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Catemeric Hydrogen Bonding in (+)- and (±)-endo-Camphorcarboxylic Acid

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Abstract. 4,7,7-Trimethyl-3-oxobicyclo[2.2.1]heptane-2-*endo*-carboxylic acid (I), (+)-$C_{11}H_{16}O_3$, M_r = 196·246, monoclinic, $P2_1$, a = 10·712 (3), b = 6·724 (3), c = 7·136 (3) Å, β = 95·07 (3)°, V(234 K) = 512·0 (4) Å^3, Z = 2, D_m(295 K) = 1·25 (1), D_x[295 K; V = 515·0 (5) Å^3] = 1·266 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 0·98 cm^{-1}, F(000) = 212, T = 234 (1) K, R = 0·058 for 638 observed reflections. (II), (±)-$C_{11}H_{16}O_3$, M_r = 196·246, monoclinic, $P2_1/c$, a = 10·849 (2), b = 6·751 (3), c = 14·248 (2) Å, β = 94·96 (1)°, V(252 K) = 1039·6 (5) Å^3, Z = 4, D_m(295 K) = 1·24 (1), D_x[295 K; V = 1046·0 (6) Å^3] = 1·246 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 0·96 cm^{-1}, F(000) = 424, T = 252 (1) K, R = 0·065 for 1290 observed reflections. In both the (+)-enantiomer (I) and the racemate (II) the crystal is composed of single-strand helical chains parallel to the b axis, produced by infinite repetition of a hydrogen bond linking the carboxylic acid of one molecule with the ketone of an adjacent screw-related molecule, so that each hydrogen-bonding helix contains molecules of only one chirality. The packing in (II), whose c cell dimension is doubled relative to (I), corresponds to stacked pairs of ($P2_1$) cells packed as in (I), with alternating chirality in the c direction.

Introduction. Our exploration of hydrogen-bonding patterns in keto carboxylic acids (Leiserowitz, 1976; Vanderhoff, Thompson & Lalancette, 1986; Lalancette, Slifer & Thompson, 1989; Lalancette, Vanderhoff & Thompson, 1990) has led us to examine the title compounds. Our attention was drawn to these materials for several specific reasons. The

geometry of β-keto acids appears attractive for internal hydrogen bonding. However, to our knowledge no evidence for this in the solid state has ever appeared. There is considerable literature treating the putative existence and importance of such hydrogen bonding in solution, in part because it has been implicated indirectly in the thermal instability of these compounds (Hay & Bond, 1967; Grande & Rosenfeld, 1980). Their thermal decarboxylation is known to proceed by way of a six-centered internal hydrogen transfer, whose obvious precursor would be the corresponding internally hydrogen-bonded structure (Logue, Pollack & Vitullo, 1975). However, evidence also exists in favor of other mechanisms (Ferris & Miller, 1963; Kayser, Brault, Pollack, Bantia & Sadoff, 1983). As a class, β-keto carboxylic acids are usually so thermally unstable that they are seldom available commercially. Not only was the title structure an exception, but both enantiomers were available, thus placing the racemate at our disposal as well. We were interested not merely in the hydrogen-bonding pattern, but in seeing whether it would be altered by the presence *versus* the absence of the second enantiomer and the change in space group required (Eliel & Kofron, 1953; Walborsky, Barash, Young & Impastato, 1961; Simpson & Marsh, 1966).

Experimental. The (+)-enantiomer [(I); Baptista (1976)] was purchased from Aldrich Chemical Co. (m.p. 393–396 K) and recrystallized from water by slow evaporation at 295 K; densities were measured by flotation in carbon tetrachloride–cyclohexane. An elongated platelet 1·40 × 0·09 × 0·20 mm was mounted on a glass fiber; attempts to cleave these crystals were unsuccessful. Data ($2\theta_{max}$ = 60°, −15 ≤ h ≤ 15,

