The distances involved in the contacts between the perchlorate ion and the surrounding antipyrine groups are listed in Table 7. The intramolecular and intermolecular approaches involving the atoms in the antipyrine groups are given in Table 8 and are indicated in Fig. 6. These correspond to the expected van der Waal interactions.

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The Crystal Structure of 2,6-Dimethylbenzoic acid

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Crystals of 2,6-dimethylbenzoic acid have been studied by three-dimensional X-ray methods. They are monoclinic, space group $P2_1/a$, with four molecules in a cell of dimensions $a=15{\cdot}24$, $b=4{\cdot}04$ $c=13{\cdot}16$ Å, $\beta=94°8'$. The structure was solved by Patterson methods and refined by Fourier and differential Fourier syntheses. R is 0·168 for 958 reflexions. The structure consists of hydrogen-bonded dimers. The carboxyl group is rotated, out of the benzene plane, through 53°31′ and there are bond-angle distortions.

Introduction

So far as we know little has been done about the molecular structure of methyl derivatives of benzoic acid. Ossorio (1960), has studied the ultraviolet absorption spectra of benzoic, toluic and dimethylbenzoic acids, and discussed the spectra in terms of the resonance theory and of steric inhibition of resonance. There is a close proximity of the methyl groups to the carboxyl group in 2,6-dimethylbenzoic acid. Thus interactions between these groups are expected. The angle between the carboxyl group and the benzene ring, estimated from ultraviolet absorption spectra, is close to 60°.

The study of related compounds was initiated by Sim, Robertson & Goodwin (1955), with the determination of the crystal structure of benzoic acid. Later, Ferguson & Sim (1961, 1962), studied the molecular overcrowding in isomorphous acids, *o*-chlorobenzoic acid and *o*-bromobenzoic acid. Finally, Brown & Marsh (1963), have described the molecular structure of 2-amino-3-methylbenzoic acid.

The present work gives an account of the crystal and molecular structure of 2,6-dimethylbenzoic acid.

Crystal data

A sample of highly purified 2,6-dimethylbenzoic acid was kindly furnished by Dr M. Colomina of our Institute. Colorless crystals of the acid were obtained by slow evaporation of a solution in an ethanol–chloroform mixture at room temperature. The crystals are prisms elongated along the b axis, and belong to the monoclinic system. The crystal data are:

$a = 15{\cdot}24 \pm 0{\cdot}01$ Å
$b = 4{\cdot}04 \pm 0{\cdot}01$
$c = 13{\cdot}16 \pm 0{\cdot}01$
$\beta = 94°8'$
$D_m = 1{\cdot}21$ g.cm^{-3}, $D_x = 1{\cdot}227$ g.cm^{-3}, $Z = 4$
Space group, $P2_1/a$.

The cell dimensions were determined from rotation and equatorial layer line Weissenberg photographs.

Experimental

The intensity data were recorded on multiple-film equi-inclination Weissenberg photographs with Cu $K\alpha$ radiation. No absorption corrections were applied. The recorded data consisted of four layers with the crystal mounted on the b axis, and three layers with the crystal mounted on the c axis. The intensities were measured visually with a calibrated intensity strip. A total of 958 independent reflexions were measured. The unobserved reflexions were assigned intensities of half the minimum observable value. The data were reduced to structure amplitudes in the usual way and placed on a common scale by a least-squares method described by Rollett & Sparks (1960).

Determination of the structure

The (010) *projection*

The Patterson projection $P(u,w)$ was calculated from the value F_o^2 for the 120 observed non-zero $h0l$ reflexions. This projection indicates the molecular orientation and shows that the molecules are nearly perpendicular to the b axis. Before the positions of the atoms were fixed, however, a preliminary isotropic temperature factor was obtained from a Wilson plot, and a sharpened Patterson function $P(u,w)$ was calculated. The values $|F_{h0l}^2|$ were multiplied by the factor $(1/\hat{f}) \exp(2B \sin^2\theta/\lambda^2)(2 \sin \theta/\lambda)^4 \exp[-(4{\cdot}4 \sin \theta/\lambda)^2]$ (*cf.* Donohue & Trueblood, 1952; Brown & Marsh, 1963). The new projection shows clearly the symmetrical distribution of intramolecular vector peaks around the origin. With the help of some low-order structure factors the approximate position of the molecule projected on (010) was soon found, and the agreement index for F_o and F_c with the coordinates for all atoms obtained of the two-dimensional Patterson map was 0·32. The electron density projection $\varrho(x,z)$ was calculated. An isotropic temperature factor $\exp(-2{\cdot}50 \sin^2\theta/\lambda^2)$ was used in the calculation of structure factors $h0l$ and the disagreement index R decreased to 0·24.

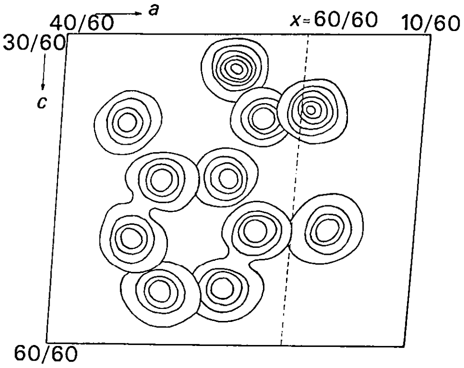

Fig. 1. A composite diagram of the last electron-density function; the contours are drawn at equal intervals of 1·5 Å^{-3}, starting from 1·5 Å^{-3}.

Three-dimensional refinement

In order to obtain the y parameters, a three-dimensional sharpened Patterson function was calculated, using the same sharpening function as for the (010) projection. The interpretation of the three-dimensional Patterson function was carried out by the use of stereographic projections for all maxima at distances 1·4 Å (distance between neighbouring atoms in the ring) and 2·4 Å (distance between alternate atoms also in the ring). With the coordinates derived from it, a check was made of all the interatomic peaks over the complete synthesis. The result was completely satisfactory since the (x,z) parameters from the (010) projection were also confirmed. With the set of x,y,z, parameters given by the three-dimensional Patterson function an R index of 0·33 was obtained for all observed reflexions. Those parameters were refined by three-dimensional reiterative electron density and structure factor calculations, using at first only the reflexions with $\sin \theta < 0{\cdot}700$. The R value decreased to 0·23. The last three-dimensional Fourier synthesis is shown in Fig. 1.

A difference Fourier synthesis was calculated in order to refine the atomic positions and also to locate the hydrogen atoms. This map showed shifts for the atomic positions and also slight anisotropy in the **b** direction. It was also possible to locate three hydrogen atoms attached to the carbon atoms of the benzene ring. The methyl hydrogen and the hydroxyl hydrogen atoms were not found in this difference Fourier synthesis. The R value was down to 0·205 for all observed reflexions.

The refinement was continued by two cycles of differential synthesis with individual isotropic temperature factors for all atoms, and two cycles of differential synthesis with anisotropic temperature factors. When the shifts were less than the standard deviations the refinement was stopped. The final R index was 0·168 for all observed reflexions.

