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Refinement of the Crystal and Molecular Structure of 1,2,4-Triazole (C₂H₃N₃) at Low Temperature

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The crystal structure of 1,2,4-triazole has been redetermined on the basis of three-dimensional X-ray data obtained by low temperature automatic diffractometric methods. At -160°C , crystals of the compound are orthorhombic with the space group symmetry *Pbca* and lattice parameters $a=9.729 \pm 0.002$, $b=9.334 \pm 0.004$, and $c=6.977 \pm 0.002$ Å. The structure based on 746 independent reflections has been refined anisotropically to a disagreement factor of 0.051. The hydrogen atom not previously located in the room temperature structure determination of 1,2,4-triazole has now been found. Accordingly the compound can be designated as 1-hydrogen-1,2,4-triazole. The geometry of the triazole ring is consistent with that found in other triazole compounds but differs significantly from the geometry previously reported for 1,2,4-triazole. N-H \cdots N and C-H \cdots N hydrogen bonds of lengths 2.82 and 3.30 Å, respectively, link the molecules together to generate infinite corrugated sheets lying approximately perpendicular to the *c* axis.

Introduction

1,2,4-Triazole can exist in two tautomeric forms designated I and II in Fig. 1. The crystal structure of the compound was determined by Deuschl (1965) at room temperature. However, since Deuschl was not able to locate the nitrogen-bonded hydrogen atom, he could not specify whether 1,2,4-triazole existed solely as form I or form II, or as a mixture of both.

Deuschl's results also seemed to indicate that the geometry of the triazole ring in 1,2,4-triazole was significantly different from its geometry in the phosphoryl triazole compounds (Goldstein & Ladell, 1969). In particular, two of the angles in the triazole ring deviated by four times their estimated standard deviations from the average values of the corresponding angles in seven phosphoryl triazole compounds. In order to explain these differences, a redetermination of the structure of 1,2,4-triazole was undertaken. The investigation was carried out at a low temperature (-155°C) so as to facilitate the localization of the possibly tautomeric hydrogen atom and improve the resolution of the other atoms.

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Experimental

Clear, colorless, needle-like crystals of 1,2,4-triazole were obtained by slow evaporation of a solution of the compound (commercial grade) in a solvent consisting of equal volumes of water and propanol. The crystals acquire a yellowish color upon prolonged standing at room temperature after X-ray irradiation.

Lattice parameters were measured on a PAILRED diffractometer by the ' ω difference' method (Ladell, 1969) at room temperature (23°C) and at -160°C . As Table 1 shows, our room temperature values for the lengths of the **a** and **c** axes differ at the 95% significance level from the values reported by Deuschl (1965). However, our calculated X-ray density of $1.394 \pm 0.001 \text{ g.cm}^{-3}$ at room temperature agrees well with his measured density of 1.392 g.cm^{-3} .

Table 1. Comparison of lattice parameter measurements on 1,2,4-triazole

	Room T^*	+23°C†	-160°C†
$a(\text{\AA})$	9.69 ± 0.04	9.769 ± 0.002	9.729 ± 0.002
$b(\text{\AA})$	9.38 ± 0.04	9.366 ± 0.002	9.334 ± 0.004
$c(\text{\AA})$	7.14 ± 0.03	7.195 ± 0.002	6.977 ± 0.002
$V(\text{\AA}^3)$	649 ± 5	658.3 ± 0.3	633.6 ± 0.3
$d_c(\text{g.cm}^{-3})$	1.40 ± 0.01	1.394 ± 0.001	1.439 ± 0.001

* Deuschl (1965).

† Present study.

A crystal $0.3 \times 0.4 \times 1.0 \text{ mm}$ was mounted on a PAILRED diffractometer with its long direction parallel to the ω rotation axis and ten levels of data ($0kl-9kl$) were recorded in the automatic mode with the use of crystal-monochromatized Cu $K\beta$ radiation. The experimental procedures employed during data collection will be described elsewhere (Goldstein & Ladell, 1969). Upper-level measurements in zones perpendicular to the **b**-2**a** axis provided the intensities of the $h00$ reflections which were not accessible to the automatic mode in the first setting. The temperature was kept constant during the measurements with a set-point deviation controller (Abowitz & Ladell, 1968). However, approximately halfway through the data collection the thermocouple was inadvertently displaced from its initial position. The temperature scale was recalibrated after completion of the data collection and the final temperature was found to be -150°C . Although the intensities of the same reflections measured at both temperatures varied slightly, no significant change was observed in the lattice parameters at the two different temperatures. The initial temperature was estimated from an earlier calibration to be approximately -160°C .

A total of 1524 reflections were measured over a period of 10 days. The 839 independent reflections obtained upon final correlation represented approximately 75% of the number of reflections available to the Cu $K\beta$ sphere and somewhat more than 100% of the number of reflections available to the Cu $K\alpha$ sphere.

