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The Crystal Structure of 2,3-Dimethylbenzoic Acid

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The crystal structure of 2,3-dimethylbenzoic acid has been determined from three-dimensional X-ray data. The triclinic unit cell of dimensions $a = 6.895$, $b = 9.018$, $c = 6.846$ Å, $\alpha = 97^\circ 22'$, $\beta = 110^\circ 50'$, $\gamma = 95^\circ 40'$ contains two molecules. The space group is $P\bar{1}$. Positions of some atoms in the molecule deviate from a planar configuration owing to molecular overcrowding. The carboxyl group is somewhat distorted from the benzene ring.

Introduction

The determination of the crystal structure of 2,3-dimethylbenzoic acid was undertaken as a continuation of previous studies (Anca, Martínez-Carrera & García-Blanco, 1967; Florencio & Smith, 1970; Cano, Martínez-Carrera & García-Blanco, 1970) to

Fig. 1. Difference electron-density map showing hydrogen atoms contoured at intervals of 0·1 e.Å⁻³ beginning at 0·3 e.Å⁻³.

investigate existing interactions between methyl groups and the carboxyl group in these derivatives of benzoic acid. In the present paper we paid attention to the effect of the position of the methyl groups on the bond lengths and bond angles in the case of an asymmetric molecule.

Experimental

A purified specimen of 2,3-dimethylbenzoic acid was kindly supplied by Dr Colomina of this Institute. Single crystals were obtained by slow evaporation in ethyl alcohol.

Unit-cell parameters were derived by a least-squares fit to the 2θ values of 30 high-order reflexions measured, using a single crystal, on a General Electric XRD-6 diffractometer with Co $K\alpha$ radiation ($\lambda = 1.7902$ Å).

Parameters of the triclinic cell are:

$a = 6.895$ Å	$\alpha = 97^\circ 22'$	$D_m = 1.25$ g.cm⁻³
$b = 9.018$	$\beta = 110^\circ 50'$	$D_x = 1.27$ g.cm⁻³
$c = 6.846$	$\gamma = 95^\circ 40'$	$Z = 2$

The molecule was assumed to be planar and centrosymetric based on the structures of other analogous benzoic acids. Therefore, the space group chosen was
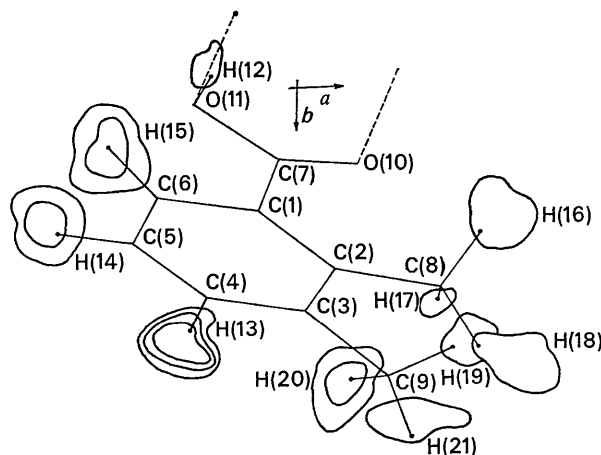
Table 1. *Observed and calculated structure factors*

H	K	L	FOBS	FCAL
-11	1		2.9	2.7-
-11	2		2.2	2.6
-11	3		2.6	2.3-
-10			1.9	2.0
-10	1		3.9	4.0
-10	2		9.0	9.5-
-10	3		1.4	1.2
-9	2		2.3	2.4-
-9	1		4.0	4.4
-9			1.4	1.6
-9	2		7.7	8.2-
-9	3		6.1	5.9
-9	5		2.7	2.4-
-9	6		2.9	2.6-
-8	1		2.1	1.5
-8			1.4	1.7-
-8	1		1.5	1.5
-8	2		6.6	6.7
-8	3		3.5	2.9-
-8	5		2.2	2.3-
-8	6		2.6	2.6-
-7	1		7.1	7.3-
-7			9.9	9.2

Table 1 (cont.)

(Structure-factor listing with columns H K L, FOBS, FCAL, reproduced in several blocks across the page.)

PĪ rather than P1. This assumption was later confirmed by the structural analysis.

Two-dimensionally integrated equi-inclination Weissenberg data were collected for the *a* axis (zones 0*kl*–4*kl*) and for the *c* axis (zones *hk*0–*hk*5) using the multiple-film technique. Intensity data were recorded for two crystals, reduced separately, and subsequently compared and averaged.

