

## A Highly Substituted *trans*-Fused Bicyclo[5.3.0]decene

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### Abstract

The title compound, 2,4-dimethyl-9-oxabicyclo[5.3.0]-dec-5-ene-1,3-diol deuteriochloroform solvate, C<sub>11</sub>H<sub>18</sub>O<sub>3</sub>·CDCl<sub>3</sub>, has a seven-membered and a five-membered ring which are *trans*-fused and are affected by angle strain. There are three types of intermolecular hydrogen bonding present in the structure, namely, O—H···OH [O···O 2.774 (2) Å], O—H···O [O···O 2.837 (2) Å] and C—D···OH [C···O 3.043 (2) Å].

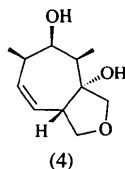
### Comment

Our objective was to design a strategy which would rapidly assemble the *trans*-fused bicyclo[5.3.0] ring system and be sufficiently flexible to incorporate substitution within the rings and/or at the periphery. The 5,7-fused ring system is found in many natural products (Rigby, 1988). Our overall plan, outlined in the scheme below, relies on an intramolecular cyclization process in which C—C bond formation is accompanied by the rupture of a C—O bond.



X = CH<sub>2</sub>, O, S, N—Me

The relative stereochemistry of the title bicyclo[5.3.0] molecule (4) was established by this X-ray structure determination and is consistent with an intramolecular anionic attack of the olefin in an *exo*-S<sub>N</sub>2' fashion (Lautens & Kumanovic, 1995). The product contains five contiguous stereocentres and a new ring, as well as a tertiary bridgehead hydroxy moiety.



In the title molecule, the seven-membered ring has a half-chair conformation (Ladd & Palmer, 1985). Atoms

C2, C3, C4 and C5 form a least-squares plane [maximum deviation from the plane of 0.009 (1) Å for atom C4], with atoms C1, C7 and C6 displaced from it by 0.950 (3), 0.523 (4) and -0.443 (3) Å, respectively. The seven-membered ring is *trans*-fused [torsion angle O14—C1—C2—H2 -177.3 (12)°] to the five-membered ring, which has an envelope conformation. Atoms C1, C8, O9 and C10 form a plane [maximum deviation 0.094 (1) Å for atom O9], with atom C2 displaced from it by -0.585 (2) Å.

The magnitudes of the internal angles of the seven-membered ring in (4) are significantly distorted by strain. The sum of the internal angles of the seven-membered ring is 838.2 (1)°, which is significantly larger than the expected sum, 787.5°, based on orbital hybridization principles. The internal angles in the five-membered ring, on the other hand, tend to be smaller than expected. The most significant value is 101.6 (1)° for C1—C2—C8. This appears to compensate for the angular distortion present in the seven-membered ring.

There are three different types of hydrogen bonding present in the crystal structure. Firstly, molecules are linked by intermolecular O—H···OH hydrogen bonds *via* 2<sub>1</sub> screw axes to form infinite chains in the *y* direction [O12···O14(-*x*, ½ + *y*, ½ - *z*) 2.774 (2) Å]. There are also O—H···O hydrogen bonds between molecules, symmetry related by glide planes, which form chains in the *z* direction [O14···O9(*x*, -½ - *y*, ½ + *z*) 2.837 (2) Å]. The asymmetric unit of the structure contains one CDCl<sub>3</sub> molecule which is rotationally disordered about the C—D bond axis giving two sites for each Cl atom. This solvent molecule is hydrogen bonded through C—D···OH [C15···O12 3.043 (2) Å] interactions to give the third type of hydrogen bonding. The overall structure consists of layers of hydrogen-

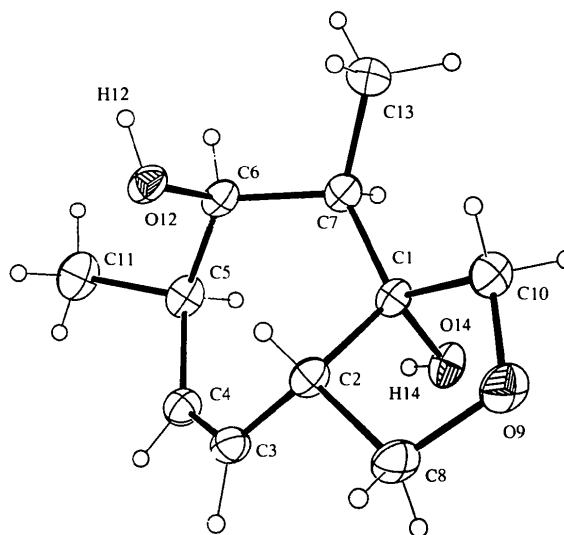


Fig. 1. View of the title molecule with the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small spheres.

