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The Crystal Structure of 2,4,6-Trimethylbenzoic Acid

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Crystals of 2,4,6-trimethylbenzoic acid are monoclinic with space group $C2/c$ and have eight molecules in the unit cell. The structure has been determined by Patterson and trial and error methods and refined by Fourier and three-dimensional differential syntheses. The benzene ring is planar, and C–C distances average 1·391 Å; the carboxyl group however is twisted 48°29′ from this plane. All intermolecular contacts correspond to normal van der Waals interactions.

Introduction

The study of the structure of 2,4,6-trimethylbenzoic acid has been carried out in an attempt to determine the characteristics of the interactions between the methyl groups and the carboxyl group in this molecule.

Similar studies on this kind of interaction in other organic molecules have been reported by several authors: Ferguson & Sim (1961, 1962) on *o*-bromobenzoic acid, and *o*-chlorobenzoic acid, and Brown & Marsh (1963) on 2-amino-3-methylbenzoic acid, found similar values for the angle between the plane of the benzene ring and the plane of the carboxyl group. Anca, Martínez-Carrera & García-Blanco (1967) found a much larger tilt in 2,6-dimethylbenzoic acid, which corresponds to a compound bisubstituted in the *ortho* position relative to the carboxyl group. Lai & Marsh (1967) found a much smaller angle in *p*-aminobenzoic acid. The present study shows that in this respect 2,4,6-trimethylbenzoic acid posseses the properties of both *ortho* and *para* substituted compounds.

Experimental

Crystals of 2,4,6-trimethylbenzoic acid were readily grown from solution in ethanol. A prismatic needle of length 0·30 mm and 0·10 × 0·15 mm section was used for collection about the *b* axis, and a tabular crystal of 0·20 × 0·25 mm for collection about the *a* axis. The crystal data, obtained from measurements on zero level Weissenberg photographs about the two axes, are:

$a = 15{\cdot}21 \pm 0{\cdot}01$ Å
$b = 7{\cdot}02 \pm 0{\cdot}01$
$c = 17{\cdot}54 \pm 0{\cdot}01$
$\beta = 90°43'$
$D_m = 1{\cdot}16$ g.cm^{-3}, $D_x = 1{\cdot}156$ g.cm^{-3}, $Z = 8$

Systematic absences are: hkl with $h+k \neq 2n$, $h0l$ with $l \neq 2n$, corresponding to two possible space groups, $C2/c$ and Cc; the first space group was confirmed by solution of the structure.

X-ray intensities were collected from multiple-film equi-inclination Weissenberg photographs with Cu $K\alpha$ radiation. Eight layers recorded by rotation about **b** and five layers recorded by rotation about **a** were measured photometrically. Copper radiation allows a maximum of 1217 unique reflexions, representing 66% of the possible observable number. Unobserved reflexions were included by taking one half of the minimum observable intensity.

Data from the two axes were corrected for Lorentz and polarization factors and those of the non-zero layers for the spot extension factor also. No correction for absorption was made.

The data were reduced to structure amplitudes in the usual way, and placed on the same relative scale by means of a comparison of common reflexions on different films. Observed and calculated structure factors are given in Table 1.

Determination of the structure

Because the molecule was presumed to be planar and centrosymmetric, as is the case in other analogous acids, and because there are just eight molecules in the unit cell, it seemed likely that the space group was the centrosymmetric one, $C2/c$, rather than Cc. Accordingly the molecules were centred either at (000) or at $(\frac{1}{4}\frac{1}{4}0)$, these being the two unique centres of symmetry in $C2/c$.

The positions and orientations of the molecules were determined by computing the structure factors of seven $h00$, four $0k0$ and eleven $00l$ reflexions as a function of a rotation matrix, and also by interpretation of a sharpened three-dimensional Patterson function.

The $F(hkl)^2$ were multiplied by the factor

$$(1/f)\exp(2B\sin^2\theta/\lambda^2)\,(2\sin\theta/\lambda)^4\exp[-(4{\cdot}4\sin\theta/\lambda)^2]$$

(Donohue & Trueblood, 1952; Brown & Marsh, 1963).

In this way a set of x,y,z coordinates for the heavy atoms was obtained. Structure factors were calculated

