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Crystal Structures and Photochemistry of α -Cyclopentyl-4-carboxypropiofenone* and α -Cyclooctyl-4-carboxypropiofenone†–Acetic Acid (1:1 Mixed Carboxylic Acid Dimer)

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Abstract

The structures and photochemistry of two α -cycloalkylpropiofenones have been studied for comparison with related acetophenones. Crystal data: $Cu K\alpha_1$, $\lambda = 1.54056 \text{ \AA}$, $T = 295 \text{ K}$; cyclopentyl derivative, $C_{15}H_{18}O_3$, $M_r = 246.31$, triclinic, $P\bar{1}$, $a = 5.867 (1)$, $b = 10.291 (1)$, $c = 11.583 (2) \text{ \AA}$, $\alpha = 87.43 (1)$, $\beta = 80.11 (1)$, $\gamma = 78.25 (1)^\circ$, $V = 674.5 (5) \text{ \AA}^3$, $Z = 2$, $D_x = 1.212 \text{ g cm}^{-3}$, $\mu = 6.4 \text{ cm}^{-1}$, $F(000) = 264$, $R = 0.076$ for 1328 reflections; cyclooctyl derivative, $C_{18}H_{24}O_3$, $C_2H_4O_2$, $M_r = 348.44$, triclinic, $P\bar{1}$, $a = 7.1567 (5)$, $b = 7.7031 (5)$, $c = 18.1728 (2) \text{ \AA}$, $\alpha = 97.162 (5)$, $\beta = 94.670 (6)$, $\gamma = 104.331 (6)^\circ$, $V = 956.5 (1) \text{ \AA}^3$, $Z = 2$, $D_x = 1.209 \text{ g cm}^{-3}$, $\mu = 6.6 \text{ cm}^{-1}$, $F(000) = 376$, $R = 0.044$ for 1586 reflections. The α -methyl substituents have resulted in large changes in molecular conformation relative to the acetophenone analogues, with rotations of about 100° about the C(carbonyl)–C(α) bonds, and rotations of the carbonyl groups out of the aromatic planes by 27° . The cyclopentyl ring is disordered over two envelope conformations and the cyclooctyl ring has a boat–chair

conformation; the propiofenone moieties occupy equatorial sites on the cycloalkyl rings, with molecular parameters being favourable for photochemical reaction *via* hydrogen abstraction. The photoproduct ratios are relatively insensitive to reaction medium, with a trend to increased amounts of cyclization products with increasing cycloalkyl ring size. The cyclopentyl crystal structure contains the usual hydrogen-bonded carboxylic acid dimers, but the cyclooctyl compound exhibits an unusual arrangement, each α -cyclooctyl-4-carboxypropiofenone molecule forming a pair of hydrogen bonds with an acetic acid molecule, *i.e.* the structure contains a mixed acid dimer.

Introduction

Previous crystal structure studies of α -cycloalkylacetophenones (Fig. 1, $Z = H$) have given detailed information on the structural aspects of the photochemical fragmentation or cyclization reactions (Norrish type II reaction) in the solid state and in solution (Evans & Trotter, 1988*a,b*). These reactions are believed to proceed *via* γ -H abstraction to give a 1,4-biradical, which either undergoes cleavage of the α – β bond to yield cycloalkene and acetophenone, or cyclizes to cyclobutanol (Fig. 2). Correlation of the structural and photochemical data leads to several important conclusions. (1) The acetophenone grouping occupies an equatorial site on the non-planar cycloalkyl ring in all

* α -Cyclopentyl- α -methyl-4-carboxyacetophenone; 1-(4-carboxyphenyl)-2-cyclopentylpropan-1-one; 4-(2-cyclopentylpropionyl)-benzoic acid.

† α -Cyclooctyl- α -methyl-4-carboxyacetophenone; 1-(4-carboxyphenyl)-2-cyclooctylpropan-1-one; 4-(2-cyclooctylpropionyl)-benzoic acid.

the molecules, with a γ -H atom suitably oriented for abstraction by carbonyl O, at an H...O abstraction distance of about 2.7 Å. (2) The photoproduct ratios are relatively insensitive to reaction medium, so that the reactions appear to be controlled mainly by intramolecular forces. (3) Variation in aromatic ring substituent(s) X (Fig. 1) produces little change in molecular structure or geometry, and does not influence the photochemical behaviour greatly (Ariel & Trotter, 1985). (4) Increase in cycloalkyl ring size (n , Fig. 1) leads to increased amounts of cyclization products, which have *cis*-fused ring junctions for the smaller, and *trans*-fused ring junctions for the larger cycloalkyl rings, and to increased amounts of cyclization products with OH *trans* to the adjacent ring-junction H atom. This dependence of the photochemical reactions on cycloalkyl ring size can be correlated with angles between biradical p orbitals (Fig. 2) and with related ring torsion angles, with the detailed geometry of the biradicals (as deduced from the reactant geometries), and with the steric stability of the photoproducts.

