C1	0.0953 (2)	0.4610 (2)	0.2955 (4)	0.0493 (6)
C2	0.2009 (2)	0.4990 (2)	0.2218 (4)	0.0531 (6)
C3	0.2141 (2)	0.6101 (2)	0.1942 (4)	0.0548 (7)
C4	0.1227 (2)	0.6799 (2)	0.2399 (4)	0.0565 (7)
C5	0.0183 (2)	0.6428 (2)	0.3166 (5)	0.0622 (8)
C6	0.0054 (2)	0.5316 (2)	0.3461 (4)	0.0565 (7)
C7	0.1531 (2)	0.2788 (2)	0.3783 (4)	0.0555 (7)
C8	0.0117 (3)	0.1424 (3)	0.2588 (7)	0.0814 (11)
C9	0.1906 (4)	0.0890 (3)	0.4371 (7)	0.0845 (11)

Table 4. *Selected geometric parameters ($\mathring{A}$, °) for (2)*

O1—C7	1.374 (3)	N2—C4	1.465 (4)
O1—C1	1.391 (3)	C1—C6	1.377 (4)
O2—C7	1.211 (4)	C1—C2	1.382 (4)
O3—N2	1.223 (5)	C2—C3	1.378 (4)
O4—N2	1.227 (4)	C3—C4	1.374 (4)
N1—C7	1.327 (4)	C4—C5	1.375 (4)
N1—C9	1.454 (5)	C5—C6	1.381 (4)
N1—C8	1.457 (4)		
C7—O1—C1	119.9 (2)	C3—C2—C1	118.6 (2)
C7—N1—C9	118.6 (3)	C4—C3—C2	119.5 (2)
C7—N1—C8	124.2 (3)	C3—C4—C5	122.1 (2)
C9—N1—C8	117.2 (3)	C3—C4—N2	119.0 (3)
O3—N2—O4	123.7 (3)	C5—C4—N2	118.9 (3)
O3—N2—C4	118.4 (3)	C4—C5—C6	118.4 (3)
O4—N2—C4	118.0 (3)	C1—C6—C5	119.7 (3)
C6—C1—C2	121.6 (3)	O2—C7—N1	126.3 (3)
C6—C1—O1	115.9 (2)	O2—C7—O1	122.8 (2)
C2—C1—O1	122.4 (2)	N1—C7—O1	110.8 (2)

For both (1) and (2), H atoms were placed in calculated sites riding on the C atoms to which they were attached. Isotropic displacement parameters were fixed at 0.08 $\mathring{A}^2$.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ZORTEP* (Zsolnai, 1994); software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1035). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Baker, H. M., Blackwell, L. F., Brown, R. L., Buckley, P. D., Dobbs, A. J., Hardman, M. J., Hill, J. P., Kitson, K. E., Kitson, T. M. & Baker, E. N. (1994). *J. Mol. Biol.* **241**, 263–264.
Burr, M. & Koshland, D. E. (1964). *Proc. Natl Acad. Sci, USA,* **52**, 1017–1024.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Kagan, H. (1979). *Organic Stereochemistry*. London: Edward Arnold.
Kitson, T. M. (1989). *Biochem. J.* **257**, 579–584.
Kitson, T. M. & Freeman, G. H. (1993). *Bioorg. Chem.* **21**, 354–365.
Kitson, T. M. & Kitson, K. E. (1994). *Biochem. J.* **300**, 25–30.
Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for Crystal Structure Refinement*. University of Göttingen, Germany.
Zsolnai, L. (1994). *ZORTEP. Interactive Graphics Program*. University of Heidelberg, Germany.

A Pinacol Precursor to a Chiral Spiro Compound

William P. Schaefer,[a] Lawrence M. Henling,[a] Henry C. McBay[b]† and John Abulu[b]

[a]Beckman Institute, California Institute of Technology, Pasadena, California 91125, USA, and [b]Department of Chemistry, Clark-Atlanta University, Atlanta, Georgia 30314, USA

Abstract

The dimer of 1-indanolyl obtained from the UV photolysis of 1-indanone in 2-propanol is *trans*-α,α'-biindanyl-α,α'-diol, $(C_9H_9O)_2$. There are two almost identical molecules in the asymmetric unit linked by a hydrogen-bonding system that extends along the *a* axis. Bond distances and angles are as expected.