$0 \le k \le 9$, $0 \le l \le 9$) were collected on a Syntex $P2_1$ diffractometer with a graphite monochromator using Mo $K\alpha$ radiation; 15 high-angle reflections were used to calculate the orientation matrix and best cell dimensions. Space group $P2_1$ was chosen on the basis of the screw axis on b and confirmed by successful solution and refinement of the structure. With three standard reflections recorded every 47 reflections ($\pm 1.06\%$), 1609 unique reflections were measured in the θ–2θ scan mode. Of these, 971 were unobserved and 638 had $I \ge 3\sigma(I)$; the low percentage of reflections observed was probably due to the low power at which the diffractometer was run during this data cycle. After accurate measurement of the three pairs of parallel crystal faces, one of which was normal to b, absorption corrections were made based on Howells' analytical expression for polyhedra (Alcock, 1970) (min. = 1.009, max. = 1.021). The structure was solved using $MULTAN80$; all non-H atoms were found from the best E map (CFOM = 2.59) and all hydrogens were found in difference Fourier maps. H-atom positional parameters were not refined; their isotropic thermal parameters were fixed at $(B + 1)$ Å^2, where B is the value for the atom to which the H is bound. All non-H atoms were refined with anisotropic thermal parameters; $\Sigma w||F_o| - |F_c||^2$ was minimized; the isotropic extinction parameter was refined to 0.3 (2); $R = 0.058$, $wR = 0.055$, $S = 1.76$, the weighting scheme chosen was σ weights, last cycle max. $\Delta/\sigma = 0.015$, av. = 0.003, final difference Fourier max. = 0.18, min. = 0.15 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 racemic modification (II) was crystallized by slow evaporation at 295 K of a toluene solution of equal weights of commercial (Aldrich Chemical Co. (+)- and (−)-enantiomer; the same solution also produced thinner crystals of the enantiomers in the same apparent crystal habit. The density was measured as described for (I). A crystal $0.50 \times 0.13 \times 0.65$ mm was used to collect the data ($2\theta_{max} = 50°$, $0 \le h \le 13$, $0 \le k \le 8$, $-17 \le l \le 17$). Space group $P2_1/c$ was chosen on the basis of absent reflections ($h0l$ with $l \ne 2n$ and $0k0$ with $k \ne 2n$ absent). With three standard reflections recorded every 17 reflections ($\pm 1.82\%$), 1977 unique reflections were collected. Of these, 687 were unobserved and 1290 had $I > 3\sigma(I)$. Absorption corrections, made after accurately measuring the three pairs of parallel crystal faces normal to the principal crystal axes, were applied as described above, min. = 1.047, max. = 1.065. All non-H atoms were found ($MULTAN80$) from the best E map (CFOM = 2.90) and all hydro-

gens were found in subsequent difference Fourier maps. H-atom positional parameters and their isotropic thermal parameters were set as described for (I); $\Sigma w||F_o| - |F_c||^2$ was minimized; the isotropic extinction parameter was refined to 0.09 (3); $R = 0.065$, $wR = 0.083$, $S = 1.29$, $w = 1/\sigma^2$ with $\sigma = 0.013 \times F_o + 4.821$ for $F_o \le 230.0$, $\sigma = 0.081 \times F_o - 11.650$ for $F_o > 230.0$, last cycle max. $\Delta/\sigma = 0.056$, av. = 0.004, final difference Fourier max. = 0.30, min. = 0.15 e Å^{-3}. The empirical weighting function was derived from a smoothed plot of the average values of $|\Delta F|/|F_o|$ for various ranges of $|F_o|$; the atomic scattering factors were applied as described above.

Discussion. Tables 1 and 2 list positional and isotropic thermal parameters* for (I) and (II), respectively. Table 3 lists interatomic distances and interatomic angles for (I) and (II).

Fig. 1 presents a view of molecule (I) with its numbering scheme, which also applies to (II). Fig. 2(a) is a partial packing diagram for (I) which shows the catemeric (Leiserowitz, 1976) hydrogen-bonding arrangement linking the carboxylic acid of each molecule to the ketone of the next, along b. For the cell chosen, each of the two contained molecules participates in H bonding to molecules outside its own cell to which it is screw-related along the b axis, generating single-strand helices with axes parallel to b. Fig. 3(a) is a full packing diagram, viewed down the helical axis (b), of an adjacent pair of cells chosen to facilitate comparison with (II) [Fig. 3(b)]. Since the H-bonding chains are a cell length apart in both a and c, the closest proximity of adjacent helical axes is 7.136 Å.