Final parameters and accuracy

The atomic parameters with their standard deviations are listed in Table 1. The bond angles and bond lengths are shown in Table 2. The mean standard deviation is 0·01 Å in bond lengths and 0·2° in bond angles. The

Table 1. *The atomic parameters*

	Fractional coordinates with e.s.d. in parentheses			Anisotropic temperature coefficients* (Å^2)					
	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}
C(1)	0·4025 (0·0004)	−0·0302 (0·0016)	0·2289 (0·0004)	1·56	0·44	1·20	−0·01	0·07	0·10
C(2)	0·4530 (0·0004)	−0·1414 (0·0016)	0·3156 (0·0004)	1·54	0·70	1·00	−0·30	0·05	−0·09
C(3)	0·4129 (0·0004)	−0·1505 (0·0019)	0·4079 (0·0005)	1·93	1·48	1·12	−0·07	0·10	0·06
C(4)	0·3265 (0·0005)	−0·0455 (0·0021)	0·4161 (0·0005)	2·81	1·29	1·29	−0·38	0·10	0·74
C(5)	0·2791 (0·0004)	0·0699 (0·0020)	0·3287 (0·0006)	1·84	2·24	2·38	−0·36	−0·04	0·62
C(6)	0·3155 (0·0004)	0·0736 (0·0018)	0·2344 (0·0005)	2·38	1·81	2·38	−0·20	0·02	0·12
C(7)	0·5471 (0·0004)	−0·2644 (0·0019)	0·3142 (0·0005)	1·65	1·51	2·07	0·32	−0·13	−0·16
C(8)	0·4455 (0·0003)	−0·0155 (0·0017)	0·1278 (0·0004)	1·74	2·37	1·21	−0·47	−0·02	0·20
C(9)	0·2595 (0·0005)	0·2080 (0·0023)	0·1422 (0·0006)	2·13	2·21	2·16	0·55	0·39	−0·34
O(1)	0·5163 (0·0003)	0·1251 (0·0016)	0·1223 (0·0003)	2·05	2·08	2·04	−0·02	−0·01	−0·13
O(2)	0·4054 (0·0003)	−0·1647 (0·0016)	0·0527 (0·0003)	2·88	3·21	1·61	−0·76	−0·52	0·33

* In the expression $f^0 \exp\,[-\frac{1}{4}(B_{11}h^2a^{*2}+\ldots\ldots\ldots+B_{13}2hla^*c^*)]$.

Table 2. *Bond lengths and valence angles*

C(1)–C(2)	1·403 Å	C(2)–C(1)–C(6)	121·3°
C(2)–C(3)	1·399	C(1)–C(2)–C(3)	117·8
C(3)–C(4)	1·396	C(2)–C(3)–C(4)	122·2
C(4)–C(5)	1·394	C(3)–C(4)–C(5)	118·2
C(5)–C(6)	1·395	C(4)–C(5)–C(6)	121·5
C(6)–C(1)	1·399	C(5)–C(6)–C(1)	118·8
C(2)–C(7)	1·519	C(1)–C(2)–C(7)	123·9
C(1)–C(8)	1·525	C(3)–C(2)–C(7)	118·2
C(6)–C(9)	1·531	C(1)–C(6)–C(9)	122·8
C(8)–O(1)	1·226	C(5)–C(6)–C(9)	118·3
C(8)–O(2)	1·276	C(2)–C(1)–C(8)	118·5
C(8)–C(9)	2·994	C(6)–C(1)–C(8)	120·1
C(8)–C(7)	2·980	C(1)–C(8)–O(1)	120·3
O(1)–C(7)	2·984	C(1)–C(8)–O(2)	116·4
O(2)–C(9)	2·996	O(1)–C(8)–O(2)	123·2

Table 4. *Displacements* (Å) *of the atoms from the various planes*

(i) Plane through all atoms
(ii) Plane through benzene ring atoms
(iii) Plane through C(1), C(8), O(1), O(2) atoms

	(i)	(ii)	(iii)
C(1)	−0·006	−0·001	−0·003
C(2)	−0·065	0·010	−0·984
C(3)	−0·080	−0·008	−0·977
C(4)	−0·003	−0·003	−0·015
C(5)	0·084	0·013	0·960
C(6)	0·059	−0·010	0·966
C(7)	−0·168	−0·011	−2·081
C(8)	0·024	0·033	0·011
C(9)	0·175	0·027	2·081
O(1)	0·835	0·885	−0·004
O(2)	−0·854	−0·885	−0·004

Table 3. *Intermolecular distances less than* 4 Å

The following Roman numbers give the symmetry relationship of the atoms concerned

I	(x,	y,	z)	VI	($-\frac{1}{2}+x$,	$-\frac{1}{2}-y$,	z)
II	(x,	$1+y$,	z)	VII	($1-x$,	$-y$,	$-z$)
III	(x,	$-1+y$,	z)	VIII	($-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	z)
IV	($1-x$,	$-y$,	$1-z$)	IX	($1-x$,	$-y$,	$-z$)
V	($\frac{1}{2}-x$,	$\frac{1}{2}+y$,	$1-z$)				

Atom	i	Atom	j	$d(ij)$	Atom	i	Atom	j	$d(ij)$
C(1)	I	C(2)	II	3·828 Å	C(7)	I	O(1)	III	3·537 Å
C(1)	I	C(6)	II	3·859	C(8)	I	C(8)	VII	3·859
C(1)	I	C(7)	II	3·915	C(8)	I	O(1)	III	3·638
C(1)	I	C(9)	III	3·894	C(8)	I	O(1)	VII	3·412
C(2)	I	C(6)	III	3·908	C(8)	I	O(2)	II	3·617
C(2)	I	C(7)	II	3·823	C(8)	I	O(2)	VII	3·480
C(3)	I	C(3)	IV	3·670	C(9)	I	O(1)	VIII	3·758
C(3)	I	C(4)	III	3·852	C(9)	I	O(2)	II	3·623
C(6)	I	C(9)	III	3·778	O(2)	I	O(2)	VII	3·548
C(5)	I	C(7)	VI	3·737	O(1)	I	O(2)	VII	2·673*
C(4)	I	C(5)	III	3·808	O(1)	I	O(2)	II	3·412
C(4)	I	C(4)	V	3·890	O(1)	I	O(1)	VII	3·376
C(3)	I	C(5)	III	3·855	C(9)	I	O(2)	IX	3·497

* Hydrogen bond.