Comment

The diol dimer described here, (I), was prepared in the hope that intramolecular hydrogen bonding would lock it in the correct conformation for enantioselective rearrangement during pinacol rearrangement to produce a spiro compound with a chiral spiro atom. The molecule was the one expected, but all the hydrogen

(I)
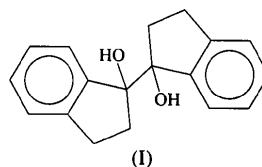
bonding is intermolecular, this despite IR studies on the compound in solution which indicated intramolecular hydrogen bonding (McBay & Abulū, 1994). In the crystal, the diol molecules form hydrogen-bonded pairs about centers of symmetry with O$\cdots$O distances 2.716 (3) and 2.725 (3) Å; the O$\cdots$H distances are 1.94 (3) and 1.99 (3) Å, with O—H$\cdots$O angles of 152 (3) and 148 (3)°. These pairs are each bonded to

† Deceased 23 June 1995.

two non-symmetry-related pairs by two other hydrogen bonds: O1b—HO1b···O2a and O1a—HO1a···O2b (1 + *x*, *y*, *z*) with O···O distances 2.784 (3) and 2.776 (3) Å, H···O distances 2.11 (3) and 2.04 (4) Å and O—H···O angles 162 (4) and 163 (4)°. This results in a chain of dimers, molecules *a*, *b*, *a*, *b*..., hydrogen bonded along the *a* axis with all hydrophilic O atoms involved (Fig. 2). The exteriors of the chains have the hydrophobic groups showing; there are no interchain hydrogen bonds.
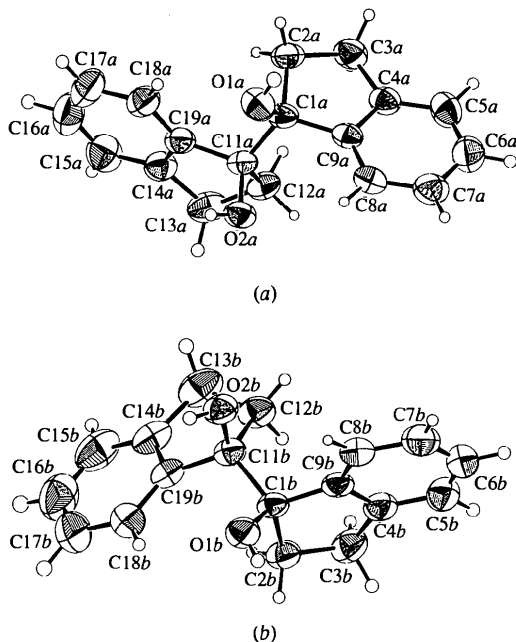
Bond distances and angles are normal when compared with values given by Allen *et al.* (1987) or, for distances involving the C atoms linked to O atoms, with the average of five identical fragments found in the Cambridge Crystallographic Database (Allen, Kennard & Taylor, 1983). The relevant distances are compared in Table 3, where the values for the present compound are the averages of the four chemically equivalent distances in the two molecules (except there are only two distances for C1—C11).

(a)

(b)

Fig. 1. *ORTEP*II (Johnson, 1976) drawings of the two independent molecules showing the atom-numbering system. Non-H atoms are shown as 50% probability ellipsoids.
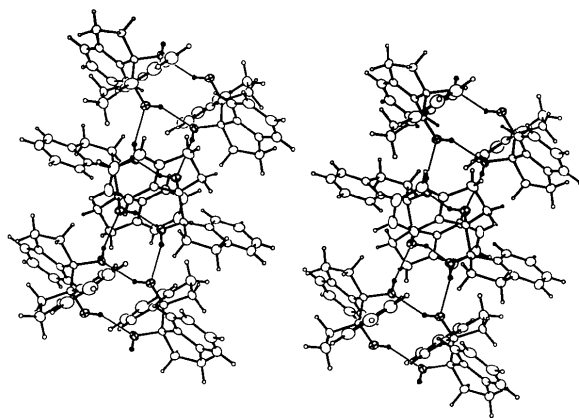

Fig. 2. A stereoview showing the hydrogen bonding, with non-H atoms shown as 20% probability ellipsoids.

Experimental

This dimer was the major product obtained by treating 1-indanone with magnesium amalgam and $TiCl_4$ in tetrahydrofuran following the procedure outlined by Ahond *et al.* (1968). (The minor product was *trans*-α,α'-dehydrobiindanyl.)

