$C_{18}H_{15}NO_2$

C15A	0.9589 (5)	0.3335 (5)	−0.2228 (4)	0.046 (5)
C16A	1.0342 (6)	0.2846 (6)	−0.2580 (4)	0.051 (5)
C17A	1.1288 (6)	0.3802 (6)	−0.3057 (4)	0.053 (5)
O18A	0.8688 (4)	0.6830 (4)	−0.1833 (3)	0.071 (4)
C19A	0.8227 (7)	0.7627 (7)	−0.1584 (6)	0.090 (8)
O20A	0.6516 (4)	0.1940 (4)	−0.0680 (3)	0.065 (4)
C21A	0.5447 (7)	0.1404 (8)	−0.0142 (6)	0.080 (7)
C1B	1.1408 (5)	0.7573 (5)	0.0314 (4)	0.048 (5)
C2B	1.0217 (6)	0.6721 (6)	0.0118 (5)	0.063 (5)
C3B	0.9648 (6)	0.5486 (5)	0.0437 (5)	0.052 (5)
C4B	1.0305 (5)	0.5118 (5)	0.0945 (4)	0.043 (4)
C5B	1.2242 (5)	0.5650 (5)	0.1731 (4)	0.046 (5)
N6B	1.4302 (5)	0.6457 (4)	0.2470 (4)	0.054 (4)
C7B	1.6466 (6)	0.7979 (6)	0.3003 (5)	0.057 (5)
C8B	1.7390 (6)	0.9234 (7)	0.2955 (5)	0.065 (6)
C9B	1.7260 (6)	1.0098 (6)	0.2483 (5)	0.064 (6)
C10B	1.6211 (5)	0.9730 (5)	0.1997 (4)	0.050 (5)
C11B	1.3360 (5)	0.8145 (5)	0.1122 (4)	0.045 (4)
C12B	1.2125 (5)	0.7260 (5)	0.0882 (4)	0.044 (5)
C13B	1.1558 (5)	0.6000 (5)	0.1195 (4)	0.043 (4)
C14B	1.3461 (6)	0.6551 (5)	0.1954 (4)	0.052 (5)
C15B	1.4001 (5)	0.7801 (5)	0.1647 (4)	0.042 (4)
C16B	1.5246 (5)	0.8468 (5)	0.2026 (4)	0.045 (4)
C17B	1.5388 (5)	0.7609 (5)	0.2525 (4)	0.045 (4)
O18B	0.9837 (4)	0.3928 (4)	0.1263 (3)	0.051 (3)
C19B	0.8640 (6)	0.2988 (6)	0.0969 (5)	0.062 (6)
O20B	1.2049 (4)	0.8773 (4)	0.0020 (3)	0.060 (3)
C21B	1.1417 (7)	0.9157 (7)	−0.0542 (6)	0.077 (7)

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

C1A—O20A	1.379 (8)	C1B—O20B	1.362 (7)
C4A—O18A	1.368 (8)	C4B—O18B	1.374 (7)
N6A—C14A	1.408 (9)	N6B—C14B	1.371 (10)
N6A—C17A	1.387 (11)	N6B—C17B	1.380 (6)
O18A—C19A	1.412 (12)	O18B—C19B	1.421 (7)
O20A—C21A	1.425 (9)	O20B—C21B	1.421 (11)
C12A—C1A—O20A	114.0 (6)	C12B—C1B—O20B	113.9 (5)
C2A—C1A—O20A	124.7 (6)	C2B—C1B—O20B	125.4 (6)
C3A—C4A—O18A	126.3 (7)	C3B—C4B—O18B	124.6 (6)
C13A—C4A—O18A	113.7 (6)	C13B—C4B—O18B	115.1 (6)
C14A—N6A—C17A	109.0 (5)	C14B—N6B—C17B	109.6 (5)
C5A—C14A—N6A	128.7 (5)	C5B—C14B—N6B	130.0 (5)
N6A—C14A—C15A	107.6 (5)	N6B—C14B—C15B	109.5 (6)
N6A—C17A—C16A	109.1 (6)	N6B—C17B—C16B	108.4 (5)
N6A—C17A—C7A	128.5 (6)	N6B—C17B—C7B	130.1 (6)
C4A—O18A—C19A	116.3 (6)	C4B—O18B—C19B	117.1 (5)
C1A—O20A—C21A	117.9 (6)	C1B—O20B—C21B	117.6 (5)

Data collection, cell refinement and data reduction: *SDP* (Frenz, 1978). Structure solution: *SHELXS*86 (Sheldrick, 1985). Structure refinement: *SHELX*76 (Sheldrick, 1976). Calculation of geometrial parameters: *PARST* (Nardelli, 1983). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1976). All H atoms were located from a difference Fourier map and were refined isotropically.

