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The Crystal Structure of 1,4-Dimethyl-5-ethyl-5-hydroxy- Δ^2 -1,2,3-triazoline

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1,4-Dimethyl-5-ethyl-5-hydroxy- Δ^2 -1,2,3-triazoline ($C_6H_{13}N_3O$) crystallizes in space group $P2_12_12_1$ (No. 19) with $a = 11.530$ (8), $b = 11.839$ (7), and $c = 5.862$ (3) Å, $Z = 4$. The structure was solved by direct methods and refined by the full-matrix least-squares method to an R of 0.050, using 1578 diffractometric X-ray intensities. Two symmetry-related reflexions were measured for each of the 841 independent reflexions. The triazoline ring adopts an envelope conformation with C(5) at the flap of the envelope. The alkyl groups are all equatorial whereas the hydroxy group is axial. The structure is held together by one intermolecular $OH \cdots N$ hydrogen bond and van der Waals forces.

Introduction

Nuclear magnetic resonance studies (Olsen, 1969) on 5-hydroxy- and 5-amino-triazolines have directed interest towards conformation studies of the five-membered ring system triazoline. A deshielding effect was observed on substituents at C(4) situated *cis* with respect to a nitrogen or oxygen atom attached to C(5). This effect could arise from an interaction of the C(4) substituent with the lone pair of the heteroatom at C(5), but it might also be ascribed to an envelope-like conformation of the triazoline ring system (Olsen, 1969). This X-ray crystallographic investigation was undertaken in order to distinguish between these two possibilities, and the result supports the latter interpretation. A series of structure determinations is now

being planned in cooperation with C. E. Olsen, Department of Organic Chemistry, The Royal Veterinary and Agricultural University, Copenhagen, in order to investigate the conformation of the triazoline ring as a function of different substituents.

Experimental

1,4-Dimethyl-5-ethyl-5-hydroxy- Δ^2 -1,2,3-triazoline was prepared (Olsen, 1969) and crystallized for data collection by C. E. Olsen. Colourless orthorhombic crystals elongated along the c axis were formed from an ether solution. Weissenberg and precession photographs showed that $h00$ were absent for $h \neq 2n$, $0k0$ for $k \neq 2n$, and $00l$ for $l \neq 2n$, so the space group was $P2_12_12_1$ (No. 19). The compound had been prepared as a racemate.

This space group is non-centrosymmetric, so crystals of different chirality had to be present. A solution of a single crystal did indeed rotate the plane of polarized light.

The unit-cell dimensions obtained from least-squares refinement of a series of diffractometer-measured θ angles ($\lambda = 0.71069 \text{ \AA}$) were $a = 11.530(8)$, $b = 11.839(7)$ and $c = 5.862(3) \text{ \AA}$, $V = 800.2 \text{ \AA}^3$. The formula weight is $143.2 (\text{C}_6\text{H}_{13}\text{N}_3\text{O})$. Only a rough determination of the density was possible as the crystals were soluble in the available liquids, but the approximate density (1.24 g cm^{-3}) agreed sufficiently well with the density calculated (1.19 g cm^{-3}) to establish the number of mol-

ecules per unit cell, $Z = 4$. The linear absorption coefficient, $\mu(\text{Mo } K\alpha)$ is 0.90 cm^{-1} .

All X-ray data were obtained from a crystal $0.3 \times 0.4 \times 0.45 \text{ mm}$ on a Nonius 3-circle automatic diffractometer with graphite monochromated $\text{Mo } K\alpha$ radiation. The compound is very sensitive to moisture, so the crystal was sealed in a glass capillary. The c axis of the crystal was oriented along the φ axis of the goniometer. The ω scanning mode was used with a scan speed of 1.2° per min. Each reflexion was scanned over a range of 1.2° . Background was measured on each side of the reflexion for half the scanning time. Each of the 841 independent reflexions in the range $2.5^\circ < \theta < 25^\circ$ was measured twice. 1578 of the 1655 reflexions (hkl and $\bar{h}\bar{k}l$) measured had structure factors greater than 2.5 times their corresponding standard deviations obtained from counting statistics and were considered observed. The two measurements of each independent reflexion were compared and a reliability index for the observed reflexions was found to be $R = \sum(F_1 - F_2) / \sum \frac{1}{2}(F_1 + F_2) = 0.038$, but the reflexions from both octants were used independently in the least-squares refinement. A standard reflexion was remeasured after each 25 reflexions. No absorption correction was applied.

