organic papers

A chiral C_2 axially symmetric naphthalene derivative of a bicyclooctane diketal

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The crystal structure of the title compound, $(-)$-(4R,5R,-4''R,5''R)-dispiro[4,5-dimethyl-1,3-dioxalane-2,3'-[1',5'-(naph-thalene-1,8-diyl)bicyclo[3.3.0]octane]-7',2''-(4'',5''-dimethyl-1'',3''-dioxalane)], $C_{26}H_{30}O_4$, contains two independent molecules in the asymmetric unit separated by normal van der Waals distances. The five-membered rings in the *trans*-2,3-dimethyl-1,4-dioxaspiro[4.4]nonane moieties exhibit envelope conformations and the acenaphthene moieties are essentially planar. The conformations of a dioxacyclopentane ring in the two molecules are different. The molecular dimensions in both molecules are as expected.

Comment

This project was designed to prepare chiral naphthalene systems with C_2 symmetry for subsequent use as a chiral catalytic transfer agent [$Cr(CO)_3$ from naphthalene to prochiral arene]. The reaction of acenaphthoquinone, (I), and 1,3-acetonedicarboxylate, (II), led to diketone (III), which upon reaction with two equivalents of $(-)$-(2R,3R)-butane-2,3-diol, (IV), gave the bis-ketal (V). To assess the potential regiochemistry of the two C_2 axial symmetric naphthalene rings toward $Cr(CO)_3$ complexation, an X-ray structure of (V) was determined and is presented in this paper.
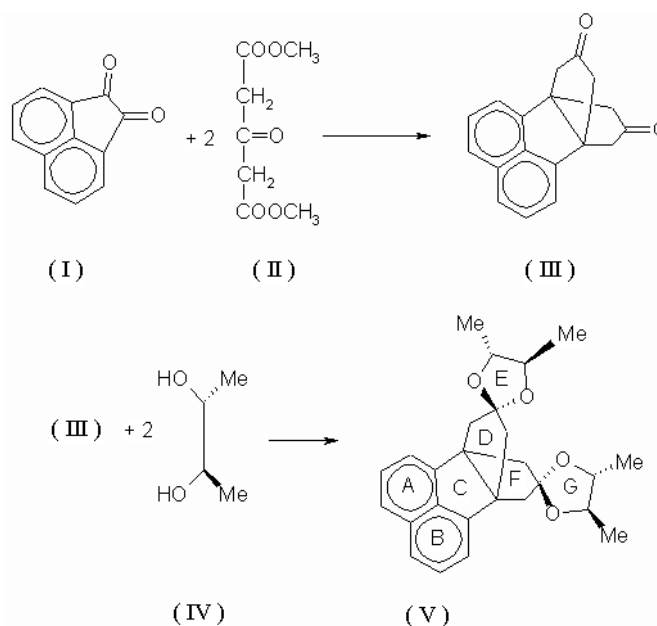
The asymmetric unit of (V) is composed of two independent molecules 1 and 2 wherein an acenaphthene moiety has been fused with two *trans*-2,3-dimethyl-1,4-dioxaspiro[4.4]nonane moieties (Figs. 1 and 2). The conformations of the dioxa-
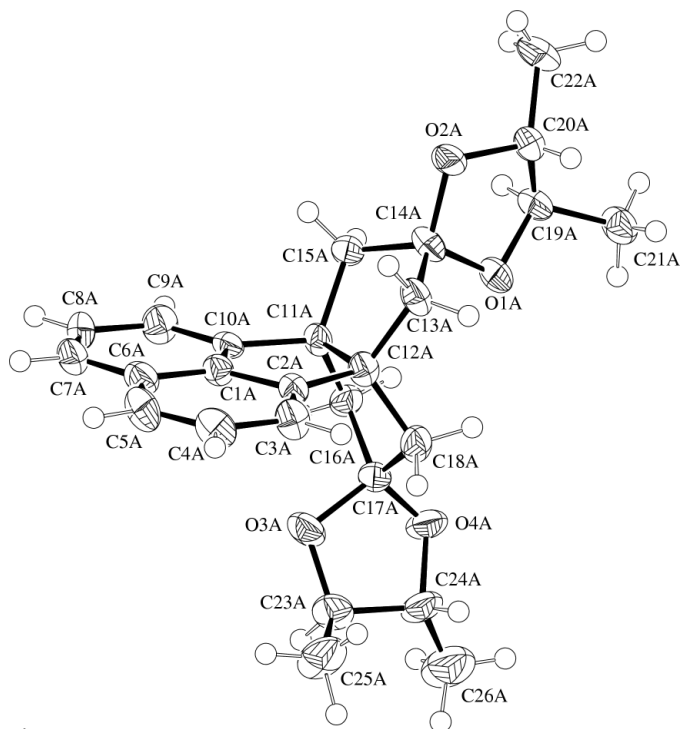
Figure 1
*ORTEP*II (Johnson, 1976) drawing of molecule 1 of (V). Displacement ellipsoids have been plotted at the 50% probability level.
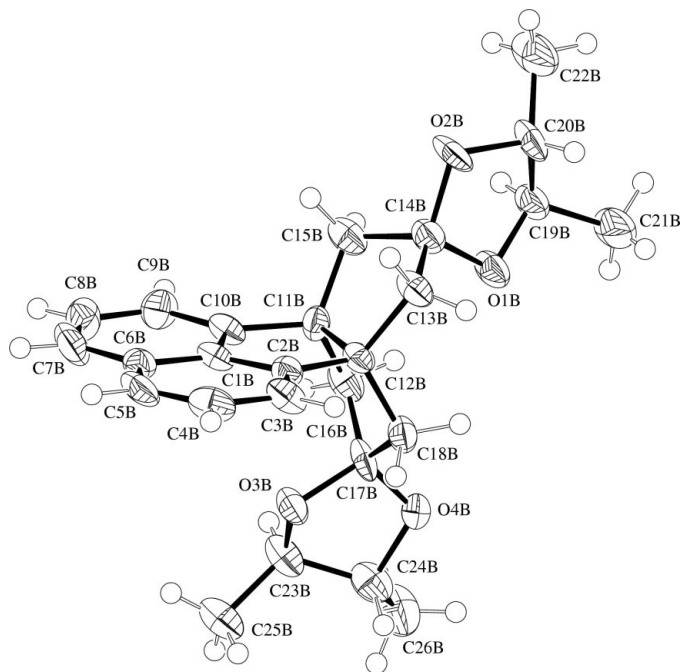

