The Molecular Structure and Tautomer Equilibrium of Gaseous 1,2,3-Triazole Studied by Microwave Spectroscopy, Electron Diffraction and *Ab Initio* Calculations*

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Begtrup, M., Nielsen, C. J., Nygaard, L., Samdal, S., Sjøgren, C. E. and Sørensen, G. O., 1988. The Molecular Structure and Tautomer Equilibrium of Gaseous 1,2,3-Triazole Studied by Microwave Spectroscopy, Electron Diffraction and *Ab Initio* Calculations. – Acta Chem. Scand., Ser. A 42: 500–514.

1,2,3-Triazole has been studied by microwave spectroscopy, by gas-phase electron diffraction, and by *ab initio* calculations.

The analysis of the microvawe spectra of the parent molecule, the $^{15}N_3$ species and the corresponding *N*-deuteriated species reveals the molecule to exist as a mixture of two planar tautomers: a 1*H* form with C_s symmetry and a 2*H* form with C_{2v} symmetry. The dipole moments of the tautomers have been measured as μ_{1H} = 4.38(3) D and μ_{2H} = 0.218(12) D for the 1*H* and 2*H* forms of the $^{15}N_3$ species, respectively. The relative abundance of the tautomers, estimated from intensity measurements, is 1*H*:2*H* ~ 1:1000 at room temperature.

Fully optimized geometries have been calculated for the two tautomeric forms of 1,2,3-triazole at the Hartree-Fock SCF level employing a basis set of double zeta quality. The calculations show the 2*H* form to be the more stable, the energy difference being $\Delta E_{1H \to 2H}$ = −14.7 kJ mol⁻¹.

The structural refinement of a planar C_{2v} model of the 2*H* tautomer was carried out based upon the electron-diffraction data in combination with the measured rotational constants (corrected to A_z, B_z and C_z). An r_a^0 model corrected for isotopic differences was used in the combined analysis, and the *u* values and the various correction terms needed were obtained from normal coordinate calculations based on a simplified valence force field. The bond distances (r_a) and the independent valence angles ($\angle_a$) thus obtained are: r_{NH} = 1.017(1), r_{CH} = 1.105 (3), r_{CC} = 1.405(2), r_{CN} = 1.346(2) and r_{NN} = 1.323(1) Å, and $\angle_{NNN}$ = 117.1(1) and $\angle_{CCH}$ = 133.0(5)°.

Dedicated to Professor Otto Bastiansen on his 70th birthday

The investigation of 1,2,3-triazole by microwave spectroscopy started twenty years ago as an extension of work on pyrrole[1] and pyrazole.[2] As the dipole moment of 1,2,3-triazole, measured in benzene solution, was known to be 1.77 D[3] we expected to find a strong spectrum of one or both

tautomers (Fig. 1) and were at the time very surprised that only one extremely weak spectrum was observed.

Simultaneously, the Bangor microwave group assigned the spectrum by microwave double resonance.[4] Somewhat later a highly enriched *N*-deuterio sample was prepared and a spectrum assigned,[5] confirming that the tautomer found by both groups was indeed the asymmetric 1*H* form.

Prior to these microwave studies the IR spec-

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* A preliminary report of the microwave work has been given elsewhere, see Ref. 10. Since then we have extended the work and reassigned one of the spectra.

trum of 1,2,3-triazole as well as of a ca. 50 % N-deuteriated sample was investigated.[6] The spectra were interpreted in terms of the asymmetric tautomer, mainly on the basis of the IR vapour phase contours. Apparently five C type bands are found in the vapour phase spectra, which is in perfect agreement with the selection rule for C_s symmetry, whereas only three are expected for the $2H$ form with C_{2v} symmetry.

Recently, $1H$- and $2H$-1,2,3-triazole were observed directly by low temperature ^1H NMR.[7] The observed $1H$ form was found to be predominant in toluene solution at 175 K. The relative amount of the $2H$ form was reported to increase with decreasing dipole moment of the solvent, with decreasing concentration, and with increasing temperature. The thermodynamic parameters of the tautomeric equilibrium were determined and used to show that the $2H$ form amounts to more than 97 % at 300 K at 0.05 M concentration in toluene.

Shortly after the publication of the microwave studies[4] the dipole moments of the two N-methyl-1,2,3-triazoles in benzene solution were reported,[8] revealing very large differences in the moments for the 1-methyl and 2-methyl isomers: 4.46 and 0.37 D, respectively. Triazole itself was remeasured in benzene solution as well. These results led to the expectation of the $2H$ form of 1,2,3-triazole as the dominant tautomer in benzene solution, and we planned to make a new search for this tautomer in the gas phase, although it was expected that the dipole moment of the $2H$ form would be very small.[5]

Nuclear quadrupole patterns of the microwave lines were studied at high resolution by Blackman et al. for the parent and 1-D species of $1H$-1,2,3-triazole[9]. No $2H$ lines were observed in that study.

Considering the experimental difficulties in finding and assigning microwave lines of the $1H$ form caused by (i) low population and (ii) line broadening by nuclear quadrupole coupling, it was considered essential to prepare a sample highly enriched with $^{15}N_3$. We could thereby avoid the quadrupole patterns, concentrate the line intensities, and a search for the $2H$ form would then be more favourable. The "missing" tautomer, which turned out to constitute more than 99 % of the mixture, was eventually found in the microwave spectra and a preliminary report was presented.[10]

A few years later the gas phase tautomerism of 1,2,3-triazole was studied by photoelectron spectroscopy and by HONDO calculations,[11] and very recently these calculations were extended to the SCF level including configuration interaction.[12] The geometries employed in the latter calculations were those resulting from the minimum basis HONDO calculations,[11] and no geometry optimisation was attempted. The conclusion presented[11] was in agreement with our results: the $2H$ tautomer is by far the dominant form. However, the ab initio geometries were so utterly in disagreement with our own geometric models of the tautomers that we decided to extend the microwave study of 1,2,3-triazole with a gas-phase electron diffraction investigation and more elaborate ab initio calculations at the Hartree-Fock SCF level including full geometry optimisation for the two tautomeric forms.

From electron diffraction experiments the interatomic distances are determined directly. The individual values of closely spaced bond distances cannot be determined accurately; only their average can. However, even with complex distance overlaps a molecular structure can be determined accurately if a reasonable molecular force field is available and when rotational constants are included in the analysis.

