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10-Carboxy-Δ^1-octal-2-one and 10-Carboxy-*cis*-decal-2-one: Structures and Intermolecular Hydrogen-Bonding Patterns

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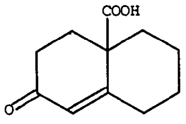
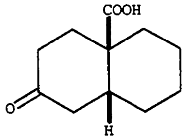
Abstract. (I) 2,3,4,4a,5,6,7,8-Octahydro-2-oxo-napthalene-4a-carboxylic acid, $(\pm)$-$C_{11}H_{14}O_3$, M_r = 194·230, monoclinic, $P2_1/n$, a = 12·943 (3), b = 11·951 (2), c = 6·346 (1) Å, β = 92·84 (2)°, V (245 K) = 975·4 (3) Å^3, V (295 K) = 990·1 (8) Å^3, Z = 4, D_m (295 K) = 1·26 (1), D_x (295 K) = 1·303 g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ = 7·8 cm^{-1}, F(000) = 416, T = 245 (1) K, R = 0·052 for 870 observed reflections. In (I), the crystal is composed of single-strand helical chains with axes parallel to b, produced by repetition of a hydrogen bond linking the carboxylic acid of each molecule with the ketone of an adjacent screw-related molecule; each helix contains molecules of only one chirality. (II) *cis*-Perhydro-2-oxo-naphthalene-4a-carboxylic acid, $(\pm)$-$C_{11}H_{16}O_3$, M_r = 196·246, monoclinic, $P2_1/c$, a = 12·053 (2), b = 15·194 (3), c = 11·348 (2) Å, β = 102·27 (1)°, V (251 K) = 2076·9 (6) Å^3, V (295 K) = 2095·6 (6) Å^3, Z = 8, D_m (295 K) = 1·28 (1), D_x (295 K) = 1·272 g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ = 7·6 cm^{-1}, F(000) = 848, T = 251 (1) K, R = 0·048 for 1722 observed reflections. In (II), enantiomers are paired by mutual hydrogen bonding of carboxyl groups, leaving the ketone carbonyl groups uninvolved. The differences in hydrogen bonding between (I) and (II) are related to observable differences in solid-state IR carbonyl stretching frequencies.

Introduction. In our exploration of hydrogen-bonding patterns in keto carboxylic acids (Leiserowitz, 1976; Vanderhoff, Thompson & Lalancette, 1986; Lalancette, Slifer & Thompson, 1989; Lalancette, Vanderhoff & Thompson, 1990, 1991), we have examined the title compounds. Our attention was drawn particularly to the octalone (I) because of anomalies in the solid-state IR spectrum which we suspected to be connected with hydrogen bonding (Vanderhoff, Lalancette & Thompson, 1990). With both (I) and its *cis*-saturated analog (II) – in which the IR anomalies were absent – available to us, we undertook low-temperature X-ray studies to determine unambiguously the solid-state hydrogen-bonding patterns.



(I)



(II)

In a study of a compound closely related to (I) and (II), Chadwick & Dunitz (1979) showed that 10-carboxy-*cis*-decal-3-one adopts a catemeric or chain-like hydrogen-bonding pattern in the solid state. This hydrogen-bonding mode in keto acids is associated in a few known cases with the types of IR anomalies we had seen in (I) (Amagaya, Takai, Ogihara & Iitaka, 1977; Takai, Amagaya & Ogihara, 1977; Jefferies, Payne, Raston & White, 1981; Vanderhoff, Thompson & Lalancette, 1986; Lalancette, Vanderhoff & Thompson, 1991), but is far less common in keto acids than the usual carboxyl dimer which leaves the ketone uninvolved, of which several dozen examples appear in the literature. Among racemic compounds, we have previously noted the occurrence of centrosymmetrically related racemic pairs of single-strand helices (Vanderhoff, Thompson & Lalancette, 1986; Lalancette, Vanderhoff & Thompson, 1991), and among single enantiomers, a single-strand (Lalancette, Vanderhoff & Thompson, 1991) and a triple-strand helix (Lalancette, Slifer & Thompson, 1989). In addition we are aware of several reports by others describing hydrogen-bonding chains in keto acids (Amagaya, Takai, Ogihara & Iitaka, 1977; Precigoux, Busetta & Hospital, 1977; Chadwick & Dunitz, 1979; Fortier, DeTitta, Fronckowiak, Smith & Hauptman, 1979; Carpy, Goursolle & Leger, 1980; Jefferies, Payne, Raston & White, 1981; Preut, Kreiser, Mueller & Jones, 1985; Bertolasi, Ferretti & Gilli, 1982; Peeters, Blaton & De Ranter, 1983).

