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1*H*-Tetrazol-5(4*H*)-one

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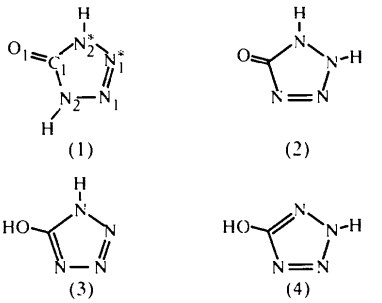
Abstract

The molecular structure determination of the title compound, CH_2N_4O, determined by X-ray crystallography reveals it to be 1*H*-tetrazol-5(4*H*)-one, not 5-hydroxytetrazole which had been generally accepted; 1*H*-tetrazol-5(4*H*)-one is the keto form with C_{2v} symmetry. *Ab initio* calculations at the MP2/6–31G* level also indicate that 1*H*-tetrazol-5(4*H*)-one is the most stable tautomer.

Comment

Four structural isomers, (1)–(4), can be written for the title compound. Hattori *et al.* (1953) reported that 5-hydroxytetrazole, (3), was the generally accepted form and that the crystal system was tetragonal. Furthermore, they studied another unstable form, the crystal system of which was probably triclinic (Hattori *et al.*, 1953). However, recent studies suggested that isomer (1) is acceptable because this compound has a keto group. We have identified the molecular structure of this compound by X-ray crystallography.



The most stable isomer obtained in the solid state is the keto form with C_{2v} symmetry. The ring is essentially planar, the largest deviation from the least-squares plane being 0.005 Å (N1). The bond lengths are quite different from normal ones. The N1—N2 length of 1.351 (2) Å is clearly shorter than other N—N single-bond lengths. The N—N bond lengths in hydrazine (H_2N—NH_2) and *N,N,N′,N′*-tetramethylhydrazine [$(CH_3)_2N$—$N(CH_3)_2$] are 1.449 and 1.42 Å, respectively (Sasada, 1984). Similarly, the C1—N2 bond length of 1.348 (2) Å is shorter than that of 1.47 Å in ethylenediamine ($NH_2C_2H_4NH_2$) and that of 1.46 Å in *N,N,N′,N′*-tetramethylhydrazine. Also, the N1=N1* double-bond length of 1.275 (3) Å is longer than the normal ones; for example, the N=N bond length in azomethane (CH_3N=NCH_3) is 1.247 Å (Sasada, 1984). Such intermediate lengths between single- and double-bond lengths should arise because the electrons in the π orbitals are delocalized over the ring. The C1=O1 bond length of 1.241 (3) Å is longer than expected; for example, that in acetone is 1.213 Å. However, this is not due to the delocalization of the electrons, but to intermolecular electrostatic interactions. The shortest intermolecular distance between the O atom and an H atom is 1.93 Å.

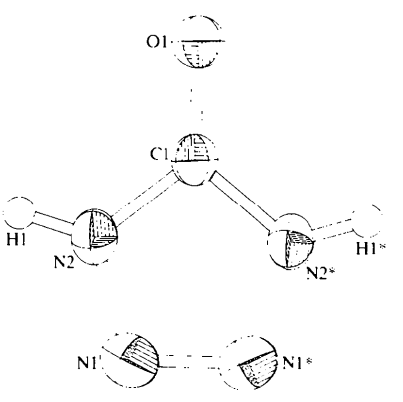


Fig. 1. View of the title molecule with the atomic numbering scheme and with non-H atoms represented by 50% probability ellipsoids. Superscript * denotes the symmetry transformation *y, x, −z, i.e.* code (i) in Table 2.

Ab initio calculations also support the observation that isomer (1) is the most stable, although they do not consider the intermolecular interaction. At the MP2/6–31G* level, the relative energies of isomers (2), (3) and (4) with respect to that of the isomer (1) are 123.3, 71.4 and 26.7 kJ mol^{-1}, respectively. Isomer (2) has not been reported and the energy difference between isomer (1) and isomer (3) is sufficiently large so that isomer (3) also should not exist under normal temperature and pressure. A similar tendency was obtained at the HF/6–31G* level.

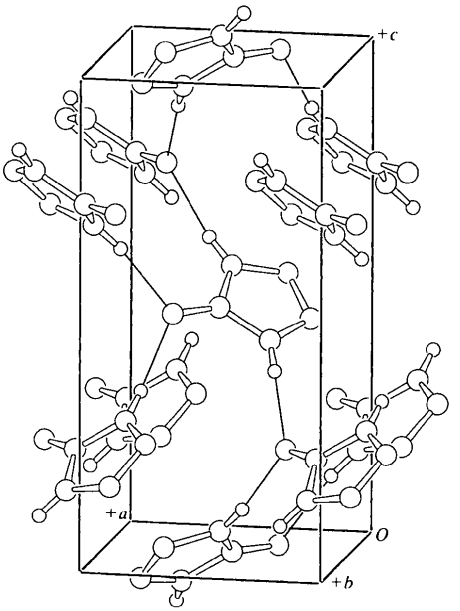


Fig. 2. Packing diagram illustrating the hydrogen bonds by thin lines.

Experimental

The compound was synthesized according to the published procedure of Moeller (1957). The crystal used for analysis was obtained by recrystallization from 2-propanol.

