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

O1—N	1.201 (4)	C1—C2	1.199 (4)
O2—N	1.175 (4)		
O1—N—O2	122.9 (3)	Si—C1—C2	177.9 (3)

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual.* Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *LSFM* in *MolEN.* Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIF IN* in *MolEN.*

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Structure and Photochemistry of Four Adamantylacetophenones

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Abstract

The photochemistry and crystal structures of four α-adamantylacetophenones have been studied, namely, 1-(4-fluorophenyl)-2-(tricyclo[3.3.1.1^{3,7}]dec-1-yl)-ethanone [(1*a*), $C_{18}H_{21}FO$], 1-(4-cyanophenyl)-2-(tricyclo[3.3.1.1^{3,7}]dec-1-yl)ethanone [(1*b*), $C_{19}H_{21}NO$], 1-(4-cyanophenyl)-2-(3-methyltricyclo[3.3.1.1^{3,7}]dec-1-yl)ethanone [(1*c*), $C_{20}H_{23}NO$] and 1-(4-carboxyphenyl)-2-(3-methyltricyclo[3.3.1.1^{3,7}]dec-1-yl)ethanone [(1*d*), $C_{20}H_{24}O_3$]. All four molecules adopt fairly similar conformations, with short γH···O contacts permitting hydrogen abstraction in the photochemical reactions. However, three of the compounds, (1*a*), (1*b*) and (1*d*), are photostable in the solid state and possible reasons for this unreactivity are considered.

Comment

Study of the photochemical Norrish type II γ-hydrogen-abstraction reaction of α-adamantylacetophenones is simplified by the fact that products formed by cleavage of the intermediate 1,4-biradicals are not possible, since they would include the highly strained adamantene (Evans & Trotter, 1989*a*,*b*; Jones *et al.*, 1994). For reactants of type (1) (R = H), the favoured products are two cyclobutanols, with *cis*-OH, (2), or *trans*-OH substituents (relative to the ring junction H atom). The major photoproduct is usually the *trans*-OH isomer, which is presumably more stable than the *cis*-OH isomer, since the latter exhibits greater steric repulsions between a pseudo-axial aryl substituent on the folded four-membered ring and the adamantyl group. Production of the *trans*-OH isomer involves rotation of the adamantyl group by about 90° from the observed solid-state molecular conformation of the adamantylacetophenones; since even the solid-state photoreactions yield the *trans*-OH isomer as the major product, rotation of the approximately spherical adamantyl group appears to be a preferred (energetically favourable) reaction pathway.

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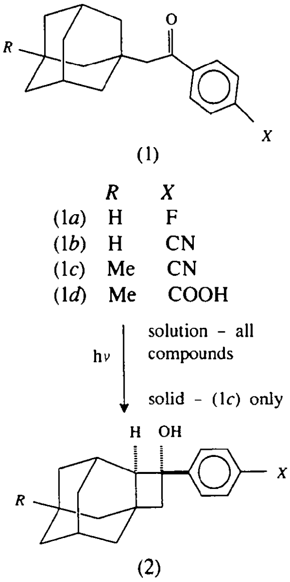


(1)

	R	*X*
(1*a*)	H	F
(1*b*)	H	CN
(1*c*)	Me	CN
(1*d*)	Me	COOH

(2)

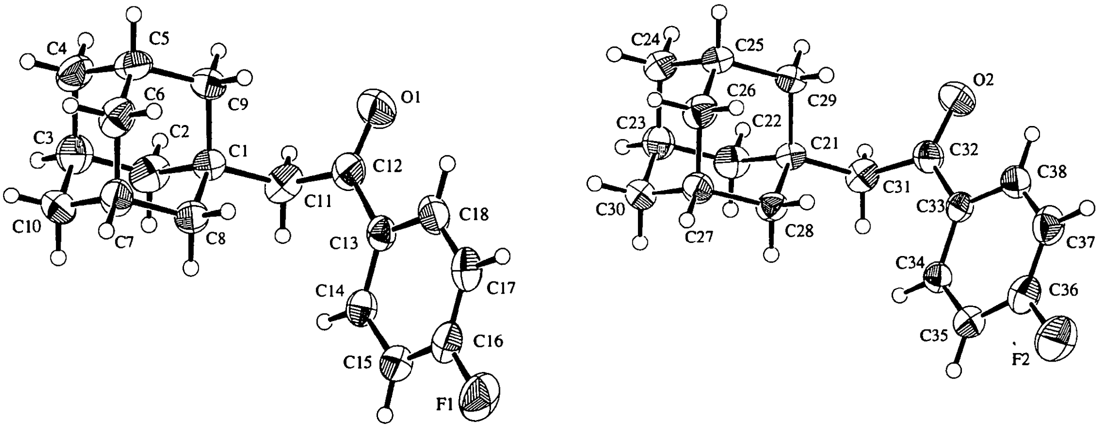
The situation is different for 3-methyl-substituted adamantylacetophenones [(1), *R* = Me], where the presence of the 3-methyl substituent reduces the symmetry of the biradical intermediate and results in six possible cyclization photoproducts, three with *cis*-OH and three with *trans*-OH arrangements (Evans & Trotter, 1989*b*). The major solid-state photoproduct is that isomer (a *cis*-OH) which involves minimum change of molecular conformation during the photoreaction; apparently, rotation of the adamantyl group is now a much less favourable process as a result of the presence of the bulky 3-methyl substituent.