Change of substituent at the α position (Z in Fig. 1) has been shown to alter the photochemical behaviour in related systems, with α -methyl substitution resulting in increased amounts of cyclization photoproducts (Lewis & Hilliard, 1970). This has been attributed to steric interactions between the α -methyl group and the aromatic ring preventing the attainment of a conformation favourable for cleavage.

The present paper investigates the effects of α -methyl substitution in α -cycloalkylacetophenones on molecular conformation and geometry, and examines any consequent changes in photochemical behaviour. The number of compounds which could be studied is limited, since only the 4-carboxy derivatives are solid at room temperature. Crystal structures are determined for α -cyclopentyl- and α -cyclooctyl-4-carboxypropio-phenones (Fig. 1, $X = \text{CO}_2\text{H}$, $Z = \text{Me}$, $n = 5$ and 8). Difficulty was encountered in obtaining suitable crystals, especially for the cyclooctyl compound, for which crystals finally obtained from acetic acid proved to be a 1:1 complex. Crystal data were also obtained for the cycloheptyl derivative ($n = 7$), but disorder prevented a detailed crystal structure solution.

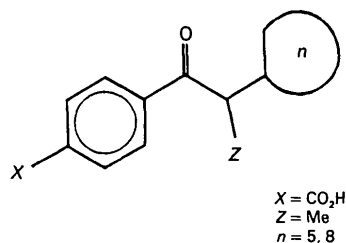


Fig. 1. α -Cycloalkylpropio-phenones (n = number of C atoms in cycloalkyl ring).

Experimental

Crystals of the cyclopentyl compound, $\text{CO}_2\text{H-Me-5R}$, show {100}, {010} and {001} forms, dimensions 0.2 × 0.2 × 0.2 mm [cyclooctyl compound, $\text{CO}_2\text{H-Me-8R}$, {001} plates, 0.2 × 0.3 × 0.1 mm], Enraf-Nonius CAD-4F diffractometer, lattice parameters from 25 reflections with $\theta = 35\text{--}50^\circ$. Intensities for $\theta \leq 75^\circ$, hkl : -6 to 6, -12 to 12, 0 to 13 [0 to 8, -8 to 8, -21 to 21], ω -2 θ scan, ω -scan width $(0.90 + 0.14 \tan \theta)^\circ$ [$(0.80 + 0.14 \tan \theta)^\circ$] at 1.4–10° min⁻¹, extended 25% on each side for background measurement, three standard reflections, no decay [uniform 60% decay of all three standards, owing to slow volatilization of the crystal; the great difficulty encountered in obtaining a crystal of this material precluded recollection of the data with precautions to prevent decay; correction made for the decay by multiplying the intensities by $I_o(\text{standards})/I_t(\text{standards}, t = \text{time})$, Lp but no absorption corrections, 2284 [3366] reflections measured, 1328 [1586] with $I \geq 3\sigma(I)$, where $\sigma^2(I) = S + 4(B_1 + B_2) + (0.04I)^2$, with $S = \text{scan}$, B_1 and $B_2 = \text{background counts}$.

Many attempts to solve the structure of $\text{CO}_2\text{H-Me-5R}$ by direct methods were unsuccessful. The orientation and position of a 4-carboxyacetophenone dimer fragment was determined from the Patterson function, and the remainder of the structure then obtained from electron-density maps. Refinement was

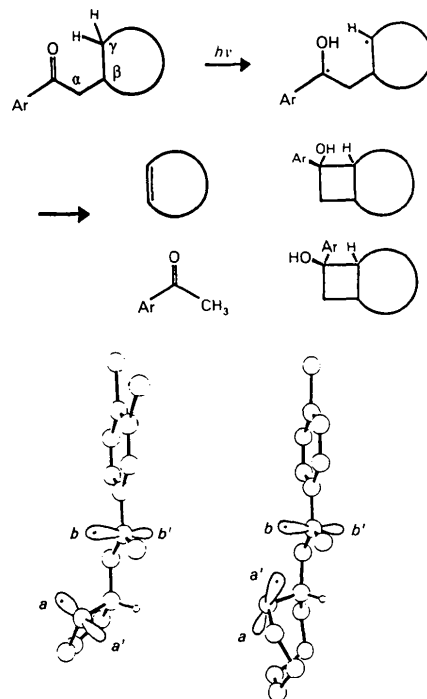


Fig. 2. The Norrish type II reaction and orientation of the radical p -orbitals for cyclopentyl- and cyclooctylacetophenones.