Crystal data

$C_{18}H_{18}O_2$	Mo $K\alpha$ radiation
$M_r = 266.34$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 25
$P\bar{1}$	reflections
$a = 10.798\,(3)$ Å	$\theta = 7\text{--}11°$
$b = 12.100\,(3)$ Å	$\mu = 0.074$ mm^{-1}
$c = 12.359\,(3)$ Å	$T = 294$ K
$\alpha = 106.24\,(2)°$	Thin needle
$\beta = 104.27\,(3)°$	$0.52 \times 0.12 \times 0.10$ mm
$\gamma = 103.54\,(2)°$	Clear
$V = 1420.6\,(6)$ Å^3	
$Z = 4$	
$D_x = 1.25$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.047$
diffractometer	$\theta_{max} = 25°$
ω scans	$h = -12 \rightarrow 12$
Absorption correction:	$k = -14 \rightarrow 14$
none	$l = -14 \rightarrow 14$
10095 measured reflections	3 standard reflections
4995 independent reflections	frequency: 150 min
4995 observed reflections	intensity decay: within
[All reflections used, F_o^2	counting statistics
positive and negative]	

Refinement

Refinement on F^2	$w = 1/\sigma^2(F_o^2)$
$R(F) = 0.043$ for 2646	$(\Delta/\sigma)_{max} = <0.02$
reflections with	$\Delta\rho_{max} = 0.31$ e Å^{-3}
$F_o^2 > 3\sigma(F_o^2)$	$\Delta\rho_{min} = -0.30$ e Å^{-3}
$wR(F^2) = 0.008$ on F^2 for	Extinction correction: none
4995 reflections	Atomic scattering factors
$S = 1.38$	from *International Tables*
4995 reflections	*for X-ray Crystallography*
505 parameters	(1974, Vol. IV)
All H-atom parameters	
refined	

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

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

	x	y	z	U_{eq}
C1a	0.6926 (2)	0.1845 (2)	0.1995 (2)	0.0424 (6)
C2a	0.8155 (3)	0.2109 (3)	0.3109 (3)	0.0539 (7)
C3a	0.8716 (3)	0.3489 (3)	0.3782 (3)	0.0594 (9)
C4a	0.8086 (2)	0.4002 (2)	0.2891 (2)	0.0470 (7)
C5a	0.8426 (3)	0.5198 (3)	0.2941 (3)	0.0587 (8)
C6a	0.7728 (3)	0.5468 (3)	0.2011 (3)	0.0649 (9)
C7a	0.6706 (3)	0.4559 (3)	0.1038 (3)	0.0622 (8)
C8a	0.6375 (3)	0.3362 (3)	0.0977 (2)	0.0508 (7)
C9a	0.7068 (2)	0.3091 (2)	0.1915 (2)	0.0423 (6)
C11a	0.5573 (2)	0.1221 (2)	0.2115 (2)	0.0412 (6)
C12a	0.5234 (3)	0.1992 (3)	0.3148 (2)	0.0504 (7)
C13a	0.4271 (3)	0.1062 (3)	0.3440 (3)	0.0629 (8)
C14a	0.4744 (2)	−0.0026 (2)	0.3133 (2)	0.0529 (7)
C15a	0.4514 (3)	−0.1018 (3)	0.3499 (3)	0.0709 (9)
C16a	0.5044 (4)	−0.1923 (3)	0.3093 (3)	0.0792 (10)
C17a	0.5784 (3)	−0.1845 (3)	0.2346 (3)	0.0728 (9)
C18a	0.6007 (3)	−0.0866 (3)	0.1969 (2)	0.0561 (7)
C19a	0.5485 (2)	0.0053 (2)	0.2373 (2)	0.0453 (6)
O1a	0.6989 (2)	0.1024 (2)	0.0933 (2)	0.0584 (5)
O2a	0.4494 (2)	0.0994 (2)	0.1036 (2)	0.0501 (5)
C1b	0.1758 (2)	0.2368 (2)	0.0924 (2)	0.0406 (6)
C2b	0.2819 (3)	0.3288 (2)	0.0684 (3)	0.0508 (7)
C3b	0.3380 (3)	0.4478 (3)	0.1767 (3)	0.0605 (8)
C4b	0.2957 (2)	0.4110 (2)	0.2721 (2)	0.0518 (7)
C5b	0.3394 (3)	0.4767 (3)	0.3940 (3)	0.0689 (10)
C6b	0.2955 (3)	0.4231 (4)	0.4677 (3)	0.0764 (11)
C7b	0.2084 (3)	0.3050 (3)	0.4223 (3)	0.0683 (9)
C8b	0.1625 (3)	0.2387 (3)	0.3001 (3)	0.0528 (7)
C9b	0.2064 (2)	0.2930 (2)	0.2257 (2)	0.0426 (6)
C11b	0.0292 (2)	0.2162 (2)	0.0165 (2)	0.0431 (6)
C12b	−0.0123 (3)	0.3308 (3)	0.0458 (3)	0.0565 (8)
C13b	−0.1159 (3)	0.3180 (3)	−0.0709 (3)	0.0757 (10)
C14b	−0.0770 (3)	0.2399 (3)	−0.1657 (3)	0.0621 (8)
C15b	−0.1102 (3)	0.2229 (4)	−0.2870 (4)	0.0839 (11)
C16b	−0.0647 (4)	0.1451 (4)	−0.3582 (4)	0.0954 (13)
C17b	0.0134 (4)	0.0834 (4)	−0.3115 (3)	0.0835 (11)
C18b	0.0488 (3)	0.1009 (3)	−0.1909 (3)	0.0622 (8)
C19b	0.0040 (2)	0.1799 (2)	−0.1176 (2)	0.0483 (7)
O1b	0.1911 (2)	0.1182 (2)	0.0608 (2)	0.0529 (5)
O2b	−0.0627 (2)	0.1269 (2)	0.0409 (2)	0.0538 (5)