Table 1. *Observed and calculated structure factors*

Unobserved reflexions are marked with an asterisk

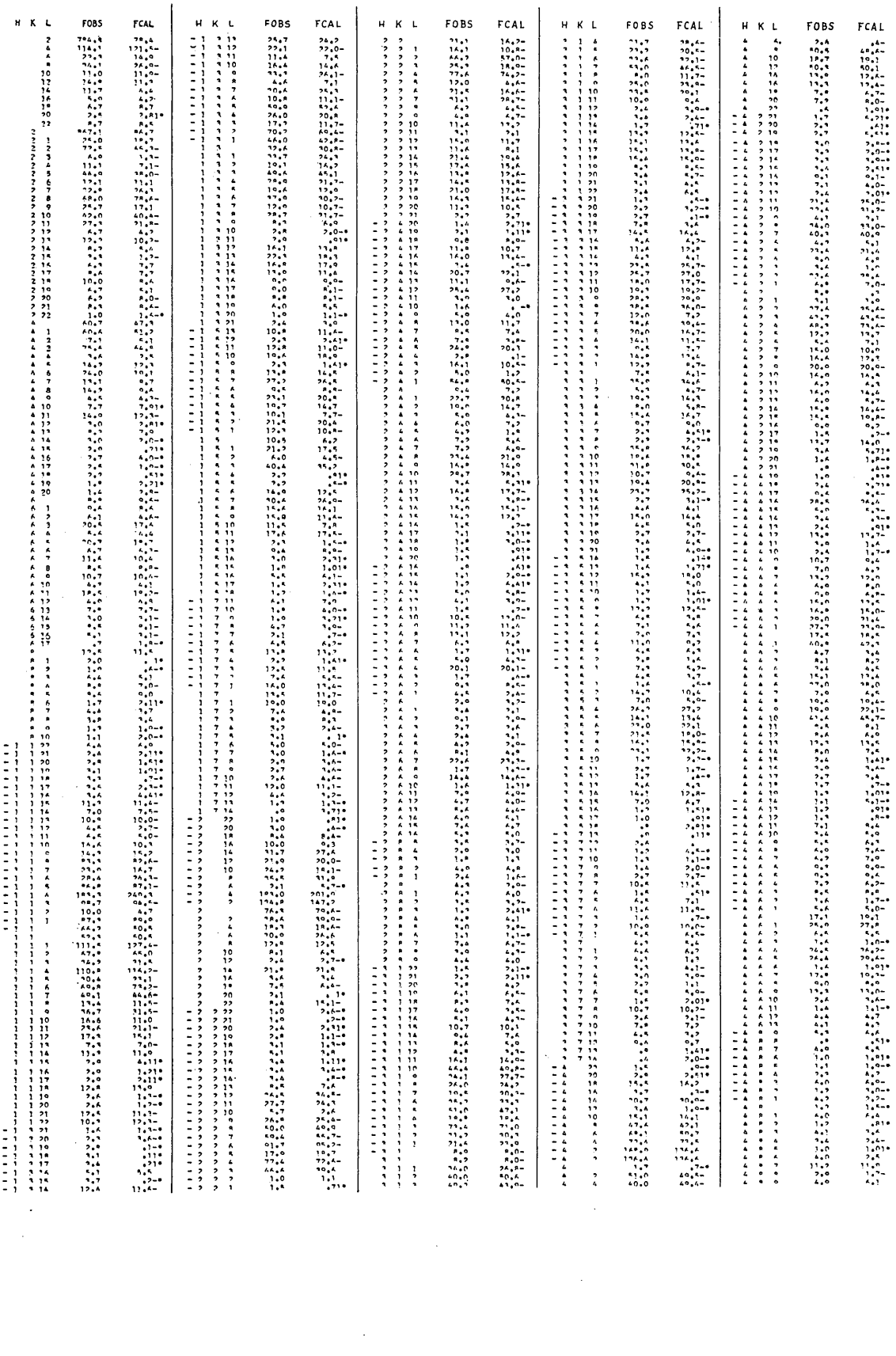
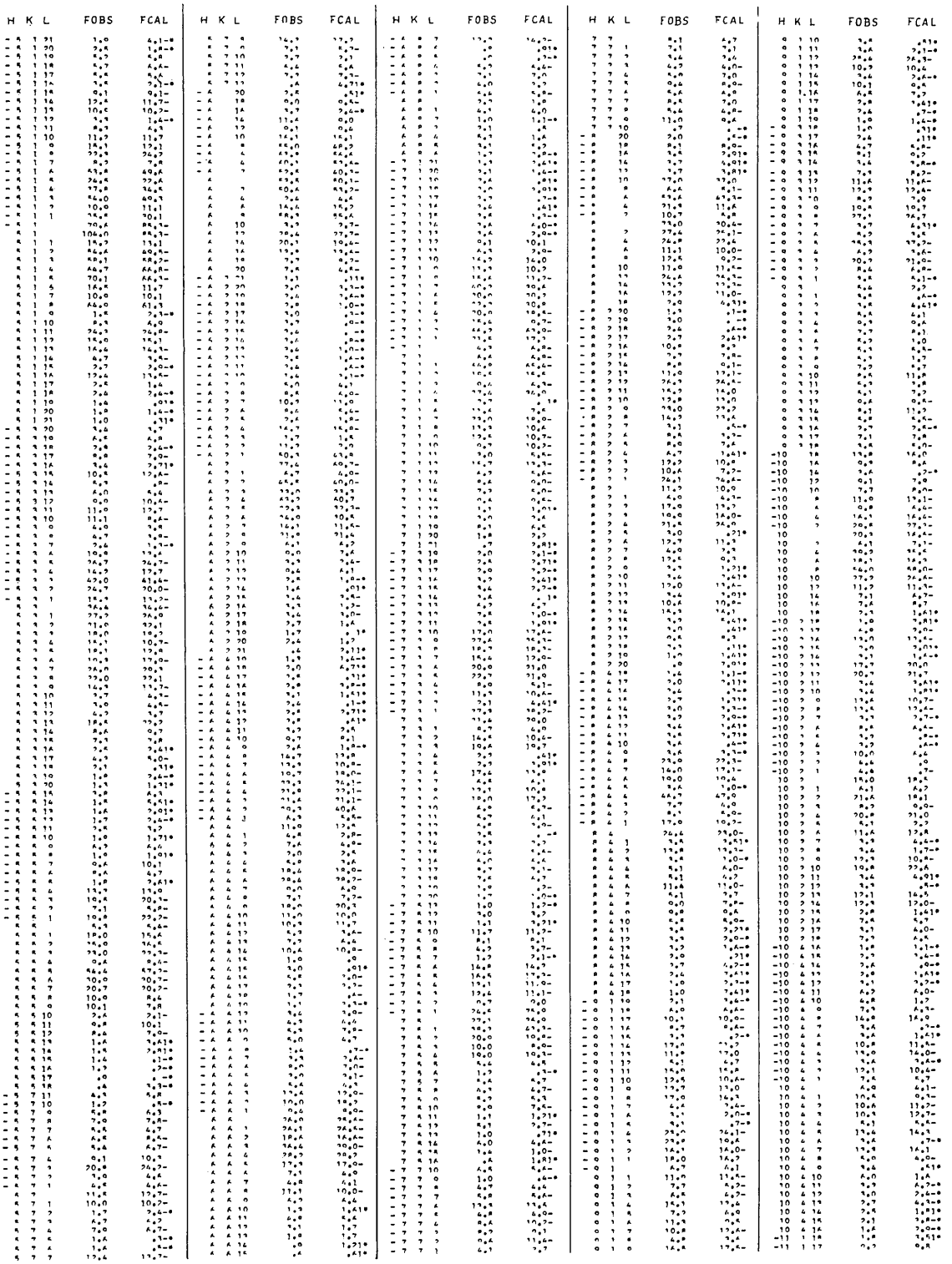


Table 1 (*cont.*)



for the model derived from these coordinates. The reliability index, defined in the usual way, amounted to 0·58.