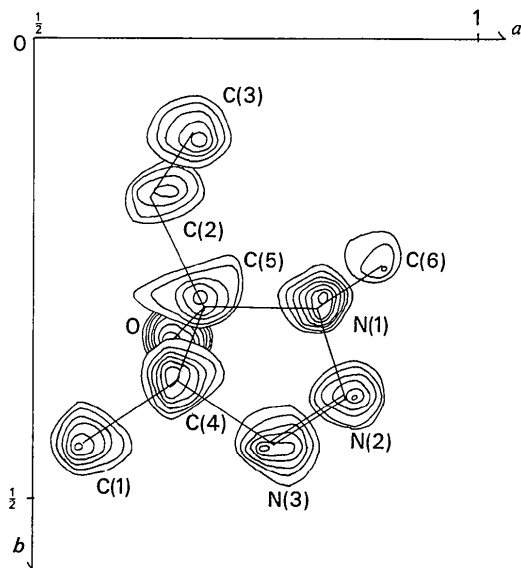


Fig. 1. 1,4-Dimethyl-5-ethyl-5-hydroxy- Δ^2 -1,2,3-triazoline. Sections from a three-dimensional E map computed on the basis of 101 phases found by tangent refinement. The contours are evenly spaced. The final positions of the non-hydrogen atoms are indicated.

Determination and refinement of the structure

The structure was determined by a computer application of the tangent formula (Karle & Hauptman, 1956). Preliminary symbolic addition (Karle & Karle, 1966) suggested a starting set of six reflexions, three of which were fixed to define the origin and one to define the enantiomorph. The phase value of the remaining two were given symbols and the most probable values found from \sum_2 relations. The tangent formula was then applied to obtain a total of 101 phases for reflexions with $|E| \geq 1.5$. E maps were computed with the phases obtained for the two most probable choices for the unknown symbols. One of these showed the full

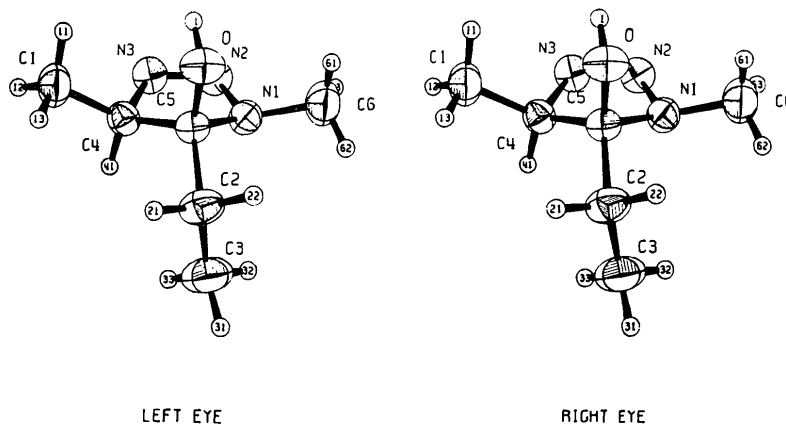


Fig. 2. Stereoscopic drawing of the 1,4-dimethyl-5-ethyl-5-hydroxy- Δ^2 -1,2,3-triazoline molecule. The non-hydrogen atoms are represented by their thermal ellipsoids scaled to enclose 50% probability.

Table 1. Observed and calculated structure factors ($\times 10$) for 1,4-dimethyl-5-ethyl-5-hydroxy- Δ^2 -1,2,3-triazoline. Unobserved reflexions are designated with an asterisk. The columns are h , $|F_o|$, $|F_c|$, ϕ_o and ϕ_c . The phases are in millicycles.

Table with columns: h, |Fo|, |Fc|, phi_o, phi_c. Rows list structure factor data for various hkl reflections, including observed and calculated values and phases.

structure. A composite projection is shown in Fig. 1. The structure factor calculation gave an R of 0.23 [$R = \sum w(|F_o| - |F_c|) / \sum F_o$].