Figure 2
*ORTEP*II (Johnson, 1976) drawing of molecule 2 of (V). Displacement ellipsoids have been plotted at the 50% probability level.

cyclopentane ring (*G*) in the two molecules are different from each other. The molecular dimensions in both molecules are as expected with mean bond distances: C$sp3$—C$sp3$ 1.526 (17), C$sp3$—C$sp2$ 1.515 (12), O—C$sp3$ 1.434 (16) and C—C$_{aromatic}$ 1.393 (16) Å.
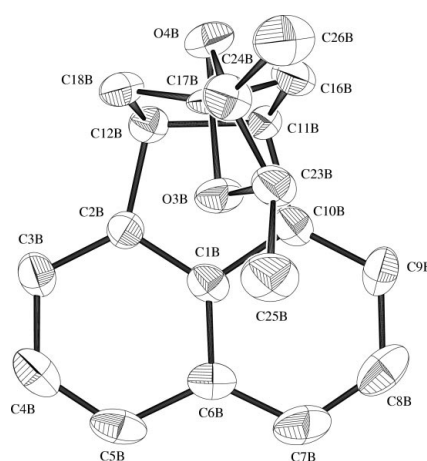

Figure 3
Facial projection of molecule 2 of (V); the second ketal and H atoms have been omitted for clarity.