Table 5. *Observed and calculated structure factors*

H	K	L	FOBS	FCAL
18			4.8	5.2
16			5.9	6.6-
14			14.9	15.0-
12			7.0	7.4
10			8.1	6.0
8			27.4	22.0-
6			31.9	35.7-
4			23.8	25.8
18		1	4.1	5.7-
16		1	9.1	8.4-
12		1	6.0	4.6
10		1	8.1	5.9-
8		1	11.4	9.4-
6		1	2.3	1.4
-4		1	24.2	17.0
-6		1	24.5	24.3-
-8		1	41.4	44.5
-10		1	23.7	22.2
-12		1	9.6	7.6
-14		1	7.9	5.4-
-16		1	14.6	14.6
18		2	[illegible]	[illegible]
16		2	11.8	12.1-
14		2	6.6	5.6-
6		2	14.6	13.1-
4		2	3.8	3.7-
2		2	4.2	2.6
-2		2	10.0	9.9
-4		2	36.1	45.8-
-6		2	15.1	9.3
-8		2	30.7	22.6
-10		2	20.0	15.7
-12		2	24.3	23.2
-14		2	19.4	17.8
-16		2	7.5	8.0
18		3	4.0	2.9
16		3	13.9	13.8-
14		3	5.2	3.0
12		3	28.5	25.7-
10		3	16.8	17.4-
8		3	29.6	29.6-
6		3	24.7	19.5-
4		3	7.7	6.3
2		3	29.9	33.6
-2		3	21.1	23.4-
-4		3	26.7	33.2-
-6		3	16.2	11.2-
-8		3	3.9	2.5-
-10		3	14.0	13.1
-18		3	8.4	8.3
14		4	8.4	5.6-
12		4	7.4	7.1-
10		4	28.7	25.1
8		4	23.3	20.8-
4		4	34.7	33.1-
2		4	27.2	30.0-
		4	35.5	46.3-
-2		4	4.6	8.8-
-4		4	40.7	53.8-
-8		4	7.7	5.5
-12		4	6.5	2.9
-14		4	8.2	5.0-
18		5	7.4	9.9-
14		5	7.5	6.4
12		5	39.8	46.6
10		5	11.1	8.2
8		5	11.1	7.1-
6		5	16.6	13.0-
4		5	36.8	36.4-
2		5	10.5	5.4
		5	31.8	26.4-
-2		5	52.2	72.7-
-4		5	40.1	57.7-
-6		5	18.5	14.9
-10		5	31.1	35.0
-12		5	12.7	7.8-
-14		5	17.5	14.5-
-16		5	7.7	7.4-
-18		5	8.0	5.9-
16		6	10.0	10.1
14		6	14.8	17.5
12		6	5.8	3.1
10		6	24.1	25.9-
6		6	21.7	17.4-
4		6	39.7	48.3
2		6	29.0	21.7
		6	17.0	10.0-
-2		6	33.1	27.8-
-4		6	29.4	29.5
-6		6	2.9	2.7
-8		6	18.4	15.7
-10		6	23.9	23.2-
-12		6	37.3	48.4-
-14		6	8.6	6.7-
-16		6	8.6	6.5-
-18		6	10.3	9.6
16		7	7.7	10.3
14		7	6.3	4.6
6		7	10.7	9.6
4		7	32.6	26.8
		7	24.7	18.5
-2		7	24.3	18.7
-4		7	22.3	20.1
-6		7	7.9	4.6
-10		7	35.0	40.2-
-14		7	10.3	7.4-
16		8	7.9	7.5
14		8	6.9	7.3
12		8	6.4	7.2
8		8	9.5	10.7
6		8	10.4	9.1
4		8	25.1	20.1
2		8	11.4	7.4
-2		8	7.7	7.3-
-4		8	7.3	6.2
-6		8	21.1	15.8
-8		8	9.1	8.4
-10		8	13.9	11.6
-12		8	10.0	7.0
-14		8	5.3	4.7-
-16		8	10.2	8.2
14		9	9.7	8.3-
12		9	13.7	14.5-
8		9	9.8	9.1-
6		9	16.0	12.1
4		9	24.3	19.9
2		9	9.2	5.3
		9	26.8	21.7
-2		9	11.6	8.2
-4		9	21.8	15.6
-6		9	14.9	8.7
-14		9	9.8	7.4
-16		9	6.2	4.7
12		10	7.8	8.3-
10		10	15.8	14.2-
8		10	18.0	18.0-
6		10	17.9	14.4
2		10	30.7	32.0
		10	5.1	3.7-
-2		10	11.9	9.0-
-4		10	11.5	6.3
-10		10	5.5	3.0
-14		10	5.5	2.0
-16		10	12.6	10.7
12		11	8.1	9.1-
8		11	13.1	11.7
6		11	13.1	11.0
4		11	5.5	3.0
2		11	21.8	18.6-
		11	43.0	59.4-
-2		11	2.8	2.1-
-6		11	19.8	18.5
-8		11	10.9	9.9
-14		11	19.6	18.5
12		12	3.3	3.9-
10		12	4.2	3.5
8		12	5.8	4.5
4		12	12.6	10.9-
2		12	31.9	34.2-
-6		12	7.4	5.9
-8		12	20.0	19.3-
-12		12	10.6	8.0
-14		12	7.4	6.5
4		13	9.1	6.5-
-2		13	5.1	2.6-
-4		13	9.3	8.1
-6		13	14.3	11.8-
-8		13	9.2	3.8-
-10		13	5.3	4.2-
-12		13	9.3	7.9-
8		14	12.1	10.8
4		14	8.5	7.2-
2		14	15.8	16.3-
		14	7.5	5.4-
-10		14	7.7	5.6-
6		15	5.3	5.0-
		15	7.1	7.3
-4		15	12.6	11.7
-6		15	6.7	5.3-
-8		15	2.9	2.3-
4		16	9.4	8.6
		16	8.7	7.5
-4		16	11.8	8.0
-2		16	18.5	21.0
-6		16	5.1	4.7-
18	1		3.1	4.3
16	1		5.2	7.9-
15	1		8.9	10.0
14	1		8.8	10.1-
12	1		12.8	15.6-
11	1		11.0	11.4-
10	1		7.8	6.5
8	1		4.3	4.7
7	1		22.9	24.5
6	1		11.9	10.0
5	1		7.9	10.0-
4	1		28.2	39.6-
3	1		17.7	15.5
18	1	1	4.0	4.6
17	1	1	5.8	9.1
16	1	1	4.8	6.7-
15	1	1	5.4	5.4
14	1	1	3.7	5.6-
12	1	1	11.8	15.3-
11	1	1	5.1	3.4
10	1	1	13.2	13.0-
9	1	1	13.8	11.6
8	1	1	20.3	20.3-
7	1	1	6.7	5.4-
6	1	1	16.8	13.2-
5	1	1	5.9	6.7-
4	1	1	33.9	39.9-
3	1	1	34.0	45.4-
2	1	1	31.0	37.2
	1	1	11.2	10.0
-1	1	1	37.4	46.4
-2	1	1	38.3	50.1
-3	1	1	12.5	10.4-
-4	1	1	13.5	12.2-
-5	1	1	24.9	24.4
-6	1	1	19.1	15.9-
-7	1	1	2.2	3.4-
-8	1	1	21.2	20.0-
-9	1	1	21.8	23.4-
-10	1	1	3.9	1.4-
-11	1	1	2.8	3.7-
-15	1	1	9.1	9.4-
15	1	2	5.6	7.2
12	1	2	4.6	5.6-
11	1	2	5.7	6.3
10	1	2	14.4	15.8
9	1	2	7.8	6.1
8	1	2	8.7	8.2