Two subsequent three-dimensional Fourier syntheses were computed using only the terms with sin $\theta < 0{\cdot}8$ in the first Fourier synthesis and with all the observed

Table 1 (*cont.*)

H	K	L	FOBS	FCAL
-11	1	16	10.7	11.7
-11	1	15	6.0	6.6
-11	1	14	5.7	5.7-
-11	1	13	3.3	.5-*
-11	1	12	7.3	7.8-
-11	1	11	3.5	.8-*
-11	1	10	3.6	1.1-*
-11	1	9	3.6	1.81*
-11	1	8	3.6	4.8-*
-11	1	7	6.9	6.8
-11	1	6	10.8	8.0-
-11	1	5	6.7	6.7
-11	1	4	15.6	12.3-
-11	1	3	11.7	9.5
-11	1	2	3.3	7.4-*
-11	1	1	3.3	2.01*
-11	1		20.7	33.8
11	1	1	20.3	18.6
11	1	2	20.5	20.6
11	1	3	6.2	6.8-
11	1	4	16.4	18.0-
11	1	5	25.1	26.9-
11	1	6	8.5	10.6
11	1	7	3.3	.5-*
11	1	8	23.6	25.1-
11	1	9	22.1	21.6
11	1	10	26.0	26.9-
11	1	11	9.3	9.7
11	1	12	8.6	9.5
11	1	13	3.3	.8-*
11	1	14	5.8	5.6
11	1	15	2.9	.91*
11	1	16	2.6	.71*
11	1	17	2.2	2.01*
11	1	18	1.6	3.41*
-11	3	17	1.6	1.01*
-11	3	16	2.2	.6-*
-11	3	15	6.2	6.4-
-11	3	14	2.9	.21*
-11	3	13	3.1	2.01*
-11	3	12	6.7	7.5
-11	3	11	3.5	5.21*
-11	3	10	3.6	.91*
-11	3	9	9.3	8.8-
-11	3	8	7.2	7.5-
-11	3	7	7.6	7.3-
-11	3	6	3.8	1.41*
-11	3	5	7.2	7.9-
-11	3	4	9.9	11.1
-11	3	3	3.7	2.5-*
-11	3	2	7.5	3.6
-11	3	1	9.2	10.6
11	3		9.2	8.1
11	3	1	5.3	5.8
11	3	2	3.7	.11*
11	3	3	3.7	3.31*
11	3	4	3.8	6.6-*
11	3	5	3.8	1.51*
11	3	6	15.4	18.9
11	3	7	5.9	5.3
11	3	8	5.3	6.9
11	3	9	5.7	4.6-
11	3	10	3.6	.5-*
11	3	11	10.5	11.9-
11	3	12	3.3	.1-*
11	3	13	3.0	.2-*
11	3	14	2.8	3.6-*
11	3	15	2.4	4.51*
11	3	16	2.0	1.91*
11	3	17	1.2	5.5-*
-12		16	9.3	5.2-
-12		14	3.2	2.0-*
-12		12	3.6	2.0-*
-12		10	3.7	.41*
-12		8	9.8	9.2-
-12		6	9.5	11.9-
-12		4	7.8	4.3
-12		2	10.1	7.8-
12			7.7	6.6
12		2	41.8	36.1
12		4	46.2	45.5-
12		6	50.7	53.3-
12		8	3.8	1.21*
12		10	3.7	.21*
12		12	3.5	.1-*
12		14	3.1	3.61*
12		16	2.6	1.61*
-12	2	17	1.5	5.11*
-12	2	16	2.0	4.51*
-12	2	15	2.4	4.51*
-12	2	14	2.6	1.71*

H	K	L	FOBS	FCAL
-12	2	13	2.9	2.8-*
-12	2	12	3.0	5.0-*
-12	2	11	3.2	1.3-*
-12	2	10	3.3	1.11*
-12	2	9	3.4	1.41*
-12	2	8	3.4	1.5-*
-12	2	7	10.1	7.5
-12	2	6	3.4	1.31*
-12	2	5	3.4	1.2-*
-12	2	4	26.9	27.7
-12	2	3	19.5	20.5-
-12	2	2	11.8	9.8
-12	2	1	4.8	1.2
12	2		11.9	11.9-
12	2	1	11.6	13.2-
12	2	2	19.1	19.3
12	2	3	3.4	.7-*
12	2	4	7.8	6.7
12	2	5	3.4	.4-*
12	2	6	4.0	4.8
12	2	7	3.4	.4-*
12	2	8	5.7	6.2
12	2	9	8.1	8.7
12	2	10	7.7	7.3-
12	2	11	4.9	4.6
12	2	12	4.3	3.1
12	2	13	6.7	4.7-
12	2	14	10.8	10.1
12	2	15	2.2	2.91*
12	2	16	4.0	4.1
12	2	17	1.1	3.41*
-12	4	14	1.9	.5-*
-12	4	13	2.2	.81*
-12	4	12	2.5	.9-*
-12	4	11	2.7	1.41*
-12	4	10	2.9	6.11*
-12	4	9	6.0	6.6-
-12	4	8	5.9	6.2
-12	4	7	3.3	2.0-*
-12	4	6	3.4	3.8-*
-12	4	5	8.5	7.5
-12	4	4	3.5	3.7-*
-12	4	3	3.5	1.11*
-12	4	2	11.6	9.7-
-12	4	1	6.2	4.1
12	4		11.8	13.1-
12	4	1	3.5	2.11*
12	4	2	3.5	1.11*
12	4	3	13.8	16.1
12	4	4	5.4	4.4-
12	4	5	4.0	3.8
12	4	6	5.2	2.3-
12	4	7	10.4	12.8-
12	4	8	3.2	1.11*
12	4	9	7.8	8.1-
12	4	10	2.9	.2-*
12	4	11	2.7	1.6-*
12	4	12	4.3	2.2-*
12	4	13	3.8	4.2-
12	4	14	1.6	2.9-*
-13	1	16	1.9	3.3-*
-13	1	15	2.3	1.1-*
-13	1	14	2.6	1.91*
-13	1	13	2.9	.51*
-13	1	12	3.1	1.6-*
-13	1	11	3.3	4.61*
-13	1	10	4.8	1.4-
-13	1	9	3.5	3.61*
-13	1	8	6.5	4.6
-13	1	7	3.6	1.5-*
-13	1	6	11.3	12.0-
-13	1	5	3.6	4.6-*
-13	1	4	3.6	1.51*
-13	1	3	12.7	10.8-
-13	1	2	26.6	26.8
-13	1	1	3.6	1.81*
-13	1		14.5	12.7-
13	1	1	21.9	21.0-
13	1	2	11.9	11.5-
13	1	3	3.6	2.6-*
13	1	4	3.6	1.71*
13	1	5	20.7	19.5
13	1	6	12.7	13.2-
13	1	7	11.8	10.8
13	1	8	3.5	1.2-*
13	1	9	3.4	1.5-*
13	1	10	3.3	5.01*
13	1	11	3.2	3.41*
13	1	12	3.0	2.91*
13	1	13	8.4	5.6
13	1	14	2.5	1.91*

