the major conformer of the cation is represented in Fig. 1, and a view of the cation showing both conformations is given in Fig. 2. Atoms C(4) and C(5) in the six-carbon bridge are disordered. This disorder is effectively a racemization and results in an approximate mirror plane of symmetry for the cation perpendicular to and bisecting the N(1)···N(8) vectors. Site occupancy for C(4), C(5) refined to 0·658 (5) and for C(4′), C(5′) to 0·342 (5). The two conformations for the six-carbon bridge which result (see Table 2) are both similar to that observed in the inside-protonated [6.4.3]diamine (Alder *et al.*, 1988). The conformation of the five-carbon bridge is similar to those observed in the inside-protonated [5.4.3]diamine and [5.5.2]diamine (White *et al.*, 1988*a,b*), having an approximate plane of symmetry; the three-carbon bridge has the typical envelope-like conformation (Alder *et al.*, 1988; White *et al.*, 1988*a*). The bicyclic cation has a number of close intramolecular H···H contacts (see Table 2*d*). The strain imposed by these close contacts is taken up to some degree by an opening of the C—C—C angles; the average C—C—C angle is 116·7 (7)° compared with the idealized value of 109·5° (this average does not include those angles from the six-carbon bridge which are disordered). The inside proton is localized towards N(8) [N(8)—H = 1·19 (3), N(1)···H 1·49 (3) Å], the N—H—N angle is 154 (3)° and the N···N distance is 2·610 (5) Å. This can be contrasted with a number of inside-protonated bicyclic diamines; for [6.4.3]diamines [N···N = 2·663 (4), N—H 0·95 (2), 1·77 (2) Å (Alder *et al.*, 1988)], for [5.4.3]diamine [N···N 2·555 (3), N—H 1·30 (3), 1·30 (2) Å (White *et al.*, 1988*a*)], for [5.5.2]diamine [N···N = 2·555 (7), N—H 1·09 (5), 1·67 (5) Å (White *et al.*, 1988*b*)] and for the [4.4.4]diamine [N···N = 2·526 (3) Å] and an apparently symmetrical linear N—H—N system (Alder *et al.*, 1983).

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Crystal Structure and Photochemistry of Two α-Cycloalkyl-4-carboxyacetophenones

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Abstract. The photochemical behaviour of two α-cycloalkylacetophenones has been correlated with the crystal and molecular structural data. In both cases Mo $K\alpha_1$ radiation was used, $\lambda = 0{\cdot}70930$ Å, $T = 295$ K. α-Cyclopentyl-4-carboxyacetophenone,* $C_{14}H_{16}O_3$, $M_r = 232{\cdot}28$, triclinic, $P\bar{1}$, $a = 10{\cdot}809$ (2), $b = 22{\cdot}683$ (4), $c = 5{\cdot}091$ (1) Å, $\alpha = 94{\cdot}68$ (1), $\beta = 92{\cdot}74$ (1), $\gamma = 77{\cdot}97$ (2)°, $V = 1216{\cdot}1$ (4) Å^3, $Z = 4$ (2 molecules per asymmetric unit), $D_x = 1{\cdot}268$ g cm^{-3}, $\mu = 0{\cdot}8$ cm^{-1}, $F(000) = 496$, $R = 0{\cdot}056$ for 2129 reflections. α-Cyclooctyl-4-carboxyacetophenone,† $C_{17}H_{22}O_3$, $M_r = 274{\cdot}36$, triclinic, $P\bar{1}$, $a = 6{\cdot}6335$ (6), $b = 9{\cdot}7489$ (12), $c = 11{\cdot}5888$ (14) Å, $\alpha = 80{\cdot}658$ (10), $\beta = 88{\cdot}449$ (8), $\gamma = 88{\cdot}344$ (10)°, $V = 739{\cdot}0$ (2) Å^3, $Z = 2$, $D_x = 1{\cdot}233$ g cm^{-3}, $\mu = 0{\cdot}8$ cm^{-1}, $F(000) = 296$, $R = 0{\cdot}042$ for 2135 reflections. The molecular conformations and geometries are very similar to those of related chloro derivatives, except that one of the independent molecules of the cyclopentyl compound has a conformation which involves a 100° rotation about the C(carbonyl)—C_α bond from that observed in all the other molecules. All the molecules have geometries which are favourable for photochemical reaction *via* hydrogen abstraction processes, and increasing amounts of cyclization products with increasing cycloalkyl ring size can be correlated with changing angles between biradical *p* orbitals.

