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Key indicators

Single-crystal X-ray study
T = 170 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
Disorder in main residue
R factor = 0.047
wR factor = 0.139
Data-to-parameter ratio = 14.3

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

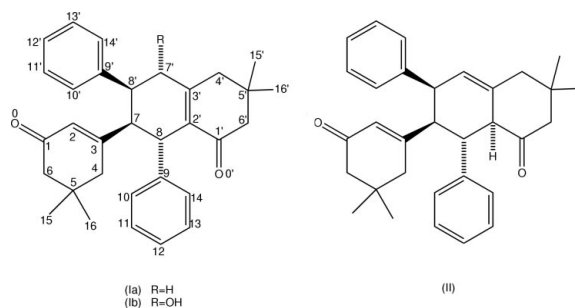
6,7-*cis*-7,8-*trans*-3,3-Dimethyl-7-(5,5-dimethyl-3-oxo-1-cyclohexenyl)-6,8-diphenyl-1,2,3,4,5,6,7,8-octahydronaphthalen-1-one

An X-ray diffraction study has established the structure of the title compound, $\text{C}_{32}\text{H}_{36}\text{O}_2$, obtained from benzaldehyde and isophorone under Claisen–Schmidt conditions.

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Comment

Two possible structures, including (*Ia*) without stereochemistry, were proposed for the high-melting condensation products formed in up to 59% yield from mixtures of isophorone, aromatic aldehydes, sodium hydroxide, and ethanol (Kabas, 1966). From its ^1H , HSQC, and HMBC NMR spectra, the benzaldehyde product was determined to have the constitution (*Ia*), but the stereochemistry remained in doubt. An X-ray study has firmly established structure (*Ia*), including the stereochemistry. The torsion angle between HC7 and HC8 is close to 90° , showing why coupling between these protons is not observed in the NMR spectra (given as supporting information). It was proposed that compound (*Ia*) was formed by a sequence involving two Michael additions, but a Diels–Alder reaction of benzylideneisophorone with itself to give (II) followed by base-catalysed double-bond isomerization to (*Ia*) seems more likely; a precedent is found in the Diels–Alder reaction of benzylideneisophorone with maleic anhydride (Kabas, 1966). Difference maps revealed a small peak at a C–O distance [1.41 (2) \AA] from C7, suggesting that 10% of the sample had air-oxidized to the alcohol (*Ib*).



Experimental

Crystals suitable for structural determination were grown by slow evaporation from a deuterio-chloroform solution of the compound.

Crystal data

$\text{C}_{32}\text{H}_{36}\text{O}_2$
 $M_r = 452.61$
Monoclinic, $P2_1/c$
 $a = 12.2381 (9) \text{ \AA}$
 $b = 21.8866 (15) \text{ \AA}$
 $c = 10.3089 (7) \text{ \AA}$
 $\beta = 113.690 (1)^\circ$
 $V = 2528.6 (3) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.193 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 4886 reflections
 $\theta = 2.4\text{--}22.4^\circ$
 $\mu = 0.07 \text{ mm}^{-1}$
 $T = 170 (2) \text{ K}$
Block, colorless
 $0.30 \times 0.15 \times 0.10 \text{ mm}$

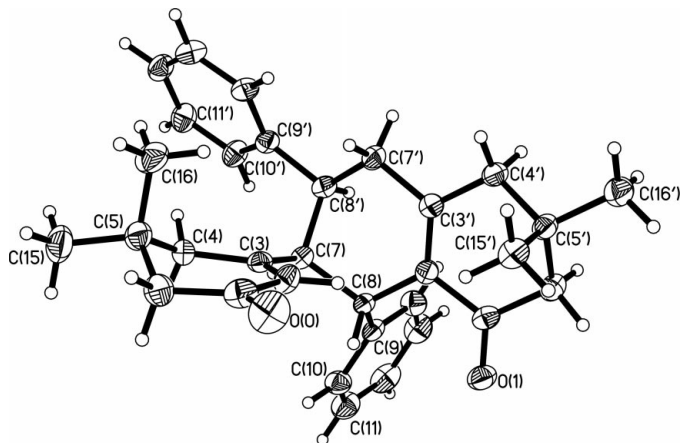


Figure 1
Displacement ellipsoid plot rendered with 50% probability ellipsoids (Bruker, 1997b).

Data collection

SMART1000 CCD area-detector
diffractometer
 φ and ω scans
23714 measured reflections
4484 independent reflections
2142 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.099$

$\theta_{\text{max}} = 25.1^\circ$
 $h = -14 \rightarrow 14$
 $k = -26 \rightarrow 26$
 $l = -12 \rightarrow 12$
61 standard reflections
every 3636 reflections
intensity decay: 0.1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.139$
 $S = 0.94$
4484 reflections
313 parameters
H atoms treated by a mixture of
independent and constrained
refinement

$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.25 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.21 \text{ e } \text{\AA}^{-3}$
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0024 (8)

H atoms were placed at idealized positions, constrained to ride on the atom to which they were bonded and given displacement parameters equal to 1.2 or 1.5 times U_{iso} of that bonded atom. Residual electron density ($> 0.5 \text{ e}^- \text{ per } \text{\AA}^3$) was discovered in later difference maps, located approximately 1.4 \AA from C7' and 0.4 \AA from H7'A. As the distance was nearly an ideal alcoholic C—O bond length, the residual density was assigned to an O atom, O3B. The neighboring proton (H7'A) and O3B were modeled as two parts of a disordered group, with the relative occupancies of the two parts allowed to refine. The final occupancies of the two parts were 88.566 (7)% for the proton and 11.434 (7)% for O3B. No protons were modeled for O3B. The resultant difference map was greatly improved.

Data collection: *SMART* (Bruker, 1997a); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997a); program(s) used to solve structure: *SHELXTL* (Bruker, 1997b); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This structure was determined in the Molecular Structure Laboratory of the Department of Chemistry, University of Arizona, Tucson AZ 85721. The SMART1000 diffractometer was gratefully obtained with funds provided by NSF grant CHE9610374.

References

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Bruker (1997b). *SHELXTL*. Version 5.0. Bruker AXS Inc., Madison, Wisconsin, USA.
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