Among four further derivatives, (1*a*)–(1*d*), which have now been studied, the behaviour of (1*c*) conforms to the general principles described above, with the major product of solid-state photolysis (93%) being the *cis*-OH compound (2*c*). The three compounds (1*a*), (1*b*) and (1*d*) are unusual in that they react in solution but are photostable in the solid state. This suggested that these compounds might crystallize with molecular comformations that preclude facile γH abstraction. Crystal structure analyses show in fact that all four molecules, (1*a*)–(1*d*), have quite similar conformations (Fig. 1). For (1*a*) (two independent molecules), (1*b*) and (1*c*), the conformations are very similar to each other (Fig. 1), with one γH atom (on C9) suitably oriented for abstraction by oxygen, with H···O distances of 2.57–2.81 Å (Table 1) [further H···O contacts, hydrogen on C9, or on C8 for (1*b*), are in the range 3.03–3.40 Å]; angular parameters (Table 1) are also in the ranges found for other (reactive) molecules. For (1*d*), the conformations are somewhat different. For one of the (two) independent molecules, the conformation shows rotation of about 100° around C11—C12 [with respect to compounds (1*a*)–(1*c*)], so that γH atoms on C9 and C8 are close to oxygen, 2.57 and 2.50 Å (Table 1). The second molecule of (1*d*) exhibits a rotation of about 120° about C21—C31 (Fig. 1, equivalent to C1—C11 in the other molecules), thus placing the O atom between C9 and C2 (C29 and C22 in Fig. 1), with two γH···O distances of 2.47 and 2.51 Å. For (1*d*), angular parameters are also favourable for γH abstraction.

Thus, in the crystal of (1*c*), the molecular conformation is suitable for abstraction of a γH atom (on C9) by oxygen, with subsequent interaction between the biradical π-orbital lobes (on C9 and C12, lobes facing towards the viewer in Fig. 1), to form a new C9—C12 bond, with reduction of the C9···C12 non-bonded distance of 2.988 (4) Å to a C9—C12 bonded distance of about 1.54 Å. This results in formation of the *cis*-OH isomer, (2), with minimum atomic movement. This structure for (2) is in accord with the detailed NMR data (Yang, 1993). One final point on the photochemistry of (1*c*) is that the crystals are chiral (space group $P2_12_12_1$), although the crystal sample presumably contains some amount of each of the two enantiomorphous crystals. Photolysis of a single crystal of (1*c*) produced (2) in optically active form, $[\alpha]_D = -29°$ (room temperature, 10 mg ml^{-1} chloroform solution), although attempts to measure the enantiomeric excess, with a chiral HPLC column and NMR shift reagents, were unsuccessful.

