The crystal structure viewed down the *c* axis is shown in Fig. 2. All the functional groups except N(3) of molecules *A* and *B* participate in hydrogen bonding. The geometry of the hydrogen bonds together with the symmetry code are summarized in Table 3. The cytosine bases of molecules A^{i} and B^{iii} are overlapped in nearly parallel to form a pair of molecules: base separation is about 3·3 Å, the dihedral angle being 0·8 (1)°. The molecules A^{i} and B^{iii} are related by a pseudo-twofold axis along **a**, and are joined together by hydrogen bonds (1) and (2) (Table 3). The pairs are stacked along **c** to form a column through the hydrogen bonds (3) and (4). The columns are held together by the hydrogen bonds (5) to (8) along **a** and (9) to (11) along **b** to complete the whole structure.

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Structure of α-2-Norbornyl-4-chloroacetophenone*

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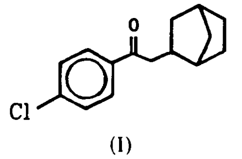
Abstract. $C_{15}H_{17}ClO$, $M_r = 248·75$, monoclinic, $P2_1/a$, $a = 8·836$ (2), $b = 10·222$ (1), $c = 14·578$ (2) Å, $\beta = 95·828$ (7)°, $V = 1309·9$ (3) Å^3, $Z = 4$, $D_x = 1·261$ g cm^{-3}, Mo $K\alpha_1$, $\lambda = 0·70930$ Å, $\mu = 2·6$ cm^{-1}, $F(000) = 528$, $T = 295$ K, $R = 0·037$ for 1227 reflections. Bond lengths and angles are normal, and torsion angles are very similar to those in related cycloalkylacetophenones. H···O abstraction distances are favourable for photochemical reaction, and photoproduct ratios can be rationalized in terms of angles between biradical *p* orbitals.

Introduction. Previous structural and photochemical studies of α-cycloalkylacetophenones have yielded correlations between photochemical behaviour and molecular parameters, and have in particular indicated the dependence of photoproduct ratios on cycloalkyl ring size (Evans & Trotter, 1988*a*,*b*). As an example of a molecule with a conformationally rigid ring system an α-norbornylacetophenone (I) has now been examined.



(I)

Experimental. Colourless crystals, 0·20 × 0·25 × 0·30 mm, Enraf–Nonius CAD-4F diffractometer, lattice parameters from 24 reflections with $\theta = 12–18°$. Intensities for $\theta \leq 25°$, *hkl* 0 to 10, 0 to 12, −17 to 17, ω–2θ scan, ω-scan width $(0·90 + 0·35\tan\theta)°$ at 1·1–6·7° min^{-1}, extended 25% on each side for background measurement, three standard reflections (no

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* 2-(*exo*-2-Bicyclo[2.2.1]heptyl)-1-(4-chlorophenyl)ethanone.

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decay), Lp but no absorption corrections, 2296 independent reflections measured, 1227 with $I \geq 3\sigma(I)$, where $\sigma^2(I) = S + 4(B_1 + B_2) + (0{\cdot}04I)^2$, S = scan, B_1 and B_2 = background counts. Structure determined by direct methods, refined by full-matrix least squares on F, H atoms from a difference map, $w = 1/\sigma^2(F)$, scattering factors from *International Tables for X-ray Crystallography* (1974), locally written, or locally modified versions of standard computer programs (Evans & Trotter, 1988*a*), final $R = 0{\cdot}037$, $wR = 0{\cdot}044$ for 1227 reflections, $S = 1{\cdot}5$, 154 parameters (non-H atoms, plus 68 H-atom parameters), $R = 0{\cdot}117$ for all 2296 reflections, $\Delta/\sigma = 0{\cdot}03$ (mean), 0·20 (maximum), maximum final difference density ±0·17 e Å^{-3}.

Discussion. Final positional parameters are in Table 1, and other data have been deposited.* The molecule (Fig. 1) contains a norbornyl group with normal bond lengths and angles (Table 2); C—C = 1·511–1·541 (5), mean 1·527 Å, C(11)—C(15)—C(14) bridgehead angle = 94·0 (3)°, other angles = 100·9–109·9 (3), mean 103·6°. The acetophenone moiety occupies an *exo* site on the norbornyl nucleus. The aromatic ring is nearly planar [$\chi^2 = 27{\cdot}7$, maximum atomic displacement from mean plane = 0·007 (3) Å], with C—C = 1·368–1·388 (4), mean 1·379 Å, C—C—C = 117·7–121·5 (3), mean 120·0°, and C—Cl = 1·732 (3) Å; the carbonyl group is almost coplanar with the aromatic ring (angle = 1·4°).

