

N(14) du noyau principal de la seconde [distances O(28)—H(O28) = 0,97 et H(O28)···N(14) = 1,83 Å]. Les différentes chaînes ainsi créées laissent apparaître des cavités où viennent s'insérer les molécules de tétrahydrofuranne. Chaque molécule de tétrahydrofuranne est liée à la molécule de grossularine II par une liaison hydrogène entre l'atome d'azote N(1) du groupement indole et l'atome d'oxygène de la molécule de tétrahydrofuranne. Les environnements sont tels que l'atome d'oxygène de cette molécule de tétrahydrofuranne se trouve de façon statistique de part et d'autre du plan moyen défini par les quatre atomes de carbone. Les deux positions sont différenciées par les lettres *A* et *B*. La corrélation importante entre le facteur de multiplicité et le facteur de température de l'atome d'oxygène O(29) n'a pas permis d'affiner ce facteur de multiplicité.

Nous avons pris une valeur de 0,7 pour la position *A* et de 0,3 pour la position *B*, ce qui a permis d'obtenir des facteurs de température semblables pour ces deux atomes dont les positions sont pratiquement symétriques par rapport au plan moyen de la molécule de tétrahydrofuranne. La distance de l'atome d'oxygène

O(29)*A* au plan moyen défini par les atomes C(30), C(31), C(32) et C(33) (plan 3) est de 0,46 (1) Å et celle de l'atome O(29)*B* de 0,61 (1) Å. On peut remarquer que l'atome d'hydrogène H(N1) est approximativement à égale distance de ces deux positions: H(N1)···O(29)*A* = 1,87 Å et H(N1)···O(29)*B* = 1,94 Å.

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2-Cyclohexyl-1-(4-methoxyphenyl)-2-phenylethanone

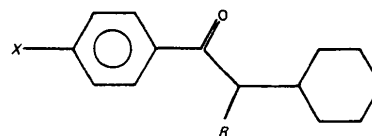
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Abstract. C₂₁H₂₃O₂, *M_r* = 307.41, monoclinic, *C*2, *a* = 22.7637 (25), *b* = 5.7299 (3), *c* = 13.3155 (13) Å, β = 93.101 (5)°, *V* = 1734.2 (3) Å³, *Z* = 4, *D_x* = 1.177 g cm⁻³, Cu *K*α, λ = 1.5418 Å, μ = 5.57 cm⁻¹, *F*(000) = 660, *T* = 295 K, final *R* = 0.049 for 1404 observed reflections. The carbonyl-containing side chain is equatorial with respect to the chair-shaped cyclohexane ring. The equatorial γ-hydrogen atom is 2.70 Å from the ketone O atom (axial hydrogen 3.90 Å), which is near to the upper limit for hydrogen abstraction. The photochemical behaviour has not been established.

Introduction. The geometric requirements for γ-hydrogen abstraction by carbonyl oxygen (Norrish type II reaction) have been studied for six cyclohexylacetophenones: (1) (*X* = CH₃, Cl, CH₂O, COOH, CN) and (2) (Ariel, Ramamurthy, Scheffer & Trotter, 1983; Ariel & Trotter, 1985, 1986).



- (1) *R* = H; *X* = CH₃, Cl, CH₂O, COOH, CN
 (2) *R* = Me; *X* = COOH
 (3) *R* = Ph; *X* = OCH₃

The present paper describes the crystal structure of (3), although it has not been possible to obtain a satisfactory account of the photochemical behaviour.

Experimental. Crystal size 0.1 × 0.2 × 0.5 mm, m.p. 378–379 K, CAD-4 diffractometer, graphite-monochromatized Cu *K*α radiation, lattice parameters from setting of 25 reflections with 40 ≤ θ ≤ 48°. 1572 unique reflections with θ ≤ 65°, *h* = -26–+26, *k* = 0–6, *l* = 0–15; ω-θ scan, ω scan width (1.0 + 0.14 tan θ)°,