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* 1-(4-Carboxyphenyl)-2-cyclopentylethanone; 4-cyclopentylmethylcarbonylbenzoic acid.

† 1-(4-Carboxyphenyl)-2-cyclooctylethanone; 4-cyclooctylmethylcarbonylbenzoic acid.

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Introduction. The structural aspects of the photochemical fragmentation or cyclization (Norrish type II reaction) of α-cycloalkyl-4-chloroacetophenones have previously been studied (Evans & Trotter, 1988). Correlation of the structural and photochemical data indicates that the photochemical behaviour is governed by intramolecular forces, and an increase in the amount of cyclization products with increasing cycloalkyl ring size can be rationalized qualitatively in terms of changing torsion angles. The present paper extends these investigations to the 4-carboxy derivatives. The crystal structure of the cyclohexyl compound (CO_2H-6R) has previously been determined (Ariel & Trotter, 1985), and the structures of the cyclopentyl (CO_2H-5R) and cyclooctyl (CO_2H-8R) derivatives are now described; suitable crystals of the cyclobutyl and cycloheptyl compounds could not be obtained.

Experimental. Crystals of the cyclopentyl compound, CO_2H-5R, are colourless [001] prisms, 0·20 × 0·20 × 0·40 mm [cyclooctyl compound, CO_2H-8R, {100}, {010}, {001}, $\{01\bar{1}\}$ forms, 0·3 × 0·3 × 0·4 mm], Enraf–Nonius CAD-4F diffractometer, lattice parameters from 25 reflections with $\theta = 15$–$23°$, reduced cell with orientation $c < a < b$, two obtuse angles for CO_2H-5R [$\theta = 14$–$22°$, orientation $a < b < c$, all angles acute for CO_2H-8R]. Intensities for $\theta \leq 25°$ [27·5°], $hkl = 0$ to 12, −25 to 26, −6 to 6 [−8 to 8, −12 to 0, −15 to 14], ω–2θ scan, ω scan width (1·00 + 0·35tanθ)° [(0·90 + 0·35tanθ)°] at 0·8–6·7 [1·5–10·0]° $\min^{-1}$, extended 25% on each side for background measurement, three standard reflections (no decay), Lp corrections, 4241 [3380] reflections measured, 2129 [2135] 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.

Initial attempts to determine the structure of CO_2H-5R by direct methods were unsuccessful. All reflections with h odd are systematically weak, so that there is a subcell with $a' = a/2$. Renormalization of the data did not assist with a direct-methods solution, and the structure was determined by Patterson methods. With the assumption of the presence of two approximately centrosymmetrical 4-carboxyacetophenone fragments linked across a centre of symmetry by hydrogen bonding, the orientation and position of these fragments were determined from the Patterson map. An electron-density map (h even reflections only) revealed two possible orientations for the five-membered cycloalkyl ring. Placing one of these orientations on a dimer centred at (0,0,0) and the other on a dimer at ($\frac{1}{2}$,0,0) gave a trial structure, for which least-squares refinement quickly converged, but at $R(h \text{ even}) = 0{\cdot}16$, $R(h \text{ odd}) = 0{\cdot}52$. A shift of origin by $x = \frac{1}{4}$ and a redistribution of the two five-membered ring orientations resulted in a structure with two *non*-centrosymmetric hydrogen-bonded dimers in the unit cell, related to each other by a space-group centre of symmetry. Refinement then proceeded smoothly. Two outer atoms of each five-membered ring showed evidence of disorder, and the attached H atoms were fixed in calculated positions; the carboxyl H atoms were found (and refined) as single full-weight atoms near the centres of the O···O hydrogen bonds, although these are probably means of two disordered sites. $w = 1/\sigma^2(F)$, scattering factors from *International Tables for X-ray Crystallography* (1974), locally written, or locally modified versions of standard computer programs (Evans & Trotter, 1988), final $R = 0{\cdot}056$ (0·053 for h even, 0·068 for h odd), $wR = 0{\cdot}078$ for 2129 reflections, $S = 2{\cdot}9$, 307 parameters (non-hydrogen atoms, plus 96 H parameters), $R = 0{\cdot}115$ for all 4241 reflections, $\Delta/\sigma = 0{\cdot}005$ (mean), 0·25 (maximum), final difference density $\pm 0{\cdot}26$ e Å^{-3}.

