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7β-Hydroxy-7α-(3-propargyl)-3-methyl-spiro[5.5]undec-2-en-1-one

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Abstract

The title compound, $C_{15}H_{20}O_2$, contains two six-membered rings, one of which is in a chair conformation while the other assumes an envelope shape. The molecules form dimers which are connected by C—H···O hydrogen bonds donated by the propargyl residue. The hydrogen-bonding pattern is composed of finite cooperative C≡C—H···O—H···O≡C chains.

Comment

Terminal alkynes of the present type are used as starting materials for the synthesis of steroids (Nasipuri, 1992). The crystal structure of the title compound, (I), was determined to study the intermolecular contacts of the propargyl residue, which is usually involved in C—H···X hydrogen bonding if suitable acceptors, X, are available (Desiraju, 1991).

(I)
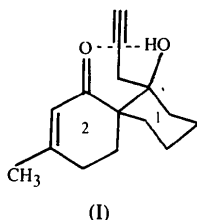
Compound (I) crystallizes in a non-centrosymmetric space group with a pair of enantiomeric molecules (A, B) per asymmetric unit. For molecule A, the molecular conformation and the atomic numbering scheme are shown in Fig. 1. Ring 1 is in a chair conformation and Ring 2 adopts an envelope shape. The ring-puckering parameters (following Cremer & Pople, 1975) for Rings 1 and 2 of both molecules are given in Table 3. The hydroxy group forms an intermolecular hydrogen bond to O=C with O···O = 2.668 (4) Å (Table 4). Molecules A and B form a pseudo-centrosymmetric dimer, with a non-crystallographic centre of symmetry at x/a = 0.123 (3), y/b = 0.519 (6), z/c = 0.344 (6). The molecules are connected by mutual C—H···O hydrogen bonds donated by the propargyl residues and accepted by the hydroxy groups (Fig. 2) (H···O ≃ 2.37 Å, for normalized H-atom positions). Within this dimer, the two molecules are tilted with respect to each other, so that true centrosymmetry is disturbed [this is reflected in non-zero dihedral angles between corresponding molecular planes; *e.g.* the least-squares-planes through rings 1(A) and 1(B) form an angle of 7.0 (2)°, and those through rings 2(A) and 2(B) form an angle of 8.8 (2)°].
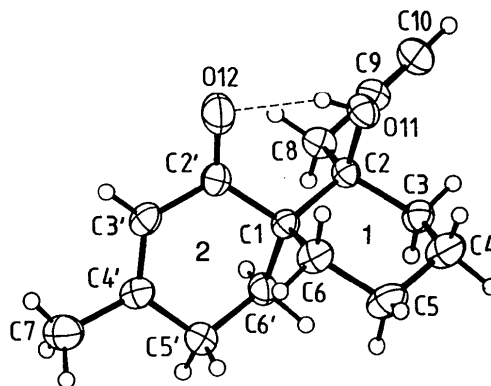

Fig. 1. Molecular structure and atomic numbering scheme of molecule A. Displacement ellipsoids are drawn at the 30% probability level.
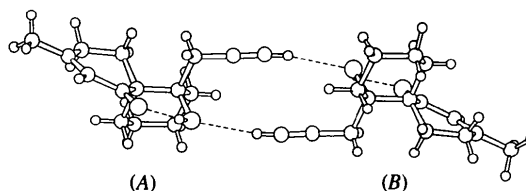

(A)   (B)

Fig. 2. The pseudo-centrosymmetric dimer formed by molecules A and B. Hydrogen bonds are shown as dashed lines.