extended 25% on each side for background measurement, horizontal aperture (2.0+tan θ)mm, vertical aperture 4 mm; absorption (max. transmission factor 0.94, min. 0.74) and Lp corrections; three standard reflections. Systematic absences (hkl absent if $h+k=2n$) allow space groups $C2$, Cm or $C2/m$. Choice of $C2$ confirmed by E statistics, Patterson function and successful solution of structure and refinement. Structure solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined by full-matrix least squares using *SHELX76* (Sheldrick, 1976) minimizing $\sum w(|F_o| - |F_c|)^2$. Positions of all H atoms calculated, methyl hydrogens refined as rigid CH₃ group possessing C_3 symmetry, thermal parameters of all H atoms refined isotropically. 234 parameters, consisting of 72 positional parameters, 138 anisotropic and 23 isotropic thermal parameters, and a scale factor. Final $R=0.049$, $wR=0.046$ for 1404 reflections for which $F \geq 3\sigma(F)$, where $\sigma^2(I) = S + 2B + [0.04(S-B)]^2$, S = scan count, B = time-averaged background count. $R=0.059$, $wR=0.048$ for all data, $w=1/\sigma^2(F)$, $(\Delta/\sigma)_{\max}=0.06$, $\pm 0.18 \text{ e } \text{Å}^{-3}$ in final difference synthesis; atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965). Space group $C2$ is chiral, so the unit cell contains only one enantiomorph; since the bulk material is racemic, the crystal may well be twinned, but the absence of heavy atoms precludes the use of anomalous dispersion to study the phenomenon. The configuration depicted was chosen arbitrarily.

Discussion. Final atomic coordinates are in Table 1, bond distances, bond angles and selected torsion angles in Table 2.* A stereoview of the molecular conformation is in Fig. 1. The $C(sp^3)-C(sp^3)$ bond distances (Table 2) are in the range 1.505 (6)–1.542 (4) Å, mean 1.525 Å; $C(8)-C(9) = 1.542 (4)$ Å is the longest bond, possibly due to steric effects. The cyclohexane ring angles are in the range 109.3 (3)–113.1 (3)°, mean 111.3°; this ring has a chair conformation with torsion angles $\pm 53.2 (4)-56.9 (5)^\circ$, mean 55.2°, similar to an ideal chair conformation with 111.5° valency angles (torsion angle = 55°; Bucourt & Hainaut, 1965).

Compound (3) crystallizes in a similar conformation to the five derivatives of (1), and to (2), in that the carbonyl-containing side chain is equatorial with respect to the chair-shaped cyclohexane ring (Ariel & Trotter, 1986). However, while in (2) the $CH(R)C_6H_{11}$

Table 1. *Atom coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{Å}^2 \times 10^3$)*

	x	y	z	U_{eq}^*
O(1)	1345 (1)	492	2445 (2)	86
O(2)	3720 (1)	-2009 (6)	4803 (2)	71
C(1)	2531 (1)	-3605 (7)	2962 (2)	51
C(2)	3059 (1)	-3770 (7)	3522 (2)	55
C(3)	3224 (1)	-2001 (7)	4188 (2)	54
C(4)	2865 (1)	-37 (7)	4269 (2)	55
C(5)	2349 (1)	121 (7)	3698 (2)	52
C(6)	2164 (1)	-1651 (6)	3035 (2)	46
C(7)	1596 (1)	-1398 (7)	2464 (2)	56
C(8)	1314 (1)	-3467 (6)	1875 (2)	49
C(9)	643 (1)	-3564 (7)	1976 (2)	52
C(10)	492 (2)	-3848 (10)	3076 (3)	82
C(11)	-168 (2)	-4079 (12)	3190 (3)	104
C(12)	-418 (2)	-6125 (11)	2571 (3)	92
C(13)	-282 (1)	-5864 (10)	1483 (3)	76
C(14)	372 (1)	-5579 (8)	1357 (2)	57
C(15)	4070 (2)	-4041 (9)	4852 (3)	80
C(16)	1497 (1)	-3354 (6)	802 (2)	45
C(17)	1350 (1)	-1457 (7)	184 (2)	55
C(18)	1508 (1)	-1416 (8)	-804 (3)	64
C(19)	1815 (1)	-3268 (8)	-1200 (3)	67
C(20)	1964 (1)	-5135 (8)	-586 (3)	63
C(21)	1808 (1)	-5193 (7)	394 (2)	54

* U_{eq} is one third the trace of the diagonalized anisotropic temperature factor matrix.