bonded molecules of (4) with disordered hydrogen-bonded molecules of  $\text{CDCl}_3$  sandwiched between layers (Fig. 2). The disorder does not affect the hydrogen bonding.

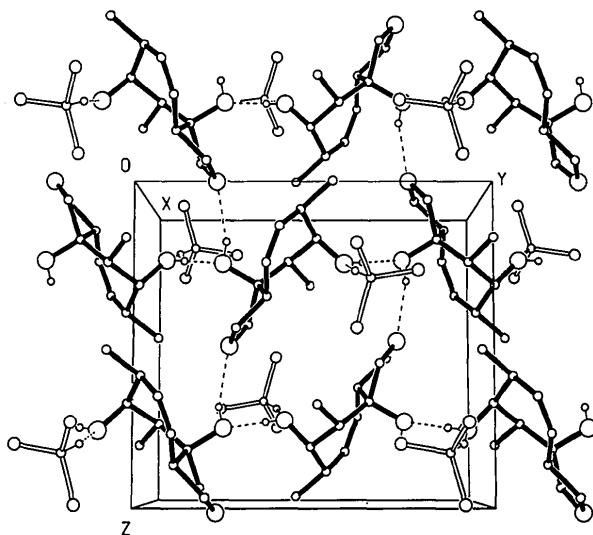
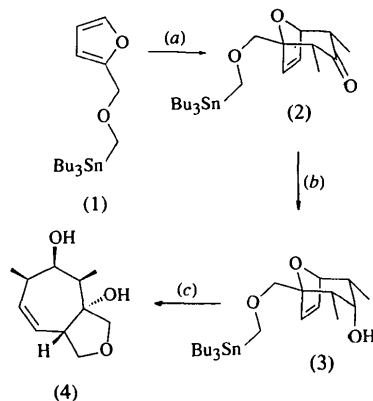


Fig. 2. View perpendicular to the  $bc$  plane showing a hydrogen-bonded layer. Atoms are drawn as open spheres and only the H atoms involved in hydrogen bonds (shown by dashed lines) have been included. Only one of the disorder sites has been shown for the Cl atoms.

## Experimental

The oxabicyclo[3.2.1] substrate (3) employed in this study was prepared in three steps using [4+3] cycloaddition as the key step. The  $\alpha$ -(tributylstannyl)methyl ether of furfuryl alcohol (1) was prepared by the methods of Still & Mitra (1978), Still, McDonald, Collum & Mitra (1979), Seyferth & Andrews (1971) and Still (1978), using KH and  $\text{Bu}_3\text{SnCH}_2\text{I}$ . Noyori's [4+3] cycloaddition (Sato & Noyori, 1978) was employed for the synthesis of the oxabicyclo[3.2.1] substrate (2). The method involves the generation of an oxyallyl cation



- (a) [4 + 3] cycloaddition  
 (b) L-Selectride<sup>®</sup>, THF, 195 K  
 (c) MeLi (5 eq.), THF, 195 → 273 K, 2 h

from  $\alpha, \alpha'$ -dibromopentan-3-one (Ashcroft & Hoffman, 1978; Clarke & Heathcock, 1976) and Zn/Ag couple (Clarke & Heathcock, 1976), followed by cycloaddition to furan (1) to form (2). Following the cycloaddition (22% yield), ketone (2) was stereoselectively reduced with L-selectride (Chiu, 1994). Alcohol (3) was investigated in the cyclization reaction. The feasibility of the intramolecular ring opening of the oxabicyclo[3.2.1] compounds was explored using the stannyl ether (3). In a typical experiment, (3) was treated with 5 eq. of MeLi in tetrahydrofuran at 195 K for 5 min to generate the  $\alpha$ -oxy organolithium species (Broka & Shen, 1989; Broka, Lee & Shen, 1988). Upon warming to 273 K and stirring for 2 h, the bicyclo[5.3.0] tetrahydrofuran (4) was produced in 85% yield. Crystals of (4) were obtained from  $\text{CDCl}_3$ .