Of these reflections, 170 had net intensities smaller than twice the standard deviation in the measurements and were considered to be accidentally absent or 'unobservable'. Since observable intensities could be found out to the edge of the Cu $K\beta$ sphere for the particular crystal employed, the advantage of using Cu $K\beta$ instead of Cu $K\alpha$ radiation is evident. Mo $K\alpha$ radiation, which would have provided a larger number of reflections, was unsuitable because the crystal was too small.

The semi-automatic processing of PAILRED data will be described in another paper (Goldstein & Ladell, 1969). Appropriate corrections were applied for the Lorentz, double polarization and absorption factors. In the calculation of the absorption correction, the crystal was assumed to approximate to a cylinder of 0.35 mm average diameter ($\mu = 6.65 \text{ cm}^{-1}$ for Cu $K\beta$ radiation). In the correlation procedure a factor of the form $K \exp(-Bs^2)$, where K and B are positive quantities and $s = (\sin \theta)/\lambda$, was applied to the part of the data collected at -160°C to reduce all the data to an independent set of reflections normalized to -150°C . The values of K and B were deduced both from a comparison of equivalent intensities in common to the two groups of reflections as functions of $(\sin \theta)/\lambda$, and from separate partial least-squares refinements of the two data sets. No corrections for secondary extinction were applied at this stage.

Refinement

Refinement proceeded in space group $Pbca$ by full-matrix least-squares method with the coordinates for the carbon and nitrogen atoms reported by Deuschl (1965) as starting parameters. The least-squares program was a modified version of the UCLA program of Gantzel, Sparks & Trueblood (1961) which minimizes the quantity $\sum w(\Delta F)^2$. Volume III of *International Tables for X-ray Crystallography* (1962) provided the atomic scattering factor curves for C(valence), N(neutral), and H. Near the end of the refinement the atomic scattering curve for hydrogen previously used was replaced by the scattering curve for the bonded hydrogen atom calculated by Stewart, Davidson & Simpson (1965). The use of the latter resulted in more reasonable isotropic temperature factors for the hydrogen atoms, the net effect being to increase

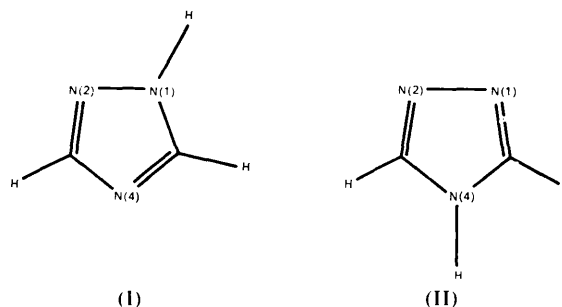


Fig. 1. Two possible tautomeric forms of 1,2,4-triazole.

the values of these factors by approximately 2.3 \AA^2 . The weights of the observational equations were taken proportional to $1/\sigma^2(F)$ where

$$\sigma(F) = \sqrt{|F_o|^2 + \sigma(F^2) - |F_o|},$$

$$\sigma(F^2) = |F_o|^2 \sqrt{(C_T + t^2 C_B)/(C_T - t C_B)^2 + \varepsilon_I^2},$$

C_T = total ω -scan count,

C_B = total background count,

t = ratio of ω -scan time to background count time,

ε_I = constant specifying the relative error introduced into the measurements from instrumental instabilities (0.02 was used in the present case), and

$|F_o|$ = observed structure factor.

As indicated earlier, initial refinement was carried out separately on the two parts of the data in order to establish a suitable scaling function. Additional isotropic least-squares refinement based on all observed reflections followed the final correlation to a unique data set. A difference Fourier map calculated at this stage [$(\sin \theta)/\lambda \leq 0.60$] clearly revealed the position of all the hydrogen atoms as peaks of height 0.66, 0.63 and 0.43 $e.\text{\AA}^{-3}$ for atoms H(5), H(3) and H(1), respectively. A hydrogen atom was definitely attached to atom N(1) and no indication was found for the presence of any hydrogen atoms near atoms N(4) or N(2). All other positive peaks were smaller than the ones found and only two were as large as 0.40 $e.\text{\AA}^{-3}$. Further least-squares refinement with anisotropic temperature factors for the carbon and nitrogen atoms and isotropic temperature factors for the hydrogen atoms brought convergence to a conventional disagreement factor of 0.085 for all 652 observed reflections.