Of all possible reflexions, 960 (60%) were recorded. The remaining reflexions (of non-observable intensity) were allocated intensities according to $I = \frac{1}{2}I_{min}$.

The intensity data of each layer line were corrected for effects due to Lorentz and polarization factors in the usual way. No absorption corrections were applied.

Determination of the structure

Since the Ī21 reflexion was the strongest one, it was assumed that the molecule lay near this plane. Hence, for convenience the molecule was chosen to lie on this plane with an orientation that was in best agreement with the vector set found in a sharpened three-dimensional Patterson function. The $F(hkl)^2$ were multiplied by the factor:

$$(1/f) \exp (2B \sin^2 \theta/\lambda^2)(2 \sin \theta/\lambda)^4 \exp [-(4\cdot4 \sin \theta/\lambda)^2]$$

(Donohue & Trueblood, 1952; Brown & Marsh, 1963). A structure-factor calculation with the set of coordinates found gave an *R* index of 0·48. A Fourier synthesis was performed and the *R* value dropped to 0·31 for all observed reflexions. Isotropic temperature factor $\exp (-2\cdot7 \sin^2 \theta/\lambda^2)$ was used in calculating structure factors. Further refinement of the structure

was carried out by means of three cycles of differential synthesis with individual isotropic temperature factors and five cycles of differential synthesis with anisotropic temperature factors (not considering the hydrogen atoms).

When the shifts were less than the standard deviations the refinement was stopped. The final *R* index was 0·095 for all observed reflexions.

A three-dimensional difference Fourier synthesis, based on the last cycle of differential synthesis, was calculated to obtain the positions of the hydrogen atoms including structure factors with sin θ < 0·6. A composite map of the difference electron density obtained is shown in Fig. 1. All hydrogen atoms clearly appear. They were given isotropic *B* values of 5·0 Å², and their parameters were not refined. Final structure factors, including the contribution of the hydrogen atoms, decreased *R* to 0·091 for all observed reflexions. Observed and calculated structure factors are listed in Table 1. Structural parameters are listed in Tables 2 and 3.

Table 2. *Hydrogen-atom parameters*

	x/a	y/b	z/c
H(12)	−0·190	−0·030	−0·135
H(13)	−0·205	0·340	−0·930
H(14)	−0·480	0·185	−0·880
H(15)	−0·377	0·063	−0·570
H(16)	0·380	0·225	−0·320
H(17)	0·300	0·320	−0·160
H(18)	0·405	0·393	−0·295
H(19)	0·330	0·395	−0·670
H(20)	0·120	0·448	−0·830
H(21)	0·245	0·520	−0·600

Table 3. *Atomic parameters for the non-hydrogen atoms*

E.s.d.'s are in parentheses.

	x/a	y/b	z/c	B_{11}*	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}
C(1)	−0·0793	0·1760	−0·4339	3·12	2·89	2·60	0·34	0·86	1·28
	(0·007)	(0·0003)	(0·0007)						
C(2)	0·0833	0·2680	−0·4629	1·59	2·21	2·43	0·44	0·29	0·76
	(0·0006)	(0·0003)	(0·0007)						
C(3)	0·0309	0·3286	−0·6519	3·16	2·68	3·35	0·43	0·99	1·44
	(0·0007)	(0·0003)	(0·0006)						
C(4)	−0·1712	0·2974	−0·8008	3·03	3·45	2·52	0·62	1·19	0·99
	(0·0007)	(0·0003)	(0·0006)						
C(5)	−0·3321	0·2072	−0·7730	3·30	4·32	2·88	0·42	1·13	0·46
	(0·0007)	(0·0004)	(0·0007)						
C(6)	−0·2813	0·1456	−0·5859	2·84	3·41	2·95	0·16	0·75	1·01
	(0·0007)	(0·0003)	(0·0004)						
C(7)	−0·0393	0·1031	−0·2386	1·80	2·76	2·62	0·12	0·72	0·81
	(0·0005)	(0·0003)	(0·0006)						
C(8)	0·3057	0·3012	−0·3048	1·91	5·35	4·33	−0·62	2·38	0·53
	(0·0007)	(0·0004)	(0·0007)						
C(9)	0·1983	0·4289	−0·6944	5·28	5·04	4·95	−0·08	2·38	2·38
	(0·0008)	(0·0004)	(0·0008)						
O(10)	0·1247	0·1183	−0·0937	2·54	5·24	2·95	−0·96	2·06	0·36
	(0·0004)	(0·0003)	(0·0004)						
O(11)	−0·2074	0·0189	−0·2421	3·20	6·11	3·50	−0·60	2·71	0·81
	(0·0005)	(0·0003)	(0·0005)						

* In the expression $F_o \exp\left[-\frac{1}{4}(B_{11}h^2a^{*2}+ \ldots +B_{31}2hla^*c^*)\right]$

Discussion

Molecular dimensions are summarized in Fig. 2 and Table 4.

