN}^- and bonding n_{NN}^+ combinations of the lone pairs of the imino nitrogens of the symmetrical 4H (**C**) form.

Although the difference in the spectra of compounds **A** and **B** is not as pronounced, we nonetheless observe a notable change in the position of the bands corresponding to ionization of the halogen lone pair, especially the n_X^σ pairs. This may be explained by the differing interactions according to position 3 or 5 of the halogen, between the pair n_X^σ and the combinations n_{NN}^- and n_{NN}^+ of the imino nitrogens.

As shown by the data in Table 1, the n_{NN}^+ orbital indeed has a node on carbon 3 and a non-negligible weight on carbon 5. When we consider overlapping, this will be shown by a non-negligible interaction between these two orbitals during a halogen substitution on position 5.

Orbital n_{NN}^-, however, exhibits a localization which is practically the same on positions 3 and 5. The destabilization effect observed for the lone pair n_X seems to originate primarily from an inductive effect which is stronger for 3-halogeno 1,2,4-(1H)-triazole than for 5-halogeno (inductive effects are a function of the localization of orbitals, since they depend on the eigenvectors $c_{i\mu}^2$[36]).

Table 2. Experimental ionization potentials (eV) of chloro-1,2,4-triazoles (fixed structure models).

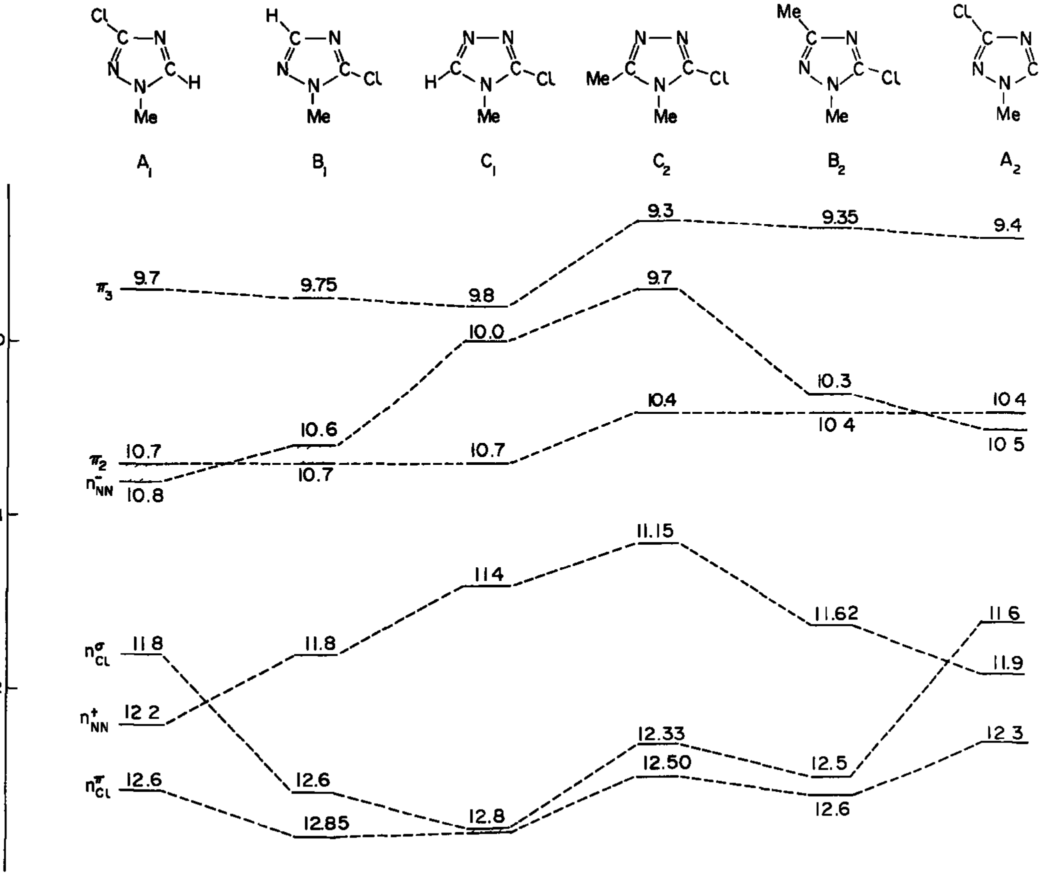
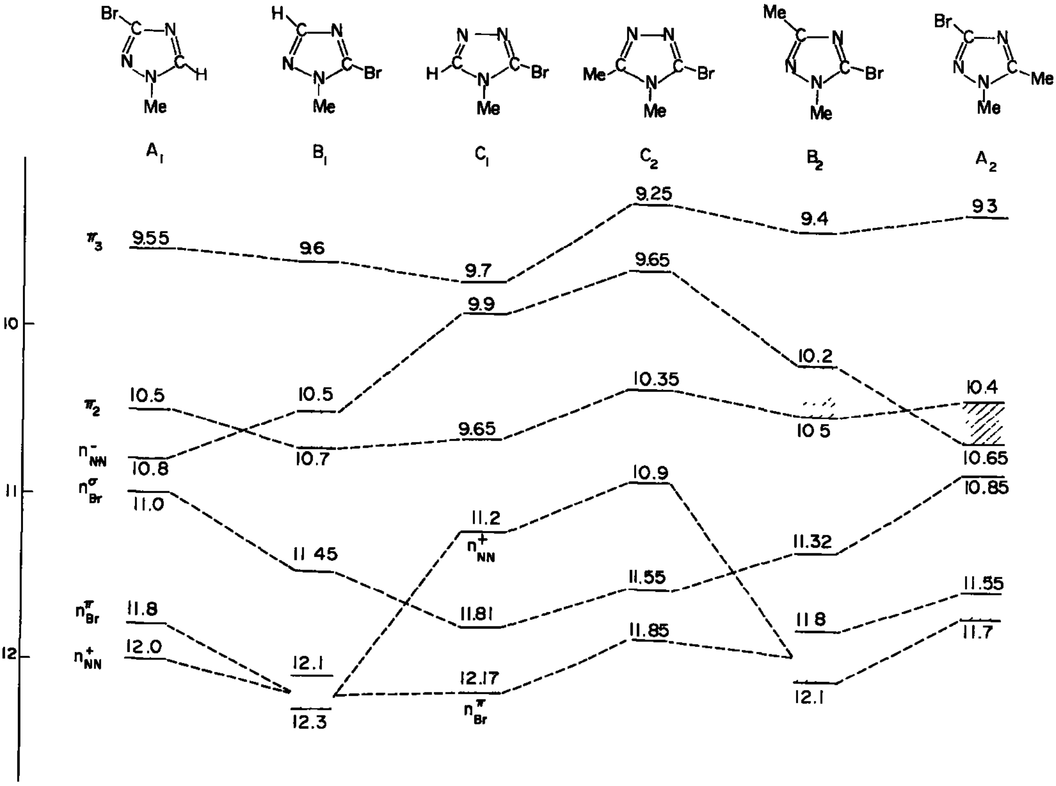


