2717 measured reflections
2113 independent reflections
1132 reflections with $I > 2\sigma(I)$
3 standard reflections every 97 reflections
intensity decay: 1.84%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.150$
$S = 1.03$
2111 reflections
143 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 0.0808P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 0.210$ e Å^{-3}
$\Delta\rho_{\min} = -0.150$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.084 (14)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (II)*

O1—C3	1.219 (3)	O3—C8	1.317 (3)
O2—C8	1.196 (3)		
O2—C8—C1	124.0 (3)	O3—C8—C1	112.1 (3)
C8—C1—C7a—C7	−57.2 (4)	C7a—C1—C8—O2	−103.5 (3)

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O4	0.75 (3)	1.87 (3)	2.615 (3)	170 (4)
O4—H4*A*···O2^{i}	0.77 (3)	2.18 (3)	2.845 (3)	144 (3)
O4—H4*B*···O1^{ii}	0.90 (3)	1.86 (3)	2.754 (3)	172 (3)
C4—H4···O1^{iii}	0.93	2.54	3.402 (3)	155
C1—H1···O1^{iv}	0.95	2.54	3.387 (3)	149

Symmetry codes: (i) $-x, -y, -z$; (ii) $x-1, y-1, z$; (iii) $2-x, 2-y, 1-z$; (iv) $x-1, y, z$.

For both (I) and (II), the H-atom treatment for the organic portion is the same. All non-carboxyl H atoms were found in electron-density difference maps but replaced in calculated positions and allowed to refine as riding models on their appropriate C atoms. The carboxyl H atom was found in an electron-density difference map and was allowed to refine with its displacement parameter fixed at 0.08 Å^2. The displacement parameter of the single methylene H atom on C1 was allowed to refine alone and the pair of H atoms on C2 as a group. The displacement parameters for the four aromatic H atoms were allowed to refine as a group. For the hydrate (II), the water H atoms were found in an electron-density difference map; they were allowed to refine with their displacement parameters fixed at 0.08 Å^2.

For both compounds, data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXTL* (Sheldrick, 1994); program(s) used to refine structures: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1331). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1842–1845

2,4,5-Trimethylbenzoic Acid

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(*Received 24 March 1997; accepted 24 June 1997*)

Abstract

The X-ray structure of the title compound, $C_{10}H_{12}O_2$, has been determined. The carboxyl and its *o*-methyl group display typical evasive in-plane splaying away from each other. The carboxyl is coplanar with the benzene ring and displays some minor disordering; the *para*-methyl group shows rotational disorder. Pairs of molecules form centrosymmetric carboxyl dimers [O···O 2.640 (2) Å].

Comment

Our continuing study of hydrogen bonding in keto-carboxylic acids, where four different basic hydrogen-bonding modes have been documented (Coté, Thompson & Lalancette, 1996), is currently being extended to include several simple unelaborated acids (Lalancette, Stringer & Coté, 1996). In the absence of other functional groups, carboxylic acids normally aggregate in the solid state as dimers (Leiserowitz, 1976). Rare instances

Acta Crystallographica Section C
ISSN 0108-2701 © 1997

are known of catemeric hydrogen-bonding patterns, as in formic (Holtzberg, Post & Fankuchen, 1953; Nahringbauer, 1978) and acetic acids (Jones & Templeton, 1958; Nahringbauer, 1970).

For benzoic acids, numerous published X-ray structures exist for simple substitution patterns (Miller, Curtin & Paul, 1974). A feature of long-standing interest in these compounds is the response of the carboxyl group to crowding by substituents at the *ortho* position(s). For benzoic acid itself, the carboxyl lies only 1.9 (2)° from coplanarity (Sim, Robertson & Goodwin, 1955), but sterically demanding *ortho* substituents typically produce twisting of the carboxyl from coplanarity as well as an evasive in-plane splaying of both of the carboxyl—C1—C2-substituent internal angles. Pertinent cases include *o*-chlorobenzoic acid (Ferguson & Sim, 1962), whose angles of twist and for combined in-plane splay (*i.e.* combined excess beyond the 120° expected at each site) are 13.7 and 7.2°, respectively, and *o*-bromobenzoic acid (Ferguson & Sim, 1961), whose corresponding angles are 18.3 and 8.3°. These angles are 17 and 10° in *o*-iodobenzoic acid (Gougoutas, 1977), which also shows significant warping of the aromatic ring; the case is similar for 3-iodo-2-naphthoic acid, where the corresponding angles are 20.0 and 10° (Gougoutas & Toeplitz, 1977).