Table 4. *Bond lengths and valence angles with e.s.d.'s in parentheses*

C(1)–C(2)	1·415 Å	C(1)—C(2)—C(3)	117·4°
	(0·006)		(0·3)
C(2)–C(3)	1·410	C(2)—C(3)—C(4)	120·3
	(0·005)		(0·4)
C(3)–C(4)	1·375	C(3)—C(4)—C(5)	122·5
	(0·005)		(0·4)
C(4)–C(5)	1·394	C(4)—C(5)—C(6)	117·6
	(0·006)		(0·4)
C(5)–C(6)	1·404	C(5)—C(6)—C(1)	120·8
	(0·006)		(0·3)
C(6)–C(1)	1·383	C(1)—C(2)—C(8)	123·2
	(0·005)		(0·4)
C(1)–C(7)	1·514	C(8)—C(2)—C(3)	119·4
	(0·005)		(0·3)
C(2)–C(8)	1·500	C(2)—C(3)—C(9)	120·4
	(0·006)		(0·4)
C(3)–C(9)	1·529	C(9)—C(3)—C(4)	119·3
	(0·006)		(0·4)
C(7)–O(10)	1·189	C(1)—C(7)—O(10)	125·2
	(0·004)		(0·3)
C(7)–O(11)	1·313	C(1)—C(7)—O(11)	113·1
	(0·004)		(0·3)
		O(10)-C(7)-O(11)	121·7
			(0·3)

The benzene-carbon atoms and the two methyl groups show small, but in some cases significant, deviations from the expected coplanarity with respect to the best plane through the benzene-ring atoms. Two atoms, *i.e.* carboxyl C(7) and methyl C(8), are displaced 0·022 and 0·025 Å from this

plane, respectively. This is ascribed to steric interaction between the methyl groups and the carboxyl group. The carboxyl group is twisted around the bond C(1)–C(7) in such a way that a calculated best plane through C(1), C(7), O(10) and O(11) forms an angle of 10°1′ with the plane through the benzene ring. Equations of the several planes, together with deviations of the atoms from the planes, are shown in Table 5.

Table 5. *Molecular least-squares planes*

Description of planes:

I: C(1), C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(9), O(10), O(11)
II: C(1), C(2), C(3), C(4), C(5), C(6)
III: C(1), C(7), O(10), O(11)

Equations of planes:

(Coefficients are direction cosines relative to orthogonal axes. X' Y and Z' are also orthogonal coordinates in Å.)

I: $-0·4219X' + 0·7749Y + 0·4545Z' + 0·0848 = 0$
II: $-0·4216X' + 0·7781Y + 0·4493Z' + 0·1190 = 0$
III: $-0·4389X' + 0·7644Y + 0·4561Z' + 0·0665 = 0$

Deviations	I	II	III
C(1)	0·016	0·003	0·000
C(2)	0·009	−0·001	−0·036
C(3)	0·002	0·001	−0·054
C(4)	−0·006	0·002	−0·046
C(5)	0·004	0·004	−0·008
C(6)	0·004	−0·005	0·004
C(7)	0·001	−0·022	−0·001
C(8)	−0·010	−0·025	−0·073
C(9)	−0·008	−0·004	−0·094
O(10)	0·013	−0·015	0·001
O(11)	−0·024	−0·049	0·000

Bond lengths and bond angles in the benzene ring agree remarkably well with corresponding values found in the literature (mean values 1·397 Å and 120°).
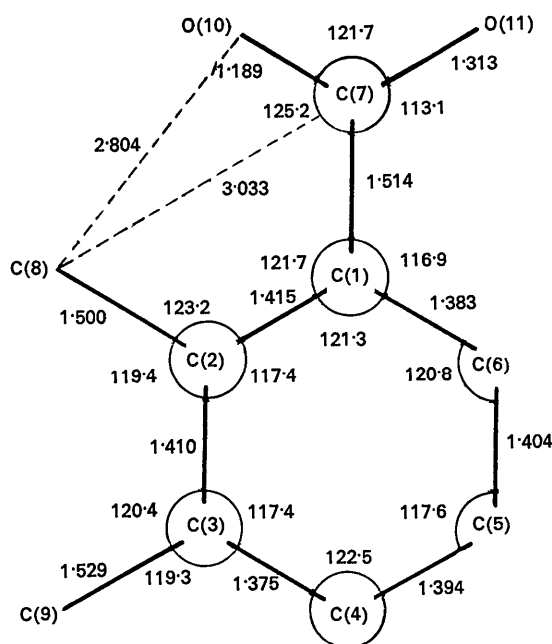
Fig. 2. Bond lengths and angles in the 2,3-dimethylbenzoic acid molecule.

