

Fig. 4. Comparison of structure of perhexiline with that of an antihistamine containing aromatic rings (carbinoxamine). Atomic labels followed by (p) = perhexiline and by (c) = carbinoxamine. Perhexiline solid lines, carbinoxamine broken lines. Hydrogen and chlorine atoms have been removed for clarity.

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1-(4-Carboxyphenyl)-2-cyclohexyl-2-methylethanone

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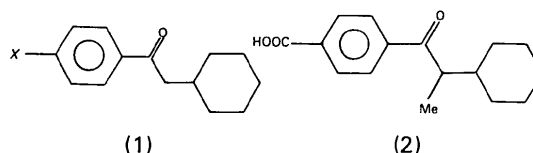
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Abstract. IUPAC name: 4-[(1-cyclohexylethyl)-carbonyl]benzoic acid. $C_{16}H_{20}O_3$, $M_r = 260.33$, monoclinic, $P2_1/n$, $a = 6.264$ (1), $b = 23.977$ (3), $c = 9.731$ (1) Å, $\beta = 100.072$ (6)°, $V = 1439.0$ (3) Å³, $Z = 4$, $D_x = 1.201$ g cm⁻³, $Cu K\alpha$, $\lambda = 1.5418$ Å, $\mu = 6.21$ cm⁻¹, $F(000) = 560$, $T = 295$ K, final $R = 0.058$ for 1678 observed reflections. The carbonyl-containing side chain is equatorial with respect to the chair-shaped cyclohexane ring. The crystal contains centrosymmetric carboxylic-acid dimers.

Introduction. Irradiation of five derivatives of compound (1) ($X = CH_3, Cl, CH_3O, COOH$, and CN) in the solid state results in a Norrish type II reaction, *i.e.* γ -H abstraction by the carbonyl O leading to cleavage and

cyclization (Ariel, Ramamurthy, Scheffer & Trotter, 1983; Ariel & Trotter, 1985); the geometric requirements for the abstraction of the γ -H have been established. The present crystallographic study was undertaken to determine whether a methyl substituent in the α -position, as in compound (2), changes the molecular conformation and thus changes the solid-state reactivity.



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Experimental. D_m not determined. Crystal size 0.2 × 0.2 × 0.5 mm, m.p. 434–435 K; CAD-4 diffractometer, graphite-monochromatized Cu $K\alpha$ radiation; lattice parameters from setting of 23 reflections with $40 \leq \theta \leq 49^\circ$; 1951 unique reflections with $\theta \leq 60^\circ$; ω - $\frac{2}{3}\theta$ scan, ω -scan width $(1.0 + 0.3 \tan \theta)^\circ$, extended 25% on each side for background measurement, horizontal aperture $(2.0 + \tan \theta)$ mm, vertical aperture 4 mm; absorption and L_p corrections; three standard reflections, no significant variation. Structure solved by direct methods using *SHELX76* (Sheldrick, 1976) and refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$. The carboxyl H atom was located in a difference synthesis; the positions of all other H atoms were calculated; methyl H atoms were refined as a rigid CH_3 group possessing C_3 symmetry; the temperature factors of all H atoms were refined isotropically. 198 parameters refined, consisting of 63 positional parameters, 114 anisotropic temperature factors, 20 isotropic temperature factors and a scale factor. Final $R = 0.058$, $wR = 0.056$ for 1678 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. $R = 0.067$, $wR = 0.059$ for all data. $w = 1/\sigma^2(F)$. $(\Delta/\sigma)_{\max} = 0.07$. $\Delta\rho = \pm 0.14 e \text{ \AA}^{-3}$ in final difference synthesis. Atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965). No correction for secondary extinction.

ring is $21.1 (1)^\circ$ in (2), compared to $2.7 (1)$ – $13.3 (2)^\circ$ in compounds (1). Here again the equatorial γ -H atom, H_e [H(101)], is closer to O(1) (2.73 Å) than the axial γ -H atom, H_a [H(102)] (3.54 Å). However, the 2.73 Å distance is close to the suggested upper limit of 2.72 Å (van der Waals radii sum) for H abstraction (Appel, Jiang, Scheffer & Walsh, 1983). The angle τ , the degree

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

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
O(1)	-2655 (3)	4026 (1)	-2414 (2)	81
O(2)	5648 (2)	4845 (1)	3382 (2)	73
O(3)	2558 (3)	4760 (1)	4184 (2)	79
C(1)	2751 (3)	4276 (1)	-537 (2)	59
C(2)	3731 (3)	4459 (1)	769 (2)	58
C(3)	2578 (3)	4511 (1)	1843 (2)	51
C(4)	385 (4)	4376 (1)	1604 (3)	62
C(5)	-592 (3)	4195 (1)	298 (3)	60
C(6)	545 (3)	4145 (1)	-784 (2)	49
C(7)	-681 (3)	3976 (1)	-2185 (2)	56
C(8)	498 (4)	3726 (1)	-3255 (2)	58
C(9)	1145 (3)	3119 (1)	-2808 (2)	57
C(10)	-789 (4)	2736 (1)	-2803 (3)	75
C(11)	-84 (4)	2150 (1)	-2306 (4)	85
C(12)	1448 (4)	1904 (1)	-3181 (3)	87
C(13)	3398 (4)	2280 (1)	-3191 (4)	87
C(14)	2692 (4)	2869 (1)	-3683 (3)	78
C(15)	3642 (3)	4716 (1)	3218 (2)	56
C(16)	-821 (5)	3778 (1)	-4730 (3)	79