Two cycles of isotropic full-matrix refinement led to an R of 0.13. A difference Fourier synthesis at this stage showed all the hydrogen atoms except the one bonded to C(4). The positions of the hydrogen atoms were in accordance with those calculated from the positions of the atoms to which they are bonded. In the following cycles of full-matrix anisotropic least-squares refinement, the hydrogen atoms were included in the structure-factor calculation, but their parameters were not refined. The refinement ceased at $R = 0.08$. A difference Fourier map calculated at this stage showed negative regions around one of the nitrogen atoms [N(1)] and at the position of the hydrogen atom H(41), which was bonded to one of the carbon atoms

of the ring, and also a positive region round the carbon C(4). This indicated that the assignment of the ring atoms was wrong and the positions of C(4) and N(1) were interchanged, as well as those of N(2) and N(3). A new position of H(41) was calculated. One cycle of anisotropic refinement reduced R to 0.06, which verified this assignment. Further anisotropic refinement in which the hydrogen positions were included, but the isotropic temperature factor of hydrogen was fixed at $B = 5.00 \text{ \AA}^2$, led to $R = 0.050$ (1578 reflexions, less than not included). At this stage the shifts were less than 0.3 times the corresponding standard deviations (average shift/error 0.04).

During the later stages of refinement, the weighting scheme was $1/w = 1.6 - 0.31|F| + 0.028|F|^2 + 0.0005|F|^3$, with the maximum allowed weight set to 10. A final analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of F_o and

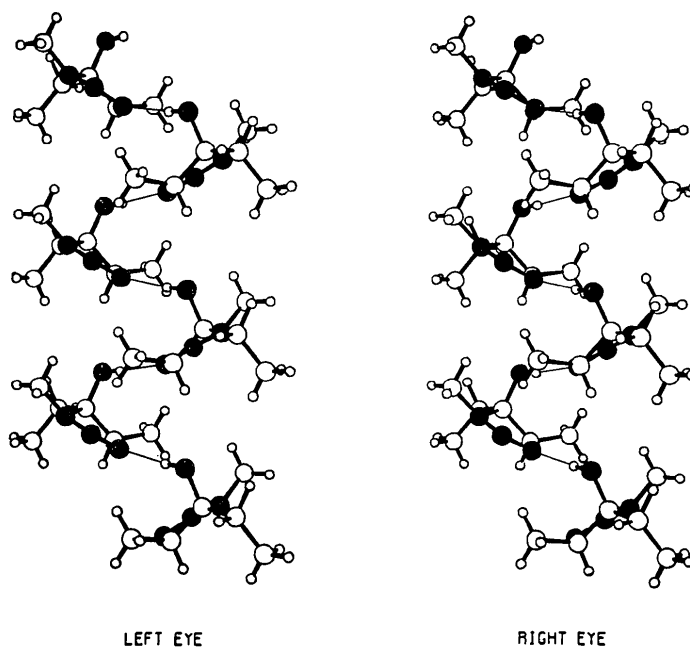


Fig. 3. Stereoscopic drawing of a series of 1,4-dimethyl-5-ethyl-5-hydroxy-2,1,2,3-triazoline molecules related by the twofold screw axis parallel to the c axis. The O-H...N hydrogen bond is shown.

Table 2. Final atomic parameters (and e.s.d.'s)

$$\text{T.F.} = \exp \{ -2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl) \}.$$

