Microwave Spectrum of 1-Deuterio-1,2,3-Triazole

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Summary Analysis of the microwave spectrum of a highly enriched sample of *N*-deuterio-1,2,3-triazole has shown unambiguously that the unsymmetric tautomer of 1,2,3-triazole is present in the vapour phase.

Like 1,2,4-triazole[1], 1,2,3-triazole may exist in either the 1*H*- or 2*H*-form. Combined i.r., ^{1}H n.m.r., ^{14}N n.m.r., and mass spectral data leave some uncertainty about which tautomeric form of 1,2,3-triazole is present in the liquid and the gas phase.[2]

The microwave spectrum of the parent species of 1,2,3-triazole was interpreted in terms of the 1*H*-form.[3] The assignment was made by double resonance, but only *a*-type transitions could be found. Since both *a*- and *b*-type transitions are symmetry-allowed in the 1*H*-form (but only one selection rule, *a* or *b*, in the 2*H*-form), this is not a conclusive proof of which tautomer is present in the gas phase. Stiefvater *et al.*[3] suggested, however, that the assigned spectrum arises from the 1*H*-form rather than from the 2*H*-form, based on model calculations of the two tautomers.

Previous attempts to obtain *N*-deuterio-1,2,3-triazole of high isotopic purity have been unsuccessful.[4] However, 98% enrichment was achieved by stirring an 8% etheral solution of the protio-compound[5] for 1 h at 20 °C with 99·8% D_2O (10 mol. equiv.) saturated with KCl. Pre-dried equipment and chemicals were used. Two additional exchange cycles gave after final drying ($MgSO_4$), removal of the ether, and distillation, 55% of *N*-deuterio-1,2,3-triazole.

The microwave spectrum of the deuteriated sample was assigned by conventional methods on a Stark-modulated spectrograph. Several lines were observed, and the rotational constants determined by rigid-rotor-fitting of six lines with low J values, $A = 9967{\cdot}7$, $B = 9160{\cdot}3$, and $C = 4771{\cdot}9$ MHz. This spectrum was assigned to the 1-deuterio-form for the following reasons: (i) The spectrum contained both *a*- and *b*-type transitions (only one type is symmetry-allowed for the 2-deuterio-form). (ii) The rotational constants A and B both change from their parent values (only one of these would change for the 2-deuterio-form). (iii) The substitution co-ordinates of H(1) are $|a|$ 1·563 Å and $|b|$ 1·372 Å, and the inertial axes rotate on substitution by 36°. [H(2) would have one co-ordinate = 0 and a rotation upon substitution of 0° or 90°]. (iv) The H(1) distance from the centre of mass is 2·08 Å which compares favourably with 2·07 Å in pyrazole[6] and 2·12 Å in pyrrole.[7]

No lines were found which could be attributed to the 2-deuterio-form. However, its presence cannot be excluded, since an almost vanishing dipole moment of the 2*H*-form of 1,2,3-triazole must be expected. Recent dipole measurements[8] of the two *N*-methylated derivatives of 1,2,3-triazole at 25 °C in benzene gave μ 4·46 D for 1-methyl-1,2,3-triazole and μ0·37 D for 2-methyl-1,2,3-triazole. Comparing these values with the microwave results, μ 1·74 D for pyrrole[7] and μ 2·12 D for 1-methylpyrrole,[9] the 1*H*-form can be expected to have a dipole moment around 4·1 D, whereas the dipole moment of the 2*H*-form must be much smaller $[0{\cdot}37 \pm (2{\cdot}12 - 1{\cdot}74) = 0{\cdot}75 \text{ or } -0{\cdot}01 \text{ D}]$. The microwave spectrum of the 2*H*-form would therefore be very difficult to find in the rich spectrum of the 1*H*-form. We find it probable, however, that the 2*H*-form is present in comparable amounts, since the spectrum of the 1*H*-form is much weaker than one would expect considering the large dipole moment, 4·1 D, estimated above.

The proposed dipole moment for the 1*H*- and 2*H*-forms, 4·1 D and 0·75 or 0·01 D, respectively, suggest that both tautomers of 1,2,3-triazole are present in benzene solution, where the dipole moment[8] is 1·85 D at 25 °C and 2·08 D at 45 °C. Since the extent of hydrogen bonding between two or more molecules is unknown, the relative amount of the tautomers can only be guessed.

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