TTF)$_2$Br.C$_2$H$_4$(OH)$_2$ may also be possible, since it involves all the Br anions, just like the salts (BEDT-TTF)$_3$Br$_2$(H$_2$O)$_2$ (Urayama *et al.*, 1987) and (BEDT-TTF)$_3$Cl$_2$.(H$_2$O)$_2$ (Mori & Inokuchi, 1987*a*,*b*; Rosseinsky *et al.*, 1988). Unfortunately, determination of O-atom positions is not sufficiently accurate to allow us to draw definite conclusions about the system of anion hydrogen bonds in the crystal.

The molecular structures of cation radicals *A* and *B* (Table 2) are analogous to the structure of BEDT-TTF with a formal charge of $+\frac{1}{2}$ in the (BEDT-TTF)$_4$Cd$_2$I$_6$ (Gritsenko, Konovalikhin, Dyachenko, Lyubovskaya & Zhilyaeva, 1990), (BEDT-TTF)$_4$(Hg$_2$Cl$_6$).C$_6$H$_5$Cl (Dyachenko, Gritsenko, Mkoyan, Shilov & Atovmyan, 1991), (BEDT-TTF)$_4$-(Hg$_2$Br$_6$).C$_6$H$_5$Cl and (BEDT-TTF)$_4$(Hg$_2$Br$_6$) salts investigated by us.

The BEDT-TTF molecules in (BEDT-TTF)$_2$Br.C$_2$H$_4$(OH)$_2$ are not planar, only the TTF fragments are planar. In molecule *A*, the rest of the atoms are displaced out of the TTF fragment plane by 0.01–0.62 Å, and in molecule *B* by 0.01–0.55 Å. Ethylene carbons are disordered in accordance with their high $B_{\rm eq}$ values (Table 1).

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9-Oxobicyclo[3.3.1]nonane-1-carboxylic Acid: Structure and Hydrogen-Bonding Pattern

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Abstract. (I) C$_{10}$H$_{14}$O$_3$, $M_r = 182.220$, orthorhombic, *Ibam*, $a = 12.795$ (2), $b = 13.178$ (2), $c = 11.092$ (2) Å, V(246 K) = 1870.2 (5), V(295 K) = 1891.8 (4) Å^3, $Z = 8$, D_m(295 K) = 1.26 (1), D_x(295 K) = 1.280 g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 7.80$ cm^{-1}, $F(000) = 784$, $T = 246$ (1) K, $R = 0.047$ for 418 observed reflections. Compound (I) adopts a conformation having two flattened chair cyclohexanone rings, with the plane of the carboxyl group orthogonal to that of the ketone. Pairs of molecules form centrosymmetric dimers by mutual hydrogen bonding of carboxyl groups, leaving the ketone carbonyls uninvolved. The two conformationally enantiomeric arrangements of the carboxyl group are disordered in the crystal.

Introduction. Simple crystalline keto carboxylic acids have four known hydrogen-bonding states which dictate or affect the intermolecular association. By far the most common has carboxyl groups paired by mutual hydrogen bonding in which the ketone is not involved (Leiserowitz, 1976; Lalancette, Vanderhoff

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& Thompson, 1990; Lalancette, Thompson & Vanderhoff, 1991; Thompson, Vanderhoff & Lalancette, 1991). A much less-common pattern involves an intermolecular carboxyl-to-ketone hydrogen bond repeated infinitely along one cell axis to yield a chain, or catemer (Vanderhoff, Thompson & Lalancette, 1986; Lalancette, Slifer & Thompson, 1989; Lalancette, Vanderhoff & Thompson, 1990, 1991; Lalancette, Thompson & Vanderhoff, 1991). A third, seldom observed, arrangement is an internal hydrogen bond (Griffe, Durant & Pieret, 1972; Sheldrick & Trowitzsch, 1983; Abell, Morris & McKee, 1990; Halfpenny, 1990). One instance is known of an acid-to-ketone dimer (Abell, Trent & Morris, 1991).

The geometry of β-keto acids appears attractive for internal hydrogen bonding (Toffoli, Khodadad & Rodier, 1988). Indeed, a considerable literature suggests the existence and importance of such hydrogen bonding in solution, in part because it has been implicated indirectly in the thermal instability of β-keto acids (Hay & Bond, 1967; Grande & Rosenfeld, 1980). Their thermal decarboxylation is known to proceed by a six-centered internal hydrogen transfer, for which the corresponding internally hydrogen-bonded structure seems a logical precursor (Logue, Pollack & Vitullo, 1975). However, to our knowledge, no evidence for this hydrogen-bonding mode in simple crystalline β-keto acids has ever appeared and thus far it has been encountered only in γ- or 4-keto acids, requiring a *seven*-membered hydrogen-bonding ring.

