Phenyl[2,4,6-tris(1-methylethyl)phenyl]-methanethione and 4-Methoxyphenyl[2,4,6-tris(1-methylethyl)phenyl]methanethione

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Abstract

The two title compounds, $C_{22}H_{28}S$ and $C_{23}H_{30}OS$, respectively, have almost identical molecular structures, but different crystal structures. The two parts of each molecule are approximately perpendicular to each other, with $S \cdots \gamma H$ distances of 3.06 and 3.02 Å, respectively, suitable for H-atom abstraction in photochemical reactions.

Comment

Thioketones undergo photochemical H-atom abstraction reactions *via* their $(\pi,\pi^*)^1$ excited states, in contrast to their oxygen analogues which react *via* their $(n,\pi^*)^3$ states (Wagner, 1971; Wagner & Park, 1991; de Mayo, 1976; Ramamurthy, 1985; Maciejewski & Steer, 1993). To determine the molecular parameters associated with the photochemical reactions of thioketones, the 2,4,6-triisopropylthiobenzophenone derivatives, (1a) and (1b), have been synthesized and their crystal structures and photochemistry have been studied, for comparison with the known structures and photochemistry of the analogous benzophenones, (1c) and (1d) (Ito, Matsuura & Fukuyama, 1988).

(1n)

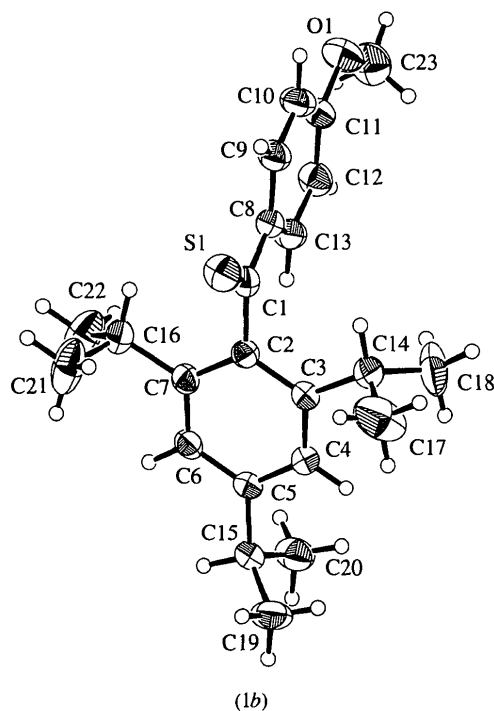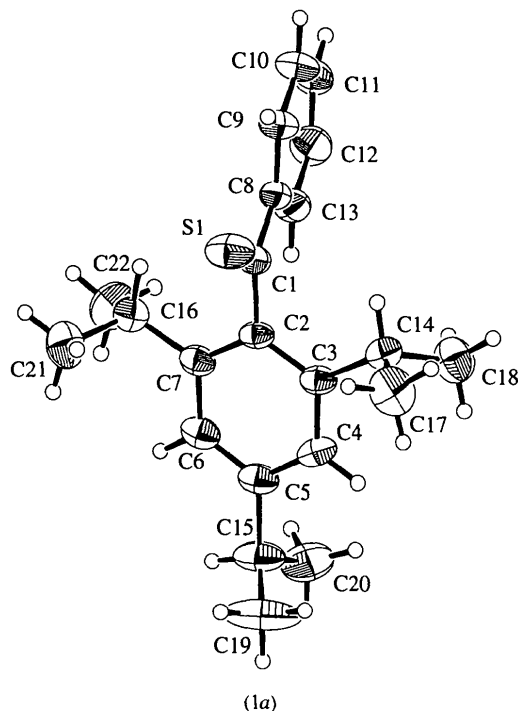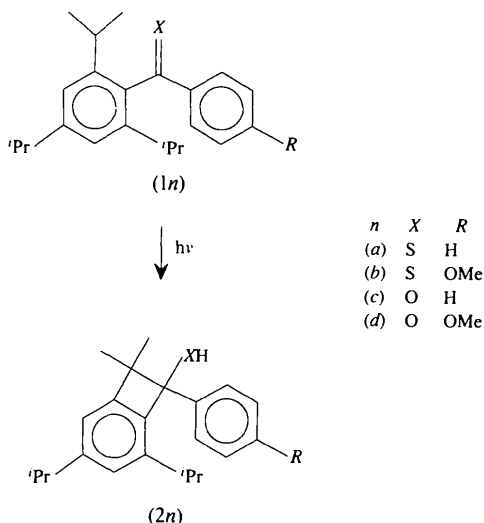|	n	X	R
(a)		S	H
(b)		S	OMe
(c)		O	H
(d)		O	OMe

