The Microwave Spectrum and Dipole Moment of 1,2,4-Triazole: Identification of Tautomer in Vapour Phase

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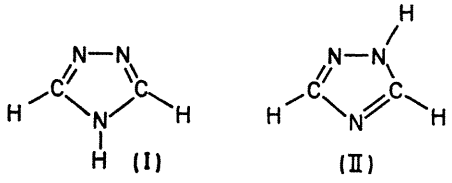
Summary An analysis of the microwave spectrum of 1,2,4-triazole has shown that the molecule is planar and exists predominantly in the unsymmetrical tautomeric form in the vapour phase.

1,2,4-TRIAZOLE may exist in two tautomeric forms, (I) and (II). Structure (II) is believed[1] to be the more stable in the solid phase at −155 °C and this tautomer will possess components of the dipole moment along both of the in-plane inertial axes, *a* and *b*, whereas the other tautomer will have only one component, since it has C_{2v} symmetry. Therefore an analysis of the microwave spectrum could indicate which is the more stable tautomer in the gas phase at room temperature.

Crystallographic structural data[1] were used to predict the approximate spectrum which was then analysed to give $A = 10{\cdot}24514(5)$, $B = 9{\cdot}83215(5)$, $C = 5{\cdot}01522(5)$ GHz and an inertial defect of 400 a.m.u. pm^2, confirming the expectation of planarity for the molecule. About 60 transitions were assigned either to μ_a or μ_b type transitions and fell within 2 MHz of the final predicted values, using the above rotational constants and the rigid rotor approximation. No other lines were observed that could be attributed to tautomer (I).

Experimental and calculated values of the dipole moment of 1,2,4-*triazole*

Method	μ_a (D)	μ_b (D)	μ_{total} (D)	Ref.
Microwave ..	$0{\cdot}8_2$	$2{\cdot}5_9$	$2{\cdot}7_2$	this work
Dioxan solution ..	—	—	3·27	ref. 2
VESCF	0·75	2·20	2·33	this work
CNDO/2 . ..	0·92	2·93	3·07	this work



Stark effect measurements on the $3_{12}—3_{21}$, $4_{22}—4_{31}$, $3_{22}—3_{21}$, $4_{32}—4_{31}$ lines gave values of $\mu_a = 0{\cdot}82$ (10), $\mu_b = 2{\cdot}59$ (10), $\mu_{total} = 2{\cdot}72$ (12) D. These values are in good agreement with solution measurements[2] and those calculated by us using the π-electron VESCF method[3] and the all-valence-electron CNDO/2[4] method (Table). (The agreement could be fortuitous, especially since we had to estimate the molecular geometry for the molecular orbital calculations.)

The nitrogen nuclear quadrupole coupling of the three nitrogens causes some of the low J lines to be at least 4 MHz broad. An analysis of this hyperfine structure is in progress and the results will be reported later.

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