by full-matrix least squares on F . High apparent thermal motion and anomalous geometry indicated disorder of the five-membered cyclopentyl ring over two molecular conformations related by rotation of $\sim 180^\circ$ about C(8)–C(9) and some rotation about C(7)–C(8). The disorder was treated by splitting each ring-atom site, and C(15), into two isotropic atoms (Fig. 1). The alternative of a $P1$ model was examined by using one set of the split positions for one of the molecules in the unit cell, and the other set for the second molecule, which has opposite chirality at C(8) (the bulk material is racemic); there was no supercell such as that found for α -cyclopentyl-4-carboxyacetophenone (Evans & Trotter, 1988*b*). The following points are relevant to the $P1$ refinement: (i) the least-squares matrix was poorly conditioned, with many high correlation coefficients between parameters of related atoms; (ii) the R factors were not significantly improved over the $P\bar{1}$ structure (although the $P1$ refinement was not taken to convergence because of the poorly conditioned matrix); (iii) a difference synthesis showed residual density which suggested $P\bar{1}$ symmetry; (iv) there are no anomalously short intermolecular distances involving disordered atoms in $P\bar{1}$, so that each orientation can occupy the molecular site; (v) previous experience with five-membered rings indicates that disorder is a not-uncommon phenomenon; (vi) previous experience with possible disordered systems indicates that centrosymmetric disordered models usually fit the data better than non-centrosymmetric (pseudo-centrosymmetric) ordered models. The $P1$ model was therefore discarded, and refinement of the disordered $P\bar{1}$ structure proceeded. Initial refinement indicated approximately equal occupancies of two disordered sites, and the occupancy factors were fixed at 50%; isotropic thermal parameters were used for the half-weight disordered atoms (it might have been possible to refine these atoms with anisotropic parameters, but the more-conservative use of isotropic parameters was adopted). H atoms were fixed in calculated positions (except for the carboxyl H atom, which could not be located on a difference map). The appropriate weighting scheme was derived by analyzing values of $w\Delta F^2$; this analysis indicated that $w = 1$ for all reflections with $I \geq 3\sigma(I)$ gave uniform values of $w\Delta F^2$ averaged over ranges of $|F_o|$, $\sin\theta/\lambda$ and Miller indices, and these unit weights were used in the final refinement cycles. 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 $R = 0.076$ (the high value is probably due to difficulty in treating the disorder), $wR = 0.066$ for 1328 reflections, $S = 2.8$, 133 parameters, $R = 0.115$ for all 2284 reflections, $\Delta/\sigma = 0.005$ (mean), 0.040 (maximum), maximum final difference density $\pm 0.30 \text{ e } \text{Å}^{-3}$.

The $\text{CO}_2\text{H-Me-8R}$ structure could also not be solved by direct methods. The Patterson map could not be

interpreted in terms of 4-carboxyacetophenone hydrogen-bonded dimers, but an orientation and position were derived for a carboxyacetophenone fragment. Electron-density maps then revealed the remainder of the structure, which was found to contain an α -cyclooctyl-4-carboxypropio-phenone molecule, linked by two carboxyl-type hydrogen bonds to an acetic acid molecule. Refinement then proceeded normally, with H atoms located on a difference map and refined with isotropic thermal parameters, $w = 1/\sigma^2(F)$ gave uniform average values of $w\Delta F^2$ over ranges of $|F_o|$, $\sin\theta/\lambda$ and Miller indices. Final $R = 0.044$, $wR = 0.047$ for 1586 reflections, $S = 1.7$, 226 parameters (non-H atoms, plus 112 H-atom parameters), $R = 0.125$ for all 3366 reflections, $\Delta/\sigma = 0.007$ (mean), 0.100 (maximum), maximum $\Delta\rho \pm 0.22 \text{ e } \text{Å}^{-3}$.

Crystal data for α -cycloheptyl-4-carboxypropio-phenone, $\text{CO}_2\text{H-Me-7R}$, are: $\text{C}_{17}\text{H}_{22}\text{O}_3$, $M_r = 274.36$, triclinic, $P\bar{1}$, $a = 6.601$ (5), $b = 9.822$ (4), $c = 12.069$ (8) Å, $\alpha = 92.67$ (2), $\beta = 95.96$ (2), $\gamma = 99.48$ (3)°, $V = 766.0 \text{ Å}^3$, $Z = 2$, $D_x = 1.189 \text{ g cm}^{-3}$, $\mu = 6.5 \text{ cm}^{-1}$, $F(000) = 296$. Intensity data were measured and the structure determined and refined to $R = 0.10$. However extensive disorder in the seven-membered ring prevented accurate determination of the important molecular parameters, and the analysis was abandoned. The cycloheptyl derivative has a chiral centre at C(8), and the same considerations apply with reference to $P1/P\bar{1}$ as described above for the cyclopentyl compound; the disorder is much more severe for the cycloheptyl molecule, with an apparently planar seven-membered ring, but very large apparent thermal parameters perpendicular to the pseudo-ring plane.