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Experimental. The octalone [(I), m.p. 401–403 K; Thompson & Shah, 1983] was crystallized from 95% ethanol by slow evaporation at 295 K; its density was measured by flotation in carbon tetrachloride–toluene. A truncated pyramid, having facial center-to-center distances of 0·38, 0·28 and 0·25 mm, was mounted on a glass fiber. At low temperature, 15 high-angle reflections were used to calculate the orientation matrix and best cell dimensions, and space group $P2_1/n$ was chosen on the basis of the extinct reflections. Data were collected on a Syntex $P2_1$ diffractometer with a graphite monochromator using Cu $K\alpha$ radiation. With three standard reflections recorded every 27 reflections ($\pm$1·8%), 1016 unique reflections were measured in the θ–2θ scan mode ($2\theta_{\max} = 114{\cdot}9°$, $0 \le h \le 14$, $0 \le k \le 13$, $-7 \le l \le 7$); 146 were unobserved [$I < 3\sigma(I)$] and 870 had $I \ge 3\sigma(I)$. After accurate measurement of the six crystal faces, the parallel pair of which was normal to a principal crystal axis, absorption corrections were made based on Howells' analytical expression for polyhedra (min. = 1·124, max. = 1·166). The structure was solved using *MULTAN*80; all non-H atoms were found from the best E map (CFOM = 3·00) and all H atoms were found in subsequent difference Fourier maps. H-atom positional parameters were refined, and their isotropic thermal parameters were set at $(B + 1)$ Å^2, where B was the value for the atom to which the H was bound. All non-H atoms were refined with anisotropic thermal parameters; $\sum||F_o| - |F_c||^2$ was minimized; $R = 0{\cdot}052$, $wR = 0{\cdot}064$, $S = 1{\cdot}31$, $w = 1/\sigma^2$ with $\sigma = 0{\cdot}010F_o + 4{\cdot}570$ for $F_o \le 210{\cdot}0$, $\sigma = 0{\cdot}029F_o + 0{\cdot}693$ for $F_o > 210{\cdot}0$, last cycle max. $\Delta/\sigma = 0{\cdot}0176$, av. = 0·0027, final difference Fourier max. = 0·19, min. = 0·06 e Å^{-3}. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 72–98) and no anomalous-dispersion corrections were used. The computer programs used have been previously referenced (Lalancette, Vanderhoff & Thompson, 1990).

