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(6b*R*,10a*S*)-6b,10a-Dimethyl-10,10a-dihydro-9*H*-fluoranthene

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Key indicators

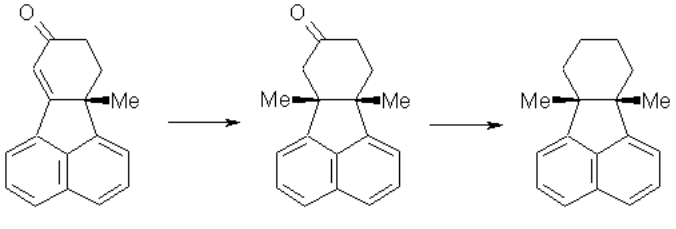
Single-crystal X-ray study
T = 200 K
Mean σ(C–C) = 0.007 Å
R factor = 0.054
wR factor = 0.214
Data-to-parameter ratio = 11.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

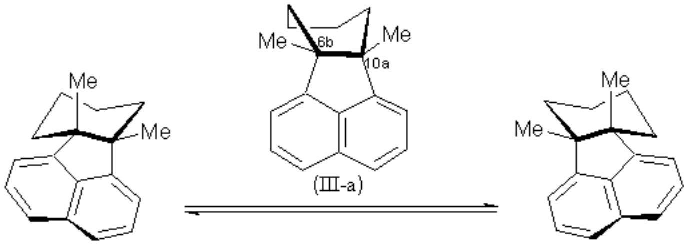
The crystal structure of the title compound, $C_{18}H_{20}$, contains molecules which are separated by normal van der Waals distances. The methyl groups attached at the junction of the acenaphthylene and cyclohexyl rings are *cis* with respect to each other. The naphthalene ring in the acenaphthylene moiety is essentially planar, with the remaining two C atoms lying 0.206 (6) and 0.253 (6) Å on opposite sides of the plane of the naphthalene ring. The five-membered ring adopts an envelope conformation and the cyclohexyl ring is in a slightly flattened chair conformation. The molecular dimensions are as expected.

Comment

In order to simplify the number of possible $Cr(CO)_3$ isomers of a chiral naphthalene and to maximize the chiral environment for the subsequent $Cr(CO)_3$ transfer, it was desirable to use a C_2-axially symmetric naphthalene, and the *trans* isomer of (III) appeared to be an ideal target for the subsequent preparation of a homochiral $Cr(CO)_3$ complex (Simion, 1996). The conjugate addition of lithium dimethylcuprate to the partially resolved enone (I) produced the ketone (II) as a single isomer that upon Wolff–Kishner reduction led to the formation of the title compound, (III), as a *cis*-isomer, instead of the target *trans*-isomer. NMR spectroscopy was not decisive in establishing the *cis*- or *trans*- ring junction in (III). Therefore, an X-ray structure determination was carried out to investigate the nature of the ring junction. The high *cis*-stereoselectivity observed in this kinetically controlled



(I) (II) (III)



(III-a)

(III-b) (III-c)

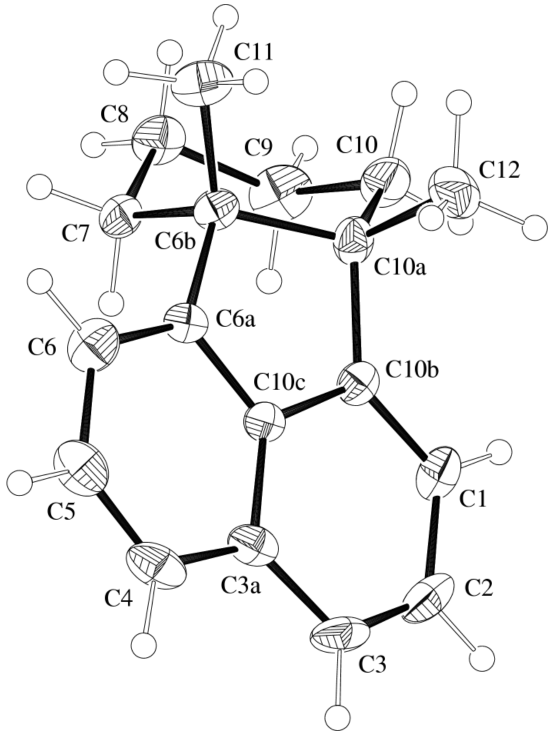


Figure 1
*ORTEP*II (Johnson, 1976) drawing of (III). Displacement ellipsoids have been plotted at the 30% probability level.

conjugate addition of organocuprate reagents to the enone (I) is similar to the one observed in bicyclo[4.4.0]enones which form mainly the corresponding *cis*-decalin products (Posner, 1972).

Compound (III), while having no chirality in a C_s boat conformation (III-a), may adopt two chiral chair conformations in the crystal (III-b and III-c). Selection of a single crystal is then equivalent to a spontaneous resolution (Jacques *et al.*, 1981). This is the case with the crystal selected for this study in which compound (III) crystallizes in the non-centrosymmetric space group $P2_12_12_1$ in a chiral chair conformation, (III-b), with a *P* 6b*R*, 10a*S* specified stereochemistry. The stereochemistry for the two chair conformations may be specified as *P* 6b*R*, 10a*S* for (III-b) and *M* 6b*R*, 10a*S* for (III-c); a view down the C6*b*—C10*a* bond and clockwise rotation of the front groups to the equivalent back-groups = *P*, and anticlockwise rotation = *M*. However, the occurrence of a spontaneous resolution is not demonstrable through the measurement of optical activity since the conformers interconvert very rapidly in solution.