The hydrogen bonds form finite cooperative C≡C—H···O—H···O=C chains (Figs. 2 and 3), which constitutes a stronger hydrogen-bonding pattern than isolated O—H···O and C—H···O hydrogen bonds. We

have observed related cooperative arrangements in similar compounds (Lakshmi, Subramanian, Rajagopalan, Koellner & Steiner, 1995).
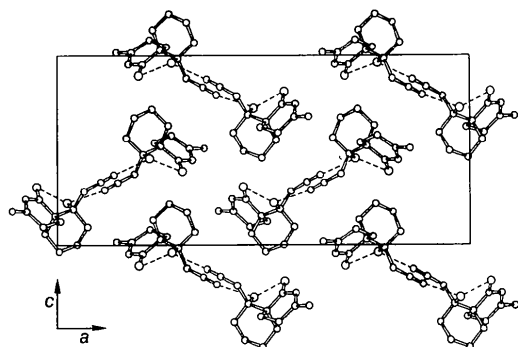

Fig. 3. Crystal packing arrangement. For clarity, H atoms are omitted. Hydrogen bonds are shown as dashed lines.

Experimental

The compound was prepared by the propargylation of 9-methylspiro[5.5]undec-2-ene-1,7-dione. The density D_m was measured by flotation in KI/H_2O.

Crystal data

$C_{15}H_{20}O_2$	Cu $K\alpha$ radiation
$M_r = 232.31$	$\lambda = 1.54184$ Å
Orthorhombic	Cell parameters from 23
$Pna2_1$	reflections
$a = 27.700\,(3)$ Å	$\theta = 20\text{–}34°$
$b = 7.630\,(4)$ Å	$\mu = 0.569$ mm^{-1}
$c = 12.382\,(1)$ Å	$T = 293\,(2)$ K
$V = 2617\,(1)$ Å^3	Rectangular block
$Z = 8$	$0.6 \times 0.4 \times 0.4$ mm
$D_x = 1.179$ Mg m^{-3}	Pale yellow
$D_m = 1.180$ Mg m^{-3}	

Data collection

Enraf–Nonus CAD-4 diffractometer	$\theta_{max} = 59.81°$
ω scans	$h = 0 \rightarrow 31$
Absorption correction:	$k = 0 \rightarrow 8$
none	$l = 0 \rightarrow 13$
2034 measured reflections	3 standard reflections
2034 independent reflections	frequency: 60 min
1990 observed reflections	intensity decay: <2%
$[I > 2\sigma(I)]$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.002$
$R(F) = 0.047$	$\Delta\rho_{max} = 0.246$ e Å^{-3}
$wR(F^2) = 0.118$	$\Delta\rho_{min} = -0.258$ e Å^{-3}
$S = 1.126$	Extinction correction: none

2034 reflections
467 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + 0.1154P^2 + 0.1113P]$
where $P = (F_o^2 + 2F_c^2)/3$

Atomic scattering factors
from *International Tables for Crystallography* (1992, Vol. C)