The decalone [(II), m.p. 386–387 K; Thompson & Shah, 1983] was crystallized and its density measured as described above. A rod, 0·62 × 0·22 × 0·14 mm, was mounted on a glass fiber. The orientation matrix and best cell dimensions at low temperature were calculated as described above, and space group $P2_1/c$ was chosen on the basis of the extinct reflections. With three standard reflections recorded every 27 reflections ($\pm$1·4%), 2552 unique reflections were measured in the θ–2θ scan mode ($2\theta_{\max} = 110°$, $0 \le h \le 13$, $0 \le k \le 16$, $-12 \le l \le 12$); 830 were unobserved [$I < 3\sigma(I)$] and 1722 had $I \ge 3\sigma(I)$. Absorption corrections were applied as described above after accurately measuring the three pairs of parallel crystal faces, each of which was normal to a principal crystal axis (min. = 1·086, max. = 1·301). The structure was solved using *MULTAN*80 and all non-H atoms were found from the best E map (CFOM = 3·00). The carboxyl H atoms were found in difference Fourier maps; all other H atom positions were calculated with fixed geometry. H-atom positional parameters were not refined and their isotropic thermal parameters were set at $(B + 1)$ Å^2, where B was the value for the atom to which the H was bound. All non-H atoms were refined with anisotropic thermal parameters; $\sum||F_o| - |F_c||^2$ was minimized; $R = 0{\cdot}048$, $wR = 0{\cdot}056$, $S = 1{\cdot}39$, $w = 1/\sigma^2$ with $\sigma = 0{\cdot}011F_o + 2{\cdot}525$ for $F_o \le 42{\cdot}0$, $\sigma = -0{\cdot}048F_o + 5{\cdot}033$ for $F_o > 42{\cdot}0$, last cycle max. $\Delta/\sigma = 0{\cdot}0297$, av. = 0·0062, final difference Fourier max. = 0·22, min. = 0·14 e Å^{-3}. Atomic scattering factors were applied as described above.

Discussion. Table 1 lists positional and isotropic thermal parameters* and Table 2 lists bond and interatomic distances and angles, for both (I) and (II).

Fig. 1 presents a view of the asymmetric unit of (I) with its numbering scheme. As expected, the ketone ring has the half-chair and the non-ketone ring the chair conformation. The carboxyl group has its carbonyl turned away from the ketone, with the plane of the carboxyl at an angle of 19·2 (4)° relative to the plane defined by C(9), C(10) and C(11). Fig. 2 shows the helical hydrogen-bonding arrangement in (I), created by repetition of a hydrogen bond linking the carboxyl of each molecule to the ketone of an adjacent screw-related molecule of identical chirality, along *b*. Fig. 3 shows that the single-strand helices with opposite chirality but parallel axes passing through the cell do not interpenetrate each other in the center of the cell, but will do so where they extend beyond the *ab* and *bc* cell faces.

Fig. 4 presents a view of the asymmetric unit of (II) with its numbering scheme, which is identical to that for (I), since the two are isoskeletal. The molecule on the right has the same absolute configuration at C(10) as that chosen for Fig. 1. The asymmetric unit consists of a configurationally enantiomeric pair of molecules with essentially identical (but enantiomeric) chair conformations. However, as may be seen in the figure, the two molecules cannot be related by a true mirror, since the rotational conformations of the carboxyl groups differ in the two by about 180°. The two molecules in the asymmetric unit also have several significantly different bond lengths and angles (Table 2) as well as

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53922 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and isotropic thermal parameters for* (Å²) (I) *and* (II)

$$B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2ab\cos\gamma)\beta_{12} + (2ac\cos\beta)\beta_{13} + (2bc\cos\alpha)\beta_{23}].$$

