

Acta Cryst. (1995). **C51**, 2377–2381

1,2;3,4-Bis{8',11'-dioxo[4.3.3]propella-(3',4')}benzene: a Bis(propellene) from Prehnitene

KATARZYNA STADNICKA AND WOJCIECH ŻEŚLAWSKI

*Faculty of Chemistry, Jagiellonian University,
ul. Ingardena 3, 30-060 Kraków, Poland*

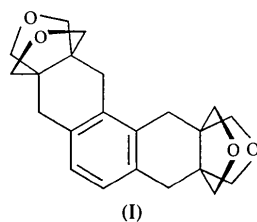
(Received 2 February 1995; accepted 6 June 1995)

Abstract

The asymmetric unit of the title compound, 1,3,3a,4,7,7a,8,10,10a,11,12,12a-dodecahydro-3a,12a:7a,10a-bis(methoxymethano)phenanthro[2,3-c:6,7-c']difuran, $C_{22}H_{26}O_4$, contains two U-shaped molecules related by a pseudo-twofold screw axis. Each of the molecules displays its own pseudo-mirror plane. All the tetrahydrofuran rings have envelope forms and the cyclohexane rings adopt boat conformations. There are only weakly dispersive intermolecular interactions.

Comment

Cyclization of a 1.1,2.2-tetrasubstituted ring leads, in general, to the formation of a 1.2-dispiran or the isomeric propellane (Ginsburg, 1987). Both, the complexity of the transannular effects and strain in the ring systems makes *a priori* prediction of the final product difficult (Jamrozik, 1985). The present work was undertaken to verify the molecular structure of the title bis(propellane), (I), the synthesis of which has been reported recently (Jamrozik & Żeślowski, 1994).



According to the observed systematic absences, two possible space groups were considered: $Pcam$ (No. 57, D_{2h}^{11}) and $Pca2_1$ (No. 29, C_{2h}^2). Although the unit cell contains eight molecules, no reasonable solution was found in the centrosymmetric space group, mainly because $Pcam$ implies the presence of a mirror plane perpendicular to [001]. Eventually, the structure was successfully solved in space group $Pca2_1$ with two symmetry-independent molecules in the unit cell.

Each of the molecules *A* and *B* displays a pseudo-mirror plane intersecting the benzene ring bonds C1—C6 and C3—C4 of molecule *A* and C31—C36 and

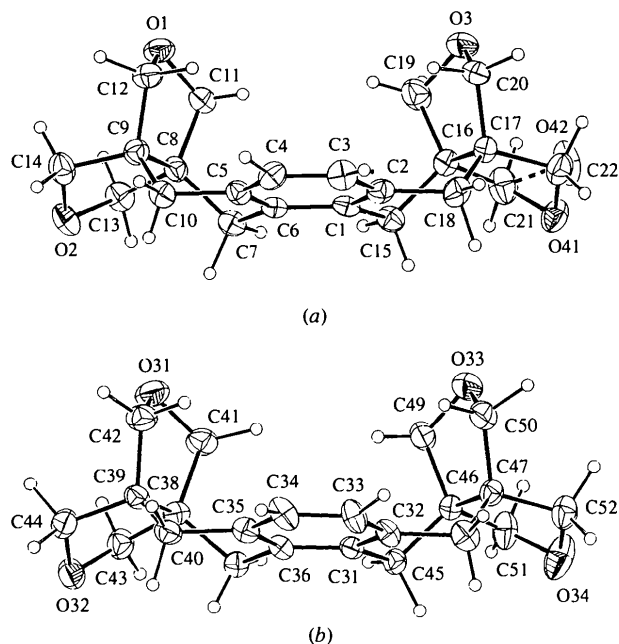


Fig. 1. Views of (a) molecule *A* and (b) molecule *B*, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level (ORTEP II; Johnson, 1976). One O atom of molecule *A* is disordered between two positions, O41 and O42, with site-occupancy factors of 0.76 (3) and 0.24 (3), respectively.

C33—C34 of molecule *B* (cf. Fig. 1). The mirror planes, described by the equations $2.6421x + 9.7739y - 11.7861z = -5.9918$ and $-2.7567x + 9.5604y + 12.6420z = 4.8772$, for *A* and *B*, respectively, make angles of about 60.5° and are oblique with respect to the crystallographic axes. The two symmetry-independent molecules have similar dimensions except for minor differences in bond lengths and valence angles (Table 2). The benzene rings of both molecules are planar with maximum deviations from planarity of 0.017 (6) and 0.018 (7) Å for *A* and *B*, respectively, and with an average C—C distance of 1.392 (18) for *A* and 1.389 (5) Å for *B*. The bond lengths of the cyclohexene rings [average 1.505 (49) for *A* and 1.511 (55) Å for *B*] show a gradual increase in length from the value characteristic for aromatic rings towards that expected for the conjoining bond.* Mean values of the remaining C—C bonds of the five-membered rings are 1.531 (13) and 1.528 (10) Å for *A* and *B*, respectively, whereas average C—O distances are 1.425 (28) and 1.423 (11) Å. The mean value of the endocyclic angles in the aromatic ring is $120.0(15)^\circ$ and deviations from the mean value exceed 3σ only for C2—C3—C4 in *A* and C33—C34—C35 in *B*. The endocyclic angles fall into two groups characteristic of the cyclohexene ring: those at