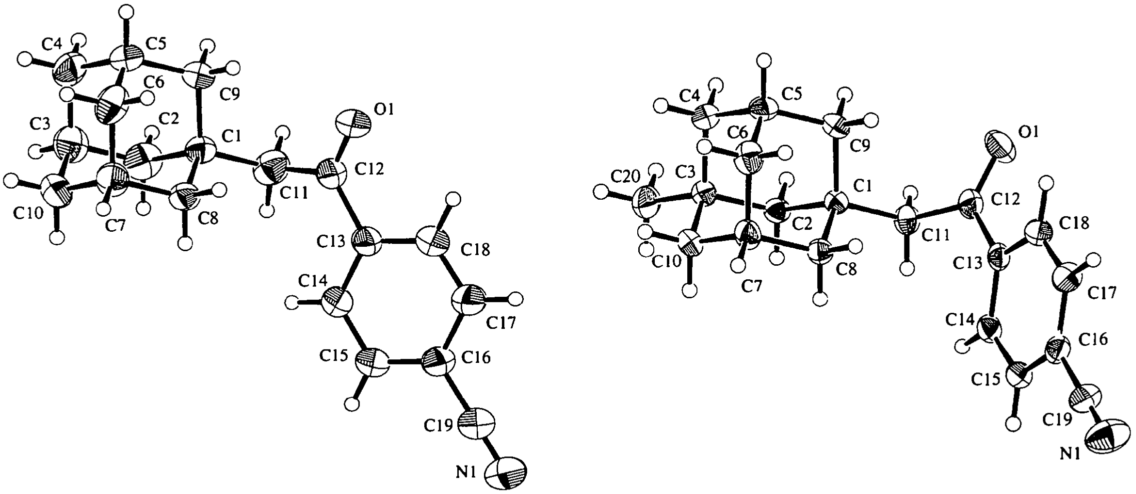
For (1*a*), (1*b*) and (1*d*), the molecular conformations (Fig. 1 and Table 1) are also favourable for γH abstraction, so that the non-reactivity in the solid state cannot be ascribed to unsuitable γH···O interactions. A possibly relevant difference between the reactive (1*c*) and unreactive (1*a*), (1*b*) and (1*d*) molecules is that if (as likely) the closest γH atom is abstracted in each case, then the C···C distances involved in the new bond formation are 2.988 Å in (1*c*) and 3.029 Å in (1*a*) (2.993 Å in the second molecule, but this has a rather longer γH···O distance of 2.81 Å), 3.201 Å in (1*b*), and 3.229 and 3.218 Å in the two (1*d*) molecules. Hydrogen abstraction may occur, with the biradical intermediates undergoing reverse hydrogen transfer, to re-form the starting materials, in preference to forming the new C—C bond. However, the slightly longer distances in (1*a*), (1*b*) and (1*d*) scarcely seem sufficiently long to preclude reaction (since they are all < 3.4 Å, the sum of the van der Waals radii). Another possible explanation for the unreactivity in the solid state is that the molecular motion involved in the reaction, even though minimum, is hindered by intermolecular interactions. However, inspection of the molecular packings (diagrams in the supplementary material) does not reveal any obvious impediments to the reaction process. The exact reason for the photostability of these three ketones is, therefore, still unclear.

The crystal structure of (1*a*) contains two molecules in the asymmetric unit. Independent molecules are related by pseudo-centres of inversion at, for example, $\frac{5}{8},\frac{1}{4},z$ (choice of origin along *c* arbitrary in $Pca2_1$); the deviations of the pairs of pseudo-related atoms



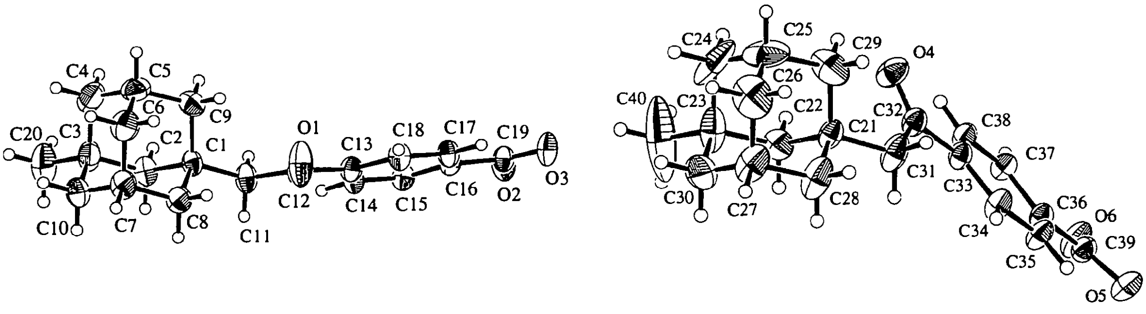
Compound (1*a*) Molecule 1

Compound (1*a*) Molecule 2



Compound (1*b*)

Compound (1*c*)



Compound (1*d*) Molecule 1

Compound (1*d*) Molecule 2

Fig. 1. Views of the title molecules (33% probability displacement ellipsoids). For compound (1*d*) molecule 2, the molecule shown has the opposite chirality to that of the molecule given in the deposited coordinate table and shown in Fig. 2.