(I)	*x*	*y*	*z*	B_{eq}/B_{iso}
O(1)	0·1164 (2)	−0·0451 (2)	0·1880 (4)	4·69 (1)
O(2)	0·2742 (3)	0·3373 (3)	0·6956 (6)	7·10 (2)
O(3)	0·2253 (2)	0·3184 (3)	0·3640 (5)	5·94 (2)
C(1)	0·0434 (3)	0·1197 (3)	0·3113 (6)	3·09 (2)
C(2)	0·1212 (3)	0·0327 (3)	0·3171 (6)	3·35 (2)
C(3)	0·2104 (3)	0·0437 (4)	0·4744 (7)	4·30 (2)
C(4)	0·1790 (3)	0·1057 (3)	0·6697 (7)	4·23 (2)
C(5)	0·0759 (4)	0·2648 (4)	0·8140 (6)	4·64 (2)
C(6)	0·0138 (4)	0·3714 (4)	0·7710 (8)	5·34 (2)
C(7)	−0·0680 (4)	0·3511 (4)	0·5975 (7)	5·11 (2)
C(8)	−0·0205 (3)	0·3092 (3)	0·3973 (7)	4·01 (2)
C(9)	0·0499 (3)	0·2105 (3)	0·4351 (5)	2·96 (2)
C(10)	0·1291 (3)	0·2204 (3)	0·6175 (5)	3·29 (2)
C(11)	0·2141 (3)	0·3005 (3)	0·5665 (7)	3·59 (2)
H(C1)	−0·0010 (4)	0·0113 (4)	0·0199 (7)	4·08
H(C3)	0·0234 (4)	−0·0030 (5)	0·0504 (8)	5·30
H′(C3)	0·0268 (4)	0·0083 (4)	0·0403 (8)	5·30
H(C4)	0·0236 (4)	0·0117 (4)	0·0776 (8)	5·23
H′C(4)	0·0127 (4)	0·0060 (4)	0·0741 (8)	5·23
H(C5)	0·0129 (4)	0·0272 (4)	0·0921 (9)	5·63
H′(C5)	0·0024 (4)	0·0203 (5)	0·0860 (8)	5·63
H(C6)	−0·0022 (4)	0·0398 (5)	0·0903 (9)	6·34
H′(C6)	0·0062 (4)	0·0436 (5)	0·0727 (9)	6·34
H(C7)	−0·0110 (4)	0·0421 (5)	0·0572 (8)	6·10
H′(C7)	−0·0118 (4)	0·0294 (5)	0·0641 (9)	6·10
H(C8)	−0·0072 (4)	0·0292 (4)	0·0285 (8)	5·00
H′(C8)	0·0028 (4)	0·0371 (4)	0·0339 (8)	5·00
H(O3)	0·0289 (5)	0·0375 (5)	0·0364 (8)	6·93
(II)				
O(1)	0·4661 (2)	−0·1167 (2)	0·0336 (3)	5·54 (2)
O(2)	0·8005 (2)	0·0485 (2)	−0·0528 (2)	4·41 (1)
O(3)	0·8619 (3)	0·0619 (2)	0·1443 (3)	5·48 (1)
C(1)	0·6384 (3)	−0·0638 (3)	0·1558 (3)	4·26 (2)
C(2)	0·5652 (3)	−0·0968 (3)	0·0402 (4)	4·02 (2)
C(3)	0·6169 (3)	−0·0982 (3)	−0·0684 (3)	4·52 (2)
C(4)	0·7412 (3)	−0·1268 (3)	−0·0429 (3)	4·11 (2)
C(5)	0·9367 (3)	−0·1207 (3)	0·0950 (4)	4·91 (2)
C(6)	0·9437 (4)	−0·2171 (3)	0·1353 (4)	5·43 (2)
C(7)	0·8895 (4)	−0·2290 (3)	0·2443 (4)	5·18 (2)
C(8)	0·7672 (3)	−0·1958 (3)	0·2171 (4)	4·51 (2)