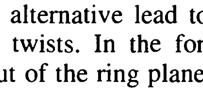
A particularly interesting case is *o*-toluic acid (Katayama, Furusaki & Nitta, 1967), in which these angles are 0 and 7°, respectively. Here a single *o*-methyl group causes in-plane splaying comparable with that in *o*-chlorobenzoic acid, but is insufficient to force the carboxyl from coplanarity with the ring. Evidently benzoic acids will endure considerable in-plane angle strain before suffering a loss of resonance stabilization.

Since estimates of steric bulk suggest that methyl and chloro substituents are closely comparable in size, the additional deformation in the *o*-chloro case may involve dipolar repulsions as well. This conclusion is supported by the relatively weak correlation between these deformations and estimates of purely steric size (Newman, 1956; Quayle, 1953; Isemura, 1965) within the entire above series of *o*-substituted benzoic acids.

Besides *o*-toluic acid, only two X-ray structures are known for *o*-methylbenzoic acids that are not *o*,*o*-disubstituted. In 2-methyl-5-nitrobenzoic acid (Tinant, Declercq, Van Meerssche & Exner, 1988), the angles for carboxyl twist and combined in-plane splay are 3 and 7.1/7.5° (two molecules in the asymmetric unit), respectively. The case of 2,3-dimethylbenzoic acid (Smith, Florencio & Garcia-Blanco, 1971), in which the angles in question are 10 and 4.9°, suggests that packing forces may contribute significantly to the balance between these two modes of steric strain avoidance.

For *o*-methyl groups, the extreme case is represented by 2,6-dimethylbenzoic (Anca, Martinez-Carrera & Garcia-Blanco, 1967) and 2,4,6-trimethylbenzoic acids (Florencio & Smith, 1970; Benghiat & Leiserowitz, 1972), where overcrowding and the absence of the in-plane-splay alternative lead to more drastic out-of-plane carboxyl twists. In the former case, the carboxyl is rotated out of the ring plane by 53.5°, while in the trimethyl species the twist is 48.5°.

We were interested in studying these deformations in other polysubstituted *o*-methylbenzoic acids, and have examined the case of 2,4,5-trimethylbenzoic acid, (I), containing one methyl group each in the *ortho*, *meta* and *para* positions.



(I)

The dimeric hydrogen-bonding in (I) is illustrated in Fig. 1. Within experimental error, the acid group and benzene ring are coplanar, with a twist of only 1.0 (4)°. However, the carboxyl and *o*-methyl groups are splayed away from each other, with C2—C1—C7 and C1—C2—C8 angles of 122.5 (2) and 124.6 (2)°, respectively, for a combined in-plane splay of 7.1°. As documented above, this figure appears to be typical for benzoic acids that are *o*-monosubstituted with groups of modest size.

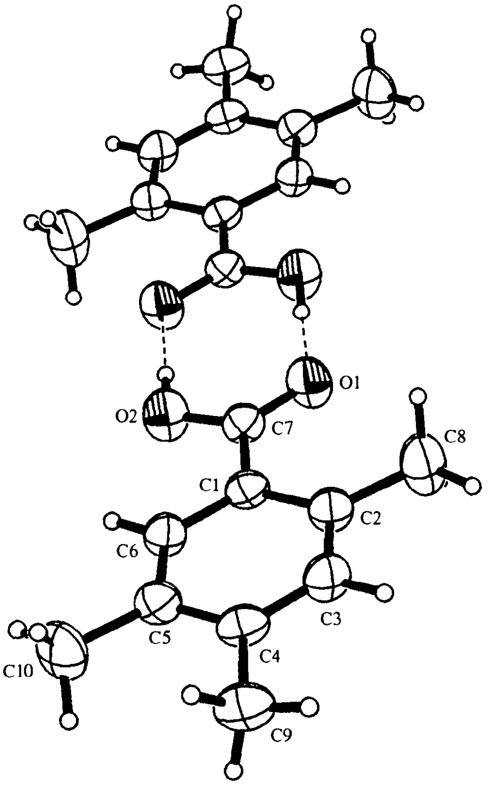


Fig. 1. *ORTEP*II (Johnson, 1976) plot of (I) showing a centrosymmetric dimer pair, with the numbering scheme. The principal rotamer for the methyl group (C9) *para* to the acid is shown. Ellipsoids are drawn at the 40% probability level.