Experimental

$^{15}N_3$-1,2,3-Triazole. In an ampoule, $^{15}N_3$ sodium azide (95 % enriched; supplier Isocommerz, Leipzig, DDR) (249 mg) was covered with dry benzene (4.0 ml). The benzene was frozen by cooling to $-78\,°C$. Propiolic acid (1.0 ml) was added. When frozen, conc. hydrochloric acid (0.5 ml) and a magnet stirring bar were added. The ampoule was sealed under nitrogen. After stirring at 20 °C for 1 h, heating to 75 °C within ca. 15 min (oil bath), and stirring at 75 °C for 3 h the benzene was decanted off. The residue was dissolved in water (12 ml) at 60 °C and acidified to pH ca. 3 (hydrochloric acid). Removal of the water, extraction with boiling 10 % aqueous acetone (10 + 4×5 ml) with cooling to 0 °C before filtration through activated carbon, removal of the solvents, and drying (1 mmHg, P_2O_5, 2 d) gave $^{15}N_3$-4-carboxy-1,2,3-triazole; the latter was heated in a sealed 60 ml thick walled ampoule, by stirring in an oil bath, to 230 °C for 15 min (safety shield). The ampoule was cooled to $-196\,°C$ and

opened under nitrogen. Extraction with dry ether (5×2 ml), pressure filtration through activated carbon, removal of the ether and short path distillation gave 240 mg (91 %) of *[15]N3-1,2,3-triazole* as a colourless oil. The identity and purity of the product were checked by ^{1}H, ^{13}C and ^{15}N NMR spectroscopy.[13]

Microwave spectra. Microwave spectra were recorded at room temperature and at pressures less than 20 mTorr in the 8–40 GHz region using a Hewlett-Packard 8460A MRR spectrometer controlled by a microprocessor which in turn was linked to the local host computer.[14] Stark voltages up to the maximum possible (4000 V cm^{-1}) were applied, but often this was not sufficient to modulate the lines. The measured transition frequencies are believed to be accurate to within 0.05 MHz.

Since most of the lines (39) of 1-D substituted 1*H*-1,2,3-triazole were measured as far back as in 1971[5] using a Stark-modulated spectrometer with video recording, their frequencies are considerably less accurate. In the least-squares analysis the measurements were therefore weighted in accordance with uncertainties ranging from 0.3 to 1.0 MHz.

Electron diffraction. The electron-diffraction experiments were carried out with a Balzer's Eldigraph KD-G2[15,16] for nozzle-to-plate distances of 498.19 and 248.32 mm, using Kodak Electron Image plates and a nozzle temperature of 96 °C. The wavelength of the electron beam was 0.05865 Å (estimated standard deviation of 0.1 %), as calibrated against diffraction patterns of benzene using r_a(CC) = 1.3975 Å as standard. Six plates were used for both camera distances in the structural analysis. The optical densities (*D*) were recorded on a Joyce Loebl densitometer, and the densities were processed[17] using a blackness correction of $1 + 0.03D + 0.09D^2 + 0.03D^3$. A modification function $s/|f'_N|^2$ was applied, and a background subtraction program was used to subtract the background on the modified form employing polynomials of the 7th and 9th degree for the long and short camera distances, respectively. The program works essentially in the same way as that described by L. Hedberg.[18] The six modified molecular intensity curves were averaged for each of the two camera distances, and these two average curves were used simultaneously in the least-squares analysis. The intensity data cover the range of $2.00 \leq s \leq 15.25$ Å^{-1} with data intervals $\Delta s = 0.125$ Å^{-1} for the long camera
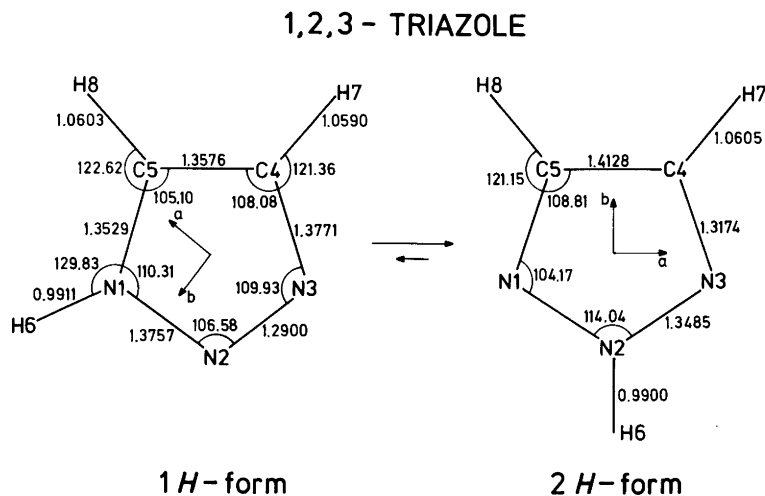
1,2,3 - TRIAZOLE

Fig. 1. The *ab initio* molecular models (double zeta basis) of 1,2,3-triazole drawn to scale. Computed energies: −240.422405 hartree (2*H* form) and −240.416798 hartree (1*H* form). Bond lengths in Å and angles in degrees. Computed dipole moments and gross atomic charges: μ = (0, 0.52, 0), q_{N1} = −0.345, q_{N2} = −0.273, q_C = −0.027, q_{H6} = 0.408, q_{H7} = 0.268 (2*H* form) and μ = (4.95, 0.08, 0) D, q_{N1} = −0.345, q_{N2} = 0.008, q_{N3} = −0.341, q_{C4} = −0.055, q_{C5} = 0.072, q_{H6} = 0.399, q_{H7} = 0.267, q_{H8} = 0.279 (1*H* form).

distance, and $4.00 \leq s \leq 30.00$ Å^{-1} with $\Delta s = 0.25$ Å^{-1} for the short camera distance.

The scattering amplitudes and phases[17] were calculated using the partial wave method[19] based upon analytical Hartree-Fock potentials for C and N atoms,[20] and the best electron density of bonded hydrogen for the H atoms.[21] The inelastic scattering factors were those of Tavard et al.[22]

Ab initio calculations

Restricted Hartree-Fock level calculations were performed using a gradient version of the program MOLECULE.[23,24] The geometry relaxation was continued until all cartesian forces on the atomic coordinates were less than 0.001 atomic units.

A $7s3p$ basis set, developed for the first row atoms,[25] has proved its merit as a medium-sized basis set capable of giving equilibrium geometries in agreement with experimental values. This set was therefore chosen as a starting set for carbon and nitrogen. For hydrogen, a $4s$ primitive set[26] was employed and the primitive sets were contracted to double zeta quality, $4s2p$ on C and N, and $2p$ on H, the orbital exponents on hydrogen being scaled by a factor of (1.2^2).[27]

The computed equilibrium geometries of the $1H$ and $2H$ tautomers of 1,2,3-triazole are given in Fig. 1, where also the dipole moments and the gross atomic charges have been included. The calculations show the $2H$ tautomer to be the more stable, with an energy difference of $\Delta E_{1H \to 2H} = -14.7$ kJ mol^{-1}, which corresponds roughly to a ratio of $1H{:}2H \sim 1{:}200$ at room temperature.