Table 3. Experimental ionization potentials (eV) of bromo-1,2,4-triazoles (fixed structure models).



Thus, we observe (Table 2) the pair n^{σ}_{Cl} at 11.8 eV for the 3-chloro derivative (the ionization potential associated with the combinations n^{-}_{NN} and n^{+}_{NN} appear at 10.8 eV and 12.2 eV), while in the case of the 5-chloro derivative, the pair n^{σ}_{Cl} is associated with the ionization potential observed at 12.6 eV; the combination n^{-}_{NN} corresponds to the second ionization potential at 10.6 eV (weaker inductive effect) and the combination n^{+}_{NN} to 11.8 eV (interaction between this combination and the pair n^{σ}_{Cl} of the halogen).

In the case of bromo derivatives (Table 3), we similarly observe a destabilization of the combination n^{-}_{NN} and a stabilization of the n^{σ}_{Br} orbital when passing from the 3-bromo to the 5-bromo compound. Considering the initial order of energy in this case, we also observe a stabilization of the combination n^{+}_{NN}.

If we consider the π system, the molecular π_2 orbital, as a result of its negligible localization on carbon 5, tends to be slightly more destabilized by n^{π}_{X} in compound **A** than in compound **B**, particularly for the brominated derivatives, in which inductive effects are of a lesser magnitude. In spite of this n^{π}_{X}/π_2 interaction, the n^{π}_{X} orbital is slightly more stabilized in **B** than in **A**, which can result only from the interaction with π_3. This interaction is undoubtedly stronger than the first, since, unlike all the other molecular orbitals of the ring and in spite of the stabilizing inductive effect of the halogens, π_3 is considerably more destabilized in the halogenated compounds than in nonsubstituted 1,2,4-triazole. The order of energy of this π_3 orbital is relatively constant between **A** and **B**, however, which may be explained by a buffering action of the inductive power of the halogen.

In conclusion, the photoelectron spectra of forms **A**, **B** and **C** are highly specific, regardless of the nature of the halogen (Cl or Br). This is particularly true for the position of the bands associated with the ionization of halogen lone pairs σ and π. It should be remembered that their assignment was unequivocally performed by the HeI/HeII irradiation transition.

B. *Free models.* Table 4 shows the values of the vertical ionization potentials of the 1,2,4-triazole derivatives halogenated and methylated on position 3 or 5. According to these data, it is clear that the non-Me and C-Me compounds exhibit the same tautomeric form for a given halogen be it Cl or Br. Since the evolution of the molecular orbitals observed between the two compounds is on the same

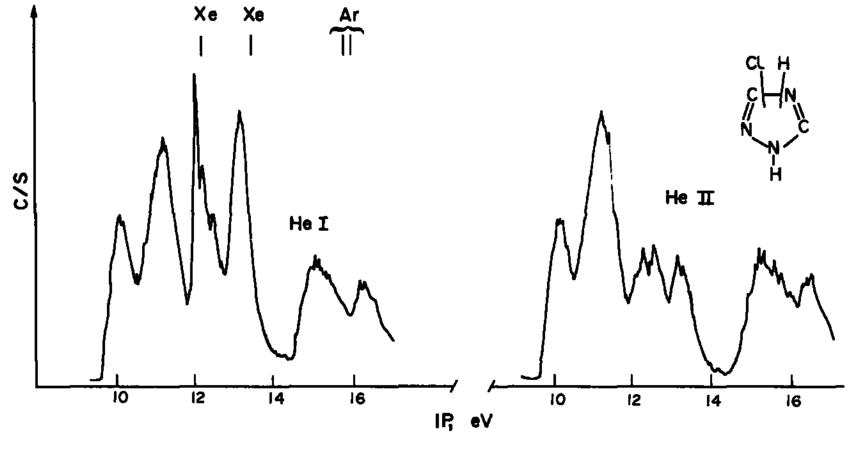


Fig. 8. Photoelectron spectrum (HeI, HeII) of C-chloro-1,2,4-(1H)-triazole.

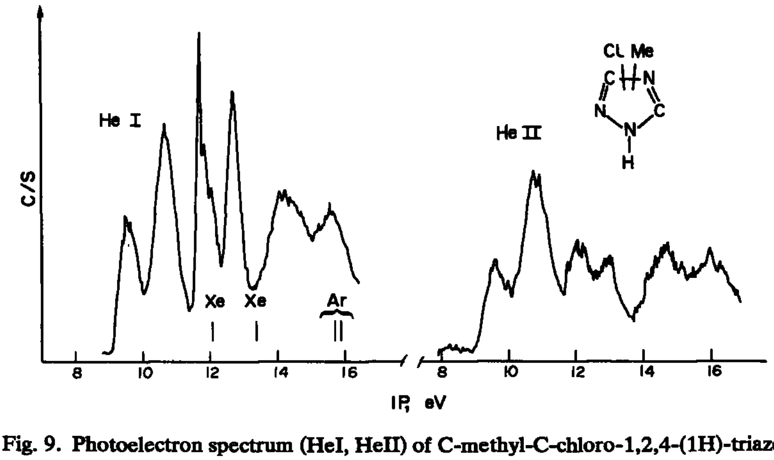


Fig. 9. Photoelectron spectrum (HeI, HeII) of C-methyl-C-chloro-1,2,4-(1H)-triazole.