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Absolute Configuration of N,N-{(1S)-1-[(1-Methoxy-1-methyl)ethyl]tetramethylene}-(1R,6R,7R)-9,9-diethoxy-1-methyl-2-oxo-bicyclo[4.3.0]nonane-7-sulfonamide

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Abstract

The title compound, $C_{22}H_{39}NO_6S$, is obtained by an intramolecular cyclization of the adduct resulting

from the Michael addition of a chiral homoenolate to a cyclic α-enone. Its absolute stereochemistry is unambiguously established and this will provide an insight into the mechanism of the addition step of the reaction.

Comment

The development of synthetic methods that allow the efficient construction of cyclopentanoids has been an objective of organic chemists throughout the last decade. A few years ago, we described a two-step [3 + 2] annulation yielding highly functionalized fused cyclopentanes (De Lombaert, Nemery, Roekens, Carretero, Kimmel & Ghosez, 1986). We are now developing an asymmetric version of this sequence. The first step is the enantioselective Michael addition of the chiral homoenolate equivalent (1) to a cyclic α-enone. Intramolecular cyclization of the resulting adduct (2) produces the title compound (3) in an optically pure crystalline form.

(1)

(2)

(3)
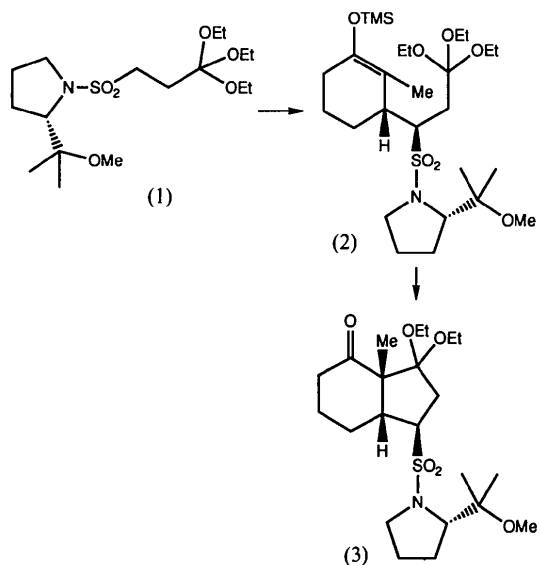
The absolute stereochemistry of (3) is established unambiguously; each of the three asymmetric atoms C1, C6 and C7 has the *R* configuration. The *S* configuration at C22 is retained from that of the chiral homoenolate (1). This result should assist in the determination of a mechanistic model for the Michael addition step (Huart & Ghosez, 1994).

The cyclohexanone adopts a distorted half-chair conformation with the twofold axis through the midpoints of the C1—C2 and C4—C5 bonds ($\Delta C_2 = 9°$) (Duax, Weeks & Rohrer, 1976). The five-membered pentane ring has an envelope conformation with C8 at the flap ($\Delta C_s = 4.5°$) and the five-membered pyrrolidine ring forms a half-chair with the twofold axis through C22 ($\Delta C_2 = 5.4°$).

The N atom is pyramidal, as the sum of the valence angles is 349.4° and it is 0.29 Å out of the plane through atoms S18, C22 and C25. The N—SO$_2$ bond length of 1.637 (2) Å is within the expected range (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987).
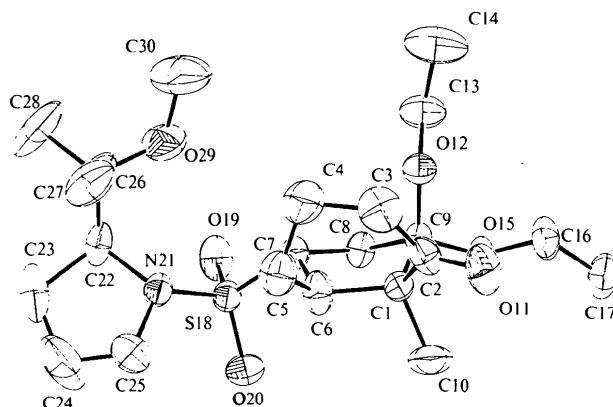