The effect of extinction was pronounced and could not be neglected since some of the observed structure factors were reduced by as much as 50%. The first order correction for secondary extinction (Zachariasen, 1963 and 1965) was therefore inadequate, and the more

general expression derived by Zachariasen (1967) had to be employed. The expression was adapted to upper-level equi-inclination geometry with the aid of Whittaker's formulae (Whittaker, 1953) for the normal and parallel components in double polarization and was used in the following form

$$F_{\text{corr}} = F_o \sqrt{p/(Y1 + Y2)}.$$

The quantities are identified as follows:

F_{corr} = fully-corrected observed structure factor,

F_o = observed structure factor after correction for the absorption, Lorentz and polarization factors but before the extinction correction,

$p = p_1 + p_2$ = total double polarization factor,

$p_1 = [1 - B + qB \cos^2 \nu \sin^2 Y/(1 - B)]/(1 + q)$
= normal component of double polarization,

$p_2 = q \cos^2 2\theta/(1 + q)(1 - B)$

= parallel component of double polarization,

$B = \sin^2 \nu \cos^2 \nu (1 + \cos Y)^2 = \tan^2 \nu (1 + \cos 2\theta)^2$,

$Y_1 = p_1 f(X_1)$, $Y_2 = p_2 f(X_2)$,

$X_1 = 3g \text{ Lp}_1 F_c^2$, $X_2 = 3g \text{ Lp}_2 F_c^2$,

$g = \alpha \{t + m(\bar{T} - t)\}$,

$f(X) = (\tanh |X|)/|X|$ if $X \leq 1$

$= (\tan^{-1} |X|)/|X|$ if $X > 1$, and

F_c = calculated structure factor, m = parametric constant, and $q = \cos^2 2\theta_m$ where θ_m is the monochromator angle.

The remaining symbols other than ν and θ are those appearing in Zachariasen's (1967) paper. The application of this expression with $t = 3 \times 10^{-4}$, and $m = 4.2$ to all observed reflections reduced the disagreement factor to 0.059. Further refinement of the carbon, nitrogen and hydrogen atoms led to slight changes in the positional coordinates, improved the planarity of the triazole ring, and yielded a disagreement factor

Table 2. Final fractional positional coordinates and temperature factor parameters for all atoms*

(a) Non-hydrogen atoms†									
	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	-66 (2)	-846 (2)	2102 (2)	45 (2)	54 (1)	92 (3)	-1 (3)	-6 (4)	10 (4)
N(2)	250 (2)	-2031 (2)	1072 (2)	68 (2)	52 (1)	103 (3)	-21 (3)	-1 (4)	-13 (4)
C(3)	1597 (2)	-1928 (2)	915 (3)	63 (2)	58 (2)	97 (3)	12 (3)	23 (4)	-3 (4)
N(4)	2149 (2)	-764 (2)	1775 (2)	43 (2)	63 (1)	112 (3)	3 (3)	-9 (4)	-3 (4)
C(5)	1064 (2)	-113 (2)	2505 (3)	47 (2)	51 (2)	103 (3)	-0 (3)	-10 (4)	-7 (4)

(b) Hydrogen atoms‡				
	x/a	y/b	z/c	B
H(1)	-106 (2)	-058 (2)	250 (4)	3.8 (0.5) \AA^2
H(3)	200 (2)	-267 (2)	021 (4)	3.0 (0.5)
H(5)	105 (2)	076 (2)	316 (4)	2.1 (0.5)

* The values in parenthesis are the estimated standard deviations obtained from the inverse of the diagonal elements of the least-squares full matrix.

† All values have been multiplied by 10^4 . The β_{ij} 's are the coefficients that were used in the expression for the temperature factor given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

‡ The values of the fractional coordinates have been multiplied by 10^3 .

Table 3. Observed and calculated structure factors for the present structure on an absolute scale

The columns are, respectively, l , $|F_o|$ and F_c . Unobservable reflections are labelled with U . The reflections labelled with A disobeyed the extinction conditions for $Pbca$ whereas those labelled with an asterisk have a value of $|F_c|$ much smaller than the corresponding value of $|F_o|$.

<p>0 20.28 -77.98 1 4.67 -100.23 2 17.98 -17.87 3 0.81U 1.12</p>	<p>0 13.79 14.40 1 10.37 11.26 2 1.81 1.72 3 7.94 -8.00 4 6.45 6.28</p>	<p>2 7.46 -7.14 3 5.22 5.75 4 10.79 10.84 5 4.86 -5.01 6 0.85U 0.20</p>	<p>1 1.90 1.68 2 5.75 5.59 3 0.84U 0.84U 4 1.12U -0.00 5 0.93 35.77 6 11.92 -11.92 7 0.50U 0.00 8 0.50U 0.00</p>	<p>1 0.52U 0.27 2 1.77 -1.77 3 5.28 -5.50 4 0.84U -0.84U 5 0.84U 0.84U 6 0.84U -2.13 7 0.84U -0.84U 8 0.84U -0.84U</p>	<p>5 3.24 3.48 6 5.68 5.91 7 3.81 3.82 8 15.84 -16.08 9 0.00U 0.00 10 1.85U 1.85U 11 8.98 9.19 12 0.84U -0.84U 13 6.95 -6.77 14 0.84U 0.00</p>	<p>0 8.16 8.52 1 10.44 10.53 2 15.54 15.54 3 12.08 11.09 4 17.74 -17.74 5 1.74 1.74 6 10.59 11.20 7 18.58 18.58 8 12.08 11.09 9 17.74 -17.74 10 1.74 1.74 11 10.59 11.20 12 18.58 18.58 13 12.08 11.09 14 17.74 -17.74 15 1.74 1.74 16 10.59 11.20 17 18.58 18.58 18 12.08 11.09 19 17.74 -17.74 20 1.74 1.74 21 10.59 11.20 22 18.58 18.58 23 12.08 11.09 24 17.74 -17.74 25 1.74 1.74 26 10.59 11.20 27 18.58 18.58 28 12.08 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after convergence of 0.051 for the observed reflections. The disagreement factor is 0.056 when all measured reflections allowed in the space group *Pbca* are included. During the final least-squares cycle, the maximum shifts in the coordinates and temperature factors were 0.9σ and 1.2σ , respectively, and the mean shifts 0.3σ .

