Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	U_{eq}
O1*A*	0.11628 (11)	−0.0167 (3)	0.41256 (9)	0.0177 (3)
O2*A*	0.18514 (12)	0.3602 (3)	0.36350 (10)	0.0195 (3)
N1*A*	0.36618 (14)	−0.2275 (3)	0.41995 (11)	0.0149 (3)
C1*A*	0.2055 (2)	0.1312 (3)	0.38363 (12)	0.0139 (3)
C2*A*	0.34707 (15)	0.0176 (3)	0.36696 (11)	0.0133 (3)
C3*A*	0.3628 (2)	−0.0190 (4)	0.25875 (12)	0.0160 (3)
C4*A*	0.4075 (2)	0.2312 (5)	0.21567 (15)	0.0260 (4)
C5*A*	0.4308 (3)	0.2170 (6)	0.10901 (15)	0.0363 (6)
C6*A*	0.2304 (2)	−0.1279 (4)	0.20399 (13)	0.0222 (3)
O1*B*	0.62713 (12)	0.5636 (3)	0.40883 (9)	0.0175 (2)
O2*B*	0.70429 (15)	0.9557 (3)	0.38462 (11)	0.0241 (3)
N1*B*	0.88872 (15)	0.3764 (3)	0.39427 (11)	0.0182 (3)
C1*B*	0.7143 (2)	0.7198 (4)	0.38167 (12)	0.0156 (3)
C2*B*	0.8385 (2)	0.6041 (3)	0.33698 (12)	0.0158 (3)
C3*B*	0.7967 (2)	0.5281 (4)	0.23100 (12)	0.0179 (3)
C4*B*	0.9163 (2)	0.4018 (6)	0.18619 (14)	0.0338 (6)
C5*B*	0.8842 (2)	0.3372 (6)	0.07956 (15)	0.0369 (6)
C6*B*	0.7421 (4)	0.7567 (6)	0.17339 (15)	0.0536 (9)

Table 2. *Selected geometric parameters (Å, °)*

O1*A*—C1*A*	1.264 (2)	O1*B*—C1*B*	1.269 (2)
O2*A*—C1*A*	1.257 (2)	O2*B*—C1*B*	1.255 (2)
N1*A*—C2*A*	1.497 (2)	N1*B*—C2*B*	1.500 (2)
C1*A*—C2*A*	1.537 (2)	C1*B*—C2*B*	1.540 (2)
C2*A*—C3*A*	1.546 (2)	C2*B*—C3*B*	1.544 (2)
C3*A*—C6*A*	1.532 (3)	C3*B*—C6*B*	1.518 (3)
C3*A*—C4*A*	1.537 (3)	C3*B*—C4*B*	1.528 (3)
C4*A*—C5*A*	1.531 (3)	C4*B*—C5*B*	1.526 (3)
O2*A*—C1*A*—O1*A*	125.0 (2)	O2*B*—C1*B*—O1*B*	125.8 (2)
O2*A*—C1*A*—C2*A*	117.73 (15)	O2*B*—C1*B*—C2*B*	118.4 (2)
O1*A*—C1*A*—C2*A*	117.2 (2)	O1*B*—C1*B*—C2*B*	115.7 (2)
N1*A*—C2*A*—C1*A*	109.27 (13)	N1*B*—C2*B*—C1*B*	109.09 (14)
N1*A*—C2*A*—C3*A*	110.72 (14)	N1*B*—C2*B*—C3*B*	109.72 (15)
C1*A*—C2*A*—C3*A*	112.31 (13)	C1*B*—C2*B*—C3*B*	110.85 (13)
C6*A*—C3*A*—C4*A*	112.7 (2)	C6*B*—C3*B*—C4*B*	111.7 (2)
C6*A*—C3*A*—C2*A*	111.71 (14)	C6*B*—C3*B*—C2*B*	109.9 (2)
C4*A*—C3*A*—C2*A*	109.6 (2)	C4*B*—C3*B*—C2*B*	111.97 (14)
C5*A*—C4*A*—C3*A*	114.5 (2)	C5*B*—C4*B*—C3*B*	114.4 (2)
O1*A*—C1*A*—C2*A*—N1*A*	−19.0 (2)	O1*B*—C1*B*—C2*B*—N1*B*	−41.4 (2)
N1*A*—C2*A*—C3*A*—C6*A*	79.4 (2)	N1*B*—C2*B*—C3*B*—C6*B*	178.4 (2)
N1*A*—C2*A*—C3*A*—C4*A*	−154.95 (14)	N1*B*—C2*B*—C3*B*—C4*B*	−56.9 (2)
C2*A*—C3*A*—C4*A*—C5*A*	178.3 (2)	C2*B*—C3*B*—C4*B*—C5*B*	−176.4 (2)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A**	H···*A*†	*D*···*A*	*D*—H···*A**
N1*A*—H1*A*···O2*A*^{i}	0.92 (3)	1.95(3)	1.841	2.859 (2)	170 (2)
N1*A*—H2*A*···O1*B*^{i}	0.89 (3)	1.89(3)	1.751	2.778 (2)	175 (3)
N1*A*—H3*A*···O1*B*^{ii}	0.86 (2)	2.07(2)	1.931	2.839 (2)	148 (2)
N1*B*—H1*B*···O2*B*^{i}	0.93 (4)	1.94(4)	1.837	2.851 (3)	168 (3)
N1*B*—H2*B*···O2*A*^{iii}	0.85 (3)	2.13(3)	1.961	2.948 (2)	161 (4)
N1*B*—H2*B*···O1*A*^{iii}	0.85 (3)	2.35(4)	2.230	3.023 (2)	136 (3)
N1*B*—H3*B*···O1*A*^{iv}	0.85 (2)	1.91(3)	1.735	2.760 (2)	174 (2)

