The Crystal Structure of Trimellitic Acid for the Pseudo-cell

Fusao TAKUSAGAWA, Ken HIROTSU, and Akira SHIMADA

Department of Chemistry, Faculty of Science, Osaka City University, Sugimoto-cho, Sumiyoshi-ku, Osaka 558

(Received March 19, 1973)

The crystal structure of trimellitic acid(benzene-1,2,4-tricarboxylic acid) for the pseudo-cell was determined by the method of X-ray diffraction. The crystal is monoclinic, with the space group of I2/c and with $a=15.91$, $b=61.35$, $c=8.99$ Å, and $\beta=95.4°$. The appearence of diffraction patterns strongly indicated the existence of the pseudo-cell with $b/5$ and with the space group of I2/c. The structure of the pseudo-cell was determined by the symbolic addition method. The final R value is 13.6%. There is no intramolecular hydrogen bond between the adjacent carboxyl groups, and one of these carboxyl groups twists greatly out of the plane of a benzene ring so that the repulsion between the oxygen atoms is reduced. Each molecule is joined, through three kinds of hydrogen bonds, with three neighboring molecules. These hydrogen bonds are formed between the carboxyl groups related by the center of symmetry and the two-fold axis. The molecular dimensions and packing obtained by the refinement for the pseudo-cell do not seem to contain unacceptable results.

In a series of benzene derivatives which are substituted with one to six carboxyl groups, the crystal structures of several members have already been studied by means of X-ray studies to obtain valuable information in the field of crystal chemistry: benzoic acid,[1] phthalic acid,[2,3] isophthalic acid,[4] terephthalic acid,[5] trimesic acid,[6] hemimellitic acid,[7] pyromellitic acid,[8,9] and mellitic acid.[10] Since the trimellitic acid has a pair of adjacent carboxyl groups, just like phthalic acid, hemimellitic acid, pyromellitic acid, and mellitic acid, it is of interest to elucidate the steric hindrance of these carboxyl groups. There has been no intramolecular hydrogen bond between the adjacent carboxyl groups in these crystals. Hence, it is also of interest to examine the hydrogen bond formation in this crystal and also to compare the molecular dimensions of this compound with those of other similar carboxylic acids.

Experimental

The crystal was obtained in the form of a colorless plate by recrystallization from an aqueous solution. The cell dimensions were measured from zero-layer Weissenberg photographs, which were calibrated with superimposed Al powder lines. They are given with other crystal data in Table 1. The density was determined by the flotation method in a mixture of tetrachloromethane and benzene.

The diffraction patterns strongly suggest the existence of a pseudo-cell with the parameters shown in Table 1. The intensity data were collected for the 0—8 layers around the a and b(pseudo-cell) axes by the use of the multiple-film equi-inclination Weissenberg technique with Cu$K\alpha$ radiation. The intensities of the diffraction spots were estimated visually by comparison with a calibrated intensity standard. The characteristics of the intensity data were as follows:

$k=5n$, Strong reflections

$k=5n\pm2$, Weak reflections

$k=5n\pm1$, Absent

The intensity distribution in $0kl$ is shown in Fig. 1. There were 1424 independent reflections for the pseudo-cell ($k=5n$), while about 3500 reflections were measured for the real cell. The data were corrected for spot shape and for Lorentz and polarization factors. No absorption correction was

Table 1. Crystal data for trimellitic acid

Molecular formula		$C_6H_3(COOH)_3$	
Molecular weight		210.15	
		Real-cell	Pseudo-cell
Crystal system		Monoclinic	Monoclinic
Space group		I2/c	I2/c
Cell dimensions;	a	15.91±0.02 Å	15.91±0.02 Å
	b	61.35±0.06	12.27±0.01
	c	8.99±0.01	8.99±0.01
	β	95.4 ±0.1°	95.4 ±0.1°
	V	8733 ±5 Å^3	1746 ±1 Å^3
Z		40	8
Density(calc.)		1.60 g/cm^3	
Density(obs.)		1.58	

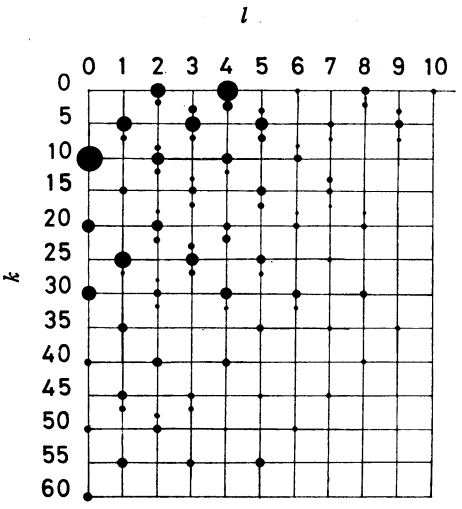

Fig. 1. Intensity distribution of $0kl$ reflections.

1) G. A. Sim, J. M. Robertson and T. H. Goodin, *Acta Crystallogr.*, **8**, 157 (1955).
2) H. Jaggi, *Z. Kristallogr.*, **109**, 3 (1957).
3) W. Nowacki and H. Jaggi, *ibid.*, **109**, 272 (1957).
4) R. Alcala and S. M. Carrera, *Acta Crystallogr.*, **B28**, 1671 (1972).
5) M. Bailery and C. J. Brown, *ibid.*, **22**, 387 (1966).
6) D. J. Duchamp and R. E. Marsh, *ibid.*, **B25**, 5 (1969).
7) F. Takusagawa and A. Shimada, This Bulletin, **46**, 2998 (1973).
8) F. Takusagawa, K. Hirotsu, and A. Shimada, *ibid.*, **44**, 1274 (1971).
9) F. Takusagawa, K. Hirotsu, and A. Shimada, *ibid.*, **42**, 3368 (1969).
10) S. F. Darlow, *Acta Crystallogr.*, **14**, 159 (1961).

TABLE 2. THE OBSERVED AND CALCULATED STRUCTURE FACTORS

F_o, F_c and DF have been multiplied by 5. The unobserved reflection is indicated by an asterisk. The reflection with the $|F_o-F_c|/|F_o|$ larger than 0.3 is indicated by a plus sign.

