Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

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

	x	y	z	U_{eq}
Cl1	0.2157 (1)	0.0875 (1)	0.3753 (1)	0.052 (1)
O1	0.8448 (2)	0.4361 (4)	0.7673 (4)	0.084 (1)
O2	0.9236 (2)	0.5259 (4)	0.6148 (5)	0.095 (1)
O3	0.6372 (2)	0.4483 (2)	0.5403 (3)	0.047 (1)
O4	0.4635 (2)	0.0496 (2)	0.6888 (3)	0.050 (1)
N1	0.7355 (2)	0.2605 (3)	0.5288 (4)	0.050 (1)
N2	0.5189 (2)	0.2664 (3)	0.6281 (4)	0.049 (1)
N3	0.3067 (2)	0.1741 (3)	0.7209 (4)	0.043 (1)
C1	0.8598 (2)	0.4416 (4)	0.6448 (5)	0.056 (1)
C2	0.8068 (3)	0.3573 (5)	0.5041 (5)	0.056 (1)
C3	0.6598 (2)	0.3144 (3)	0.5558 (3)	0.038 (1)
C4	0.6007 (2)	0.1986 (3)	0.6029 (4)	0.044 (1)
C5	0.4588 (2)	0.1866 (3)	0.6752 (3)	0.035 (1)
C6	0.3823 (2)	0.2757 (3)	0.7105 (4)	0.042 (1)
C7	0.9801 (4)	0.6212 (10)	0.7402 (14)	0.138 (3)

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

O1—C1	1.199 (5)	N2—C5	1.315 (4)
O2—C1	1.305 (4)	N2—C4	1.445 (4)
O2—C7	1.465 (9)	N3—C6	1.473 (4)
O3—C3	1.231 (3)	C1—C2	1.487 (6)
O4—C5	1.220 (3)	C3—C4	1.500 (4)
N1—C3	1.322 (4)	C5—C6	1.506 (4)
N1—C2	1.441 (4)		
C1—O2—C7	117.2 (5)	O3—C3—C4	121.7 (3)
C3—N1—C2	122.2 (3)	N1—C3—C4	114.9 (3)
C5—N2—C4	121.7 (3)	N2—C4—C3	111.3 (3)
O1—C1—O2	124.8 (4)	O4—C5—N2	123.0 (3)
O1—C1—C2	125.0 (3)	O4—C5—C6	121.6 (3)
O2—C1—C2	110.2 (4)	N2—C5—C6	115.4 (2)
N1—C2—C1	113.4 (3)	N3—C6—C5	110.2 (2)
O3—C3—N1	123.4 (3)		

Table 3. *Comparison of torsion angles* (°) *in compounds* (I)–(IV)

	(I)	(II)	(III*a*)	(III*b*)	(IV)
N3—C6—C5—N2	164.8	158.5	−149.9	−161.8	164.9 (3)
C6—C5—N2—C4	172.1	−178.2	−176.7	176.1	174.5 (3)
C5—N2—C4—C3	−153.3	−72.1†	177.6	−165.9	−177.7 (3)
N2—C4—C3—N1	159.7	163.7	−171.5	174.5	−179.2 (3)
C4—C3—N1—C2	−178.5	−176.2	−178.5	−176.1	−170.9 (3)
C3—N1—C2—C1	−80.1†	85.5†	172.8	172.8	68.5(5)†
N1—C2—C1—O1	172.7	177.5	−172.6	−168.8	177.7 (6)

† The atoms involved in these angles are not constrained by intermolecular interactions.

The metric symmetry of the title compound is orthorhombic but the diffraction symmetry and systematic extinctions are compatible only with monoclinic space group $P2_1/c$.

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1258). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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An Indanyl Precursor to a Chiral Spiro Compound

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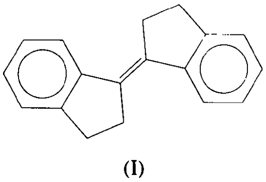
Abstract

The dimer of α-indanylcarbene obtained after UV irradiation of the lithium salt of the tosylhydrazone of 1-indanone in benzene is *trans*-α,α'-dehydrobiindanyl, $(C_9H_8)_2$. The asymmetric unit is planar within ±0.02 Å; the two halves are related by a center of symmetry and joined by a double bond.