Crystal data

CH_2N_4O	Mo $K\alpha$ radiation
M_r = 86.05	λ = 0.7107 Å
Tetragonal	Cell parameters from 25 reflections
$P4_12_12$	θ = 10.5–19.6°
a = 5.4965 (2) Å	μ = 0.1464 mm^{-1}
c = 11.137 (1) Å	T = 296 K
V = 336.45 (3) Å^3	Prism
Z = 4	0.26 × 0.21 × 0.20 mm
D_x = 1.699 Mg m^{-3}	Colourless
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.021
ω scans with profile analysis	θ_{max} = 27.3°
Absorption correction: none	h = 0 → 7
487 measured reflections	k = 0 → 7
279 independent reflections	l = 0 → 10
226 reflections with $F > 3\sigma(F)$	3 standard reflections every 100 reflections intensity decay: 0.54%

Refinement

Refinement on F	$\Delta\rho_{max}$ = 0.132 e Å^{-3}
R = 0.028	$\Delta\rho_{min}$ = −0.124 e Å^{-3}
wR = 0.040	Extinction correction: Zachariasen (1963) type 2 Gaussian isotropic
S = 1.36	Extinction coefficient: 1040.7
226 reflections	Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)
30 parameters	
H atoms not refined	
$w = 1/[\sigma^2(F_o) + 0.000625\|F_o\|^2]$	
$(\Delta/\sigma)_{max}$ = 0.004	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a^i a^j \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
O1	0.3169 (2)	x	0	0.0371
N1	0.6901 (3)	0.8113 (3)	0.0385 (1)	0.0428
N2	0.4843 (3)	0.6862 (3)	0.0627 (1)	0.0333
C1	0.4766 (3)	x	0	0.0273

Table 2. *Selected geometric parameters (Å, °)*

O1—C1	1.241 (3)	N2—C1	1.348 (2)
N1'—N1	1.275 (3)	N2—H1	0.83
N1—N2	1.351 (2)		
N1—N1'—N2	107.81 (9)	O1—C1—N2	128.8 (1)
N1—N2—C1	111.0 (1)	N2—C1—N2'	102.4 (2)
O1—C1—N2—N1	179.7 (1)	N2—N1—N1'—N2'	−1.1 (3)
N1'—N1—N2—C1	0.9 (2)	N1—N2—C1—N2'	−0.34 (10)

Symmetry code: (i) $y, x, -z$.

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N2'—H1'···O1	0.83	1.93	2.758 (2)	171.2

Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{4} - z$; (ii) $y - \frac{1}{2}, \frac{1}{2} - x, z - \frac{1}{4}$.

The structure was solved by direct methods and difference Fourier synthesis, and refined by full-matrix least-squares methods, with anisotropic displacement parameters for all non-H atoms. H atoms were located from a difference electron-density map and included in the structure-factor calculations, but were not refined. All *ab initio* calculations were performed with the *Gaussian*94 program package (Frisch *et al.*, 1995). Structure (1) was optimized with C_{2v} symmetry; the other structures were obtained by full optimization.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1003). Services for accessing these data are described at the back of the journal.

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(7*R*,8*S*,10b*R*)-7,8-Dihydroxy-1,5,6,7,8,9,-10,10b-octahydro-3*H*-1,3-oxazolo[4,3-*a*]isoquinolin-3-one

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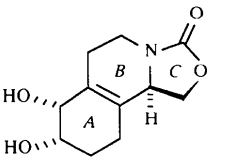
Abstract

The title compound, $C_{11}H_{15}NO_4$, was synthesized as an intermediate in a synthesis of the morphine skeleton. The two six-membered rings adopt $^4H_3$ half-chair conformations. The five-membered ring is in an envelope (*E*) conformation. Chains of the molecules hydrogen bonded through the allylic hydroxyl and carbonyl groups extend along the *b* axis. These chains are cross-linked along the [101] direction by hydrogen bonds between the adjacent secondary OH group and the allylic O atom [allylic O···O(x, $1+y$, z) 2.836 (2) Å, O—H···O 133 (2)°; secondary hydroxyl O···O($\frac{1}{2}+x$, $\frac{3}{2}-y$, $1-z$) 2.751 (2) Å, O—H···O 174 (2)°].

Comment

In the past 40 years, numerous total syntheses of morphine have been published [for a recent review see Hudlicky *et al.* (1996), and references therein]. We recently reported a chemo-enzymatic synthesis of the morphine skeleton in which the title compound, (1), was synthesized in one of the intermediate steps (Butora *et al.*, 1996). Attempts have been made to relate the absolute stereochemistry at C10b to either C7 or C8 using standard spectroscopic techniques. Careful coupling-constant analysis (^{1}H NMR, various solvents) suggested the absolute stereochemistry shown below. Although nuclear Overhauser enhancement experiments seemed to support these conclusions, final proof was sought from a single-crystal X-ray structure determination. As the absolute stereochemistry at C7 and C8 is set enzymatically (Stabile *et al.*, 1995), this also provided proof of the absolute stereochemistry of (1) as shown.



(1)

The bond lengths and angles in (1) are in good agreement with counterparts observed in other organic compounds (Allen *et al.*, 1987). The molecules of (1) have two six-membered rings fused through the C6a=C10a double bond, which has the only zero-value endocyclic torsion angle in either ring. The planar geometry around the double bond forces the ring conformations to deviate from a more stable chair conformation. Consequently, rings *A* and *B* adopt half-chair conformations which may be described as $^4H_3$ according to Boeyens (1978) terminology. Ring *A* has C8 and C9 at distances of −0.465 (3) and 0.294 (3) Å, respectively, from the plane of C6a, C7, C10a and C10, while N4 and C5 are at distances of −0.340 (3) and 0.303 (4) Å, respectively, from the plane of C6, C6a, C10a and C10b. Ring *C* adopts an envelope conformation with C10b occupying the flap position at a distance of 0.382 (3) Å from the plane of C1, O2, C3 and N4.

Each molecule of (1) is involved in two intermolecular hydrogen bonds. One hydrogen bond between O7—H7 and O1 results in a chain of molecules extending