Fig. 1. PLATON (Spek, 1990) drawing of the title molecule. The displacement ellipsoids are drawn at the 50% probability level.
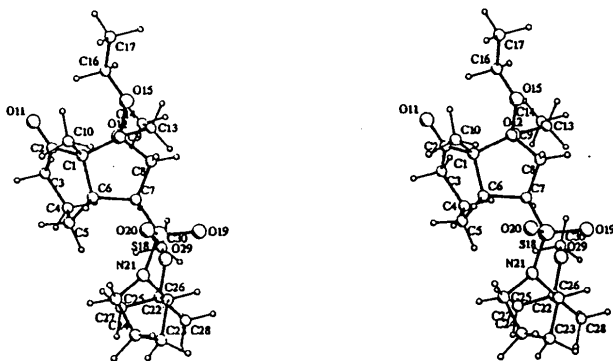

Fig. 2. A stereoscopic drawing of the title molecule with atom labelling (PLUTO; Motherwell & Clegg, 1978).

Experimental

Crystal data

C$_{22}$H$_{39}$NO$_6$S	Cu $K\alpha$ radiation
M_r = 445.62	λ = 1.54178 Å
Orthorhombic	Cell parameters from 19
$P2_12_12_1$	reflections
a = 7.636 (1) Å	θ = 10–30°
b = 8.911 (1) Å	μ = 1.49 mm^{-1}
c = 34.895 (3) Å	T = 291 K
V = 2374.5 (4) Å^3	Parallelepiped
Z = 4	0.36 × 0.28 × 0.24 mm
D_x = 1.25 Mg m^{-3}	Colourless
	Crystal source: from
	pentane/ethyl ether

Data collection

Huber four-circle diffractom-eter	$R_{int} = 0.038$
	$\theta_{max} = 67.5°$
θ–2θ scans	$h = -9 \to 9$
Absorption correction:	$k = 0 \to 10$
none	$l = 0 \to 41$
4899 measured reflections	1 standard reflection
4269 independent reflections	monitored every 50
4059 observed reflections	reflections
$[I > 2.5\sigma(I)]$	intensity decay: 11%

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.01$
$R = 0.058$	$\Delta\rho_{max} = 0.71$ e Å^{-3}
$wR = 0.067$	$\Delta\rho_{min} = -0.77$ e Å^{-3}
$S = 0.59$	Atomic scattering factors
4059 reflections	from *International Tables*
272 parameters	*for X-ray Crystallography*
$w = 1/[\sigma^2(F) + 0.02456F^2]$	(1974, Vol. IV)

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}
C1	0.4187 (3)	0.6249 (3)	0.8572 (1)	0.036 (1)
C2	0.5687 (4)	0.6985 (4)	0.8348 (1)	0.045 (1)
C3	0.5912 (6)	0.8668 (5)	0.8333 (1)	0.069 (1)
C4	0.4558 (8)	0.9533 (4)	0.8597 (1)	0.079 (2)
C5	0.4373 (5)	0.8705 (5)	0.8970 (1)	0.061 (1)
C6	0.3441 (4)	0.7232 (4)	0.8903 (1)	0.050 (1)
C7	0.1431 (3)	0.7342 (3)	0.8831 (1)	0.034 (1)
C8	0.0985 (3)	0.6015 (3)	0.8576 (1)	0.036 (1)
C9	0.2559 (3)	0.5927 (3)	0.8309 (1)	0.032 (1)
C10	0.4896 (5)	0.4789 (5)	0.8746 (1)	0.063 (1)
O11	0.6745 (3)	0.6227 (4)	0.8184 (1)	0.066 (1)
O12	0.2594 (2)	0.7073 (2)	0.8031 (1)	0.038 (1)
C13	0.1068 (4)	0.7249 (4)	0.7792 (1)	0.057 (1)
C14	0.1451 (7)	0.8301 (7)	0.7478 (1)	0.094 (2)
O15	0.2491 (3)	0.4483 (2)	0.8143 (1)	0.040 (1)
C16	0.3659 (5)	0.4162 (4)	0.7834 (1)	0.053 (1)
C17	0.3647 (6)	0.2505 (4)	0.7772 (1)	0.066 (1)
S18	0.0195 (1)	0.7259 (1)	0.9263 (1)	0.035 (1)
O19	-0.1609 (3)	0.7235 (3)	0.9156 (1)	0.051 (1)
O20	0.0861 (4)	0.6028 (3)	0.9488 (1)	0.061 (1)
N21	0.0634 (3)	0.8814 (3)	0.9493 (1)	0.040 (1)
C22	-0.0729 (4)	0.9978 (4)	0.9536 (1)	0.050 (1)
C23	-0.0610 (7)	1.0375 (6)	0.9971 (1)	0.081 (2)
C24	0.0672 (10)	0.9321 (9)	1.0140 (1)	0.112 (3)
C25	0.1742 (6)	0.8761 (5)	0.9846 (1)	0.067 (1)
C26	-0.0462 (5)	1.1308 (4)	0.9262 (1)	0.065 (1)
C27	0.1281 (6)	1.2104 (4)	0.9322 (2)	0.080 (2)
C28	-0.1926 (9)	1.2429 (6)	0.9306 (2)	0.117 (2)
O29	-0.0531 (5)	1.0611 (3)	0.8886 (1)	0.073 (1)
C30	-0.0384 (10)	1.1504 (7)	0.8556 (2)	0.108 (2)