Each of the three methyl groups in (I) lies in the ring plane, and the methyl group bound to C4 displays rotational disorder. The H atoms on this methyl (C9) were modeled with two sets of three H atoms, defining a regular hexagon. The rotamer ratio found in this modeling for the C9 methyl H atoms was 74:26 (2); Fig. 1 shows only the predominant rotamer. The *ortho*-methyl H atoms are staggered with respect to the carboxyl O atom and show no disorder. Calculations with an ordered carboxyl (Borthwick, 1980) put the distances between the carbonyl O atom and the nearest C8 H atoms at 2.42 and 2.51 Å. For a singly bonded O atom at the same site, these calculated distances are 2.19 and 2.29 Å. Thus, these interactions are measurably worse for C—O···H—C than for C═O···H—C, although evidently not such as to suppress all carboxyl disorder.

In (I), the C—O bond distances are 1.230 (2) and 1.289 (2) Å, and the C—C—O angles are 115.2 (2) and 122.4 (2)°, indicating some minor disordering for the carboxyl. Typical C—O distances and C—C—O angles cited for highly ordered carboxyl groups are 1.21 and 1.31 Å, and 112 and 123° (Borthwick, 1980).

The solid-state (KBr) IR spectrum of (I) displays C═O stretching absorption shifts typical for a dimer, at 1681 cm^{-1}. In CCl_4, this is shifted to 1688 cm^{-1}, indicating a lower average carboxyl coplanarity in solution.

Experimental

The title compound is commercially unavailable and was synthesized in 67% yield from 5-bromo-1,2,4-trimethylbenzene by carbonation of the Grignard reagent (Bowen, 1955; Smith & Stanfield, 1949). Recrystallization from *p*-xylene yielded X-ray-quality crystals (m.p. 422–424 K).

Crystal data

$C_{10}H_{12}O_2$
$M_r = 164.20$
Triclinic
$P\bar{1}$
$a = 7.065\,(2)$ Å
$b = 7.199\,(1)$ Å
$c = 9.726\,(2)$ Å
$\alpha = 105.61\,(1)^\circ$
$\beta = 103.46\,(1)^\circ$
$\gamma = 99.61\,(1)^\circ$
$V = 449.2\,(2)$ Å^3
$Z = 2$
$D_x = 1.214$ Mg m^{-3}
$D_m = 1.21\,(1)$ Mg m^{-3}
D_m measured by flotation in CCl_4/cyclohexane

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 11 reflections
$\theta = 20.2$–26.8°
$\mu = 0.083$ mm^{-1}
$T = 296\,(2)$ K
Parallelepiped
0.60 × 0.40 × 0.12 mm
Colorless

Data collection

Siemens *P*4 diffractometer
$2\theta/\theta$ scans
Absorption correction: face-indexed numerical
$T_{\min} = 0.970$, $T_{\max} = 0.991$
3460 measured reflections
1730 independent reflections
1050 reflections with $F > 4\sigma(F)$

$R_{\rm int} = 0.062$
$\theta_{\max} = 26^\circ$
$h = -8 \rightarrow 8$
$k = -8 \rightarrow 8$
$l = -11 \rightarrow 11$
3 standard reflections every 97 reflections intensity decay: 1.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.149$
$S = 1.025$
1730 reflections
121 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0667P)^2 + 0.0179P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 0.182$ e Å^{-3}
$\Delta\rho_{\min} = -0.196$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C7	1.230 (2)	C1—C7	1.493 (2)
O2—C7	1.289 (2)		
O1—C7—O2	122.4 (2)	O2—C7—C1	115.2 (2)
O1—C7—C1	122.4 (2)	C7—O2—H2	114.2 (14)
C6—C1—C7—O1	−179.7 (2)	C6—C1—C7—O2	−0.4 (3)
C2—C1—C7—O1	0.0 (3)	C2—C1—C7—O2	179.4 (2)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1^{i}	0.92 (3)	1.72 (3)	2.640 (2)	178 (2)

Symmetry code: (i) $1 - x, -y, -z$.