H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF
K=L=	0	0		4	124	-128	4	-10	29	26	3	-9	37	47	-9	-8*	0	0	0	-4	43	39	4	15*	0	4	-4
2	87	102	-14	6	52	59	-6	-8	42	-31	-10	-7+	37	-12	-25	-6*	0	-11	11	-2	86	63	22	17*	0	-2	2
4	54	-46	-8	8	47	50	-3	-6	30	-22	-8	-5	71	-53	-18	-4*	0	2	-2	0	44	35	8	K=L=	4	2	
6	71	-62	-9	10	57	66	-8	-4*	0	-7	7	-3+	21	-35	13	-2*	0	9	-9	2	98	102	-4	-18*	0	-6	6
8+	9	-2	-7	12*	0	-8	8	-2	93	100	-7	-1	68	-79	10	0*	0	-8	8	4+	15	-8	-7	-16	14	-12	-2
10+	24	40	-16	14*	0	4	-4	0+	28	8	19	1	116	-116	0	K=L=	2	11		6	100	97	2	-14*	0	-4	4
12*	0	5	-5	16	23	23	0	2	48	38	9	3	245	-263	17	-3*	0	10	-10	8*	0	-17	17	-12+	15	10	5
14*	0	-10	10	18+	0	5	-5	4	12	9	3	5	90	75	14	K=L=	3	0		10	93	-89	-3	-10+	13	9	4
16*	0	-3	3	K=L=	1	2		6	14	11	3	7	43	44	-1	1	227	228	0	12+	29	20	9	-8	76	-67	-8
18*	0	1	-1	-17*	0	-4	4	8	23	-25	1	9*	0	-2	2	3+	7	14	-7	14*	0	-8	8	-6+	31	-15	-16
K=L=	0	2		-15*	0	-10	10	10*	0	-9	9	11	28	-25	-2	5	137	-118	-18	K=L=	3	6		-4	73	-57	-15
-16*	0	19	-19	-13*	0	-10	10	K=L=	1	8		13*	0	0	0	7	67	-47	-20	-17*	0	1	-1	-2	177	-175	-1
-14*	0	9	-9	-11*	0	0	0	-15*	0	0	0	15	41	-36	-5	9*	0	10	-10	-15+	6	12	-5	0	140	-145	4
-12*	0	-8	8	-9	112	-111	-1	-13*	0	5	-5	17	18	-14	-3	11+	52	29	22	-13*	0	-5	5	2	266	-285	19
-10	81	66	14	-7	61	59	2	-11*	0	1	-1	K=L=	2	4		13*	0	-1	1	-11	18	20	-1	4	151	-157	6
-8	157	-152	-5	-5	28	28	0	-9*	0	-1	1	-18*	0	4	-4	15	39	-33	-5	-9+	19	-12	-6	6+	38	20	17
-6	163	119	44	-3	97	98	-1	-7	12	-14	1	-16*	0	-13	13	17*	0	9	-9	-7*	0	0	0	8	37	43	-6
-4	384	432	-48	-1	93	96	-2	-5	19	17	2	-14*	0	-14	14	K=L=	3	1		-5	69	-49	-19	10	42	32	10
-2	286	299	-13	1	33	-42	9	-3	24	18	6	-12	18	19	+1	-18*	0	-1	1	-3	67	-49	-18	12	35	-27	-7
0	163	178	-15	3	228	-229	1	-1	33	39	-5	-10*	0	-1	1	-16*	0	1	-1	-1*	0	-2	2	14	11	9	1
2+	22	14	8	5*	0	8	-8	1+	17	24	-6	-8+	22	15	7	-14	32	-33	1	1	29	-34	4	16	9	6	2
4	216	233	-16	7	28	-20	-8	3	29	-22	-7	-6+	23	-8	-14	-12	17	-21	3	3	55	-48	-7	K=L=	4	3	
6	75	-96	21	9	136	131	5	5+	28	6	22	-4+	12	19	-7	-10*	0	4	-4	5	64	45	18	-17*	0	3	-3
8	80	84	-3	11	23	25	-2	7	57	43	14	-2	133	-146	12	-8	71	63	8	7	121	-129	7	-15*	0	-8	8
10	39	-37	-1	13*	0	15	-15	K=L=	1	9		0	97	105	-8	-6	56	62	-6	9	20	-19	0	-13	11	11	0
12	30	-26	-4	15	21	19	1	-12*	0	-3	3	2+	40	26	13	-4	17	-12	-5	11	52	-39	-13	-11	46	-43	-2
14*	0	0	0	17+	18	10	7	-10*	0	3	-3	4	58	-52	-6	-2	179	175	3	K=L=	3	7		-9+	14	21	-7
16	21	-22	0	K=L=	1	3		-8*	0	5	-5	6	18	21	-3	0	41	-33	-8	-16*	0	0	0	-7*	0	4	-4
K=L=	0	4		-18*	0	1	-1	-6+	14	-4	-9	8+	27	-18	-8	2	102	-111	9	-14*	0	3	-3	-5+	24	-1	-22
-14	31	28	3	-16*	0	2	-2	-4+	32	-21	-10	10	61	70	-8	4	54	42	11	-12*	0	2	-2	-3	109	88	21
-12*	0	-2	2	-14*	0	4	-4	-2	46	-40	-5	12*	0	0	0	6	112	-101	-10	-10*	0	6	-6	-1	123	-114	-9
-10*	0	-5	5	-12	68	-57	-10	0	47	38	8	14	45	-32	-12	8	59	64	-5	-8	28	21	7	1+	7	3	4
-8	32	-29	-3	-10+	14	-20	6	2	50	45	4	K=L=	2	5		10	21	19	2	-6+	34	-17	-17	3	173	186	-12