In comparison with the structures of $1H$- and $2H$-1,2,3-triazole obtained by HONDO calculations[11] (minimum basis set), our SCF minimum energy structures of the two tautomers each have ca. 3 % shorter bond distances but roughly the same valence angles. The energy difference, $\Delta E_{1H \to 2H} = -15.9$ kJ mol^{-1}, calculated with the HONDO program (with a double zeta basis set)[11] is close to our result. However, the corresponding results from the very recent SCF and SCF-CI calculations,[12] -70 and -92 kJ mol^{-1}, respectively, cannot be taken as evidence in a discussion of the tautomeric equilibrium because the geometries resulting from the HONDO minimum basis set calculations[11] were assumed. The ab initio results will be further commented upon in the subsequent chapters.
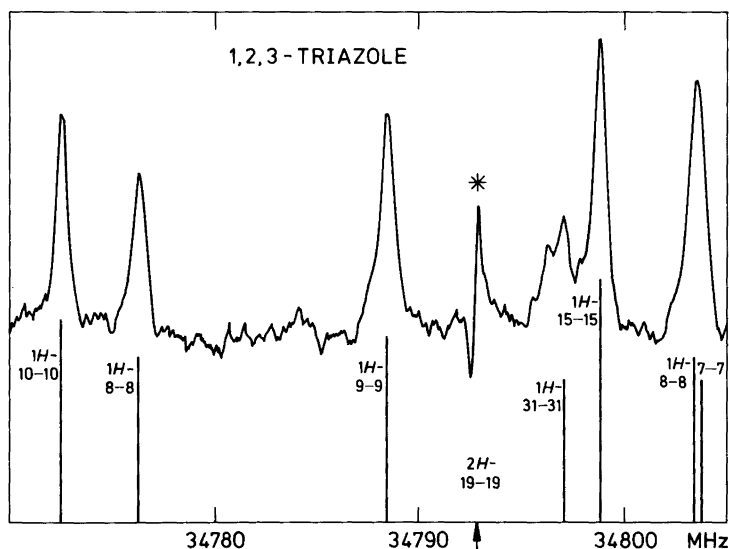

Fig. 2. Detail of the microwave spectrum of 1,2,3-triazole, parent species. 10 mTorr, 20 °C, 2000 V cm^{-1}, 25 kHz step length, 20 spectra added. The $2H$ line marked with an asterisk is not fully modulated, whereas all the other ($1H$) lines are Stark resolved at this field.

Analysis of microwave spectra

Assignment of the spectral lines to either the 1H or the 2H tautomer was easily accomplished on the basis of the large differences in their Stark effects. At moderate Stark fields of about 1000 V cm^{-1} the lines of the 1H tautomer appear fully modulated whereas the lines of the 2H tautomer, due to the very small dipole moment, are either totally absent or – for the high-J Q-lines – only visible as unmodulated lines appearing as a first-order derivative recording. An example of this can be seen already in the recording of the initial investigation (Fig. 2 in Ref. 4). Further examples are given in Figs. 2 and 3.

The $^{15}N_3$ enriched sample. After the assignment of a large number of lines of the 1H tautomer, the spectrum of a very near oblate symmetric rotor with a small dipole moment (lines difficult to modulate) and alternating spin weights (5:3) consistent with a model of the 2H tautomer was found and assigned. The dipole moments of both tautomers were measured (see below).

Parent 1,2,3-triazole. Prior to the search for the 2H tautomer the earlier data for the 1H tautomer were extended by new measurements. Some lines with a slow Stark effect as in the $^{15}N_3$-2H tautomer were observed but not assigned at that time.

The preliminary electron-diffraction results and *ab initio* calculations resulted in models of the tautomers which pointed to a reassignment of the first microwave 2H spectrum to the 2-D,$^{15}N_3$ species instead of to the 2-H,$^{15}N_3$ species. We therefore resumed the microwave investigation and soon found lines in the spectra from the 2-H,$^{15}N_3$ species. These lines were assigned and measured.

A possible explanation for the fact that we first found spectral lines of deuteriated 2H tautomer is that triazole is a very effective "cleansing agent" for the microwave cell. It takes several days to saturate the equipment and get observable lines. In the meantime, most of the history of the cell is presented and several different spectra can be observed. Any labile bonded deuterium on the cell walls may exchange with the N-bonded hydrogen in 1,2,3-triazole.
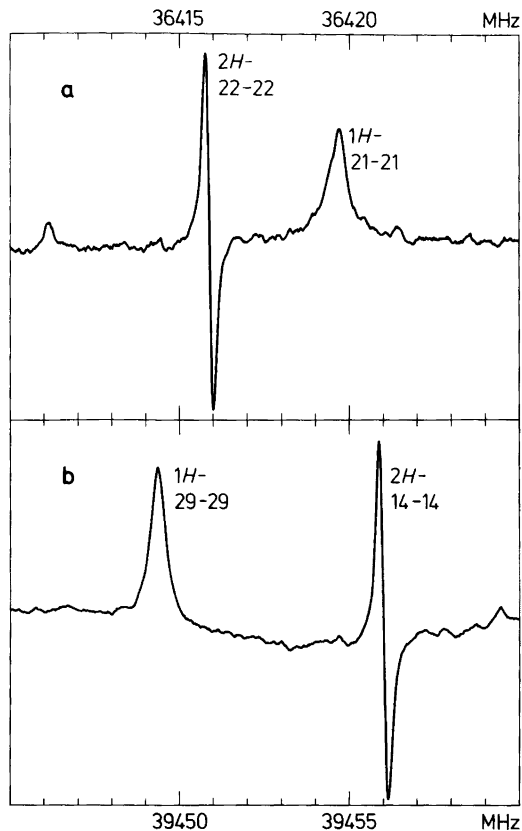
With the improved molecular model we again

Fig. 3. Two details of the microwave spectrum of 1,2,3-triazole, $^{15}N_3$ species. (a) 5 mTorr, 20 °C, 2000 V cm^{-1}, 25 kHz step length, 20 spectra added. The 2H line is $22_{17,5} \rightarrow 22_{18,4}$ and the 1H line is $21_{17,5} \rightarrow 21_{17,4}$. (b) as in a, except 3000 V cm^{-1}. The 2H line is $14_{11,4} \rightarrow 14_{12,3}$ and the 1H line is $29_{24,6} \rightarrow 29_{24,5}$.

returned to the parent sample of 1,2,3-triazole in order to assign the 2H spectrum.

The latest step was a collection of the data for the 1-D species of the 1H tautomer, published earlier only in part.[5]

For the 1H parent species most of the lines were quadrupole broadened, but none of the measured lines had to be corrected for quadrupole hyperfine structure.

For the 2H parent species some lines were observed as triplets similar to the patterns caused by two equivalent nitrogen quadrupoles (e.g. Ref. 28, Fig. 2). The observed triplets for 2H-1,2,3-triazole were consistent with model val-

ues as follows: $\chi_{aa} = -3$ MHz, $\chi_{bb} = 2$ MHz, $\chi_{cc} = 1$ MHz for N1 and N3, whereas the coupling from N2 was neglected.

An analysis of the narrow quadrupole patterns was not attempted, since the Stark effect gave splittings of the same magnitude or less.

Tables of the experimental microwave frequencies can be obtained from one of the authors (L.N.) upon request. They have also been deposited at the Microwave Data Center at the National Bureau of Standards, Gaithersburg, Maryland, U.S.A.

