Hydrogen bonds and C—H···O interactions in 2-(2-methylbenzyl)malonic acid at 150 K

Roger E. Gerkin

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA
Correspondence e-mail: gerkin@chemistry.ohio-state.edu

The title compound, $C_{11}H_{12}O_4$, crystallized in the centrosymmetric space group *Pbca* with one molecule as the asymmetric unit. The two hydrogen bonds have O_D···O_A distances of 2.667 (2) and 2.628 (2) Å, and O—H···O angles of 179 (2) and 177 (2)°. Each hydrogen bond forms an $R_2^2(8)$ cyclic dimer about a center of symmetry. The leading intermolecular C—H···O interaction has an H···O distance of 2.66 Å and a C—H···O angle of 160°. Taken together with the hydrogen bonds, it results in a three-dimensional network of interactions. The structure is compared with that of a close analog, benzylmalonic acid.

Comment

This report is one of a series on hydrogen bonding and C—H···O interactions in carboxylic acids. The title acid, (I), crystallized in the centrosymmetric space group *Pbca* with one molecule as the asymmetric unit. The refined molecule and the labeling scheme are given in Fig. 1. In the carboxyl groups, the C—O distances are somewhat less than usually observed, and the C=O distances are somewhat greater. The carboxyl O atoms are nonetheless ordered, as shown by the orientations of their substantially largest principal displacement components almost normal to the planes of their carboxyl groups (see, *e.g.* Fitzgerald & Gerkin, 1993). Moreover, although the refined O3—H1O3 distance, 1.23 (2) Å, is larger then usual and the isotropic displacement parameter of H1O3 is large, the interpretation of H1O3 as an ordered H atom is supported by the fact that H1O3 and H1O1 appeared as the top two peaks in the Fourier difference map after all other atoms were refined, and by the absence of any suitable residual electron-density peak near O4. Such a location of H1O3 is, of course, consistent with a flatter-than-usual potential function between the O atoms in the dimer. Thus, this is a case in which a neutron-diffraction determination would be of particular interest. Two hydrogen bonds and one leading intermolecular C—H···O interaction (Taylor & Kennard, 1982; Steiner & Desiraju, 1998) are present in this structure; five additional intermolecular C—H···O interactions of somewhat lesser significance are also present. The geometric parameters of all

these are given in Table 2. The results of basic first- and second-level graph-set analysis (Bernstein *et al.*, 1995) involving the three leading interactions, labeled *a–c* for this purpose in the order of their appearance in Table 2, are given in Table 3. Each hydrogen bond forms an $R_2^2(8)$ cyclic dimer about a center of symmetry. The chains given in Table 3 propagate along [100], [010], [010] and [001] in the order of their appearance. Thus, a three-dimensional network of interactions is formed by the three leading interactions. A stereodiagram (Fig. 2) includes examples of each of these interactions.

(I)
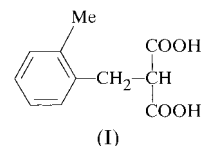
The phenyl ring in (I) is closely planar, the maximum deviation of a C atom from the best-fit plane describing them being 0.005 (2) Å, while the mean deviation is 0.003 (2) Å. The molecular configuration can be characterized in good part by the dihedral angles between the following planes: (1) the phenyl-ring plane; (2) the plane defined by C1, C2 and C3; (3) the carboxyl plane C1, O1 and O2; and (4) the carboxyl plane C3, O3 and O4. The values are as follows: (1)∧(2) 60.4 (2), (1)∧(3) 84.9 (2), (1)∧(4) 64.9 (2), (2)∧(3) 89.6 (2), (2)∧(4) 4.6 (2) and (3)∧(4) 88.2 (2)°. Fig. 2 makes some of these relations apparent, as well as illustrating the alternating layers, along the *c* axis, of hydrocarbon and carboxyl portions of molecules. For structural comparisons, benzylmalonic acid at room temperature [hereafter, (II)] (Lepore *et al.*, 1975) appears particularly well suited. With respect to the dihedral angles just characterized for (I), the corresponding values for (II) are, respectively, 57.1 (4), 77.5 (5), 53.6 (4), 83.9 (5), 3.5 (5) and 83.7 (6)°. These values support the conclusion that (I) and (II) have very similar molecular conformations. Despite their similar molecular conformations, (I) and (II) pack quite differently, as demonstrated by their (conventional) hydrogen bonding. Whereas for (I), the first- and second-level graph-set descriptors are $R_2^2(8)$, $R_2^2(8)$ and $C_2^2(12)$, for (II) they are $C(6)$, $R_2^2(12)$, and $C_2^2(8)$.