Symmetry codes: (i) $x, y-1, z$; (ii) $1-x, y-\frac{1}{2}, 1-z$; (iii) $1+x, y, z$; (iv) $1-x, \frac{1}{2}+y, 1-z$.

* Experimental H-atom positions. † Normalized (Taylor & Kennard, 1983) hydrogen bonds with d(N—H) = 1.030 Å.

Amino-group H atoms were refined isotropically, other H atoms were placed geometrically. Refinement then allowed the H atoms to move along the C—H bond direction with the C—H distance being kept constant for all H atoms on the same C atom. The U_{iso} values were fixed at 1.2 × U_{eq} of the bonded atom, except that a free variable for U_{iso} was refined for each of the four methyl groups.

Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1156). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Dalhus, B. & Görbitz, C. H. (1996). *Acta Chem. Scand.* **50**. In the press.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Taylor, R. & Kennard, O. (1983). *Acta Cryst.* B**39**, 133–138.

Torii, K. & Iitaka, Y. (1971). *Acta Cryst.* B**27**, 2237–2246.

Acta Cryst. (1996). C**52**, 1466–1470

1,3-Adamantanedicarboxylic Acid and 1,3-Adamantanediacetic Acid

CHRISTOPHER GLIDEWELL[a]* AND GEORGE FERGUSON[b]

[a]*School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland, and* [b]*Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1. E-mail: cg@st-andrews.ac.uk*

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Abstract

The structure of 1,3-adamantanedicarboxylic acid (tricyclo[3.3.1.1^{3,7}]decane-1,3-dicarboxylic acid), $C_{12}H_{16}O_4$, consists of hydrogen-bonded chains of molecules related by a glide plane. In 1,3-adamantanediacetic acid (tricyclo[3.3.1.1^{3,7}]decane-1,3-diacetic acid), $C_{14}H_{20}O_4$, the asymmetric unit comprises two hydrogen-bonded molecules and these bimolecular units are in turn linked by hydrogen bonds across centres of inversion to give chains.

Comment

The crystal structures of dicarboxylic acids in which the two acidic functions are at sites remote from one another on a rigid three-dimensional framework exhibit a range of hydrogen-bonding patterns. The structures of bicyclo[2.2.2]octane-1,4-dicarboxylic acid (Ermer &