Comment

In an attempt to prepare a spiro compound with a chiral spiro atom resulting from enantioselective migration during pinacol rearrangement, we sought to make a *vic*-glycol as a precursor. If the *vic*-glycol is locked into the proper conformation by hydrogen bonding, the enantioselective migration might be facilitated. Thus, from alkene to epoxide to *vic*-glycol seemed a likely route. The alkene chosen for the mock-up study was *trans*-α,α'-dehydrobiindanyl, (I).



(I)

The molecule displays normal geometry (Fig. 1, Table 2). C—C (aromatic) bonds average 1.390 (9) Å and the C1=C1^i double bond is 1.351 (1) Å [symmetry code: (i) $\frac{3}{2} - x, \frac{3}{2} - y, -z$]. All H-atom parameters were refined; C—H bonds average 0.991 (13) Å and the two H—C—H angles average 105.9 (16)°. The U_{ij} values of the heavy atoms are given in Table 3. Even though the data were collected at room temperature, the final difference map clearly shows the bonding electrons in the molecule (Fig. 3). The largest peaks in the final difference map are shown in Fig. 3, which displays residual density between every pair of C atoms except C1 and C1^i.

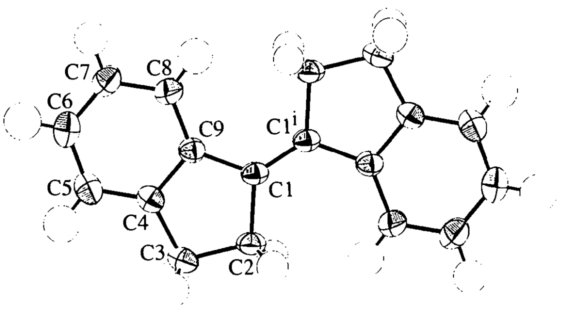


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the molecule with 50% probability ellipsoids. H atoms are shown as plain spheres with their refined parameters.

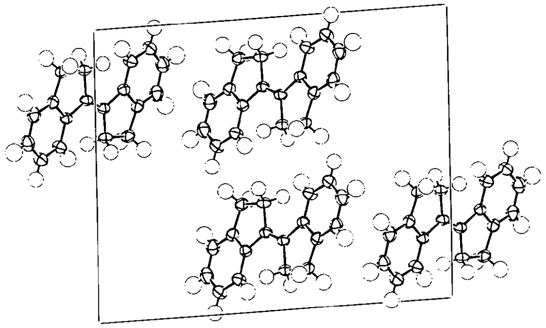


Fig. 2. An *ORTEP*II (Johnson, 1976) drawing of the contents of a unit cell, with a unit cell outlined. Atoms are shown as in Fig. 1; the view is perpendicular to the *ac* plane.

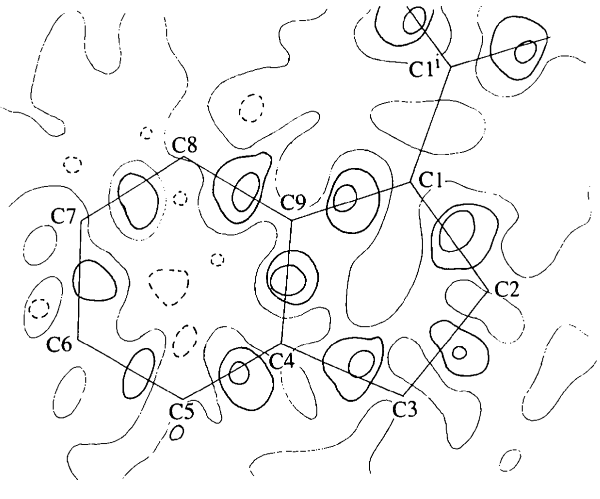


Fig. 3. A difference map in the plane of the asymmetric unit at the end of refinement. Contours are at −0.1 (dashed), 0 (thin line), and 0.1 and 0.2 e Å^{-3} (heavy lines).