Eight weak reflections of the type $0kl$ with k odd, and $hk0$ with h odd were observed (see Table 3). Although these may have been spurious reflections caused by multiple diffraction the possibility that the space group $P2_12_12_1$ is a more appropriate description of the crystal symmetry cannot be excluded. In view of the paucity and low intensity of the extra reflections, the structural model obtained by refining in the space group *Pbca* cannot be distinguished from a model appropriate to the space group $P2_12_12_1$.

Results

The refined parameters and their estimated standard deviations for all the atoms in the asymmetric unit of 1,2,4-triazole are given in Table 2. Table 3 lists the observed and calculated structure factors for all the unique reflections for which measurements were made. For unobservable reflections, *i.e.* those for which the net intensity was less than twice the standard deviation in the measurement, the value of the observed structure factor is half the standard deviation in the measurement properly scaled. The reflections marked with a letter or an asterisk were given zero weight in the final stages of the least-squares refinement. Those la-

beled with a *U* are the unobservable reflections (including space group extinct reflections which were measured); those labeled with an *A* are the observed reflections violating the extinction conditions for space group *Pbca*; and finally those marked by an asterisk are observed reflections for which the calculated structure factor was much less than the observed value.

Fig. 2 shows the bond angles and distances calculated from the final set of coordinates. The values in parenthesis have been corrected for librational motion. The average estimated standard deviations are 0.003 Å in the C–C and C–N distances, 0.02 Å in the C–H and N–H distances, 0.2° in the angles that do not involve hydrogen atoms, and 1.4° in the other angles. The geometry of the triazole ring in the present structure is more consistent with the geometry observed in the phosphoryl triazole compounds than the geometry of the ring reported in Deuschl's room temperature structure (Deuschl, 1965) as illustrated in Table 4 which provides comparisons of the internal bond angles of the triazole rings in the present structure, Deuschl's structure, and the average values of the corresponding angles in seven phosphoryl triazole compounds. The deviations of the values in columns 2 and 3 from those in column 4 are shown in the last two columns. Since the phosphoryl group in each of the triazole derivatives was assumed to be attached to atom N(1) in the calculation of the average values, the small deviations listed in column 5 confirm our finding that the tautomeric hydrogen atom of 1,2,4-triazole is located on atom N(1).

It is interesting to note that the two angles in Deuschl's structure which differ most from the corresponding angles in the structures of the phosphoryl triazole compounds are the same angles which differ most from the corresponding angles in the present structure and both involve atom C(5). Similarly, a comparison of the bond lengths in the two structure determinations of 1,2,4-triazole (Table 5) shows that the largest differences between corresponding distances in the two sets occur in the bonds to atom C(5), namely N(4)–C(5) and N(1)–C(5). The implications of these observations will be discussed later.

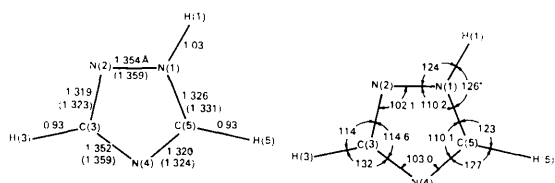


Fig. 2. Numbering scheme and bond distances in Å (left) and bond angles in degrees (right) for 1,2,4-triazole.

Table 4. Comparison of bond angles ($^\circ$) in triazole rings*

Angle	Low T^\dagger	Rm T^\ddagger	Substituted§	Deviations**	
				Low T	Rm T
N(1)–N(2)–C(3)	102.1	101.8	101.8 (1.2)	0.3	0
N(2)–C(3)–N(4)	114.6	114.5	115.8 (0.9)	–1.2	–1.3
C(3)–N(4)–C(5)	103.0	104.3	103.2 (0.5)	–0.2	1.1
N(4)–C(5)–N(1)	110.1	107.1	110.7 (0.6)	–0.6	–3.6
C(5)–N(1)–N(2)	110.2	112.2	108.6 (0.8)	1.6	3.6

* The estimated standard deviations in the low temperature and room temperature structures of 1,2,4-triazole are 0.2° and 0.9° , respectively.

