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An Enantiopure Isobornylsulfinylcyclohexene Derivative, $C_{19}H_{30}O_5S$

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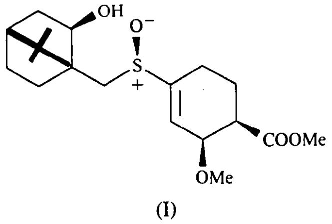
Abstract

The crystal structure of the title compound {methyl ($1R,2R,R_S$)-2-methoxy-4-[($1S,2R,4R$)-2-hydroxy-10-bornylsulfinyl]cyclohex-3-enecarboxylate}, $C_{19}H_{30}O_5S$, has been determined by X-ray diffraction. The structure shows an intramolecular hydrogen bond between the hydroxyl group and the sulfinyl O atom.

Comment

In the course of work on asymmetric Diels–Alder syntheses involving homochiral sulfinyldienes (Aversa, Bonaccorsi, Giannetto, Jafari & Jones, 1992; Aversa, Bonaccorsi, Giannetto & Jones, 1994), we isolated the title compound (I), as yet unknown, by reaction of (R_S,E)-1-methoxy-3-[(1S)-isobornyl-10-sulfinyl]buta-1,3-diene with methyl acrylate in the presence of $LiClO_4$ (Adams, Jones, Aversa, Bonaccorsi & Giannetto, 1993). This adduct and its transformation products from removal of the chiral auxiliary, have arrays of functionality which are suitable for further manipulation to give synthetically useful optically active compounds.



(I)

The structure of (I) was established by X-ray crystallographic analysis in order to elucidate its molecular conformation and to assign the configurations of the new chiral centres generated in the Diels–Alder cycloaddition (Adams, Jones, Aversa, Bonaccorsi & Giannetto, 1993): the known configuration of the isobornyl group was used as an internal standard. The isobornylsulfinyl moiety present in (I) is closely related to a family of isobornyl derivatives which have found wide use in asymmetric synthesis as chiral auxiliaries (Oppolzer, 1984). Although previous papers deal with X-ray structures of molecules showing (1S)-isobornyl-10-sulfinyl or -sulfonyl frames (De Lucchi, Marchioro, Valle & Modena, 1985; De Lucchi, Lucchini, Marchioro, Valle & Modena, 1986; Arai, Hayashi, Koizumi, Shiro & Kuriyama, 1988; Arai, Matsui, Koizumi & Shiro, 1991; Arai *et al.*, 1991), to the best of our knowledge the articles refer to tables of crystal data available as supplementary material, without emphasizing particular aspects of the structural geometry.

The results of the X-ray structure analysis of (I) are given in Tables 1 and 2. This analysis shows (Fig. 1) that the cyclohexene ring has a planar four-atom fragment [C(2), C(1), C(6), C(5) about the double bond, r.m.s. deviation 0.003 Å, displacements of C(3) and C(4) of −0.492 (10) and +0.233 (9) Å, respectively]. The methoxy atom O(2) is displaced from this plane by −1.253 (6) Å, that is, in a direction opposite to that of the adjacent C(4) atom; the methoxycarbonyl group is equatorial. The two four-atom planes of the tricyclic isobornyl residue [C(10), C(11), C(12), C(13) and C(10), C(13), C(14), C(15)] are each approximately planar (r.m.s. deviations 0.007 and 0.005 Å, respectively) and mutually inclined at 108.0 (8)°; they are inclined to the C(10), C(13), C(16) plane at 123.3 (7) and 128.7 (8)°, respectively. Atom C(15) carries a substituent hydroxyl group which forms an intramolecular hydrogen bond to the sulfinyl O atom [O(1)···O(5) 2.708 (12) Å]. There is no intermolecular hydrogen bonding.

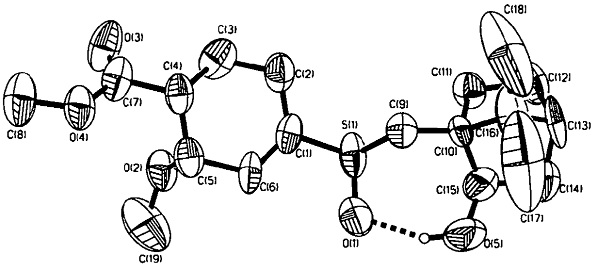


Fig. 1. Displacement ellipsoid plot (50% probability level) of (I) showing the atom-numbering scheme and intramolecular hydrogen bonding. Most of the H atoms have been omitted for clarity.