* The term conjoining is widely used for the $(C_{sp^3})_3-C-C-(C_{sp^3})_3$ bond type, common to three propellane rings (Tobe, 1992). The length of such a bond is significantly longer (1.588 Å) than that of a typical single C—C bond, which is estimated as 1.530 Å (Allen *et al.*, 1987).

the bond common to benzene [average 116.2(1) in *A* and 116.9(15)° in *B*], and the remaining [average 112.3(4) in *A* and 112.5(11)° in *B*]. The average values of the endocyclic angles of the five-membered rings are 104.7(15) for *A* and 104.4(17)° for *B*.

Ring-puckering parameters and asymmetry parameters are given in Table 3. The tetrahydrofuran rings have envelope conformations (*C_s*) and the cyclohexene rings adopt boat conformations (*C_s*), unlike in cyclohexene in the vapour phase where a half-chair (*C₂*) form was determined by electron diffraction as the most stable conformation for the isolated molecule (Chiang & Bauer, 1969). In the crystal structure of 8,11-dithia[4.3.3]propella-3-ene (Herbstein *et al.*, 1986) both the five-membered and the cyclohexene rings were found to have *C₂* symmetry (twist and screw-boat conformations, respectively), while in its PdCl₂ complex *C_s* symmetry was observed for all the rings (*i.e.* envelope and boat conformations) due to specific interactions with Pd²⁺. In the title compound, the boat form of the cyclohexene moiety may be stabilized by the influence of the two tetrahydrofuran rings at the conjoining bond. All the rings are of the same symmetry, in agreement with the non-mixing rule observed for this class of propellanes (Herbstein *et al.*, 1986). Al-

though rapid fluctuation of the six-membered ring conformations was observed in solution by ¹H NMR spectroscopy (Jamrozik & Żesławski, 1994), only one of the possible conformations is present in the crystal structure and both symmetry-independent molecules are U-shaped.

The shortest intramolecular contacts were found between the benzyl H atoms, which are coplanar with the aromatic ring [2.02(6) in *A*, 2.12(8) Å in *B*]. Distances between H atoms at C11 and C19 of *A* and C41 and C49 of *B* are equal to the sum of the van der Waals radii within the limit of error. The packing projected along [010] is depicted in Fig. 2. Intermolecular interactions are purely weak dispersive. There are no H...H intermolecular distances less than 2.19(10) Å.

Finally, we note that closer inspection of the atomic coordinates of the two independent molecules using the program *PARST* (Nardelli, 1983) revealed that although the molecules *A* and *B* could be considered as related by a pseudo-twofold screw axis: 2(0, 0.495, 0) 0.125, y, 0.281, and one can find a pseudo centre of symmetry at (0.376, 0.245, 0.282) which brings the molecule *A* at (*x* + 1/2, -*y*, *z*) close to *B* (Fig. 2), the probability for such a symmetry element appearing is low, as verified by the χ^2 test. For the twofold screw axis the sums $\sum_i (\Delta_i/\sigma_i)^2$ for the *x*, *y* and *z* coordinates are 45.66, 30.62 and 5.16, respectively, and for the centre of symmetry, 45.68, 30.54 and 5.16, respectively. The theoretical value is $\chi^2 = 38.90$ at 95% for 26 degrees of freedom (only non-H atoms were taken into account). It can be seen in Fig. 2 that the pseudo-symmetry elements together with the true glide plane *a*, perpendicular to [010], form a pseudo space group *P2₁/a* with the same lattice parameters *a* and *b* as in *Pca2₁*, but with a β angle of 103°. The new unit cell also contains two symmetry-independent molecules, but in this description glide plane *c* (which is evident in the observed systematic absences) is lost. The existence of a pseudo centre of symmetry makes any simple physical test for non-centrosymmetry (*e.g.* of pyroelectricity) non-relevant in distinguishing between space groups *Pca2₁* and *Pcam* of this particular structure.