Discussion

Final positional parameters are in Table 1, and other data have been deposited.* Both structures contain hydrogen-bonded carboxylic acid dimers (Fig. 3). For $\text{CO}_2\text{H-Me-5R}$ the dimeric units contain the usual arrangement of carboxylate groups hydrogen bonded about a centre of symmetry; $\text{CO}_2\text{H-Me-8R}$ contains an unusual arrangement with each carboxyacetophenone molecule forming a pair of hydrogen bonds with an acetic acid molecule, *i.e.* the structure contains a mixed acid dimer. The carboxyl groups are disordered in both structures, since C–O distances (Table 2) are 1.260 and 1.271 (6), mean 1.266 Å for $\text{CO}_2\text{H-Me-5R}$, and 1.252–1.274 (3), mean 1.262 Å for $\text{CO}_2\text{H-Me-8R}$, with C–C–O angles 117.9 and 118.5 (5), and 117.8–119.4 (4)°. The carboxyl H atom could not be located

* Lists of anisotropic thermal parameters, H-atom positions, torsion angles and structure factors, and packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44900 (48 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional (fractional $\times 10^4$, primed atoms $\times 10^3$) and isotropic thermal parameters ($U \times 10^3 \text{ \AA}^2$), with standard deviations in parentheses*

	$U_{\text{eq}} = \frac{1}{3} \times \text{trace of the diagonalized } U \text{ tensor.}$			$U_{\text{eq}}/U_{\text{iso}}$
	<i>x</i>	<i>y</i>	<i>z</i>	
CO₂H-Me-5R				
C(1)	-4232 (8)	-4498 (5)	-1898 (4)	63
C(2)	-5291 (9)	-5573 (6)	-1965 (5)	77
C(3)	-4360 (9)	-6787 (5)	-1556 (5)	78
C(4)	-2326 (9)	-6984 (5)	-1055 (4)	62
C(5)	-1267 (9)	-5906 (5)	-977 (4)	67
C(6)	-2190 (9)	-4676 (5)	-1402 (4)	68
C(7)	-5394 (11)	-3167 (6)	-2340 (5)	79
C(8)	-3886 (10)	-2148 (5)	-2782 (5)	76
C(14)	-1268 (10)	-8309 (5)	-603 (5)	70
O(1)	-7497 (7)	-2953 (4)	-2359 (4)	114
O(2)	670 (7)	-8436 (4)	-219 (3)	89
O(3)	-2334 (7)	-9248 (4)	-638 (4)	99
C(9)'	-343 (2)	-217 (1)	-416 (1)	71 (3)
C(10)'	-220 (3)	-353 (1)	-466 (1)	107 (4)
C(11)'	-68 (3)	-323 (2)	-583 (1)	120 (5)
C(12)'	-50 (3)	-188 (2)	-583 (1)	97 (5)
C(13)'	-178 (2)	-124 (1)	-468 (1)	81 (4)
C(15)'	-483 (3)	-88 (2)	-227 (2)	136 (7)
C(9)''	-233 (2)	-256 (1)	-386 (1)	68 (3)
C(10)''	-349 (2)	-295 (1)	-487 (1)	84 (3)
C(11)''	-187 (2)	-277 (1)	-599 (1)	90 (4)
C(12)''	34 (3)	-218 (2)	-557 (2)	115 (6)
C(13)''	-76 (2)	-161 (1)	-446 (1)	78 (3)
C(15)''	-554 (2)	-71 (1)	-272 (1)	84 (4)
CO₂H-Me-8R				
C(1)	2646 (4)	-113 (4)	6758 (1)	48
C(2)	2538 (6)	-1666 (4)	6263 (2)	60
C(3)	978 (5)	-2344 (5)	5721 (2)	61
C(4)	-534 (5)	-1518 (4)	5670 (2)	52
C(5)	-403 (6)	53 (4)	6163 (2)	64
C(6)	1179 (5)	741 (4)	6690 (2)	61
C(7)	4316 (5)	690 (4)	7352 (2)	57
C(8)	5434 (5)	-486 (4)	7691 (2)	58
C(9)	4184 (5)	-1577 (4)	8223 (1)	53
C(10)	3988 (6)	-335 (5)	8928 (2)	69
C(11)	2036 (7)	-656 (6)	9203 (3)	89
C(12)	1187 (9)	-2386 (7)	9511 (3)	114
C(13)	734 (9)	-4148 (8)	8958 (3)	114
C(14)	2242 (11)	-5206 (7)	8951 (4)	120
C(15)	4332 (9)	-4180 (7)	9015 (2)	97
C(16)	4995 (8)	-3186 (6)	8381 (2)	82
C(17)	-2254 (5)	-2304 (4)	5110 (2)	56
C(18)	7437 (7)	600 (8)	8060 (3)	91
O(1)	4697 (4)	2320 (3)	7587 (1)	81
O(2)	-2348 (4)	-3760 (3)	4695 (1)	76
O(3)	-3563 (4)	-1463 (3)	5077 (1)	74
C(19)	-6669 (5)	-4328 (5)	3639 (2)	62
C(20)	-8325 (8)	-5083 (7)	3042 (3)	80
O(4)	-5411 (4)	-5225 (3)	3722 (1)	76
O(5)	-6542 (4)	-2835 (3)	4030 (1)	78