7	1	2	8.7	6.2
6	1	2	9.7	8.7-
5	1	2	9.5	6.3
4	1	2	32.2	33.9-
3	1	2	16.7	17.2-
2	1	2	40.7	50.0-
1	1	2	25.1	26.8
	1	2	38.9	52.1-
-1	1	2	8.8	6.1-
-2	1	2	9.3	5.6
-3	1	2	4.7	6.1
-4	1	2	24.0	24.2-
-5	1	2	8.4	7.2
-7	1	2	30.8	23.4-
-8	1	2	11.2	10.7-
-9	1	2	3.5	2.6-
-10	1	2	6.5	7.4
-11	1	2	10.3	9.0-
-13	1	2	7.8	9.7-
-14	1	2	7.8	9.7
-15	1	2	10.0	11.0-
18	1	3	2.3	3.0-
17	1	3	3.0	3.9
16	1	3	2.0	.5-
15	1	3	3.9	3.8
14	1	3	4.1	2.2-
13	1	3	3.2	2.1
11	1	3	11.1	18.1
10	1	3	11.3	18.0
7	1	3	13.7	12.1
6	1	3	5.6	3.4-
5	1	3	5.4	3.9
4	1	3	23.0	29.3-
3	1	3	8.4	4.6
2	1	3	15.6	13.6-
1	1	3	8.3	6.4
	1	3	13.6	12.1
-1	1	3	20.6	17.9
-2	1	3	2.3	1.7-
-3	1	3	20.7	18.9
-4	1	3	10.1	35.1-
-6	1	3	24.6	21.7-
-8	1	3	24.6	24.5-
-9	1	3	13.5	9.9-
-10	1	3	6.4	6.3
-11	1	3	8.9	6.9-
-12	1	3	8.4	7.8
-13	1	3	7.5	5.6-
17	1	4	7.7	8.4
16	1	4	6.5	7.8
14	1	4	9.7	7.7-
13	1	4	12.3	16.0
11	1	4	14.1	13.8-
10	1	4	9.4	17.4-
9	1	4	10.1	11.2-
7	1	4	4.7	6.5
6	1	4	6.0	4.2-
4	1	4	6.7	6.8
3	1	4	28.7	25.5
2	1	4	28.1	27.3
1	1	4	24.6	22.6
	1	4	30.6	27.6
-1	1	4	20.0	16.2
-2	1	4	18.2	13.8
-3	1	4	24.0	23.2
-5	1	4	29.7	33.2
-6	1	4	21.5	17.5-
-7	1	4	5.7	3.6-
-8	1	4	21.2	17.7-
-10	1	4	5.5	6.4-
-11	1	4	8.8	5.4-
-12	1	4	15.1	15.8-
-13	1	4	8.8	5.7-
-14	1	4	9.1	9.5-
-15	1	4	4.8	4.8
13	1	5	15.7	18.0-
12	1	5	13.4	16.7
11	1	5	21.0	25.2-
10	1	5	10.3	14.8
9	1	5	9.7	13.3
8	1	5	20.5	25.6
6	1	5	16.8	13.1-
5	1	5	29.2	29.9
3	1	5	13.7	10.9
2	1	5	19.1	12.7-
1	1	5	8.9	4.5-
	1	5	34.7	32.4
-1	1	5	23.8	16.7
-2	1	5	7.1	3.4
-3	1	5	40.5	45.3
-4	1	5	6.9	4.6
-5	1	5	6.7	5.4-
-6	1	5	23.1	21.2-
-7	1	5	6.4	3.3-
-8	1	5	4.8	4.6
-9	1	5	11.8	9.9-
-10	1	5	7.8	4.6
-11	1	5	12.5	11.6-
-12	1	5	8.8	7.8
-13	1	5	18.4	20.7
-14	1	5	5.1	2.9
-15	1	5	9.3	7.9
-16	1	5	8.9	7.6-
-17	1	5	5.4	6.1
14	1	6	8.6	9.1
13	1	6	16.3	17.7-
12	1	6	11.2	12.8
11	1	6	9.4	9.3
10	1	6	14.3	12.9
9	1	6	6.3	3.7
8	1	6	8.4	5.6
7	1	6	15.6	10.2
6	1	6	14.0	8.7-
5	1	6	4.2	2.9
4	1	6	14.0	10.2
3	1	6	31.7	24.5-
2	1	6	16.3	14.7
1	1	6	6.4	8.5
	1	6	26.2	20.2
-1	1	6	28.1	21.6
-2	1	6	19.3	15.7-
-3	1	6	9.2	7.3-
-4	1	6	10.5	8.0-
-5	1	6	21.2	18.7-
-6	1	6	9.5	9.8-
-8	1	6	25.8	28.8
-9	1	6	14.8	12.9-
-10	1	6	15.1	14.3
-11	1	6	27.6	34.8
-12	1	6	15.2	15.2
-13	1	6	14.5	14.8
-14	1	6	8.8	8.3-
-15	1	6	3.8	3.6
15	1	7	7.0	7.4-
12	1	7	11.1	10.7-
8	1	7	13.3	13.2-
5	1	7	22.2	20.8-
4	1	7	16.1	10.6
3	1	7	8.2	5.5-
2	1	7	25.9	23.2
1	1	7	7.4	5.1-
	1	7	28.5	23.1
-1	1	7	19.1	11.2-
-2	1	7	29.0	21.3
-3	1	7	22.1	16.2-
-4	1	7	7.3	4.2
-6	1	7	14.5	8.7
-7	1	7	8.2	6.0-
-8	1	7	6.7	5.1
-9	1	7	23.8	24.6
-11	1	7	16.3	13.0
-13	1	7	8.6	7.5-
-14	1	7	9.3	7.5-
-15	1	7	5.7	4.1
-16	1	7	7.1	6.1
-17	1	7	7.5	7.7-
8	1	8	16.1	15.3-
5	1	8	5.6	3.5-
4	1	8	12.9	10.6-
3	1	8	18.5	14.5-
2	1	8	16.1	11.6
1	1	8	9.9	7.4-
	1	8	15.3	10.4
-1	1	8	16.3	11.2-
-2	1	8	3.8	4.1-
-4	1	8	12.0	7.9-
-5	1	8	10.5	7.5-
-6	1	8	8.9	6.2
-8	1	8	5.6	4.1
-9	1	8	6.3	2.9
-10	1	8	16.6	17.2
-11	1	8	9.4	9.8-
-13	1	8	8.5	6.5
-15	1	8	6.3	4.7-
15	1	9	5.9	5.3
14	1	9	4.8	6.2
8	1	9	9.4	7.6-
7	1	9	10.9	9.5
6	1	9	2.7	.7
5	1	9	12.9	11.5-
4	1	9	10.7	8.3-
1	1	9	16.3	12.0-
	1	9	28.9	26.3-
-1	1	9	19.1	15.6-
-2	1	9	21.4	16.6-
-4	1	9	10.8	10.6-
-5	1	9	11.0	8.6-
-6	1	9	7.4	6.2
-8	1	9	14.8	15.4
-10	1	9	11.4	12.4
14	1	10	3.7	5.6-
11	1	10	5.1	5.2
10	1	10	7.8	7.5-
9	1	10	12.5	12.6
8	1	10	9.5	9.7-
6	1	10	9.0	8.8-
5	1	10	9.0	8.1-
3	1	10	13.1	9.9-
2	1	10	11.8	8.6
1	1	10	22.6	20.3-
-1	1	10	24.4	20.9
-2	1	10	7.1	7.0
-3	1	10	5.2	4.4
-4	1	10	14.9	13.1-
-8	1	10	6.7	8.5-
-10	1	10	6.5	6.8-
-15	1	10	7.0	7.0-
11	1	11	9.1	9.2
10	1	11	8.7	9.7-
8	1	11	5.4	5.9-
7	1	11	9.9	9.6-
6	1	11	8.7	7.7-
4	1	11	14.9	13.5
3	1	11	10.9	8.4-
1	1	11	32.2	32.6
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-4	1	11	11.4	9.2-
-7	1	11	11.5	12.9-
-12	1	11	11.1	10.5-
-13	1	11	10.0	7.2-
-14	1	11	6.6	5.5-
12	1	12	5.7	7.1
9	1	12	4.7	4.1-
8	1	12	7.3	8.6
6	1	12	6.2	6.7