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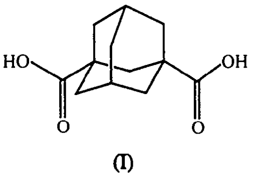
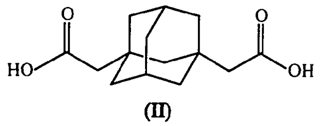
Dunitz, 1969) and 1,12-dicarboxy-1,12-dicarba-*closo*-dodecaborane(12) (Centore, Ciajolo, Tuzi, Komarova, Rusanov & Vasnev, 1994) are both characterized by the formation of chains of molecules in which the molecules are connected by eight-membered [O=C—O—H]$_2$ hydrogen-bonded rings similar to those found in the dimeric forms of monocarboxylic acids. Such chain formation is the typical mode of aggregation for non-cage dicarboxylic acids (Leiserowitz, 1976); amongst dicarboxylic acids based upon carbocyclic non-cage frameworks it occurs, for example, in the structures of *trans*-1,4-cyclobutanedicarboxylic acid (Margulis & Fischer, 1967), terephthalic acid (Bailey & Brown, 1967), *trans*-1,4-cyclohexanedicarboxylic acid (Dunitz & Strickler, 1966; Luger, Pleith & Ruban, 1972), the *cis* and *trans* isomers of 1,3-cyclohexanedicarboxylic acid (van Koningsveld, 1984), and camphoric acid (Barnes, Paton, Blyth & Howie, 1991). On the other hand, the crystal structure of 1,4-cubanedicarboxylic acid (Ermer & Lex, 1987), whose carbon framework is closely related to that of bicyclo[2.2.2]octanedicarboxylic acid (D_{3d} molecular symmetry rather than D_{3h}), shows an entirely different hydrogen-bonding scheme, with the formation of layers of hydrogen-bonded molecules. In contrast to these extended structures, the crystal structure of ferrocene-1,1′-dicarboxylic acid contains finite dimers in both its monoclinic (Palenik, 1967) and triclinic (Takusagawa & Koetzle, 1979) modifications. Seeking a cage-based dicarboxylic acid which both forms extended chains and has no axial symmetry, so that the possible rotation of the eight-membered [O=C—O—H]$_2$ rings about C—C bonds (Furic, 1984) could in principle be distinguished from any motion of the framework by the use of solid-state NMR spectroscopy, we selected two acids containing the adamantane framework, namely, 1,3-adamantanedicarboxylic acid, (I), and 1,3-adamantanediacetic acid, (II), and report here their structures.



(I)



(II)

Molecules of (I), $C_{10}H_{14}(COOH)_2$ (Fig. 1), are connected by O—H···O hydrogen bonds into chains (Fig. 2) parallel to the **a** direction and generated by the glide plane, the two independent intermolecular O···O distances being 2.693 (2) and 2.661 (2) Å. The hydroxyl H atoms are ordered, but the eight-membered [O=C—O—H]$_2$ rings do not include any element of crystallographic symmetry. Since the two hydrogen bonds within these rings are crystallographically different, the first-level graph set (Bernstein, Davis, Shimoni & Chang, 1995) is *DD* and the second-level graph set is $R_2^2(8)$; since the overall hydrogen-bonding pattern is a 'chain of rings', with a chain motif *C*(8), it can be described by the extended notation $C(8)[R_2^2(8)]$ (Bernstein, Davis, Shimoni & Chang, 1995). The apparent simplicity of this structure is marred by the occurrence of positional disorder. Some 10% of the molecules are displaced by *ca* 2.0 Å from the major component (see *Experimental*), resulting in two alternative cage positions which have interlinked rings, which in turn leads to the generation of two parallel strings of molecules with occupancies of 0.9 and 0.1, respectively. Within any string, however, there is sufficient space for the [O=C—O—H]$_2$ rings to rotate about the C1—C11 and C3—C13 bonds.

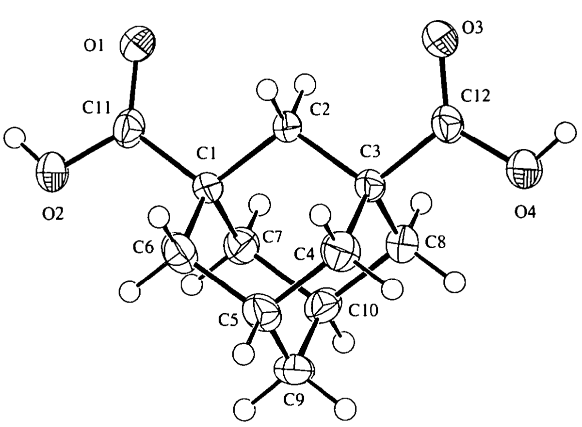


Fig. 1. A view of compound (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

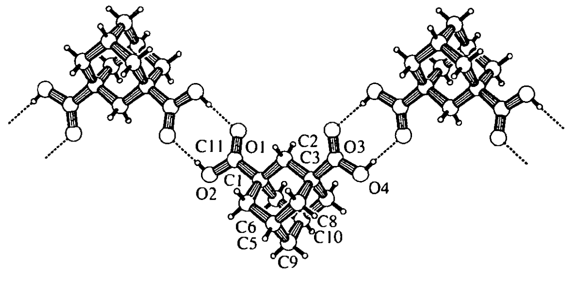


Fig. 2. A view of the chain structure of compound (I).