C(9)	0·7604 (3)	−0·0986 (3)	0·1803 (3)	3·69 (2)
C(10)	0·8141 (3)	−0·0832 (2)	0·0688 (3)	3·55 (2)
C(11)	0·8238 (3)	0·0148 (3)	0·0482 (4)	3·86 (2)
O(1′)	0·4089 (2)	0·3411 (2)	0·0467 (3)	6·40 (2)
O(2′)	0·8397 (2)	0·2319 (2)	0·1048 (3)	5·19 (1)
O(3′)	0·7581 (2)	0·2214 (2)	−0·0889 (2)	4·52 (1)
C(1′)	0·6044 (3)	0·3247 (3)	0·1408 (3)	4·34 (2)
C(2′)	0·5064 (3)	0·3344 (3)	0·0343 (3)	4·09 (2)
C(3′)	0·5349 (3)	0·3286 (3)	−0·0882 (3)	4·21 (2)
C(4′)	0·6434 (3)	0·3772 (3)	−0·0979 (3)	3·87 (2)
C(5′)	0·8472 (3)	0·4176 (3)	−0·0010 (4)	4·36 (2)
C(6′)	0·8281 (3)	0·5150 (3)	0·0175 (4)	5·04 (2)
C(7′)	0·7904 (4)	0·5323 (3)	0·1364 (4)	5·42 (2)
C(8′)	0·6876 (4)	0·4774 (3)	0·1438 (3)	4·49 (2)
C(9′)	0·7084 (3)	0·3797 (3)	0·1299 (3)	3·69 (2)
C(10′)	0·7439 (3)	0·3596 (2)	0·0087 (3)	3·29 (2)
C(11′)	0·7834 (3)	0·2651 (3)	0·0115 (4)	3·62 (2)
H(C1)	0·6422	−0·0012	0·1509	5·26
H′(C1)	0·6047	−0·0783	0·2220	5·26
H(C3)	0·6103	−0·0413	−0·1052	5·52
H′(C3)	0·5734	−0·1353	−0·1283	5·52
H(C4)	0·7725	−0·1156	−0·1111	5·11
H′(C4)	0·7439	−0·1892	−0·0312	5·11
H(C5)	0·9816	−0·0867	0·1581	5·91
H′(C5)	0·9679	−0·1148	0·0251	5·91
H(C6)	1·0204	−0·2353	0·1552	6·43
H′(C6)	0·9045	−0·2531	0·0705	6·43
H(C7)	0·9325	−0·1976	0·3112	6·18
H′(C7)	0·8908	−0·2898	0·2659	6·18
H(C8)	0·7351	−0·2036	0·2861	5·51
H′(C8)	0·7231	−0·2301	0·1540	5·51
H(C9)	0·8036	−0·0660	0·2458	4·69
H(O3)	0·8540	0·1240	0·1450	6·48
H(C1′)	0·5806	0·3402	0·2125	5·34
H′(C1′)	0·6265	0·2643	0·1468	5·34
H(C2′)	0·4731	0·3503	−0·1475	5·21
H′(C2′)	0·5431	0·2681	−0·1074	5·21
H(C4′)	0·6278	0·4388	−0·1013	4·87
H′(C4′)	0·6642	0·3622	−0·1713	4·87
H(C5′)	0·8657	0·4089	−0·0773	5·36
H′(C5′)	0·9092	0·3995	0·0610	5·36
H(C6′)	0·7726	0·5371	−0·0477	6·04
N′(C6′)	0·8971	0·5460	0·0188	6·04
H(C7′)	0·7726	0·5932	0·1417	6·42
H′(C7′)	0·8508	0·5187	0·2024	6·42
H(C8′)	0·6248	0·4958	0·0829	5·49
H′(C8′)	0·6667	0·4878	0·2187	5·49
H(C9′)	0·7730	0·3612	0·1934	4·69
H(O3′)	0·7730	0·1650	−0·0800	5·52