The CO_2H-8R structure was also determined by Patterson methods, in terms of centrosymmetric hydrogen-bonded dimers. The only complicating feature was the existence of disordered half-occupied sites for the carboxyl H atoms. Final $R = 0{\cdot}040$, $wR = 0{\cdot}050$ for 2135 reflections, $S = 1{\cdot}9$, 181 parameters (non-hydrogen atoms, plus 92 H parameters), $R = 0{\cdot}077$ for all 3380 reflections, $\Delta/\sigma = 0{\cdot}004$ (mean), 0·078 (maximum), maximum $\Delta\rho$ +0·15 to −0·23 e Å^{-3}.

Discussion. Final positional parameters are in Table 1, and other data have been deposited.* The structures both contain hydrogen-bonded dimers (Fig. 1); for CO_2H-5R these dimers are *non*-centrosymmetric, but CO_2H-8R contains the more usual centrosymmetric dimers. In both structures, the carboxyl groups appear to be disordered, since C—O distances are all in the range 1·241–1·283 (4) Å (Table 2), and the carboxyl H atoms show disorder over two sites; the O—H···O distances are 2·616 (4) and 2·624 (4) Å in CO_2H-5R, and 2·634 (2) Å in CO_2H-8R. In CO_2H-5R, molecules pack in parallel planes [approximately $(24\bar{1})$], with perpendicular distance of 3·48 Å between aromatic rings. The molecules are further stacked parallel to their long axes, so that hydrophilic and hydrophobic regions alternate along **b**. In CO_2H-8R, nearest-neighbour molecules pack around centres of symmetry with 3·44 Å spacing between aromatic ring planes.

The aromatic rings in both compounds show small but not structurally significant deviations from exact planarity ($\chi^2 = 6{\cdot}3$ and 21·4 for CO_2H-5R, 40·9 for CO_2H-8R), with maximum displacement of C atoms from mean planes of 0·009 (3) Å. The two aromatic

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* Lists of anisotropic thermal parameters, H-atom positions and thermal parameters, bond lengths and angles involving H, torsion angles and structure factors, and packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44686 (52 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* × 10^4) *and equivalent isotropic thermal parameters* ($U_{\text{eq}} \times 10^3$ Å^2), *with e.s.d.'s in parentheses*

