(*b*) *Entre deux plans successifs:* Étant donnée la disposition des molécules dans les miroirs $z=0$ et $z=\frac{1}{2}$ (Fig. 2) il apparaît que la seule distance critique entre atomes appartenant à des couches voisines est C(1)–Cl'' dont la valeur est 3,28 Å. Cette distance est inférieure à la somme des rayons de van der Waals si l'on admet pour ceux-ci les valeurs de 1,8 Å pour l'ion Cl^- et 1,7 Å pour la demi-épaisseur du cycle pyridinique. Bien que les valeurs couramment admises pour ces rayons de van der Waals comportent une certaine imprécision, il semble qu'il y ait ici une légère contraction dans l'empilement des couches moléculaires. On peut attribuer ce fait à une certaine attraction électrostatique entre l'ion chlore Cl'' chargé négativement et les charges positives apparaissant sur l'atome N par suite de la fixation du proton ou sur l'atome C(2) par suite de la mobilité des liaisons π conjuguées de la chaîne latérale et du noyau (effet de résonance).

La facilité de clivage des cristaux perpendiculairement à l'axe *c* indique, par ailleurs, que les forces de cohésion entre couches moléculaires parallèles sont relativement faibles.

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The Structure of p-Nitrobenzoic Acid*

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The structure of *p*-nitrobenzoic acid has been refined with the help of three-dimensional data. The molecular dimensions are compared with those of *p*-nitroaniline and *p*-nitrophenol; the variations are interpreted as being due to minor contributions from quinonoid valence-bond structures in the latter compounds.

Introduction

A preliminary structure analysis of *p*-nitrobenzoic acid was reported earlier (Sakore & Pant, 1965). A three-dimensional refinement of the structure has now been undertaken because the precision of the preliminary analysis was too low to reveal the influence of the substituted groups on the molecular geometry. The structures of some substituted nitrobenzenes having electron donor groups like NH_2 and OH in *para* positions have recently been determined with great accuracy (Trueblood, Goldish & Donohue, 1961; Coppens & Schmidt, 1965*a*, *b*); it is of interest to compare the molecular dimensions in these structures with those in *p*-nitrobenzoic acid, which has an electron withdrawing substituent (carboxyl group) *para* to the nitro group.

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Table 1. *Final atomic and thermal parameters*

Atom	*x*	*y*	*z*	*B*
C(1)	0·4157 ± 0·0004	0·4986 ± 0·0011	0·0897 ± 0·0003	2·83 Å
C(2)	0·4899 ± 0·0004	0·6398 ± 0·0011	0·1299 ± 0·0003	3·34
C(3)	0·4584 ± 0·0004	0·8352 ± 0·0011	0·1696 ± 0·0003	3·23
C(4)	0·3530 ± 0·0004	0·8894 ± 0·0011	0·1659 ± 0·0003	3·30
C(5)	0·2787 ± 0·0004	0·7479 ± 0·0011	0·1272 ± 0·0003	3·47
C(6)	0·3101 ± 0·0004	0·5507 ± 0·0011	0·0885 ± 0·0003	2·99
C(7)	0·4538 ± 0·0004	0·2883 ± 0·0011	0·0486 ± 0·0003	3·10
N	0·3185 ± 0·0004	0·0898 ± 0·0009	0·2093 ± 0·0002	3·78
O(1)	0·5464 ± 0·0003	0·2422 ± 0·0008	0·0492 ± 0·0002	3·87
O(2)	0·3802 ± 0·0003	0·1559 ± 0·0008	0·0144 ± 0·0002	3·79
O(3)	0·3823 ± 0·0003	0·1767 ± 0·0008	0·2508 ± 0·0002	4·56
O(4)	0·2310 ± 0·0003	0·1699 ± 0·0008	0·1987 ± 0·0002	4·34
H(1)	0·4115 ± 0·0026	0·0382 ± 0·0065	−0·0076 ± 0·0015	3·80

Experimental

The crystal data reported earlier (Sakore & Pant, 1965) are: $a=12{\cdot}97$, $b=5{\cdot}07$, $c=21{\cdot}43$ Å; $\beta=96{\cdot}4°$; space group, $A2/a$; $\varrho_o=1{\cdot}600$ g.cm^{-3}, $\varrho_c=1{\cdot}585$ g.cm^{-3} for $Z=8$; μ for Cu $K\alpha$, 13·8 cm^{-1}.

Table 2. *Observed and calculated structure factors*

The low angle reflexions not shown in the table are cut off by the beam stop.