-6	130	124	6	-8	124	133	-8	4	22	-18	-4	-7+	34	18	15	12	41	46	-4	-4+	6	2	4	5+	8	-13	4
-4	21	-19	-1	-6	124	115	9	K=L=	1	10		-5	111	-94	-17	14*	0	1	-1	-2	50	47	3	7+	8	4	3
-2	202	204	-1	-4	85	85	0	-9*	0	4	-4	-3+	15	-8	-7	16	16	-11	-4	0	31	-26	-5	9	39	-40	1
0	377	-396	19	-2	120	-134	13	-7*	0	0	0	-1	35	-33	-2	18*	0	1	-1	2	100	88	11	11	16	-17	1
2+	17	7	10	0	262	278	-16	-5*	0	-7	7	1	36	32	4	K=L=	3	2		4*	0	2	-2	13*	0	-4	4
4+	153	200	-47	2*	0	8	-8	-3*	0	0	0	3	22	20	2	-17*	0	5	-5	6	24	-25	0	15+	24	16	7
6	91	93	-1	4	348	368	-19	-1*	0	-1	1	5	44	-43	-1	-15+	26	16	9	8+	15	-10	-5	K=L=	4	4	
8	46	39	-12	6	43	-51	8	1	20	14	5	7	46	-40	-5	-13	19	17	1	10*	0	4	-4	-18*	0	-6	6
10	50	-55	5	8	94	-80	-14	K=L=	1	11		9	148	144	4	-11	30	-35	4	K=L=	3	8		-16*	0	6	-6
12	66	-71	5	10	25	22	2	-8*	0	-7	7	11	22	-24	2	-9	106	105	1	-15*	0	0	0	-14*	0	-8	8
14*	0	16	-16	12*	0	-4	4	-6+	5	-11	5	13*	0	-7	7	-7	64	-59	-5	-13*	0	-7	7	-12	39	-28	-10
16+	20	-26	6	14	43	32	11	-4	11	12	-1	K=L=	2	6		-5	86	72	14	-11*	0	-1	1	-10*	0	6	-6
K=L=	0	6		16+	13	-2	-11	K=L=	2	0		-18*	0	0	0	-3	58	-61	3	-9*	0	-4	4	-8	30	28	2
-16*	0	-4	4	K=L=	1	4		0	458	-495	36	-16*	0	4	-4	-1+	15	-22	7	-7	46	47	0	-6	50	-40	-9
-14*	0	4	-4	-15*	0	-10	10	2	184	195	-10	-14*	0	-1	1	1	21	26	-5	-5+	30	-21	-9	-4	9	-10	0
-12*	0	12	-12	-13	34	-31	-2	4	37	35	2	-12*	0	-8	8	3	22	19	3	-3	75	-65	-10	-2	169	-147	-21
-10*	0	4	-4	-11	24	-21	-3	6+	10	5	5	-10*	0	2	-2	5	133	-123	-9	-1	21	-19	-2	0	31	34	-2
-8	39	36	3	-9	20	18	2	8+	17	-9	-7	-8+	23	-15	-8	7	87	90	-2	1+	13	-8	-5	2	51	-43	-8
-6	14	-13	-1	-7	50	53	-3	10	75	-65	-9	-6*	0	4	-4	9	118	-125	6	3+	16	8	7	4	79	80	-1
-4	176	-164	-12	-5	29	-29	0	12*	0	11	-11	-4	44	53	-8	11+	20	-13	-7	5	46	-41	-4	6	43	-50	6
-2	44	-43	0	-3+	32	-19	-13	14*	0	8	-8	-2+	19	-26	7	13	24	-19	-4	7	64	-56	-7	8	16	13	3
0*	0	4	-4	-1	11	-13	1	16*	0	11	-11	0	51	45	5	15	33	-23	-9	K=L=	3	9		10	57	-56	-1
2	69	70	-1	1	44	50	-5	18+	9	-3	-6	2	17	-13	-3	17+	24	-14	-9	-12	8	9	0	12	38	41	-2
4	86	-88	1	3	28	37	-8	K=L=	2	1		4	27	22	4	K=L=	3	3		-10*	0	-10	10	14	34	24	10
6	20	15	4	5	93	89	3	-17*	0	8	-8	6	44	47	-3	-18*	0	-3	3	-8*	0	-2	2	K=L=	4	5	
8	50	41	8	7	87	83	4	-15*	0	7	-7	8	50	-57	6	-16*	0	-7	7	-6*	0	1	-1	-17*	0	4	-4
10*	0	3	-3	9	29	29	0	-13	32	27	4	10	33	-26	-6	-14	17	-17	0	-4+	2	-3	1	-15*	0	3	-3
12*	0	-12	12	11	40	49	-9	-11*	0	3	-3	12*	0	9	-9	-12	39	41	-2	-2	10	9	0	-13*	0	5	-5
K=L=	0	8		13	70	60	9	-9	38	41	-2	K=L=	2	7		-10+	26	-13	-13	0	10	8	1	-11	36	-36	0
-14*	0	-6	6	15*	0	-10	10	-7	124	108	16	-17*	0	0	0	-8+	18	-9	-8	2+	15	0	-14	-9	14	12	1
-12*	0	4	-4	K=L=	1	5		-5	306	311	-5	-15*	0	-1	1	-6	108	103	5	4+	16	10	6	-7*	0	-12	12
-10*	0	7	-7	-16*	0	-4	4	-3	264	-253	-11	-13*	0	3	-3	-4	44	40	3	K=L=	3	10		-5	52	46	5
-8*	0	7	-7	-14	12	8	3	-1	93	-74	-19	-11*	0	-16	16	-2+	37	23	14	-11*	0	5	-5	-3+	34	19	15