Experimental

Following the procedure of Frimer, Weiss & Rosental (1994), 4 g of the lithium salt of the tosylhydrazone of 1-indanone was irradiated in benzene solution for 2.5 h using a 450 W Hanovia lamp (UV). From this solution was isolated 2.1 g of yellow solid which was recrystallized from 95% ethanol. The X-ray crystals were cleaved from these large chunks (m.p. 438–441 K). ^{1}H and ^{13}C NMR spectra were recorded.

Crystal data

$C_{18}H_{16}$
$M_r = 232.32$
Monoclinic
$C2/c$
$a = 13.758\ (5)$ Å
$b = 5.391\ (1)$ Å
$c = 16.844\ (4)$ Å
$\beta = 93.00\ (3)°$
$V = 1247.6\ (6)$ Å^3
$Z = 4$
$D_x = 1.24$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.4–13.4°$
$\mu = 0.065$ mm^{-1}
$T = 296$ K
Triangular prism (irregular)
$0.52 \times 0.44 \times 0.37$ mm
Pale yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
7190 measured reflections
1781 independent reflections
1781 observed reflections [all reflections used, F_o^2 positive and negative]

$R_{\text{int}} = 0.010$ for 155 duplicates; GOF 1.01 for 1781 reflections
$\theta_{\text{max}} = 30°$
$h = -19 \rightarrow 19$
$k = -7 \rightarrow 7$
$l = -20 \rightarrow 20$
3 standard reflections
frequency: 150 min
intensity decay: within statistical expectations

Refinement

Refinement on F^2
$R(F^2 > 0) = 0.050$
$R[F^2 > 3\sigma(F^2)] = 0.044$
$wR(F^2) = 0.011$
$S = 2.95$
1781 reflections
115 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\text{max}} < 0.005$

$\Delta\rho_{\text{max}} = 0.28$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.16$ e Å^{-3}
Extinction correction: Larson (1967)
Extinction coefficient: $0.95\ (22) \times 10^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

B_{iso} for H atoms; $U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for non-H atoms.

	x	y	z	B_{iso}/U_{eq}
C1	0.7657 (1)	0.6578 (2)	0.0246 (1)	0.0326 (2)
C2	0.8682 (1)	0.5483 (2)	0.0287 (1)	0.0382 (2)
C3	0.8688 (1)	0.3406 (3)	0.0913 (1)	0.0425 (3)
C4	0.7672 (1)	0.3367 (2)	0.1196 (1)	0.0373 (2)
C5	0.7294 (1)	0.1765 (3)	0.1745 (1)	0.0489 (3)
C6	0.6332 (1)	0.1989 (3)	0.1932 (1)	0.0521 (3)
C7	0.5753 (1)	0.3823 (3)	0.1577 (1)	0.0489 (3)
C8	0.6123 (1)	0.5428 (2)	0.1027 (1)	0.0436 (3)
C9	0.7093 (1)	0.5208 (2)	0.0822 (1)	0.0336 (2)
H2*A*	0.9189 (10)	0.676 (3)	0.0427 (8)	4.0 (3)
H2*B*	0.8852 (10)	0.485 (3)	−0.0251 (8)	3.8 (3)
H3*A*	0.9177 (11)	0.374 (3)	0.1362 (9)	4.6 (4)
H3*B*	0.8853 (11)	0.177 (3)	0.0685 (9)	4.8 (4)
H5	0.7725 (11)	0.050 (3)	0.1986 (9)	5.3 (4)
H6	0.6052 (12)	0.087 (3)	0.2323 (10)	5.6 (4)
H7	0.5065 (11)	0.403 (3)	0.1723 (9)	4.3 (3)
H8	0.5700 (11)	0.670 (3)	0.0795 (10)	5.0 (4)