† Present structure.

‡ Room temperature structure as determined by Deuschl (1965).

§ Average of values from previously determined structures containing a substituted triazole ring (Goldstein & Ladell, 1969). The root mean square deviations in the average values are given in parentheses.

** Deviations from the average values in the substituted triazoles.

Table 5. Comparison of bond distances (\AA) in the low temperature and room temperature structures of 1,2,4-triazole*

	Low T †	Room T ‡	Difference
N(1)–N(2)	1.359	1.354	–0.005
N(2)–C(3)	1.323	1.330	0.007
C(3)–N(4)	1.359	1.353	–0.006
N(4)–C(5)	1.324	1.352	0.028
N(1)–C(5)	1.331	1.344	0.013

* The estimated standard deviations in the bond lengths are approximately 0.003 \AA in the low temperature study and 0.014 \AA in the room temperature study.

† Present structure.

‡ Deuschl (1965).

The bond lengths in the triazole ring of the present structure can be described very satisfactorily in terms of contributions from the five resonance forms (shown in Fig. 3) to the ground state of the molecule. A comparison of the bond lengths derived from the refined parameters with the lengths calculated on the basis of contributions of 31%, 27%, 19%, 19%, and 4% for forms *A*, *B*, *C*, *D*, and *E*, respectively, is given in Table 6. The theoretical values agree very well with the experimentally derived distances after the latter have been corrected for librational motion. Pauling's expression (Pauling, 1948) relating the bond lengths r to the double bond character b , namely

$$r = r_1 - (r_1 - r_2)3b/(2b + 1),$$

was employed with $r_2 = 1.24 \text{ \AA}$ for N–N and 1.28 \AA for C–N bonds and $r_1 = 1.47 \text{ \AA}$ (Bryden, 1958).

Table 6. Comparison of observed bond distances and their derived double bond characters b with those calculated on the basis of the resonance form contributions in Fig. 3

	Observed		Calculated	
	Distance	b	Distance	b
N(1)–N(2)	1.359 \AA	0.23	1.359 \AA	0.23
N(2)–C(3)	1.323	0.51	1.325	0.50
C(3)–N(4)	1.359	0.31	1.360	0.31
N(4)–C(5)	1.324	0.51	1.325	0.50
N(1)–C(5)	1.331	0.46	1.332	0.46

Form *A*, as expected, makes the largest contribution to the ground state since it is the only neutral resonance form possible for the compound. The negative charges on atoms N(2) and N(4) in forms *B* and *C*, respectively, suggest that these forms should be stabilized by hydrogen bonding. The large contributions of these resonance forms are consistent with this explanation since nitrogen atoms N(2) and N(4) are both probably involved in hydrogen bonding, atom N(4) forming a strong intermolecular $N \cdots H-N$ hydrogen bond with atom N(1), and atom N(2) a weak intermolecular $N \cdots H-C$ hydrogen bond with atom C(5). The small contribution of form *E* is also in accord

with this scheme since participation of atom C(5) in hydrogen bonding would tend to prevent the localization of a negative charge on that atom.

There is nothing unusual about the short C–H bonds since shortened C–H bond lengths are a common feature of X-ray determined structures (Stewart *et al.*, 1965). There is no obvious explanation, however, for the large difference in the N(2)–C(3)–H(3) and N(4)–C(3)–H(3) angles.

The best least-squares plane passing through the non-hydrogen atoms of the reference molecule in the present structure can be represented by the equation:

$$0.10855X - 0.52088Y + 0.84670Z = 1.64670,$$

where X, Y, Z are orthogonal coordinates in \AA measured along the crystallographic axes \mathbf{a}, \mathbf{b} and \mathbf{c} , respectively (Schomaker, Waser, Marsh & Bergman, 1959). Table 7 lists the displacements of the atoms from the best least-squares planes through the non-hydrogen atoms of the 1,2,4-triazole molecule in the low temperature structure (present structure) and the room temperature structure (Deuschl, 1965). Deviations of the ring from planarity are negligible in the present structure. In the room temperature study, however, although the deviations do not appear to be highly significant, they can be seen from the last column to be attributable completely to a displacement of atom C(5) by 0.06 \AA from the plane of the other four non-hydrogen atoms. Indeed, comparison of the atomic coordinates in the room temperature and low temperature studies reveals that the major differences between the two sets occur in the coordinates of atom C(5) and in the z/c coordinate in particular. One can therefore account for the significant deviations of the bond angles and distances in the room temperature study from their corresponding values in the present structure in terms of a displacement of atom C(5) from its correct position.