Table 2. *Bond lengths (\AA), bond angles ($^\circ$) and selected torsion angles ($^\circ$), with standard deviations in parentheses*

CO₂H-Me-5R			
C(1)–C(2)	1.386 (6)	C(8)–C(15)'	1.43 (2)
C(1)–C(6)	1.392 (6)	C(8)–C(9)''	1.436 (11)
C(1)–C(7)	1.510 (7)	C(8)–C(15)''	1.596 (14)
C(2)–C(3)	1.356 (7)	C(9)'–C(10)'	1.53 (2)
C(3)–C(4)	1.390 (7)	C(9)''–C(13)''	1.537 (15)
C(4)–C(5)	1.391 (6)	C(10)'–C(11)'	1.54 (2)
C(4)–C(14)	1.490 (7)	C(11)'–C(12)'	1.42 (2)
C(5)–C(6)	1.376 (6)	C(12)'–C(13)'	1.52 (2)
C(7)–C(8)	1.523 (7)	C(9)''–C(10)''	1.56 (2)
C(7)–O(1)	1.212 (6)	C(9)''–C(13)''	1.534 (15)
C(14)–O(2)	1.271 (6)	C(10)''–C(11)''	1.50 (2)
C(14)–O(3)	1.260 (6)	C(11)''–C(12)''	1.69 (2)
C(8)–C(9)'	1.569 (12)	C(12)''–C(13)''	1.43 (2)
CO₂H-Me-8R			
C(2)–C(1)–C(6)	119.1 (5)	C(7)–C(8)–C(9)'	107.8 (6)
C(2)–C(1)–C(7)	118.1 (5)	C(7)–C(8)–C(15)'	112.5 (9)
C(6)–C(1)–C(7)	122.7 (5)	C(9)''–C(8)–C(15)'	115.6 (9)
C(1)–C(2)–C(3)	120.8 (5)	C(4)–C(14)–O(2)	118.5 (5)
C(2)–C(3)–C(4)	120.9 (5)	C(4)–C(14)–O(3)	117.9 (5)
C(3)–C(4)–C(5)	118.5 (5)	O(2)–C(14)–O(3)	123.6 (5)
C(3)–C(4)–C(14)	121.9 (5)	C(8)–C(9)''–C(10)'	113.6 (9)
C(5)–C(4)–C(14)	119.6 (5)	C(8)–C(9)''–C(13)''	111.3 (9)
C(4)–C(5)–C(6)	120.8 (5)	C(10)''–C(9)''–C(13)''	104.4 (10)
C(1)–C(6)–C(5)	119.8 (4)	C(9)''–C(10)''–C(11)''	105.2 (11)
C(1)–C(7)–C(8)	119.2 (5)	C(10)''–C(11)''–C(12)''	108.0 (13)
C(1)–C(7)–O(1)	118.9 (5)	C(11)''–C(12)''–C(13)''	110.2 (12)
C(8)–C(7)–O(1)	121.8 (5)	C(9)''–C(13)''–C(12)''	104.3 (11)
CO₂H-Me-8R			
C(1)–C(2)	1.386 (4)	C(9)–C(16)	1.541 (4)
C(1)–C(6)	1.375 (4)	C(10)–C(11)	1.495 (5)
C(1)–C(7)	1.495 (4)	C(11)–C(12)	1.516 (6)
C(2)–C(3)	1.375 (4)	C(12)–C(13)	1.531 (7)
C(3)–C(4)	1.387 (4)	C(13)–C(14)	1.505 (6)
C(4)–C(5)	1.391 (4)	C(14)–C(15)	1.496 (7)
C(4)–C(17)	1.480 (4)	C(15)–C(16)	1.505 (5)
C(5)–C(6)	1.371 (5)	C(17)–O(2)	1.255 (3)
C(7)–C(8)	1.503 (4)	C(17)–O(3)	1.265 (3)
C(7)–O(1)	1.229 (3)	C(19)–C(20)	1.488 (5)
C(8)–C(9)	1.554 (4)	C(19)–O(4)	1.274 (3)
C(8)–C(18)	1.522 (5)	C(19)–O(5)	1.252 (3)
C(9)–C(10)	1.539 (4)		
C(2)–C(1)–C(6)	118.7 (3)	C(8)–C(9)–C(10)	111.3 (3)
C(2)–C(1)–C(7)	122.5 (3)	C(8)–C(9)–C(16)	109.6 (3)
C(6)–C(1)–C(7)	118.8 (3)	C(10)–C(9)–C(16)	114.2 (3)
C(1)–C(2)–C(3)	120.3 (4)	C(9)–C(10)–C(11)	117.2 (3)
C(2)–C(3)–C(4)	120.9 (3)	C(10)–C(11)–C(12)	120.5 (4)
C(3)–C(4)–C(5)	118.4 (3)	C(11)–C(12)–C(13)	116.2 (4)
C(3)–C(4)–C(17)	120.7 (3)	C(12)–C(13)–C(14)	117.1 (5)
C(5)–C(4)–C(17)	120.9 (3)	C(13)–C(14)–C(15)	118.2 (4)
C(4)–C(5)–C(6)	120.2 (4)	C(14)–C(15)–C(16)	117.6 (5)
C(1)–C(6)–C(5)	121.4 (3)	C(9)–C(16)–C(15)	119.2 (4)
C(1)–C(7)–C(8)	120.8 (3)	C(4)–C(17)–O(2)	118.9 (3)
C(1)–C(7)–O(1)	118.7 (3)	C(4)–C(17)–O(3)	117.8 (3)
C(8)–C(7)–O(1)	120.4 (3)	O(2)–C(17)–O(3)	123.3 (3)
C(7)–C(8)–C(9)	109.1 (3)	C(20)–C(19)–O(4)	118.0 (4)
C(7)–C(8)–C(18)	111.9 (3)	C(20)–C(19)–O(5)	119.4 (4)
C(9)–C(8)–C(18)	113.6 (3)	O(4)–C(19)–O(5)	122.6 (3)