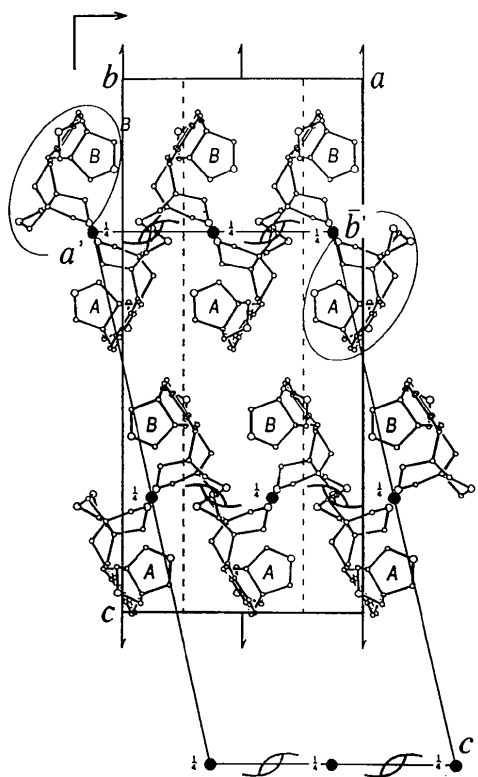


Fig. 2. Packing diagram of the structure projected along [010]. Only non-H atoms are shown; O atoms are shown as open circles bigger than those for C atoms. Single molecules *A* and *B* are marked at positions (*x* + 1, *y*, *z*) and (*x* - 1/2, *y*, -*z*), respectively. The symmetry elements of space group *Pca2₁* are introduced together with those of the pseudo space group *P2₁/a* [2(0, 1/2, 0) 1/8, *y*, 1/4 + 0.031, and $\bar{1}$ (3/8, 1/4, 1/4 + 0.031)].

Experimental

(I) was obtained from prehnitene in four steps, with the final step being the cyclization by reaction of the suitable octol with KHSO₄ at 423 K. Crystals suitable for X-ray diffraction were obtained from an acetic acid solution by slow evaporation at room temperature. *D_m* was measured by flotation in aqueous KI solution.

Crystal data

C₂₂H₂₆O₄
M_r = 354.43
 Orthorhombic
Pca2₁
a = 12.380(2) Å
b = 11.194(2) Å
c = 26.892(5) Å

Mo *K*α radiation
 λ = 0.7107 Å
 Cell parameters from 35 reflections
 θ = 2.8–12.2°
 μ = 0.086 mm⁻¹
T = 293(2) K

$V = 3726.7$ (11) Å³
 $Z = 8$
 $D_x = 1.263$ Mg m⁻³
 $D_m = 1.26$ (2) Mg m⁻³

Data collection

Kuma KM-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction:
 none
 3003 measured reflections
 2271 independent reflections
 1755 observed reflections
 $[I > 2\sigma(I)]$
 $R_{\text{int}} = 0.0203$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.0317$
 $wR(F^2) = 0.0709$
 $S = 1.146$
 2270 reflections
 679 parameters
 H atoms refined isotropically; riding model for H521 and H522 only
 $w = 1/[\sigma^2(F_o^2) + (0.0552P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = -0.037$
 $\Delta\rho_{\text{max}} = 0.175$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.119$ e Å⁻³

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

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

Molecule A	x	y	z	U_{eq}
O1	-0.2010 (3)	-0.3847 (4)	0.3971 (2)	0.0572 (10)
O2	0.0201 (4)	-0.5549 (3)	0.4637	0.0590 (11)
O3	-0.1045 (3)	0.0836 (4)	0.3014 (2)	0.0667 (13)
O41†	0.1900 (7)	0.1827 (6)	0.3004 (4)	0.060 (3)
O42‡	0.122 (4)	0.1971 (16)	0.2768 (10)	0.079 (13)
C1	0.0689 (4)	-0.0613 (5)	0.4130 (2)	0.0387 (13)
C2	0.0332 (4)	0.0463 (6)	0.4348 (3)	0.044 (2)
C3	-0.0274 (5)	0.0404 (6)	0.4773 (3)	0.0483 (15)
C4	-0.0520 (5)	-0.0650 (6)	0.5012 (3)	0.048 (2)
C5	-0.0151 (4)	-0.1702 (5)	0.4814 (2)	0.0396 (13)
C6	0.0450 (4)	-0.1706 (5)	0.4373 (3)	0.0382 (13)
C7	0.0789 (4)	-0.2913 (5)	0.4180 (3)	0.0444 (14)
C8	-0.0156 (4)	-0.3802 (5)	0.4168 (3)	0.0405 (13)
C9	-0.0828 (4)	-0.3785 (5)	0.4660 (2)	0.0437 (14)
C10	-0.0380 (5)	-0.2902 (5)	0.5042 (3)	0.0439 (14)
C11	-0.0989 (5)	-0.3519 (6)	0.3772 (3)	0.0493 (15)
C12	-0.1966 (4)	-0.3448 (6)	0.4479 (3)	0.053 (2)
C13	0.0240 (6)	-0.5097 (6)	0.4140 (4)	0.051 (2)
C14	-0.0778 (7)	-0.5091 (6)	0.4840 (4)	0.056 (2)
C15	0.1287 (5)	-0.0497 (6)	0.3650 (3)	0.0447 (14)
C16	0.0698 (5)	0.0335 (5)	0.3285 (3)	0.0427 (14)
C17	0.0361 (4)	0.1539 (4)	0.3526 (3)	0.0443 (14)
C18	0.0629 (5)	0.1585 (5)	0.4080 (3)	0.051 (2)
C19	-0.0342 (7)	-0.0192 (7)	0.3102 (4)	0.067 (3)
C20	-0.0862 (5)	0.1581 (6)	0.3425 (3)	0.055 (2)
C21	0.1451 (7)	0.0723 (6)	0.2858 (3)	0.067 (2)
C22	0.0990 (6)	0.2463 (6)	0.3218 (3)	0.058 (2)
Molecule B				
O31	0.4643 (3)	0.0989 (4)	0.1684 (2)	0.0698 (12)
O32	0.2320 (3)	-0.0488 (4)	0.0989 (2)	0.0600 (12)

