

ORGANIC COMPOUNDS

Acta Cryst. (1997). **C53**, 1255–1256

(Z)-1-Benzoyl-4-*tert*-butyl-1-methylcyclohexane and (Z)-4-*tert*-Butyl-1-methyl-1-thiobenzoylcyclohexane†

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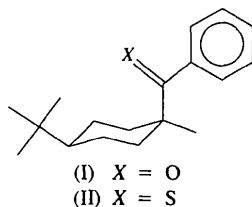
(Received 5 February 1997; accepted 7 April 1997)

Abstract

Both title molecules, $C_{18}H_{26}O$ and $C_{18}H_{26}S$, contain six-membered cyclohexane rings with chair conformations, equatorial 1-methyl and 4-*tert*-butyl substituents, and axial 1-benzoyl or 1-thiobenzoyl substituents, respectively. The substituent carbonyl and thiocarbonyl groups are oriented with the O and S atoms close to axial H atoms in the cyclohexane rings, thus accounting for the observed photochemical reactivity.

Comment

The materials were synthesized as part of a study of asymmetric induction in the photochemistry of ketones (Leibovitch *et al.*, 1996; Leibovitch, 1997). Each molecule of (I) and (II) contains a six-membered cyclohexane ring with a chair conformation, with torsion angles ± 54.2 – 57.9 (3) and 51.3 – 57.2 (2) $^\circ$, respectively. The 1-methyl and 4-*tert*-butyl substituents are in equatorial positions, and the 1-benzoyl and 1-thiobenzoyl substituents are in axial sites. The phenyl groups are rotated considerably out of the planes of the carbonyl and thiocarbonyl groups; O—C—C torsion angles are 136.3 (3) and -41.6 (4) $^\circ$, and S—C—C torsion angles are 128.9 (2) and -48.3 (2) $^\circ$, for the benzoyl, (I), and thiobenzoyl compound, (II), respectively. Bond lengths and angles are normal; C=O 1.220 (3) and C=S 1.622 (2) Å.



† Alternative names: *cis*-[4-(1,1-dimethylethyl)-1-methylcyclohexyl]-phenylmethanone and *cis*-[4-(1,1-dimethylethyl)-1-methylcyclohexyl]-phenylmethanethione.

The carbonyl and thiocarbonyl groups are oriented approximately normal to the C4...C1 axes of the cyclohexane rings; O/S—C7—C1—C6 torsion angles are 26.5 (3) and 35.5 (2) $^\circ$ in the two compounds. This brings the O and S atoms reasonably close to the axial H atoms on C5, with O...H 2.69 and S...H 3.03 Å, distances which are suitable for H-atom abstraction in the photochemical reactions (Leibovitch *et al.*, 1996) (the more distant axial H atoms on C3 are at 3.57 and 4.05 Å).

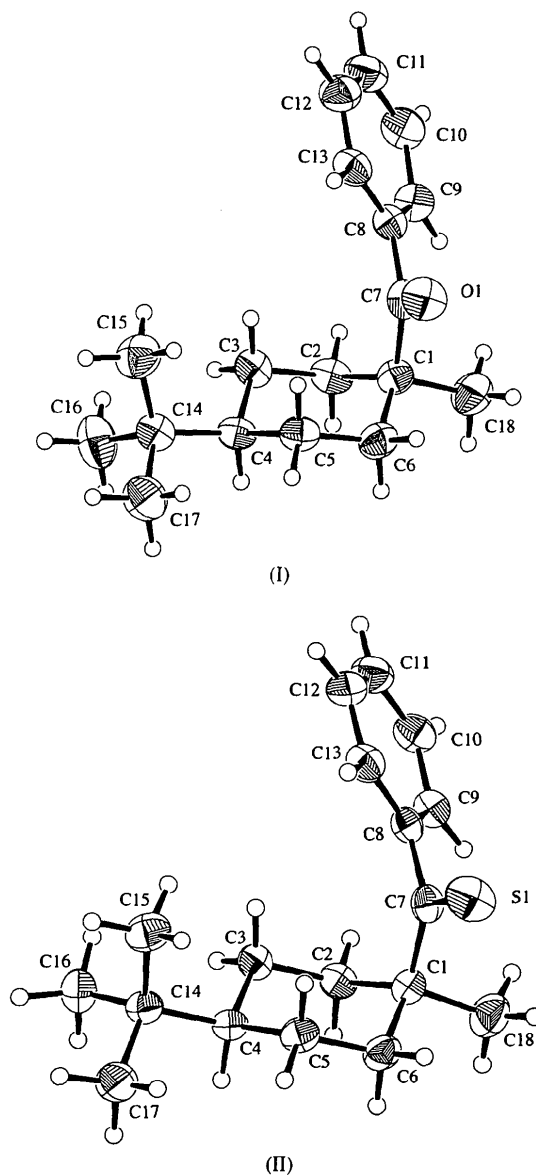


Fig. 1. Views of the two title molecules with 33% probability displacement ellipsoids.