(2n)

(1a)

(1b)

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

The two compounds, (1a) and (1b), have almost identical molecular structures (Fig. 1), but different crystal structures. In each molecule, the two parts are almost exactly perpendicular to each other. The S1—

C1—C2—C3 and S1—C1—C2—C7 torsion angles are −84.1 (2) and 95.3 (2)° in (1a), and −90.8 (2) and 90.0 (2)° in (1b), respectively (in the molecules in Fig. 1; the crystals are racemates). Related benzophenones exhibit similar conformations (Ito *et al.*, 1988; Fu, Scheffer & Trotter, 1997).

Thioketones (1a) and (1b) exhibit absorption maxima in the visible (600 nm, n,π^*) and UV (320 nm, π,π^*) regions of the spectrum. Irradiation with visible light produces no photochemical reaction, but UV irradiation (λ > 290 nm) of benzene solutions or of crystals leads to photoproducts (2a) and (2b). The geometrical parameters relevant to these photochemical H-atom abstraction reactions are d, ω, Δ and θ, which are the S$\cdots\gamma$H distance, the angular displacement of the γH from the thiocarbonyl plane, and the C=S$\cdots$H and C—H$\cdots$S angles, with ideal values of 3.00 Å, 90, <90 and 180°, respectively (for π,π^*; 3.00 Å, 0, 90 and 180 for n,π^*) (Fu, Scheffer & Trotter, 1996). The measured values for the S$\cdots$(γH on C14) interactions in (1a) and (1b) (Fig. 1) are 3.06 Å, 51, 52, 118° and 3.02 Å, 50, 53, 125°, respectively; the S$\cdots$(γH on C16) distances are slightly longer, 3.28 and 3.18 Å. The parameters deviate from the ideal values, but not unreasonably so. Fairly similar parameters have been measured for the ketones (Ito *et al.*, 1988), with expected shorter O$\cdots\gamma$H distances of 2.88–2.97 Å.

Bond lengths and angles in the two thiobenzophenones, (1a) and (1b), are close to normal values; C=S = 1.628 (2) and 1.639 (2) Å, which is close to the length of 1.636 (9) Å reported for thiobenzophenone (Rindorf & Carlsen, 1979).

Experimental

The title materials were synthesized from the corresponding ketones (Fu, 1994; details have been deposited with the supplementary material).

Compound (1a)

Crystal data

C$_{22}$H$_{28}$S
M_r = 324.52
Monoclinic
$P2_1/n$
a = 9.218 (2) Å
b = 16.055 (4) Å
c = 13.804 (2) Å
β = 94.89 (2)°
V = 2035.5 (7) Å^3
Z = 4
D_x = 1.059 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 24 reflections
θ = 15.0–18.1°
μ = 0.150 mm^{-1}
T = 294 K
Prism
0.60 × 0.40 × 0.30 mm
Blue

Data collection

Rigaku AFC-6S diffractometer
ω–2θ scans
Absorption correction:
  ψ scans (North, Phillips & Mathews, 1968)
  T_{min} = 0.928, T_{max} = 1.000
6476 measured reflections
5930 independent reflections

2059 reflections with I>3σ(I)
R_{int} = 0.024
θ_{max} = 30.03°
h = 0 → 12
k = 0 → 22
l = −19 → 19
3 standard reflections
  every 200 reflections
  intensity decay: 0.26%

Refinement

Refinement on F^2
$R(F)$ = 0.051
$wR(F^2)$ = 0.155
S = 1.31
5930 reflections
208 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + 0.00051(F_o^2)^2]$

$(\Delta/\sigma)_{max}$ = 0.021
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}
Extinction correction: none
Scattering factors from
  International Tables for Crystallography (Vol. C)

Compound (1b)