4	1	12	7.3	6.4
3	1	12	20.6	22.4
2	1	12	17.2	15.8-
1	1	12	20.2	17.6
	1	12	13.4	11.8-
-1	1	12	9.0	7.8-
-2	1	12	18.1	18.2-
-5	1	12	10.1	11.4-
-8	1	12	5.0	6.5
-9	1	12	6.7	6.2
-10	1	12	5.1	5.2-
-13	1	12	9.1	6.8-
10	1	13	5.7	5.0-
4	1	13	5.5	6.0
3	1	13	8.0	6.5
2	1	13	8.1	8.5
	1	13	5.6	6.7
-1	1	13	7.4	6.7
-7	1	13	7.6	7.3
-4	1	14	7.0	7.6
-9	1	14	4.6	5.3
-10	1	14	5.7	6.8-
6	1	15	5.2	5.5
5	1	15	2.5	3.1
2	1	15	7.2	5.9-
-3	1	15	8.5	6.8-
-4	1	15	1.3	2.1
-5	1	15	9.1	8.8-
-6	1	15	7.6	6.5
-1	1	16	7.9	8.3-
-3	1	16	12.0	12.8-
18	2		4.0	5.5
17	2		4.7	4.5-
13	2		9.6	11.1
11	2		5.9	5.5
10	2		9.9	10.3
8	2		13.3	10.0-
7	2		7.4	5.4
6	2		12.0	13.5
5	2		18.6	15.3
4	2		13.4	10.5-
3	2		44.8	55.5
2	2		15.7	12.3-
1	2		7.2	5.7
	2		12.5	9.9
16	2	1	4.7	4.3-
15	2	1	7.3	8.8
14	2	1	4.0	3.6-
13	2	1	5.5	5.1
12	2	1	7.4	4.9-
11	2	1	11.6	10.7
10	2	1	14.1	10.0-
9	2	1	11.7	11.9
8	2	1	8.9	4.9-
7	2	1	4.0	4.6
6	2	1	8.2	10.8
5	2	1	30.3	30.5
2	2	1	33.1	45.8
1	2	1	8.2	8.3-
	2	1	5.4	6.4-
-1	2	1	8.0	4.9-
-2	2	1	3.0	1.7-
-3	2	1	10.4	6.3-
-4	2	1	4.2	3.8-
-5	2	1	26.7	24.9
-6	2	1	17.1	14.9-
-7	2	1	13.2	12.0
-8	2	1	7.8	7.8-
-9	2	1	8.3	6.1
-11	2	1	12.6	11.2-
-12	2	1	12.8	10.7-
-14	2	1	4.1	6.3
-16	2	1	6.9	8.0
16	2	2	8.0	8.2
14	2	2	6.8	5.5-
13	2	2	7.8	8.0
12	2	2	8.1	4.4-
11	2	2	7.4	6.3
10	2	2	19.4	19.7-
9	2	2	16.9	15.2-
8	2	2	4.4	1.2
6	2	2	4.5	4.5
5	2	2	5.6	7.3
4	2	2	27.0	27.2
3	2	2	9.9	10.1
2	2	2	4.5	2.5-
1	2	2	35.2	42.3
	2	2	15.9	11.8-
-3	2	2	19.5	18.4
-5	2	2	21.2	19.4
-6	2	2	18.6	15.2
-7	2	2	14.0	13.0
-9	2	2	8.4	6.5
-10	2	2	8.9	11.0-
-12	2	2	8.7	7.1-
-13	2	2	7.3	5.7-
-14	2	2	6.8	5.5
15	2	3	8.2	7.3-
11	2	3	16.9	17.9-
8	2	3	25.7	29.4
7	2	3	12.6	11.2
6	2	3	7.0	6.0
5	2	3	15.9	15.6
3	2	3	33.5	36.6
2	2	3	34.0	38.5-
1	2	3	4.7	3.0-
	2	3	16.5	14.2-
-1	2	3	13.0	9.6-
-2	2	3	16.4	14.9-
-3	2	3	13.9	11.5
-4	2	3	19.6	19.8
-5	2	3	8.6	9.2
-7	2	3	14.6	14.8
-9	2	3	9.6	8.3
-10	2	3	7.3	4.0
-11	2	3	6.2	3.9-
-12	2	3	12.3	11.3
-14	2	3	11.8	11.0
-15	2	3	11.9	12.8
11	2	4	3.2	2.5-
10	2	4	20.5	17.0
9	2	4	5.6	4.1
8	2	4	14.5	10.0
7	2	4	18.3	17.7-
6	2	4	7.3	3.2
5	2	4	8.3	5.8
3	2	4	15.4	15.8-
2	2	4	19.2	18.1-
1	2	4	13.0	8.9-
	2	4	7.2	6.3
-1	2	4	5.9	4.1-
-3	2	4	6.0	3.7
-4	2	4	7.9	6.2-
-5	2	4	7.2	6.8
-6	2	4	15.0	17.5-
-7	2	4	19.9	19.8
-8	2	4	11.3	7.7
-9	2	4	5.8	4.6
-12	2	4	17.6	17.4
-13	2	4	13.1	13.3
-14	2	4	2.3	1.5-
15	2	5	11.2	11.5
13	2	5	5.7	4.2-
12	2	5	11.5	7.9
11	2	5	11.1	11.4-
9	2	5	23.4	26.8-
7	2	5	17.4	15.8-
4	2	5	17.5	17.3-
3	2	5	6.3	7.1-
2	2	5	4.6	1.7
1	2	5	9.3	9.5-
	2	5	14.9	14.4
-1	2	5	19.6	23.0-
-3	2	5	4.2	3.1
-4	2	5	11.9	11.1
-5	2	5	15.1	15.0
-6	2	5	12.5	11.2
-7	2	5	19.5	19.5
-9	2	5	7.3	3.6-
-12	2	5	7.6	5.7-
-13	2	5	11.4	11.5-
-14	2	5	13.6	15.0-
14	2	6	13.8	16.2
13	2	6	11.4	13.7-
12	2	6	6.9	3.5
11	2	6	8.6	8.1-
10	2	6	9.5	6.7
9	2	6	7.8	8.6-
7	2	6	14.0	12.1
6	2	6	12.6	11.4-
5	2	6	6.6	3.4
4	2	6	13.0	11.8-
3	2	6	8.7	7.3-
1	2	6	21.7	27.4-
	2	6	15.3	16.1-
-1	2	6	4.5	4.4-
-2	2	6	6.8	4.7
-3	2	6	4.9	4.8-
-4	2	6	14.7	13.6
-5	2	6	7.9	5.2
-7	2	6	19.4	18.1-
-8	2	6	10.6	10.5
-9	2	6	19.9	22.0-
-11	2	6	10.8	10.5-
-12	2	6	10.0	8.7-
-14	2	6	6.2	5.0
-15	2	6	13.9	14.6
13	2	7	6.7	6.0
12	2	7	7.9	7.3-
10	2	7	5.5	4.3
9	2	7	4.5	2.8
8	2	7	8.8	6.8-
7	2	7	11.0	9.4
6	2	7	10.3	11.5
5	2	7	5.5	5.3-
4	2	7	5.0	4.8-
3	2	7	9.1	8.2-
1	2	7	9.8	8.9-
	2	7	6.4	4.9-
-1	2	7	16.3	15.9-
-2	2	7	15.7	14.8
-3	2	7	12.2	11.2-
-5	2	7	7.6	6.3-
-6	2	7	5.2	4.2
-7	2	7	19.6	21.5-
-8	2	7	9.9	7.9-
-10	2	7	14.9	11.6-
-11	2	7	5.8	2.9-
-12	2	7	5.9	5.8
-13	2	7	7.6	6.5
12	2	8	8.6	6.5-
10	2	8	8.3	5.3-
7	2	8	5.9	4.9
6	2	8	7.0	5.8-
4	2	8	8.0	8.5-
2	2	8	11.4	10.7
1	2	8	16.1	17.6-
	2	8	16.3	15.0
-1	2	8	5.0	2.8-
-2	2	8	20.5	25.6
-3	2	8	14.7	14.8
-6	2	8	9.2	6.8-
-8	2	8	21.5	24.0-
-9	2	8	8.3	6.6-
-11	2	8	11.4	13.5-
9	2	9	5.9	7.3
8	2	9	7.2	4.1-
7	2	9	8.7	7.5
6	2	9	13.1	11.8-
5	2	9	10.6	9.6
	2	9	16.3	16.5