Experimental

The title compounds were synthesized according to the methods of Leibovitch *et al.* (1996) and Leibovitch (1997).

Compound (I)*Crystal data*

C₁₈H₂₆O
M_r = 258.40
 Orthorhombic
*Pna*2₁
a = 20.120 (4) Å
b = 13.075 (4) Å
c = 6.149 (4) Å
V = 1618 (1) Å³
Z = 4
D_x = 1.061 Mg m⁻³
D_m not measured

Cu *Kα* radiation
 λ = 1.5418 Å
 Cell parameters from 24 reflections
 θ = 12.7–24.0°
 μ = 0.480 mm⁻¹
T = 294 K
 Needle
 0.30 × 0.10 × 0.10 mm
 Colourless

Data collection

Rigaku AFC-6S diffractometer
 ω -2 θ scans
 Absorption correction:
 ψ scans (North, Phillips & Mathews, 1968)
 T_{\min} = 0.962, T_{\max} = 1.000
 1814 measured reflections
 1814 independent reflections

1052 reflections with $I > 3\sigma(I)$
 θ_{\max} = 77.64°
 h = -25 → 0
 k = 0 → 16
 l = 0 → 7
 3 standard reflections every 200 reflections
 intensity decay: 29%

Refinement

Refinement on F^2
 $R(F)$ = 0.037
 $wR(F^2)$ = 0.110
 S = 1.12
 1814 reflections
 172 parameters
 H atoms not refined
 $w = 1/[\sigma^2(F_o^2) + 0.00063(F_o^2)^2]$
 $(\Delta/\sigma)_{\max}$ = 0.0006

$\Delta\rho_{\max}$ = 0.20 e Å⁻³
 $\Delta\rho_{\min}$ = -0.22 e Å⁻³
 Extinction correction: Zachariasen (1967)
 Extinction coefficient: 2.7 (6) × 10⁻⁶
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (II)*Crystal data*

C₁₈H₂₆S
M_r = 274.46
 Orthorhombic
Pbca
a = 12.853 (1) Å
b = 32.252 (3) Å
c = 7.945 (1) Å
V = 3293.5 (6) Å³
Z = 8
D_x = 1.107 Mg m⁻³
D_m not measured

Cu *Kα* radiation
 λ = 1.5418 Å
 Cell parameters from 23 reflections
 θ = 42.3–50.4°
 μ = 1.568 mm⁻¹
T = 294 K
 Prism
 0.12 × 0.10 × 0.10 mm
 Purple

Data collection

Rigaku AFC-6S diffractometer
 ω -2 θ scans

2327 reflections with $I > 3\sigma(I)$
 θ_{\max} = 77.68°

Absorption correction: $h = 0 \rightarrow 16$
 ψ scans (North, Phillips & Mathews, 1968) $k = 0 \rightarrow 40$
 T_{\min} = 0.699, T_{\max} = 0.855 $l = 0 \rightarrow 10$
 3492 measured reflections 3 standard reflections
 3492 independent reflections every 200 reflections
 intensity decay: 12%

Refinement

Refinement on F^2
 $R(F)$ = 0.047
 $wR(F^2)$ = 0.119
 S = 2.36
 3492 reflections
 173 parameters
 H atoms not refined
 $w = 1/[\sigma^2(F_o^2) + 0.00005(F_o^2)^2]$
 $(\Delta/\sigma)_{\max}$ = 0.016

$\Delta\rho_{\max}$ = 0.32 e Å⁻³
 $\Delta\rho_{\min}$ = -0.31 e Å⁻³
 Extinction correction: Zachariasen (1967)
 Extinction coefficient: 2.2 (1) × 10⁻⁶
 Scattering factors from *International Tables for Crystallography* (Vol. C)

The structures are not isomorphous, with space groups *Pna*2₁ ($Z = 4$) and *Pbca* ($Z = 8$), for the carbonyl and thiocarbonyl compounds, respectively.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structures: *SIR92* (Altomare, Cascarano, Giacovazzo & Guagliardi, 1993) for (I); *SHELXS86* (Sheldrick, 1985) for (II). For both compounds, program(s) used to refine structures: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1298). Services for accessing these data are described at the back of the journal.

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