H	K	L	FOBS	FCAL
13	1	15	5.0	4.0
13	1	16	2.8	3.3
-13	3	15	1.6	1.51*
-13	3	14	2.1	3.21*
-13	3	13	2.5	.91*
-13	3	12	2.7	1.0-*
-13	3	11	5.7	3.2
-13	3	10	3.2	.11*
-13	3	9	4.4	7.0-
-13	3	8	14.0	15.7
-13	3	7	16.8	15.9-
-13	3	6	3.6	2.71*
-13	3	5	5.9	5.8
-13	3	4	13.7	13.9-
-13	3	3	9.2	8.3
-13	3	2	3.7	.7-*
-13	3	1	7.5	7.5-
13	3		3.7	3.4-*
13	3	1	5.3	.9
13	3	2	4.3	8.5
13	3	3	6.0	6.3-
13	3	4	11.0	14.2
13	3	5	5.2	3.5-
13	3	6	3.6	1.61*
13	3	7	3.5	4.4-*
13	3	8	3.4	2.0-*
13	3	9	4.7	5.2-
13	3	10	3.1	.51*
13	3	11	2.9	1.81*
13	3	12	3.8	3.2
13	3	13	2.4	2.4-*
13	3	14	1.9	.21*
13	3	15	1.2	1.1-*
-14		14	2.4	2.11*
-14		12	3.0	1.81*
-14		10	12.7	14.4-
-14		8	9.7	8.1-
-14		6	8.4	8.4
-14		4	3.7	3.0-*
-14		2	8.4	6.8
14			8.6	7.3-
14		2	24.0	25.8-
14		4	3.7	3.0-*
14		6	3.7	.9-*
14		8	3.6	3.0-*
14		10	3.3	2.3-*
14		12	2.9	2.41*
14		14	2.3	2.61*
-14	2	15	1.3	2.51*
-14	2	14	1.9	1.1-*
-14	2	13	2.2	.6-*
-14	2	12	2.5	2.41*
-14	2	11	2.7	1.2-*
-14	2	10	4.1	2.7-
-14	2	9	3.0	.6-*
-14	2	8	6.0	5.5
-14	2	7	10.1	11.8-
-14	2	6	11.6	10.4
-14	2	5	5.5	6.5-
-14	2	4	14.0	13.8-
-14	2	3	13.9	14.7
-14	2	2	3.4	.61*
-14	2	1	8.1	8.3
14	2		18.8	19.3
14	2	1	5.5	4.5
14	2	2	10.8	7.8
14	2	3	4.8	3.4
14	2	4	3.3	1.41*
14	2	5	3.3	2.71*
14	2	7	3.2	4.21*
14	2	8	3.1	1.21*
14	2	9	3.0	.31*
14	2	10	2.8	2.21*
14	2	11	2.6	3.21*
14	2	12	5.9	3.6
14	2	13	2.1	3.61*
14	2	14	4.5	1.2-
14	2	15	.6	1.1-*
-14	4	12	8.7	11.6
-14	4	11	5.5	5.6-
-14	4	10	2.2	2.11*
-14	4	9	2.4	3.61*
-14	4	8	15.0	14.4-
-14	4	7	2.7	3.21*
-14	4	6	7.1	5.8-
-14	4	5	3.0	.71*
-14	4	4	3.0	3.5-*
-14	4	3	3.1	3.61*
-14	4	2	3.1	3.3-*
-14	4	1	3.1	1.9-*
14	4		3.1	.1-*

H	K	L	FOBS	FCAL
14	4	1	3.1	3.21*
14	4	2	3.1	2.11*
14	4	3	4.4	5.7-
14	4	4	3.0	1.81*
14	4	5	4.2	5.2-
14	4	6	2.8	.3-*
14	4	7	2.7	1.71*
14	4	8	2.5	2.0-*
14	4	9	2.3	3.8-*
14	4	10	2.1	2.3-*
14	4	11	1.9	1.6-*
14	4	12	1.9	.1*
-15	1	14	1.6	4.7-*
-15	1	13	2.1	4.01*
-15	1	12	2.4	1.4-*
-15	1	11	2.6	2.5-*
-15	1	10	2.8	.21*
-15	1	9	3.0	6.7-*
-15	1	8	4.0	4.0-
-15	1	7	4.6	2.3-
-15	1	6	3.3	8.81*
-15	1	5	6.8	3.7
-15	1	4	4.9	5.5
-15	1	3	4.0	7.5
-15	1	2	11.2	5.1-
-15	1	1	3.5	.61*
-15	1		3.5	.81*
15	1	1	11.5	8.5
15	1	2	3.5	2.9-*
15	1	3	5.3	6.6
15	1	4	3.4	4.3-*
15	1	5	3.3	2.81*
15	1	6	6.6	5.4-
15	1	7	6.1	6.0
15	1	8	4.4	1.3-
15	1	9	4.6	4.3
15	1	10	3.9	2.1
15	1	11	4.3	4.6
15	1	12	9.2	7.4
15	1	13	6.7	5.4
15	1	14	1.3	3.71*
-15	3	12	1.7	3.21*
-15	3	11	10.1	10.6-
-15	3	10	5.3	5.2
-15	3	9	2.6	. -*
-15	3	8	7.4	6.6-
-15	3	7	12.4	11.3
-15	3	6	5.9	6.5-
-15	3	5	3.2	.1*
-15	3	4	3.2	3.01*
-15	3	3	3.3	3.5-*
-15	3	2	8.6	6.9
-15	3	1	3.4	5.11*
15	3		6.1	7.1
15	3	1	3.3	2.8-*
15	3	2	3.3	.51*
15	3	3	3.3	1.11*
15	3	4	3.2	2.1-*
15	3	5	3.1	3.8-*
15	3	6	3.0	.1*
15	3	7	2.9	.8-*
15	3	8	2.7	2.21*
15	3	9	2.5	2.2-*
15	3	10	2.3	4.3-*
15	3	11	2.0	2.4-*
15	3	12	1.4	.7-*
-16		12	5.1	6.4-
-16		10	4.8	6.1
-16		8	7.7	6.6
-16		6	3.2	. -*
-16		4	3.4	1.3-*
-16		2	8.2	5.2-
-16			3.3	5.0-*
16		2	8.8	9.3-
16		4	7.7	6.3-
16		6	3.2	.4-*
16		8	8.0	5.4
16		10	2.5	4.51*
-16	2	12	1.3	2.01*
-16	2	11	1.8	1.3-*
-16	2	10	2.1	3.31*
-16	2	9	4.1	3.7-
-16	2	8	2.5	1.4-*
-16	2	7	4.4	3.3
-16	2	6	2.0	.2-
-16	2	5	2.8	6.11*
-16	2	4	2.9	7.51*
-16	2	3	2.9	1.3-*
-16	2	2	3.0	3.01*
-16	2	1	5.1	3.7-
16	2		3.0	.3-*