For the hydrogen atoms an isotropic temperature factor $U = 0.063 \text{ \AA}^2$ was used. Thermal parameters are in $\text{\AA}^2 \times 10^2$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O	0.66368 (13)	0.32806 (13)	0.4406 (2)	5.45 (8)	4.18 (8)	3.73 (8)	-0.96 (7)	1.14 (7)	-0.27 (6)
N(1)	0.82269 (13)	0.28830 (13)	0.1960 (3)	3.53 (8)	3.81 (8)	5.02 (10)	-0.14 (7)	-0.10 (8)	0.07 (8)
N(2)	0.85626 (15)	0.38812 (15)	0.1035 (3)	3.74 (8)	4.57 (9)	4.64 (10)	-0.56 (7)	0.67 (8)	0.28 (8)
N(3)	0.77425 (13)	0.43881 (15)	0.0080 (3)	4.19 (9)	4.56 (9)	4.56 (10)	-0.70 (7)	0.4 (8)	0.86 (9)
C(1)	0.55804 (19)	0.4403 (2)	0.0614 (5)	4.10 (10)	5.40 (12)	6.45 (16)	0.63 (10)	-0.79 (11)	0.47 (13)
C(2)	0.6432 (2)	0.17026 (18)	0.2027 (5)	5.36 (12)	3.51 (10)	6.30 (15)	-0.88 (9)	0.51 (12)	-0.43 (10)
C(3)	0.6836 (3)	0.1020 (2)	-0.0009 (7)	7.20 (17)	4.63 (14)	9.1 (2)	-0.26 (12)	0.30 (19)	-2.57 (14)
C(4)	0.66713 (17)	0.36977 (16)	0.0296 (4)	3.66 (9)	4.01 (10)	3.89 (11)	-0.26 (8)	-0.12 (9)	0.13 (8)
C(5)	0.69558 (16)	0.28825 (16)	0.2233 (3)	3.56 (9)	3.40 (9)	3.47 (9)	-0.28 (8)	0.36 (8)	-0.02 (8)
C(6)	0.8979 (3)	0.2431 (2)	0.3724 (6)	5.39 (14)	5.57 (14)	7.8 (2)	0.47 (11)	-1.67 (14)	0.84 (15)

Table 2 (*cont.*)

	<i>x</i>	<i>y</i>	<i>z</i>
H(1)	0.687 (3)	0.398 (3)	0.453 (6)
H(11)	0.561 (3)	0.487 (3)	0.205 (6)
H(12)	0.547 (3)	0.483 (3)	-0.075 (6)
H(13)	0.494 (3)	0.387 (3)	0.080 (6)
H(21)	0.560 (3)	0.186 (3)	0.199 (6)
H(22)	0.663 (3)	0.137 (3)	0.369 (6)
H(31)	0.665 (3)	0.023 (3)	0.008 (6)
H(32)	0.762 (3)	0.087 (3)	0.002 (6)
H(33)	0.671 (3)	0.133 (3)	-0.138 (7)
H(41)	0.660 (3)	0.330 (3)	-0.119 (6)
H(61)	0.873 (3)	0.272 (3)	0.522 (6)
H(62)	0.889 (3)	0.163 (3)	0.376 (6)
H(63)	0.962 (3)	0.270 (3)	0.346 (6)

$\sin \theta$ showed a smooth distribution indicating the validity of the weighting scheme.

Observed and calculated structure factors are listed in Table 1 and the final atomic parameters in Table 2.

The input tapes for the diffractometer were produced on a GIER computer by *INDIFF* (Sørensen, unpublished). The remaining calculations were performed on the IBM 360/75 and later the IBM 370/165 computer at NEUCC, Lundtofte, Denmark. The N.R.C.2A Picker data reduction program (Ahmed, revised by Alcock and Sørensen) and the X-RAY System (Stewart, Kundell & Baldwin, 1970) were used. The drawings were prepared by *ORTEP* (Johnson, 1965).

Description and discussion of the structure

The 1,4-dimethyl-5-ethyl-5-hydroxy- Δ^2 -1,2,3-triazoline molecule and the atomic labelling used are shown in Fig. 2. The molecules related by the twofold screw axis parallel to the *c* axis are linked together by hydrogen bonds to form a quasi-helical chain, Fig. 3. The hydrogen bond is from a hydroxyl group to one of the double-bonded nitrogen atoms [N(3)] in the next molecule. As shown in Fig. 4, which is a projection along the *c* axis, these chains are held together only by van der Waals forces. The shortest distances are all between hydrogen atoms and greater than twice the van der Waals radius.