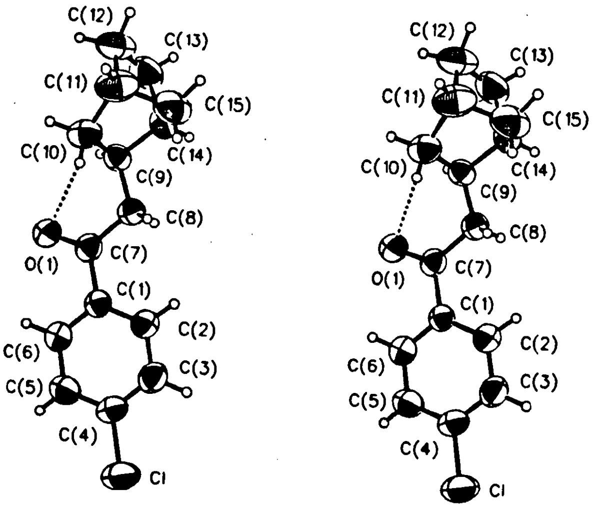

Fig. 1. Stereoview of the α-2-norbornyl-4-chloroacetophenone molecule, with 50% probability ellipsoids for non-H atoms, and arbitrary circles for H atoms. The dotted line indicates the O···γ-H(*exo*) distance of 2·98 Å.

Table 1. *Final positional* (*fractional* × 10^4, Cl × 10^5) *and equivalent isotropic thermal parameters* (U × 10^3 Å^2), *with standard deviations in parentheses*

$U_{eq} = \frac{1}{3}$ × trace of diagonalized U tensor.

	x	y	z	U_{eq}
Cl	30240 (10)	38053 (9)	80857 (5)	87
O(1)	4605 (3)	2392 (2)	3830 (1)	78
C(1)	3662 (3)	3487 (2)	5069 (2)	51
C(2)	2846 (3)	4508 (3)	5401 (2)	60
C(3)	2655 (4)	4616 (3)	6324 (2)	65
C(4)	3286 (3)	3694 (3)	6927 (2)	59
C(5)	4129 (4)	2679 (3)	6630 (2)	66
C(6)	4311 (3)	2583 (3)	5701 (2)	60
C(7)	3866 (3)	3315 (3)	4073 (2)	55
C(8)	3149 (4)	4285 (3)	3390 (2)	58
C(9)	3326 (3)	3975 (2)	2381 (2)	55
C(10)	2400 (4)	2773 (3)	2015 (2)	72
C(11)	1398 (4)	3302 (4)	1198 (2)	93
C(12)	2355 (5)	3611 (5)	416 (2)	91
C(13)	3272 (6)	4811 (4)	783 (3)	96
C(14)	2715 (4)	5058 (4)	1730 (2)	78
C(15)	1036 (5)	4659 (5)	1543 (3)	100

Table 2. *Bond lengths* (Å) *and angles* (°), *with standard deviations in parentheses*

Cl—C(4)	1·732 (3)	C(8)—C(9)	1·528 (4)
O(1)—C(7)	1·220 (3)	C(9)—C(10)	1·541 (4)
C(1)—C(2)	1·383 (4)	C(9)—C(14)	1·521 (4)
C(1)—C(6)	1·388 (4)	C(10)—C(11)	1·511 (5)
C(1)—C(7)	1·493 (4)	C(11)—C(12)	1·520 (5)
C(2)—C(3)	1·377 (4)	C(11)—C(15)	1·520 (6)
C(3)—C(4)	1·368 (4)	C(12)—C(13)	1·536 (6)
C(4)—C(5)	1·372 (4)	C(13)—C(14)	1·533 (5)
C(5)—C(6)	1·383 (4)	C(14)—C(15)	1·536 (5)
C(7)—C(8)	1·499 (4)		

C(2)—C(1)—C(6)	117·7 (3)	C(8)—C(9)—C(10)	113·4 (2)
C(2)—C(1)—C(7)	123·3 (3)	C(8)—C(9)—C(14)	112·7 (2)
C(6)—C(1)—C(7)	119·0 (2)	C(10)—C(9)—C(14)	102·8 (2)
C(1)—C(2)—C(3)	121·5 (3)	C(9)—C(10)—C(11)	103·6 (3)
C(2)—C(3)—C(4)	119·3 (3)	C(10)—C(11)—C(12)	109·9 (3)
Cl—C(4)—C(3)	119·6 (2)	C(10)—C(11)—C(15)	101·1 (3)
Cl—C(4)—C(5)	119·2 (2)	C(12)—C(11)—C(15)	102·1 (4)
C(3)—C(4)—C(5)	121·2 (3)	C(11)—C(12)—C(13)	102·6 (3)
C(4)—C(5)—C(6)	118·9 (3)	C(12)—C(13)—C(14)	103·8 (3)
C(1)—C(6)—C(5)	121·4 (3)	C(9)—C(14)—C(13)	108·4 (3)
O(1)—C(7)—C(1)	119·7 (3)	C(9)—C(14)—C(15)	101·1 (3)
O(1)—C(7)—C(8)	121·4 (2)	C(13)—C(14)—C(15)	100·9 (3)
C(1)—C(7)—C(8)	118·9 (2)	C(11)—C(15)—C(14)	94·0 (3)
C(7)—C(8)—C(9)	115·1 (2)		