Compound (II), $C_{10}H_{14}(CH_2COOH)_2$ (Fig. 3), has two molecules in the asymmetric unit, denoted *A* and *B*, which are joined by O—H···O hydrogen bonds, with two independent O···O distances of 2.643 (5) and 2.663 (5) Å. One carboxyl group of each molecule participates in the formation of the usual eight-membered [O=C—O—H]$_2$ ring. The two hydrogen bonds within this ring are crystallographically different, so that the first-level graph set is *DD* and the second-level graph set is $R_2^2(8)$. The bimolecular structural unit thus formed then acts as a conventional dicarboxylic acid containing two independent and free carboxyl groups; each of these groups forms a centrosymmetric hydrogen-bonding motif of type $R_2^2(8)$, with a carboxyl group from another bimolecular unit, thus forming chains of type $-A-B-B'-A'-A-$, where the pairs of molecules *A* and *A'*, and *B* and *B'* are related by centres of inversion. The O···O distances between the asymmetric units are 2.644 (5) and 2.659 (5) Å. As in compound (I), the hydrogen bonding in (II) forms a chain of rings, but in (II), the chain motif is *C*(10). The chains run parallel to the **c** direction and there are four such chains running through each unit cell, with $[O{=}C{-}O{-}H]_2$ rings of different chains lying across the centres of inversion at $(0,0,\frac{1}{2})$, $(0,\frac{1}{2},\frac{1}{2})$, $(\frac{1}{2},0,\frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$.

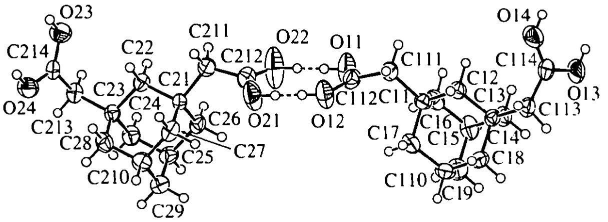


Fig. 3. A view of the asymmetric unit in compound (II) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

The principal differences between the two independent molecules of compound (II) arise from the conformations adopted by the two exocyclic CH_2COOH fragments. These are best defined by reference to the C—C bond directions C*n*11—C*n*17 and C*n*13—C*n*18 [*n* = 1 (molecule *A*), 2 (molecule *B*)], which lie parallel to the apical C*n*10—H directions. In molecule *A*, the torsion angles C17—C11—C111—C112 and C18—C13—C113—C114 are −56.5 (5) and 171.5 (3)°, respectively, while the corresponding angles in molecule *B* are 65.2 (5) and 58.8 (4)°, respectively; thus only in molecule *B* does one of the carboxyl groups lie antiperiplanar to the reference C—C direction. On the other hand, the O—C—C—C torsion angles in the two independent molecules of (II) are very similar (Table 4). The intramolecular distances are all comparable with those in related systems (Leiserowitz, 1976; Ermer & Bödecker, 1981; van Koningsveld, 1984; Ermer, 1988; Bélanger-Gariépy, Brisse, Harvey, Gilson & Butler, 1990) and all are typical of their bond types in general (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987).

Within the chains formed by compound (I) the hydroxyl H atoms are all ordered, whereas in compound (II), the hydroxyl H atoms are disordered equally over two sites, as judged from the peak heights in difference maps, regardless of whether the eight-membered $[O{=}C{-}O{-}H]_2$ ring is, or is not, strictly centrosymmetric. In both of the closest analogues of (I), *i.e.* the ordered low-temperature phase of 1-adamantanecarboxylic acid (Bélanger-Gariépy, Brisse, Harvey, Gilson & Butler, 1990) and 1,3,5,7-adamantanetetracarboxylic acid (Ermer, 1988), the hydroxyl H atoms are fully ordered. They are similarly fully ordered in di-1-adamantylmethane-3,3'-dicarboxylic acid (Ermer & Bödecker, 1981). The corresponding H atoms, however, are partially disordered, with site occupancies of 0.7 and 0.3 in 1,12-dicarboxy-1,12-dicarba-*closo*-dodecaborane(12) (Centore, Ciajolo, Tuzi, Komarova, Rusanov & Vasnev, 1994), and fully disordered in bicyclo[2.2.2]octane-1,4-dicarboxylic acid (Ermer & Dunitz, 1969). Attention has previously been drawn (Leiserowitz, 1976) to the occurrence of a continuum of behaviour in dimeric monocarboxylic acids from systems having fully ordered hydroxyl H atoms to those having the hydroxyl H atoms fully disordered over two equally populated sites.