$$U_{\text{eq}} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
CO_2H-5R				
C(1)	7152 (3)	−1893 (2)	−9384 (7)	44
C(2)	8254 (3)	−1941 (2)	−7792 (8)	48
C(3)	8342 (4)	−1517 (2)	−5742 (8)	46
C(4)	7345 (3)	−1037 (1)	−5239 (7)	43
C(5)	6251 (3)	−983 (2)	−6826 (7)	50
C(6)	6158 (3)	−1407 (2)	−8840 (8)	47
C(7)	6988 (3)	−2355 (2)	−11603 (7)	48
C(8)	8068 (4)	−2868 (2)	−12235 (8)	50
C(9)	7806 (3)	−3322 (2)	−14451 (8)	53
C(10)	6800 (5)	−3671 (2)	−13873 (12)	82
C(11)	7187 (6)	−4287 (2)	−15256 (14)	126
C(12)	8426 (6)	−4349 (2)	−16241 (14)	129
C(13)	8951 (4)	−3804 (2)	−15156 (14)	85
C(14)	7427 (3)	−576 (2)	−2998 (7)	44
O(1)	5983 (2)	−2305 (1)	−12817 (6)	76
O(2)	6518 (2)	−148 (1)	−2589 (5)	61
O(3)	8452 (2)	−653 (1)	−1588 (5)	60
C(1′)	7829 (3)	1892 (1)	9204 (7)	42
C(2′)	6733 (3)	1933 (2)	7626 (7)	47
C(3′)	6648 (4)	1500 (2)	5574 (8)	47
C(4′)	7658 (3)	1024 (1)	5091 (6)	41
C(5′)	8747 (4)	975 (2)	6695 (8)	50
C(6′)	8824 (4)	1403 (2)	8725 (8)	50
C(7′)	7983 (4)	2359 (2)	11381 (7)	51
C(8′)	6953 (4)	2911 (2)	11828 (8)	52
C(9′)	6962 (4)	3375 (2)	9816 (8)	54
C(10′)	8200 (5)	3558 (2)	9565 (15)	79
C(11′)	7879 (5)	4191 (2)	8575 (12)	103
C(12′)	6529 (5)	4428 (2)	8985 (12)	98
C(13′)	6033 (5)	3975 (2)	10381 (13)	83
C(14′)	7583 (3)	563 (2)	2899 (7)	45
O(1′)	8954 (3)	2301 (1)	12751 (5)	73
O(2′)	8503 (2)	133 (1)	2474 (5)	60
O(3′)	6562 (2)	635 (1)	1465 (5)	61
CO_2H-8R				
C(1)	4867 (2)	1726 (1)	3977 (1)	37
C(2)	2873 (2)	1353 (2)	4169 (1)	43
C(3)	1778 (3)	953 (2)	3285 (1)	43
C(4)	2668 (2)	950 (2)	2192 (1)	39
C(5)	4652 (3)	1336 (2)	1988 (1)	46
C(6)	5752 (3)	1716 (2)	2877 (1)	46
C(7)	6133 (2)	2127 (2)	4927 (1)	39
C(8)	5084 (2)	2389 (2)	6040 (1)	40
C(9)	6373 (2)	3016 (2)	6888 (1)	37
C(10)	6986 (3)	4500 (2)	6361 (2)	47
C(11)	9125 (3)	4898 (2)	6585 (2)	58
C(12)	9691 (3)	5035 (2)	7832 (2)	59
C(13)	9656 (3)	3697 (2)	8719 (2)	53
C(14)	7782 (3)	3486 (2)	9509 (2)	56
C(15)	5758 (3)	3812 (2)	8938 (2)	53
C(16)	5169 (3)	2908 (2)	8048 (2)	50
C(17)	1497 (2)	535 (2)	1238 (1)	43
O(1)	7943 (2)	2209 (1)	4782 (1)	57
O(2)	−282 (2)	129 (1)	1469 (1)	61
O(3)	2331 (2)	598 (2)	242 (1)	64

rings in CO_2H-5R are almost parallel, but are shifted from coplanarity by 0·24 Å along the plane normals (0·14 Å between carboxyl-group planes). The carbonyl and carboxyl groups in CO_2H-5R are planar and close to coplanar with the aromatic rings, with all mean planes tilted no more than 6° with respect to each other. In CO_2H-8R, the carboxyl group is nearly coplanar with the aromatic ring, but the carbonyl group is rotated 12° out of the ring plane; the two carboxyl groups of the dimer are displaced by 0·20 Å from coplanarity. Bond lengths and angles in the aromatic rings (Table 2) are normal, with C—C = 1·362–1·391, mean 1·385 Å, and C—C—C = 118·3–121·2, mean 120·0°, in the two structures.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and some torsion angles* (°) *with e.s.d.'s in parentheses*