Rotational constants. The line frequencies were fitted using an effective Hamiltonian incorporating quartic and sextic centrifugal distortion terms. For planar, near oblate symmetric rotors the planarity defect (i.e. the deviation of τ_{bcbc} and τ_{caca} from zero) is negligible and the planarity relations[29] were therefore invoked in rewriting the quartic centrifugal distortion operator in a form involving the following four parameters:

$$D_1 = \tau_{abab} + 2\,\tau_{cccc}$$

$$D_2 = \tau_{aaaa} + \tau_{bbbb} - 2\,\tau_{abab} - 8\,\tau_{cccc}$$

$$D_3 = \tau_{aaaa} - \tau_{bbbb}$$

$$D_4 = \tau_{cccc}$$

These combinations were chosen since D_2 and D_3 vanish for an oblate symmetric top. As in previous investigations[28] of planar near oblate rotors, the contributions to the line frequencies are small for these two constants and almost vanishing for D_4, when τ_{cccc} enters the combinations in D_1 and D_2. For this reason, D_4 could only be fitted with physically reasonable results for two of the investigated species (the 1-H,[15]N_3 and 2-D,[15]N_3 species). In all other cases D_4 was constrained to the value -2.0 kHz confirmed by the force constant calculations. Despite the indeterminability of D_4 it was necessary in most cases to include the sextic term H_{JK} in the analysis. The spectroscopic constants are given in Tables 1 and 2 together with the derived asymmetry parameter, $\varkappa$, and inertial moments and defect. Furthermore, the maximum J-value and the number of observed lines are given together with the standard deviation of the least squares fit, σ.

Dipole moments. The dipole moments of the two tautomers of 1,2,3-triazole were determined for the [15]N_3 species of the $1H$ form and for the 2-D,[15]N_3 species of the $2H$ form. The Stark voltages were calibrated against the OCS transitions assuming a dipole moment of $\mu_{OCS} = 0.71521$ D.[30]

For the $1H$ tautomer the Stark effect of six transitions was studied, three of R-type and three of Q-type. With the electric field strength varying

Table 1. Rotational constants, $\varkappa$, moments of inertia, inertial defect and centrifugal distortion constants (see text) for 1H-1,2,3-triazole. Conversion factor 505376 MHz uÅ^2.

Species	Parent	1-D	[15]N_3
A/MHz	10030.785(8)	9967.85(4)	9742.714(5)
B/MHz	9870.675(8)	9160.36(4)	9452.439(5)
C/MHz	4972.933(8)	4771.79(4)	4795.665(4)
$\varkappa$	0.93668841(10)	0.689191(2)	0.88264745(6)
I_a/uÅ^2	50.38249(4)	50.7006(2)	51.87220(3)
I_b/uÅ^2	51.19974(4)	55.1699(3)	53.46514(3)
I_c/uÅ^2	101.6253(2)	105.9091(9)	105.38184(9)
ID/uÅ^2	0.04310(9)	0.0386(5)	0.04449(5)
D_1/kHz	$-11.524(10)$	$-11.1(4)$	$-10.964(9)$
D_2/kHz	0.502(3)	0.3(2)	1.027(5)
D_3/kHz	0.637(2)	$-3.8(2)$	$-0.0353(16)$
D_4/kHz	-2 fixed	-2 fixed	$-1.1(3)$
H_{JK}/Hz	0.071(3)	$-0.4(4)$	0.0174(5)
J_{max}	49	22	60
Lines	88	48	138
σ/MHz	0.058	^{a}	0.044

^{a} 1.08 times estimated uncertainties used in weighting.

Table 2. Rotational constants, ϰ, moments of inertia, inertial defect and centrifugal distortion constants (see text) for 2*H*-1,2,3-triazole. Conversion factor 505376 MHz uÅ^2.

Species	Parent	$^{15}N_3$	2-D,$^{15}N_3$
A/MHz	10252.006(13)	10000.139(7)	9320.226(8)
B/MHz	9776.969(13)	9318.480(7)	9266.541(8)
C/MHz	5002.448(10)	4821.741(6)	4645.134(8)
ϰ	0.8190183(7)	0.7367298(4)	0.97703365(4)
I_a/uÅ^2	49.29533(6)	50.53690(3)	54.22357(4)
I_b/uÅ^2	51.69046(7)	54.23375(4)	54.53772(4)
I_c/uÅ^2	101.0257(2)	104.81194(14)	108.79687(18)
ID/uÅ^2	0.0400(2)	0.04130(8)	0.03557(9)
D_1/kHz	−11.5(3)	−10.69(3)	−9.690(11)
D_2/kHz	0.69(2)	0.50(3)	−0.006(6)
D_3/kHz	1.93(2)	1.14(4)	−3.2740(4)
D_4/kHz	−2 fixed	−2 fixed	−1.8(6)
H_{JK}/Hz	−0.1(3)		−0.003(2)
J_{max}	23	25	49
Lines	44	45	89
σ/MHz	0.096	0.058	0.042

from 100 to 1000 V cm^{-1} the Stark effects were quadratic with the field within the accuracy of the experiment. However, at larger field strengths some of the Stark coefficients displayed significant deviations from quadratic behaviour. The second-order Stark shifts are given in Table 3, from which the dipole moment μ_{1H} = 4.38(3) D may be derived; the uncertainty given in parentheses represents the 3σ-limit. The *ab initio* calculated dipole moment (Fig. 1) is 4.95 D pointing roughly from N3 towards C5. Unfortunately, the individual components cannot be compared to the experimental values directly because the position of the 1*H*-1,2,3-triazole molecule in the principal axis system of the $^{15}N_3$ species is not known. The direction of the *ab initio* calculated dipole moment may be off by 20–30°. Further, the molecule is near oblate and a slight change in the structure parameters may cause a large rotation of the *a,b* principal axes. However, a rough estimate of the dipole moment components may be obtained by rotating the coordinate system relative to the *ab initio* model of the molecule in such a way that the coordinates of the *N*-bonded hydrogen/deuterium correspond to the experimental values (see later). This procedure yields (μ_a/D,μ_b/D) = (4.7,−1.4) and (3.0,−3.9) for the parent and the 1-D species, respectively. The results are at least in agreement with the fact that *b*-type transitions dominate the microwave spectrum of

the 1-D species, whereas most lines in the spectrum of the parent species are of *a*-type.

As mentioned before, we measured the spectrum of the 2-D,$^{15}N_3$ species by accident. Under

Table 3. Second-order Stark coefficients and uncertainties[a] (MHz cm^2 V^{-2}) for the $^{15}N_3$ species of 1*H*-1,2,3-triazole.