It is noteworthy, in view of the controversy concerning the intramolecular proton dynamics in carboxylic acid dimers (Furic, 1984; Meier, Meyer, Ernst, Stöckli, Furrer, Hälg & Anderson, 1984; Nagaoka, Terao, Imashiro, Hirota & Hayashi, 1984), that within each crystallographically independent $[O{=}C{-}O{-}H]_2$ ring in compounds (I) and (II), the thermal motion of the O atoms is much greater than that of the neighbouring C atoms and further, is very anisotropic, with the largest components of the motion in the directions normal to the planes of the $[O{=}C{-}O{-}H]_2$ rings.

Experimental

Samples of both (I) and (II) were obtained from the Aldrich Chemical Company. Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of methanol solutions.

Compound (I)

Crystal data

$C_{12}H_{16}O_4$
$M_r = 224.25$
Monoclinic
$P2_1/a$
$a = 6.7341\ (6)$ Å
$b = 19.760\ (2)$ Å
$c = 8.1797\ (15)$ Å
$\beta = 102.085\ (9)°$
$V = 1064.3\ (2)$ Å^3
$Z = 4$
$D_x = 1.399$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 8.15–13.65°$
$\mu = 0.104$ mm^{-1}
$T = 294\ (1)$ K
Plate
0.29 × 0.29 × 0.15 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none

$R_{\text{int}} = 0.009$
$\theta_{\max} = 26.9°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 25$
$l = 0 \rightarrow 10$

2489 measured reflections
2304 independent reflections
989 observed reflections
[$I > 2\sigma(I)$]

3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0499$
$wR(F^2) = 0.1458$
$S = 0.863$
2304 reflections
199 parameters
H atoms riding (C—H 0.97–0.98, O—H 0.82 Å)
$w = 1/[\sigma^2(F_o^2) + (0.0824P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.013$

$\Delta\rho_{\max} = 0.281$ e Å^{-3}
$\Delta\rho_{\min} = -0.213$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0084 (4)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (I)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.3175 (3)	0.25339 (9)	0.5842 (2)	0.0411 (6)
O2	0.4515 (4)	0.15943 (10)	0.7121 (2)	0.0472 (6)
O3	0.0752 (3)	0.25680 (9)	−0.0268 (2)	0.0411 (6)
O4	−0.0477 (4)	0.16291 (9)	−0.1620 (2)	0.0488 (6)
C1	0.2727 (4)	0.14872 (12)	0.4306 (3)	0.0254 (6)
C2	0.2032 (4)	0.19347 (11)	0.2758 (3)	0.0250 (5)
C3	0.1135 (4)	0.15048 (12)	0.1225 (3)	0.0246 (6)
C4	0.2786 (5)	0.10059 (13)	0.0902 (3)	0.0350 (7)
C5	0.3456 (5)	0.05535 (13)	0.2441 (3)	0.0367 (7)
C6	0.4352 (5)	0.09903 (13)	0.3967 (3)	0.0348 (7)
C7	0.0876 (4)	0.10831 (12)	0.4629 (3)	0.0305 (7)
C8	−0.0690 (4)	0.10994 (12)	0.1566 (3)	0.0316 (7)
C9	0.1641 (5)	0.01576 (12)	0.2776 (3)	0.0393 (8)
C10	0.0014 (4)	0.06476 (13)	0.3096 (3)	0.0327 (7)
C11	0.3499 (4)	0.19215 (13)	0.5828 (3)	0.0295 (6)
C12	0.0451 (4)	0.19563 (13)	−0.0281 (3)	0.0292 (6)
O1*A*	0.549 (6)	0.2554 (9)	0.473 (3)	0.160 (8)
O2*A*	0.666 (6)	0.1608 (14)	0.608 (2)	0.160 (8)
O3*A*	0.296 (6)	0.2545 (9)	−0.136 (4)	0.160 (8)
O4*A*	0.156 (5)	0.1599 (14)	−0.258 (3)	0.160 (8)
C1*A*	0.521 (3)	0.1503 (9)	0.319 (2)	0.160 (8)
C2*A*	0.435 (3)	0.1943 (7)	0.166 (2)	0.160 (8)
C3*A*	0.361 (3)	0.1488 (9)	0.0137 (18)	0.160 (8)
C4*A*	0.539 (3)	0.1067 (12)	−0.021 (2)	0.160 (8)
C5*A*	0.625 (3)	0.0626 (9)	0.132 (3)	0.160 (8)
C6*A*	0.699 (2)	0.1081 (11)	0.285 (3)	0.160 (8)
C7*A*	0.355 (4)	0.1027 (12)	0.354 (2)	0.160 (8)
C8*A*	0.194 (2)	0.1013 (11)	0.049 (3)	0.160 (8)
C9*A*	0.459 (4)	0.0151 (7)	0.167 (3)	0.160 (8)
C10*A*	0.280 (3)	0.0572 (10)	0.201 (3)	0.160 (8)
C11*A*	0.580 (4)	0.1942 (9)	0.473 (2)	0.160 (8)
C12*A*	0.270 (4)	0.1930 (9)	−0.134 (2)	0.160 (8)