Intraannular torsion angles

	This work	Boat-chair*
9–10	-96.9	-102.2
10–11	66.9	65.0
11–12	-64.5	-65.0
12–13	96.3	102.2
13–14	-40.9	-44.7
14–15	-66.2	-65.0
15–16	65.6	65.0
16–9	40.3	44.7

* Hendrickson (1967).

for CO₂H-Me-5R, and those for CO₂H-Me-8R refined to positions essentially in the centres of the hydrogen bonds, which are probably means of two disordered sites. The O–H...O distances are 2.606 (6) Å in CO₂H-Me-5R, and 2.618 and 2.647 (3) Å in CO₂H-Me-8R.

The aromatic rings in both molecules are not far from planar ($\chi^2 = 2.9$ and 58.2), with maximum deviation 0.014 (4) Å. The carboxyl groups are nearly coplanar with the rings, but the carbonyl groups are rotated out of the ring planes by 27° in both molecules. Bond lengths and angles are in the ranges 1.36–1.39 Å and 118–121°.

The cyclopentyl ring is disordered over two conformations, one a C(9) envelope and the other a

C(13) envelope (Fig. 3). As a result of the disorder the atomic positions are not very accurately established, and bond lengths and angles show rather wide

Double-primed atoms

111.6 (6)

108.9 (6)

118.9 (7)

118.5 (5)

117.9 (5)

123.6 (5)

113.6 (9)

111.3 (9)

103.6 (9)

105.2 (11)

106.6 (10)

108.0 (13)

110.2 (12)

102.0 (12)

106.6 (11)

variations (Table 2). The cyclooctyl ring has a boat-chair conformation, with intraannular torsion angles in good agreement with ideal values (Table 2). Bond lengths are normal, 1.495–1.541 (4–7), mean 1.516 Å, and bond angles show the usual increase over tetrahedral values, 114.2–120.5 (4), mean 117.5°.