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 of (2) is in Fig. 1. The $C(sp^3)$ – $C(sp^3)$ bond distances (Table 2) are in the range 1.509 (2)–1.553 (2) Å, mean 1.527 Å. The longest bond C(8)–C(9) = 1.553 (2) Å is relatively stretched, possibly due to steric effects. The cyclohexane-ring angles are in the range $110.5 (1)$ – $111.7 (1)^\circ$, mean 111.2° ; this ring has a chair conformation with torsion angles $\pm 55.1 (3)$ – $56.0 (3)^\circ$, mean 55.5° , similar to an ideal chair conformation with 111.5° valency angles (torsion angle 55° ; Bucourt & Hainaut, 1965).

Compound (2) crystallizes in a similar conformation to the five derivatives of (1), in that the carbonyl-containing side chain is equatorial with respect to the chair-shaped cyclohexane ring (Ariel & Trotter, 1985). However, the $CH(CH_3)C_6H_{11}$ group is rotated about the C(7)–C(8) bond by about 100° relative to compounds (1). The angle between the ketone group [plane of C(6), C(7), C(8) and O(1)] and the aromatic

Table 2. Bond lengths (Å), bond angles ($^\circ$) and selected torsion angles ($^\circ$)

C(1)–C(2)	1.382 (2)	C(9)–C(10)	1.521 (2)
C(2)–C(3)	1.376 (2)	C(10)–C(11)	1.528 (2)
C(3)–C(4)	1.391 (2)	C(11)–C(12)	1.509 (2)
C(4)–C(5)	1.380 (2)	C(12)–C(13)	1.520 (3)
C(5)–C(6)	1.376 (2)	C(13)–C(14)	1.531 (2)
C(1)–C(6)	1.397 (2)	C(9)–C(14)	1.520 (2)
C(6)–C(7)	1.499 (2)	C(3)–C(15)	1.472 (2)
C(7)–O(1)	1.223 (2)	C(15)–O(2)	1.276 (2)
C(7)–C(8)	1.503 (2)	C(15)–O(3)	1.256 (2)
C(8)–C(9)	1.553 (2)	C(8)–C(16)	1.531 (2)
C(3)–C(2)–C(1)	121.3 (1)	C(16)–C(8)–C(7)	111.5 (1)
C(6)–C(1)–C(2)	119.8 (1)	C(16)–C(8)–C(9)	114.3 (1)
C(4)–C(3)–C(2)	119.1 (1)	C(10)–C(9)–C(8)	113.4 (1)
C(15)–C(3)–C(2)	120.4 (1)	C(14)–C(9)–C(8)	111.9 (1)
C(15)–C(3)–C(4)	120.4 (1)	C(14)–C(9)–C(10)	110.5 (1)
C(5)–C(4)–C(3)	119.5 (1)	C(11)–C(10)–C(9)	111.7 (1)
C(6)–C(5)–C(4)	121.8 (1)	C(12)–C(11)–C(10)	111.0 (2)
C(5)–C(6)–C(1)	118.5 (1)	C(13)–C(12)–C(11)	111.3 (2)
C(7)–C(6)–C(1)	123.5 (1)	C(14)–C(13)–C(12)	111.1 (1)
C(7)–C(6)–C(5)	117.9 (1)	C(13)–C(14)–C(9)	111.5 (2)
C(6)–C(7)–O(1)	118.7 (1)	C(3)–C(15)–O(2)	118.3 (2)
C(8)–C(7)–O(1)	121.1 (1)	C(3)–C(15)–O(3)	119.4 (1)
C(8)–C(7)–C(6)	120.2 (1)	O(2)–C(15)–O(3)	122.3 (2)
C(9)–C(8)–C(7)	108.4 (1)		
C(1)–C(6)–C(7)–O(1)	-159.0 (2)	C(16)–C(8)–C(9)–C(10)	-60.6 (3)
C(1)–C(6)–C(7)–C(8)	23.7 (3)	C(16)–C(8)–C(9)–C(14)	65.3 (3)
C(5)–C(6)–C(7)–O(1)	18.4 (3)	C(8)–C(9)–C(10)–C(11)	-177.9 (2)
C(5)–C(6)–C(7)–C(8)	-158.9 (2)	C(8)–C(9)–C(14)–C(13)	177.5 (2)
O(1)–C(7)–C(8)–C(9)	-103.2 (2)	C(14)–C(9)–C(10)–C(11)	55.5 (3)
O(1)–C(7)–C(8)–C(16)	23.4 (3)	C(10)–C(9)–C(14)–C(13)	-55.1 (3)
C(6)–C(7)–C(8)–C(9)	74.0 (2)	C(9)–C(10)–C(11)–C(12)	-56.0 (3)
C(6)–C(7)–C(8)–C(16)	-159.4 (2)	C(10)–C(11)–C(12)–C(13)	55.7 (3)
C(7)–C(8)–C(9)–C(10)	64.4 (2)	C(11)–C(12)–C(13)–C(14)	-55.5 (3)
C(7)–C(8)–C(9)–C(14)	-169.7 (2)	C(12)–C(13)–C(14)–C(9)	55.4 (3)