If the foregoing conclusion is valid, one can surmise that 1,2,4-triazole has essentially the same structure at room temperature as at -155°C and therefore exists primarily as the asymmetric tautomer (form II in Fig. 1). This deduction conforms with the observation

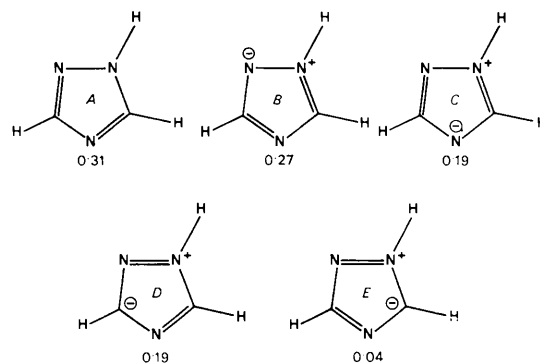


Fig. 3. Resonance forms of 1,2,4-triazole.

Table 7. Atomic displacements (\AA) from the best least-squares planes through the non-hydrogen atoms of the triazole ring in the low temperature and room temperature structures

	Low T^*	Room T^\dagger	
	I	II	III‡
N(1)	-0.001	0.013	0
N(2)	0.001	-0.015	0
C(3)	-0.000	-0.004	-0.002
N(4)	-0.000	0.011	0
C(5)	0.000	-0.015	-0.062
H(1)	-0.002		
H(3)	-0.018		
H(5)	-0.038		

* Present structure.

† Based on Deuschl's results (1965).

‡ Plane through atoms N(1), N(2) and N(3).

that in the alkylation, acylation or phosphorylation of 1,2,4-triazole and its 3- and/or 5- substituted derivatives, substitution of the tautomeric hydrogen atom occurs primarily at atoms N(1) and N(2) and seldom, if at all, at atom N(4) (Atkinson & Polya, 1954; Gehlen & Winzer, 1956; Potts & Crawford, 1962; van den Bos, Schipperheyn & van Deursen, 1966).

The thermal vibrational ellipsoids derived from the temperature parameters of the non-hydrogen atoms are tabulated in Table 8. Difficulty was encountered in applying Cruickshank's rigid body treatment to the non-hydrogen atoms of the molecule because of a degeneracy introduced by the apparent molecular symmetry. However, by assuming the translational motion of the center of gravity of the molecule to be isotropic with an average mean square displacement amplitude of 0.0208 \AA^2 and subtracting its contribution, it was possible to isolate the effect of molecular libration on the thermal motions of the atoms. The remaining thermal motion can then be described reasonably well in terms of librational oscillations of approximately 4.0° , 4.0° and 2.5° amplitude about the three mutually perpendicular axes ω_1 , ω_2 and ω_3 , respectively, shown in Fig. 4. The axis ω_1 is perpendicular to the plane of the molecule and intersects the plane at a point which is located approximately 1 \AA from atom N(1), 1.2 \AA from atom N(4), and 0.6 \AA from atom C(5). The axes ω_2 and ω_3 lie in the plane of the molecule, ω_2 being

oriented such that it is perpendicular to bond C(3)–N(4) and passes through atom N(1), whereas ω_3 is parallel to bond C(3)–N(4) and approximately 1.5 \AA from it. This description is consistent with the hydrogen bonding scheme.

Table 8. Atomic thermal vibration ellipsoids derived from temperature factors*

	U_{ii}	C_1	C_2	C_3
N(1)	251	2118	-7574	-6176
	220	6676	5737	-4747
	207	7137	-3118	6272
N(2)	344	9161	-3949	0693
	258	2110	3279	-9208
	202	3410	8582	3837
C(3)	330	8784	3196	3554
	256	-1214	8684	-4808
	214	-4622	3791	8016
N(4)	285	2107	6834	-6990
	274	-0800	7247	6844
	203	9743	-0883	2074
C(5)	265	3939	2680	-8792
	227	-5637	8260	-0007
	215	7261	4959	4764

* All values have been multiplied by 10^4 . Each line provides the mean square displacement U_{ii} (\AA^2) along a particular principal axis whose direction cosines with respect to the crystallographic axes a , b and c are C_1 , C_2 and C_3 , respectively.

If the relationship between X-ray determined temperature factors and absolute temperatures suggested by Lonsdale & El Sayed (1965) is used to calculate the thermal parameters expected for 1,2,4-triazole at room temperature from the low temperature results, one obtains temperature factors which are more isotropic than, but similar in magnitude to, those observed for the triazole ring in the phosphoryl triazole compounds (Goldstein & Ladell, 1969). However these expected parameters are quite different from those reported by Deuschl. His values are considerably lower than the expected values and show much more thermal anisotropy. The refined temperature factors of the hydrogen atoms in the present structure are all greater than the average temperature factors of the atoms to which they are attached. Since by far the largest thermal motion is exhibited by the tautomeric hydrogen atom, one can understand the difficulty encountered by Deuschl in attempting to locate the tautomeric hydrogen atom in his room temperature study.