Table 2. *Bond and interatomic distances* (Å) *and angles* (°) *for* (I) *and* (II)

Parentheses contain e.s.d.'s for the least significant digit

	(I)	(II)	(II)′
C(1)—C(2)	1·448 (5)	1·502 (5)	1·506 (5)
C(1)—C(9)	1·340 (5)	1·532 (5)	1·534 (5)
C(2)—C(3)	1·494 (5)	1·495 (6)	1·504 (6)
C(3)—C(4)	1·517 (6)	1·527 (6)	1·526 (5)
C(4)—C(10)	1·544 (5)	1·531 (5)	1·542 (5)
C(5)—C(6)	1·523 (6)	1·532 (6)	1·519 (6)
C(5)—C(10)	1·548 (6)	1·552 (5)	1·548 (5)
C(6)—C(7)	1·510 (7)	1·528 (6)	1·536 (6)
C(7)—C(8)	1·523 (6)	1·525 (6)	1·511 (6)
C(8)—C(9)	1·503 (5)	1·532 (6)	1·520 (6)
C(9)—C(10)	1·512 (5)	1·556 (5)	1·555 (5)
C(10)—C(11)	1·506 (5)	1·516 (6)	1·511 (5)
O(1)—C(2)	1·238 (4)	1·219 (4)	1·217 (5)
O(2)—C(11)	1·186 (4)	1·232 (5)	1·238 (4)
O(3)—C(11)	1·318 (5)	1·304 (5)	1·298 (4)
O(3)—H(O3)	1·06 (6)	0·948	0·877
O(3)—O(1)″	2·652 (4)		
O(3)—O(2)′		2·625 (4)	2·690 (4)
H(O3)—O(1)″	1·60 (6)		
H(O3)—O(2)′		1·700	1·815
C(2)—C(1)—C(9)	122·9 (3)	114·0 (3)	113·4 (3)
C(1)—C(2)—C(3)	117·9 (4)	117·0 (3)	116·2 (3)
C(1)—C(2)—O(1)	120·7 (3)	121·5 (4)	121·8 (4)
C(3)—C(2)—O(1)	121·3 (3)	121·4 (4)	121·8 (4)
C(2)—C(3)—C(4)	111·1 (3)	114·3 (3)	114·0 (3)
C(3)—C(4)—C(10)	112·6 (3)	113·7 (3)	113·7 (3)
C(6)—C(5)—C(10)	113·2 (3)	113·4 (3)	113·4 (3)
C(5)—C(6)—C(7)	109·9 (4)	110·5 (4)	111·7 (3)
C(6)—C(7)—C(8)	111·3 (4)	111·0 (3)	110·7 (3)
C(7)—C(8)—C(9)	113·0 (4)	111·5 (3)	112·2 (4)
C(1)—C(9)—C(8)	121·4 (3)	112·1 (3)	111·6 (3)
C(1)—C(9)—C(10)	122·2 (3)	110·5 (3)	110·3 (3)
C(8)—C(9)—C(10)	116·3 (3)	111·1 (3)	111·4 (3)
C(4)—C(10)—C(5)	109·3 (3)	110·8 (3)	110·8 (3)
C(4)—C(10)—C(9)	110·8 (3)	110·1 (3)	110·0 (3)
C(4)—C(10)—C(11)	108·0 (3)	110·3 (3)	111·9 (3)
C(5)—C(10)—C(9)	109·4 (3)	109·4 (3)	109·1 (3)
C(5)—C(10)—C(11)	108·3 (3)	106·7 (3)	106·7 (3)
C(9)—C(10)—C(11)	111·1 (3)	109·4 (3)	108·1 (3)
C(10)—C(11)—O(2)	123·3 (4)	122·9 (3)	121·3 (3)
C(10)—C(11)—O(3)	115·4 (3)	115·8 (4)	117·0 (3)
O(2)—C(11)—O(3)	120·9 (4)	121·4 (4)	121·7 (4)
C(11)—O(3)—H(O3)	103· (3)	122·3	113·3
C(2)—O(1)—H(O3)″	125· (2)		
C(11)—O(2)—H(O3)′		124·1	128·9
C(11)—O(3)—O(1)″	110·1 (2)		
C(11)—O(3)—O(2)′		113·1 (3)	111·4 (2)
O(3)—H(O3)—O(1)″	168· (5)		
O(3)—H(O3)—O(2)′		164·0	176·3

(II) and (II′) are, respectively, the right- and the left-hand molecules in the asymmetric unit shown in Fig. 4. For column (II′) the primed and unprimed designations are to be reversed, *e.g.* O(3)—O(2)′ is read O(3)′—O(2) and C(11)—O(3)—O(2)′ is read C(11)′—O(3)′—O(2). The ″ indicates that the atom is in an adjacent molecule related by $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

other slight deviations from a local mirror plane, so that the pair as a unit has distinct asymmetry beyond that conferred by the carboxyl conformations. As may also be seen in Fig. 4, the paired carboxyl groups are not coplanar [dihedral angle 150·9 (5)°].

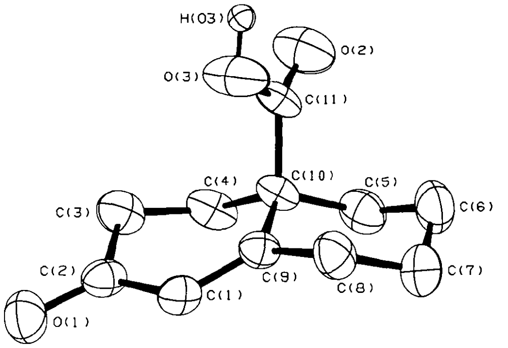

Fig. 1. The atom-numbering scheme for compound (I). The same numbering applies to (II).