The torsion angles, φ_1 = C(7)—C(8)—C(9)—C(10) = 69·4 (4)° and φ_2 = O(1)—C(7)—C(8)—C(9) = 3·9 (4)° are close to ideal values of 60 and 0°, respectively, as found for the cycloalkylacetophenones (Evans & Trotter, 1988*a*); the ψ torsion angle, C(14)—C(9)—C(10)—C(11), is constrained to be close to 0° [0·8 (3)°] by the rigid norbornyl ring system. Both γ-H atoms on C(10) are reasonably favourably sited for abstraction by oxygen in a photochemical reaction. The *exo*-H atom on C(10) has abstraction

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[*] Lists of anisotropic thermal parameters, H-atom positions, bond lengths and angles involving H atoms, torsion angles, structure factors, and a packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44941 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

parameters, *d*, τ and Δ (Evans & Trotter, 1988*a*)* of 2·98 Å, 44° and 75°, respectively, in a boat-like reaction geometry, while *endo* H is slightly less favourably situated, at 3·13 Å, 26° and 100°, in a chair-like geometry.

α-Norbornyl-4-chloroacetophenone undergoes the Norrish type II reaction upon irradiation in solution and in the solid state (Omkaram, 1986), giving cyclization products with a four-membered ring formed by C(7)···C(10) bonding, and *p*-chloroacetophenone and norbornene *via* C(8)—C(9) bond cleavage. The cyclization-to-cleavage ratio is again relatively insensitive to reaction medium (Evans & Trotter, 1988*a,b*), with cyclization of 13±1% in benzene and acetonitrile solutions and in the solid state. Thus the photoreaction seems to be governed by intra- rather than intermolecular forces, and cleavage is the predominant process. The biradical *p*-orbital angles (Evans & Trotter, 1988*a*)* are $\theta_{\rm C=O}=94$, $\theta_\gamma=40$, $\theta_{pp}=64°$. The θ_γ angle is not far from the range of 51–69° found in cyclobutyl- and cyclopentylacetophenones, and the product ratios are very similar, so that cleavage does again seem to be favoured by lower values of θ_γ. The ψ torsion angle of close to 0° also favours cleavage, and the strain involved in fusing an additional four-membered ring to the norbornyl nucleus makes cyclization less likely. No data are available on the cyclization product ratios, since the products are only formed in small amounts.

The molecules are oriented in the unit cell with their long axes along **c**, with the directions of the long axes alternating along **b**.* Nearest neighbours pack around centres of symmetry with the aromatic rings separated by 3·62 Å.

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* d = O···H abstraction distance, τ = angle between the O···H vector and the carbonyl plane, Δ = C=O···H; the biradical *p* orbitals are taken at right angles to the carbonyl (C=O) and C(9)—C(10)—C(11) (γ) planes, and the angles quoted are between these orbitals and the C(8)—C(9) bond.

* For packing diagram, see deposition footnote.

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Structure of α-Cycloheptyl-4-methylacetophenone*

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Abstract. $C_{16}H_{22}O$, M_r = 230·35, monoclinic, $P2_1/a$, a = 16·287 (4), b = 5·5518 (7), c = 15·533 (3) Å, β = 99·95 (1)°, V = 1383·4 (5) Å^3, Z = 4, D_x = 1·106 g cm^{-3}, Mo $K\alpha_1$, λ = 0·70930 Å, μ = 0·6 cm^{-1}, $F(000)$ = 504, T = 295 K, R = 0·042 for 1227 reflections. The molecular conformation and geometry are similar to those of related molecules, with the acetophenone grouping occupying an equatorial site on the twist-chair cycloheptyl ring. Parameters are favourable for photochemical hydrogen abstraction, d = 2·68 Å, τ = 49°, Δ = 76°, and photoproduct ratios fit the previously established correlations with angles between biradical *p* orbitals.

Introduction. Previous studies of series of α-cycloalkyl-4-chloro- and -4-carboxyacetophenones have led to useful correlations between molecular structure parameters and photoproduct ratios (Evans & Trotter, 1988*a,b*). The present paper describes the structure and photochemistry of a 4-methyl derivative (Me-7R).

Experimental. Colourless {100} plates, cut crystal with dimensions 0·20 × 0·25 × 0·35 mm, Enraf–Nonius CAD-4F diffractometer, monochromatized Mo $K\alpha$ radiation, lattice parameters from 25 reflections with θ = 11–21°. Intensities for $\theta \le 25°$, hkl −18 to 18, 0 to 6, 0 to 18, ω–2θ scan, ω-scan width (0·85 + 0·35tanθ)° at 1·5–10° min^{-1}, extended 25% on each side for background measurement, three stan-

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* 2-Cycloheptyl-1-(4-methylphenyl)ethanone.

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