organic compounds

Conformation of hydrogen-bonded dimeric *o*-methyl-substituted benzoic acids

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Molecules of 2,4-dimethylbenzoic acid, $C_9H_{10}O_2$, form typical centrosymmetric hydrogen-bonded dimers. The carboxyl group is twisted with respect to the benzene ring and the methyl group in the *ortho* position shows evasive in-plane splaying. The relation between the in-plane splaying and the twist angle of the carboxyl group for various *ortho*-substituted dimeric derivatives of benzoic acid is presented. It shows how the steric strains are released depending on the numbers and positions of the substituents.

Comment

2,4-Dimethylbenzoic acid, (I), was obtained by the acetylation of *m*-xylene by acetic acid in the presence of P_2O_5 as catalyst. According to Kosolapoff (1947), in the course of this reaction mono- and diacetyl derivatives of *m*-xylene form, and the latter is found in the high-boiling fraction. Our studies reveal that the compound is actually 2,4-dimethylbenzoic acid, (I).


(I)
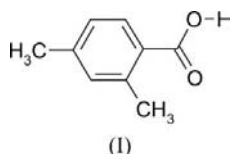
Molecules of (I) crystallize in the form of centrosymmetric hydrogen-bonded dimers. One such dimer is presented in Fig. 1, along with the atom-numbering scheme. The carboxyl group in (I) shows C—O bond-length alteration, with distances of 1.3085 (19) and 1.2251 (18) Å. The relevant C—C—O angles are also different, at 114.34 (14) and 124.02 (14)°. The differences between these bond lengths (Δd) and angles ($\Delta\varphi$) obey the relation given by Borthwick (1980), *i.e.* $\Delta\varphi = -100 \times \Delta d$ (φ in degrees and d in Å). The carboxyl group is twisted with respect to the benzene ring. The dihedral angle between the plane of the benzene ring and the plane formed by atoms O1/O2/C1 is 14.06 (3)°. The methyl group in the *ortho* position is splayed away from the carboxyl group and

this is illustrated by the different values of the C2—C3—C8 and C4—C3—C8 angles, which are 124.23 (14) and 118.57 (14)°, respectively. In contrast, the C4—C5—C9 and C6—C5—C9 angles are nearly equal and the methyl group in the *para* position is located symmetrically.

The centrosymmetric hydrogen-bonded dimer of (I) is described using the common motif which occurs in most other monocarboxylic acids (Leiserowitz, 1976), namely $R_2^2(8)$ (Etter, 1990) (Fig. 1). The H1···O2^i and O1···O2^i distances are 1.71 (3) and 2.646 (2) Å, respectively, and the O1—H1···O2^i angle is 176 (3)° [symmetry code: (i) $-x, -y, 1 - z$]. The molecular packing of (I) is best described as comprising puckered sheets of carboxylic acid hydrogen-bonded dimers but there are no significant interactions between dimers.

The observed in-plane splaying and the noncoplanarity of the carboxyl group and the benzene ring indicate that the molecular conformation is influenced by the presence of a methyl group in the *ortho* position. In other methylbenzoic acid derivatives, it was found that there are two ways in which the steric strain caused by the closeness of a carboxyl and a methyl group can be relieved (Barcon *et al.*, 1997). First of all, the carboxyl and the *o*-methyl groups exhibit evasive in-plane splaying, Δ. This parameter was calculated by adding the values of the C2—C3—C8 and C4—C3—C8 angles and subtracting 240° from the sum. The second possibility for relieving steric strain is a twist of the carboxyl group around the C_{ar}—$C_{carboxyl}$ bond. To examine these parameters for benzoic acid derivatives, we performed a search of the Cambridge Structural Database (CSD, Version 5.28 of August 2007; Allen, 2002; Bruno *et al.*, 2002). The following restrictions were made: $R < 10\%$, at least one methyl group present in an *ortho* position, and the remaining substituents restricted to be only H, methyl, Cl or Br. Moreover, only acids forming hydrogen-bonded dimeric structures were taken into account. In the case of two acids, namely 2-methylbenzoic acid (Byrn *et al.*, 1993) and 2,4,6-trimethylbenzoic acid (Gdaniec *et al.*, 2003), structural data for the acid molecules acting as guest molecules or found in cocrystals were also included. This provided us with a set of 14 molecules. The angle of twist and the angle for combined in-plane splay have been calculated for (I) and all the structures obtained from the CSD search. In the case of acids with methyl groups in both *ortho* positions, the in-plane splay was taken as the mean of the two values.
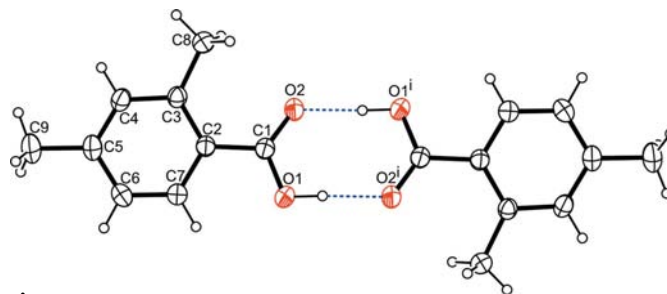
Figure 1
The hydrogen-bonded dimeric motif of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines. [Symmetry code: (i) $-x, -y, 1 - z$.]
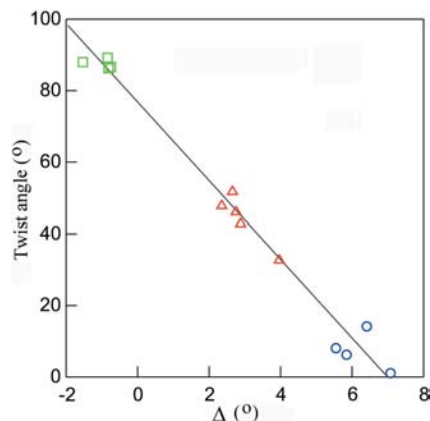
Figure 2
A scatter plot showing the relation between the in-plane splaying, Δ, and the twist angle of the carboxyl group. Data corresponding to mono-*ortho*-substituted acids are represented by circles, triangles show the data for di-*ortho*-substituted molecules and squares denote the group of pentasubstituted benzoic acid derivatives.