The asymmetric unit of (III) is composed of molecules separated by normal van der Waals distances wherein an acenaphthylene has been fused with a *cis*-cyclohexyl ring (Fig. 1). The molecular dimensions are as expected with mean bond distances: $Csp^3—Csp^3$ 1.54 (2), $Csp^3—Csp^2$ 1.523 (1), and $C—C_{aromatic}$ 1.40 (2) Å. The C6*b*—C10*a* distance at the junction of the cyclohexyl and acenaphthylene rings is significantly longer than expected for a $Csp^3—Csp^3$ single bond at a value of 1.586 (6) Å; the corresponding distance in similar structures, acenaphthoquinone diketal (Parvez *et al.*, 2001*a*) and a naphthalene derivative of a bicyclooctane diketal (Parvez *et al.*, 2001*b*) have been reported to be 1.585 (8) and 1.613 (12) Å, respectively.

The naphthalene ring in the acenaphthylene moiety is essentially planar, with C6*b* and C10*a* 0.206 (6) and 0.253 (6) Å, respectively, on opposite sides of the plane of the naphthalene ring atoms; the maximum deviation of any atom from the mean plane of the naphthalene ring is 0.034 (3) Å. The five-membered ring fused to the naphthalene ring exhibits a C6*b*-envelope conformation, with C6*b* 0.385 (6) Å, out of the least-squares plane of the remaining ring atoms. The cyclohexyl ring adopts a slightly distorted chair conformation caused by the fusion of the acenaphthylene and cyclohexyl rings, with torsion angles in the range ±41.0 (5)–62.5 (5)°.

Experimental

Preparation of (I): enone (I) was prepared (Simion, 1996) from (±)-2-methyl-1-acenaphthenone according to a general protocol reported for the enantioselective elaboration of quaternary carbon centers through Michael-type alkylation of chiral imines (Revial & Pfau, 1992).

Preparation of (II): a solution of (I) (2.34 g, 10 mmol) in 75 ml dry ether was added to a solution of lithium dimethylcuprate prepared from CuI (9.40 g, 48.2 mmol) and MeLi (1.5 M in ether) (66.7 ml, 100 mmol) and cooled to 195 K. After completion of the addition, the reaction mixture was warmed to 253 K and stirred for 1 h, and quenched with saturated NH_4Cl. The organic layer was washed with brine and dried ($MgSO_4$). Evaporation, followed by recrystallization (pentane) gave 2.22 g, m.p. 382–384 K, $[\alpha]^{23}{}_D = 114.14°$ (*c* = 0.079, $CHCl_3$), ee = 47% [(+)-diethyl tartrate ketal, GC].

Preparation of (III): a mixture of (II) (2.50 g, 0.01 mol), 80% hydrazine hydrate (26.40 g, 0.66 mol), hydrazine dihydrochloride (8.40 g, 0.80 mol) and triethylene glycol, 225 g, was heated at 403 K for 2.5 h. After adding KOH pellets (85%) (14.5 g, 0.22 mol), the temperature was gradually raised to 483 K by distilling out the low-boiling material, and the reaction mixture was heated at this temperature for 2.5 h. After cooling, the reaction mixture was diluted with water and extracted with ether. The organic layer was washed with 1 *N* HCl, and then with brine, and dried ($MgSO_4$). Evaporation of the solvent, followed by recrystallization (hexane) gave 1.88 g (yield 80%), m.p. 393–395 K. Spectroscopic data for (I), (II), and (III) are available (Simion, 1996).

Crystal data

$C_{18}H_{20}$
$M_r = 236.34$
Orthorhombic, $P2_12_12_1$
$a = 13.332$ (3) Å
$b = 13.791$ (3) Å
$c = 7.440$ (2) Å
$V = 1367.9$ (6) Å^3
$Z = 4$
$D_x = 1.148$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.0$–15.0°
$\mu = 0.06$ mm^{-1}
$T = 200$ (2) K
Prism, colorless
0.60 × 0.47 × 0.38 mm

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
1819 measured reflections
1819 independent reflections
1073 reflections with $I > 2\sigma(I)$
$\theta_{max} = 27.5°$

$h = 0 \rightarrow 17$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 9$
3 standard reflections
every 200 reflections
intensity decay: <0.1%

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Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.113P)^2 + 0.398P]$
$R[F^2 > 2\sigma(F^2)] = 0.054$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.214$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.11$	$\Delta\rho_{\max} = 0.31$ e Å^{-3}
1819 reflections	$\Delta\rho_{\min} = -0.27$ e Å^{-3}
165 parameters	
H-atom parameters constrained	

The space group, $P2_12_12_1$, was uniquely determined from the systematic absences. The H atoms were located from difference maps and were included at geometrically idealized positions with C—H = 0.95–0.99 Å, in a riding mode with isotropic displacement parameters equal to 1.2 (non-methyl) and 1.5 (methyl) times the displacement parameters of the atoms to which they were attached. As the compound has only C and H atoms, we did not measure any Friedel pairs of reflections; our analysis only determines the relative stereochemistry.

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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