Table 2. *Bond lengths (Å), bond angles (°) and torsion angles (°)*

C(1)–C(2)	1.382 (4)	C(12)–C(13)	1.505 (6)
C(2)–C(3)	1.386 (5)	C(13)–C(14)	1.516 (5)
C(3)–C(4)	1.398 (5)	C(9)–C(14)	1.529 (5)
C(4)–C(5)	1.368 (4)	C(3)–O(2)	1.357 (4)
C(5)–C(6)	1.395 (5)	C(15)–O(2)	1.411 (6)
C(1)–C(6)	1.403 (5)	C(8)–C(16)	1.511 (4)
C(6)–C(7)	1.473 (4)	C(16)–C(17)	1.393 (5)
C(7)–O(1)	1.224 (4)	C(17)–C(18)	1.383 (5)
C(7)–C(8)	1.541 (5)	C(18)–C(19)	1.390 (6)
C(8)–C(9)	1.542 (4)	C(19)–C(20)	1.377 (6)
C(9)–C(10)	1.532 (5)	C(20)–C(21)	1.371 (5)
C(10)–C(11)	1.525 (6)	C(16)–C(21)	1.396 (5)
C(11)–C(12)	1.526 (8)		
C(6)–C(1)–C(2)	121.3 (3)	C(14)–C(9)–C(8)	110.7 (3)
C(3)–C(2)–C(1)	119.6 (3)	C(14)–C(9)–C(10)	109.3 (3)
C(2)–C(3)–O(2)	124.9 (3)	C(11)–C(10)–C(9)	112.2 (3)
C(4)–C(3)–O(2)	115.2 (3)	C(12)–C(11)–C(10)	110.7 (4)
C(4)–C(3)–C(2)	119.9 (3)	C(13)–C(12)–C(11)	110.7 (4)
C(5)–C(4)–C(3)	119.9 (3)	C(14)–C(13)–C(12)	111.9 (3)
C(6)–C(5)–C(4)	121.6 (3)	C(13)–C(14)–C(9)	113.1 (3)
C(5)–C(6)–C(1)	117.7 (3)	C(17)–C(16)–C(8)	121.5 (3)
C(7)–C(6)–C(1)	123.5 (3)	C(21)–C(16)–C(8)	120.5 (3)
C(7)–C(6)–C(5)	118.8 (3)	C(21)–C(16)–C(17)	118.0 (3)
C(6)–C(7)–O(1)	119.6 (3)	C(18)–C(17)–C(16)	120.6 (3)
C(8)–C(7)–O(1)	119.3 (3)	C(19)–C(18)–C(17)	120.6 (4)
C(8)–C(7)–C(6)	121.1 (3)	C(20)–C(19)–C(18)	118.7 (3)
C(9)–C(8)–C(7)	111.7 (3)	C(21)–C(20)–C(19)	121.0 (4)
C(16)–C(8)–C(7)	108.7 (3)	C(20)–C(21)–C(16)	121.0 (3)
C(16)–C(8)–C(9)	114.1 (2)	C(15)–O(2)–C(3)	118.7 (3)
C(10)–C(9)–C(8)	111.2 (3)		
C(1)–C(6)–C(7)–O(1)	-168.6 (3)	C(8)–C(9)–C(10)–C(11)	-176.9 (3)
C(1)–C(6)–C(7)–C(8)	10.5 (5)	C(8)–C(9)–C(14)–C(13)	176.0 (3)
C(5)–C(6)–C(7)–O(1)	12.4 (5)	C(14)–C(9)–C(10)–C(11)	-54.4 (4)
C(5)–C(6)–C(7)–C(8)	-168.5 (3)	C(10)–C(9)–C(14)–C(13)	53.2 (4)
O(1)–C(7)–C(8)–C(9)	-41.1 (4)	C(9)–C(10)–C(11)–C(12)	56.9 (5)
O(1)–C(7)–C(8)–C(16)	85.7 (4)	C(10)–C(11)–C(12)–C(13)	-56.4 (5)
C(6)–C(7)–C(8)–C(9)	139.8 (3)	C(11)–C(12)–C(13)–C(14)	55.3 (5)
C(6)–C(7)–C(8)–C(16)	-93.4 (4)	C(12)–C(13)–C(14)–C(9)	-54.9 (5)
C(7)–C(8)–C(9)–C(10)	-60.2 (4)	C(7)–C(8)–C(16)–C(17)	-61.3 (4)
C(7)–C(8)–C(9)–C(14)	178.0 (3)	C(9)–C(8)–C(16)–C(17)	64.1 (4)
C(16)–C(8)–C(9)–C(10)	176.0 (3)	C(7)–C(8)–C(16)–C(21)	120.2 (3)
C(16)–C(8)–C(9)–C(14)	54.3 (4)	C(9)–C(8)–C(16)–C(21)	-114.5 (3)