The scatter graph (Fig. 2) shows the relation between the twist of the carboxyl group and the in-plane splay. The data are separated into three clusters. The points at the bottom right-hand corner correspond to the structures of mono-*ortho*-substituted acids. The value of Δ ranges from 5.6 to 7.1°, whereas that of the twist angle ranges from 1.0 to 14.1°. The parameters of the benzoic acid derivatives with a methyl group in both *ortho* positions and with both *meta* positions vacant lie in the middle cluster. In this cluster, the values of Δ and the twist fall in the ranges 2.4–4.0 and 32.6–51.6°, respectively. It should be noted that for pure 2,4,6-trimethylbenzoic acid measured at 100 K (Wilson & Goeta, 2004), the values of Δ and the twist angle are 2.9 and 42.7°, respectively. When the same compound forms a cocrystal with 1,4-bis(pentafluorophenyl)butadiyne (Gdaniec *et al.*, 2003), these values change to 4.0 and 32.6°, respectively. Moreover, the data provided by Wilson & Goeta (2004) for pure 2,4,6-trimethylbenzoic acid measured at different temperatures in the range 100–290 K show small changes of the parameters in question. At the top left-hand corner of Fig. 2, there is a cluster of points which corresponds to the pentasubstituted acids. The buttressing effect (Westheimer, 1956) of the substituents in the *meta*-position hinders the in-plane splaying but a twist angle of approximately 90° is observed.

Summarizing, the observed relationship shows that the in-plane splaying and the twist angle of the carboxyl group are interdependent parameters with a correlation factor of 0.98 (4). Steric strains introduced by substituents in the *ortho* position are primarily released by in-plane splaying. However, if the buttressing effect of groups in the *meta* positions occurs, in-plane splaying is unfavourable. Thus, the twist of the carboxyl group becomes significant and approaches 90° with a loss of resonance stabilization. The structures of 2,4,6-trimethylbenzoic acid molecules in various molecular environments are good examples of the fact that the molecular conformation is also to some extent dependent on other

factors, such as crystal packing forces and weak intermolecular interactions.

Experimental

The synthesis of the title compound was carried out according to the procedure described by Kosolapoff (1947). *m*-Xylene was treated with acetic acid in the presence of P_2O_5 as catalyst and the high-boiling fraction was purified by distillation under reduced pressure. Crystals of (I) suitable for X-ray studies were obtained by sublimation.

Crystal data

$C_9H_{10}O_2$	$V = 786.8\ (3)\ \text{Å}^3$
$M_r = 150.17$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 5.4656\ (12)\ \text{Å}$	$\mu = 0.09\ \text{mm}^{-1}$
$b = 13.660\ (2)\ \text{Å}$	$T = 293\ (2)\ \text{K}$
$c = 10.6755\ (19)\ \text{Å}$	$0.25 \times 0.20 \times 0.15\ \text{mm}$
$\beta = 99.182\ (16)°$	

Data collection

Siemens *P*3 diffractometer	$R_{int} = 0.014$
1551 measured reflections	2 standard reflections
1399 independent reflections	every 70 reflections
953 reflections with $I > 2\sigma(I)$	intensity decay: 4.1%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	H atoms treated by a mixture of
$wR(F^2) = 0.106$	independent and constrained
$S = 1.02$	refinement
1399 reflections	$\Delta\rho_{max} = 0.14\ \text{e}\ \text{Å}^{-3}$
108 parameters	$\Delta\rho_{min} = -0.13\ \text{e}\ \text{Å}^{-3}$

H atoms were positioned geometrically and constrained to ride on their parent atoms, with C—H = 0.93–0.96 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(methyl C). The methyl group in the *para* position (C9) was modelled as an idealized disordered rotating group with a refined occupancy factor of 0.62 (2) for the major conformer. The carboxyl H atom was located in a difference Fourier map and its positional and isotropic displacement parameters were freely refined.

Data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991); cell refinement: *P3/P4-PC Diffractometer Program*; data reduction: *XDISK* (Siemens, 1991); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.3085 (19)	O2—C1	1.2251 (18)
O1—C1—O2	121.63 (14)	C2—C3—C8	124.23 (14)
O1—C1—C2	114.34 (14)	C4—C5—C9	121.52 (16)
O2—C1—C2	124.02 (14)	C6—C5—C9	120.86 (16)
C4—C3—C8	118.57 (14)		
O1—C1—C2—C3	165.38 (15)	O2—C1—C2—C3	−14.6 (3)

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3135). Services for accessing these data are described at the back of the journal.

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