Table 5 (*cont.*)

H	K	L	FOBS	FCAL
-1	2	9	18.6	21.8
[illegible]	2	9	3.6	2.1-
-4	2	9	12.1	12.5-
-6	2	9	9.4	6.5-
-7	2	9	8.8	9.9-
-9	2	9	14.0	16.3-
-10	2	9	9.1	9.3
10	2	10	5.2	3.7-
9	2	10	8.3	9.5
7	2	10	10.0	10.2
6	2	10	5.8	5.9
5	2	10	14.0	16.9
4	2	10	6.2	4.9
2	2	10	9.3	8.3
1	2	10	5.6	5.2
-1	2	10	7.9	7.0-
-2	2	10	19.1	22.9-
-4	2	10	6.2	3.0-
-5	2	10	10.1	7.5
-6	2	10	8.8	8.5-
-8	2	10	6.8	5.4
-9	2	10	8.0	7.9
-10	2	10	5.6	5.1
-11	2	10	4.7	3.0
-12	2	10	4.5	3.9
8	2	11	4.6	4.4
7	2	11	5.5	3.3
5	2	11	8.4	6.6-
4	2	11	11.7	12.8
3	2	11	14.4	17.1-
	2	11	8.3	4.5-
-1	2	11	7.3	8.7
-3	2	11	20.3	26.5
-5	2	11	6.1	6.1
-6	2	11	6.0	5.7-
-7	2	11	5.9	6.9
-8	2	11	5.4	5.0
-11	2	11	5.9	5.6
5	2	12	9.8	11.1-
3	2	12	6.5	5.8
2	2	12	11.2	13.9-
1	2	12	8.0	9.5
-1	2	12	10.3	11.7
-2	2	12	5.6	4.3-
-3	2	12	5.2	4.3
-5	2	12	5.8	5.7-
-6	2	12	8.0	7.3
4	2	13	8.9	12.4-
1	2	13	7.7	8.5-
	2	13	5.5	4.3-
-3	2	13	5.4	5.7-
-5	2	13	4.0	4.4-
2	2	14	7.6	10.5
-3	2	14	4.4	3.5-
-4	2	14	5.2	7.9-
13	3		5.6	4.2
10	3		4.5	2.0-
9	3		8.2	7.0
8	3		9.8	8.8-
5	3		4.8	4.4-
4	3		20.9	19.6-
3	3		11.3	12.1
2	3		11.0	12.3-
1	3		8.0	10.4
15	3	1	5.3	6.2-
12	3	1	5.8	5.6
10	3	1	10.7	11.4-
9	3	1	13.3	10.9
8	3	1	9.4	7.2
7	3	1	5.6	3.1
6	3	1	11.3	10.6-
5	3	1	15.1	13.6
4	3	1	11.0	10.5-
3	3	1	6.7	5.3-
2	3	1	6.0	4.0
1	3	1	3.7	1.6
	3	1	6.5	6.8-
-2	3	1	5.4	3.5-
-3	3	1	5.2	3.3-
-4	3	1	8.4	8.6-
-6	3	1	8.3	8.1-
-7	3	1	8.0	8.1
-9	3	1	5.5	2.9
-10	3	1	8.5	7.4
-11	3	1	9.1	9.6
-12	3	1	5.4	5.0
-13	3	1	4.6	4.0
15	3	2	4.7	4.8-
13	3	2	7.2	5.7
12	3	2	9.1	9.7-
11	3	2	9.3	7.1
9	3	2	8.4	6.9
8	3	2	6.9	3.4
7	3	2	13.2	15.7-
6	3	2	13.0	14.4-
5	3	2	22.0	25.9-
4	3	2	21.5	22.0
3	3	2	21.0	22.8-
2	3	2	9.5	9.9-
1	3	2	10.3	12.3
	3	2	2.9	.1-
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-4	3	2	13.1	13.1-
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15	3	3	4.2	4.3
14	3	3	4.9	5.4
13	3	3	5.7	4.3
10	3	3	6.9	3.8
9	3	3	18.0	18.9-
8	3	3	14.6	17.8-
7	3	3	24.2	29.1-
6	3	3	8.4	3.7
5	3	3	14.2	11.9-
4	3	3	7.5	9.6-
3	3	3	13.9	9.6
2	3	3	13.1	13.8-
1	3	3	18.7	16.5
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-3	3	3	8.9	9.3-
-4	3	3	6.2	5.4
-5	3	3	12.2	11.8-
-6	3	3	8.3	4.3
-7	3	3	12.6	14.4
-10	3	3	8.9	11.0-
-13	3	3	11.7	12.4-
-14	3	3	12.0	14.0-
-15	3	3	6.9	7.0-
14	3	4	3.8	.8
11	3	4	5.6	5.7-
8	3	4	10.6	8.8
6	3	4	15.5	13.5
5	3	4	4.1	4.1
4	3	4	9.2	6.9-
3	3	4	12.6	9.8
2	3	4	10.1	8.7
	3	4	13.8	15.1-
-1	3	4	12.0	14.0-
-2	3	4	4.2	2.2-
-3	3	4	13.8	15.3-
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14	3	5	4.6	4.2-
10	3	5	6.8	8.4
9	3	5	6.2	3.2-
8	3	5	15.2	13.8
7	3	5	6.2	5.2-
6	3	5	9.3	9.6
5	3	5	5.9	5.0-
4	3	5	7.8	7.7
3	3	5	8.3	7.5
2	3	5	5.3	5.1
1	3	5	8.6	8.1-
	3	5	4.9	4.8
-2	3	5	7.5	6.6
-3	3	5	8.9	9.3-
-4	3	5	9.6	9.4-
-5	3	5	9.5	9.0-
-6	3	5	11.9	9.5-
-7	3	5	7.0	5.9-
-8	3	5	6.2	6.7-
-11	3	5	5.3	4.1-
-13	3	5	5.8	6.0
-14	3	5	9.9	9.6
13	3	6	5.0	3.7-
10	3	6	5.8	4.7
9	3	6	8.6	7.6-
6	3	6	6.3	4.6-
5	3	6	6.1	6.0
4	3	6	5.7	4.5-
3	3	6	5.8	5.8
2	3	6	9.2	11.6
-2	3	6	8.1	8.3
-3	3	6	9.9	11.1-
-4	3	6	5.2	5.4
-5	3	6	5.3	3.4
-6	3	6	6.1	6.2
-8	3	6	12.1	10.7
-14	3	6	8.0	7.5-
11	3	7	4.6	4.2
9	3	7	10.0	10.5
8	3	7	3.2	2.0-
7	3	7	7.9	7.5
6	3	7	2.6	2.3-
5	3	7	7.2	6.9
3	3	7	10.9	14.4
2	3	7	7.1	4.5-
1	3	7	8.6	8.6
	3	7	5.3	4.3-
-1	3	7	5.7	3.8-
-2	3	7	9.0	9.5
-3	3	7	9.9	9.2-
-4	3	7	6.1	2.6-
-5	3	7	9.2	8.0-
-6	3	7	15.7	17.5
-7	3	7	8.9	7.9-
-8	3	7	6.2	6.7
-9	3	7	6.6	5.0
5	3	8	12.8	16.5
3	3	8	5.9	6.9
2	3	8	6.2	4.5-
1	3	8	4.8	2.2-
	3	8	11.2	11.9
-1	3	8	14.1	15.5-
-2	3	8	10.1	11.9-
-3	3	8	9.2	8.7-
-5	3	8	8.4	7.2
-7	3	8	16.7	21.9
-8	3	8	7.4	9.6-
-9	3	8	9.9	10.6
-10	3	8	6.0	6.7
7	3	9	5.0	3.8
6	3	9	8.3	8.8-
4	3	9	9.1	8.3-
3	3	9	8.8	8.8-
1	3	9	7.7	7.2-
-1	3	9	6.2	7.2-
-3	3	9	17.6	21.4
-4	3	9	11.7	15.0
-5	3	9	17.9	21.7
-7	3	9	9.2	12.6
-8	3	9	7.7	9.3
-9	3	9	5.2	4.6-
6	3	10	8.3	10.1-
4	3	10	6.8	8.5-
-1	3	10	6.1	7.2
-2	3	10	6.0	6.4
-3	3	10	7.7	7.5
-4	3	10	7.3	8.1-
4	3	11	8.3	8.5
3	3	11	4.8	7.4-
-2	3	11	7.7	11.5-
-4	3	11	7.9	11.4-
-8	3	11	4.3	6.2-
5	3	12	9.1	12.6-
-3	3	12	5.0	6.3