Conformation of the molecule

The interatomic distances and angles, uncorrected for thermal motion, are given in Table 3, and shown in Fig. 5. The triazoline ring adopts an envelope conformation. The atoms N(1), N(2), N(3), and C(4) lie in one plane which forms an angle of 27.5° with the plane defined by C(4), C(5), and N(1). The equation of the least-squares plane through N(1), N(2), N(3), and C(4) is $-2.5072x + 5.4914y + 5.0344z = 0.5072 \text{ \AA}$ in direct space. The standard deviation of the atoms from the plane is 0.0006 \AA , *i.e.*, this part of the ring is planar within experimental error. The torsional angles in the ring are given in Table 4. The three alkyl groups are in equatorial positions, whereas the hydroxy group is axial. The molecule has nearly symmetry *m*, as the ethyl and hydroxy group atoms H(31), C(3), C(2),

C(5), O, and H(1) lie roughly in a plane perpendicular to the planar part of the ring.

Table 3. *Interatomic distances (Å) and angles (°)*

O—C(5)	1.407 (2)	N(2)—N(1)—C(5)	109.11 (14)
N(1)—N(2)	1.357 (2)	N(2)—N(1)—C(6)	115.81 (17)
N(1)—C(5)	1.474 (3)	C(5)—N(1)—C(6)	121.09 (19)
N(1)—C(6)	1.452 (4)	N(1)—N(2)—N(3)	112.38 (16)
N(2)—N(3)	1.252 (2)	N(2)—N(3)—C(4)	109.01 (17)
N(3)—C(4)	1.486 (3)	C(3)—C(2)—C(5)	115.4 (2)
C(1)—C(4)	1.521 (3)	N(3)—C(4)—C(1)	113.31 (17)
C(2)—C(3)	1.514 (4)	N(3)—C(4)—C(5)	103.46 (15)
C(2)—C(5)	1.527 (3)	C(1)—C(4)—C(5)	115.72 (19)
C(4)—C(5)	1.526 (3)	O—C(5)—N(1)	110.98 (15)
		O—C(5)—C(2)	105.96 (17)
		O—C(5)—C(4)	113.93 (16)
		N(1)—C(5)—C(2)	112.64 (16)
		N(1)—C(5)—C(4)	97.62 (15)
		C(2)—C(5)—C(4)	115.76 (18)

Table 4. *Torsional angles (°) in the triazoline ring*

N(1)—N(2)—N(3)—C(4)	0
N(2)—N(3)—C(4)—C(5)	17.9
N(3)—C(4)—C(5)—N(1)	-26.0
C(4)—C(5)—N(1)—N(2)	27.6
C(5)—N(1)—N(2)—N(3)	-19.1

The N(1)—N(2) distance of $1.357 (2) \text{ \AA}$ corresponds to a bond order of 1.5 (Sabesan & Venkatesan, 1971), whereas the N(2)—N(3) distance of $1.252 (2) \text{ \AA}$ does not

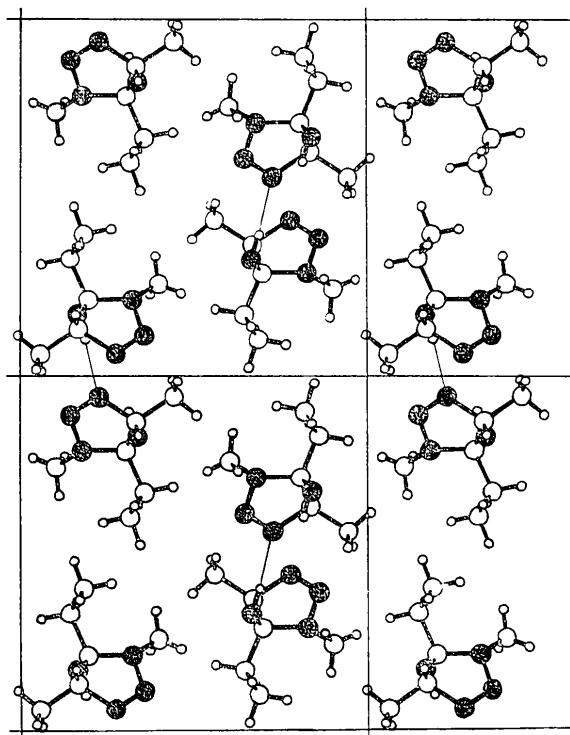


Fig. 4. Projection of the structure along the *c* axis. The *a* axis is horizontal, the *b* axis vertical.

differ significantly from the normal double bond length. Electrophilic reagents are known to attack the molecule at N(3) (Olsen, 1969); this is in accordance with a significant contribution of a resonance structure which has the double bond between N(1) and N(2) and a negative charge at N(3).