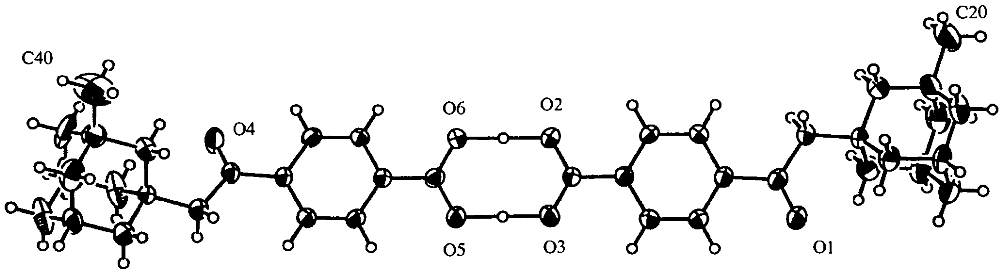


Fig. 2. The non-centrosymmetric hydrogen-bonded dimer of two independent molecules of (1*d*).

from exact centrosymmetry are in the range 0.066–0.526 (6) Å. Compound (1*d*) also contains two independent molecules, which form a non-centrosymmetric hydrogen-bonded dimer (Fig. 2), O···O = 2.614 and 2.629 (5) Å; a similar arrangement is found in a related cyclopentylacetophenone derivative (Evans & Trotter, 1988). The four carboxyl C—O bonds are equal in length [average 1.268 (3) Å], indicating disorder of the carboxyl groups.

Experimental

The title materials were synthesized from the adamantylacetyl chlorides (details in the supplementary material).

Compound (1*a*)

Crystal data

$C_{18}H_{21}FO$
M_r = 272.36
Orthorhombic
$Pca2_1$
a = 12.802 (3) Å
b = 11.181 (3) Å
c = 20.281 (2) Å
V = 2903.0 (9) Å^3
Z = 8
D_x = 1.246 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 22.7–30.5°
μ = 0.672 mm^{-1}
T = 294 K
Prism
0.25 × 0.20 × 0.20 mm
Colourless

Data collection

Rigaku AFC-6S diffractometer
ω–2θ scans
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{\min}$ = 0.854, $T_{\max}$ = 0.874
3086 measured reflections
3086 independent reflections

1960 reflections with $I > 3\sigma(I)$
$\theta_{\max}$ = 77.59°
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 14$
$l = -25 \rightarrow 0$
3 standard reflections every 200 reflections intensity decay: 1.6%

Refinement

Refinement on F^2
$R(F)$ = 0.042
$wR(F^2)$ = 0.125
S = 1.10
3086 reflections
360 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + 0.00106(F_o^2)^2]$

$(\Delta/\sigma)_{\max}$ = 0.0007
$\Delta\rho_{\max}$ = 0.27 e Å^{-3}
$\Delta\rho_{\min}$ = −0.35 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (1*b*)

Crystal data

$C_{19}H_{21}NO$
M_r = 279.38
Monoclinic
$P2_1/a$
a = 11.617 (2) Å
b = 6.643 (6) Å
c = 20.868 (2) Å
β = 103.27 (1)°
V = 1567 (2) Å^3
Z = 4
D_x = 1.184 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 23 reflections
θ = 41.9–49.3°
μ = 0.529 mm^{-1}
T = 294 K
Prism
0.45 × 0.30 × 0.30 mm
Colourless

Data collection

Rigaku AFC-6S diffractometer
ω–2θ scans
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{\min}$ = 0.782, $T_{\max}$ = 0.853
3669 measured reflections
3205 independent reflections

2048 reflections with $I > 3\sigma(I)$
$R_{\rm int}$ = 0.017
$\theta_{\max}$ = 77.48°
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 8$
$l = -26 \rightarrow 25$
3 standard reflections every 200 reflections intensity decay: 0.3%

Refinement

Refinement on F
R = 0.057
wR = 0.171
S = 1.673
3205 reflections
190 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + 0.0009(F_o^2)^2]$

$(\Delta/\sigma)_{\max}$ = 0.0027
$\Delta\rho_{\max}$ = 0.19 e Å^{-3}
$\Delta\rho_{\min}$ = −0.33 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (1*c*)