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and bond distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42466 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

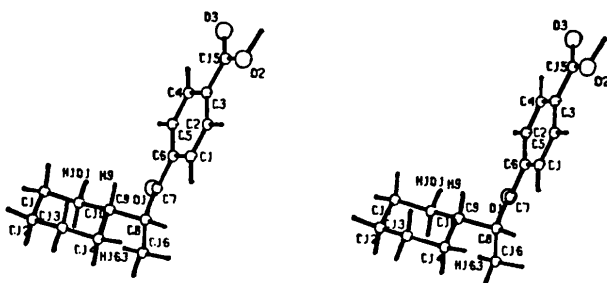


Fig. 1. Stereoscopic view of (2) with crystallographic atomic labelling.

to which the H being abstracted lies outside the mean plane of the carbonyl group, is 65° for H_e , and 39° for H_a [in (1) the corresponding values are 45 and 35° , respectively]. The $\cos^2\tau$ dependence of abstraction, suggested by Wagner (1976), would reduce the relative reactivity of H_e by a factor of 6. The angle Δ , between the H in question and the C(7)—O(1) bond, is 73° for H_e , and 75° for H_a [in (1) the equivalent values are 90 and 66° , respectively], quite distorted from the ideal 90° . Abstraction of H_e would involve a chair-shaped six-membered transition state, in contrast to the boat geometry in compounds (1).

In compounds (1) H_β [H(9)] is in a favourable position for β -abstraction (although no such products are isolated), the O(1) \cdots H β distance being 2.6 Å, $\tau_\beta = 7-13^\circ$, and $\Delta_\beta = 82^\circ$. In contrast, in (2), H(9) is 3.55 Å from O(1), τ_β is 28° , and $\Delta_\beta = 30^\circ$. Another β -H atom, H(163) on the methyl group C(16), is 2.60 Å away from O(1), its $\tau = 3^\circ$, and $\Delta = 83^\circ$. The photochemical behaviour of compound (2) is not yet fully established.

The molecules of (2) form centrosymmetric carboxylic-acid dimers (Fig. 2) with O(2) \cdots O(3) 2.62 Å. The two carboxyl O atoms, O(2) and O(3), are not very distinguishable; C(15)—O(2) is 1.276 (2) Å and C(15)—O(3) is 1.256 (2) Å. The same holds for their bond angles, C(3)—C(15)—O(2) 118.3 (2), C(3)—

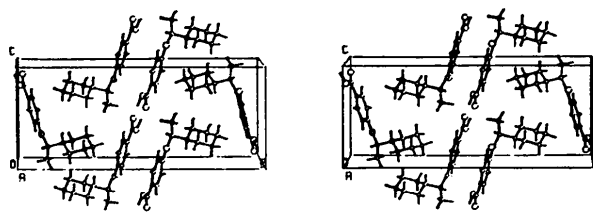


Fig. 2. Stereo packing diagram of (2).

C(15)—O(3) 119.4 (1) $^\circ$. However, a difference Fourier synthesis resolved only one carboxylic H atom, H(O), at 1.23 Å away from O(2). The hydrogen-bonding distance O(3) \cdots H(O) is 1.39 (4) Å and the O(3) \cdots H(O)—O(2) angle is 180° . The carboxyl group may be somewhat disordered, but the X-ray room-temperature data could not define this disorder more precisely. The angle between the carboxyl group and the aromatic ring is 1.4 (2) $^\circ$.

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13-Oxatetracyclo[7.4.2.0^{3,15}.0^{11,14}]pentadecane-6,12-dione

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Abstract. C₁₄H₁₈O₃, $M_r = 234.29$, orthorhombic, *Pbca*, $a = 16.409$ (5), $b = 13.911$ (5), $c = 10.506$ (8) Å, $V = 2398$ (3) Å³, $Z = 8$, $D_m = 1.288$,

$D_x = 1.298$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 0.841$ cm⁻¹, $F(000) = 1008$, $T = 295$ K, $R = 0.056$ for 1154 observations. The structure analysis confirms

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