Experimental

The enantiopure adduct was synthesized in 67% yield *via* the asymmetric Diels–Alder reaction of homochiral (R_S,E)-1-methoxy-3-[(1S)-isobornyl-10-sulfinyl]buta-1,3-diene with methyl acrylate in the presence of $LiClO_4$ as a Lewis acid catalyst (Adams, Jones, Aversa, Bonaccorsi & Giannetto, 1993). The compound was crystallized from ethyl acetate–petroleum ether (b.p. 313–333 K).

Crystal data

$C_{19}H_{30}O_5S$
$M_r = 370.51$
Orthorhombic
$P2_12_12_1$
$a = 6.755\ (5)$ Å
$b = 7.068\ (7)$ Å
$c = 40.62\ (5)$ Å
$V = 1939\ (3)$ Å^3
$Z = 4$
$D_x = 1.269$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 18 reflections
$\theta = 2\text{–}7°$
$\mu = 0.183$ mm^{-1}
$T = 288$ K
Block
0.60 × 0.40 × 0.20 mm
Colourless

Data collection

Nicolet $R3$ diffractometer
ω scans
Absorption correction: none
3655 measured reflections
2241 independent reflections
1567 observed reflections $[F > 3\sigma(F)]$
$R_{\text{int}} = 0.0357$

$\theta_{\text{max}} = 20°$
$h = 0 \rightarrow 6$
$k = -6 \rightarrow 6$
$l = -39 \rightarrow 39$
1 standard reflection monitored every 200 reflections
frequency: 300 min
intensity decay: none

Refinement

Refinement on F
$R = 0.0766$
$wR = 0.0773$
$S = 1.710$
1567 reflections
226 parameters
H atoms placed in calculated positions using a riding model

Unit weights applied
$(\Delta/\sigma)_{\text{max}} = 0.013$
$\Delta\rho_{\text{max}} = 0.55$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.51$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S(1)	0.5183 (5)	0.8788 (3)	0.3572 (1)	0.078 (1)
O(1)	0.7218 (13)	0.8751 (12)	0.3419 (2)	0.132 (4)
O(2)	0.3270 (11)	0.4195 (9)	0.2796 (1)	0.077 (3)
O(3)	−0.1132 (11)	0.2478 (10)	0.3008 (2)	0.101 (3)
O(4)	0.1451 (10)	0.0464 (10)	0.3015 (1)	0.075 (3)
O(5)	0.9436 (10)	1.0385 (13)	0.3896 (3)	0.158 (5)
C(1)	0.4017 (15)	0.6575 (13)	0.3492 (2)	0.062 (4)
C(2)	0.2019 (14)	0.6315 (14)	0.3632 (2)	0.077 (4)
C(3)	0.0713 (14)	0.5092 (14)	0.3405 (3)	0.084 (4)
C(4)	0.1839 (13)	0.3320 (12)	0.3305 (2)	0.061 (4)
C(5)	0.3760 (14)	0.3782 (14)	0.3123 (2)	0.067 (4)
C(6)	0.4848 (17)	0.5453 (12)	0.3265 (2)	0.068 (4)
C(7)	0.0498 (16)	0.2092 (14)	0.3083 (2)	0.072 (4)
C(8)	0.0416 (18)	−0.0763 (14)	0.2800 (2)	0.099 (5)
C(9)	0.5584 (14)	0.8529 (12)	0.4009 (2)	0.060 (3)
C(10)	0.6152 (12)	1.0359 (11)	0.4169 (2)	0.047 (3)
C(11)	0.4506 (14)	1.1807 (12)	0.4180 (2)	0.072 (4)
C(12)	0.5125 (18)	1.3165 (13)	0.4459 (2)	0.088 (5)
C(13)	0.7112 (19)	1.2341 (14)	0.4570 (2)	0.086 (5)
C(14)	0.8566 (19)	1.2799 (17)	0.4280 (3)	0.112 (6)
C(15)	0.7853 (14)	1.1466 (15)	0.4020 (3)	0.089 (4)
C(16)	0.674 (2)	1.0232 (15)	0.4543 (2)	0.100 (5)
C(17)	0.867 (3)	0.9131 (18)	0.4595 (3)	0.236 (11)
C(18)	0.514 (3)	0.9474 (18)	0.4753 (3)	0.254 (14)
C(19)	0.476 (3)	0.387 (2)	0.2565 (2)	0.148 (7)