In both structures the propiophenone moieties occupy equatorial sites on the cycloalkyl rings (Fig. 3). The presence of the α -methyl substituent has resulted in

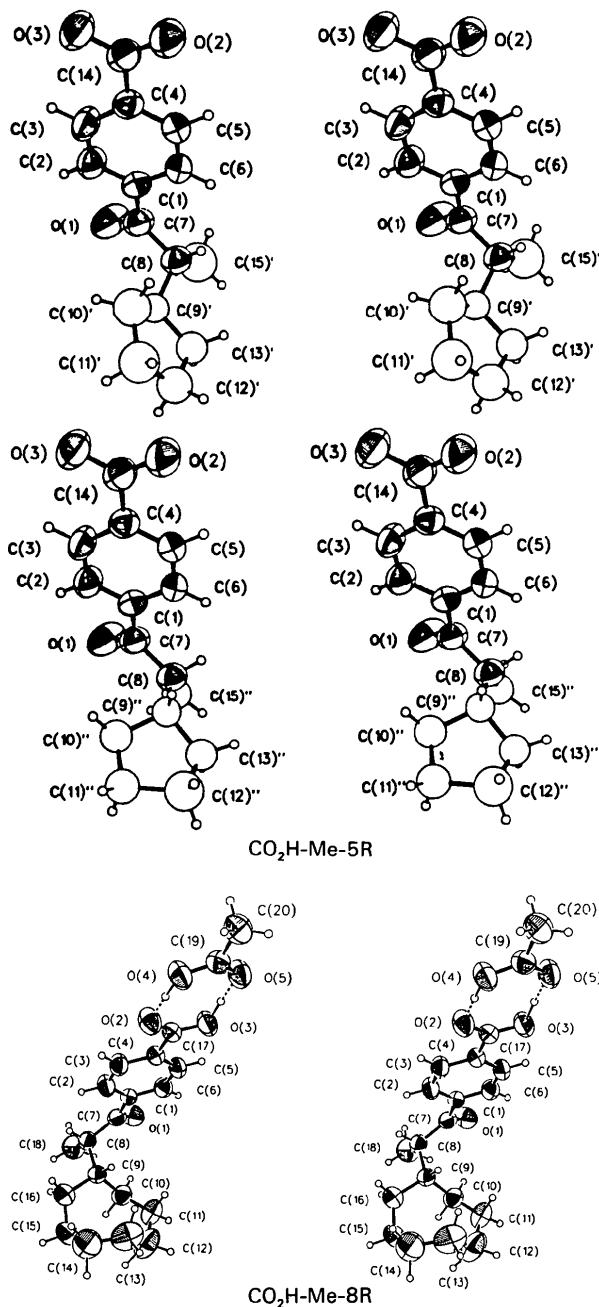


Fig. 3. Stereoviews of the two conformers of $\text{CO}_2\text{H-Me-5R}$ and of $\text{CO}_2\text{H-Me-8R}$.

Table 3. *Molecular conformations, H-abstraction and biradical geometries, and photoproduct ratios for α -cycloalkyl-4-carboxyacetophenones*

Torsion angles (°)	$\text{CO}_2\text{H-Me-5R}$		$\text{CO}_2\text{H-Me-6R}^\dagger$	$\text{CO}_2\text{H-Me-8R}^*$
	1	2		
$\varphi_1 = \text{C}(7)\text{-C}(8)\text{-C}(9)\text{-C}(10)$	-59	53	64	70
$\varphi_2 = \text{O}(1)\text{-C}(7)\text{-C}(8)\text{-C}(9)$	-77	-110	-103	-102
Carbonyl/ring	27	27	21	27
$\varphi = \text{C}(8+n)\text{-C}(9)\text{-C}(10)\text{-C}(11)$	-26	25	56	97
H-abstraction parameters				
d (Å)	3.46	3.10	2.73	2.59
τ (°)	56	50	65	50
Δ (°)	58	73	73	79
Biradical p -orbital angles (°)‡				
$\theta_{\text{C=O}}$	23	28	23	21
θ_r	61	69	88	52
θ_{pp}	60	106	83	70
% Cyclization§				
Benzene	53 (¶)		61 (¶)	66 (64)
Acetonitrile	68 (¶)		75 (¶)	57 (69)
Solid state	55 (0)		68 (66)	70 (85)
% <i>cis</i> -OH cyclobutanol				
	¶		¶	¶

* Torsion angles listed for $\text{CO}_2\text{H-Me-8R}$ are for the enantiomorph of the molecule given in Table 1, for comparison purposes; the crystals are racemic.

† Ariel & Trotter (1986a).

‡ See Evans & Trotter (1988a) for definitions.

§ Numbers in parentheses are for the corresponding acetophenones [Fig. 1, $Z = \text{H}$; Evans & Trotter (1988b)]. Data for 5R and 6R are from Omkaram (1986), for 8R from Harkness (1986).