Table 2. *Selected geometric parameters (Å, °) for (I)*

O1—C11	1.230 (3)	C3—C12	1.512 (3)
O2—C11	1.305 (3)	C3—C8	1.540 (4)
O3—C12	1.225 (3)	C3—C4	1.549 (4)
O4—C12	1.312 (3)	C4—C5	1.532 (3)
C1—C11	1.512 (3)	C5—C9	1.524 (4)
C1—C2	1.535 (3)	C5—C6	1.534 (3)
C1—C6	1.538 (4)	C7—C10	1.532 (3)
C1—C7	1.549 (4)	C8—C10	1.530 (3)
C2—C3	1.531 (3)	C9—C10	1.525 (4)
O1—C11—O2	122.9 (2)	O3—C12—O4	122.9 (2)
O1—C11—C1	122.4 (2)	O3—C12—C3	123.6 (2)
O2—C11—C1	114.7 (2)	O4—C12—C3	113.6 (2)
C2—C1—C11—O1	14.5 (4)	C2—C3—C12—O3	5.8 (4)

Compound (II)

Crystal data

$C_{14}H_{20}O_4$
$M_r = 252.30$
Monoclinic
$P2_1/a$
$a = 23.677$ (14) Å
$b = 7.739$ (5) Å
$c = 14.730$ (14) Å
$\beta = 110.23$ (5)°
$V = 2533$ (3) Å^3
$Z = 8$
$D_x = 1.323$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 5.90$–13.35°
$\mu = 0.096$ mm^{-1}
$T = 294$ (1) K
Very thin plate
0.41 × 0.39 × 0.01 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4602 measured reflections
4427 independent reflections
2002 observed reflections
[$I > 2\sigma(I)$]

$R_{\rm int} = 0.022$
$\theta_{\max} = 24.9$°
$h = -28 \rightarrow 26$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0654$
$wR(F^2) = 0.1860$
$S = 0.967$
4427 reflections
326 parameters
H atoms riding (C—H 0.97–0.98, O—H 0.83 Å)
$w = 1/[\sigma^2(F_o^2) + (0.0886P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.249$ e Å^{-3}
$\Delta\rho_{\min} = -0.206$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0002 (7)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O11	0.4227 (2)	0.1970 (4)	−0.1489 (2)	0.0761 (11)
O12	0.4190 (2)	0.0259 (4)	−0.0317 (2)	0.0678 (10)
O13	0.42339 (13)	−0.5512 (4)	−0.5339 (2)	0.0593 (9)
O14	0.49458 (14)	−0.5368 (5)	−0.3901 (2)	0.0623 (9)
C11	0.3918 (2)	−0.1761 (5)	−0.2469 (3)	0.0347 (9)
C12	0.4170 (2)	−0.3380 (5)	−0.2797 (3)	0.0345 (9)
C13	0.3700 (2)	−0.4268 (5)	−0.3655 (3)	0.0332 (9)
C14	0.3485 (2)	−0.2968 (5)	−0.4488 (3)	0.0433 (11)
C15	0.3225 (2)	−0.1368 (6)	−0.4178 (3)	0.0475 (12)
C16	0.3700 (2)	−0.0518 (5)	−0.3319 (3)	0.0439 (10)
C17	0.3380 (2)	−0.2290 (6)	−0.2185 (3)	0.0430 (11)
C18	0.3167 (2)	−0.4769 (6)	−0.3343 (3)	0.0448 (11)
C19	0.2692 (2)	−0.1884 (6)	−0.3888 (3)	0.0576 (13)
C110	0.2904 (2)	−0.3142 (6)	−0.3044 (3)	0.0474 (11)
C111	0.4432 (2)	−0.1009 (6)	−0.1597 (3)	0.0460 (11)
C112	0.4270 (2)	0.0490 (6)	−0.1110 (3)	0.0451 (11)
C113	0.3950 (2)	−0.5928 (5)	−0.3959 (3)	0.0415 (10)
C114	0.4408 (2)	−0.5597 (5)	−0.4411 (3)	0.0416 (10)
O21	0.4101 (2)	0.2992 (4)	0.0724 (3)	0.0802 (11)
O22	0.4192 (2)	0.4659 (4)	−0.0404 (3)	0.1011 (15)