intermolecular distances less than 4·0 Å are listed in Table 3. The equation of the best plane through all the atoms in the molecule, calculated by the method of Schomaker, Waser, Marsh & Bergman (1959), is

$$0{\cdot}2599X'+0{\cdot}9512Y+0{\cdot}1667Z'-1{\cdot}9283=0$$

where X', Y, Z' (in Å) are referred to orthogonal axes a, b and c'. The deviations of the atoms from this plane, given in column (i) of Table 4, show that the molecule is non-planar.

The equation of the plane through the carbon atoms of the benzene ring is

$$0{\cdot}3101X'+0{\cdot}9313Y+0{\cdot}1912Z'-2{\cdot}2972=0\,.$$

The plane through the carboxyl group and C(1) of the benzene ring is

$$-0{\cdot}4743X'+0{\cdot}8466Y-0{\cdot}2417Z'+3{\cdot}6328=0\,.$$

The displacements of atoms from these planes are given in Table 4.

The angle between the plane of the carboxyl group and the plane of the benzene ring is 53°31′. Calculated and observed structure factors are given in Table 5.

Discussion

The bond lengths and angles in the benzene ring show a very slight variation of hexagonal symmetry (Fig. 2 and Table 2). The average value for the distance C–C in the ring is 1·398 Å, in good agreement with the values for the C–C distance in aromatic compounds of 1·395 Å found in the literature (*International Tables for X-ray Crystallography*, 1962).

The bond lengths, C(2)–C(7) (1·519 Å) and C(6)–C(9) (1·531 Å) are a little different. However this difference is not significant in terms of the calculated standard deviations.

The distance C(1)–C(8) is 1·525 Å, slightly higher than the value 1·479 Å for the sp^2 state of hybridization. Probably this is due to intramolecular overcrowding. Ferguson & Sim (1961) found a distance of 1·521 Å for C(aromatic)–C(carboxylic) in *o*-chlorobenzoic acid, which they interpreted in terms of intramolecular overcrowding.

The fact that the C(8)–O(1) bond (1·226 Å) is shorter than C(8)–O(2) (1·276 Å) supports the conclusion that the hydrogen atom is attached to O(2) and not to O(1).

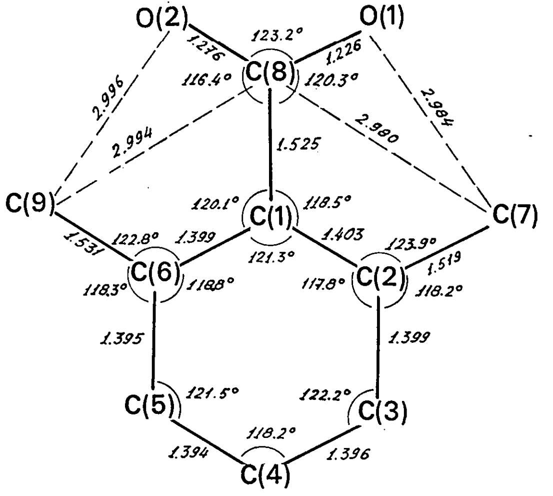

Fig. 2. Bond lengths and angles in the 2,6-dimethylbenzoic acid molecule.

This conclusion is also in agreement with the fact that the angle O(2)–C(8)–C(1) (116·4°) is smaller than O(1)–C(8)–C(1) (120·3°). The angle O(1)–C(8)–O(2) is 123·2°.

The molecule is fundamentaly plane except for the oxygen atoms. Column (ii) of Table 4 shows the deviation of each atom from the best plane of the six ring atoms as determined by least squares when all the ring atoms were weighted equally. The extra-ring atoms C(7), C(8), C(9) are staggered slightly above and below the best ring plane, and are probably indicative of an overcrowded molecular structure. The strain in a planar model for the molecule is relieved by a rotation of the carboxyl group around the exocyclic C(1)–C(8) bond, so that the angle between the planes of the benzene ring and the carboxyl group is 53°31′. This angle is in good agreement with the value of 60° calculated from ultraviolet spectra and it is greater than the values found in other benzoic acids. This angle of tilt is 13°7′ in *o*-chlorobenzoic acid (Ferguson & Sim, 1962), 18°3′ in *o*-bromobenzoic acid (Ferguson & Sim, 1961) and 6·7° in *o*-fluorobenzoic acid (Krausse & Dunken, 1966; Ferguson & Islam, 1966). The twist of the carboxyl group is caused by the methyl groups in the *ortho* position. The oxygen atoms produce also some distortion in the deviation of the methyl groups from the plane. It is probable that such displacements of the methyl groups correspond to the methyl C–O and methyl C=O interactions. The exocyclic valence angles C(1)–C(6)–C(9) and C(1)–C(2)–C(7) are increased from the normal value of 120° to 122·8 and 123·9° respectively, while the adjacent angles C(5)–C(6)–C(9) and C(3)–C(2)–C(7) are decreased to 118·3 and 118·2° respectively. The intermolecular distances C(9)···O(2) (2·996 Å), C(7)···O(1) (2·984 Å) and C(9)···C(8) (2·994 Å), C(7)···C(8) (2·980 Å) are also shorter than the sums of van der Waals radii [3·40 Å and 4·00 Å respectively; Pauling (1960)] (Table 2 and Fig. 2).