Transition	|*M*|	Stark coefficients
$1_{1,0} \rightarrow 2_{1,1}$	0	−2.37 (3)×10^4
$1_{1,1} \rightarrow 2_{1,2}$	0	3.53 (3)×10^{-4}
	1	2.49 (3)×10^{-4}
$2_{0,2} \rightarrow 3_{0,3}$	1	8.20 (25)×10^{-6}
$3_{0,3} \rightarrow 3_{2,2}$	2	−1.04 (1)×10^{-5}
	3	−1.54 (2)×10^{-5}
$5_{3,3} \rightarrow 5_{3,2}$	4	2.31 (7)×10^{-6}
	5	3.63 (10)×10^{-6}
$6_{4,3} \rightarrow 6_{4,2}$	3	2.86 (10)×10^{-6}
	4	4.84 (10)×10^{-6}
	5	7.67 (20)×10^{-6}
	6	1.03 (2)×10^{-5}

Dipole moment: μ_{1H} = 4.38 (3) D
μ_a = 4.08 (3) D, μ_b = 1.59 (4) D

[a]Uncertainties given in parentheses represent three standard deviations where the uncertainties of the Stark voltages have been included.

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the given experimental conditions only one transition of this species, viz. $2_{1,2} \rightarrow 3_{1,3}$, was suitable for dipole moment measurement, the other low-J transitions being either too weak or perturbed by close lying lines. The Stark effect is extremely slow for this transition and only the $|M| = 2$ component could be measured. At 4000 V cm^{-1}, the $|M| = 0$ and 1 components were only shifted ca. -0.05 and 0.30 MHz, respectively, from the zero-field position. Although the line shape and line intensity were affected by this, the line position was not. Computer simulations of the Stark patterns at different field strengths indicated the maximum shift in line peak position to be ca. 0.005 MHz, i.e. less than the accuracy with which we could measure the Stark shift itself.

The Stark effect of the $|M| = 2$ component of the $2_{1,2} \rightarrow 3_{1,3}$ transition is quadratic with the applied field. The shift is $1.16(5) \times 10^{-7}$ MHz cm^2 V^{-2} corresponding to a dipole moment $\mu_{2H} = 0.218(12)$ D. In principle, the dipole moment of the $2H$ form could also be obtained from an analysis of the unresolved Stark patterns of the medium-J Q-type transitions. However, our attempts in this direction did not improve the accuracy in the dipole moment. For comparison, the ab initio calculated dipole moment of the $2H$ tautomer (Fig. 1) is 0.52 D, with N2 being the negatively charged end.

Relative population of tautomers. The population ratio of the two tautomers, $1H:2H$, was estimated from an analysis of the two details of the microwave spectrum of the triple ^{15}N sample shown in Fig. 3.

It was described above that the $2H$ lines were incompletely modulated and, hence, their linewidth and intensity could not be measured directly. In order to find the relative line intensities for the two tautomers, the recordings were compared to simulated patterns, whereby both linewidth and hypothetical peak height for the $2H$ lines could be extracted by a fitting procedure. The linewidth for the $2H$ tautomer was found to be 0.30(5) MHz, which is significantly less than the corresponding value for the $1H$ tautomer, viz. 0.50 MHz or more. For the $J = 22$ and $J = 14$ $2H$ lines shown in Fig. 3, the ratios between the hypothetical and the observed peak heights (under the specified experimental conditions) were found to be 2.5(5) and 2.1(4), respectively.

Analysis of the two details in Fig. 3 gave con-

sistent values of the population ratio $1H:2H = 1.0(2) \times 10^{-3}$, corresponding to $\Delta E_{1H \rightarrow 2H} = -19$ kJ mol^{-1}, which is a considerably larger energy difference than predicted by the ab initio calculations.

Analysis of electron-diffraction data

Calculation of vibrational quantities. We have adopted and slightly modified a valence force field for pyrrole[31] for calculating the root-mean-square amplitudes of vibration, u, and other vibrational quantities for the $2H$ tautomer of 1,2,3-triazole. The pyrrole force field has been developed from a similar force field for thiophene,[32] and both force fields probably give an accurate description of the potential surface for the molecules.

The modification of the pyrrole force field[31] merely consists of neglecting all force constants involving the α-hydrogens. The calculated vibrational frequencies appear reasonable – there is no complete vibrational study – and the centrifugal distortion constants and the inertial defects are also in fair agreement with our observations.

It is not surprising that the u values are insensitive to modifications of the force field necessary to reproduce the vibrational frequencies and the centrifugal distortion constants. However, the harmonic corrections[33,34] to the ground state rotational constants, $\delta B_{vib} = 0.5 \Sigma \alpha_i \sim B_z - B_0$, are more sensitive to variations in the force field and they are probably only correct to within 10 %. The electronic and centrifugal distortion contributions to B_0 are much smaller than δB_{vib} and have been neglected.

Structure analysis. According to the microwave analysis and the ab initio calculations the $1H/2H$ tautomer mixture consists of more than 99 % of the symmetric $2H$ form at room temperature. Hence, even at 96 °C, i.e. the nozzle temperature in the experiment, the amount of the $1H$ form is far below the "detection" limit for electron diffraction. Accordingly, the diffraction data have been analyzed in terms of a single tautomer, $2H$, with C_{2v} symmetry. The molecular geometry of this model can be described by the following seven independent structure parameters: r_{NN}, r_{CN}, r_{CC}, r_{NH}, r_{CH}, $\angle_{NNN}$ and $\angle_{CCH}$.

The root-mean-square amplitudes of vibration,[35] u, and the perpendicular amplitude correc-

Table 4. Calculated and refined vibrational amplitude quantities (Å) for 2*H*-1,2,3-triazole.[a]

Distance	r_a	$u_T{}^b$	$u_{refined}$		K_T	u_0	K_0
N1–N2	1.323	0.0440	0.0435 }	(6)[c]	0.0019	0.0436	0.0017
N1–C5	1.346	0.0437	0.0432 }		0.0022	0.0433	0.0020
C4–C5	1.405	0.0495			0.0020	0.0488	0.0018
N2–H6	1.017	0.0713	0.063 }	(4)[c]	0.0327	0.0713	0.0251
C4–H7	1.105	0.0762	0.068 }		0.0187	0.0762	0.0174
N1···N3	2.256	0.0500	0.051 }	(1)[c]	0.0006	0.0486	0.0005
N1···C4	2.231	0.0520	0.053 }		0.0007	0.0505	0.0006
N2···C4	2.087	0.0510	0.050 (2)		0.0008	0.0496	0.0007
N1···H6	2.034	0.0954			0.0151	0.0946	0.0114
N1···H7	3.309	0.0902	0.089 }		0.0053	0.0891	0.0048
N2···H7	3.123	0.0908	0.089 }	(10)[c]	0.0056	0.0898	0.0051
C4···H6	3.044	0.0871	0.085 }		0.0092	0.0861	0.0071
N1···H8	2.102	0.0990			0.0091	0.0981	0.0083
C4···H8	2.297	0.0983			0.0085	0.0972	0.0078
H6···H7	4.030	0.1196			0.0106	0.1186	0.0087
H7···H8	2.898	0.1541			0.0112	0.1516	0.0103

[a] u values not refined were constrained to their calculated values. Uncertainties correspond to one standard deviation as resulting from the least-squares refinement using a diagonal weight matrix. [b] T corresponds to a nozzle temperature of 96 °C. [c] Refined in one group.

tion coefficients,[35] K, were calculated from an approximate force field as already described. The asymmetry parameters,[36] $\varkappa$, for bonded atomic pairs were estimated from the diatomic approximation by $\varkappa = \frac{1}{6}a_3 \cdot u^4$, where a_3, the cubic anharmonicity constant, was assumed equal to 2.0 Å^{-1} for the NN, CN and CC bonds,[37] and to 2.6 Å^{-1} for the CH and NH bonds.[38,39] The $\varkappa$ values for all the non-bonded atomic pairs were ignored. Correction for shrinkage was incorporated in the analysis by refining a geometrically consistent r_α structure,[33] and the calculated u and K values for the parent molecule are given in Table 4 together with the refined u values.