Plate
 $0.3 \times 0.3 \times 0.1$ mm
 Colourless

$\theta_{\text{max}} = 25.0^\circ$
 $h = 0 \rightarrow 14$
 $k = 0 \rightarrow 13$
 $l = -32 \rightarrow 0$
 3 standard reflections
 monitored every 50
 reflections
 intensity variation: <1.5%

Extinction correction:
 SHELXL93 (Sheldrick,
 1993)

Extinction coefficient:
 0.0043 (7)

Atomic scattering factors
 from *International Tables
 for Crystallography* (1992,
 Vol. C, Tables 4.2.6.8 and
 6.1.1.4)

Absolute configuration:
 Flack (1983) parameter
 = 0.46 (1.80)

O33	0.3589 (4)	0.5830 (4)	0.2670 (2)	0.0695 (13)
O34	0.0678 (4)	0.6834 (4)	0.2646 (3)	0.091 (2)
C31	0.1963 (4)	0.4382 (5)	0.1521 (3)	0.0385 (15)
C32	0.2302 (5)	0.5460 (5)	0.1321 (3)	0.0440 (14)
C33	0.2943 (5)	0.5486 (6)	0.0897 (3)	0.056 (2)
C34	0.3243 (6)	0.4414 (6)	0.0682 (3)	0.054 (2)
C35	0.2888 (4)	0.3325 (5)	0.0865 (2)	0.0439 (14)
C36	0.2237 (4)	0.3314 (5)	0.1291 (3)	0.0382 (13)
C37	0.1884 (5)	0.2092 (5)	0.1469 (3)	0.0433 (14)
C38	0.2808 (4)	0.1174 (5)	0.1471 (3)	0.0408 (13)
C39	0.3499 (4)	0.1180 (5)	0.0984 (2)	0.0430 (14)
C40	0.3150 (5)	0.2143 (5)	0.0616 (3)	0.0480 (14)
C41	0.3645 (5)	0.1445 (7)	0.1879 (3)	0.059 (2)
C42	0.4644 (5)	0.1386 (7)	0.1181 (3)	0.057 (2)
C43	0.2368 (7)	-0.0103 (5)	0.1489 (4)	0.055 (2)
C44	0.3312 (6)	-0.0081 (6)	0.0780 (5)	0.059 (2)
C45	0.1312 (5)	0.4478 (5)	0.2002 (3)	0.0422 (14)
C46	0.1854 (5)	0.5322 (5)	0.2371 (3)	0.0406 (14)
C47	0.2217 (4)	0.6544 (4)	0.2138 (3)	0.0415 (13)
C48	0.1961 (6)	0.6607 (6)	0.1580 (3)	0.053 (2)
C49	0.2919 (6)	0.4837 (6)	0.2574 (4)	0.054 (2)
C50	0.3415 (5)	0.6604 (6)	0.2250 (3)	0.059 (2)
C51	0.1093 (7)	0.5698 (6)	0.2779 (3)	0.063 (2)
C52	0.1563 (5)	0.7455 (5)	0.2439 (3)	0.059 (2)

† Occupancy = 0.76 (3).

‡ Occupancy = 0.24 (3).