Crystal data

$C_{20}H_{23}NO$
M_r = 293.41

Mo $K\alpha$ radiation
λ = 0.7107 Å

Orthorhombic
$P2_12_12_1$
$a = 12.021$ (3) Å
$b = 20.149$ (3) Å
$c = 6.655$ (2) Å
$V = 1611.9$ (5) Å^3
$Z = 4$
$D_x = 1.209$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 18.9$–20.8°
$\mu = 0.069$ mm^{-1}
$T = 294$ K
Prism
0.70 × 0.50 × 0.50 mm
Colourless

Data collection

Rigaku AFC-6*S* diffractometer
ω–2θ scans
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{\min} = 0.806$, $T_{\max} = 1.000$
2687 measured reflections
2687 independent reflections

1780 reflections with $I > 3\sigma(I)$
$\theta_{\max} = 30.02°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 28$
$l = 0 \rightarrow 9$
3 standard reflections every 200 reflections intensity decay: 0.07%

Refinement

Refinement on F^2
$R(F) = 0.048$
$wR(F^2) = 0.153$
$S = 1.45$
2687 reflections
199 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + 0.00109(F_o^2)^2]$

$(\Delta/\sigma)_{\max} = 0.0002$
$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (1*d*)

Crystal data

$C_{20}H_{24}O_3$
$M_r = 312.41$
Triclinic
$P\overline{1}$
$a = 12.987$ (3) Å
$b = 18.439$ (5) Å
$c = 7.281$ (2) Å
$\alpha = 101.23$ (2)°
$\beta = 98.32$ (2)°
$\gamma = 91.12$ (2)°
$V = 1690.3$ (7) Å^3
$Z = 4$
$D_x = 1.228$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 23 reflections
$\theta = 17.5$–20.1°
$\mu = 0.081$ mm^{-1}
$T = 294$ K
Plate
0.70 × 0.60 × 0.10 mm
Colourless

Data collection

Rigaku AFC-6*S* diffractometer
ω–2θ scans
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{\min} = 0.696$, $T_{\max} = 1.000$
10 263 measured reflections
9849 independent reflections

3156 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.031$
$\theta_{\max} = 29.99°$
$h = 0 \rightarrow 18$
$k = -25 \rightarrow 25$
$l = -10 \rightarrow 10$
3 standard reflections every 200 reflections intensity decay: 0.24%

Refinement

Refinement on F^2
$R(F) = 0.079$
$wR(F^2) = 0.248$
$S = 2.02$
4268 reflections (to $\theta = 25°$, $> 0.5\sigma$)
416 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + 0.00181(F_o^2)^2]$

$(\Delta/\sigma)_{\max} = 0.0003$
$\Delta\rho_{\max} = 0.39$ e Å^{-3}
$\Delta\rho_{\min} = -0.38$ e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 2.1 (6) × 10^{-6}
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Comparison of selected molecular dimensions (Å, °) of the title compounds*

	(1*a*)-1	(1*a*)-2	(1*b*)	(1*c*)	(1*d*)-1	(1*d*)-2
d	2.64	2.81	2.57	2.73	2.57/2.50	2.47/2.51
ω	59	63	33	63	45/14	9/50
Δ	80	72	94	74	90/100	100/87
θ	112	106	121	110	121/121	122/122
D	3.029 (6)	2.993 (6)	3.201 (3)	2.988 (4)	3.117 (7) 3.229 (7)	3.218 (7) 3.049 (7)
$\varphi(9,1)$	177.7 (3)	177.2 (3)	177.8 (2)	177.2 (2)	176.4 (4)	−177.6 (5)
$\varphi(1,11)$	55.9 (4)	47.1 (4)	72.7 (2)	53.2 (3)	56.7 (6)	−69.3 (6)
$\varphi(11,12)$	−84.7 (5)	−91.6 (4)	−67.6 (3)	−92.0 (3)	16.8 (8)	22.8 (7)
$\varphi(12,13)$	11.1 (5)	8.9 (5)	−17.0 (3)	26.3 (4)	−6.0 (7)	−17.1 (7)

Notes: γH on C9 [C9 and C8 or C2 for (1*d*)-1 or (1*d*)-2],
$d = \text{O}\cdots\gamma\text{H}$ (ideal value < 2.72 Å),
ω = angular displacement of γH from the CO plane (ideal 0°),
$\Delta = \text{C}{=}\text{O}\cdots\gamma\text{H}$ (ideal value 90°),
$\theta = \gamma\text{C}{-}\gamma\text{H}\cdots\text{O}$ (ideal value 180°),
$D = \text{(O)C}\cdots\gamma\text{C}$ (ideal value <3.4 Å),
$\varphi(9,1)$ = C5—C9—C1—C11,
$\varphi(1,11)$ = C9—C1—C11—C12,
$\varphi(11,12)$ = C1—C11—C12—O1,
$\varphi(12,13)$ = C11—C12—C13—C14.