Selected bond distances and angles of (I) are given in Table 1. All distances and angles fall within normal limits. In
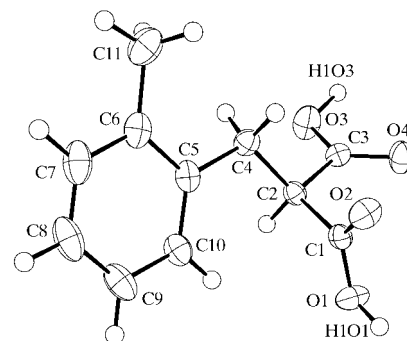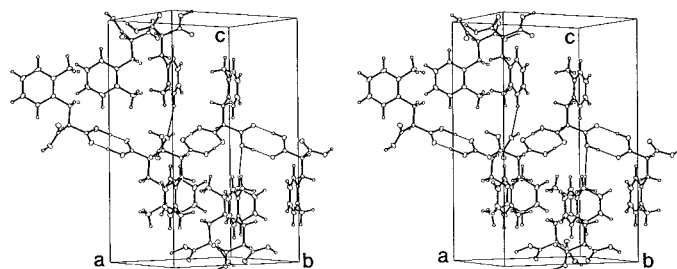

Figure 1
Labeling scheme for (I) with displacement ellipsoids at the 50% probability level.

organic compounds

Figure 2
Packing stereodiagram of (I), with the origin at the rear lower right. The finer interatomic lines depict interactions *a–c* (Tables 2 and 3).

(I), the closest intermolecular approaches, excluding pairs of atoms in hydrogen-bonded carboxyl groups or in the tabulated C—H···O interactions, are between O1 and O3^{vii} [symmetry code: (vii) $x - \frac{1}{2}, \frac{1}{2} - y, -z$] and fall short of the corresponding Bondi (1964) van der Waals radius sum by 0.10 Å.

Experimental

Compound (I) was obtained as a finely crystalline white powder from a sample in Dr M. S. Newman's chemical collection. Slow evaporation of a solution of this material in ether produced a suitable experimental sample. A synthesis is described by Harvey *et al.* (1982).

Crystal data

$C_{11}H_{12}O_4$
$M_r = 208.21$
Orthorhombic, *Pbca*
$a = 11.3705$ (2) Å
$b = 9.7132$ (2) Å
$c = 19.0382$ (3) Å
$V = 2102.65$ (11) Å^3
$Z = 8$
$D_x = 1.315$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 38 725 reflections
$\theta = 1.07–27.47°$
$\mu = 0.100$ mm^{-1}
$T = 150$ K
Cut column, colorless
$0.23 \times 0.12 \times 0.12$ mm

Data collection

Nonius KappaCCD diffractometer
ω scans with κ offsets
38 725 measured reflections
2408 independent reflections
1777 reflections with $I > 2\sigma_I$

$R_{int} = 0.056$
$\theta_{max} = 27.47°$
$h = -14 \rightarrow 14$
$k = -12 \rightarrow 12$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R(F) = 0.048$
$wR(F^2) = 0.085$
$S = 1.97$
2408 reflections
145 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma_{cs}^2 + (0.018I)^2]$
$(\Delta/\sigma)_{max} = 0.0003$
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}
Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: 5.5 (10) $\times 10^{-7}$

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.2886 (15)	O3—C3	1.2742 (14)
O2—C1	1.2360 (14)	O4—C3	1.2532 (14)
O1—C1—O2	124.2 (2)	C3—C2—C4	110.2 (2)
O1—C1—C2	114.5 (2)	O3—C3—O4	123.7 (2)
O2—C1—C2	121.3 (2)	O3—C3—C2	115.8 (2)
C1—C2—C3	109.6 (2)	O4—C3—C2	120.5 (2)
C1—C2—C4	113.2 (2)		

Table 2
Hydrogen-bonding geometry and leading C—H···O interactions (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O1···O2^i	0.93 (2)	1.73 (2)	2.667 (2)	179 (2)
O3—H1O3···O4^{ii}	1.23 (2)	1.40 (2)	2.628 (2)	177 (2)
C7—H7···O1^{iii}	0.98	2.66	3.593 (2)	160
C7—H7···O3^{iv}	0.98	2.73	3.475 (2)	133
C8—H8···O2^v	0.98	2.77	3.540 (2)	136
C10—H10···O4^{vi}	0.98	2.80	3.591 (2)	139
C2—H2···O4^{vi}	0.98	2.83	3.734 (2)	154
C2—H2···O2^{vi}	0.98	2.85	3.642 (2)	138

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

Table 3
Basic first- and second-level graph-set descriptors involving interactions designated *a–c* in the order given in Table 2.

	a	*b*	*c*
a	$R_2^2(8)$	$C_2^2(12)$	$C_2^2(12)$
b		$R_2^2(8)$	$C_2^2(14)$
c			$C(8)$

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1995); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Fitzgerald, L. J. & Gerkin, R. E. (1993). *Acta Cryst.* C**49**, 1952–1958.
Harvey, R. G., Cortez, C. & Jacobs, S. A. (1982). *J. Org. Chem.* **47**, 2120–2125.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Lepore, U., Lepore, G. C. & Ganis, P. (1975). *Acta Cryst.* B**31**, 2874–2876.
Molecular Structure Corporation (1995). *TEXSAN*. Version 1.7. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Steiner, T. & Desiraju, G. R. (1998). *J. Chem. Soc. Chem. Commun.* pp. 891–892.
Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.
Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.
Zachariasen, W. H. (1968). *Acta Cryst.* A**24**, 212–216.