-6	38	-33	-5	-12*	0	9	-9	1	181	-190	8	-9*	0	-18	18	0	62	54	8	-9*	0	-2	2	-1	29	-24	-5
-4+	38	-14	-24	-10*	0	6	-6	3	110	-110	0	-7	29	21	8	2	78	76	1	-7*	0	-3	3	1+	15	-6	-8
-2	68	-78	10	-8+	28	-19	-9	5	39	-37	-1	-5*	0	17	-17	4	61	53	7	-5*	0	6	-6	3	81	66	15
0	85	-61	-24	-6	120	108	12	7+	71	-43	-28	-3*	0	13	-13	6+	14	6	7	-3*	0	9	-9	5	86	78	8
2+	55	-29	-25	-4	30	-24	-5	9	135	-121	-14	-1*	0	-5	5	8	97	99	-2	-1*	0	-3	3	7	77	-78	1
4	49	59	-10	-2	58	67	-9	11	30	35	-4	1+	32	-21	-11	10+	23	-1	-22	1	37	-32	-4	9	101	-101	0
6	10	-7	-2	0	165	160	5	13	50	-47	-2	3	84	72	11	12*	0	-5	5	K=L=	4	0		11	29	23	5
8*	0	-5	5	2	53	46	7	15*	0	-7	7	5	57	52	4	14	47	-42	-4	0	335	-380	45	13	15	-12	-3
K=L=	0	10		4	118	114	3	17*	0	-14	14	7	64	60	3	16	14	12	1	2	143	-157	14	K=L=	4	6	
-4+	22	-12	-9	6	14	15	-1	K=L=	2	2		9*	0	-14	14	K=L=	3	4		4	175	-182	7	-16*	0	-1	1
-2	42	-38	-3	8	23	-24	0	-18*	0	3	-3	K=L=	2	8		-17*	0	-6	6	6	39	-33	-6	-14*	0	-1	1
0*	0	1	-1	10+	12	-16	4	-16*	0	-2	2	-14*	0	3	-3	-15	29	21	8	8	56	-49	-6	-12*	0	-1	1
2	33	-28	-4	12	57	-58	0	-14*	0	-4	4	-12*	0	-5	5	-13	38	34	4	10	50	45	4	-10+	16	-9	-7
K=L=	1	0		14*	0	0	0	-12*	0	-13	13	-10*	0	0	0	-11	26	21	4	12	17	-15	-1	-8+	16	-9	-7
3	137	153	-16	K=L=	1	6		-10	41	-40	-1	-8*	0	2	-2	-9*	0	-12	12	14	9	11	-2	-6+	5	8	-3
5	21	-27	5	-17*	0	-1	1	-8	136	123	13	-6*	0	-9	9	-7	103	-94	-8	16	19	-15	-3	-4+	6	13	-7
7	74	-92	18	-15*	0	-9	9	-6	80	-64	-16	-4*	0	12	-12	-5	79	70	9	18*	0	1	-1	-2	59	74	-14
9	21	-24	2	-13*	0	1	-1	-4+	15	-22	6	-2	24	24	0	-3+	13	-4	-8	K=L=	4	1		0	50	41	8
11*	0	-6	6	-11*	0	-10	10	-2	142	124	17	0*	0	6	-6	-1	112	-101	-11	-17*	0	-5	5	2+	53	35	17
13*	0	4	-4	-9*	0	8	-8	0	111	-107	-4	2*	0	7	-7	1	127	-141	14	-15+	11	-2	-8	4	81	73	7
15	20	19	0	-7*	0	-9	9	2+	58	-39	-19	4	47	-36	-10	3	53	-44	-8	-13+	11	-4	-6	6	138	-127	-11
17*	0	-2	2	-5	28	25	3	4	179	-178	-1	6	21	-20	-1	5	60	47	12	-11+	22	-15	-7	8+	17	-8	-8
K=L=	1	1		-3+	28	37	-9	6	50	49	0	8	24	19	5	7	27	23	4	-9	28	-27	-1	10+	15	-10	-4
-18*	0	-4	4	-1*	0	8	-8	8	31	-36	4	K=L=	2	9		9	36	-32	-4	-7	73	80	-6	K=L=	4	7	
-16+	22	-15	-7	1	35	36	0	10	24	27	-2	-9*	0	4	-4	11	114	-99	-14	-5	75	-63	-11	-15*	0	1	-1
-14*	0	-9	9	3	133	141	-8	12	41	46	-5	-7*	0	0	0	13	118	-83	-35	-3	95	92	3	-13+	16	-1	-15
-12	19	-24	5	5*	0	2	-2	14*	0	-5	5	-5*	0	13	-13	15	20	15	4	-1	147	128	19	-11*	0	11	-11
-10*	0	2	-2	7	39	38	1	16*	0	1	-1	-3	36	41	-4	K=L=	3	5		1	27	26	0	-9+	15	5	10
-8+	26	-12	-13	9	12	15	-3	18	14	-14	0	-1	32	31	1	-16*	0	8	-8	3	202	-218	15	-7	15	-15	0
-6	229	-218	-10	11+	46	31	14	K=L=	2	3		1*	0	9	-9	-14*	0	1	-1	5	130	-118	-11	-5+	6	-1	-4
-4	715	709	6	K=L=	1	7		-17*	0	-4	4	3	65	50	14	-12*	0	-3	3	7	81	76	5	-3	81	-84	3
-2	48	53	-5	-16+	9	2	7	-15*	0	11	-11	5	15	18	-2	-10+	26	16	9	9	90	81	8	-1	64	57	6
0	77	-86	9	-14*	0	2	-2	-13*	0	-21	21	K=L=	2	10		-8	21	20	1	11	40	-42	1	1	122	102	19
2	111	-112	1	-12	15	13	2	-11	71	67	4	-10*	0	0	0	-6+	15	10	4	13	25	24	1	3	119	-114	0