For compounds (1*a*) and (1*c*), the opposite polarity and enantiomorph, respectively, gave the same *R* factors as the reported structures. For (1*d*), the equality of the carboxyl C—O distances and diffuse difference-map peaks for the carboxyl H atoms indicated disorder of the carboxyl groups, and the H atoms were fixed at the centres of the hydrogen bonds; these H atoms are probably disordered about these central sites. The data for (1*d*) are rather poor (thin plate), resulting in a high *R* factor and anomalous displacement ellipsoids for C24 and C40.

For all compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1351). Services for accessing these data are described at the back of the journal. Details of the syntheses and photochemistry of the title compounds, together with packing diagrams for compounds (1*b*) and (1*c*), have also been deposited.

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3-(4-Cyanophenyl)-2,2-dimethyl-1-phenylpropane-1-thione†

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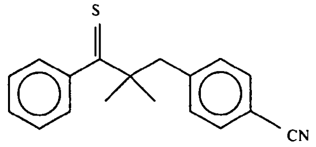
Abstract

The title molecule, $C_{18}H_{17}NS$, contains an all-*trans* arrangement of the central aliphatic system and exhibits an intramolecular S···βH contact of 2.71 Å, which is favourable for hydrogen abstraction in a photochemical reaction. The angular parameters (describing the orientation of the H atom relative to the thiocarbonyl plane) are close to those expected for reaction *via* the (n,π^*) excited state.

Comment

Photolysis of thioketones proceeds *via* the (π,π^*) excited state, with hydrogen abstraction preferably from the δ position, but with γ or ε abstraction in some derivatives (Couture *et al.*, 1981). For thioketones which have only βH atoms available, reaction appears to occur by two separate pathways, following (π,π^*) or (n,π^*) excitations, to give cyclopropylthiols as photoproducts. In our study of the molecular parameters involved in hydrogen abstraction in the photochemical reactions of thioketones (Fu *et al.*, 1997), we have determined the crystal structure of one of the compounds described by Couture *et al.* (1981), namely, 3-(4-cyanophenyl)-2,2-dimethyl-1-phenylpropane-1-thione, (1) [3-(4-cyanophenyl)thiopivalophenone, compound (7*b*), in Couture *et al.* (1981)]. This compound reacts in solution *via* βH-atom abstraction, to yield a mixture of *cis* and *trans* cyclopropylthiols.



(I)

The title molecule (Fig. 1) contains an all-*trans* arrangement of the central aliphatic chain, with both aromatic rings roughly normal to the plane of the chain [torsion angles: C2—C1—C6—C7 −102.4 (3), C2—C1—C6—C11 79.4 (4), C2—C3—C12—C13 −95.6 (4) and C2—C3—C12—C17 88.1 (4)°]. There are intramolecular S···βH (on C3) contacts of 2.71 (H atom on the right in Fig. 1) and 2.93 Å (H atom on the left). The relevant parameters in the hydrogen abstractions are *d*, ω, Δ and θ (S···βH, angular displacement of βH from the thiocarbonyl plane, C=S···H and C—H···S), with ideal values: for (π,π^*), <3.0 Å, 90, <90, 180°, and

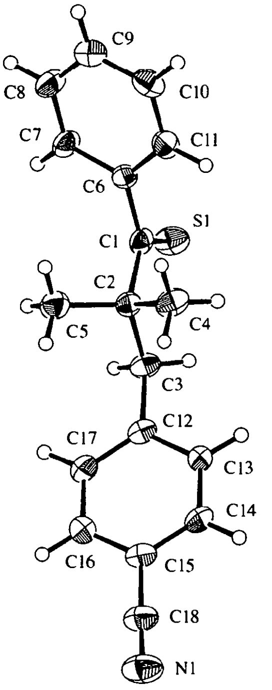


Fig. 1. View of the title molecule (33% probability displacement ellipsoids).

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† Alternative name: 4-(2-methyl-2-thiobenzoylpropyl)benzonitrile.