The shorter intermolecular atomic separations in the present structure are listed in Table 9. The H \cdots H separations are normal and have not been included. The short N(1) \cdots N(4) distance (2.821 \AA) represents a strong N–H \cdots N hydrogen bond which links together neighboring molecules related by the a -glide to form chains of molecules running approximately parallel to the a axis. The hydrogen bond is not quite linear, with values of 160.5° and 12.5° for the N(1)–H(1) \cdots N(4) and H(1)–N(1) \cdots N(4) angles, respectively, and is considerably shorter than most N–H \cdots N hydrogen bonds ordinarily encountered (Fuller, 1959). This

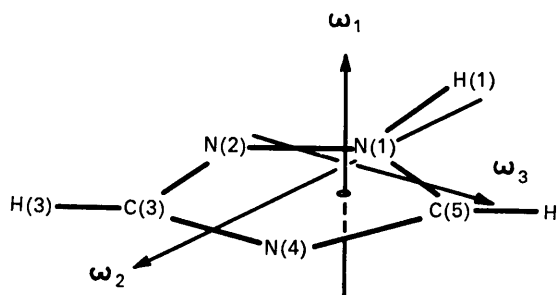


Fig. 4. Illustration of molecular librational motions observed in present structure.

Table 9. Short intermolecular atomic separations

Atom 1	Atom 2	Symmetry*	Distance
N(4)	H(1)	<i>H</i>	1.83 Å
H(5)	N(2)	<i>C</i>	2.48
C(3)	H(1)	<i>H</i>	2.83
C(5)	H(1)	<i>H</i>	2.83
N(4)	N(1)	<i>H</i>	2.821
C(5)	N(2)	<i>C</i>	3.300
N(1)	N(1)	<i>E</i>	3.333
N(2)	C(5)	<i>E</i>	3.445
N(1)	C(5)	<i>E</i>	3.474
C(3)	C(3)	$G(0, -1, 0)$	3.648
C(5)	C(3)	$G(0, -1, 0)$	3.681

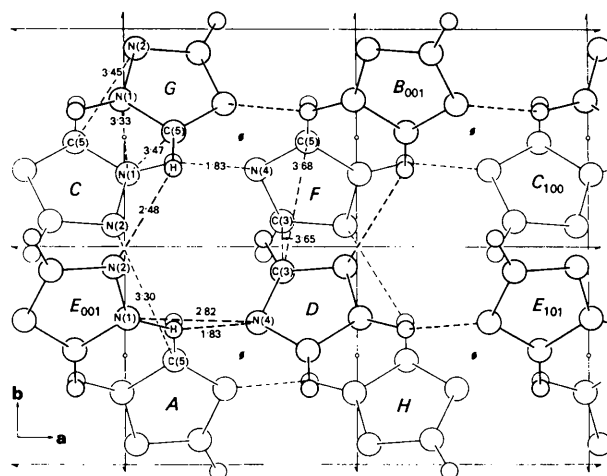
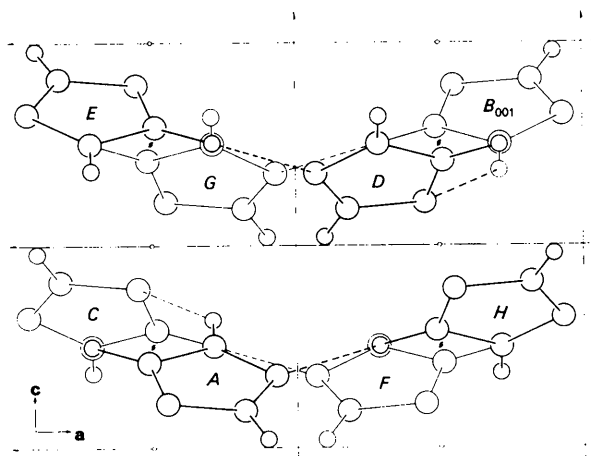
* The characters tabulated here and shown in Figs. 5 and 6 denote the symmetry operations, and the numbers in parenthesis the additional unit translations along the crystallographic axes *a*, *b* and *c*, respectively, which must be applied to obtain the coordinates of atom 2 from those of atom 1. If the coordinates of atom 1 are *x*, *y*, *z*, then application of the symmetry operations denoted by *A*, *B*, *C*, *D*, *E*, *F*, *G*, and *H* yields coordinates for atom 2 at *x*, *y*, *z*; $\frac{1}{2} + x, \frac{1}{2} - y, -z$; $-x, \frac{1}{2} + y, \frac{1}{2} - z$; $\frac{1}{2} - x, -y, \frac{1}{2} + z$; $-x, -y, -z$; $\frac{1}{2} - x, \frac{1}{2} + y, z$; $x, \frac{1}{2} - y, \frac{1}{2} + z$; and $\frac{1}{2} + x, y, \frac{1}{2} - z$, respectively.

shortening implies that a large residual positive charge is localized on atom N(1) (Wallwork, 1962), a deduction which agrees well with the contention we previously made that resonance forms *B* to *D* in Fig. 3 must make important contributions to the ground state of the molecule. A similar explanation would account for the short N-H...N bonds observed in other compounds of the same type, e.g. 2.76 Å in 5-aminotetrazole monohydrate (Britts & Karle, 1967), 2.86 Å in imidazole (Martinez-Carrera, 1966) and 2.88 Å in 3-hydrazino-5-thio-1,2,4-triazole (Senko & Templeton, 1956).