Besides a "standard" electron-diffraction analysis, a joint structural analysis based upon the electron-diffraction data and the rotational constants for the parent, $^{15}N_3$ and the 2-D,$^{15}N_3$ species of 2*H*-1,2,3-triazole was also undertaken. First, the effective rotational constants for the vibrational ground state, B_0, were transformed into zero-point rotational constants, B_z, as previously described. The corresponding r_z structure should be compared to the r_α^0 structure derived from the electron-diffraction data. Second, the r_z structure is (by nature) different for different isotopic molecules. Hence, the isotopic changes in

the bond distances were estimated from the corresponding differences in the calculated u and K values. Bonded atomic pairs were treated in the diatomic approximation and the isotopic changes in the zero-point bond lengths were estimated by:[34,40,41]

$$\delta r_z = \frac{3}{2} a_3 \cdot \delta <\Delta z^2> - \delta K$$

i.e.

$$r^0{}_{\alpha(ref.)} - r^0{}_{\alpha(isotope)} = \frac{3}{2} a_3 \cdot \{(u^0_{ref})^2 - (u^0_{isotope})^2\} - \{K^0_{ref.} - K^0_{isotope}\}$$

where u^0 and K^0 are the root-mean-square amplitudes and perpendicular amplitudes of vibration at 0 K, respectively, and a_3 is the previously mentioned anharmonicity constant.

For the correction to r_α^0, two different approaches have been suggested in the literature,[33,34] viz:

$$r_\alpha^0 = r_g - \frac{3}{2} a_3 (u_T{}^2 - u_0{}^2) - K_0 \tag{1}$$

and[42,43]

$$r_\alpha^0 = r_g - \frac{3}{2} a_3 (u_T{}^2 - u_0{}^2) - K_T \qquad (2)$$

where[33,34]

$$r_g = r_\alpha + K \quad \text{and} \quad r_a = r_g - \frac{u^2}{r}.$$

The merits and drawbacks of the two approaches have been discussed,[42,43] and it is generally expected that eqn. (1) does not account properly for the shrinkage effect at increasing temperatures while K_T, entering eqn. (2), usually is calculated to be too large when large amplitude motions are involved.

The relative weights of the electron-diffraction data and the rotational constants in the least-squares structure refinement are not obvious. As previously mentioned, the uncertainties in the B_z rotational constants have been estimated as 10 % of the vibrational correction $\delta B_{vib} = B_z - B_0$. Hence, we have weighted the B_z rotational constants in such a way that calculated uncertainties in the B_α^0 rotational constants were approximately equal to 10 % of δB_{vib}.

Results and discussion

Structure of 2H-1,2,3-triazole. The final structure parameters obtained from an analysis of the electron-diffraction data alone and from the joint microwave/electron-diffraction analyses are given in Table 5, where also the *ab initio* r_e structure has been included. In Table 6 the effective rotational constants, B_0, and the derived zero-point constants, B_z, are compared to their counterparts, B_α^0, derived from the r_α^0 structure and the *ab initio* calculated equilibrium values, B_e. The molecular intensity and radial distribution curves corresponding to the joint analysis are shown in Figs. 4 and 5, respectively, while the correlation matrix is given in Table 7.

As can be seen from Fig. 5 and Table 4, the most important distances are grouped around 1.35 and 2.15 Å, which makes it imperative to have reliable u and K values available for the analysis. In column A of Table 5, the structural parameters obtained from an analysis of the electron-diffraction data alone are given. The correlation between r_{CN}, r_{NN} and $\angle_{NNN}$ is rather large, which is also reflected in the estimated uncertainties in the calculated rotational constants (Table 6). Although the differences between the B_z and the B_α^0 rotational constants are small, in general

Table 5. Structure parameters (Å, degrees) for 2H-1,2,3-triazole.[a]

	A ED r_a	B ED+MW r_a	C ED+MW r_a	D ED+MW r_a	E ED+MW r_a	F ED+MW r_α^0	G ED+MW $r_e{}^c$	H ab initio r_e
r_{NH}	1.026(7)	1.020(1)	1.017(1)	1.025(1)	0.994(1)	0.997	0.997	0.990
r_{CH}	1.099(4)	1.103(4)	1.105(3)	1.105(3)	1.113(5)	1.092	1.069	1.061
r_{CC}	1.401(3)	1.405(2)	1.405(2)	1.406(2)	1.409(3)	1.405	1.398	1.413
r_{CN}	1.347(3)	1.346(2)	1.346(2)	1.346(2)	1.321(2)	1.345	1.339	1.317
r_{NN}	1.323(2)	1.323(1)	1.323(1)	1.323(1)	1.343(1)	1.323	1.317	1.349
$\angle_{NNN}$	117.3(2)	117.1(1)	117.1(1)	117.1(1)	114.05	117.1	117.1	114.05
$\angle_{CCH}$	130.8(18)	133.4(5)	133.0(5)	133.1(5)	133.3(8)	133.0	133.0	130.0
$R_{ED}{}^b$	3.13	3.12	3.12	3.14	5.27			
$R_{MW}{}^b$	0.192	0.009	0.007	0.007	0.013			

[a] For definition of the different bond distances, Ref. 33. The uncertainties in brackets represent one standard deviation as resulting from the least-squares refinement. They do not include the uncertainty in the electron wavelength, and correlation among the electron-diffraction data has not been incorporated.
Column A: only ED data used; B: eqn. (1), but no correction for isotopic differences (see text); C: as B, but with correction for isotopic differences; D: eqn. (2) and with correction for isotopic differences; E: as for C, but $\angle_{NNN}$ fixed at the *ab initio* calculated value; F: as for C, but corrected to r_α^0; G: As for F, but corrected to r_e by using the approximation $r_e = r_\alpha^0 - \frac{3}{2} a_3 \cdot u_0{}^2$. [b] $R = [\Sigma w_i \Delta_i{}^2 / \Sigma w_i I_{i(obs)}{}^2]^{1/2} \cdot 100$, where $\Delta_i = I_{i(obs)} - I_{i(calc)}$ and w_i is the weight function. [c] Estimated.

Table 6. Rotational constants (MHz) for 2H-1,2,3-triazole as observed by microwave spectroscopy and calculated from different electron-diffraction models and by *ab initio* methods.