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

C1a—C2a	1.553 (4)	C1b—C2b	1.548 (4)
C1a—C9a	1.514 (3)	C1b—C9b	1.512 (3)
C1a—C11a	1.542 (3)	C1b—C11b	1.549 (3)
C1a—O1a	1.436 (3)	C1b—O1b	1.439 (3)
C2a—C3a	1.533 (4)	C2b—C3b	1.532 (4)
C3a—C4a	1.507 (4)	C3b—C4b	1.504 (4)
C4a—C5a	1.387 (4)	C4b—C5b	1.388 (4)
C4a—C9a	1.383 (3)	C4b—C9b	1.386 (4)
C5a—C6a	1.376 (5)	C5b—C6b	1.369 (5)
C6a—C7a	1.383 (5)	C6b—C7b	1.380 (5)
C7a—C8a	1.384 (4)	C7b—C8b	1.392 (5)
C8a—C9a	1.383 (4)	C8b—C9b	1.381 (4)
C11a—C12a	1.536 (4)	C11b—C12b	1.531 (4)
C11a—C19a	1.520 (3)	C11b—C19b	1.526 (4)
C11a—O2a	1.445 (3)	C11b—O2b	1.438 (3)
C12a—C13a	1.530 (5)	C12b—C13b	1.534 (5)
C13a—C14a	1.506 (4)	C13b—C14b	1.501 (5)
C14a—C15a	1.388 (4)	C14b—C15b	1.395 (5)
C14a—C19a	1.385 (4)	C14b—C19b	1.389 (4)
C15a—C16a	1.381 (5)	C15b—C16b	1.366 (6)
C16a—C17a	1.370 (5)	C16b—C17b	1.377 (6)
C17a—C18a	1.382 (5)	C17b—C18b	1.385 (5)
C18a—C19a	1.388 (4)	C18b—C19b	1.384 (4)
HO2a···O1a'ⁱ	1.94 (3)	HO2b···O1b'ⁱⁱⁱ	1.99 (3)
HO1a···O2b'ⁱⁱ	2.04 (4)	HO1b···O2a'	2.11 (3)
C9a—C1a—C2a	102.8 (2)	C9b—C1b—C2b	102.8 (2)
C11a—C1a—C2a	112.3 (2)	C11b—C1b—C2b	112.4 (2)
O1a—C1a—C2a	111.7 (2)	O1b—C1b—C2b	111.7 (2)
C11a—C1a—C9a	114.3 (2)	C11b—C1b—C9b	114.0 (2)
O1a—C1a—C9a	110.7 (2)	O1b—C1b—C9b	111.0 (2)
O1a—C1a—C11a	105.3 (2)	O1b—C1b—C11b	105.0 (2)
C3a—C2a—C1a	107.7 (2)	C3b—C2b—C1b	107.8 (2)
C4a—C3a—C2a	104.0 (2)	C4b—C3b—C2b	103.7 (2)
C5a—C4a—C3a	128.5 (2)	C5b—C4b—C3b	128.5 (3)
C9a—C4a—C3a	111.0 (2)	C9b—C4b—C3b	111.4 (2)
C9a—C4a—C5a	120.5 (2)	C9b—C4b—C5b	120.0 (3)
C6a—C5a—C4a	119.1 (3)	C6b—C5b—C4b	119.4 (3)
C7a—C6a—C5a	120.5 (3)	C7b—C6b—C5b	120.8 (3)
C8a—C7a—C6a	120.7 (3)	C8b—C7b—C6b	120.3 (3)
C9a—C8a—C7a	118.9 (3)	C9b—C8b—C7b	118.8 (3)
C4a—C9a—C1a	112.1 (2)	C4b—C9b—C1b	111.4 (2)
C8a—C9a—C1a	127.4 (2)	C8b—C9b—C1b	127.9 (2)
C8a—C9a—C4a	120.4 (2)	C8b—C9b—C4b	120.6 (2)
C12a—C11a—C1a	114.4 (2)	C12b—C11b—C1b	113.3 (2)
C19a—C11a—C1a	115.1 (2)	C19b—C11b—C1b	114.3 (2)
O2a—C11a—C1a	108.4 (2)	O2b—C11b—C1b	109.0 (2)
C19a—C11a—C12a	102.3 (2)	C19b—C11b—C12b	102.8 (2)
O2a—C11a—C12a	105.9 (2)	O2b—C11b—C12b	106.4 (2)