H	K	L	FOBS	FCAL
16	2	1	3.0	.61*
16	2	2	3.0	.4-*
16	2	3	2.9	1.01*
16	2	4	2.8	1.0-*
16	2	5	2.8	1.41*
16	2	6	2.7	3.5-*
16	2	7	4.0	5.9
16	2	8	5.7	4.6
16	2	9	5.1	4.1
16	2	10	4.3	2.7
16	2	11	4.7	4.0-
16	2	12	1.9	1.9-
-16	4	8	1.5	1.41*
-16	4	7	1.8	.81*
-16	4	6	2.0	.91*
-16	4	5	2.1	1.31*
-16	4	4	2.2	1.7-*
-16	4	3	2.3	1.8-*
-16	4	2	2.4	1.5-*
-16	4	1	2.4	.5-*
16	4		2.4	.7-*
16	4	1	2.4	1.9-*
16	4	2	2.3	1.71*
16	4	3	2.3	.61*
16	4	4	2.2	1.71*
16	4	5	2.0	4.4-*
16	4	7	1.6	4.8-*
-17	1	10	1.8	1.71*
-17	1	9	2.1	2.31*
-17	1	8	2.3	3.31*
-17	1	7	2.5	.91*
-17	1	6	2.6	.8-*
-17	1	5	2.7	1.2-*
-17	1	4	2.8	2.0-*
-17	1	3	2.8	.11*
-17	1	2	2.9	2.0-*
-17	1	1	2.9	.1*
-17	1		4.2	2.4-
17	1	1	4.9	4.8
17	1	2	5.8	5.1-
17	1	3	8.1	7.3
17	1	4	2.8	.21*
17	1	5	2.7	2.41*
17	1	6	3.6	4.0
17	1	7	2.4	1.41*
17	1	8	5.0	5.7
17	1	9	5.5	5.9
17	1	10	4.3	4.6
-17	3	8	1.6	.3-*
-17	3	7	1.9	1.7-*
-17	3	6	2.1	.1-*
-17	3	5	2.2	.1-*
-17	3	4	2.4	.11*
-17	3	3	2.4	1.81*
-17	3	2	2.5	1.81*
-17	3	1	2.5	2.11*
17	3		2.5	.61*
17	3	1	3.6	3.7-
17	3	2	2.5	.3-*
17	3	3	2.4	. -*
17	3	4	5.0	4.4
17	3	5	2.2	.61*
17	3	6	2.0	2.9-*
17	3	7	1.7	3.3-*
17	3	8	1.3	5.0-*
-18		2	9.8	9.1-
18			2.7	2.5-*
18		2	7.9	4.3
-18	2	6	1.7	.71*
-18	2	5	1.8	2.31*
-18	2	4	2.0	2.01*
-18	2	3	2.0	.2-*
-18	2	2	2.1	.61*
-18	2	1	2.1	1.6-*
18	2		2.1	1.71*
18	2	1	2.1	1.41*
18	2	2	2.1	2.3-*
18	2	3	6.5	4.4
18	2	4	1.0	.1-*
18	2	5	5.2	4.9
18	2	6	5.3	3.6
-19	1	5	1.3	1.31*
-19	1	3	1.7	3.0-*
-19	1	2	1.7	.1-*
-19	1	1	1.8	5.9-*
-19	1		3.8	2.3-
19	1	1	6.3	2.1
19	1	2	1.7	1.81*
19	1	3	1.6	.4-*
19	1	4	1.4	3.01*
19	1	5	1.0	3.21*

reflexions in the second; the set of coordinates obtained gave R values of 0·38 and 0·31 respectively. The corresponding molecular set was considered to be centred at (000). The symmetry centre at ($\frac{1}{4}\frac{1}{4}0$) was rejected, since the R value obtained on this assumption was too high.

The last three-dimensional Fourier synthesis is shown in Fig. 1.

Further refinement was attained by means of four cycles of differential synthesis with individual isotropic temperature factors for all atoms, and of six cycles of differential synthesis with anisotropic temperature factors. When the shifts were less than the standard deviations the refinement was considered to be complete. The final R index was 0·129 for all observed reflexions, and 0·160 for all reflexions.

A three-dimensional difference Fourier synthesis based on the last cycle of differential synthesis was calculated in order to obtain the positions of the hydrogen atoms. No definite peaks were observed however; only some positive regions around the carbon atoms attached to hydrogen atoms were visible.

The coordinates of the hydrogen atoms attached to the benzene ring and those of the hydrogen bond were calculated on the assumption of their planarity with the benzene ring and with the C(1)–C(7)–O(1)–O(2) plane respectively.

A three-dimensional differential synthesis was calculated with the coordinates so obtained, with the result that the hydrogen positions had to be corrected slightly. The coordinates of the hydrogen atoms of the methyl group were allocated on the basis of the tetrahedral configuration of the methyl group, taking into account the positive regions of the difference synthesis.

The coordinates of the idealized hydrogen atoms appear in Table 2.

Table 2. *Idealized hydrogen coordinates*

H(1)	0·240	−0·037	−0·005 Å
H(2)	0·250	−0·143	0·086

Table 2 (*cont.*)

H(3)	0·331	−0·043	0·051
H(4)	0·380	0·215	0·130
H(5)	0·418	0·457	0·226
H(6)	0·401	0·604	0·178
H(7)	0·358	0·609	0·251
H(8)	0·200	0·620	0·200
H(9)	0·066	0·620	0·144
H(10)	0·024	0·459	0·104
H(11)	0·026	0·443	0·181
H(12)	0·040	−0·098	0·040

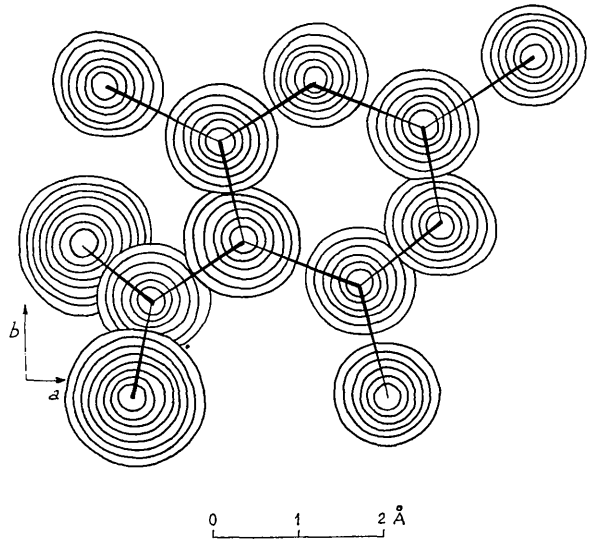


Fig. 1. 2,4,6-Trimethylbenzoic acid. A composite diagram of the final electron density function; the contours are drawn at equal intervals of 1·5 e.Å^{-3}, starting from 1·5 e.Å^{-3}.