Fig. 2(b) is a partial packing diagram for (II), revealing the same general hydrogen-bonding scheme seen in (I). As before, the helices in (II) consist of molecules of a single chirality, so that, with four molecules in the cell, there are two right- and two left-handed single-strand helices, all with axes parallel to b. Fig. 3(b) is a full packing diagram showing the arrangement of helices and their handedness for one cell, which coincides with the pair chosen in Fig. 3(a). The closest proximity of any two helical axes is one-half the cell-dimension in c, i.e. 7.124 Å. In (I) this distance was $c = 7.136$ Å; however, in (II) this distance involves helices of opposite chirality. For helices of identical handedness, the closest distance of their axes is now 10.849 Å. In spite of the replacement of alternate sheets of (+)-helices, stacked warp-fashion in the ab planes of (I), by

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Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters for* (I)

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

	x	y	z	$B_{eq}/B_{iso}(\text{Å}^2)$
O(1)	7416 (4)	5446	4983 (6)	3·55 (2)
O(2)	9584 (4)	8253 (11)	4385 (7)	4·15 (2)
O(3)	10987 (4)	8051 (12)	6873 (6)	4·64 (2)
C(1)	8625 (5)	8312 (15)	8884 (8)	3·16 (3)
C(2)	8961 (5)	6906 (13)	7273 (8)	2·68 (3)
C(3)	7657 (6)	6616 (13)	6248 (9)	3·11 (3)
C(4)	6758 (5)	7930 (13)	7157 (8)	2·93 (3)
C(5)	7189 (7)	10084 (14)	6781 (10)	3·92 (4)
C(6)	8411 (6)	10366 (15)	8056 (10)	4·17 (4)
C(7)	7301 (6)	7623 (15)	9241 (9)	3·48 (3)
C(8)	7206 (7)	5481 (16)	9888 (10)	5·09 (4)
C(9)	6676 (7)	8948 (15)	10663 (10)	5·38 (5)
C(10)	5401 (6)	7492 (14)	6600 (9)	4·01 (4)
C(11)	9855 (6)	7782 (14)	5999 (10)	3·16 (3)
H(C1)	9220	8290	9980	4·16
H(C2)	9290	5620	7820	3·68
H1(C5)	6490	10910	7390	4·92
H2(C5)	7280	10410	5480	4·92
H1(C6)	8180	11120	9280	5·17
H2(C6)	9310	10690	7600	5·17
H1(C8)	7380	4430	9120	6·09
H2(C8)	7650	5300	11140	6·09
H3(C8)	6350	5240	10310	6·09
H1(C9)	5850	8530	10360	6·38
H2(C9)	6720	10320	10280	6·38
H3(C9)	6920	8600	11920	6·38
H1(C10)	5130	6180	7020	5·01
H2(C10)	4990	7720	5340	5·01
H3(C10)	4950	8400	7380	5·01
H(O3)	11450	8550	5950	5·64

Table 2. *Fractional atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters for* (II)

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

	x	y	z	$B_{eq}/B_{iso}(\text{Å}^2)$
O(1)	7516 (2)	4896 (4)	2634 (2)	4·39 (1)
O(2)	9534 (2)	7874 (5)	2209 (2)	4·71 (1)
O(3)	10894 (2)	8073 (4)	3460 (2)	4·44 (1)
C(1)	8592 (3)	8195 (6)	4470 (2)	3·83 (2)
C(2)	8973 (3)	6733 (5)	3713 (2)	3·11 (1)
C(3)	7714 (3)	6127 (6)	3244 (2)	3·26 (1)
C(4)	6757 (3)	7330 (6)	3696 (2)	3·85 (2)
C(5)	7028 (4)	9532 (7)	3390 (3)	5·26 (2)
C(6)	8202 (4)	10130 (6)	3967 (3)	5·07 (2)
C(7)	7349 (3)	7342 (6)	4726 (2)	3·97 (2)
C(8)	7469 (5)	5316 (7)	5164 (3)	5·78 (2)
C(9)	6663 (4)	8682 (8)	5377 (3)	5·82 (2)
C(10)	5446 (4)	6657 (9)	3473 (3)	6·09 (2)
C(11)	9812 (3)	7596 (5)	3032 (2)	3·25 (1)
H(C1)	9200	8374	4998	4·83
H(C2)	9360	5579	4020	4·11
H1(C5)	6360	10385	3528	6·26
H2(C5)	7160	9563	2730	6·26
H1(C6)	8020	11126	4421	6·07
H2(C6)	8830	10492	3538	6·07
H1(C8)	7850	4410	4790	6·78
H2(C8)	7920	5401	5773	6·78
H3(C8)	6650	4821	5276	6·78
H1(C9)	7070	9480	5840	6·82
H2(C9)	6090	9529	4979	6·82
H3(C9)	6000	7974	5628	6·82
H1(C10)	4820	7600	3650	7·09
H2(C10)	5290	6340	2820	7·09
H3(C10)	5310	5410	3800	7·09
H(O3)	11320	8730	3090	5·44

Table 3. *Bond and interatomic distances* (Å) *and angles* (°) *for* (I) *and* (II)

E.s.d.'s for the least significant digit are given in parentheses.