Species	MW[a] B_0	MW+NC B_z	ED[b] B_α^0	ED+MW[c] B_α^0	ED+MW[d] B_α^0	*ab initio* B_e
Parent	10 252.006(13)	10 245.57(64)	10 213.(28)	10 245.66(29)	10 248.08(42)	10 240.
	9 776.969(13)	9 767.08(99)	9 813.(34)	9 769.33(38)	9 767.96(61)	9 775.
	5 002.448(10)	5 000.97(15)	5 004.4(31)	5 000.91(10)	5 000.13(14)	5 001.
$^{15}N_3$	10 000.139(7)	9 993.90(62)	9 962.(27)	9 993.22(28)	9 990.53(40)	9 983.
	9 318.480(7)	9 309.19(93)	9 351.(31)	9 312.53(27)	9 312.45(41)	9 315.
	4 821.741(6)	4 820.33(14)	4 823.4(29)	4 820.44(8)	4 819.79(11)	4 819.
2-D,$^{15}N_3$	9 320.227(8)	9 311.61(86)	9 351.(31)	9 312.55(27)	9 312.45(41)	9 315.
	9 266.542(8)	9 262.14(44)	9 231.(23)	9 262.37(27)	9 261.46(40)	9 243.
	4 645.134(7)	4 643.87(13)	4 645.4(33)	4 643.69(7)	4 643.44(11)	4 640.

[a]MW: microwave; NC: normal coordinate calculation; ED: electron diffraction. [b]Corresponds to model B in Table 5. [c]Corresponds to model C in Table 5. [d]Corresponds to model E ($\angle_{NNN}$ = 114.05) in Table 5.

less than 0.5 %, they are on the other hand ca. thirty times the estimated uncertainties in the B_z constants.

When the rotational constants were included in the analysis, the correlation between the structural parameters was slightly reduced and the parameters themselves slightly better determined. Exceptions to this are the structural parameters involving hydrogen, which are usually less accurately determined by electron diffraction

due to the low scattering power of hydrogen. The decreased correlation between the parameters results primarily from the fact that the non-bonded N1···N3 distance is determined by $\Delta I_b = I_b(2H,^{15}N_3) - I_b(2H,\text{parent})$.

The structure parameters obtained from a joint microwave/electron-diffraction analysis assuming that r_α^0 was identical for all isotopic species are listed in Table 5, column B. The structural parameters obtained from electron diffraction alone
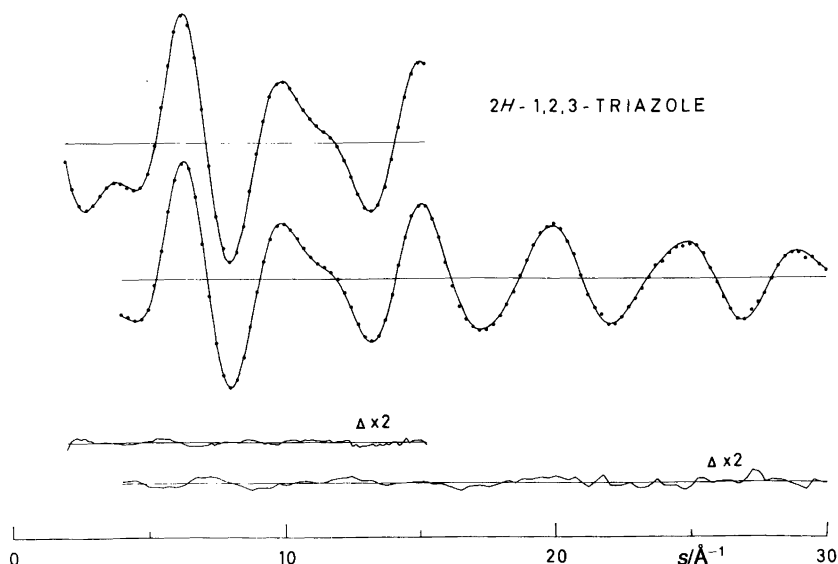

Fig. 4. Observed molecular intensity data (●) for 2H-1,2,3-triazole, and the difference curves (×2).

Fig. 5. Experimental radial distribution curve (●) for 2*H*-1,2,3-triazole, and the difference curve (×2). An artificial damping constant of $k = 0.0017$ Å² was used.

2*H*-1,2,3-TRIAZOLE
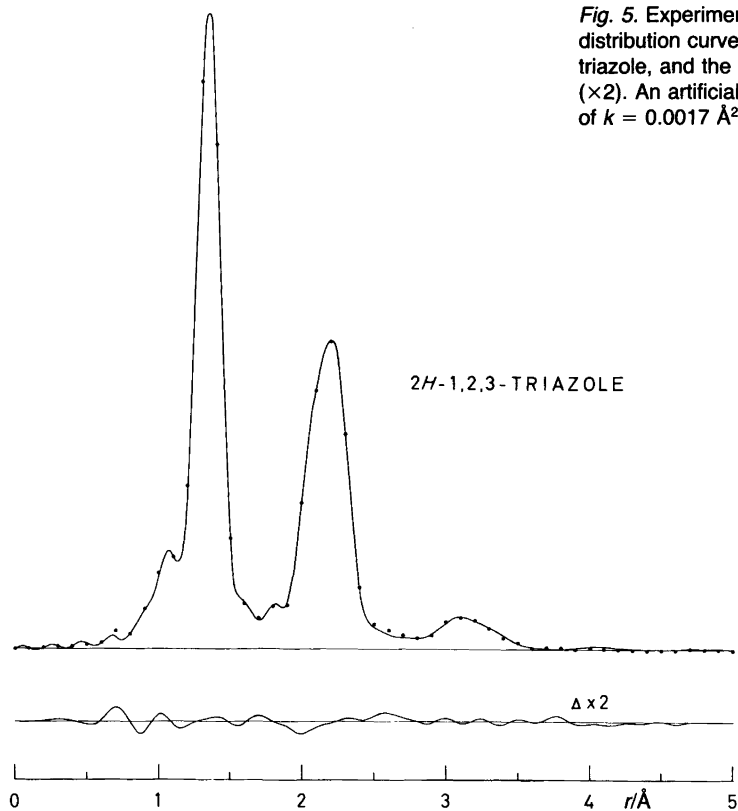
Δ×2

0   1   2   3   4   *r*/Å   5

Table 7. Correlation matrix (×100) for the least-squares structure refinement.

	r_{NH}	r_{CH}	r_{CC}	r_{CN}	r_{NN}	$\angle_{NNN}$	$\angle_{CCH}$	$u_1{}^a$	u_2	u_3	u_4	u_5	$S_l{}^b$	S_s
r_{NH}	100													
r_{CH}	−19	100												
r_{CC}	0	−70	100											
r_{CN}	74	−6	−40	100										
r_{NN}	−86	21	2	−89	100									
$\angle_{NNN}$	90	−16	−9	81	−87	100								
$\angle_{CCH}$	33	16	−56	79	−59	31	100							
u_1	16	−31	18	10	−14	14	−20	100						
u_2	−45	32	25	38	54	44	−19	−15	100					
u_3	−11	−16	23	−19	12	−13	−18	1	14	100				
u_4	0	−11	6	2	−2	−21	3	4	−24	0	100			
u_5	−18	3	2	−18	19	−20	−19	−5	30	63	−3	100		
S_l	10	−25	25	0	−10	10	−10	−16	15	30	6	19	100	
S_s	5	−27	21	−3	−5	4	−9	0	39	29	1	25	31	100

[a]Grouped u values. u_1: NH, CH; u_2: NN, CN; u_3: N⋯N, N⋯C; u_4: N⋯H, C⋯H; u_5: N2⋯C. [b]S_l and S_s are the scale factors for the long and short camera distances (see text), respectively.

and from the joint analysis are consistent, the only real difference being in the case of $\angle_{CCH}$.