The C(7)–O(10) bond of 1·189 Å is shorter than the C(7)–O(11) bond of 1·313 Å. This result suggests that the hydrogen atom is attached to the O(11) atom, and is in agreement with the value (113·1°) of the angle O(11)–C(7)–C(1) which is smaller than the 125·2° angle O(10)–C(7)–C(1). The bond length C(1)–C(7) of

1·514 Å is noticeably greater than the value of 1·479 Å reported for the sp^2 hybridization state; also, it is longer than the value found by us in the 2,4,6 trimethylbenzoic acid. The bond length C(2)–C(8) of 1·500 Å is shorter than the 1·529 Å bond length of C(3)–C(9). Nevertheless, the values found in the present work agree with the generally accepted data. Thus it may be inferred that the steric hindrance of the benzene ring and the methyl groups has no measurable influence on the bond lengths, and that the values found may be considered normal for this type of compound. The influence of the mutual interaction between the –COOH group and the two –CH₃ groups is better shown by the slight opening of the bond angles C(8)–C(2)–C(1) and C(2)–C(1)–C(7) which have values of 123·2 and 121·7° respectively and also by interatomic distances C(8)···C(7) of 3·033 Å, C(9)··· C(8) of 2·920 Å and C(8)···O(10) of 2·804 Å, which are a little shorter than the sums of the corresponding van der Waals radii (Pauling, 1960). Intermolecular distances less than 4 Å are listed in Table 6.

Atoms H(13), H(14) and H(15) are located in the benzene-ring plane. The corresponding valency angle C–C–H is about 120° and the mean distance C–H is 0·987 Å. The methyl groups have the expected tetrahedral configuration; mean values of the C–H bond and H–C–H and C–C–H angles are 0·994 Å., 106·7° and 111·9° respectively.

The structure viewed along the c axis is shown in Fig. 3 and consists of centrosymmetrical hydrogen-bonded dimers.

The O–H···O bond of 2·659 Å is similar to the values quoted for other benzoic acids. Distance

Table 6. *Intermolecular distances less than* 4 Å

Symmetry relationship of the atoms:

I:	x	y	z	V:	$-1+x$	y	$-1+z$
II:	$-x$	$-y$	$-z$	VI:	$-x$	$1-y$	$-1-z$
III:	$-x$	$-y$	$-1-z$	VII:	$-1-x$	$-y$	$-1-z$
IV:	x	y	$-1+z$	VIII:	$1-x$	$1-y$	$-z$

|	i	j		$d(ij)$		i	j		$d(ij)$
C(1)	I	C(1)	III	3·572 Å	C(4)	I	O(10)	IV	3·680 Å
C(1)	I	C(2)	III	3·972	C(4)	I	O(10)	III	3·793
C(1)	I	C(6)	III	3·987	C(4)	I	O(11)	IV	3·590
C(1)	I	C(7)	III	3·509	C(5)	I	C(7)	III	3·965
C(1)	I	C(9)	VI	3·798	C(5)	I	C(8)	V	3·861
C(1)	I	O(10)	III	3·810	C(5)	I	O(10)	V	3·544
C(1)	I	O(11)	III	3·841	C(5)	I	O(10)	III	3·545
C(2)	I	C(3)	VI	3·840	C(5)	I	O(11)	IV	3·847
C(2)	I	C(4)	VI	3·991	C(5)	I	O(11)	VII	3·641
C(2)	I	C(7)	III	3·616	C(6)	I	C(7)	III	3·681
C(2)	I	C(9)	VI	3·768	C(6)	I	C(8)	III	3·978
C(2)	I	O(11)	III	3·441	C(6)	I	C(9)	VI	3·954
C(3)	I	C(3)	VI	3·648	C(6)	I	O(10)	III	3·537
C(3)	I	C(7)	III	3·880	C(6)	I	O(11)	VII	3·400
C(3)	I	C(9)	VI	3·865	C(8)	I	C(9)	VIII	3·999
C(3)	I	O(10)	IV	3·652	C(8)	I	O(11)	III	3·772
C(3)	I	O(11)	III	3·555	C(9)	I	O(10)	IV	3·513
C(4)	I	C(7)	IV	3·715	O(10)	I	O(11)	II	2·659*
C(4)	I	C(8)	VI	3·868	O(11)	I	O(11)	II	3·603