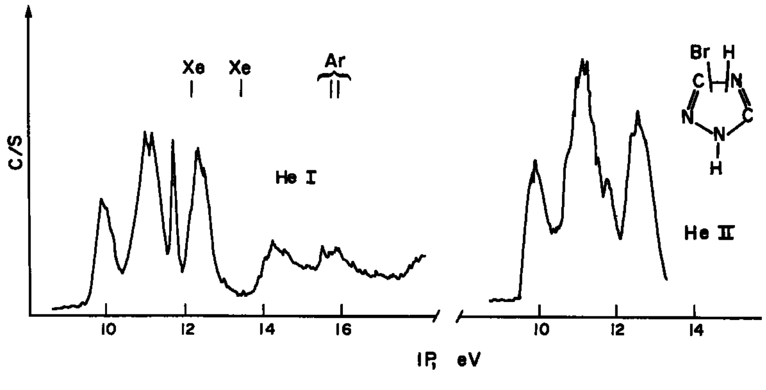


Fig. 10. Photoelectron spectrum (HeI, HeII) of C-bromo-1,2,4(1H)-triazole.

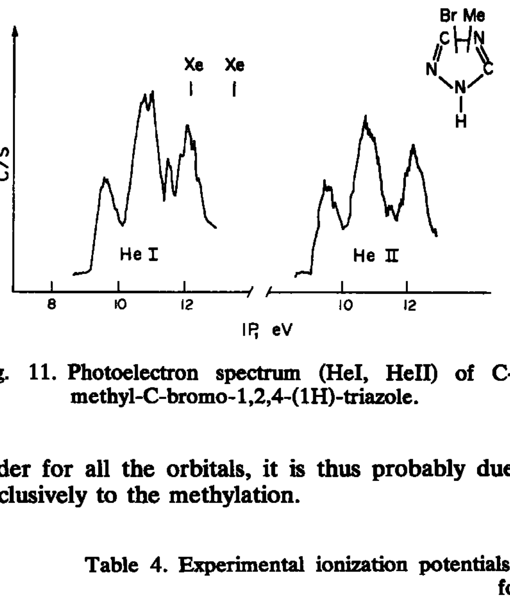


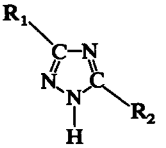
Fig. 11. Photoelectron spectrum (HeI, HeII) of C-methyl-C-bromo-1,2,4-(1H)-triazole.

order for all the orbitals, it is thus probably due exclusively to the methylation.

Although we may systematically reject the 4H tautomer (**C**), it nevertheless appears that the chlorine derivatives do not present the same form as the bromine derivatives. Indeed, the position of the spectral bands of chloro-C-methyl-1,2,4-triazole and the changes in their intensity in the HeI/HeII transition are entirely comparable to those observed in the spectrum of **A** (3-chloro), while the spectrum of the bromine homologue is inversely quite similar to that of **B** (5-bromo), particularly concerning the n^{σ}_{Br} and n^{+}_{NN} bands.

In conclusion, the analysis of the photoelectron spectra of the different halogen derivatives of 1,2,4-triazole in the vapor phase enable us to conclude that not only is the privileged form dissymetrical (1H) but also that when the halogen is chlorine there is predominance of a 3-chloro form, while in the case of bromine, the predominant form is 5-substituted.

Table 4. Experimental ionization potentials (eV) of chloro and bromo-1,2,4-triazoles (free forms).

		π	n^{-}_{NN}	π_2	n^{σ}_{X}	n^{+}_{NN}	n^{π}_{X}
R_1	R_2						
H	H	10.6	10.7	11.05		12.15	
Cl	H	10.1	11.2	11.1	12.00	12.4	13.15
Cl	Me	9.6	10.7	10.6	11.70	12.1	12.72
H	Br	9.9	11.	11.15	11.72	12.4	12.3
Me	Br	9.6	10.75	11.05	11.52	12.1	11.9

EXPERIMENTAL

The syntheses of the halogen derivatives of 1,2,4-triazole have been previously described.[37]

The photoelectron spectra were obtained with a Perkin-Elmer PS 18 spectrometer with a HeI/HeII "Helectros" light source. The spectra were calibrated with the $^2P_{1/2}$ and $^2P_{3/2}$ doublets of argon (15.755 eV and 15.93 eV) and of xenon (12.12 eV and 13.43 eV).

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