Table 2. Selected geometric parameters (Å, °)

Molecule A		Molecule B	
O1—C11	1.421 (7)	O31—C42	1.424 (8)
O1—C12	1.437 (7)	O31—C41	1.435 (7)
O2—C14	1.424 (9)	O32—C43	1.411 (10)
O2—C13	1.430 (9)	O32—C44	1.425 (9)
O3—C20	1.404 (8)	O33—C49	1.411 (8)
O3—C19	1.461 (9)	O33—C50	1.441 (8)
O41—C21	1.411 (10)	O34—C52	1.412 (7)
O41—C22	1.451 (10)	O34—C51	1.416 (8)
O42—C22	1.36 (2)		
O42—C21	1.45 (2)		
C1—C2	1.409 (9)	C31—C32	1.386 (8)
C1—C6	1.418 (8)	C31—C36	1.389 (7)
C1—C15	1.494 (8)	C31—C45	1.528 (8)
C2—C3	1.370 (9)	C32—C33	1.391 (9)
C2—C18	1.494 (9)	C32—C48	1.520 (8)
C3—C4	1.378 (9)	C33—C34	1.383 (9)
C4—C5	1.371 (8)	C34—C35	1.387 (8)
C5—C6	1.401 (7)	C35—C36	1.400 (7)
C5—C10	1.504 (8)	C35—C40	1.519 (8)
C6—C7	1.507 (8)	C36—C37	1.514 (7)
C7—C8	1.536 (8)	C37—C38	1.537 (7)
C8—C11	1.517 (8)	C38—C43	1.530 (8)
C8—C13	1.532 (8)	C38—C41	1.540 (8)
C8—C9	1.563 (7)	C38—C39	1.563 (8)
C9—C10	1.530 (8)	C39—C40	1.527 (8)
C9—C12	1.538 (8)	C39—C42	1.530 (8)
C9—C14	1.541 (9)	C39—C44	1.533 (9)
C15—C16	1.537 (9)	C45—C46	1.525 (8)
C16—C19	1.501 (10)	C46—C51	1.507 (9)
C16—C21	1.542 (9)	C46—C49	1.527 (9)
C16—C17	1.553 (8)	C46—C47	1.570 (8)
C17—C18	1.527 (9)	C47—C50	1.514 (8)
C17—C20	1.538 (8)	C47—C52	1.533 (7)
C17—C22	1.538 (8)	C47—C48	1.535 (8)
C11—O1—C12	104.2 (4)	C42—O31—C41	103.7 (5)
C14—O2—C13	105.1 (5)	C43—O32—C44	104.0 (6)
C20—O3—C19	104.2 (5)	C49—O33—C50	104.0 (6)
C21—O41—C22	103.5 (6)	C52—O34—C51	105.1 (5)
C22—O42—C21	106.4 (17)	C32—C31—C45	115.2 (5)
C2—C1—C15	116.1 (5)	C36—C31—C45	124.6 (5)
C6—C1—C15	125.1 (5)	C31—C32—C48	118.3 (5)
C3—C2—C18	125.2 (6)	C33—C32—C48	121.1 (6)
C1—C2—C18	116.2 (6)	C34—C35—C40	122.8 (5)
C4—C5—C10	123.0 (5)	C36—C35—C40	118.4 (5)
C6—C5—C10	116.3 (5)	C31—C36—C37	124.5 (5)
C5—C6—C7	116.2 (5)	C35—C36—C37	115.7 (5)
C1—C6—C7	123.9 (5)	C43—C38—C37	111.1 (5)