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

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
C1A	0.2506 (1)	0.9062 (3)	0.5307 (2)	3.50 (6)
C2A	0.2077 (1)	0.7932 (3)	0.4860 (2)	3.57 (7)
C3A	0.1680 (1)	0.7763 (4)	0.5723 (2)	4.49 (8)
C4A	0.1867 (1)	0.7033 (7)	0.6787 (3)	6.04 (12)
C5A	0.2288 (1)	0.8103 (7)	0.7231 (3)	6.28 (13)
C6A	0.2690 (1)	0.8235 (5)	0.6381 (3)	4.82 (8)
C2'A	0.2939 (1)	0.9046 (4)	0.4539 (2)	4.18 (7)
C3'A	0.3269 (1)	1.0539 (4)	0.4558 (2)	4.44 (8)
C4'A	0.3201 (1)	1.1968 (4)	0.5168 (2)	4.44 (8)
C5'A	0.2765 (1)	1.2162 (4)	0.5857 (3)	4.86 (10)
C6'A	0.2352 (1)	1.0987 (3)	0.5476 (3)	4.10 (7)
C7A	0.3559 (1)	1.3453 (7)	0.5181 (4)	6.41 (13)
C8A	0.1871 (1)	0.8754 (4)	0.3814 (3)	4.52 (8)
C9A	0.1468 (1)	0.7763 (4)	0.3348 (3)	4.63 (8)
C10A	0.1143 (1)	0.7002 (4)	0.2963 (3)	5.35 (9)
O11A	0.2229 (1)	0.6179 (2)	0.4636 (2)	4.66 (6)
O12A	0.3029 (1)	0.7789 (3)	0.3957 (2)	6.73 (9)
C1B	−0.0060 (1)	0.1332 (3)	0.1586 (2)	3.75 (7)
C2B	0.0390 (1)	0.2432 (3)	0.1952 (2)	3.78 (7)
C3B	0.0733 (1)	0.2736 (4)	0.0993 (3)	4.93 (9)
C4B	0.0487 (1)	0.3595 (7)	0.0032 (3)	6.25 (10)
C5B	0.0042 (1)	0.2559 (8)	−0.0329 (3)	6.63 (14)
C6B	−0.0301 (1)	0.2274 (5)	0.0620 (3)	4.96 (10)
C2'B	−0.0443 (1)	0.1236 (4)	0.2479 (2)	4.55 (8)
C3'B	−0.0768 (1)	−0.0270 (4)	0.2499 (2)	4.67 (7)
C4'B	−0.0739 (1)	−0.1628 (4)	0.1832 (2)	4.40 (8)
C5'B	−0.0346 (1)	−0.1729 (5)	0.1009 (4)	5.42 (10)
C6'B	0.0082 (1)	−0.0564 (4)	0.1290 (3)	4.84 (9)
C7B	−0.1093 (1)	−0.3119 (6)	0.1853 (4)	6.15 (12)
C8B	0.0652 (1)	0.1513 (5)	0.2891 (4)	5.73 (11)
C9B	0.1049 (1)	0.2514 (4)	0.3378 (3)	5.35 (9)
C10B	0.1376 (1)	0.3278 (4)	0.3762 (4)	5.85 (11)
O11B	0.0244 (2)	0.4148 (2)	0.2286 (2)	4.78 (6)
O12B	−0.0501 (1)	0.2429 (4)	0.3126 (2)	7.68 (9)

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

C1A—C2A	1.568 (4)	C1B—C2B	1.571 (4)
C1A—C6A	1.558 (5)	C1B—C6B	1.546 (5)
C1A—C2'A	1.531 (4)	C1B—C2'B	1.534 (4)
C1A—C6'A	1.544 (4)	C1B—C6'B	1.544 (4)
C2A—C3A	1.539 (4)	C2B—C3B	1.537 (5)
C2A—C8A	1.548 (5)	C2B—C8B	1.540 (6)
C2A—O11A	1.429 (3)	C2B—O11B	1.431 (4)
C3A—C4A	1.520 (6)	C3B—C4B	1.520 (6)
C4A—C5A	1.525 (7)	C4B—C5B	1.530 (7)
C5A—C6A	1.537 (6)	C5B—C6B	1.526 (6)
C2'A—C3'A	1.460 (4)	C2'B—C3'B	1.459 (5)
C2'A—O12A	1.225 (4)	C2'B—O12B	1.224 (5)
C3'A—C4'A	1.340 (5)	C3'B—C4'B	1.327 (5)
C4'A—C5'A	1.489 (5)	C4'B—C5'B	1.494 (6)
C4'A—C7A	1.504 (6)	C4'B—C7B	1.503 (6)
C5'A—C6'A	1.528 (5)	C5'B—C6'B	1.521 (5)
C8A—C9A	1.466 (5)	C8B—C9B	1.468 (6)
C9A—C10A	1.173 (5)	C9B—C10B	1.178 (6)
C2'A—C1A—C6'A	108.0 (2)	C2'B—C1B—C6'B	107.7 (2)
C6A—C1A—C6'A	111.1 (3)	C6B—C1B—C6'B	111.3 (3)
C6A—C1A—C2'A	105.6 (2)	C6B—C1B—C2'B	106.4 (2)
C2A—C1A—C6'A	111.2 (2)	C2B—C1B—C6'B	111.5 (2)
C2A—C1A—C2'A	111.8 (2)	C2B—C1B—C2'B	111.5 (2)
C2A—C1A—C6A	109.1 (2)	C2B—C1B—C6B	108.5 (2)
C1A—C2A—O11A	111.1 (2)	C1B—C2B—O11B	110.4 (2)
C1A—C2A—C8A	110.6 (2)	C1B—C2B—C8B	110.4 (3)