O23	0.48627 (13)	1.0586 (5)	0.3812 (2)	0.0626 (9)
O24	0.42233 (13)	1.0174 (4)	0.4585 (2)	0.0598 (9)
C21	0.3802 (2)	0.6702 (5)	0.1372 (3)	0.0316 (9)
C22	0.4048 (2)	0.8294 (5)	0.1994 (3)	0.0337 (9)
C23	0.3567 (2)	0.9179 (5)	0.2310 (3)	0.0331 (9)
C24	0.3049 (2)	0.9694 (5)	0.1394 (3)	0.0422 (10)
C25	0.2789 (2)	0.8111 (5)	0.0773 (3)	0.0432 (11)
C26	0.3277 (2)	0.7257 (5)	0.0475 (3)	0.0366 (10)
C27	0.3561 (2)	0.5435 (5)	0.1947 (3)	0.0421 (10)
C28	0.3335 (2)	0.7867 (5)	0.2877 (3)	0.0445 (11)
C29	0.2555 (2)	0.6839 (6)	0.1356 (3)	0.0507 (12)
C210	0.3079 (2)	0.6282 (6)	0.2258 (3)	0.0475 (11)
C211	0.4331 (2)	0.5944 (6)	0.1103 (3)	0.0483 (11)
C212	0.4192 (2)	0.4456 (6)	0.0434 (3)	0.0465 (11)
C213	0.3824 (2)	1.0828 (5)	0.2905 (3)	0.0389 (10)
C214	0.4335 (2)	1.0497 (5)	0.3832 (3)	0.0389 (10)

Table 4. *Selected geometric parameters (Å, °) for (II)*

O11—C112	1.262 (5)	O21—C212	1.256 (5)
O12—C112	1.259 (5)	O22—C212	1.244 (5)
O13—C114	1.286 (5)	O23—C214	1.262 (4)
O14—C114	1.246 (5)	O24—C214	1.251 (4)
C11—C12	1.535 (5)	C21—C22	1.525 (5)
C11—C16	1.522 (5)	C21—C26	1.530 (5)
C11—C17	1.528 (5)	C21—C27	1.529 (5)
C11—C111	1.545 (5)	C21—C211	1.553 (5)
C12—C13	1.528 (5)	C22—C23	1.533 (5)
C13—C14	1.532 (5)	C23—C24	1.531 (5)
C13—C18	1.534 (5)	C23—C28	1.533 (5)
C13—C113	1.545 (5)	C23—C213	1.547 (5)
C14—C15	1.522 (6)	C24—C25	1.526 (5)
C15—C16	1.522 (6)	C25—C26	1.522 (5)
C15—C19	1.519 (6)	C25—C29	1.530 (6)
C17—C110	1.523 (6)	C27—C210	1.519 (6)
C18—C110	1.535 (6)	C28—C210	1.524 (6)
C19—C110	1.521 (6)	C29—C210	1.533 (6)
C111—C112	1.483 (6)	C211—C212	1.477 (6)
C113—C114	1.477 (5)	C213—C214	1.501 (5)
C11—C111—C112	115.9 (3)	C21—C211—C212	116.8 (3)
O11—C112—O12	121.6 (4)	O21—C212—O22	120.7 (4)
O11—C112—C111	119.3 (4)	O21—C212—C211	120.1 (4)
O12—C112—C111	119.0 (4)	O22—C212—C211	119.1 (4)
C13—C113—C114	113.7 (3)	C23—C213—C214	114.2 (3)
O13—C114—O14	121.3 (4)	O23—C214—O24	123.1 (4)
O13—C114—C113	118.1 (4)	O23—C214—C213	117.6 (3)
O14—C114—C113	120.5 (4)	O24—C214—C213	119.3 (4)
C16—C11—C111—C112	66.0 (5)	C22—C21—C211—C212	−175.5 (4)
C17—C11—C111—C112	−56.5 (5)	C27—C21—C211—C212	65.2 (5)
C12—C11—C111—C112	−175.0 (4)	C26—C21—C211—C212	−56.9 (5)
C11—C111—C112—O12	103.1 (5)	C21—C211—C212—O22	109.6 (5)
C11—C111—C112—O11	−78.3 (5)	C21—C211—C212—O21	−73.4 (5)
C12—C13—C113—C114	−69.9 (4)	C24—C23—C213—C214	179.5 (3)
C14—C13—C113—C114	51.5 (4)	C28—C23—C213—C214	58.8 (4)
C18—C13—C113—C114	171.5 (3)	C22—C23—C213—C214	−62.5 (4)
C13—C113—C114—O14	84.0 (5)	C23—C213—C214—O24	−88.2 (5)
C13—C113—C114—O13	−94.5 (4)	C23—C213—C214—O23	92.9 (4)