In both molecules, the acenaphthene moieties (rings *A*, *B* and *C*) are essentially planar with the maximum deviation of any atom from the mean-planes being 0.051 (9) and 0.054 (9) Å for molecules 1 and 2, respectively. The five-membered rings *D*, *E*, *F* and *G* in molecule 1 exhibit C14*A*-, C19*A*-, C17*A*- and O4*A*-envelope conformations, respectively, with these atoms 0.544 (17), 0.597 (17), 0.564 (16) and 0.504 (16) Å, respectively, out of the least-squares planes of the remaining ring atoms. The corresponding rings in molecule 2 adopt C14*B*-, C19*B*-, C17*B*- and C23*B*-envelope conformations, with these atoms 0.566 (17), 0.557 (16), 0.568 (15) and 0.618 (16) Å, respectively, out of the least-squares planes of the remaining ring atoms. The molecules are separated by normal van der Waals distances. In Fig. 3, a direct facial projection of a molecule 2 of (V) is shown, where the second ketal ring and H atoms have been omitted for clarity. This view illustrates that there is a small steric differentiation of the two aromatic rings.

Experimental

The Weiss–Cook reaction (Yang-Lau *et al.*, 1976) between acenaphthoquinone, (I), and 1,3-acetonedicarboxylate, (II), led to diketone (III), which was purified by flash chromatography (SiO$_2$, 9:1 CH$_2$Cl$_2$/ethyl acetate) and recrystallized to give 62% yield, characterized by ^{1}H and ^{13}C NMR and CH analysis (Simion, 1996). Reaction of (III) with two equivalents of (−)-(2R,3R)-butane-2,3-diol, (IV) (toluene, reflux, PTSA cat. Dean–Stark trap), for 48 h gave the bis-ketal (V), which was purified by flash chromatography (SiO$_2$, 1:1 benzene/ethyl acetate) and recrystallized (pentane); 80% yield, m.p. 360 K, $[\alpha]_D^{23} = -1.3°$ (c = 0.097, CHCl$_3$).

Crystal data

C$_{26}$H$_{30}$O$_4$	$D_x = 1.222$ Mg m^{-3}
$M_r = 406.50$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 25
$a = 8.1172$ (11) Å	reflections
$b = 22.523$ (4) Å	$\theta = 10.0–15.0°$
$c = 12.5352$ (13) Å	$\mu = 0.08$ mm^{-1}
$\beta = 105.362$ (12)°	$T = 200$ (2) K
$V = 2209.9$ (5) Å^3	Prism, colourless
$Z = 4$	$0.50 \times 0.40 \times 0.32$ mm

Data collection

Rigaku AFC-6S diffractometer	$h = 0 \rightarrow 9$
$\omega/2\theta$ scans	$k = 0 \rightarrow 26$
4276 measured reflections	$l = -14 \rightarrow 14$
3990 independent reflections	3 standard reflections
2388 reflections with $I > 2\sigma(I)$	every 200 reflections
$R_{int} = 0.05$	intensity decay: <0.1%
$\theta_{max} = 25.0°$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0563P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.063$	$+ 10.0719P]$
$wR(F^2) = 0.239$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
3990 reflections	$\Delta\rho_{max} = 0.47$ e Å^{-3}
549 parameters	$\Delta\rho_{min} = -0.52$ e Å^{-3}
H-atom parameters constrained	Absolute structure: (Flack, 1983)
	Flack parameter = 0 (4)

The space group, $P2_1$, was determined from the systematic absences, packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure. Most of the H atoms were located from difference maps. All the H atoms were included at geometrically idealized positions with C—H = 0.95–1.00 Å, in a riding mode with isotropic displacement parameters 1.2 (non-methyl) and 1.5 (methyl) times the thermal displacement parameters of the atoms to which they were attached. An absolute configuration was not established in this analysis, since the absolute configuration of the starting material was already known. There is a pseudocentre of symmetry located at 0.724, 0.702, −0.011 relating some of the atoms of the two molecules in the asymmetric unit.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1994); program(s) used to solve structure: *SAPI*91 (Fan, 1991); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *TEXSAN*; software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997).

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