

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 (Å, °) 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 Å².

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: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ZORTEP* (Zsolnai, 1994); software used to prepare material for publication: *SHELXL93*.

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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.

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A Pinacol Precursor to a Chiral Spiro Compound

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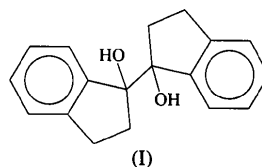
(Received 11 January 1995; accepted 27 July 1995)

Abstract

The dimer of 1-indanoyl obtained from the UV photolysis of 1-indanone in 2-propanol is *trans*- α,α' -biindanyl- α,α' -diol, (C₉H₉O)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



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...O distances 2.716 (3) and 2.725 (3) Å; the O...H distances are 1.94 (3) and 1.99 (3) Å, with O—H...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.

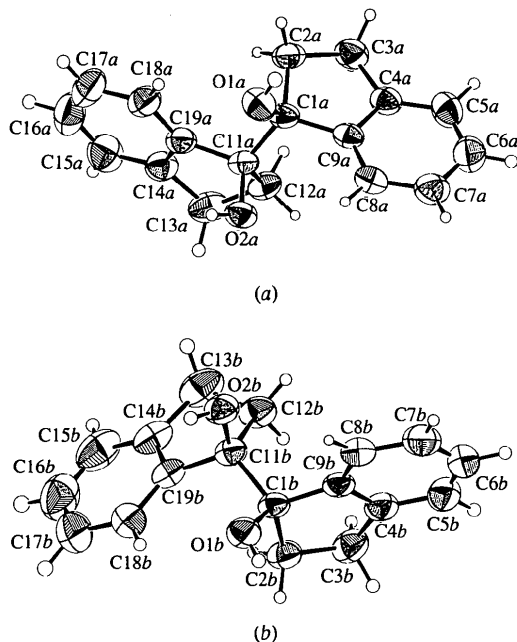


Fig. 1. ORTEPII (Johnson, 1976) drawings of the two independent molecules showing the atom-numbering system. Non-H atoms are shown as 50% probability ellipsoids.

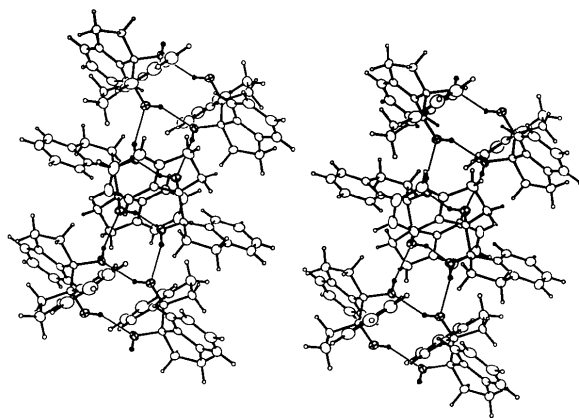


Fig. 2. A stereoview showing the hydrogen bonding, with non-H atoms shown as 20% probability ellipsoids.

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).

Experimental

This dimer was the major product obtained by treating 1-indanone with magnesium amalgam and TiCl₄ in tetrahydrofuran following the procedure outlined by Ahond *et al.* (1968). (The minor product was *trans*- α, α' -dehydrobiindanyl.)

Crystal data

C₁₈H₁₈O₂
M_r = 266.34
 Triclinic
 $P\bar{1}$
a = 10.798 (3) Å
b = 12.100 (3) Å
c = 12.359 (3) Å
 α = 106.24 (2)°
 β = 104.27 (3)°
 γ = 103.54 (2)°
V = 1420.6 (6) Å³
Z = 4
D_x = 1.25 Mg m⁻³

Mo *K* α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 7–11°
 μ = 0.074 mm⁻¹
T = 294 K
 Thin needle
 0.52 × 0.12 × 0.10 mm
 Clear

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω scans
 Absorption correction: none
 10095 measured reflections
 4995 independent reflections
 4995 observed reflections
 [All reflections used, F_o^2 positive and negative]

R_{int} = 0.047
 θ_{max} = 25°
h = -12 → 12
k = -14 → 14
l = -14 → 14
 3 standard reflections
 frequency: 150 min
 intensity decay: within counting statistics

Refinement

Refinement on F^2
 $R(F)$ = 0.043 for 2646 reflections with $F_o^2 > 3\sigma(F_o^2)$
 $wR(F^2)$ = 0.008 on F^2 for 4995 reflections
S = 1.38
 4995 reflections
 505 parameters
 All H-atom parameters refined

$w = 1/\sigma^2(F_o^2)$
 $(\Delta/\sigma)_{max} < 0.02$
 $\Delta\rho_{max} = 0.31 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.30 \text{ e \AA}^{-3}$
 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 (Å²)
$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	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 ⁱ	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 ⁱ	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.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CRYM* (Duchamp, 1964). Program(s) used to solve structure: *CRYM*. Program(s) used to refine structure: *CRYM*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *CRYM*.

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.

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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)

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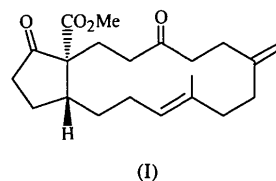
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Abstract

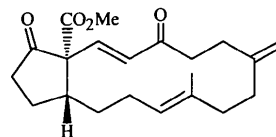
A new series of functionalized 14-membered ring compounds were synthesized by an intramolecular Michael reaction. The structures of the title compounds (I) and (II) (C₂₁H₃₀O₄ and C₂₁H₂₈O₄, respectively) were determined by single-crystal X-ray diffraction in order to confirm their relative stereochemistries.

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