CO_2H-5R			
C(1)—C(2)	1·398 (4)	C(1′)—C(2′)	1·390 (4)
C(1)—C(6)	1·390 (5)	C(1′)—C(6′)	1·390 (5)
C(1)—C(7)	1·507 (5)	C(1′)—C(7′)	1·497 (5)
C(2)—C(3)	1·373 (5)	C(2′)—C(3′)	1·388 (5)
C(3)—C(4)	1·380 (4)	C(3′)—C(4′)	1·382 (4)
C(4)—C(5)	1·389 (4)	C(4′)—C(5′)	1·390 (5)
C(4)—C(14)	1·496 (5)	C(4′)—C(14′)	1·478 (4)
C(5)—C(6)	1·362 (5)	C(5′)—C(6′)	1·370 (5)
C(7)—C(8)	1·493 (5)	C(7′)—C(8′)	1·502 (5)
C(7)—O(1)	1·213 (4)	C(7′)—O(1′)	1·222 (4)
C(8)—C(9)	1·520 (5)	C(8′)—C(9′)	1·528 (5)
C(9)—C(10)	1·524 (6)	C(9′)—C(10′)	1·496 (6)
C(9)—C(13)	1·508 (6)	C(9′)—C(13′)	1·529 (6)
C(10)—C(11)	1·499 (7)	C(10′)—C(11′)	1·525 (6)
C(11)—C(12)	1·428 (8)	C(11′)—C(12′)	1·465 (6)
C(12)—C(13)	1·519 (7)	C(12′)—C(13′)	1·494 (7)
C(14)—O(2)	1·241 (4)	C(14′)—O(2′)	1·252 (4)
C(14)—O(3)	1·280 (4)	C(14′)—O(3′)	1·283 (4)
C(2)—C(1)—C(6)	118·3 (3)	C(2′)—C(1′)—C(6′)	118·8 (3)
C(2)—C(1)—C(7)	122·7 (3)	C(2′)—C(1′)—C(7′)	122·5 (3)
C(6)—C(1)—C(7)	118·9 (3)	C(6′)—C(1′)—C(7′)	118·7 (3)
C(1)—C(2)—C(3)	120·5 (3)	C(1′)—C(2′)—C(3′)	120·5 (3)
C(2)—C(3)—C(4)	120·3 (4)	C(2′)—C(3′)—C(4′)	119·9 (4)
C(3)—C(4)—C(5)	119·6 (3)	C(3′)—C(4′)—C(5′)	119·8 (3)
C(3)—C(4)—C(14)	120·7 (3)	C(3′)—C(4′)—C(14′)	120·4 (3)
C(5)—C(4)—C(14)	119·7 (3)	C(5′)—C(4′)—C(14′)	119·8 (3)
C(4)—C(5)—C(6)	120·1 (3)	C(4′)—C(5′)—C(6′)	120·1 (4)
C(1)—C(6)—C(5)	121·2 (4)	C(1′)—C(6′)—C(5′)	121·0 (4)
C(1)—C(7)—C(8)	118·9 (3)	C(1′)—C(7′)—C(8′)	119·7 (3)
C(1)—C(7)—O(1)	119·4 (3)	C(1′)—C(7′)—O(1′)	120·4 (3)
C(8)—C(7)—O(1)	121·6 (3)	C(8′)—C(7′)—O(1′)	119·9 (4)
C(7)—C(8)—C(9)	115·3 (3)	C(7′)—C(8′)—C(9′)	112·1 (3)
C(8)—C(9)—C(10)	114·7 (4)	C(8′)—C(9′)—C(10′)	115·5 (4)
C(8)—C(9)—C(13)	113·4 (3)	C(8′)—C(9′)—C(13′)	114·0 (4)