Crystal structures have been determined for few examples of β-keto carboxylic acids, probably because as a class they are so thermally unstable as to be difficult to access and are unavailable commercially. However, those in which decarboxylation is inhibited by the necessity of introducing serious strain (*e.g.* Bredt's rule) are adequately stable. We have examined such a case, compound (I), which, as an additional point of interest, employs a bicyclo[3.3.1]nonane ring system. For this system the question of the strain of the 'wingtip' interactions in the bis-chair conformation relative to 'flagpole' plus eclipsing strain in the alternative chair–boat conformation has evoked extensive speculation, calculation and experimentation over the years (Jaime, Osawa, Takeuchi & Camps, 1983).

Experimental. Material (m.p. 407–409 K) prepared by the method of Cope & Graham (1951) was crystallized from 95% ethanol at 286 K; density was measured by flotation in carbon tetrachloride–toluene. A rectangular platelet 0.05 × 0.30 × 0.47 mm was chosen. At low temperature (246 K), 15 high-angle reflections were used to calculate the orientation matrix and best cell dimensions. On the basis of the extinct reflections, the only allowed space groups were *Ibam* and *Iba*2; refinement was carried out in each, but was successful only in *Ibam*. Data were collected on a Syntex $P2_1$ diffractometer with a graphite monochromator, using Cu $K\alpha$ radiation. With three standard reflections recorded every 47 reflections (± 4.8%), 687 unique reflections were measured in the θ–2θ scan mode ($3 < 2\theta < 115°$, $0 \le h \le 13$, $0 \le k \le 14$, $0 \le l \le 12$); 269 were unobserved [$I < 3\sigma(I)$] and 418 had $I \ge 3\sigma(I)$. After accurate measurement of the three pairs of parallel crystal faces, each of which was normal to a principal crystal axis, absorption corrections were made based on Howells' analytical expression for polyhedra ($1.04 \le A \le 1.18$) (Alcock, 1970). The structure was solved using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); all non-H atoms were found from the best E map (CFOM = 3.00) and all H atoms except the acid H were found in subsequent difference Fourier maps. H-atom positional parameters were not refined and their isotropic thermal parameters were set 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; $\sum w||F_o| - |F_c||^2$ was minimized; $R = 0.047$, $wR = 0.060$, $S = 1.31$, $w = 1/\sigma^2$ with $\sigma_i = 0.037F_o - 0.123$ for $F_o > 50.0$, $\sigma_i = -0.033F_o + 3.510$ for $F_o \le 50.0$, last cycle max. $\Delta/\sigma = 0.0031$, av. = 0.0009, final difference Fourier max. = 0.10, min. = 0.03 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 $|F_o|$. 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).

Discussion. Table 1 lists positional and isotropic thermal parameters* and Table 2 gives interatomic distances and angles for (I). Fig. 1 presents a view of the molecule with its numbering scheme. As may be seen from Fig. 1 and Table 2, both cyclohexanone rings have chair conformations, but are somewhat flattened, which moves the 'wingtips' apart where they approach each other (Webb & Becker, 1967) presumably in response to non-bonded repulsions of the *endo* H atoms at C(3) and C(7), which have a center-to-center distance of 1.94 Å (Sim, 1983).

The plane of the carboxyl group is orthogonal to that of the ketone, and Fig. 2 illustrates the for-

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54159 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0330]

Table 1. *Fractional atomic coordinates and isotropic thermal parameters* (Å^2) *for compound* (I) *with e.s.d.'s in parentheses*

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

	x	y	z	B_{eq}/B_{iso}
O(1)	0.7732 (3)	0.1523 (3)	0.5000	7.64 (3)
O(2)	0.5458 (2)	0.0894 (2)	0.5999 (2)	4.64 (1)
C(1)	0.6092 (3)	0.2385 (3)	0.5000	2.93 (2)
C(2)	0.5762 (3)	0.2941 (3)	0.6152 (4)	5.57 (2)
C(3)	0.6328 (5)	0.3926 (4)	0.6389 (4)	7.64 (3)
C(4)	0.7469 (5)	0.3899 (4)	0.6157 (5)	7.70 (3)
C(5)	0.7781 (5)	0.3335 (4)	0.5000	6.60 (4)
C(9)	0.7267 (4)	0.2317 (4)	0.5000	4.53 (3)
C(10)	0.5644 (4)	0.1314 (4)	0.5000	3.03 (2)