C11—C8—C13	112.4 (5)	C43—C38—C41	113.7 (6)	Molecule A, five-membered rings	
C11—C8—C7	113.5 (5)	C37—C38—C41	111.8 (5)	O1—C11—C8—C9—C12	τ q_2 (Å) φ_2 (°)
C13—C8—C7	111.7 (5)	C43—C38—C39	103.0 (5)	O2—C13—C8—C9—C14	0.389 (5) 176.9 (9)
C10—C9—C12	112.7 (5)	C37—C38—C39	113.7 (5)	O3—C20—C17—C16—C19	0.384 (6) 176.0 (9)
C10—C9—C14	112.8 (6)	C41—C38—C39	103.1 (4)	O41—C22—C17—C16—C21	0.388 (8) 176.5 (11)
C12—C9—C14	111.7 (6)	C40—C39—C42	112.3 (5)	O42—C21—C16—C17—C22	0.393 (9) 177.4 (10)
O1—C11—C8	106.6 (5)	C40—C39—C44	112.0 (6)		0.32 (3) 176.8 (12)
O1—C12—C9	105.0 (4)	C42—C39—C44	113.8 (6)	Molecule B, six-membered rings	
O2—C13—C8	106.1 (6)	O31—C41—C38	104.4 (5)	C35—C40	q_2 (Å) q_3 (Å) φ_2 (°) Q_T (Å) θ_2 (°)
O2—C14—C9	104.8 (6)	O31—C42—C39	106.3 (5)	C31—C32—C48—C45	0.618 (6) 0.010 (6) 122.4 (6) 0.618 (6) 89.1 (6)
C1—C15—C16	111.7 (5)	O32—C43—C38	105.7 (6)		0.673 (6) 0.005 (6) 118.9 (5) 0.673 (6) 89.6 (5)
C19—C16—C15	112.3 (5)	O32—C44—C39	106.4 (6)	Molecule B, five-membered rings	
C19—C16—C21	112.6 (7)	C46—C45—C31	111.2 (5)	O31—C41—C38—C39—C42	q_2 (Å) φ_2 (°)
C15—C16—C21	111.1 (5)	C51—C46—C45	111.8 (5)	O32—C43—C38—C39—C44	0.409 (6) -175.7 (8)
C21—C16—C17	103.2 (5)	C51—C46—C49	112.2 (7)	O33—C50—C47—C46—C49	0.392 (7) -176.1 (10)
C18—C17—C20	112.6 (5)	C45—C46—C49	113.1 (5)	O34—C52—C47—C46—C51	0.379 (7) 177.7 (11)
C18—C17—C22	113.2 (5)	C51—C46—C47	103.0 (5)		0.354 (7) 176.6 (12)
C20—C17—C22	112.5 (5)	C50—C47—C52	112.5 (5)	Asymmetry parameters (Nardelli, 1983):	
O3—C19—C16	104.7 (5)	C50—C47—C48	113.2 (5)	Molecule A	
O3—C20—C17	106.2 (5)	C52—C47—C48	112.1 (5)	C5—C10	ΔC_s
O41—C21—C16	106.1 (6)	O33—C49—C46	107.0 (5)	C1—C2—C18—C15	C7 = 0.006 (3) ΔC_s
O42—C21—C16	106.3 (11)	O33—C50—C47	106.0 (5)		C6—C5 = 0.003 (2)
O42—C22—C17	108.4 (11)	O34—C51—C46	107.1 (6)		C2—C1 = 0.021 (2)
O41—C22—C17	106.1 (6)	O34—C52—C47	106.9 (5)	O1—C11—C8—C9—C12	O1 = 0.016 (3)
C15—C1—C2—C3	176.3 (5)	C45—C31—C32—C48	-2.5 (7)	O2—C13—C8—C9—C14	O2 = 0.021 (3)
C10—C5—C6—C1	179.2 (5)	C45—C31—C36—C37	3.0 (8)	O3—C20—C17—C16—C19	O3 = 0.019 (4)
C15—C1—C6—C7	1.1 (8)	C40—C35—C36—C37	1.8 (7)	O41—C22—C17—C16—C21	O41 = 0.015 (4)
C5—C6—C7—C8	48.5 (7)	C35—C36—C37—C38	44.7 (7)	O42—C21—C16—C17—C22	O42 = 0.016 (9)
C6—C7—C8—C9	-46.3 (7)	C36—C37—C38—C39	-46.1 (7)		
C11—C8—C9—C10	-123.4 (5)	C43—C38—C39—C40	123.2 (6)	Molecule B	
C13—C8—C9—C10	119.5 (5)	C37—C38—C39—C40	2.9 (6)	C35—C40	ΔC_s
C7—C8—C9—C10	-0.8 (6)	C41—C38—C39—C40	-118.3 (5)	C31—C32—C48—C45	C37 = 0.020 (3) ΔC_s
C11—C8—C9—C12	-1.9 (6)	C37—C38—C39—C42	124.1 (5)		C48 = 0.013 (3) ΔC_s
C7—C8—C9—C12	120.8 (5)	C41—C38—C39—C42	2.9 (6)	O31—C41—C38—C39—C42	O31 = 0.024 (3)
C13—C8—C9—C14	-2.6 (6)	C43—C38—C39—C44	2.6 (6)	O32—C43—C38—C39—C44	O32 = 0.021 (4)
C7—C8—C9—C14	-122.8 (5)	C37—C38—C39—C44	-117.7 (6)	O33—C50—C47—C46—C49	O33 = 0.012 (4)
C6—C5—C10—C9	-49.3 (7)	C36—C35—C40—C39	-46.3 (7)	O34—C52—C47—C46—C51	O34 = 0.017 (4)
C8—C9—C10—C5	47.6 (6)	C38—C39—C40—C35	41.5 (7)		
C12—O1—C11—C8	41.3 (6)	C42—O31—C41—C38	44.3 (6)	Data collection: Kuma KM-4 diffractometer software. Cell refinement: Kuma KM-4 diffractometer software. Data reduction: Kuma KM-4 diffractometer software. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL93.	
C9—C8—C11—O1	-23.4 (6)	C39—C38—C41—O31	-28.2 (6)	Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1266). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.	
C11—O1—C12—C9	-42.1 (6)	C41—O31—C42—C39	-42.9 (7)	References	
C8—C9—C12—O1	26.2 (6)	C44—C39—C42—O31	-86.1 (7)	Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). <i>J. Chem. Soc. Perkin Trans. 2</i> , pp. S1–S19.	
C14—O2—C13—C8	40.6 (7)	C44—O32—C43—C38	43.1 (7)	Chiang, J. F. & Bauer, S. H. (1969). <i>J. Am. Chem. Soc.</i> 91 , 1898–1901.	
C9—C8—C13—O2	-22.2 (6)	C39—C38—C43—O32	-27.4 (6)	Cremer, D. & Pople, J. A. (1975). <i>J. Am. Chem. Soc.</i> 97 , 1354–1358.	
C13—O2—C14—C9	-41.9 (7)	C43—O32—C44—C39	-41.4 (8)	Flack, H. D. (1983). <i>Acta Cryst.</i> A39 , 876–881.	
C8—C9—C14—O2	26.5 (7)	C38—C39—C44—O32	22.8 (8)	Ginsburg, D. (1987). <i>Top. Curr. Chem.</i> 137 , 1–17.	
C2—C1—C15—C16	-47.5 (6)	C32—C31—C45—C46	-47.1 (7)	Herbstein, F. H., Ashkenazi, P., Kaftory, M., Kapon, M., Reisner, G. M. & Ginsburg, D. (1986). <i>Acta Cryst.</i> B42 , 575–601.	
C1—C15—C16—C17	49.0 (6)	C31—C45—C46—C47	47.6 (6)	Jamrozik, J. (1985). <i>Monatsh. Chem.</i> 116 , 229–235.	
C19—C16—C17—C18	118.5 (6)	C45—C46—C47—C50	-123.5 (5)	Jamrozik, J. & Żesławski, W. (1994). <i>Chem. Ber.</i> 127 , 2471–2474.	
C15—C16—C17—C18	-3.7 (6)	C49—C46—C47—C50	-1.3 (7)	Johnson, C. K. (1976). <i>ORTEPII</i> . Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.	
C21—C16—C17—C18	-123.7 (6)	C51—C46—C47—C52	-2.2 (6)	Nardelli, M. (1983). <i>Comput. Chem.</i> 7 , 95–98.	
C19—C16—C17—C20	-2.7 (7)	C45—C46—C47—C52	119.1 (5)	Sheldrick, G. M. (1990). <i>Acta Cryst.</i> A46 , 467–473.	
C15—C16—C17—C20	-124.8 (5)	C51—C46—C47—C48	-122.5 (6)		
C15—C16—C17—C22	118.3 (5)	C45—C46—C47—C48	-1.1 (6)		
C21—C16—C17—C22	-1.7 (6)	C49—C46—C47—C48	121.1 (6)		
C1—C2—C18—C17	49.5 (7)	C31—C32—C48—C47	50.6 (7)		
C16—C17—C18—C2	-44.4 (6)	C46—C47—C48—C32	-46.0 (6)		
C20—O3—C19—C16	-42.3 (8)	C50—O33—C49—C46	-41.5 (8)		
C17—C16—C19—O3	26.4 (8)	C47—C46—C49—O33	25.8 (8)		
C19—O3—C20—C17	40.6 (7)	C49—O33—C50—C47	40.1 (6)		
C16—C17—C20—O3	-23.1 (6)	C46—C47—C50—O33	-22.9 (6)		
C22—O41—C21—C16	-42.4 (10)	C52—O34—C51—C46	-39.6 (7)		
C22—O42—C21—C16	35 (3)	C47—C46—C51—O34	24.9 (7)		
C17—C16—C21—O41	27.0 (9)	C51—O34—C52—C47	37.7 (7)		
C17—C16—C21—O42	-19 (2)	C46—C47—C52—O34	-21.0 (6)		
C21—O42—C22—C17	-36 (3)				
C21—O41—C22—C17	41.2 (10)				
C16—C17—C22—O42	23 (2)				
C16—C17—C22—O41	-23.2 (8)				