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and bond distances and angles involving hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42646 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

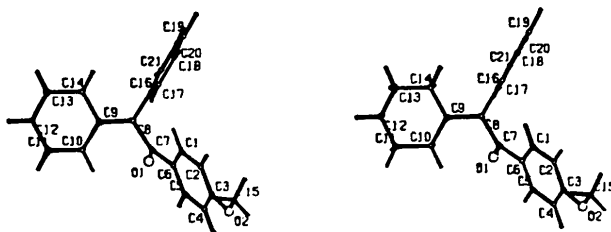


Fig. 1. Stereoscopic view of (3) with crystallographic atomic labelling.

group is rotated about the C(7)—C(8) bond by about 100° relative to (1), (3) has a conformation similar to (1), with rotation only 30° . The angle between the ketone group [plane of C(6), C(7), C(8) and O(1)] and the aromatic ring is $11.8(1)^\circ$ in (3), compared to $21.1(1)$ in (2) and $2.7(1)$ – $13.3(2)^\circ$ in (1). The equatorial γ -hydrogen, H_e [H(101)], in (3) is closer to O(1) (2.70 Å) than the axial γ -hydrogen, H_a [H(102)] (3.90 Å), the 2.70 Å distance being close to the suggested upper limit of 2.72 Å (van der Waals radii sum) for hydrogen abstraction (Appel, Jiang, Scheffer & Walsh, 1983). The angle τ (Ariel & Trotter, 1985) is 63° for H_e [45° in (1), 65° in (2)], and the Δ angle is 76° [90° in (1), 73° in (2)]. As a result of the differing torsion angles about the C(7)—C(8) bond, abstraction of H_e would involve a boat-shaped six-membered transition state, as in (1), and in contrast to the

chair-shaped geometry in (2). It has not proved possible to establish the photochemical behaviour of (3).

The angle formed between the two aromatic rings in the molecule is $64.5(1)^\circ$. Intermolecular distances correspond to van der Waals interactions.

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Structural Characterization and Synthesis of 7-Thia-1,5-diazatricyclo[7.4.1.0^{5,14}]tetradec-9(14)-ene-6,8-dithione

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Abstract. $C_{11}H_{14}N_2S_3$, $M_r = 270.42$, triclinic, $P\bar{1}$, $a = 9.514(2)$, $b = 15.411(3)$, $c = 8.780(2)$ Å, $\alpha = 101.22(2)$, $\beta = 101.60(2)$, $\gamma = 83.45(2)^\circ$, $V = 1233.1$ Å³, $D_m = 1.433(5)$, $D_x = 1.456$ Mg m⁻³, $Z = 4$, $F(000) = 568$, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.617$ mm⁻¹, $T = 295$ K, $R = 0.037$ for 3728 observed

reflections. The two crystallographically independent tricyclic molecules are found to be in an almost identical conformation. The terminal C—S bond distance has a mean value of 1.677(2) Å for the two independent molecules; the mean ring C—S bond length is 1.739(2) Å. There is a short non-bonded intramolecular contact between the terminal and the ring S atoms [mean 2.862 Å].

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