Table 2. *Interatomic distances* (Å) *and angles* (°) *for compound* (I) *with e.s.d.'s in parentheses*

C(1)—C(2)	1.533 (4)	C(1)—C(9)	1.506 (7)
C(1)—C(10)	1.523 (6)	C(2)—C(3)	1.509 (6)
C(3)—C(4)	1.483 (8)	C(4)—C(5)	1.535 (7)
C(5)—C(9)	1.494 (7)	O(1)—C(9)	1.204 (6)
O(2)—C(10)	1.261 (6)	O(2)···O(2^{i})	2.632 (5)
C(3)···C(7^{ii})	3.08 (1)	H(C3)···H(C7^{ii})	1.94
C(2)—C(1)—C(8^{ii})	112.9 (5)	C(2)—C(1)—C(9)	107.7 (3)
C(2)—C(1)—C(10)	109.8 (3)	C(9)—C(1)—C(10)	108.8 (4)
C(1)—C(2)—C(3)	115.1 (4)	C(2)—C(3)—C(4)	114.9 (5)
C(3)—C(4)—C(5)	114.4 (4)	C(4)—C(5)—C(6^{ii})	113.4 (5)
C(4)—C(5)—C(9)	108.7 (3)	C(1)—C(9)—C(5)	112.7 (4)
C(1)—C(9)—O(1)	123.0 (5)	C(5)—C(9)—O(1)	124.3 (4)
C(1)—C(10)—O(2)	118.5 (2)	O(2)—C(10)—O(3^{ii})	123.0 (4)

Symmetry code: (i) $1 - x, -y, z$; (ii) C(6), C(7), C(8) and O(3) are related to their mirror-image counterparts by $x, y, 1 - z$.

mation of centrosymmetric dimers through mutual hydrogen bonding of pairs of carboxyls. Typical C—O lengths in highly ordered carboxyl dimers are 1.31 Å for the singly bonded C—O and 1.21 Å for the C═O (Borthwick, 1980). Successful refinement of structure (I) in space group *Ibam*, which contains a mirror perpendicular to the plane of the carboxyl group, requires identical C—O bond lengths [1.261 (3) Å], whose physical significance is that the two enantiomeric arrangements of the carboxyl are totally disordered. To satisfy ourselves that this was not an artifact of the space group we attempted an independent parallel refinement in *Iba*2, which lacks the mirror. Although the latter refinement could be brought to a slightly better final level of confidence ($R = 0.041$), it gave several unrealistic and symmetrically mismatched bond lengths and angles, and produced many unacceptably high correlation coefficients beyond those obviously associated with symmetry-related pairs of atoms. We have therefore concluded that the disordering is real.

Whether these identical C—O lengths represent only static positional disorder or some dynamic process is not determinable from our data. However, a symmetrical resonance-stabilized carboxylate is excluded on the basis of the intermolecular O···O distance and the IR spectrum (Leiserowitz, 1976). A dynamic averaging process need not be rapid beyond the time scale of the X-ray experiment, and hence might be very slow and hard to distinguish from static positional disorder. However, solid-state NMR and IR experiments (Meier, Graf & Ernst, 1982; Nagaoka, Terao, Imashiro, Hirota & Hayashi, 1983) give ultralow-temperature data for certain carboxyl dimers that imply activation barriers around (4 kJ mol^{-1}) for paired tautomeric H exchange, requiring that exchange rates be of the order of 10^{10} s^{-1} at room temperature. Clearly, if these studies are correct, all such disorder in carboxylic acids

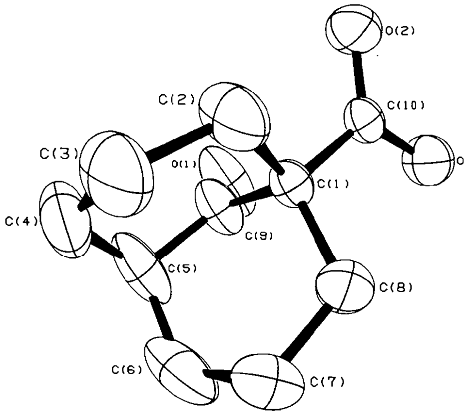

Fig. 1. A view of compound (I) consisting of the asymmetric unit (half the molecule) plus its mirror image; the numbering scheme encompasses the entire molecule. The carboxyl group is shown as found, with C—O bond lengths and C—C—O angles averaged by disordering of the two enantiomeric arrangements. The carboxyl H atom was not found and is not shown. Thermal ellipsoids are shown at the 50% probability level.