Crystal data

C$_{23}$H$_{30}$OS
M_r = 354.55
Monoclinic
$P2_1/n$
a = 11.336 (1) Å
b = 13.136 (2) Å
c = 14.240 (2) Å
β = 96.667 (9)°
V = 2106.2 (5) Å^3
Z = 4
D_x = 1.118 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 12.0–38.2°
μ = 1.362 mm^{-1}
T = 294 K
Prism
0.30 × 0.20 × 0.15 mm
Blue

Data collection

Rigaku AFC-6S diffractometer
ω–2θ scans
Absorption correction:
  ψ scans (North, Phillips & Mathews, 1968)
  T_{min} = 0.739, T_{max} = 0.815
4777 measured reflections
4348 independent reflections

2737 reflections with I>3σ(I)
R_{int} = 0.011
θ_{max} = 77.64°
h = 0 → 14
k = 0 → 16
l = −18 → 17
3 standard reflections
  every 200 reflections
  intensity decay: 0.04%

Refinement

Refinement on F^2
$R(F)$ = 0.047
$wR(F^2)$ = 0.145
S = 2.03
4348 reflections
227 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + 0.00022(F_o^2)^2]$
$(\Delta/\sigma)_{max}$ = 0.010

$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Extinction correction:
  Zachariasen (1967)
Extinction coefficient:
  0.20 (4) × 10^{-5}
Scattering factors from
  International Tables for Crystallography (Vol. C)

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: *SIR*92 (Altomare, Cascarano, Giacovazzo & Guagliardi, 1993); program(s) used to refine structures: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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4-[2,4,6-Tris(1-methylethyl)benzoyl]benzoic Acid (S)-(–)-Proline

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Abstract

The title compound, $C_{23}H_{28}O_3.C_5H_9NO_2$, is a 1:1 complex of the benzoic acid derivative and the (S)-proline zwitterion, with two formula units in the asymmetric

unit (with pseudo-symmetry relationships between the separate components). The ketone carbonyl group in each benzoic acid molecule deviates slightly from a position normal to the plane of the triisopropylphenyl ring; the deviations (of about 16°) are in opposite senses in the two molecules, so that the molecules have opposite conformational chiralities, leading to a nearly racemic photoproduct on solid-state photolysis.

Comment

The photochemistry of 2,4,6-triisopropylbenzophenone has received much attention (*e.g.* Ito *et al.*, 1983; Ito & Matsuura, 1988; Wagner & Park, 1991). Although the mechanistic details of the reaction have not been fully established, the system seemed to offer excellent prospects for solid-state asymmetric synthesis by introducing ionic chiral handles (Gudmundsdottir & Scheffer, 1990; Jones, Scheffer, Trotter & Yang, 1994; Gamlin *et al.*, 1996).

Treatment of 4-[2,4,6-tris(isopropyl)benzoyl]benzoic acid with (S)-(–)-proline in ethanol produced a 1:1 complex, (I), whose crystal structure and photochemistry have been studied.
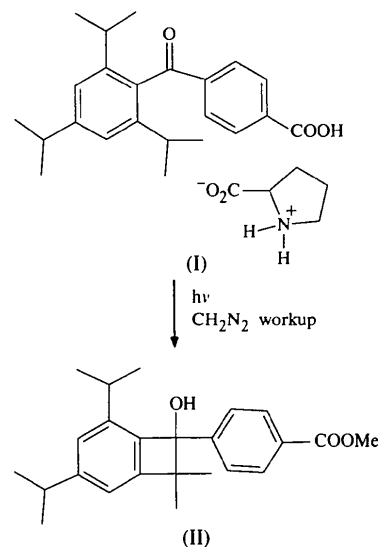
There are two independent formula units in the asymmetric unit. Proline is not sufficiently basic to form a salt with the carboxylic acid and hence the structure contains neutral acid molecules and proline zwitterions (rather than carboxylate anions and ammonium cations). In each of the acid molecules, the two parts of the molecule are not far from being perpendicular to each other (Figs. 1a and 1b), but there are significant deviations (from 90°) of the torsion angles about the C1—C2 and C24—C25 bonds. In the first molecule (Fig. 1a), the O1—C1—C2—C3 and O1—C1—C2—C7 torsion angles are −75.0 (6) and 106.8 (5)°, respectively; in the other molecule (Fig. 1b), the corresponding angles