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## Spectroscopy Letters

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597299>

## Prototropy of 1-Hydroxy-1,2,3-Triazole Studied by UV Photoelectron Spectroscopy

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**To cite this Article** Guimon, C. , Khayar, S. , Pfister-guillouzo, G. and Begtrup, M.(1987) 'Prototropy of 1-Hydroxy-1,2,3-Triazole Studied by UV Photoelectron Spectroscopy', Spectroscopy Letters, 20: 2, 105 — 110

**To link to this Article:** DOI: 10.1080/00387018708081532

**URL:** <http://dx.doi.org/10.1080/00387018708081532>

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PROTOTROPY OF 1-HYDROXY-1,2,3-TRIAZOLE  
STUDIED BY UV PHOTOELECTRON SPECTROSCOPY

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**KEY WORDS:** PES, MNDO Calculations, hydroxy triazole, prototroping, gaseous phase

A number of recent investigations have demonstrated the potential of the ultraviolet photoelectron spectroscopy by studies of gaseous equilibrium mixture at low pressure<sup>2</sup>. In particular, the method has been found applicable for studies of tautomerism<sup>3,4</sup> and prototropy<sup>5,6</sup> of heterocyclic compounds.

The present paper deals with the tautomerism of 1-hydroxy-1,2,3-triazole. The solution of this problem may contribute to the understanding of the mechanism of the action of 1-hydroxybenzo triazole, the most important catalyst in peptide synthesis<sup>7</sup>.

1-hydroxytriazole may adopt five tautomeric forms (1a-1e). According to X-ray crystallography, 1-hydroxybenzotriazole exists at the form analogous to (1a) and (1c) in the solid state depending on the solvent used for its recrystallization<sup>8</sup>. According to UV-spectra, it adopts the N-H forms analogous to (1b) and (1c) in aqueous solution<sup>9</sup>. In ethanol the less polar form (1a) predominates<sup>9</sup>. So in dimethyl sulfoxide according to <sup>13</sup>C NMR spectra<sup>10</sup>.

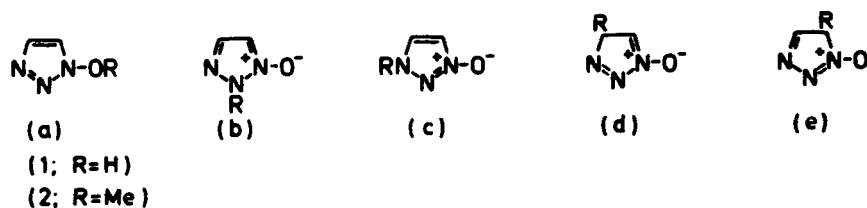
Of the tautomeric forms, only (1a-1c) are aromatic and therefore expected to be present in significant amounts. Concordantly,

the forms (1d-1e) are not observed in the  $^1\text{H}$  NMR spectra of 1-hydroxy triazole in aqueous or acetone-solution.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra as well as other classical methods failed to give further information about the tautomeric composition. Therefore photoelectron spectroscopy was employed comparing the spectrum of 1-hydroxytriazole with those of the methyl compounds (2a-2c) each possessing a fixed structure derived from the most likely tautomeric species (1a-1c), respectively. The photoelectron spectra have been compared with MNDO calculations minimizing the total energy with respect to all geometric parameters<sup>11</sup>.

### Results and discussion

The HeI photoelectron spectra of the fixed structure derivatives (2a-2c) are shown in Fig. 1-3. The ionization potentials obtained from the spectra as well as the potentials calculated by the MNDO method are presented in Table 1. Experimental and calculated potentials agree quite well according to Koopmans theorem<sup>12</sup> and exhibit characteristic trends in the series 2a, 2b and 2c. This is most obvious for the potentials associated with the  $\pi$ -orbitals of highest energy.

The ionization potential of the non-bonding  $n_{\text{O}}^{\sigma}$  orbital of pyridine-N-oxide is 9.34 eV<sup>13</sup>. Hence, a low value for this potential is expected for the triazole-N-oxides (2b) and (2c) and the second band (9.45 eV) of compound (2c) is attributed to this transition. This assignment is confirmed by the vibrational fine-structure at 1100  $\text{cm}^{-1}$  of the band, a feature also observed by the corresponding pyridine-N-oxide band. The second band (9.85 eV) of compound (2b) exhibits a less recognizable vibrational