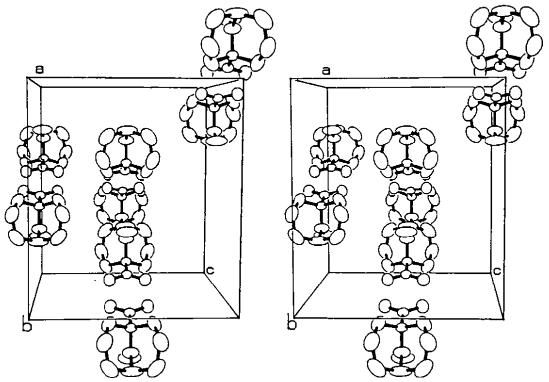

Fig. 2. A partial packing diagram for (I) in a stereoview. Four extracellular molecules are included to show the four types of symmetry-distinct centrosymmetric hyrogen-bonded carboxyl dimers (in their disordered state without carboxyl H atoms), centered on the *a* and *b* cell edges and the *ac* and *bc* faces. Thermal ellipsoids are shown at the 50% probability level.

near room temperature is dynamic, and cases of low apparent disorder merely represent lopsided equilibria which are nevertheless rapid.

Any disordering process other than a symmetrical carboxylate should produce carboxyl O and H atoms with high anisotropy, the latter elongated into a dumbbell shape or doubled along the O···O axis. The predicted O-atom shape must reflect not only averaging of the C—O lengths and C—C—O angles (Takusagawa, Hirotsu & Shimada, 1973; Dieterich, Paul & Curtin, 1974; Borthwick, 1980) but also any tilt of the carboxyl relative to its average plane (Takwale & Pant, 1971). A model based on typical lengths and angles in a coplanar and collinear carboxyl dimer predicts that, for each carboxyl O, the major in-plane ellipsoidal axis will have, as a result of total disorder, an angle of 12.5° relative to the other C—O bond (angled away from it), and 67.5° relative to its own C—O bond. The observed anisotropy of the carboxyl O atoms in (I) accords well with this; each has an ellipsoidal axis within about a degree of collinearity with the other C—O bond. Out-of-plane anisotropy for these O atoms corresponds to rotation of the carboxyl group from its average plane by no more than about 8°.

Doubling of the acid H atoms by disorder was not observable in our experimental data. Because these H atoms are diffuse even without disorder, we acquired our data at 236 K in the specific hope of defining their shape. However, the electron density which difference Fourier maps showed bridging the 2.63 Å O···O gap in the carboxyl dimer, although elongated in the O···O dimension, was so diffuse that no clear conclusions could be drawn about its shape. Attempted solutions involving half-hydrogens were not successful.

Although models of (I) can be arranged convincingly for an internal hydrogen bond, the compound does not adopt such a conformation. In fact, in the absence of additional hydrogen-bonding constraints (Destro & Marsh, 1984), every β-keto acid we are aware of whose hydrogen-bonding mode is known from X-ray crystal structure data, forms hydrogen bonds either by carboxyl dimerization (Martuscelli & Avitabile, 1967; Avitabile, Ganis & Martuscelli, 1969; Avitabile, Ganis & Lepore, 1971) or by catemerization (Lalancette, Vanderhoff & Thompson, 1991). The most obvious reason would seem to be the requirement, in six-membered rings, of achieving the optimum O—H···O angle by squeezing several of the others. Of the five simple γ-keto acids which we know to hydrogen bond internally, O—H···O angles are available for three, averaging 159°. In addition, of the keto acids we know of with catemeric carboxyl-to-ketone hydrogen bonding, this angle is available for ten, averaging 161° with none smaller than 141°. In X-ray data on 13 carboxyl dimers, Lifson, Hagler & Dauber (1979) found O—H···O angles deviating from linearity only by 0–12.4°, averaging 7.1°. It thus seems clear that this interaction operates optimally in the range 155–180°. Successful internal hydrogen-bond formation is known in several β-oxo carboxylic acids which are not strictly ketones. In these cases O—H···O angles of 153–157° are achieved at the expense of C=O···H angles of *ca* 98° (Toffoli, Khodadad & Rodier, 1988). By contrast, the latter angle varies from 122.4 to 155.7° in 11 keto acids which form intermolecular carboxyl-to-ketone hydrogen bonds.