As expected, the structure of 2,6-dimethylbenzoic acid shows the frequently observed feature of dimerization of acid molecules through hydrogen bonding between carboxyl groups about a symmetry centre. The distance O(1)···O(2) is 2·673 Å, a normal value for a hydrogen bond. Intermolecular distances have been calculated to a limit of 4·0 Å (Table 3), and the usual van der Waals distances occur. Fig. 3 shows the packing of the molecules on the (010) projection. The molecules form chains along [221], in which the dimers are joined by van der Waals forces across the line C(4)··· C(4) withdrawn $\frac{1}{2}$ in the **b** direction, giving a more compact packing in that direction.

The numerical calculations were carried out on the 7070 IBM computer (Centro de Cálculo Electrónico del C.S.I.C., Spain) using programs of the Crystallographic Laboratory of Pittsburgh University. We wish to express our thanks to Prof. G. A. Jeffrey for allowing us to use these programs. We should also like to express our appreciation to Dr R. K. MacMullan, whose assistance was invaluable in writing a Fourier program for our computer. Part of this work forms part of the Ph.D. thesis of one of us (R.A.).

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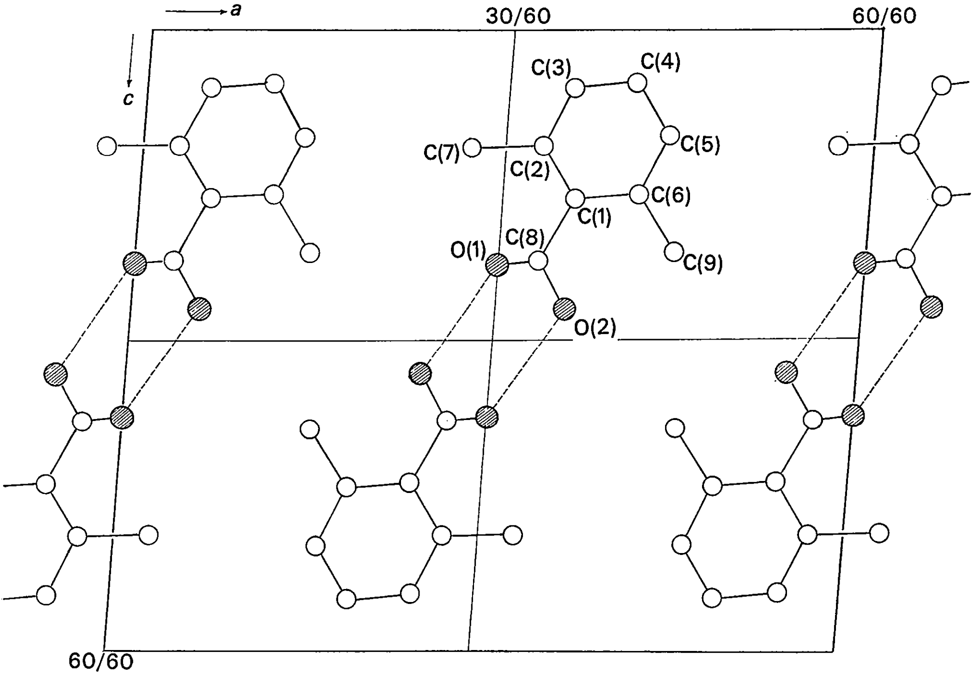

Fig. 3. 2,6-Dimethylbenzoic acid. Projection of the structure along the *b* axis.

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Structure Cristalline et Moléculaire de la Naphtohydroquinone-1,4

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The structure of naphthalene-1,4-diol was solved with the use of data from the three projections. Full-matrix least-squares refinement resulted in a final R of 0,08. The crystals are orthorombic *Pnma* with four molecules in a cell of dimensions $a=12{\cdot}67$, $b=12{\cdot}95$, $c=4{\cdot}80$ Å. The phenyl group is exactly planar but the oxygen atoms are displaced from the plane. The molecules overlap each other with an average interplanar spacing of 3·48 Å. Four hydrogen bonds per molecule have been found and their geometry is discussed. The stereochemistry of the molecule is compared with that of naphthalene.

L'étude des diol, amino-alcool et diamine naphtaléniques que nous avous entreprise complète celle des dérivés de la naphtoquinone-α et de l'hydroxycoumarine, nombre d'entre eux ayant une activité vitaminique ou antivitaminique K.

Ces études qui fournissent des comparaisons utiles entre les structures moléculaires et cristallines des composés actifs, antagonistes ou indifférents, sont menées afin de préciser sur l'exemple de ces vitamines, la notion générale d'analogie structurale utilisée par les pharmacodynamiciens.

Données expérimentales

La cristallisation de la naphtohydroquinone-α doit être conduite avec précaution. Ce produit relativement instable doit être conservé à l'abri de l'air et de la lumière; en solution, il s'oxyde et passe à l'état de naphtoquinone: nous avons dû renoncer aux essais de cristallisation par les voies classiques. Nous l'avons préparé en laboratoire selon la méthode de Fieser (1939) et cristallisé, par lent refroidissement de la solution mère, en prismes transparents de symétrie orthorhombique, allongés dans la direction **c**. Point de fusion $F=176\,^{\circ}\mathrm{C}$.

Données cristallographiques

Paramètres de la maille $a=12{,}67\pm0{,}02$ Å
$b=12{,}95\pm0{,}02$
$c=\ \ 4{,}80\pm0{,}01$
$V=788$ Å^3
Densité calculée: $d=1{,}349$ g.cm^{-3} pour 4 molécules dans la maille.
Densité mesurée: 1,35
$F(000)=336$

Les extinctions systématiques sont celles des groupes orthorhombiques $Pn2_1a$ ou $Pnma$ à 4 molécules par maille.

Les intensités des 450 taches de diffraction observables sur rétigrammes de De Jong avec la radiation Cu $K\alpha$ ont été mesurées visuellement par comparaison avec une échelle étalon. Les corrections géométrique et de polarisation ont été appliquées de la façon habituelle; il n'a pas été tenu compte de l'absorption, la section des cristaux utilisés n'excèdant pas 0,05 mm².

Détermination de la structure

L'ambiguité de groupe

Les tests de Wilson (1949) et de Howells, Phillips & Rogers (1950) indiquent une structure centrée (Fig. 1); la structure appartient au groupe *Pnma* avec 4 molécules par maille: les molécules sont donc placées sur les plans m ou perpendiculaires à ces plans. Cela ne préjuge en rien de la position des atomes d'hydrogène des 2 hydroxyles qui pourraient ne pas être symétriques par rapport au plan m: dans ce cas la symétrie réelle de la structure serait $Pn2_1a$.

Analyse de la fonction de Patterson

L'analyse a pu être developpée uniquement à partir des projections de la fonction de Patterson (obtenue au photosommateur harmonique) dans le groupe spatial *Pnma*.