Table 3. Puckering and asymmetry parameters

Puckering parameters (Cremer & Pople, 1975):

Molecule A, six-membered rings

	q_2 (Å)	q_3 (Å)	φ_2 (°)	Q_T (Å)	θ_2 (°)
C5—C10	0.664 (6)	-0.004 (6)	119.8 (5)	0.664 (6)	90.4 (5)
C1—C2—C18—C15	0.656 (6)	-0.10 (6)	117.0 (5)	0.656 (6)	90.9 (5)

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
 Tobe, Y. (1992). *Propellanes in Carboxylic Cage Compounds: Chemistry and Applications*, edited by E. Osawa & O. Youemitsu, pp. 125–153, and references therein. Weinheim: VCH.

Acta Cryst. (1995). **C51**, 2381–2383

4-Sulfonyl-1,6-dioxaspiro[4.5]decanes

INÉS ALONSO, ISABEL LÓPEZ-SOLERA AND
 PAUL R. RAITHY

*Department of Chemistry, University of Cambridge,
 Lensfield Road, Cambridge CB2 1EW, England*

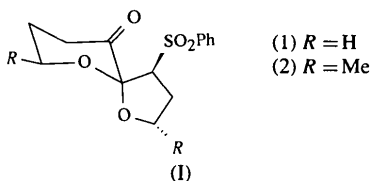
(Received 9 March 1995; accepted 10 May 1995)

Abstract

The relative configurations of 4-(phenylsulfonyl)-1,6-dioxaspiro[4.5]decan-10-one ($C_{14}H_{16}O_5S$) and its 2,7-dimethyl derivative, 2,7-dimethyl-4-(phenylsulfonyl)-1,6-dioxaspiro[4.5]decan-10-one ($C_{16}H_{20}O_5S$), are confirmed.