TABLE 2. (Continued)

H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF
5	32	-22	-9	-11*	0	7	-7	-7	53	-43	-9	-11*	0	-2	2	-15*	0	-6	6	-3+	17	-6	-11	-1*	0	-36	36
7*	0	-13	13	-9*	0	5	-5	-5+	21	-14	-6	-9*	0	0	0	-13	13	-10	-3	-1	67	-56	-11	1	43	30	12
9	23	21	1	-7	107	86	21	-3+	31	43	-12	-7+	3	12	-9	-11*	0	0	0	1*	0	1	-1	3*	12	-8	-4
K,L=	4	8		-5	64	-65	0	-1	97	-96	-1	-5+	15	-20	5	-9*	0	0	0	3	25	-27	2	K,L=	9	7	
-14*	0	-1	1	-3	78	-59	-18	1	47	-41	-6	-3	95	85	10	-7*	0	-8	8	5	72	69	3	-8*	0	-3	3
-12+	12	6	5	-1+	30	-17	-13	3	57	43	14	-1	46	-51	4	-5	64	47	16	7+	21	-14	-6	-6	26	20	6
-10+	26	-4	-21	1	33	-36	3	5	143	131	11	1	93	-108	14	-3	31	23	7	K,L=	8	4		-4+	24	-15	-8
-8+	36	-20	-16	3	72	67	5	7*	0	2	-2	3*	0	0	0	-1*	0	-3	3	-8*	0	-1	1	-2	12	15	-2
-6	50	38	12	5+	9	-16	7	9	56	50	5	5	46	-42	-4	1	32	31	0	-6+	57	38	19	0	25	29	-4
-4+	4	7	-2	7	78	-79	1	11*	0	9	-9	7*	0	-1	1	3	32	36	-4	-4+	16	0	16	K,L=	9	8	
-2	84	92	-8	9	79	-72	-7	13+	8	5	3	K,L=	6	8		K,L=	7	5		-2*	0	1	-1	-7*	0	0	0
0	34	33	0	11	21	19	1	15*	0	1	-1	-12*	0	-4	4	-16	5	4	1	0	46	48	-2	-5*	0	0	0
2+	9	-14	4	13*	0	-3	3	17	23	23	0	-10*	0	0	0	-14*	0	-3	3	2*	0	17	-17	K,L=	9	9	
4	46	-47	1	K,L=	5	5		K,L=	6	2		-8	19	16	2	-12*	0	2	-2	4*	0	-16	16	-6*	0	2	-2
6*	0	0	0	-16	8	-7	-1	-16*	0	2	-2	-6*	0	-3	3	-10	37	-29	-8	6*	0	0	0	K,L=	10	0	
K,L=	4	9		-14*	0	-3	3	-14*	0	2	-2	-4*	0	1	-1	-8	22	-22	0	8+	23	-15	-7	0+	43	29	13
-11	19	16	2	-12*	0	-4	4	-12+	15	22	-6	-2	74	-76	2	-6+	37	24	12	K,L=	8	5		2	32	-34	1
-9*	0	2	-2	-10*	0	0	0	-10	20	-21	1	0	37	34	3	-4	42	-41	-1	-7	18	13	4	4	106	-104	-2
-7	35	-28	-7	-8	14	10	4	-8	22	-21	-1	2*	0	5	-5	-2	41	28	12	-5	20	-18	-2	6	59	53	5
-5*	0	-10	10	-6	76	-74	-1	-6	76	76	0	4*	0	2	-2	0	34	-33	0	-3*	0	-18	18	8	16	-15	-1
-3*	0	-5	5	-4	23	-23	0	-4	51	-41	-10	6*	0	-7	7	2	39	30	8	-1+	39	23	15	K,L=	10	1	
-1*	0	0	0	-2	74	-60	-14	-2+	46	20	26	K,L=	6	9		4	46	33	13	1+	83	32	50	-7	54	44	10
1*	0	-6	6	0	51	50	1	0	71	61	9	-11*	0	-7	7	6	87	-96	8	3*	36	-66	30	-5	88	68	19
3*	0	0	0	2	96	-95	0	2+	26	16	10	-9*	0	-1	1	8	28	-22	-5	K,L=	8	6		-3	64	54	9
K,L=	4	10		4	84	-91	6	4	66	65	0	-7	30	34	-3	10	8	6	2	-8	18	-16	-2	-1	69	63	6
-10*	0	0	0	6	57	-60	2	6	31	-29	-1	-5+	15	-20	4	12*	0	0	0	-6*	0	12	-12	1	165	-167	2
-8*	0	7	-7	8*	0	1	-1	8	26	18	7	-3	24	-24	0	K,L=	7	6		-4	21	-14	-6	3	46	-32	-13
-6	19	14	4	10	61	55	5	10+	9	0	-9	-1	41	-46	4	-15*	0	2	-2	-2*	0	-13	13	5	25	-27	2
-4*	0	3	-3	12	19	16	3	12+	15	-22	7	1	7	-7	0	-13*	0	-2	2	0+	46	-11	-34	7+	12	16	-3
-2+	18	12	5	K,L=	5	6		14	17	-14	-3	3	32	-28	-3	-11	14	-13	0	2*	0	-31	31	K,L=	10	2	
0*	0	-7	7	-17*	0	1	-1	16*	0	6	-6	K,L=	6	10		-9*	0	0	0	4+	27	11	15	-8	40	-38	-1
K,L=	5	0		-15*	0	-3	3	K,L=	6	3		-6*	0	-3	3	-7*	0	8	-8	6*	0	27	-27	-6	43	-40	-2
1+	27	37	-9	-13*	0	-7	-7	-17+	12	7	4	-4	10	10	0	-5	32	33	-1	K,L=	8	7		-4	46	43	3
3	153	-157	4	-11*	0	-1	1	-15*	0	4	-4	-2+	9	-3	-6	-3+	15	-3	-12	-7*	0	2	-2	-2*	0	3	-3
5+	6	11	-5	-9*	0	1	-1	-13	21	-17	-4	K,L=	7	0		-1	75	60	14	-5	34	34	0	0	68	-48	-20
7	79	73	6	-7+	14	0	-13	-11+	17	-6	-11	1+	23	-14	-8	1	100	-81	-19	-3*	0	-10	10	2*	0	-2	2
9+	0	13	-12	-5	15	-15	0	-9	24	-19	-5	3	27	-19	-7	3	84	88	-4	-1+	19	7	11	4	27	-19	-7
11	22	-17	-5	-3	19	-18	-1	-7+	9	1	8	5	80	69	10	5	46	42	3	1*	0	-15	15	6*	0	-1	1
13*	0	-1	1	-1*	0	-15	15	-5+	11	-3	-7	7	16	-13	-2	7	25	25	0	K,L=	8	8		8	17	19	-2
15*	0	11	-11	1	139	139	0	-3	149	-142	-6	9	26	-23	-2	9*	0	-7	7	-8*	0	-1	1	K,L=	10	3	
17	14	-11	-3	3	97	-98	1	-1	120	110	10	11+	19	9	10	K,L=	7	7		-6	14	-10	-3	-7	67	61	5
K,L=	5	1		2	55	61	-6	1+	67	45	22	13*	0	5	-5	-12*	0	7	-7	-4+	14	-19	5	-5	9	6	2
-16+	14	7	6	4	183	-173	-9	3	73	85	-11	15*	0	7	-7	-10*	0	-5	5	-2*	0	1	-1	-3+	8	-17	9
-14+	35	24	10	6+	7	0	-6	5	67	60	7	17*	0	3	-3	-8+	10	0	-10	0	16	-19	3	-1	64	-73	8
-12*	0	6	-6	8	25	-31	5	7*	0	5	-5	K,L=	7	1		-6*	0	-11	11	K,L=	9	0		1+	12	5	7
-10	18	13	5	10	32	-40	8	9+	28	-37	8	-18*	0	-3	3	-4+	35	-22	-13	1	71	63	8	3	70	76	-6
-8+	26	-18	-8	K,L=	5	7		11	22	22	0	-16*	0	-3	3	-2	24	20	3	3	98	85	12	5	23	-19	-3
-6	47	42	5	-14*	0	-2	2	13	24	26	-2	-14*	0	7	-7	0+	16	-5	-11	5	135	-132	-3	7+	15	23	-8
-4	90	-83	-6	-12	12	-9	-2	15*	0	-3	3	-12	17	15	2	2	18	-15	-2	7+	15	-3	-12	K,L=	10	4	