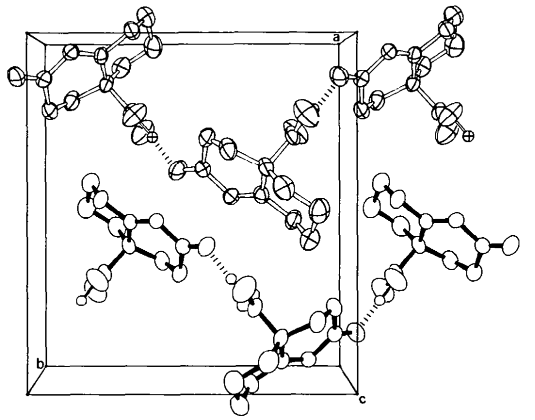

Fig. 2. A view of (I), showing the helices generated by the catemeric hydrogen bonding. Molecules configured *R* at C(10) are shown with open atoms and dark bonds; their enantiomers have sectioned atoms and open bonds.

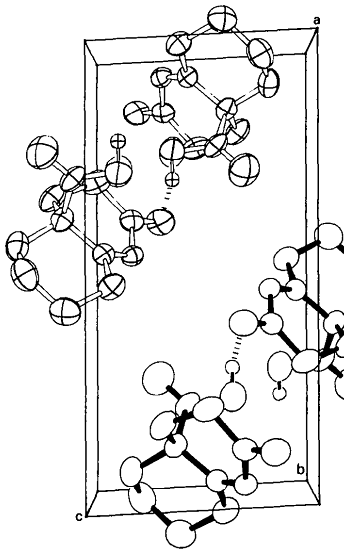

Fig. 3. A unit cell for compound (I), viewed along the axis of the helices (*b*). Helices of opposite chirality, indicated by the same shading scheme used in Fig. 2, will interpenetrate where the molecules extend beyond the *ab* and *bc* cell faces.

There is a dihedral angle of 43·4 (3)° between the plane of the carboxyl group and that defined by C(9), C(10) and C(11); the corresponding angle in the left-hand molecule is 37·7 (3)°. Fig. 5 displays the cell with two different asymmetric units, related to each other by a center of symmetry at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, and emphasizes with differential shading that each asymmetric unit contains one *RR* and one *SS* molecule.

The solid-state (KBr) IR spectrum observed for (II) is a normal one, with carbonyl stretching absorptions at 1696 and 1717 cm^{-1}. The former value is typical for carboxylic acids adopting the dimeric hydrogen-bonding pattern that is standard for these compounds; the latter value is normal for unstrained cyclic ketones (*cf.* 1715 cm^{-1} for cyclohexanone). The absorptions in (I), however, appear at 1637 and 1723 cm^{-1}, neither of which is normal for a carboxyl

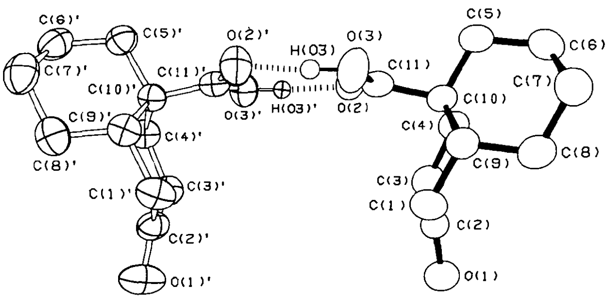

Fig. 4. The asymmetric unit of (II), with its atom-numbering scheme, in a view centered on a point midway between the two carboxyl hydrogens. A local pseudo-mirror separates the two halves of the asymmetric unit. The same shading scheme used in Figs. 2 and 3 emphasizes the opposite C(10) configurations of the molecules.