It became obvious from examination of difference maps that there was disorder in the crystal structure of (I) and by judicious use of the graphics options in *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989) it was possible to derive a set of coordinates for another diacid molecule in essentially the same orientation as the major component, but separated from it by a translation of approximately 2.0 Å. From peak heights in the maps it was deduced that occupancies of 0.9:0.1 for the two forms would be useful starting numbers for the occupancy refinement in *SHELXL*93 (Sheldrick, 1993). In the final refinement cycles, the bond lengths and angles for the minor component were restrained to be similar to those of the major component, and a common isotropic displacement parameter was refined for the minor component atoms. Final occupancies for the two components refined to 0.907 (3):0.093 (3). Difference maps for (II) showed that the carboxyl H atoms were in each case disordered over two sites. They were positioned on the line of centres and treated as riding atoms with 0.5 occupancy. Examination of the structures with *PLATON* (Spek, 1995*a*) showed that there were no solvent accessible voids in the crystal lattices.

For both compounds, data collection: *CAD*-4/*PC Software* (Enraf–Nonius 1992); cell refinement: *CAD*-4/*PC Software*; data reduction: *DATRD*2 in *NRCVAX*94. Program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990) for (I); *SOLVER* in *NRCVAX* for (II). For both compounds, program(s) used to refine structures: *NRCVAX*94 and *SHELXL*93; molecular graphics: *ORTEP*II (Johnson, 1976) as implemented in *PLATON* and *PLUTON* (Spek 1995*b*); software used to prepare material for publication: *NRCVAX*94 and *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: CF1046). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.
Bailey, M. & Brown, C. J. (1967). *Acta Cryst.* **22**, 387–391.
Barnes, J. C., Paton, J. D., Blyth, C. S. & Howie, R. A. (1991). *Acta Cryst.* C**47**, 1888–1892.
Bélanger-Gariépy, F., Brisse, F., Harvey, P. D., Gilson, D. F. R. & Butler, I. S. (1990). *Can. J. Chem.* **68**, 1163–1169.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed Engl.* **35**, 1555–1573.
Centore, R., Ciajolo, M. R., Tuzi, A., Komarova, L. G., Rusanov, A. L. & Vasnev, V. A. (1994). *Acta Cryst.* C**50**, 905–907.
Dunitz, J. D. & Strickler, P. (1966). *Helv. Chim. Acta*, **49**, 2505–2515.
Enraf–Nonius (1992). *CAD-4/PC Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
Ermer, O. (1988). *J. Am. Chem. Soc.* **110**, 3747–3754.
Ermer, O. & Bödecker, C.-D. (1981). *Chem. Ber.* **114**, 652–659.
Ermer, O. & Dunitz, J. D. (1969). *Helv. Chim. Acta*, **52**, 1861–1886.
Ermer, O. & Lex, J. (1987). *Angew. Chem. Int. Ed Engl.* **26**, 447–449.
Furic, K. (1984). *Chem. Phys. Lett.* **108**, 518–521.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Koningsveld, H. van (1984). *Acta Cryst.* C**40**, 1857–1863.
Leiserowitz, L. (1976). *Acta Cryst.* B**32**, 775–802.
Luger, P., Pleith, K. & Ruban, G. (1972). *Acta Cryst.* B**28**, 706–710.
Margulis, T. N. & Fischer, M. S. (1967). *J. Am. Chem. Soc.* **89**, 223–226.
Meier, B. H., Meyer, R., Ernst, R. R., Stöckli, A., Furrer, A., Hälg, W. & Anderson, I. (1984). *Chem. Phys. Lett.* **108**, 522–523.
Nagaoka, S., Terao, T., Imashiro, F., Hirota, N. & Hayashi, S. (1984). *Chem. Phys. Lett.* **108**, 524–525.
Palenik, G. J. (1967). *Inorg. Chem.* **8**, 2744–2749.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Spek, A. L. (1995*a*). *PLATON. Molecular Geometry Program*. Version of July 1995. University of Utrecht, Utrecht, The Netherlands.
Spek, A. L. (1995*b*). *PLUTON. Molecular Graphics Program*. Version of July 1995. University of Utrecht, Utrecht, The Netherlands.
Takusagawa, F. & Koetzle, T. F. (1979). *Acta Cryst.* B**35**, 2888–2896.