## Crystal data

$\text{C}_{11}\text{H}_{18}\text{O}_3 \cdot \text{CDCl}_3$   
 $M_r = 318.63$   
 Monoclinic  
 $P2_1/c$   
 $a = 10.125 (1) \text{ \AA}$   
 $b = 12.764 (2) \text{ \AA}$   
 $c = 11.338 (2) \text{ \AA}$   
 $\beta = 90.39 (1)^\circ$   
 $V = 1465.2 (4) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.444 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 42 reflections  
 $\theta = 5.22\text{--}12.01^\circ$   
 $\mu = 0.623 \text{ mm}^{-1}$   
 $T = 158 (2) \text{ K}$   
 Fragment cut from flat block  
 $0.35 \times 0.30 \times 0.25 \text{ mm}$   
 Colourless

## Data collection

Siemens P4 diffractometer  
 $\omega$  scans  
 Absorption correction:  
 refined from  $\Delta F$  using  
 SHELXA90 in SHELXL93  
 (Sheldrick, 1993)  
 $T_{\min} = 0.578$ ,  $T_{\max} = 0.955$   
 5320 measured reflections  
 4265 independent reflections

3220 observed reflections  
 $[I > 2\sigma(I)]$   
 $R_{\text{int}} = 0.0232$   
 $\theta_{\text{max}} = 30.01^\circ$   
 $h = -1 \rightarrow 14$   
 $k = -1 \rightarrow 17$   
 $l = -15 \rightarrow 15$   
 3 standard reflections  
 monitored every 97 reflections  
 intensity variation: <3%

## Refinement

Refinement on  $F^2$   
 $R(F) = 0.0431$   
 $wR(F^2) = 0.1183$   
 $S = 1.019$   
 4263 reflections  
 268 parameters  
 All H-atom parameters refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0593P)^2 + 0.3809P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.066$   
 $\Delta\rho_{\text{max}} = 0.526 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.271 \text{ e \AA}^{-3}$   
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{\text{eq}}$
C1	0.04551 (14)	-0.15398 (11)	0.17615 (12)	0.0175 (3)
C2	0.18329 (14)	-0.12541 (11)	0.13056 (12)	0.0189 (3)
C3	0.2927 (2)	-0.12591 (12)	0.22047 (13)	0.0222 (3)

C4	0.28810 (15)	-0.08968 (12)	0.33002 (13)	0.0223 (3)
C5	0.1769 (2)	-0.03551 (12)	0.39276 (12)	0.0226 (3)
C6	0.06617 (15)	0.00934 (11)	0.31501 (12)	0.0196 (3)
C7	-0.02465 (14)	-0.07047 (12)	0.25265 (13)	0.0198 (3)
C8	0.2040 (2)	-0.20865 (13)	0.03576 (14)	0.0263 (3)
O9	0.07558 (12)	-0.23217 (10)	-0.01145 (10)	0.0290 (3)
C10	-0.0231 (2)	-0.18267 (13)	0.06005 (13)	0.0236 (3)
C11	0.2361 (2)	0.05157 (15)	0.46984 (15)	0.0314 (4)
O12	0.12095 (11)	0.08252 (8)	0.23336 (10)	0.0215 (2)
C13	-0.1339 (2)	-0.00990 (14)	0.1889 (2)	0.0292 (3)
O14	0.05349 (12)	-0.25180 (8)	0.23963 (10)	0.0223 (2)
C1S	0.3996 (2)	0.1480 (2)	0.1667 (2)	0.0335 (4)
C11 †	0.4220 (6)	0.1114 (12)	0.0217 (5)	0.079 (2)
C12 †	0.5430 (9)	0.1095 (8)	0.2509 (10)	0.0521 (13)
C13 †	0.3618 (5)	0.2738 (4)	0.1917 (10)	0.0654 (12)
C11' ‡	0.4096 (3)	0.1599 (6)	0.0084 (2)	0.0563 (10)
C12' ‡	0.5473 (8)	0.1078 (7)	0.2249 (5)	0.0418 (6)
C13' ‡	0.3601 (4)	0.2787 (3)	0.2151 (3)	0.0418 (6)

† Occupancy = 0.47 (2).