The results of introducing an isotopic dependence into the r_α^0 structure according to the alternative eqns. (1) and (2) are given in Table 5, columns C and D, respectively. The fit to the rotational constants is slightly improved compared to model B, but otherwise only minor differences appear in the structure parameters involving hydrogen. The results of models C and D appear to differ only with respect to the r_a value for the NH distance, which can be explained by the large difference between the values for K_T and K_0, viz. 0.0327 and 0.0251 Å, respectively. The fit to the experimental data is equally good. We do not feel competent to enter into a profound discussion of which of these two schemes is the best, but we believe the main question is whether or not the NH out-of-plane bending motion should be treated as a large-amplitude motion.

A comparison of the results from the joint analysis with the results of the *ab initio* calculations in Table 5 reveals two important differences; first of all, that $r_{CN} > r_{NN}$ in the joint analysis while the *ab initio* calculations predict the reverse, and secondly, that $\angle_{NNN}$ is predicted by the *ab initio* calculations to be about 3° smaller. In order to test whether the final structure parameters could correspond to a local minimum of the least-squares surface, several sets of starting values and refinement strategies were tried. All refinements converged to the same parameter values, which indicate that the structure really corresponds to a global minimum. On the other hand, when $\angle_{NNN}$ was constrained to 114.05°, as calculated *ab initio*, r_{CN} refined to be smaller than r_{NN} as predicted *ab initio*. The results from this model are included in Table 5, column E. The fit to the rotational constants is approximately the same regardless of the constraints on $\angle_{NNN}$, while the fit to the electron diffraction data is much poorer, as reflected in the increase in the "goodness-of-fit" parameter, R.

The r_a structure in Table 5, column C was corrected to the r_α^0 structure in column F by applying eqn. (1). From the r_α^0 structure an equilibrium structure could be estimated, and the results are given in column G. This estimated r_e structure can now be compared with the *ab initio* results given in column H. As mentioned earlier, the main differences are found for the r_{CN}, r_{NN} and $\angle_{NNN}$ parameters.

It is interesting to compare vapour phase structures with structures obtained from X-ray diffraction studies of crystals. A relatively large number of 2H-1,2,3-triazole derivatives have been studied by X-ray diffraction (Ref. 44 and references therein) and the substitution and packing effects could presumably be reduced by averaging the structure parameters found for the different derivatives. The mean values obtained in this way are: $r_{CC} = 1.396$, $r_{CN} = 1.344$, $r_{NN} = 1.333$ Å and $\angle_{NNN} = 116.9°$ ("standard deviation" ca. 1%). The agreement with our vapour-phase results for 2H-1,2,3-triazole (Table 5) is close.

In view of the consistency between our vapour-phase structure of 2H-1,2,3-triazole and the "average" X-ray crystal structure of the 2H-1,2,3-triazole ring it seems evident that the basis set employed in the present *ab initio* calculations does not provide a near Hartree-Fock limit description of 2H-1,2,3-triazole. Obviously, the basis set is not flexible enough to describe the delocalized π electrons, e.g. the double bonds are calculated to be much too short and the single bonds to be longer than experimentally determined. In spite of this, the *ab initio* calculated rotational constants (Table 6) agree with the experimental values to within 0.3%. We have noticed much the same basis set deficiency when we calculated the structure of a triazole isomer,[45] vinylazide. It is obviously necessary to expand the basis set and to include polarization functions if a near Hartree-Fock limit description is required.

A comparison of the structures of 2H-1,2,3-triazole and pyrazole[2] reveals significant differences, which can all be related to the π-electron delocalization. The r_{CC} is shorter by 0.011 Å in 2H-1,2,3-triazole, r_{CN} longer by 0.014 Å and r_{NN} shorter by 0.026 Å. Hence, the π-electron delocalization is much more pronounced in 2H-1,2,3-triazole than in pyrazole. This may also explain the fact that the nitrogen-bonded hydrogen is extremely labile, and further that 1,2,3-triazole is stable at temperatures up to ca. 550 °C under low pressure conditions[46],[47] (quartz surface).

Structure of 1H-1,2,3-triazole. For the 1H-tautomer of 1,2,3-triazole we have less experimental information; however, due to the lower sym-

metry there are more independent structure parameters. Microwave data for the three isotopic species in Table 1 give the following results. The molecule is planar, of C_s symmetry and has a large dipole moment. Only a few of the thirteen geometric parameters can be derived from the moments of inertia. The position of N-bonded hydrogen(deuterium) is $(a/\text{Å}, b/\text{Å}) = (1.5636, 1.3707)$ in the parent coordinate system and $(2.0410, 0.1865)$ in the 1-D coordinate system, which means a rotation on substitution of $36.0°$. We note that the *ab initio* model has $(a/\text{Å}, b/\text{Å}) = (1.067, 1.786)$ and a substitution rotation angle of $54°$ for the same hydrogen. A large substitution rotation angle is consistent with the above-mentioned fact that the dominant transition moment changes from a to b going from the parent molecule to the 1-D species.

For the $^{15}N_3$ species, the position of all three nitrogens is involved in the change in moments of inertia by substitution, i.e. 6 parameters. These cannot be determined from the *two* independent experimental data.

As in the case of the 2*H*-tautomer, numerous X-ray studies of 1*H*-1,2,3-triazole derivatives have been reported (Ref. 44 and references therein). The average structure parameters for the ring (Fig. 1) obtained from these studies are: $r_{N1N2} = 1.355$, $r_{N2N3} = 1.309$, $r_{N3C4} = 1.370$, $r_{C4C5} = 1.378$, $r_{N1C5} = 1.356$ Å, and $\angle_{N1N2N3} = 108.2$, $\angle_{N2N3N4} = 108.2$, $\angle_{N3C4C5} = 109.9$, $\angle_{C4C5N1} = 104.4$ and $\angle_{C5N1N2} = 110.2°$. It is not surprising that much the same disagreement between the experimental and the *ab initio* calculated structure of the 2*H* tautomer is observed for the 1*H* tautomer as well. We shall refrain from further comments on the 1*H*-1,2,3-triazole structure.

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