The final structure factors, including the contribution of the hydrogen atoms, reduced R to 0·122 for all observed reflexions and to 0·155 for all reflexions.

Description of the structure

Final structure parameters and standard deviations are given in Table 3. Bond lengths and bond angles are shown in Fig. 2, and in Table 4, together with their standard deviations.

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

C(1)–C(2)	1·382 Å (0·006)	C(1)–C(2)–C(3)	120·1° (0·4)
C(2)–C(3)	1·398 (0·006)	C(2)–C(3)–C(4)	120·1 (0·4)
C(3)–C(4)	1·390 (0·006)	C(3)–C(4)–C(5)	119·2 (0·4)
C(4)–C(5)	1·380 (0·006)	C(4)–C(5)–C(6)	121·7 (0·4)
C(5)–C(6)	1·402 (0·006)	C(5)–C(6)–C(1)	118·3 (0·4)
C(6)–C(1)	1·395 (0·006)	C(6)–C(1)–C(2)	120·6 (0·4)
C(1)–C(7)	1·491 (0·006)	C(6)–C(1)–C(7)	118·4 (0·4)
C(2)–C(8)	1·547 (0·007)	C(2)–C(1)–C(7)	121·0 (0·4)
C(4)–C(9)	1·533 (0·009)	C(1)–C(2)–C(8)	123·3 (0·4)
C(6)–C(10)	1·538 (0·007)	C(3)–C(2)–C(8)	116·6 (0·4)
C(7)–O(1)	1·250 (0·006)	C(3)–C(4)–C(9)	119·9 (0·5)
C(7)–O(2)	1·286 (0·006)	C(5)–C(4)–C(9)	120·9 (0·5)

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)	0·1648 (0·0003)	0·2257 (0·0006)	0·0990 (0·0002)	4·52	2·77	2·73	−0·39	0·28	0·35
C(2)	0·2500 (0·0003)	0·1512 (0·0006)	0·0938 (0·0002)	4·67	2·94	3·35	0·16	−0·23	−0·03
C(3)	0·3185 (0·0003)	0·2483 (0·0007)	0·1331 (0·0002)	5·43	4·80	4·62	−0·06	−0·01	0·15
C(4)	0·3031 (0·0004)	0·4149 (0·0007)	0·1710 (0·0002)	5·26	4·40	3·33	−1·16	−0·35	−0·20
C(5)	0·2186 (0·0003)	0·4896 (0·0006)	0·1733 (0·0002)	5·36	3·32	3·23	−0·64	−0·60	0·76
C(6)	0·1482 (0·0003)	0·3982 (0·0006)	0·1371 (0·0002)	4·86	2·87	3·67	0·00	0·21	0·95
C(7)	0·0907 (0·0003)	0·1296 (0·0006)	0·0583 (0·0002)	3·82	2·82	3·60	−0·68	0·34	−0·22
C(8)	0·2725 (0·0004)	−0·0353 (0·0007)	0·0555 (0·0003)	7·55	3·09	5·64	0·82	−0·82	0·00
C(9)	0·3797 (0·0005)	0·5259 (0·0012)	0·2089 (0·0004)	6·88	8·76	7·66	−2·23	−2·65	−1·55
C(10)	0·0566 (0·0004)	0·4870 (0·0008)	0·1435 (0·0004)	7·08	5·74	8·17	0·66	−0·30	0·59
O(1)	0·0404 (0·0003)	0·2205 (0·0006)	0·0147 (0·0002)	5·61	4·04	7·09	−0·84	0·79	−1·91
O(2)	0·0823 (0·0003)	−0·0502 (0·0006)	0·0692 (0·0003)	8·34	3·65	7·90	−1·94	1·22	−2·84

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

Table 4 (*cont.*)

C(5)–C(6)–C(10)	117·5° (0·4)
C(1)–C(6)–C(10)	124·2 (0·4)
C(1)–C(7)–O(1)	121·0 (0·4)
C(1)–C(7)–O(2)	116·7 (0·4)
O(1)–C(7)–O(2)	122·2 (0·4)

Bond distances and angles in the benzene ring are normal (mean values 1·391 Å and 120°). The exocyclic C(2)–C(8), C(6)–C(10) and C(4)–C(9) bond lengths are 1·547, 1·538 and 1·533 Å respectively, also in good agreement with the value of 1·53 Å given for this type of bond.

The distance C(1)–C(7) of 1·491 Å is a little larger than the value of 1·479 Å reported for the sp^2 hybridization state. The same observation has been made in *o*-chlorobenzoic acid (Ferguson & Sim, 1961) and in 2,6-dimethylbenzoic acid (Anca *et al.*, 1967); in these acids the corresponding values are 1·521 and 1·525 Å respectively. This increase in bond length is a result of molecular overcrowding, and the fact that in the compound 2,4,6-trimethylbenzoic acid the corresponding increase is rather smaller may be due to the presence of the third methyl group in the *para* position.

The C(7)–O(1) bond of 1·250 Å is noticeably shorter than the C(7)–O(2) bond of 1·286 Å showing that the hydrogen atom is attached to O(2). That is also in good agreement with the value of the angle C(1)–C(7)–O(2) (116·7°), which is smaller than the angle C(1)–C(7)–O(1) (121·0°).

The equation of the least-squares plane through the carbon atoms of the benzene ring calculated according to Schomaker, Waser, March & Bergman (1959) with unit weight for all atoms is:

$$0{\cdot}1794X' + 0{\cdot}5094Y - 0{\cdot}8416Z' - 0{\cdot}2114 = 0 ,$$

where $X'YZ'$ (in Å), are referred to the orthogonal axes a, b and c'. The deviations in Å of the individual atoms from the plane are shown in column (ii) of Table 5.