C(10)—C(9)—C(13)	104·5 (4)	C(10′)—C(9′)—C(13′)	103·7 (4)
C(9)—C(10)—C(11)	106·3 (4)	C(9′)—C(10′)—C(11′)	106·0 (4)
C(10)—C(11)—C(12)	109·0 (4)	C(10′)—C(11′)—C(12′)	107·3 (4)
C(11)—C(12)—C(13)	108·0 (4)	C(11′)—C(12′)—C(13′)	107·9 (4)
C(9)—C(13)—C(12)	105·1 (4)	C(9′)—C(13′)—C(12′)	105·4 (4)
C(4)—C(14)—O(2)	119·5 (3)	C(4′)—C(14′)—O(2′)	120·0 (3)
C(4)—C(14)—O(3)	116·8 (3)	C(4′)—C(14′)—O(3′)	117·0 (3)
O(2)—C(14)—O(3)	123·7 (3)	O(2′)—C(14′)—O(3′)	123·0 (3)
CO_2H-8R			
C(1)—C(2)	1·384 (2)	C(9)—C(10)	1·538 (2)
C(1)—C(6)	1·391 (2)	C(9)—C(16)	1·535 (2)
C(1)—C(7)	1·510 (2)	C(10)—C(11)	1·522 (3)
C(2)—C(3)	1·385 (2)	C(11)—C(12)	1·531 (3)
C(3)—C(4)	1·383 (2)	C(12)—C(13)	1·525 (3)
C(4)—C(5)	1·383 (2)	C(13)—C(14)	1·522 (3)
C(4)—C(17)	1·483 (2)	C(14)—C(15)	1·516 (3)
C(5)—C(6)	1·382 (2)	C(15)—C(16)	1·526 (2)
C(7)—C(8)	1·504 (2)	C(17)—O(2)	1·264 (2)
C(7)—O(1)	1·211 (2)	C(17)—O(3)	1·259 (2)
C(8)—C(9)	1·530 (2)		
C(2)—C(1)—C(6)	119·18 (14)	C(8)—C(9)—C(10)	110·95 (13)
C(2)—C(1)—C(7)	122·29 (14)	C(8)—C(9)—C(16)	106·91 (13)
C(6)—C(1)—C(7)	118·52 (14)	C(10)—C(9)—C(16)	114·51 (14)
C(1)—C(2)—C(3)	120·57 (15)	C(9)—C(10)—C(11)	116·53 (15)
C(2)—C(3)—C(4)	119·85 (15)	C(10)—C(11)—C(12)	118·8 (2)
C(3)—C(4)—C(5)	119·98 (14)	C(11)—C(12)—C(13)	115·7 (2)
C(3)—C(4)—C(17)	120·07 (14)	C(12)—C(13)—C(14)	116·1 (2)
C(5)—C(4)—C(17)	119·95 (14)	C(13)—C(14)—C(15)	117·1 (2)
C(4)—C(5)—C(6)	120·12 (15)	C(14)—C(15)—C(16)	116·8 (2)
C(1)—C(6)—C(5)	120·3 (2)	C(9)—C(16)—C(15)	118·72 (15)
C(1)—C(7)—C(8)	118·11 (13)	C(4)—C(17)—O(2)	118·26 (15)
C(1)—C(7)—O(1)	119·70 (14)	C(4)—C(17)—O(3)	118·29 (15)
C(8)—C(7)—O(1)	122·19 (14)	O(2)—C(17)—O(3)	123·45 (15)
C(7)—C(8)—C(9)	115·83 (13)		