-2	65	-72	7	-10*	0	-7	7	K,L=	6	4		-10*	0	-1	1	4	75	-72	-2	K,L=	9	1		-8	23	26	-3
0	258	-263	5	-8+	11	-7	-4	-16*	0	5	-5	-8	51	-49	-2	6*	0	1	-1	-8	64	65	-1	-6	9	-7	-1
2	49	36	12	-6	27	24	3	-14	16	12	4	-6*	0	-3	3	K,L=	7	8		-6	54	58	-4	-4	29	30	0
4	28	28	0	-4	62	48	13	-12	16	12	3	-4	63	55	7	-11*	0	5	-5	-4+	28	-17	-11	-2*	0	4	-4
6	79	59	20	-2	81	-73	-8	-10*	0	-4	4	-2	54	-46	-7	-9*	0	-4	4	-2*	0	3	-3	0+	16	-1	-14
8	42	-44	2	0	13	-13	0	-8	22	-17	-5	0+	60	40	20	-7+	23	12	11	0	71	69	1	2	28	-31	3
10+	33	-16	-17	2	137	-123	-14	-6+	18	-4	-13	2	103	-105	2	-5*	0	-5	5	2	62	-73	10	4+	28	45	-17
12	21	-22	0	4	25	27	-1	-4	14	-18	3	4	64	-53	-11	-3*	32	-22	-10	4	23	-25	1	6	49	-58	9
14*	0	-1	1	6*	0	-9	9	-2	94	90	4	6	63	57	5	-1	54	53	0	6*	0	-13	13	8+	9	1	7
16*	0	-12	12	8	18	19	-1	0	118	-127	8	8	8	7	1	1*	0	9	-9	8	35	43	-7	K,L=	10	5	
K,L=	5	2		K,L=	5	8		2+	12	-3	-8	10*	0	10	-10	3	41	31	9	K,L=	9	2		-7*	0	3	-3
-17*	0	0	0	-13*	0	2	-2	4	19	-13	-5	12+	20	-14	-6	5	14	-10	-4	-7+	26	-14	-12	-5	37	-35	-1
-15*	0	-6	6	-11*	0	-4	4	6	106	130	-24	14+	17	-11	-5	K,L=	7	9		-5	18	-16	-1	1	56	58	-2
-13	8	9	-1	-9	10	7	3	8*	0	2	-2	16	21	15	5	-10*	0	2	-2	-3	56	50	6	3	30	27	2
-11	38	36	2	-7	56	-52	-3	10	56	-54	-1	K,L=	7	2		-8	14	14	0	-1	48	40	7	5	14	-15	1
-9*	0	-2	2	-5+	18	8	10	12	27	-24	-3	-17*	0	-4	4	-6	22	-25	2	1+	30	15	15	7+	6	8	-2
-7+	11	1	10	-3	94	93	1	14*	0	0	0	-15*	0	4	-4	-4*	0	2	-2	3+	35	25	10	K,L=	10	6	
-5+	34	17	16	-1	27	-31	4	K,L=	6	5		-13	30	-38	7	-2	14	-13	0	5*	0	6	-6	-8	11	9	2
-3	106	98	7	1	28	-27	0	-17*	0	0	0	-11*	0	3	-3	0	18	-15	-2	7	32	34	-1	-6	15	19	-4
-1+	61	-42	-18	3	54	-45	-9	-15*	0	-1	1	-9+	9	12	-2	2+	18	11	6	K,L=	9	3		0+	22	33	-10
1	247	-245	-2	5	21	-17	-4	-13*	0	0	0	-7*	0	1	-1	K,L=	7	10		-8	15	17	-1	2*	0	-9	9
3	46	39	7	K,L=	5	9		-11	13	15	-1	-5	28	-27	-1	-5*	0	-7	7	-6+	23	-13	-10	4	18	-19	0
5*	0	-6	6	-10*	0	4	-4	-9+	12	-18	5	-3	46	49	-3	-3	8	8	0	-4	52	52	0	6*	0	-8	8
7	23	-20	-2	-8+	19	-7	-11	-7	27	-29	2	-1*	0	5	-5	K,L=	8	0		-2	14	-15	1	K,L=	10	7	
9	35	26	9	-6	26	24	1	-5+	12	21	-8	1	102	86	16	0	29	25	4	0	30	36	-5	-7	18	-14	-3
11+	12	-8	-3	-4*	0	4	-4	-3*	0	10	-10	3	116	-113	-3	2	74	74	0	2	41	34	6	1	18	24	-5
13	34	-28	-5	-2*	0	-2	2	-1	82	78	3	5	62	59	2	4	88	111	-23	4	46	45	1	3+	4	1	3
15*	0	-1	1	0	18	-14	-4	1	42	32	9	7*	0	-2	2	6+	16	9	7	6*	0	10	-10	K,L=	10	8	
17*	0	2	-2	2+	26	-17	-8	3*	0	6	-6	9	57	49	8	8+	13	4	8	8+	27	41	-14	-8	8	-9	1
K,L=	5	3		K,L=	5	10		5	145	-156	10	11*	0	2	-2	K,L=	8	1		K,L=	9	4		-6+	7	-3	-4
-16*	0	-7	7	-9*	0	0	0	7	43	45	-1	13	64	57	7	-7	43	-34	-9	-7*	0	-9	9	K,L=	11	0	
-14	19	16	3	-7*	0	7	-7	9	11	-14	2	15*	0	-6	6	-5+	33	7	25	-5	22	29	-6	3	44	-40	-4
-12*	0	6	-6	-5*	0	9	-9	11*	0	-4	4	K,L=	7	3		-3	9	-8	0	-3	20	20	0	5	80	68	12
-10	9	10	0	-3	14	-15	0	K,L=	6	6		-16	18	16	1	-1	91	-102	11	-1	37	-37	0	7	32	-24	-7
-8+	14	-22	8	-1*	0	2	-2	-16*	0	-1	1	-14*	0	1	-1	1	24	-20	-3	1	35	25	10	K,L=	11	1	
-6	93	-82	-10	K,L=	6	0		-14*	0	5	-5	-12	31	-27	-4	3	46	36	10	3	44	-41	-3	+8+	16	-8	-8
-4	120	-111	-8	0	219	226	-7	-12*	0	6	-6	-10+	10	3	7	5	15	-19	3	5	91	71	19	-6	17	13	4
-2	57	-51	-5	2	37	36	1	-10*	0	-1	1	-8+	24	-12	-11	7	37	33	3	7	52	47	5	-4	70	71	-1
0	167	-177	9	4	55	42	12	-8	19	15	4	-6+	20	-10	-9	K,L=	8	2		K,L=	9	5		-2*	0	13	-13
2	46	33	13	6	90	-104	14	-6	37	-38	0	-4+	30	-42	11	-8	37	41	-4	-8*	0	-10	10	0	111	-112	1
4	102	-110	7	8+	13	19	-6	-4+	4	-5	1	-2	58	-72	14	-6*	0	1	-1	-6*	0	-14	14	2+	17	8	9
6	66	56	10	10	22	25	-2	-2+	17	-26	8	0*	0	7	-7	-4	68	65	2	-4	45	38	6	4*	0	-5	5
8	26	-22	-3	12+	8	5	3	0	61	-53	-7	2+	12	4	7	-2	61	58	2	-2+	27	42	-15	6*	0	6	-6
10	28	23	4	14	16	-16	0	2	81	64	17	4	84	90	-5	0	67	77	-9	0+	54	14	39	8	26	18	7
12	30	-31	0	16*	0	2	-2	4	15	-12	-3	6*	0	8	-8	2	74	73	1	2+	17	59	-42	K,L=	11	2	
14	8	9	0	K,L=	6	1		6+	13	8	5	8	46	-52	6	4*	0	-4	4	4	27	22	4	-7*	0	-8	8
16*	0	-6	6	-17*	0	-3	3	8	18	-17	0	10	60	-48	-12	6+	11	25	-13	6+	25	16	8	-5	39	34	0
K,L=	5	4		-15*	0	-3	3	10	17	15	2	12	19	14	5	8*	0	2	-2	K,L=	9	6		-3	95	-116	20
-17+	16	10	6	-13	13	-14	1	K,L=	6	7		14+	38	26	11	K,L=	8	3		-7*	0	-1	1	-1+	24	35	-10
-15+	14	-8	-5	-11+	13	6	6	-15*	0	1	-1	K,L=	7	4		-7	16	-20	3	-5	19	-15	-3	1*	0	23	23
-13*	0	6	-6	-9	58	-47	-10	-13*	0	1	-1	-17	11	-10	-1	-5	37	-31	-6	-3+	37	-13	-24	3	46	48	-2