	(I)	(II)
C(1)—C(2)	1·555 (9)	1·544 (5)
C(1)—C(6)	1·51 (1)	1·530 (6)
C(1)—C(7)	1·535 (8)	1·539 (5)
C(2)—C(3)	1·530 (8)	1·524 (5)
C(2)—C(11)	1·499 (8)	1·504 (5)
C(3)—C(4)	1·497 (8)	1·506 (5)
C(4)—C(5)	1·55 (1)	1·584 (6)
C(4)—C(7)	1·562 (8)	1·550 (5)
C(4)—C(10)	1·502 (8)	1·499 (6)
C(5)—C(6)	1·539 (9)	1·509 (6)
C(7)—C(8)	1·52 (1)	1·504 (6)
C(7)—C(9)	1·55 (1)	1·533 (5)
O(1)—C(3)	1·208 (7)	1·209 (4)
O(2)—C(11)	1·205 (6)	1·201 (4)
O(3)—C(11)	1·325 (7)	1·315 (4)
O(3)—H(O3)	0·922	0·854
O(3)—O(1ⁱ)	2·770 (7)	2·717 (4)
H(O3)—O(1ⁱ)	1·923	1·872
C(2)—C(1)—C(6)	107·7 (5)	107·3 (3)
C(2)—C(1)—C(7)	102·5 (5)	102·7 (3)
C(6)—C(1)—C(7)	103·3 (5)	102·6 (3)
C(1)—C(2)—C(3)	99·8 (5)	101·2 (3)
C(1)—C(2)—C(11)	114·3 (6)	114·6 (3)
C(3)—C(2)—C(11)	111·4 (5)	113·0 (3)
O(1)—C(3)—C(2)	124·5 (6)	126·6 (3)
O(1)—C(3)—C(4)	127·2 (6)	126·3 (3)
C(2)—C(3)—C(4)	108·2 (6)	107·0 (3)
C(3)—C(4)—C(5)	105·3 (5)	103·7 (3)
C(3)—C(4)—C(7)	97·7 (5)	99·4 (3)
C(3)—C(4)—C(10)	114·5 (6)	115·0 (3)
C(5)—C(4)—C(7)	101·3 (5)	100·6 (3)
C(5)—C(4)—C(10)	115·7 (5)	114·9 (4)
C(7)—C(4)—C(10)	119·8 (5)	120·7 (3)
C(4)—C(5)—C(6)	105·3 (6)	105·6 (3)
C(1)—C(6)—C(5)	102·1 (6)	102·3 (3)
C(1)—C(7)—C(4)	94·2 (5)	94·4 (3)
C(1)—C(7)—C(8)	115·1 (6)	113·1 (3)
C(1)—C(7)—C(9)	113·3 (6)	113·8 (3)
C(4)—C(7)—C(8)	112·7 (6)	113·7 (3)
C(4)—C(7)—C(9)	113·7 (6)	113·1 (3)
C(8)—C(7)—C(9)	107·6 (6)	108·3 (3)
C(2)—C(11)—O(2)	124·7 (5)	125·2 (3)
C(2)—C(11)—O(3)	112·0 (6)	111·2 (3)
O(2)—C(11)—O(3)	123·2 (6)	123·6 (3)
C(11)—O(3)—H(O3)	104·0	110·5
C(11)—O(3)—O(1ⁱ)	115·8 (5)	115·5 (2)
O(3)—H(O3)—O(1ⁱ)	152·3	170·0
C(3ⁱ)—O(1ⁱ)—H(O3)	126·2	126·9

(i) indicates that the atom is in an adjacent molecule related by (2 − x, ½ + y, 1 − z) and (2 − x, ½ + y, ½ − z) for (I) and (II), respectively.

enantiomeric sheets of (−)-helices in (II), the only substantial change in basic cell measurements is an exact (within 0·17%) doubling of the *c* cell dimension, relative to (I). The *a* and *b* dimensions are identical within 1·3%, the unique angles are identical within 0·11° and the measured densities are identical within experimental error.

The occurrence of catemeric hydrogen bonding in simple keto carboxylic acids is rare relative to the 'normal' carboxyl dimer which leaves the ketone uninvolved, of which several dozen examples appear in the literature. We have previously noted the occurrence of a racemic pair of single-strand helices related by a center of symmetry (Vanderhoff, Thompson & Lalancette, 1986) and of a triple-stranded helix arising from a single enantiomer (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, Ralston & White, 1981; Preut, Kreiser, Mueller & Jones, 1985; Bertolasi, Ferretti & Gilli, 1982; Peeters, Blaton & De Ranter, 1983).