The solid-state (KBr) IR spectrum of (I) is normal, displaying C=O stretching absorptions at 1721 cm^{-1} (ketone) and 1692 cm^{-1} (carboxyl). The corresponding Raman frequencies are 1722 cm^{-1} for the ketone and 1651 cm^{-1} for the carboxyl group. The frequency difference between IR and Raman in the latter case, 41 cm^{-1}, is at the low end of those we have observed for the carboxyl dimers we have studied (Vanderhoff, Lalancette & Thompson, 1990), the average being about 51 cm^{-1}. This frequency difference is quite small (*ca* 4 cm^{-1}) for carboxyl groups with catemeric hydrogen-bonding patterns and has been shown to be a reliable experimental diagnostic for the hydrogen-bonding mode in solid-state keto carboxylic acids (Vanderhoff, Lalancette & Thompson, 1990).

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Structures of Three 2,2-Dimethyl-3a,4,5,7a-tetrahydro-1,3-benzodioxolan-4-ols

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Abstract. $T = 295$ (1) K, λ(Cu $K\alpha$) = 1.5418 Å. (3aα,4α,5β,7aα)-5-Methoxy-2,2-dimethyl-3a,4,5,7a-tetrahydro-1,3-benzodioxolan-4-ol (2), $C_{10}H_{16}O_4$, M_r = 200.2, monoclinic, $P2_1/n$, $a = 8.264$ (1), $b = 6.988$ (1), $c = 18.288$ (1) Å, $\beta = 96.27$ (1)°, $V = 1049.8$ (3) Å^3, $Z = 4$, D_m (flotation) = 1.271 (5), D_x = 1.267 Mg m^{-3}, $\mu = 0.72$ mm^{-1}, $F(000) = 432$, final $R = 0.043$ for 1601 observed data. (3aα,4α,5β,7aα)-4-Hydroxy-2,2-dimethyl-3a,4,5,7a-tetrahydro-1,3-benzodioxolan-5-yl benzoate (3), $C_{16}H_{18}O_5$, M_r = 290.3, monoclinic, $P2_1/n$, $a = 12.792$ (1), $b = 8.937$ (1), $c = 13.089$ (1) Å, $\beta = 91.37$ (1)°, $V = 1495.9$ (2) Å^3, $Z = 4$, D_m (flotation) = 1.292 (5), D_x = 1.289 Mg m^{-3}, $\mu = 0.71$ mm^{-1}, $F(000) = 616$, final $R = 0.048$ for 1994 observed data. (3aα,4α,5α,7aα)-4-Hydroxy-2,2-dimethyl-3a,4,5,7a-tetrahydro-1,3-benzodioxolan-5-yl benzoate (4), $C_{16}H_{18}O_5$, M_r = 290.3, orthorhombic, $Pbca$, $a = 10.773$ (1), $b = 25.953$ (1), $c = 10.818$ (1) Å, $V = 3024.6$ (3) Å^3, $Z = 8$, D_m (flotation) = 1.276 (5), D_x = 1.275 Mg m^{-3}, $\mu = 0.70$ mm^{-1}, $F(000) = 1232$, final $R = 0.048$ for 2055 observed data. In each molecule the cyclohexene ring adopts a sofa conformation with C(4) lying out of the plane formed by the other five atoms. The *cis*-fused dioxolane ring adopts a conformation between a half chair and an envelope in (2) and (3), but has an envelope form in (4).

Introduction. The cyclitols and aminocyclitols (Ferrier, 1990) constitute a large class of polyfunctionalized cyclohexanes or cyclohexenes and many of these compounds display useful antibacterial (Knapp, Ornaf & Rodriques, 1983), antiviral (Datema, Romero, Legler & Schwarz, 1982; Legler, 1977), plant growth regulating (Soloway, Vogel, Le Drian & Powell, 1986, 1987) and/or insect antifeedant (Ley, Sternfeld & Taylor, 1987) properties. We are attempting to use microbially derived and commercially available dihydrocatechols [*e.g.* (1)] as starting materials for the efficient chemical synthesis of these molecules. In connection with this work we have now prepared the three cyclitols shown as (2), (3) and (4). These compounds have each been prepared (M. G. Banwell, J. N. Lambert, M. E. Reum, S. L. Richards & S. Stasi, unpublished results) in two steps from the acetonide derivative (Banwell, 1989) of (1). Very recently, an alternate synthesis of compound (2) has been reported (Hudlicky, Price, Rulin & Tsunoda, 1990). The crystal structure determinations of the three 2,2-dimethyl-3a,4,5,7a-tetrahydro-

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