The next shortest distance between non-hydrogen atoms (C(5)...N(2)=3.30 Å) is somewhat smaller than the sum of the van der Waals radii of a CH group (1.85 Å) and a nitrogen atom (1.5 Å) and could represent a weak C-H...N hydrogen bond. C-H...N hydrogen bonding has been reported in solid HCN (Dulmage & Lipscomb, 1951), where the C-H...N distance is 3.18 Å, and anomalously short C...N separations have been encountered elsewhere (Goldstein & Ladell, 1969). Moreover, it has been established from infrared evidence and X-ray determinations that the analogous C-H...O hydrogen bond exists in *o*-bromobenzoylacetylene (Ferguson & Tyrrell, 1965) and in *o*-chlorobenzoylacetylene (Ferguson & Islam, 1966), where the C-H...O distances are 3.26 and 3.21 Å, respectively, compared to an expected van der Waals separation of 3.25 Å. Sutor (1963) has tabulated a number of other C...O distances which could correspond to C-H...O hydrogen bonds. In the present case, suitable geometric conditions exist for C-H...N hydrogen bonding; the angles C(5)-H(5)...N(2) and N(2)...C(5)-H(5) are 147.1° and 24.1°, respectively, and the H(5)...N(2) distance (2.48 Å) is less than that expected from the sum of van der Waals radii (2.5-2.7 Å). The actual H(5)-N(2) distance may be even

shorter than that determined, because spherical form factors were used for the hydrogen and carbon atoms (Stewart, Davidson & Simpson, 1965).

The C-H...N hydrogen bonds would connect molecules related by the screw axes parallel to *b* and serve to link the chains of N...H-N hydrogen-bonded molecules in forming corrugated sheets of molecules approximately perpendicular to the *c* axis. The corrugation arises from the large relative tilt between adjacent molecules, 64.3° for molecules related by the *a*-glide and 62.8° for those related by the screw axis parallel to *b*. A view of these sheets down the *c* axis is shown in Fig. 5, along with some of the shorter intermolecular atomic separations (Å). The other intermolecular atomic separations are not unusually short and correspond to van der Waals interactions between the sheets. This description is in accord with the coefficient of expansion observed in the *c* direction of the crystal

Fig. 5. Molecular arrangement as viewed down the negative direction of the *c* axis.Fig. 6. Molecular arrangement as viewed down the positive direction of the *b* axis.

($254 \times 10^{-6}/^{\circ}\text{C}$) being much greater than in the **a** and **b** directions (33×10^{-6} and $28 \times 10^{-6}/^{\circ}\text{C}$, respectively). Thus, the length of the **c** axis is reduced by 3.0% when the temperature is decreased from room temperature to -160°C whereas the lengths of the **a** and **b** axes are reduced by only 0.4 and 0.3% respectively, during the same temperature span. On the other hand, the C(5)···N(2) separation remains essentially the same (3.30 Å) at both temperatures. Fig. 6 illustrates the packing of the sheets viewed down the **b** axis.

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Oxido Steroids I: The Crystal Structure of 11 β , 12 α -Dibromo-3 α , 9-oxidocholanic Acid Methyl Ester

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The crystal structure of 11 β , 12 α -dibromo-3 α , 9-oxidocholanic acid methyl ester, $\text{C}_{25}\text{H}_{38}\text{O}_3\text{Br}_2$, has been determined using three-dimensional X-ray diffraction data. This steroid crystallizes from acetone solution in the orthorhombic space group $P2_12_12_1$ with four molecules per unit cell with dimensions: $a = 14.472 \pm 0.003$, $b = 20.587 \pm 0.005$, and $c = 7.990 \pm 0.001$ Å. The *A* ring is boat shaped, and rings *B* and *C* are chair shaped. The mean plane through the atoms of the *A* ring is practically perpendicular (92°) to the mean plane of the *B* ring and the mean planes of rings *B*, *C*, and *D* are all nearly parallel to each other. The atoms forming the side chain attached to C(17), with the exception of C(21), lie approximately in a plane which is inclined to the mean plane of the *D* ring at an angle of 104° . Molecules are held together in the crystalline state by van der Waals forces.

Introduction

Investigation of the crystal structure of a variety of steroids, steroid derivatives, and steroid complexes

constitutes an integral part of the program underway in our laboratory to correlate the biological activity of steroids with their molecular structures. In as much as oxido steroids are known to be convenient intermediates for passing from mono-substituted to di-substituted compounds or *vice versa*, and that combination of these two processes can in some cases provide a means of transferring a substituent from one carbon atom to another, it is reasonable to expect that certain biologi-

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