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

S(1)—O(1)	1.510 (9)	S(1)—C(1)	1.781 (10)
S(1)—C(9)	1.802 (8)	O(2)—C(5)	1.399 (10)
O(2)—C(19)	1.395 (16)	O(3)—C(7)	1.175 (13)
O(4)—C(7)	1.347 (13)	O(4)—C(8)	1.416 (12)
O(5)—H(O5)	0.96	O(5)—C(15)	1.407 (13)
C(1)—C(2)	1.476 (14)	C(1)—C(6)	1.341 (13)
C(2)—C(3)	1.542 (14)	C(3)—C(4)	1.520 (13)
C(4)—C(5)	1.529 (13)	C(4)—C(7)	1.545 (13)
C(5)—C(6)	1.507 (13)	C(9)—C(10)	1.498 (11)
C(10)—C(11)	1.512 (12)	C(10)—C(15)	1.516 (13)
C(10)—C(16)	1.575 (13)	C(11)—C(12)	1.544 (13)
C(12)—C(13)	1.531 (17)	C(13)—C(14)	1.567 (16)
C(13)—C(16)	1.516 (15)	C(14)—C(15)	1.498 (16)
C(16)—C(17)	1.54 (2)	C(16)—C(18)	1.48 (2)
O(1)···O(5)	2.708 (12)	O(1)···H(O5)	1.81
O(1)—S(1)—C(1)	108.2 (5)	O(1)—S(1)—C(9)	105.5 (4)
C(1)—S(1)—C(9)	99.0 (4)	C(5)—O(2)—C(19)	115.7 (8)
C(7)—O(4)—C(8)	114.4 (8)	S(1)—C(1)—C(2)	116.3 (7)
S(1)—C(1)—C(6)	117.4 (8)	C(2)—C(1)—C(6)	125.0 (9)
C(1)—C(2)—C(3)	111.3 (8)	C(2)—C(3)—C(4)	109.6 (8)
C(3)—C(4)—C(5)	112.2 (7)	C(3)—C(4)—C(7)	108.9 (8)
C(5)—C(4)—C(7)	109.6 (7)	O(2)—C(5)—C(4)	107.7 (7)
O(2)—C(5)—C(6)	108.4 (7)	C(4)—C(5)—C(6)	113.3 (7)
C(1)—C(6)—C(5)	121.6 (10)	O(3)—C(7)—O(4)	126.4 (9)
O(3)—C(7)—C(4)	124.8 (9)	O(4)—C(7)—C(4)	108.6 (8)
S(1)—C(9)—C(10)	112.2 (6)	C(9)—C(10)—C(11)	114.2 (7)
C(9)—C(10)—C(15)	117.8 (7)	C(11)—C(10)—C(15)	102.7 (7)
C(9)—C(10)—C(16)	115.7 (7)	C(11)—C(10)—C(16)	101.1 (7)
C(15)—C(10)—C(16)	103.1 (8)	C(10)—C(11)—C(12)	104.2 (8)
C(11)—C(12)—C(13)	102.5 (8)	C(12)—C(13)—C(14)	104.5 (8)
C(12)—C(13)—C(16)	101.9 (9)	C(14)—C(13)—C(16)	104.7 (9)
C(13)—C(14)—C(15)	101.5 (9)	O(5)—C(15)—C(10)	116.0 (9)
O(5)—C(15)—C(14)	110.4 (9)	C(10)—C(15)—C(14)	106.6 (9)
C(10)—C(16)—C(13)	93.2 (7)	C(10)—C(16)—C(17)	112.0 (9)
C(13)—C(16)—C(17)	110.2 (11)	C(10)—C(16)—C(18)	113.3 (11)
C(13)—C(16)—C(18)	116.0 (10)	C(17)—C(16)—C(18)	111.1 (11)

The structure was solved by direct methods and refined by blocked-cascade least-squares methods. The reported structure of the correct enantiomeric form had a marginally lower R value (by 0.0003). Displacement parameters for all non-H atoms were refined anisotropically. H atoms were placed in calculated positions. The quality of the refinement was limited by the intrinsic quality of the data and by the high thermal motion of the isobornyl moiety.