The two H atoms on the ring were found in electron-density difference maps, but replaced in calculated positions and allowed to refine as riding models on their appropriate C atoms. The carboxyl (H2) was found in an electron-density difference map and its positional parameters were allowed to refine, but its displacement parameter was held at 0.080 Å^2. Electron-density difference maps in later stages of refinement revealed the rotationally disordered methyl group C9. The H atoms on this methyl group were removed and replaced with two sets of three H atoms each, such that the H atoms defined a regular hexagon. The occupancies were refined and summed to be unity. The disorder for the C9 methyl H atoms is 74 (2)/26 (2). Group $U_{\rm iso}$ values for the methyl H atoms were as follows: 0.115 (6) for the C8 methyl H atoms, 0.053 (5) for the C9 methyl H atoms and 0.115 (6) Å^2 for the C10 methyl group H atoms.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

One of us (AB) was supported by a summer internship grant from the Howard Hughes Medical Institute.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1324). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1845–1846

Bis(trimethylsilyl)acetylene

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(*Received 10 January 1997; accepted 11 April 1997*)

Abstract

The structure of the title compound, $C_8H_{18}Si_2$, at 102 K, is characterized by a centre of inversion located on the central triple bond, which is 1.208 (3) Å long.

Comment

Most transition metals form polynuclear complexes containing bridging acetylenic ligands (Varga, Mach, Schmid & Thewalt, 1994). The metal used for complexation is crucial for the strength of coordination, which is reflected, among other ways, in the elongation of the acetylenic C—C bond (Hiller *et al.*, 1996). Some of these complexes are of interest as postulated intermediates in catalytic reactions (Bonrath, Pörschke, Wilke, Angermund & Krüger, 1988) and as models for the chemisorption of unsaturated hydrocarbons to metallic surfaces of heterogeneous catalysts (Beck, Niemer & Wieser, 1993). The title compound, (I), is frequently used as a ligand in such complexation studies; therefore its molecular structure is of interest.

(I)

A crystal of (I) (m.p. 293 K) was grown using *in situ* techniques as described previously (Brodalla, Mootz, Boese & Osswald, 1985). The crystal structure analysis reveals (I) to be located on a centre of inversion. As a consequence, both trimethylsilyl groups are in staggered positions (Fig. 1). The C1—C1^{i} [symmetry code: (i) $-x, -y, 1-z$] length [1.208 (3) Å] is typical for $C\equiv C$ bonds. The C_{sp}—Si bond length is somewhat shorter than the C_{sp^3}—Si bonds (Table 2). Intramolecular steric strain between the methyl groups results in C_{sp^3}—Si—C_{sp^3} angles [110.35 (8)–111.16 (8)°] being widened by about 2–3° compared with the C_{sp}—Si—C_{sp^3} angles [107.83 (6)–108.49 (6)°]. The slight deviation of the Si—C1—C1^{i} angle [179.1 (2)°] from the idealized 180° may be due to intermolecular interactions.

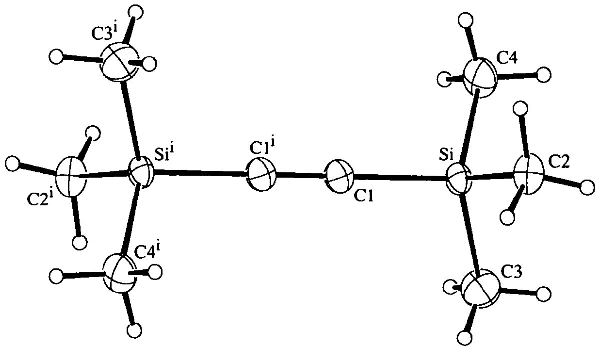

Fig. 1. A view (*ORTEP*II; Johnson, 1976) of the title molecule showing the labelling of the non-H atoms. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

The crystal was grown by zone-melting techniques in a glass capillary with a focused halogen lamp as heat source (Brodalla, Mootz, Boese & Osswald, 1985) at 292 K.