Intraanular torsion angles

Bond	This work	Boat–chair*
9–10	98·5	102·2
10–11	−68·0	−65·0
11–12	65·3	65·0
12–13	−99·4	−102·2
13–14	44·3	44·7
14–15	64·6	65·0
15–16	−67·5	−65·0
16– 9	−38·9	−44·7

* Hendrickson (1967).

Some disorder of the outer atoms of the cyclopentyl rings in both independent molecules of CO_2H-5R is indicated by large r.m.s. thermal displacements of >0·4 Å, and by apparently foreshortened C—C bond lengths of 1·43 and 1·47 (1) Å. Split-atom models were not tested for reasons previously outlined (Evans & Trotter, 1988); the disorder does not obscure structural details in other regions of the molecules. The eight-membered cyclooctyl ring has a boat–chair conformation (Fig. 1 and Table 2), with an approximate mirror plane through C(11) and C(15). Bond lengths in the ring are normal, mean 1·527 Å, and bond angles are enlarged from the tetrahedral value, range 114·5–118·8 (2)°, mean 116·8°, as found in related molecules (Evans & Trotter, 1988).

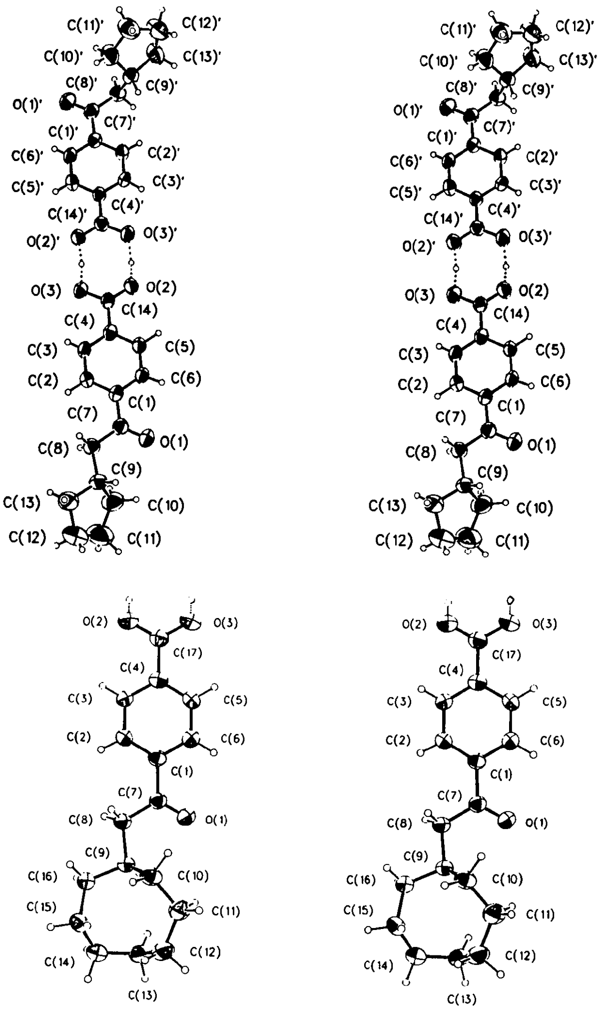

Fig. 1. Stereoviews of the molecules of CO_2H-5R (upper) and CO_2H-8R (lower).

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

	CO_2H-5R*		CO_2H-6R†	CO_2H-8R
Torsion angles (°)				
φ_1 – C(7)–C(8)–C(9)–C(10)	65	53	69	66
φ_2 = C(1)–C(7)–C(8)–C(9)	1	−101	10	11
Carbonyl/ring	3	4	11	12
ψ = C(8 + n)–C(9)–C(10)–C(11)	22	29	55	99
Hydrogen abstraction parameters				
Ring conformation	Twist-boat	Chair	Boat	Boat
d (Å)	2·69	2·93	2·60	2·69
τ (°)	29	47	44	49
Δ (°)	102	76	90	77
Biradical p-orbital angles (°)‡				
θ_{C-O}	89	25	98	99
θ_v	60	67	88	127
θ_{pp}	57	64	73	97
% Cyclization				
Benzene	§		§	64
Acetonitrile	§		§	69
Solid state	0		66	85
* *cis*-OH cyclobutanol				
Benzene	§		§	28
Acetonitrile	§		§	47
Solid state	¶		67	8

* Torsion angles listed for CO_2H-5R are for the enantiomorph of the molecules given in Table 1, for comparison purposes; the crystals are racemic.

† Ariel & Trotter (1985); torsion angles are for the enantiomorph of the molecule listed in the previous paper.

‡ See Evans & Trotter (1988) for definitions.

§ Photochemical data not obtainable.

¶ No cyclization products.

In both structures the acetophenone moieties occupy equatorial sites on the non-planar cycloalkyl rings. For CO_2H-8R this is a different equatorial position from that in Cl-8R (Evans & Trotter, 1988), but this is not unexpected, as all the equatorial positions on the cyclooctyl ring have comparable steric hindrance (Hendrickson, 1967). The conformations of the central parts of molecule 1 of CO_2H-5R (unprimed atoms in Fig. 1) and of the molecule of CO_2H-8R are similar to those of all the related molecules previously studied (Evans & Trotter, 1988). The φ_1 and φ_2 torsion angles (Table 3) are close to ideal values of 60° and 0°, respectively, and the carbonyl groups are not far from coplanar with the aromatic rings (rotations of up to 12°). Molecule 2 of CO_2H-5R (primed atoms in Fig. 1) has quite a different conformation ($\varphi_2 = -101°$), with a rotation of about 100° about the C(carbonyl)—C(α) [C(7′)—C(8′)] bond compared with molecule 1. As in the related chloro compounds (Evans & Trotter, 1988), the C(8 + n)—C(9)—C(10)—C(11) intra-annular torsion angles, ψ, increase from about 25° in CO_2H-5R to 99° in CO_2H-8R (Table 3).