¶ Photochemical data not available.

large changes in molecular conformation relative to the acetophenone compounds (Evans & Trotter 1988a,b), probably to relieve steric interactions between the methyl-group H atoms and the *ortho*-H atom of the aromatic ring. The principal changes are rotations of about 100° about the C(carbonyl)–C(α), *i.e.* C(7)–C(8), bonds, and rotations of the carbonyl groups out of the aromatic planes by 27°. Thus, the torsion angles φ_1 and φ_2 (Table 3), which are about 60 and 0°, respectively, in the cycloalkylacetophenones, are about 60 and –100° in the propiophenones. A similar conformation has been found for α -cyclohexyl-4-carboxypropionophenone (Ariel & Trotter, 1986a) (Table 3) and for one of the independent molecules in α -cyclopentyl-4-carboxyacetophenone (Evans & Trotter, 1988b). An α -phenylacetophenone derivative (Ariel & Trotter, 1986b) has a third conformation, with $\varphi_1 = 60$ and $\varphi_2 = 41$ °. As in the related acetophenones, the C(8+n)–C(9)–C(10)–C(11) intraannular torsion angles, φ , increase from 25° in $\text{CO}_2\text{H-Me-5R}$ to 97° in $\text{CO}_2\text{H-Me-8R}$.

The three propiophenones (Table 3) undergo the Norrish type II reaction in solution and in the solid state (Omkaram, 1986; Harkness, 1986). The details of the photochemistry are not as well established as for the acetophenones, principally because the presence of the α -methyl group increases the number of possible cyclization photoproducts, and these have not been

identified unambiguously. The disorder in the α -cyclopentyl-4-carboxypropiophenone structure makes it difficult to establish H-atom positions, and the closest γ -H...O distances of 3.46 and 3.10 Å in the two conformers (Table 3) are rather long for abstraction. The cyclohexyl and cyclooctyl compounds have more typical H...O distances of 2.73 and 2.59 Å, respectively, with τ angles of 65 and 50°, and Δ angles of 73 and 79° (Table 3).

As for all the acetophenones previously studied, the amounts of cyclization products for the cycloalkylpropiophenones are relatively insensitive to reaction medium (Table 3), again indicating that the photo-reactions are controlled mainly by intramolecular factors. There is a similar, although not so marked tendency for increase in cyclization with increasing cycloalkyl ring size. Despite the large changes in molecular conformation there is little difference between the cyclization-to-cleavage ratios for the aceto- and propiophenones (Table 3). The only significant change is an increase in cyclization for the cyclopentylpropiophenone, in accord with the behaviour noted previously in related systems. The cyclohexyl- and cyclooctylacetophenones give mainly cyclization products anyway, so it is perhaps not surprising that α -methyl substitution does not increase the amount of cyclization further. The radical p -orbital angles for the cycloalkylpropiophenones are in fact more favourable for cleavage than are those in the acetophenones (Table

3). The photochemical data are insufficiently well established for comment to be made on ratios of the various possible cyclobutanol photoproducts, although the geometry of the cyclooctylpropiophenone molecule suggests that *trans*-fused ring products will again predominate for the larger cycloalkyl rings.

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Structure of an Asymmetrically Substituted Tetrahydro-1,4-naphthoquinone and Conformational Energy Surfaces

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Abstract

The crystal structure of an asymmetrically substituted tetrahydro-1,4-naphthoquinone has been determined, and the structural results have been used to study the conformational inversion pathways. 2,6,7-Trimethyl-4 α ,5,8,8 α -tetrahydro-1,4-naphthoquinone, C₁₃H₁₆O₂, $M_r = 204.27$, monoclinic, $P2_1/n$, $a = 19.191$ (11), $b = 5.278$ (2), $c = 22.330$ (15) Å, $\beta = 90.70$ (3)°, $V = 2261.6$ (2.2) Å³, $Z = 8$ [two molecules, (1a) and (1b), per asymmetric unit], $D_x = 1.199$ g cm⁻³, Mo K α_1 , $\lambda = 0.70930$ Å, $\mu = 0.74$ cm⁻¹, $F(000) = 880$, $T = 295$ K, $R = 0.095$ for 1463 observed reflections. The

two crystallographically independent molecules have different conformations, each molecule being twisted such that the bridgehead H atoms are staggered, with a torsion angle of -52° for molecule (1a), 51° for (1b). Bond lengths and angles are close to normal values. Molecular-energy calculations are used to determine the energies of the two observed molecular conformers of tetrahydronaphthoquinone and of hypothetical higher-energy conformations, and thus to map the conformational energy surface. The two conformers are interconvertible (in solution) *via* higher-energy conformations, with an energy barrier of about 33 kJ mol⁻¹.

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