Scheme 1

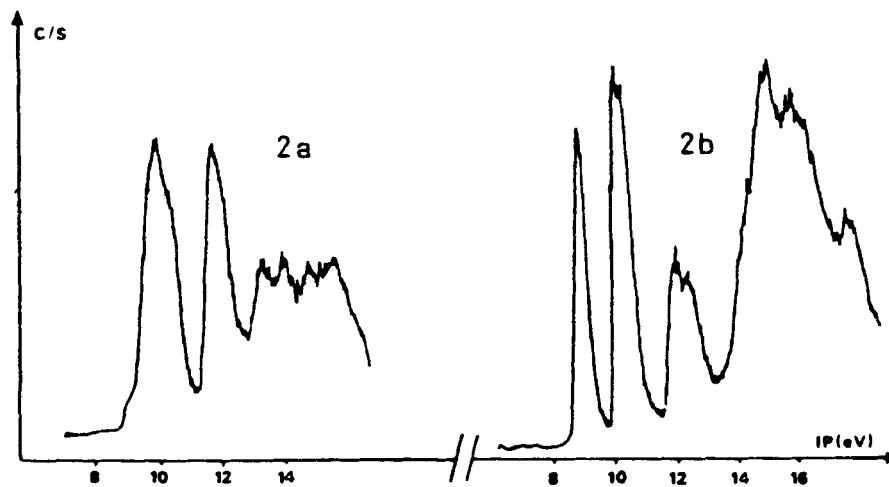


Figure 1

Figure 2

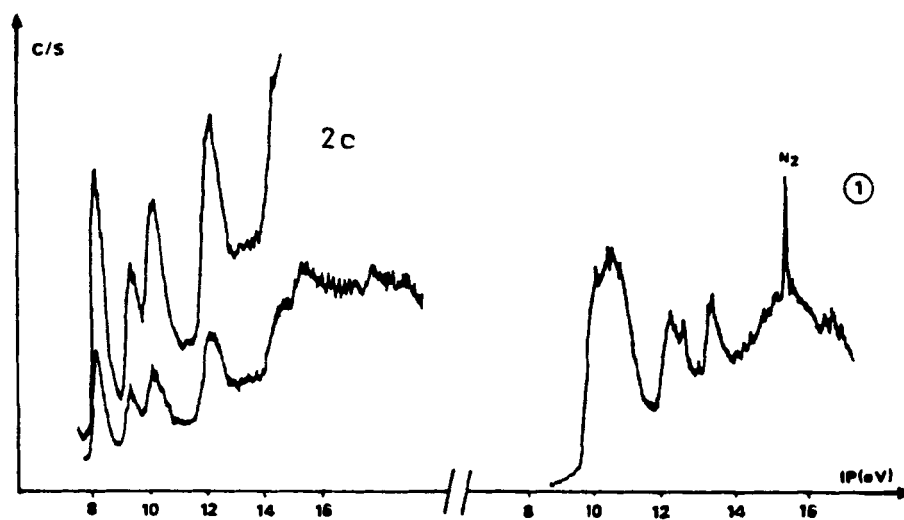


Figure 3

Figure 4

Table 1 Experimental and calculated (MNDO) ionization potentials of the methyl compounds (2a-2c) with fixed structure

Compound	Ionization potential (eV)					
(2a)	PI <sub>exp</sub>	between 9.7 and 10.7			between 11.8 and 12.4	
	PI <sub>calc.</sub>	10.22( $\pi$ )	11.19( $\pi$ )	11.82( $n_O^\pi$ )	12.78( $n_N^\sigma$ )	13.46( $n_N^{\sigma+}$ )
(2b)	PI <sub>exp</sub>	8.65	9.85		11.85	12.3
	PI <sub>calc.</sub>	9.24( $\pi$ )	10.63( $\pi$ )	11.16( $n_O^\sigma$ )	13.29( $n_N^\sigma$ )	13.52( $\pi$ )
(2c)	PI <sub>exp</sub>	8.35	9.45	10.20	between 12. and 12.5	
	PI <sub>calc.</sub>	9.02( $\pi$ )	10.66( $n_O^\sigma$ )	10.61( $\pi$ )	13.25( $\pi$ )	13.75( $n_N^\sigma$ )

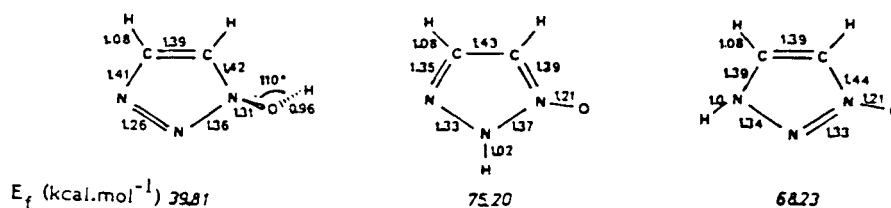
fine-structure due to partial overlap with the band resulting from the highest occupied  $\pi$ -orbital. The less satisfying accordance between the experimental and the calculated potential for the non bonding  $n_O^\sigma$ -orbital of compound (2b) demonstrates the limitations of the Koopmans approximation when dealing with non-bonding orbitals of heteroatoms. A similar inconsistency was observed in the pyridine series<sup>5</sup>.

The spectrum of 1-hydroxytriazole (1) (Fig.4) is similar to that of its O-methyl derivative (2a) (Fig.1). Even the ionization potentials of these compounds are quite similar. Small differences in band positions as well as the more significant between the bands attributed to  $n_O^\pi$ -orbitals in compounds (1) and (2a) are easily rationalized by the perturbations caused by the methyl group in (2a).

The predominance of the hydroxy form (1a) in the gas phase is confirmed by the MNDO calculations. In (1b) and (1c) conjugation between the  $\pi$ -orbitals of the oxygen and the ring exists while it is lost in (1a). In (1b) and (1c) all nitrogen atoms are planar while the substituted nitrogen is pyramidal in (1a). Despite these facts the calculated total energy increases in the order 1a < 1c < 1b. The large energy difference between (1a) and (1c) (28.4 kcal.mol<sup>-1</sup>) explains why only

Table 2 Experimental and calculated (MNDO) ionization potentials  
of 1-hydroxy-1,2,3-triazole (form 1a)

Compound	Ionization potential (eV)			
	$PI_{exp}$	between 10.1 and 11	12.3	12.5
1a	$PI_{calc}$	10.30( $\pi$ ) 11.29( $\pi$ ) 12.10( $n_N^{\sigma-}$ ) 13.24( $n_N^{\sigma+}$ ) 13.95( $n_O^{\pi}$ )		



(1a) is present in the gas phase from 20°C until the decomposition temperature of 1-hydroxytriazole.

Form (1c) is calculated to be only slightly more stable than (1b). This agrees well with the fact that the parent 1,2,3-triazole preferably adopts the unsymmetrical 1-H form in the gas phase<sup>14-16</sup> but the symmetrical 2-H form in the liquid phase<sup>17</sup>.

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Date Received: 10/14/86

Date Accepted: 11/17/86