Table 5. *Displacements* (Å) *of the atoms from the various planes*

(i) Plane through all atoms
(ii) Plane through benzene
(iii) Plane through atoms C(1), C(7), O(1), O(2)

	(i)	(ii)	(iii)
C(1)	−0·017	0·005	−0·002
C(2)	0·041	−0·007	−0·902
C(3)	0·061	0·001	−0·935
C(4)	0·008	0·007	−0·052
C(5)	−0·079	−0·010	0·860
C(6)	−0·080	0·003	0·897
C(7)	0·024	0·061	0·008
C(8)	0·126	0·008	−1·934
C(9)	0·049	0·036	−0·105
C(10)	−0·181	−0·017	1·954
O(1)	0·814	0·895	−0·003
O(2)	−0·766	−0·767	−0·003

The least-squares plane through all atoms in the molecule is:

$$0{\cdot}2201X' + 0{\cdot}4740Y - 0{\cdot}8526Z' - 0{\cdot}1630 = 0 ,$$

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

$$-0{\cdot}6104X' + 0{\cdot}1859Y + 0{\cdot}7700Z' + 0{\cdot}1142 = 0 .$$

The atoms C(8), C(9) and C(10), Table 5, show deviations above and below the best ring-plane which are larger than the deviations of the carbon atoms of the benzene ring. This fact is probably due to an overcrowded molecular structure. This molecular overcrowding is better manifested by the rotation of the carboxylic group about the exocyclic bond C(1)–C(7), the dihedral angle between the mean plane of the benzene ring and the mean plane of C(1), C(7), O(1) and O(2) being 48°29′.

The value found here, which is greater than that for other benzoic acids, is, however, smaller than the corresponding tilt of 53°31′, found by Anca *et al.* (1967) for 2,6-dimethylbenzoic acid. Such a decrease may be due to the presence of the methyl group in the *para* position.

There is a mutual interaction between the COOH group and the two CH_3 groups in *ortho* positions, resulting in a slight opening of the valence angles C(1)–C(6)–C(10) and C(1)–C(2)–C(8), which have values of 124·2 and 123·3°, and a corresponding shortening of the valence angles C(10)–C(6)–C(5) and C(8)–C(2)–C(3) which have values of 117·5 and 116·6°; all these angles differ from the normal value of 120°.

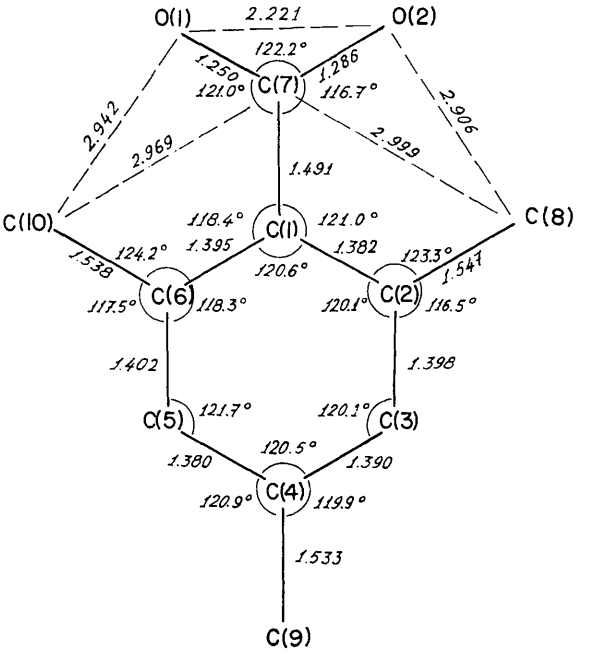


Fig. 2. Bond lengths and angles in the 2,4,6-trimethylbenzoic acid molecule.

The interatomic distances O(1)---C(10) (2·942 Å), C(8)---O(2) (2·906 Å), C(7)---C(8) (2·999 Å), and C(7)---C(10) (2·969 Å) are a little shorter than the sums of the corresponding van der Waals radii (3·40 and 4·00 Å respectively) (Pauling, 1960) which shows once more the effect of the molecular overcrowding.

Because the hydrogen atoms are not accurately placed, detailed discussion of distances and angles involving these atoms would be unjustified.

The structure, viewed along the *b* axis, is shown in Fig. 3, Molecules are held together by O–H---O hydrogen bonds forming chains along the [11$\bar{2}$] direction. These hydrogen bonds, which occur in pairs about centres of symmetry, have a length of 2·648 Å. Intermolecular distances are calculated to a limit of 4·00 Å and are shown in Table 6. Adjacent chains are held together only by van der Waals interactions, and bond lengths are normal.

All the calculations were performed on the 7070 IBM computer of the Centro de Cálculo Electronico del C.S.I.C. (Spain) with programs of the Crystallographic Laboratory of Pittsburgh University and of the Departamento de Rayos X del C.S.I.C. (Madrid, Spain). We should like to express our appreciation to Dr S. García-Blanco and to Dr S. Martínez-Carrera, whose assistance was invaluable for our work. This work forms part of the Ph. D. thesis of one of us (F. F.).