* Hydrogen bond
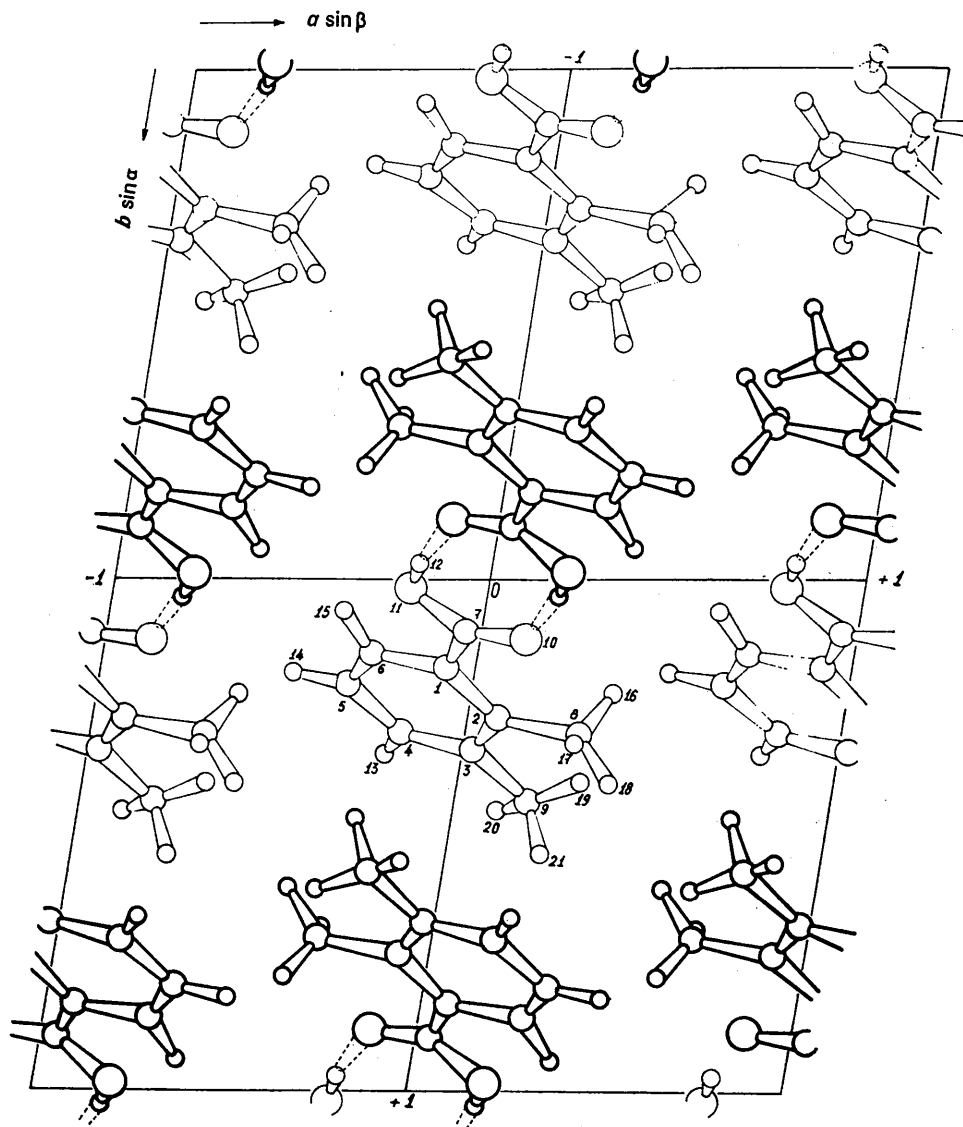
Fig. 3. 2,3-Dimethylbenzoic acid. Projection of the structure along the c axis.

O(11)–H(12) is 0·881 Å and angle C(7)–O(11)–H(12) is 116·3°.

All calculations were made on the IBM 7070 and 7090 computers of the Centro de Cálculo Electrónico C.S.I.C. Madrid. The authors thank Dr S. Martínez Carrera for continued interest and help, the staff of Instituto Torres Quevedo C.S.I.C. for making the General Electric XRD-6 diffractometer available for us, and Dr J. Fayos for assistance with the diffractometer.

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