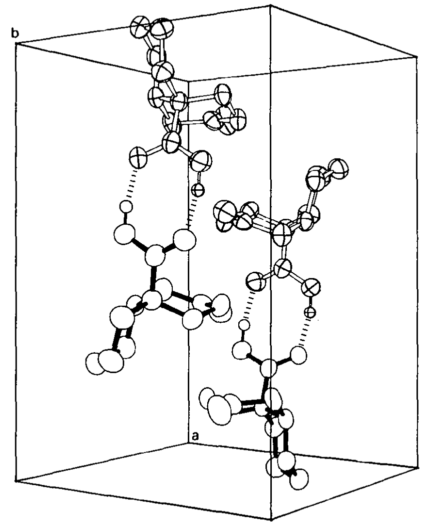

Fig. 5. A partial ($Z = 8$) packing diagram for (II), showing one pair of asymmetric units related by the center at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. Molecules of opposite configuration are differentiated as in Figs. 2–4.

group or for an α,β-unsaturated ketone (expected: *ca* 1670 cm^{-1}). These shifts are due to the unusual hydrogen-bonding arrangement in (I) and are, in fact, fairly typical for catemerically hydrogen-bonded keto carboxylic acids, as is now known from several published examples (Takai, Amagaya & Ogihara, 1977; Jefferies, Payne, Raston & White, 1981; Vanderhoff, Thompson & Lalancette, 1986; Lalancette, Vanderhoff & Thompson, 1991). Hydrogen bonding lowers the IR stretching frequency for all carbonyl groups involved, as observed for the ketone in (I) ($\Delta\nu \simeq 33$ cm^{-1}). The rise seen in (I) in the stretching frequency for the carboxyl ($\Delta\nu \simeq 25$ cm^{-1}) occurs because of the *removal* of hydrogen bonding relative to the normally observed hydrogen-bonded dimer, but is not as great as the increase reported for monomeric carboxylic acids ($\nu \simeq 1760$ cm^{-1}).

It is not clear what causes these molecules to adopt different modes of hydrogen bonding. In each of the two modes we have observed, examples are known of both conjugated and non-conjugated ketones (as well as acids), so the change does not seem attributable merely to polarity effects associated with conjugation. The other major difference between these two compounds is the obvious change in molecular shape, from the near planarity of the bicyclic system in (I) (Fig. 1) to the curvature evident in (II) (Fig. 5), and such a change might reasonably trigger a shift in hydrogen-bonding mode. However, the previously noted 10-carboxy-*cis*-decal-3-one (Chadwick & Dunitz, 1979) is nearly identical to (II) in molecular shape, [and, like (II), has a saturated ketone] and yet the two adopt different hydrogen-bonding modes. Because such slight differences are associated with dramatically different patterns of intermolecular hydrogen bonding in this ring system, it appears that the energy minima represented by these two modes must be similar in energy. It may be that they are more similar here than in the broad structural range of organic compounds, in which we have so far been able to identify more than three dozen simple keto acids which are dimeric, but just over one dozen which are catemeric.

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Structure of *m*-Xylylenediammonium Adipate Monohydrate

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Abstract. $C_8H_{14}N_2^{2+}.C_6H_8O_4^{2-}.H_2O$, $M_r = 300{\cdot}35$, monoclinic, $P2_1/c$, $a = 17{\cdot}968\,(2)$, $b = 5{\cdot}7859\,(7)$, $c = 14{\cdot}844\,(1)$ Å, $\beta = 103{\cdot}614\,(7)^\circ$, $V = 1499{\cdot}9\,(3)$ Å^3, $Z = 4$, $D_m = 1{\cdot}331$, $D_x = 1{\cdot}330$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 0{\cdot}85$ mm^{-1}, $F(000) = 648$, $T = 295$ K, $R = 0{\cdot}040$ for 2188 unique reflections. Two *m*-xylylenediammonium cations and adipate anions are held together by two kinds of strong N—H···O hydrogen bonds to form a dimer around an inversion

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