Within the present molecule, the rigidity of the bicyclic structure fixes the position of every non-H atom except the O atoms of the carboxyl group. Remarkably, in both (I) and (II), the carboxyl is turned so that its plane coincides almost exactly with the C(2)—C(3) bond, with the pair of carbonyl groups aimed in the same direction rather than away from each other. For (I), the planes defined by the carboxyl group and by C(2), C(3) and C(11) meet in a 2 (1)° dihedral angle; for (II), the angle is 2·3 (5)°. In (I), for the best plane including C(2), C(3), C(11), O(2) and O(3), the greatest deviation from the plane for any of those atoms is 0·011 Å and the mean deviation is 0·007 Å, with H(O3) lying 0·040 Å out of the plane. For (II), the greatest deviation is 0·015 Å and the mean is 0·009 Å, with H(O3) lying 0·110 Å out of the plane. In this conformation the dihedral angle between the plane of the carboxyl and that of the ketone plus its two attached C atoms is 67·3 (7)° in (I) and 63·3 (4)° in (II), a difference of 4·0°.

The solid-state infrared spectra of (I) and (II) are nearly identical, as might be anticipated from knowledge of the crystal structures. Each has three peaks in the carbonyl region of the spectrum, at 1710 ± 1, 1735 ± 2 and 1758 ± 2 cm^{-1}. Of these, the first is assigned to the ketone and is shifted some 35 cm^{-1}

to a lower wavenumber relative to camphor, whose structure differs only in the absence of the carboxyl group and can serve as a non-H-bonded model. Such a shift seems to be typical for ketone functions hydrogen bonded in this way (Amagaya, Takai, Ogihara & Iitaka, 1977; Takai, Amagaya & Ogihara, 1977; Jefferies, Payne, Ralston & White, 1981; Vanderhoff, Thompson & Lalancette, 1986). The peak around 1735 cm^{-1} is assigned to the carboxyl carbonyl and is shifted by roughly 35 cm^{-1} toward a higher wavenumber than is normal for dimerically hydrogen-bonded carboxylic acids; this shift also appears to be typical for such a change in hydrogen bonding. The peak around 1758 cm^{-1} is not specifically assigned; however, this is approximately the value usually cited for the C=O stretch of monomeric (i.e. non-hydrogen-bonded) carboxyl groups. Because the relative intensity of this band was found
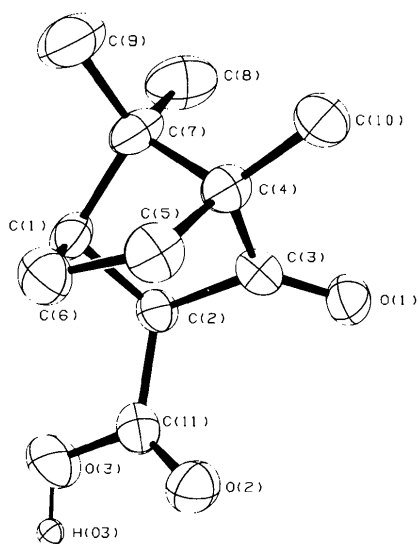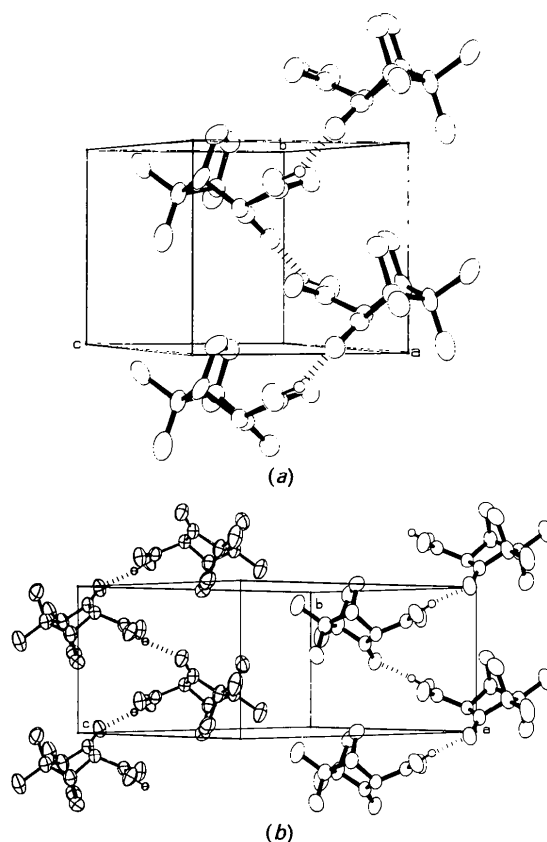