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

C1—C2	1.527 (2)	C2—H2*A*	0.999 (14)
C1—C9	1.473 (1)	C2—H2*B*	1.007 (14)
C1—C1^{i}	1.351 (1)	C3—H3*A*	1.002 (15)
C2—C3	1.538 (2)	C3—H3*B*	0.993 (15)
C3—C4	1.501 (2)	C5—H5	0.977 (16)
C4—C5	1.385 (2)	C6—H6	0.987 (17)
C4—C9	1.402 (2)	C7—H7	0.997 (15)
C5—C6	1.382 (2)	C8—H8	0.968 (16)
C6—C7	1.385 (2)		
C7—C8	1.384 (2)		
C8—C9	1.400 (2)		
C9—C1—C2	107.1 (1)	H2*A*—C2—C1	112.0 (8)
C1^{i}—C1—C2	125.2 (1)	H2*B*—C2—C1	110.3 (8)
C1^{i}—C1—C9	127.6 (1)	H2*A*—C2—C3	111.2 (8)
C3—C2—C1	106.5 (1)	H2*B*—C2—C3	112.2 (8)
C4—C3—C2	104.9 (1)	H2*B*—C2—H2*A*	104.7 (11)
C5—C4—C3	127.6 (1)	H3*A*—C3—C2	111.5 (9)
C9—C4—C3	111.3 (1)	H3*B*—C3—C2	112.1 (9)
C9—C4—C5	121.1 (1)	H3*A*—C3—C4	111.2 (9)
C6—C5—C4	119.7 (1)	H3*B*—C3—C4	110.3 (9)
C7—C6—C5	119.9 (1)	H3*B*—C3—H3*A*	107.0 (12)
C8—C7—C6	120.8 (1)	H5—C5—C4	118.1 (9)
C9—C8—C7	120.0 (1)	H5—C5—C6	122.2 (9)
C4—C9—C1	110.1 (1)	H6—C6—C5	120.7 (10)
C8—C9—C1	131.4 (1)	H6—C6—C7	119.3 (10)
C8—C9—C4	118.4 (1)	H7—C7—C6	120.3 (8)
		H7—C7—C8	118.8 (8)
		H8—C8—C7	118.5 (9)
		H8—C8—C9	121.5 (9)

Symmetry code: (i) $\frac{3}{2} - x, \frac{3}{2} - y, -z$.

Table 3. *Anisotropic displacement parameters* (Å$^2 \times 10^4$)

The form of the displacement factor is: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	269 (4)	317 (5)	395 (6)	35 (4)	32 (4)	−38 (4)
C2	277 (5)	400 (6)	469 (6)	71 (4)	29 (4)	−5 (5)
C3	370 (6)	447 (6)	452 (7)	112 (5)	−26 (5)	13 (5)
C4	392 (5)	366 (5)	359 (6)	38 (4)	−8 (4)	−17 (4)
C5	574 (8)	459 (7)	431 (7)	48 (6)	2 (5)	78 (5)
C6	615 (8)	524 (8)	429 (7)	−66 (6)	81 (6)	67 (6)
C7	435 (6)	564 (8)	478 (7)	−43 (6)	121 (5)	19 (6)
C8	354 (6)	447 (6)	513 (7)	44 (5)	94 (5)	40 (5)
C9	323 (5)	318 (5)	369 (5)	24 (4)	23 (4)	−27 (4)

The structure was solved by *MULTAN*88 (Debaerdemaeker *et al.*, 1988); all C atoms were found in the *E* map. Their positions and displacement parameters were refined and H atoms were then introduced at calculated positions. After four cycles, the H-atom parameters (positional and displacement) were included in the refinement, along with a single scale factor and a secondary extinction parameter. All refinements proceeded smoothly and quickly.

Data collection and cell refinement: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction, structure solution, structure refinement and preparation of material for publication: *CRYM* (Duchamp, 1964). Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors have been deposited with the IUCr (Reference: CR1180). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Bromo-4-[2-bromo-(*E*)-propylidene]-6-methoxy-2,5-cyclohexadien-1-one

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Abstract

The structure and stereochemistry of 2-bromo-4-[2-bromo-(*E*)-propylidene]-6-methoxy-2,5-cyclohexadien-1-one, $C_{10}H_{10}Br_2O_2$ (1), has been elucidated by X-ray crystallographic analysis. In chloroform or benzene