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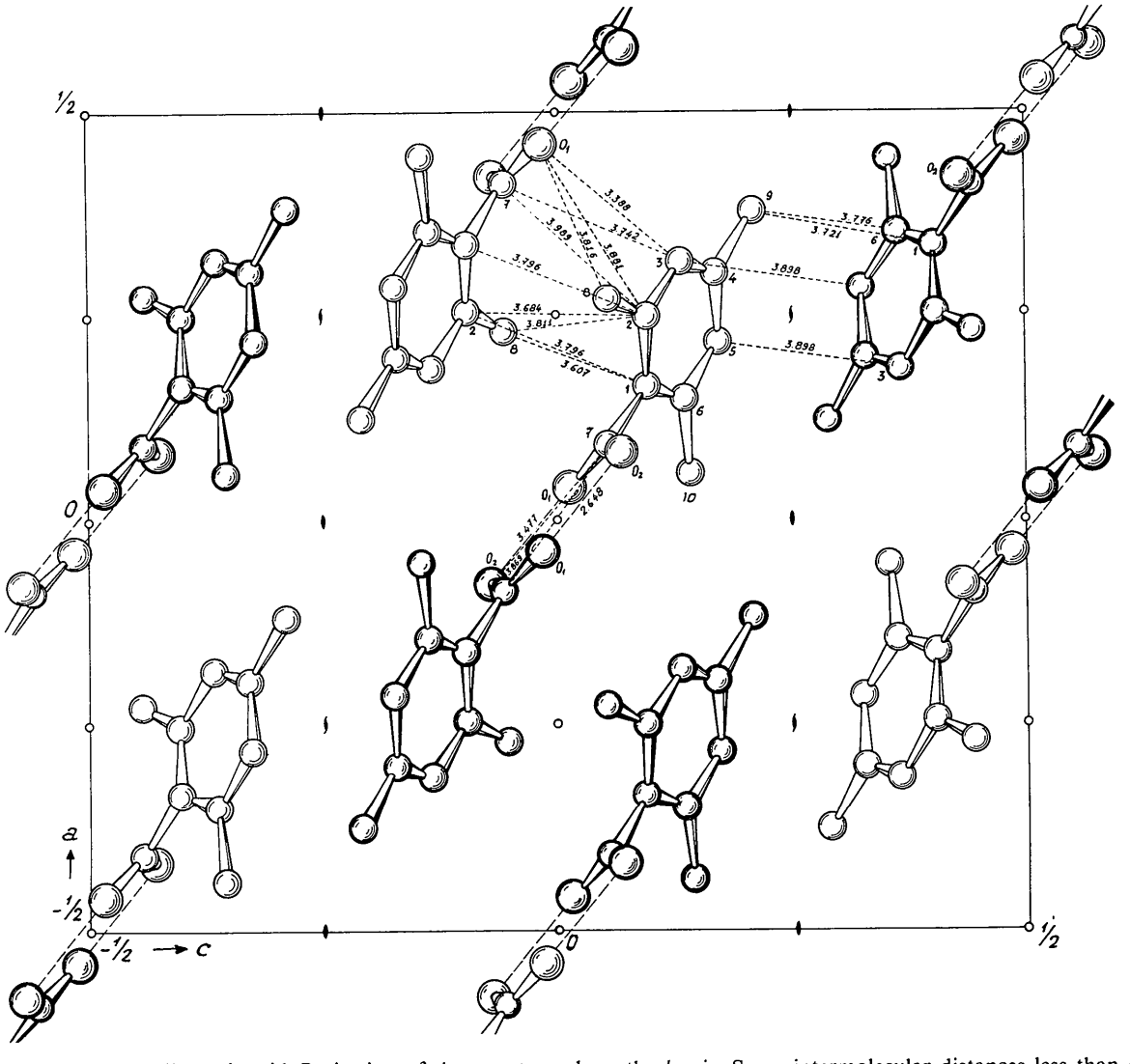

Fig. 3. 2,4,6-Trimethylbenzoic acid. Projection of the structure along the *b* axis. Some intermolecular distances less than 4·0 Å are shown.

Table 6. *Intermolecular distances less than* 4 Å

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

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

	i		*j*	*d*(*ij*)		*i*		*j*	*d*(*ij*)
C(1)	I	C(2)	II	3·796 Å	C(7)	I	O(1)	IV	3·407 Å
C(1)	I	C(8)	II	3·607	C(7)	I	O(2)	IV	3·477
C(1)	I	C(9)	III	3·721	C(8)	I	C(8)	X	3·649
C(2)	I	C(2)	II	3·684	C(8)	I	O(1)	II	3·816
C(2)	I	C(7)	II	3·989	C(9)	I	C(9)	V	3·910
C(2)	I	C(8)	II	3·811	C(9)	I	O(2)	VI	3·998
C(2)	I	O(1)	II	3·881	C(9)	I	O(2)	VII	3·963
C(3)	I	C(5)	III	3·898	C(10)	I	O(1)	VIII	3·740
C(3)	I	C(7)	II	3·742	C(10)	I	O(2)	IX	3·523
C(3)	I	O(1)	II	3·388	O(1)	I	O(1)	IV	3·372
C(6)	I	C(8)	II	3·731	O(1)	I	O(2)	IV	2·648*
C(6)	I	C(9)	III	3·776	O(2)	I	O(2)	IV	3·538
C(7)	I	C(7)	IV	3·869					

* Hydrogen bond.

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Structural Changes in the Alloy Systems of Mg–Zn–Cu and Mg–Zn–Ag Related to the Friauf–Laves Phases

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In the pseudo-binary alloy systems of $MgZn_2$–$MgCu_2$ and $MgZn_2$–$MgAg_2$ three new stacking variants were found in the homogeneity ranges of the C_{14} and C_{36} structures. These three structures can be expressed, in terms of the stacking sequence of six compound layers, as 8-layer (*AB'AB'A'CA'C*), 9-layer (*AB'ABC'BCA'C*) and 10-layer (*ABC'BCA'C'BC'B'*) type. Representation of the Friauf–Laves phases and of relevant layer structures is discussed in connexion with that of the closest packing of spheres.

Among several factors governing the crystal structures of alloy phases or intermetallic compounds, the electron concentration is important in relation to the interaction between the Fermi surface and Brillouin-zone boundaries. Laves & Witte (1936) investigated alloys of Mg-base ternary Friauf-Laves phases* and found that, when, for instance, Cu in $MgCu_2$ is replaced by a metal of higher valency, such as Zn, Al or Si, the cubic C_{15} ($MgCu_2$) structure is followed by the C_{36} ($MgNi_2$) and C_{14} ($MgZn_2$) structures as the electron-atom ratio (e/a) is increased. This work indicated a close relationship between electron concentration and crystal structure, because the phase boundaries for the above three types of structure appeared at almost the same electron concentration for various combinations of metals.

We re-investigated the pseudo-binary systems of $MgZn_2$–$MgCu_2$, $MgZn_2$–$MgAg_2$, $MgCu_2$–$MgAl_2$, $MgCu_2$–$MgSi_2$ and $MgCu_2$–$MgNi_2$, and confirmed that the crystal structures of the systems Mg–Zn–Cu and Mg–Zn–Ag were strongly governed by the electron

* The term 'Friauf–Laves phases' is used in this paper for the C_{14}, C_{15} and C_{36} type structures, since there has been confusion in specifying these types of phase. The structures of $MgCu_2$ and $MgZn_2$ were originally determined by Friauf (1927*a*,*b*) and that of $MgNi_2$ by Laves & Witte (1935). New stacking variants reported in this paper are classified in terms of structures related to Friauf–Laves phases. (We are grateful for Dr S. Samson's suggestion on this point.)