Both CO_2H-5R and CO_2H-8R, and the related CO_2H-6R (Ariel & Trotter, 1985), undergo the Norrish type II reaction in solution and in the solid state (Omkaram, 1986; Harkness, 1986). In all the molecules there is an H atom on C(10) which is suitable for abstraction by carbonyl O (Table 3). The six-membered rings formed during abstraction are mainly boat-like, although the shortest O···H distance in molecule 2 of CO_2H-5R results in a chair-like geometry (Table 3) (CO_2H-5R, molecule 2, has a second O···H distance with a boat-like geometry, but rather less favourable abstraction parameters, $d = 3{\cdot}17$ Å, $\tau = 62°$, $\Delta = 68°$). The abstraction parameters (Table 3) are very similar to those in the chloro derivatives (Evans & Trotter, 1988), and are favourable for hydrogen abstraction, with $d \sim 2{\cdot}7$ Å, $\tau \sim 40°$, and Δ not far from 90°.

Although the photochemical data are not as extensive as for the chloro derivatives, the percentage cyclization for the carboxy compounds (Table 3) again appears to be relatively insensitive to reaction medium, but increases significantly (from 0 to 85%) as the cycloalkyl ring size increases. The variation with cycloalkyl ring size again correlates qualitatively with the increasing values of the biradical *p*-orbital angles θ_v (60–127°) and ring torsion angles (22–99°) favouring cyclization over cleavage. In addition, molecule 2 of CO_2H-5R has a $\theta_{C=O}$ angle of 25°, which favours cleavage, and is perhaps responsible for the non-observance of any cyclization product in the solid state. The amount of *trans*-OH cyclobutanol cyclization product increases markedly with increasing cycloalkyl ring size, to nearly 100% for the cyclooctyl compound in the solid state, as for the chloro derivatives (the ring-junction configurations are again probably *cis* for the cyclopentyl and *trans* for the cyclooctyl products). The increasing amount of *trans*-OH photoproducts has previously been rationalized on the basis of great steric stability of the *trans*-OH photoproduct for the larger cycloalkyl rings (Evans & Trotter, 1988). Thus the photochemistry again appears to be controlled mainly by intramolecular forces.

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Structure of Bis[(−)-menthyl] Acetylenedicarboxylate

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Abstract. $C_{24}H_{38}O_4$, $M_r = 390{\cdot}57$, trigonal, $P3_121$, $a = 9{\cdot}796$ (1), $c = 21{\cdot}666$ (3) Å, $V = 1800{\cdot}6$ (3) Å^3, $Z = 3$ (molecular symmetry C_2), $D_x = 1{\cdot}080$ g cm^{-3}, Mo $K\alpha_1$, $\lambda = 0{\cdot}70926$ Å, $\mu = 0{\cdot}67$ cm^{-1}, $F(000) = 642$, $T = 295$ K, $R = 0{\cdot}040$ for 652 reflections. The molecule lies on a crystallographic twofold axis, and has a nearly linear triple C≡C bond, with the two carboxyl groups at 90° to each other; the cyclohexane ring has a chair conformation, with all substituents equatorial. Bond lengths and angles are close to expected values. The crystals undergo photoreaction, but it has not been possible to determine the details of this process.

Introduction. The production of optically active product from achiral reactant has recently been achieved by unimolecular di-π-methane photorearrangement in the solid state of a dibenzobarrelene derivative which was found to crystallize in the non-centrosymmetric space group $P2_12_12_1$ (Evans, Garcia-Garibay, Omkaram, Scheffer, Trotter & Wireko, 1986). In an effort to achieve this type of asymmetric synthesis in a controlled manner, chiral reactants (which must crystallize in a chiral space group) were synthesized. The crystal structure of one of the reagents in the syntheses, bis[(−)-menthyl] acetylenedicarboxylate, is described in the present paper. An additional point of interest is that this material itself was found to undergo photoreaction.

Experimental. Colourless rhombs, {10.1} form, dimensions about 0·4 mm, Enraf–Nonius CAD-4F diffractometer, lattice parameters from 25 reflections with $\theta = 10$–19°. Intensities for $\theta \le 27{\cdot}5°$, *hkl*: 0 to 11, 0 to 11, 0 to 28, ω–2θ scan width $(0{\cdot}65 + 0{\cdot}35\tan\theta)°$ at

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