Comment

Since the spiroketal unit is found in a wide variety of natural products (Mishima *et al.*, 1975; Kato & Scheuer, 1974), considerable attention has been focused on the development of methods for the synthesis of this moiety (Perron & Albizati, 1989). Most of these methods are based on the thermodynamically controlled acid-catalysed spiroketalization of dihydroxyketones. However, recently, some one-step convergent syntheses from two fragments have been described (Gosselin, Bonfand, Hayes & Maignan, 1994; Ann & Cohen, 1994; Boons, Downham, Kim, Ley & Woods, 1994; Carretero, Díaz & Rojo, 1994).



The structures, with the atomic numbering schemes, of the title compounds (1) and (2) are shown in Figs. 1 and 2. The non-aromatic six-membered ring has a distorted-chair conformation which is slightly flattened around the carbonyl group. This effect is greater for compound (1) [torsion angle $C8-C9-C10-C5$ $35.5(6)$ in (1) and $46.3(3)^\circ$ in (2)]. The five-membered ring conformation is slightly different in these two compounds. In (1), the ring has an envelope conformation

with $C4$ (-0.53 \AA) out of the plane defined by $O1$, $C2$, $C3$ and $C5$, whereas in (2) the ring has a half-envelope conformation with $C3$ (-0.35 \AA) and $C4$ (0.28 \AA) out of the plane defined by the other three atoms. The shortening of the $C5-O1$ and $C5-O6$ bond distances and the geometrical disposition of these groups (both in axial positions) are similar in the two compounds, probably to maximize the thermodynamic anomeric effect (Deslongchamps, Rowan, Pothier, Sauvé & Saunders, 1981). The sulfone group is in a pseudo-equatorial position in both compounds. In (2), the methyl groups $C21$ and $C71$ are in pseudo-axial and equatorial positions, respectively. The most significant difference is the conformation around the $C4-S1$ bond [torsion angle $C5-C4-S1-C11$ $-42.4(4)$ in (1) and $70.5(2)^\circ$ in (2)].

Each molecule is involved in one hydrogen bond. In (1), $C14-H14 \cdots O12^i = 2.490(6)$, $C14 \cdots O12^i = 3.408(6) \text{ \AA}$ and $C14-H14 \cdots O12^i = 169.3(1)^\circ$ [symmetry code: (i) $x, y + 1, z$]; in (2), $C4-H4 \cdots O10^{ii} = 2.550(3)$, $C4 \cdots O10^{ii} = 3.401(3) \text{ \AA}$ and $C4-H4 \cdots O10^{ii} = 145.1(1)^\circ$ [symmetry code: (ii) $1 - x, 1 - y, 2 - z$].

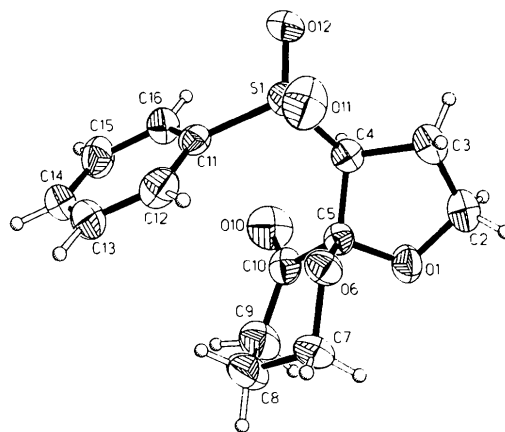


Fig. 1. Molecular structure of (1) showing 50% probability displacement ellipsoids.

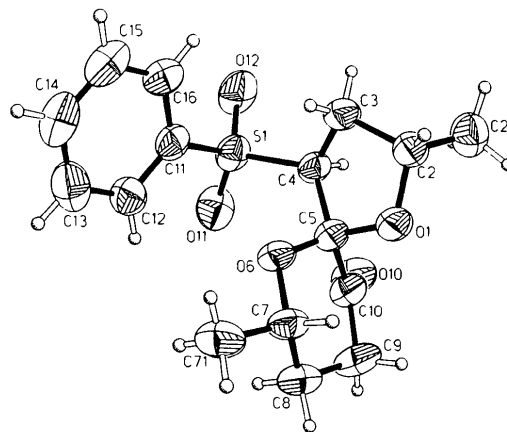


Fig. 2. Molecular structure of (2) showing 50% probability displacement ellipsoids.