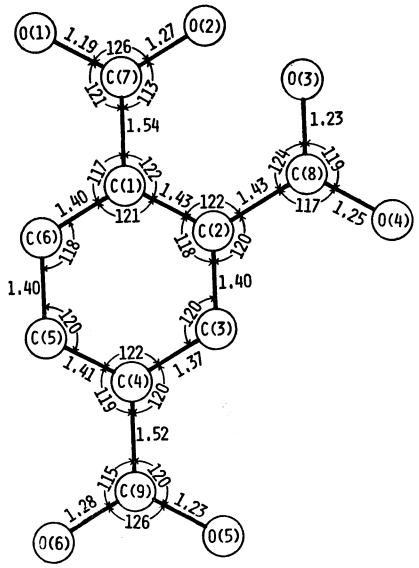

Fig. 2. Molecular dimensions of trimellitic acid. The estimated standard deviations are as follows:
C–C=0.02 Å, C–O=0.01~0.02 Å, C–C–C=0.8~1.0°, C–C–O=0.6~0.9°, O–C–O=0.5~1.0°

applied. They were then corrected and reduced to the structure factors by means of the procedure described by Hamilton, Rollet, and Sparks.[11]

Both cells, real and pseudo, were found to be monoclinic, with a space group of I2/c or Ic. The former was tentatively assumed on the basis of the statistical averages and distributions of normalized structure amplitudes in the pseudo-cell.

Phase Determination

Since the phase determination procedure for this crystal was applied only to the pseudo-cell, the indices were transformed to refer to this cell; *i.e.*, only those data with $k=5n$ were used, and the k index was divided by five. The absolute scale and approximate temperature factors were determined by means of Wilson's statistics.[12] The normalized structure amplitudes, $|E|$, were computed from these values. The symbolic addition procedure was used to determine the phases.[13] The origin was specified by assigning the signs to two linearly independent reflections.[14] Three additional E's were assigned arbitrary symbols.

Table 3. Assignment of the two origin specifying reflections and three other reflections as a starting set

h	k	l	$\|E\|$	Sign	N.I.P.[a]
4	1	3	3.34	+	88
1	10	1	3.06	−	72
9	2	5	3.40	A	50
−4	1	1	3.18	B	161
7	3	6	3.01	C	43

a) N. I. P.=Number of interaction pairs.

The starting set of phases is listed in Table 3. 114 signs for $|E|>1.5$ were determined by the application of the Σ_2 relations. From the accumulated information about the signs of the 114 reflections, it was obvious that the sign of A was +, while that of B was + and that of C was −. An E-map computed on the basis of these 114 terms revealed most of atomic positions. The peak values for all the atoms were higher than 127, the average value was 244. The maximum value of the ghost peaks was 197. A Fourier map was calculated on the basis of the structure amplitudes phased on the contributions of eight peaks(higher than 200) in order to rule out wrong peaks in the E-map.

The refinement of the positional parameters, the thermal parameters, and one scale factor was carried out by means of the block-diagonal least-squares method, with a modified version of the HBLS-IV program.[15] Four cycles of refinement with isotropic thermal parameters lowered the R value to 23.3%. At this stage of refinement, anisotropic thermal parameters were introduced; four subsequent cycles of

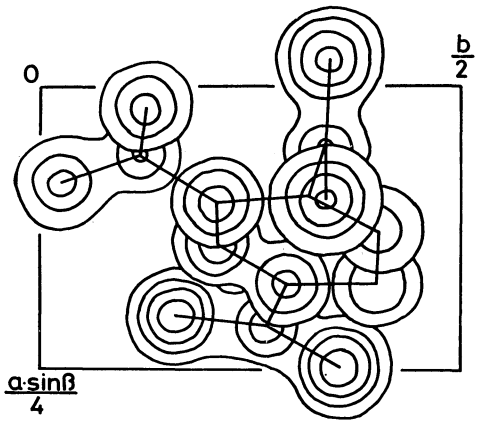

Fig. 3. Electron density map along the c axis.

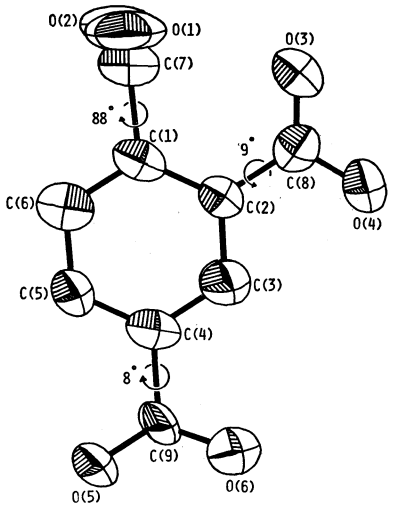

Fig. 4. Thermal ellipsoids of non-hydrogen atoms, which are scaled to include 20% probability.

11) W. C. Hamilton, J. S. Rollet and A. Sparks, *Acta Crystallogr.*, **18**, 129 (1965).
12) A. J. C. Wilson, *Nature* (London), **150**, 151 (1942).
13) J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).
14) H. Hauptman and J. Karle, *ibid.*, **12**, 93 (1959).
15) Y. Okaya and T. Ashida, HBLS-IV. The Universal Crystallographic Computing System (I), p. 65. The Crystallographic Society of Japan (1967).