‡ Occupancy = 0.53 (2).

Table 2. Selected geometric parameters (Å, °)

C1—O14	1.443 (2)	C5—C6	1.533 (2)	
C1—C10	1.529 (2)	C5—C11	1.533 (2)	
C1—C2	1.535 (2)	C6—O12	1.430 (2)	
C1—C7	1.550 (2)	C6—C7	1.541 (2)	
C2—C3	1.500 (2)	C7—C13	1.528 (2)	
C2—C8	1.527 (2)	C8—O9	1.435 (2)	
C3—C4	1.327 (2)	O9—C10	1.437 (2)	
C4—C5	1.504 (2)			
O14—C1—C10	104.23 (11)	C4—C5—C11	108.19 (14)	
O14—C1—C2	109.00 (11)	C6—C5—C11	109.78 (13)	
C10—C1—C2	100.11 (11)	O12—C6—C5	109.32 (12)	
O14—C1—C7	109.89 (11)	O12—C6—C7	111.58 (12)	
C10—C1—C7	116.06 (12)	C5—C6—C7	116.68 (12)	
C2—C1—C7	116.50 (11)	C13—C7—C6	108.09 (12)	
C3—C2—C8	111.77 (12)	C13—C7—C1	114.63 (13)	
C3—C2—C1	116.01 (12)	C6—C7—C1	115.92 (12)	
C8—C2—C1	101.62 (12)	O9—C8—C2	106.23 (12)	
C4—C3—C2	127.19 (14)	C8—O9—C10	109.23 (11)	
C3—C4—C5	129.36 (14)	O9—C10—C1	106.11 (12)	
C4—C5—C6	116.54 (12)			
D—H...A	D—H	H...A	D...A	D—H...A
O12—H12...O14 <sup>i</sup>	0.80 (2)	1.98 (2)	2.774 (2)	170 (2)
O14—H14...O9 <sup>ii</sup>	0.77 (2)	2.13 (2)	2.837 (2)	153 (2)
C1S—H1S...O12	0.90 (2)	2.21 (2)	3.043 (2)	153 (2)

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

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1194). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Ashcroft, M. R. & Hoffman, H. M. R. (1978). *Org. Synth.* **58**, 17–24.
- Broka, C. A., Lee, W. J. & Shen, T. (1988). *J. Org. Chem.* **53**, 1336–1388.
- Broka, C. A. & Shen, T. (1989). *J. Am. Chem. Soc.* **111**, 2981–2984.
- Chiu, P. (1994). PhD thesis. *Ring-Opening Reactions of Oxabicyclic Compounds: Unsymmetrical Substrates and Reduction*, p. 76. Univ. of Toronto, Canada.
- Clarke, R. D. & Heathcock, C. H. (1976). *J. Org. Chem.* **41**, 636–643.
- Ladd, M. F. C. & Palmer, R. A. (1985). *Structure Determination by X-ray Crystallography*, 2nd ed., pp. 352–354. New York: Plenum Press.
- Lautens, M. & Kumanovic, S. (1995). *J. Am. Chem. Soc.* **117**, 1954–1964.
- Rigby, J. H. (1988). *Studies in Natural Products Chemistry*, Vol. 1, edited by Atta-ur-Rahman, pp. 545–576. Amsterdam: Elsevier.
- Sato, T. & Noyori, R. (1978). *Bull. Chem. Soc. Jpn.* **51**, 2745–2746.
- Seyferth, D. & Andrews, S. B. (1971). *J. Organomet. Chem.* **30**, 151–166.
- Sheldrick, G. M. (1990). *SHELXTL/PC Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
- Siemens (1994). *XSCANS. X-ray Single Crystal Analysis System*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Still, W. C. (1978). *J. Am. Chem. Soc.* **100**, 1481–1486.
- Still, W. C., McDonald, J. H., Collum, D. B. & Mitra, A. (1979). *Tetrahedron Lett.* pp. 593–594.
- Still, W. C. & Mitra, A. (1978). *J. Am. Chem. Soc.* **100**, 1927–1928.

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## N-(p-Tolyl)phthalimide

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## Abstract

The title compound, C<sub>15</sub>H<sub>11</sub>NO<sub>2</sub>, was structurally analyzed in order to clarify the influence of the substituents on the conformational change, which has an