O2a—C11a—C19a	110.2 (2)	O2b—C11b—C19b	110.7 (2)
C13a—C12a—C11a	104.5 (2)	C13b—C12b—C11b	105.5 (2)
C14a—C13a—C12a	102.5 (3)	C14b—C13b—C12b	103.3 (3)
C15a—C14a—C13a	128.7 (3)	C15b—C14b—C13b	129.4 (3)
C19a—C14a—C13a	110.5 (2)	C19b—C14b—C13b	110.6 (3)
C19a—C14a—C15a	120.7 (3)	C19b—C14b—C15b	120.0 (3)
C16a—C15a—C14a	118.7 (3)	C16b—C15b—C14b	119.5 (4)
C17a—C16a—C15a	120.8 (3)	C17b—C16b—C15b	120.8 (4)
C18a—C17a—C16a	120.9 (3)	C18b—C17b—C16b	120.3 (4)
C19a—C18a—C17a	118.9 (3)	C19b—C18b—C17b	119.6 (3)
C14a—C19a—C11a	109.6 (2)	C14b—C19b—C11b	110.0 (2)
C18a—C19a—C11a	130.4 (2)	C18b—C19b—C11b	130.1 (2)
C18a—C19a—C14a	119.9 (2)	C18b—C19b—C14b	119.8 (3)
O2a—HO2a···O1a'ⁱ	152 (3)	O1b—HO1b···O2a'	162 (4)
O1a—HO1a···O2b'ⁱⁱ	163 (4)	O2b—HO2b···O1b'ⁱⁱⁱ	148 (3)

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $1 + x, y, z$; (iii) $-x, -y, -z$.

Table 3. *Comparison of observed and expected bond distances (Å)*

C1,11	C2,12	1.542 (10)*	1.530
C1,11	C9,19	1.518 (6)	1.547
C1,11	O1,2	1.440 (4)	1.432
C1	C11	1.546 (4)	1.546
C2,12	C3,13	1.532 (2)	1.534
C3,13	C4,14	1.505 (3)	1.510
C4,8,14,18	C5,9,15,19	1.387 (4)	1.387
C4,14	C9,19	1.386 (3)	1.397
C5,6,7,15,16,17	C6,7,8,16,17,18	1.379 (7)	1.380

* Numbers in parentheses are the sample standard deviations.

The structure was solved by *MULTAN* (Debaerdemaeker *et al.*, 1988); all heavy atoms were found in the *E* map. Their positions and isotropic displacement parameters were refined by least squares and a subsequent difference map showed peaks for most of the H atoms. The H atoms on the C atoms were initially placed by calculation; however, the final refinement included positional parameters for all atoms, anisotropic displacement parameters for the heavy atoms, isotropic displacement parameters for the H atoms and a scale factor, leading to the values reported here.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1046). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Ahond, A., Caré, A., Kan-Fan, C., Husson, H.-P., de Rostolan, J. & Potier, P. (1968). *J. Am. Chem. Soc.* **90**, 5622–5623.

Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–153.

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* pp. S1–19.

Debaerdemaeker, T., Germain, G., Main, P., Refaat, L.S., Tate, C. & Woolfson, M. M. (1988). *MULTAN88. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Universities of York, England, and Louvain, Belgium.

Duchamp, D. J. (1964). Am. Crystallogr. Assoc. Meet., Bozeman, Montana, Paper B14, p. 29.

Enraf–Nonius (1989). *CAD-4 Software.* Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Johnson, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

McBay, H. C. & Abulū. J. (1994). Unpublished results.

Acta Cryst. (1996). C52, 107–110

14-Membered Macrocycles: Methyl *trans*-(10*E*)-5-Methyl-8-methylene-11,15-dioxobicyclo[12.3.0]heptadec-4-ene-14-carboxylate, (I), and Methyl *trans*-(2*E*,10*E*)-10-Methyl-7-methylene-4,17-dioxobicyclo[12.3.0]-heptadeca-2,10-diene-1-carboxylate, (II)

MARC DROUIN,[a] GILLES BERTHIAUME[b] AND PIERRE DESLONGCHAMPS[b]

[a]Laboratoire de Diffraction des Rayons-X, Département de Chimie, Université de Sherbrooke, Sherbrooke, Quebec, Canada J1K 2R1, and [b]Laboratoire de Synthèse Organique, Département de Chimie, Université de Sherbrooke, Sherbrooke, Quebec, Canada J1K 2R1

Abstract

A new series of functionalized 14-membered ring compounds were synthesized by an intramolecular Michael reaction. The structures of the title compounds (I) and (II) ($C_{21}H_{30}O_4$ and $C_{21}H_{28}O_4$, respectively) were determined by single-crystal X-ray diffraction in order to confirm their relative stereochemistries.

Comment

The intramolecular Michael reaction has been used successfully for the synthesis of medium sized (nine- and ten-membered) rings (Deslongchamps & Roy, 1986). Recently, the formation of 14-membered rings was reported using pseudo-high-dilution techniques (Girard & Deslongchamps, 1992). In order to verify the relative ease of macrocyclization of five-membered β-ketoesters with enones and ynones, a series of new 14-membered ring compounds were synthesized from precursors differing in the nature of their Michael acceptors and in the hybridization state of one C atom (Berthiaume & Deslongchamps, 1995). X-ray diffraction analysis of the products was undertaken in order to confirm the structure and relative stereochemistry, not possible by conventional spectroscopic analysis. We report here the crystal structures of the two title 14-membered ring macrocycles, (I) and (II).
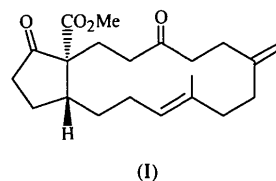
(I)
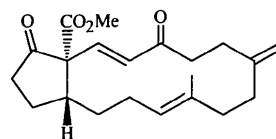
(II)

The results show the ring junction to be *trans* in both molecules and the olefin geometries to be *trans* in (I) and *trans,trans* in (II). The global conformations of the molecules are very similar. In both compounds, the methylene moiety is facing the five-membered ring. The methyl carboxylate group is equatorial to the plane defined by the atoms forming the 14-membered ring, whereas the five-membered ring is axial to this plane. In (I), C20 and C21 are facing down on the same side of the macrocycle as the five-membered ring, whereas the C4═O3 carbonyl group is facing up. In (II), C20 and C21 are also facing down, whereas the C4═O3 carbonyl group is in the plane of the 14-membered ring. Puckering analysis on the five-membered ring shows an envelope conformation in (I) and (II). C15 is 0.508 (2) Å from the plane defined by C1, C14, C16 and C17 in (I). C14 is 0.524 (10) Å from the plane defined by C1, C15, C16 and C17 in (II). In compound (I), there is no transannular close contact. In (II), the O3 ketone group and C2═C3 *trans* double bond are conjugated, as shown by the C3—C4 bond distance [1.462 (7) Å] and the O3—C4—C3—C2 torsion angle [2.6 (4)°]. This particular rigid geometry is such that H3