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

C2—C1	1.535 (4)	C6—C1	1.557 (4)
C9—C1	1.571 (3)	C10—C1	1.535 (4)
C3—C2	1.510 (5)	O11—C2	1.198 (4)
C4—C3	1.586 (7)	C5—C4	1.504 (6)
C6—C5	1.512 (5)	C7—C6	1.558 (4)
C8—C7	1.519 (3)	S18—C7	1.780 (2)
C9—C8	1.523 (3)	O12—C9	1.410 (3)
O15—C9	1.413 (3)	C13—O12	1.440 (3)
C14—C13	1.473 (5)	C16—O15	1.427 (3)
C17—C16	1.493 (5)	O19—S18	1.427 (2)
O20—S18	1.441 (2)	N21—S18	1.637 (2)
C22—N21	1.477 (4)	C25—N21	1.495 (4)
C23—C22	1.561 (5)	C26—C22	1.534 (5)
C24—C23	1.479 (9)	C25—C24	1.403 (7)
C27—C26	1.523 (6)	C28—C26	1.507 (5)
O29—C26	1.454 (5)	C30—O29	1.406 (5)
C6—C1—C2	114.3 (2)	C10—C1—C2	107.6 (3)
C9—C1—C6	104.2 (2)	C10—C1—C9	110.8 (3)
C10—C1—C6	108.1 (2)	O11—C2—C1	120.3 (3)
C3—C2—C1	121.8 (3)	C4—C3—C2	112.8 (3)
O11—C2—C3	117.8 (3)	C6—C5—C4	109.6 (3)
C5—C4—C3	109.1 (4)	C7—C6—C1	106.1 (2)
C5—C6—C1	115.5 (3)	C8—C7—C6	105.4 (2)
C7—C6—C5	115.7 (3)	S18—C7—C8	110.1 (2)
S18—C7—C6	112.6 (2)	C8—C9—C1	105.0 (2)
C9—C8—C7	102.8 (2)	O12—C9—C8	113.6 (2)
O12—C9—C1	104.8 (2)	O15—C9—C8	105.6 (2)
O15—C9—C1	115.8 (2)	C13—O12—C9	117.5 (2)
O15—C9—O12	112.1 (2)	C16—O15—C9	118.0 (2)
C14—C13—O12	109.8 (3)	O19—S18—C7	107.0 (1)
C17—C16—O15	107.7 (3)	O20—S18—O19	118.2 (2)
O20—S18—C7	107.7 (1)	N21—S18—O19	109.8 (1)
N21—S18—C7	105.8 (1)	C22—N21—S18	120.0 (2)
N21—S18—O20	107.8 (1)	C25—N21—C22	109.8 (2)
C25—N21—S18	119.6 (2)	C26—C22—N21	112.7 (3)
C23—C22—N21	102.4 (3)	C24—C23—C22	106.4 (3)
C26—C22—C23	115.0 (3)	C24—C25—N21	105.1 (4)
C25—C24—C23	108.7 (4)	C28—C26—C22	110.5 (4)
C27—C26—C22	113.1 (3)	O29—C26—C22	103.1 (2)
C28—C26—C27	109.0 (4)	O29—C26—C28	110.3 (4)
O29—C26—C27	110.7 (4)	C30—O29—C26	119.8 (3)
C9—C1—C2	111.8 (2)		

At the end of the refinement, the absolute configuration was determined by sorting the reflections according to $w^{1/2}\{[F_c(hkl)] - [F_c(-h-k-l)]\}$. Among the 100 most sensitive reflections, the signs of 98 observed and calculated differences were consistent with the absolute configuration described. Resolution was performed using *SHELXS86* (Sheldrick, 1990) and anisotropic least-squares refinement using F was performed with *SHELX76* (Sheldrick, 1976). H atoms were placed in calculated positions (C—H = 1.08 Å, H—C—H = 109.5°) with a common U_{iso} refined to 0.103 Å^2.

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