The remaining bond lengths agree with the values given in *International Tables for X-Ray Crystallography* (1962). The C-H distances are in the range 0.82–1.08 Å with a standard deviation of 0.04 Å. Bond angles which involve hydrogen are also quite normal (98–119°, e.s.d. 2–3°).

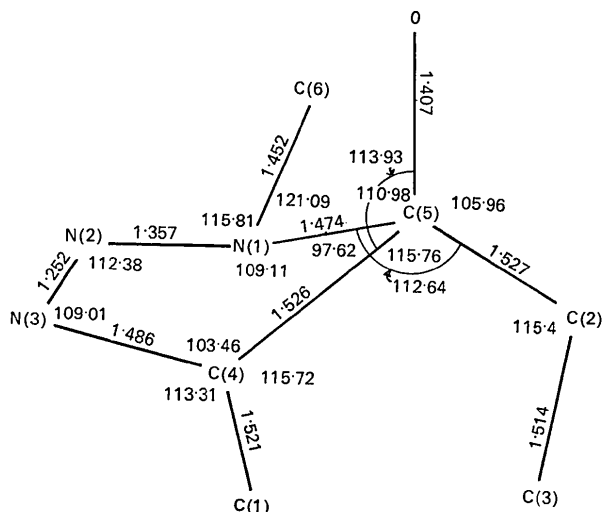


Fig. 5. Bond distances (Å) and angles (°).

The hydrogen bond

The hydrogen bond O-H(1)···N'(3) is approximately linear. The O-N distance is 2.879 (3) Å, the O-H distance 0.88 (4) Å and the N···H distance 2.01 (4) Å. The N'-H-O angle is 173 (3)°. The hydrogen bond makes an angle of 30.6° with the planar part of the ring containing the hydrogen bonded nitrogen. The C(4)-N(3)···H' angle is 136.5 (9)°, and the N(2)-N(3)···H' angle is 111.5 (9)°.

The author wishes to express her gratitude to the staff of Chemical Laboratory C, Royal Danish School of Pharmacy, and especially to lic. pharm. Alex Mehlsen Sørensen for hospitality, help and encouragement. The Danish State Foundation is thanked for placing the diffractometer at the disposal of the Laboratory.

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The Crystal Structure of Sodium Tetrasulphide, Na₂S₄

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Sodium tetrasulphide, Na₂S₄, is tetragonal and crystallizes in space group *I* $\bar{4}2d$ with cell dimensions $a = 9.5965(3)$ and $c = 11.7885(5)$ Å, and with $Z = 8$. Three-dimensional intensity data were collected with a linear diffractometer (PAILRED) using Mo $K\alpha$ radiation. Positional and anisotropic temperature-factor parameters for all atoms were refined by a full-matrix least-squares method to $R(F) = 0.030$ based on 1749 independent reflexions with $I_o > 4I$. The crystal structure is built up of unbranched S₄²⁻ ions surrounded by Na⁺ ions. The distance between different S₄²⁻ ions is about 3.60 Å. The S₄²⁻ ions lie on a twofold axis and the sulphur-sulphur bond distances are 2.074(1) Å (end) and 2.061(1) Å (middle). The sulphur-sulphur bond angle is 109.76(2)° and the dihedral angle is 97.81°. The sodium-sulphur coordination polyhedra consists of two types: a distorted tetrahedron with two pairs of distances of 2.826(1) and 2.842(1) Å and a distorted octahedron with three pairs of distances of 2.887(1), 3.043(1) and 3.081(1) Å.

Introduction

Our current work attempts to establish conditions for the formation of Na polysulphides and to determine

their structures in the solid and liquid states (Rosén & Tegman, 1972; Tegman, 1972). The structure of Na₂S₄ was studied as a part of this programme. Crystal structure determinations of sodium polysulphides can give