Table 4. The final parameters and their estimated standard deviations (in parentheses)

The coordinates have been multiplied by 10^4. The anisotropic thermal parameters are of the $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$, and have been multiplied by 10^4.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	994(7)	3199(9)	997(12)	61(5)	60(10)	103(11)	−15(10)	−61(11)	−15(16)
C(2)	1016(6)	2133(8)	1643(12)	63(5)	42(9)	88(10)	−14(9)	−47(11)	−5(13)
C(3)	1415(6)	2008(9)	3089(12)	53(5)	51(9)	116(11)	7(9)	−54(11)	2(14)
C(4)	1738(7)	2895(9)	3869(12)	60(4)	61(9)	85(10)	−4(10)	−53(11)	−8(14)
C(5)	1756(8)	3932(9)	3209(15)	88(6)	37(9)	124(13)	−13(12)	−91(15)	−7(16)
C(6)	1403(8)	4084(9)	1743(15)	77(6)	71(11)	118(12)	−27(12)	−65(14)	13(18)
C(7)	539(7)	3424(9)	−558(13)	56(4)	78(10)	97(11)	−6(10)	−43(11)	11(15)
C(8)	637(8)	1213(9)	864(13)	60(5)	48(9)	127(12)	−20(10)	−51(12)	47(16)
C(9)	2120(7)	2752(8)	5468(12)	60(4)	28(8)	97(10)	7(9)	−48(10)	−45(13)
O(1)	−195(5)	3651(8)	−716(9)	61(4)	140(9)	102(9)	−3(9)	−76(9)	50(14)
O(2)	1022(5)	3353(8)	−1595(9)	80(4)	135(9)	92(8)	38(10)	−57(9)	−38(13)
O(3)	197(7)	1283(7)	−328(12)	132(7)	60(7)	136(10)	−56(11)	−127(14)	−5(13)
O(4)	736(8)	304(7)	1478(15)	168(9)	44(8)	209(14)	−63(12)	−215(19)	31(15)
O(5)	2454(5)	3535(6)	6145(9)	77(4)	38(6)	111(8)	−8(7)	−76(9)	−29(10)
O(6)	2011(5)	1809(6)	6025(9)	74(4)	55(6)	107(8)	5(8)	−43(9)	4(11)

Table 5. Least-squares plane of benzene ring

Equation of the plane defined by six carbon atoms of benzene ring:

$$-0.915X+0.194Y+0.355Z=-0.339$$

X, Y, and Z are coordinates in Å referred to an orthogonal set of axes and parallel to the a, b, and c* axes. Deviations of atoms:

Atom	From the plane	Atom	From the plane
C(1)	0.04 Å	C(9)	0.07 Å
C(2)	0.01	O(1)	1.20
C(3)	−0.02	O(2)	−0.98
C(4)	0.03	O(3)	0.22
C(5)	−0.01	O(4)	−0.08
C(6)	−0.04	O(5)	0.04
C(7)	0.14	O(6)	0.22
C(8)	0.04		

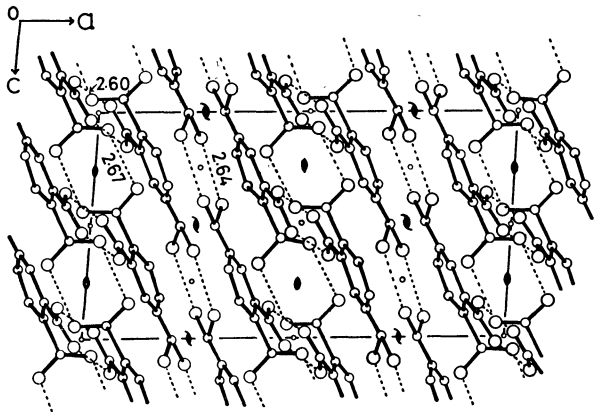

Fig. 5. A view of the crystal structure down the b axis. Hydrogen bonds are shown by broken lines.

refinement dropped the R value to 13.6%, excluding unobserved reflections. The observed and calculated structure factors are listed in Table 2.

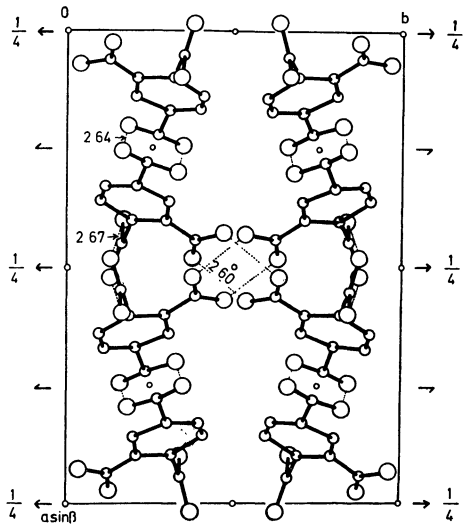

Fig. 6. A view of the crystal structure down the c axis. Hydrogen bonds are shown by broken lines.

Results and Discussion

The final positional and anisotropic thermal parameters are listed, along with their estimated standard deviations, in Table 4. Figures 3 and 4 show the electron density map along the c axis, calculated at the end of the refinement, and the thermal ellipsoids, which are scaled to include a 20% probability, respectively. The bond lengths and angles are given in Fig. 2. The equation of the least-squares plane of a benzene ring is given, along with the deviations of all the atoms from this plane, in Table 5.

A benzene ring is planar with the maximum deviation of 0.04 Å. The average values of the C(ring)–C(ring) and C(ring)–C(carboxyl) bond lengths are

1.40 and 1.49 Å, respectively. All the C–C–C bond angles lie within the range of 120±3°. In the carboxyl groups at the 1- and 4-positions, the C–O(H) and C–O bond lengths differ significantly from each other, while those of the carboxyl group at the 2-position are approximately equal. There is no intramolecular hydrogen bond between the adjacent carboxyl groups, and these groups twist by 88° (C(7)-O(1)O(2)) and 9°(C(8)O(3)O(4)) out of the plane of a benzene ring, so that the repulsion between the oxygen atoms is reduced, as is shown in Fig. 4.

The crystal structure is shown in Figs. 5 and 6. Each molecule is joined, through three kinds of hydrogen bonds (2.60, 2.64 and 2.67 Å), with three neighboring molecules. These hydrogen bonds are formed between the carboxyl groups related by the center of symmetry and the two-fold axis, as is usual in carboxylic acids.

The molecular dimensions and packing obtained by the refinement for the pseudo-cell do not seem to contain unacceptable results in comparison with other carboxylic acids[1–10] with a benzene ring. A crystal structure analysis based on the real cell is now in progress.