Data collection: Nicolet $R3$ software. Cell refinement: Nicolet $R3$ software. Data reduction: *SHELXTL* (Sheldrick, 1985). Structure solution: *SHELXTL*. Structure refinement: *SHELXTL*. Molecular graphics: *CSC CHEM-3D*, version 3.0 for Apple Macintosh. Preparation of material for publication: *SHELXTL*; Macintosh MS-Word.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: NA1130). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Anilinium Hydrogen Monofluorophosphate, $C_6H_8N^+.HPO_3F^-$

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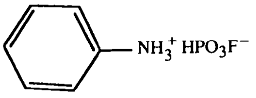
Abstract

The structure of the title compound shows a layer arrangement parallel to the *bc* plane. Two hydrogen monofluorophosphate anions are hydrogen-bonded and constitute $(H_2P_2O_6F_2)^{2-}$ anions, which are interconnected through strong N—H···O hydrogen bonds involving H atoms belonging to the $C_6H_5NH_3^+$ anilinium cations.

Comment

The monofluorophosphates of inorganic cations have been reported in several papers (Berndt, 1974; Durand, Cot & Galigné, 1974, 1978; Galigné, Durand & Cot, 1974; Durand, Granier, Cot & Galigné, 1975; Payen, Durand, Cot & Galigné, 1979; Durand, Larbot, Cot, Duprat & Dabosi, 1983; Durand, Cot, Berraho & Rafiq, 1987; Berraho, R'Kha, Vegas & Rafiq, 1992). Until now, no monofluorophosphate containing $C_6H_5NH_3^+$ organic cations has been reported.

In the present work, we describe the preparation and crystal structure of the first example of such a compound: the anilinium hydrogen monofluorophosphate, (I).



(I)

Figs. 1 and 2 give two different projections of this atomic arrangement, one along the *a* axis, the other along the *c* axis. The structure can be described as being built of atomic layers that are parallel to the *bc* plane and interact by van der Waals forces. In each layer, two HPO_3F^- anions are bonded together by means of two O(1)—H(1)···O(3) hydrogen bonds to form $(H_2P_2O_6F_2)^{2-}$ ring anions located around the inversion centres at the (0,0,0) and (1/2,1/2,0) positions.

The $C_6H_5NH_3^+$ cations are found alternately below and above the *bc* plane and are bonded to three $(H_2P_2O_6F_2)^{2-}$ dimers by means of the terminal H atoms of the NH_3 groups [N—H(7)···O(3), N—H(8)···O(2) and N—H(9)···O(2)]. The N—H distance varies according to the hydrogen-bond strength. The longest distance, N—H(9) (1.12 Å), induces a very strong hydrogen bond [N—H(9)···O(2) 1.62 Å].

The geometry of the HPO_3F^- tetrahedron is similar to that of its homologous hydrogen phosphite HPO_3H^- (Sghyar, Durand, Cot & Rafiq, 1990, 1991). It is characterized by two short and comparable P—O(2) and P—O(3) distances (1.48 Å) where the O atom is not directly linked to the H atom, and one longer P—O(1) distance (1.55 Å) to the O atom of the hydroxyl group. The lengthening of the latter distance can be correlated with the strength of the O(1)—H(1)···O(3) hydrogen bond (1.64 Å).

The averages of the P—O distances (1.508 Å) and of the F—P—O angles (105.6°) are comparable to those observed in the PO_3F^{2-} and $PO_2F_2^-$ groups. On the other hand, the average O—P—O angle (112.9°) is significantly smaller than all the values observed in the P^V oxyfluoride ions (Durand, Falius, Galigné & Cot, 1978).

The F atom of the HPO_3F^- ion, found in the *bc* plane, is only bonded to the P atom. This arrangement has been observed previously in the case of the monofluorophosphates of alkali and divalent transition metals (Durand, Granier, Cot & Galigné, 1975; Payen, Durand, Cot & Galigné, 1979; Durand, Larbot, Cot, Duprat & Dabosi, 1983; Durand, Cot, Berraho & Rafiq, 1987).