C1A—C2A—C3A	110.0 (2)	C1B—C2B—C3B	110.4 (3)
C8A—C2A—O11A	109.0 (2)	C8B—C2B—O11B	109.3 (3)
C3A—C2A—O11A	105.5 (2)	C3B—C2B—O11B	105.1 (2)
C3A—C2A—C8A	110.6 (2)	C3B—C2B—C8B	111.1 (3)
C2A—C3A—C4A	112.9 (3)	C2B—C3B—C4B	113.1 (3)
C3A—C4A—C5A	112.1 (4)	C3B—C4B—C5B	111.5 (4)
C4A—C5A—C6A	110.1 (4)	C4B—C5B—C6B	110.5 (4)
C1A—C6A—C5A	111.9 (3)	C1B—C6B—C5B	113.2 (3)
C1A—C2′A—O12A	122.0 (3)	C1B—C2′B—O12B	121.9 (3)
C1A—C2′A—C3′A	118.3 (3)	C1B—C2′B—C3′B	118.4 (3)
C3′A—C2′A—O12A	119.6 (3)	C3′B—C2′B—O12B	119.6 (3)
C2′A—C3′A—C4′A	123.8 (3)	C2′B—C3′B—C4′B	124.6 (3)
C3′A—C4′A—C7A	121.8 (3)	C3′B—C4′B—C7B	122.8 (3)
C3′A—C4′A—C5′A	121.2 (3)	C3′B—C4′B—C5′B	120.6 (3)
C5′A—C4′A—C7A	117.0 (3)	C5′B—C4′B—C7B	116.6 (3)
C4′A—C5′A—C6′A	111.9 (3)	C4′B—C5′B—C6′B	112.4 (4)
C1A—C6′A—C5′A	113.2 (2)	C1B—C6′B—C5′B	113.8 (3)
C2A—C8A—C9A	113.6 (3)	C2B—C8B—C9B	115.3 (3)
C8A—C9A—C10A	178.6 (4)	C8B—C9B—C10B	178.1 (4)

Table 3. *Ring-puckering parameters according to Cremer & Pople (1975)*

	Q (Å)	θ (°)	φ (°)
Molecule A			
Ring 1	0.580 (3)	177.0 (3)	154 (6)
Ring 2	0.460 (3)	126.8 (4)	109.2 (5)
Molecule B			
Ring 1	0.573 (4)	2.6 (4)	350 (9)
Ring 2	0.449 (3)	52.8 (4)	311.5 (6)

Table 4. *Hydrogen-bond parameters (Å, °)*

D—H···O	D—H	H···O	D···O	H_{norm}···O	D—H_{norm}···O
O11A—H···O12A	0.78 (4)	1.93 (4)	2.668 (4)	1.75	154
O11B—H···O12B	0.91 (8)	2.03 (3)	2.659 (4)	1.99	124
C10A—H···O11B	0.89 (4)	2.54 (5)	3.413 (4)	2.37	162
C10B—H···O11A	0.92 (3)	2.50 (5)	3.414 (5)	2.36	164

The structure was solved by direct methods. The initial R index for the model was 0.19. After a few cycles of full-matrix refinement the R index dropped to 0.12. All H atoms were located from difference Fourier maps and refined isotropically. The Flack χ parameter refined to −0.16 (32).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *SDP* (Frenz, 1978). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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The α-Pyridyl Nucleoside Analogue 2-Bromo-5-(2-deoxy-α-D-ribofuranosyl)pyridine

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Abstract

The structure of the title compound, $C_{10}H_{12}BrNO_3$, is reported. The ribose sugar has a C3′-*endo* pucker and the exocyclic torsion angle O5′—C5′—C4′—C3′ adopts a *gauche*+ value of 61.0 (9)°.

Comment

The determination of the structure of the title compound, (I), was undertaken in order to unequivocally assign the α-conformation at the C1′ atom following its synthesis as part of a project aimed at developing modified nucleosides for DNA triple-strand recognition. The details of the conformational features are being employed in molecular-modelling studies on triple helices with non-standard bases.

(I)