(a)

(b)

Fig. 2. (a) A partial packing diagram for (I), with extracellular molecules to show the helical hydrogen-bonding chains, in a view orthogonal to the axis of the helices (b axis). One of the two H-bonding helices, which pass along the bc cell faces, has been removed for clarity. (b) A partial packing diagram for (II), in a view orthogonal to the axis of the helices (b axis), showing two of the four helices which pass along the bc cell faces, one of each chirality. The molecules with open atoms and heavy bonds are the (+)- and those with sectioned atoms and light bonds are the (−)-enantiomer.

Fig. 1. The atom-numbering scheme, shown here for (I), applies to (II) as well.

experimentally to increase as the concentration of the keto acid in KBr was lowered, it seems likely that this band represents either monomeric carboxyl or simply the non-H-bonded carboxyl ends of broken chain fragments.

Camphorcarboxylic acid does not occur naturally; it is prepared by carboxylation of camphor, as first described some 120 years ago (Baubigny, 1868), and its full stereochemistry was long unknown. The present structure determination confirms the *endo* configuration which has been assigned to the carboxyl group of the major epimer for at least 20 years (Cervinka & Novak, 1968), although this compound is still sold by Aldrich Chemical Co. and cited in *The Merck Index* (1983) with no clear indication of *exo–endo* stereochemistry (Antkowiak & Antkowiak, 1975).
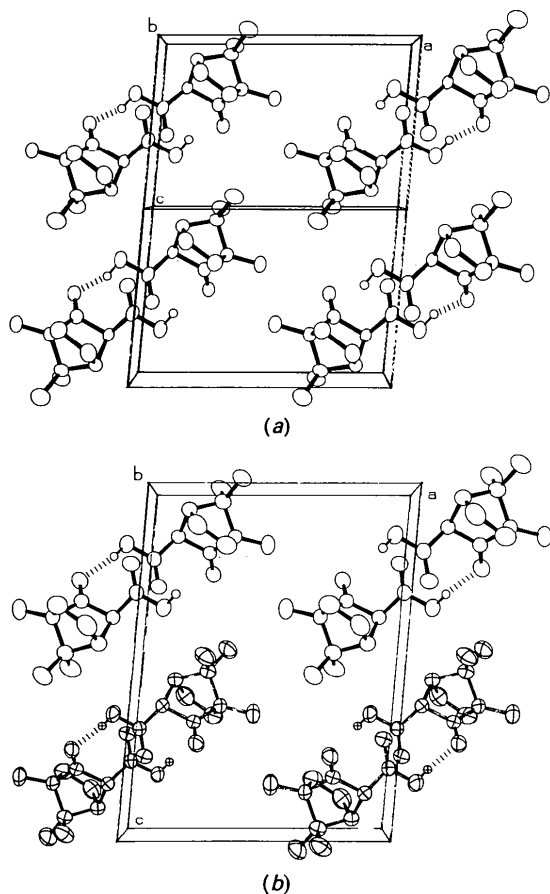
While thermal decarboxylation takes place even below the melting range (393–396 K), solid (I) appears to be more stable than some other β-keto acids (Kayser, Brault, Pollack, Bantia & Sadoff, 1983). This may conceivably be due in some way to the observed hydrogen-bonding pattern, but may also simply be because of the difficulty of introducing an additional sp^2 center into the already strained bicyclic system, as required by the decarboxylation mechanism. This difficulty is attested to by the extreme slowness of epimerization resulting from enolization, which is normally easy in β-keto acids (Antkowiak & Antkowiak, 1975).

(a)

(b)

Fig. 3. (a) A packing diagram illustrating a double unit-cell for (I), in a view along the axis of the helices (b axis), showing, for each molecule in the pair of cells, the next molecule in the helix, to which its carboxyl group is hydrogen bonded. (b) A packing diagram for (II), in a view along the axis of the helices (b axis), showing, for each molecule within the cell, the next molecule in the helix, to which its carboxyl group is hydrogen bonded. The chiralities of the molecules are indicated by differential shading as in Fig. 2(b).

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