h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc
2	0	0	22.9	24.8	8	0	22	13.3	-13.0	8	0	$\overline{20}$	23.8	-19.2	7	1	5	17.2	-16.7
4	0	0	9.5	0.4	10	0	2	9.5	- 7.5	8	0	$\overline{22}$	16.2	-10.9	8	1	5	11.1	-19.6
6	0	0	12.4	-11.2	10	0	4	<9.1	- 1.6	10	0	$\bar{2}$	<8.0	- 2.7	9	1	5	<4.0	0.0
8	0	0	4.8	2.7	10	0	6	40.0	-44.3	10	0	$\bar{4}$	13.3	-12.0	10	1	5	20.2	19.2
10	0	0	6.7	- 7.1	10	0	8	67.7	67.2	10	0	$\bar{6}$	<8.0	- 0.8	11	1	5	41.9	37.1
12	0	0	24.6	-23.9	10	0	10	44.8	39.2	10	0	$\bar{8}$	<8.0	- 1.8	12	1	5	11.4	13.3
14	0	0	9.5	- 9.0	10	0	12	10.5	3.0	10	0	$\overline{10}$	11.4	11.1	13	1	5	10.5	12.3
0	0	6	4.8	1.7	10	0	14	9.5	10.5	10	0	$\overline{12}$	10.5	10.9	14	1	5	2.9	- 2.7
0	0	8	21.9	-17.5	12	0	2	<9.2	- 2.3	10	0	$\overline{14}$	12.4	14.7	1	1	7	63.9	69.7
0	0	10	6.7	- 3.3	12	0	4	14.3	-16.6	10	0	$\overline{16}$	7.6	7.4	2	1	7	51.5	60.4
0	0	12	11.4	- 5.4	12	0	6	<8.0	5.4	10	0	$\overline{18}$	56.2	-48.7	3	1	7	11.4	14.0
0	0	14	13.3	-13.0	12	0	8	14.3	-14.3	12	0	$\bar{2}$	24.7	-20.9	4	1	7	49.6	-43.8
0	0	16	13.3	11.5	12	0	10	20.0	20.6	12	0	$\bar{4}$	17.1	-20.1	5	1	7	50.5	-45.5
0	0	18	9.5	- 8.2	12	0	12	<6.9	4.7	12	0	$\bar{6}$	24.7	-22.7	6	1	7	15.3	-11.4
0	0	20	13.3	14.4	12	0	14	7.6	7.4	12	0	$\bar{8}$	23.7	19.8	7	1	7	4.8	4.2
0	0	22	5.7	7.4	12	0	16	7.6	4.8	12	0	$\overline{10}$	23.7	17.7	8	1	7	<4.0	4.6
0	0	24	39.1	32.2	14	0	2	<8.0	0.4	12	0	$\overline{12}$	9.5	- 9.3	9	1	7	4.8	5.5
0	0	26	25.7	-19.2	14	0	4	11.4	-11.0	12	0	$\overline{14}$	17.2	15.3	10	1	7	<4.2	- 8.7
2	0	2	143.0	258.7	14	0	6	9.5	- 8.8	12	0	$\overline{16}$	26.7	-24.7	11	1	7	<4.5	3.6
2	0	4	5.7	- 7.1	2	0	$\bar{2}$	23.8	-24.0	14	0	$\bar{2}$	<8.0	- 4.3	12	1	7	<4.5	- 0.3
2	0	6	9.5	6.8	2	0	$\bar{4}$	9.5	8.4	14	0	$\bar{4}$	22.9	-21.2	13	1	7	<4.0	2.6
2	0	8	<6.0	- 2.3	2	0	$\bar{6}$	13.3	-13.5	14	0	$\bar{6}$	20.0	18.9	14	1	7	<4.0	1.9
2	0	10	88.6	-90.9	2	0	$\bar{8}$	<7.0	3.9	0	1	1	9.5	- 9.1	1	1	9	10.5	- 8.7
2	0	12	37.2	38.9	2	0	$\overline{10}$	97.2	-97.2	0	1	3	44.8	-37.3	2	1	9	23.8	25.0
2	0	14	18.1	21.2	2	0	$\overline{12}$	20.0	-23.1	0	1	5	166.8	173.9	3	1	9	62.0	55.4
2	0	16	18.1	22.5	2	0	$\overline{14}$	79.1	-80.4	0	1	7	20.0	20.9	4	1	9	<3.8	- 1.2
2	0	18	21.0	23.0	2	0	$\overline{16}$	10.5	-13.0	0	1	9	16.2	- 9.0	5	1	9	25.7	27.9
2	0	20	10.5	10.5	2	0	$\overline{18}$	21.0	22.5	0	1	11	<4.0	0.0	6	1	9	13.3	-14.5
2	0	22	3.8	5.6	2	0	$\overline{20}$	9.5	- 9.1	0	1	13	11.4	- 8.1	7	1	9	9.5	11.9
2	0	24	14.3	13.5	2	0	$\overline{22}$	27.6	26.5	0	1	15	6.7	8.5	8	1	9	19.1	-23.2
2	0	26	9.5	9.1	2	0	$\overline{24}$	13.3	-12.1	0	1	17	6.7	10.7	9	1	9	<5.8	5.8
4	0	2	31.5	-29.1	2	0	$\overline{26}$	18.1	-18.8	0	1	19	17.2	19.3	10	1	9	<6.2	6.5
4	0	4	104.9	104.5	4	0	$\bar{2}$	11.4	11.4	0	1	21	22.9	-20.5	11	1	9	10.5	11.0
4	0	6	<7.0	5.1	4	0	$\bar{4}$	85.8	-90.5	4	1	1	45.8	-46.6	12	1	9	<6.0	- 1.5
4	0	8	38.1	-32.9	4	0	$\bar{6}$	31.5	26.8	5	1	1	23.8	24.6	13	1	9	7.6	8.6
4	0	10	19.1	-16.4	4	0	$\bar{8}$	87.7	-78.4	6	1	1	19.1	-23.4	14	1	9	4.8	- 5.6
4	0	12	63.9	-60.6	4	0	$\overline{10}$	25.7	25.0	7	1	1	52.4	-53.4	1	1	11	18.1	20.4
4	0	14	19.1	20.1	4	0	$\overline{12}$	114.4	-109.4	8	1	1	49.6	45.6	2	1	11	14.3	17.8
4	0	16	9.5	11.2	4	0	$\overline{14}$	<9.2	3.9	9	1	1	10.5	11.1	3	1	11	<6.0	4.3
4	0	18	10.5	7.9	4	0	$\overline{16}$	19.1	20.6	10	1	1	14.3	-15.0	4	1	11	<6.4	0.4
4	0	20	10.5	- 7.0	4	0	$\overline{18}$	6.7	- 6.5	11	1	1	14.3	-10.9	5	1	11	20.0	19.6
4	0	22	15.3	15.9	4	0	$\overline{20}$	8.0	0.4	12	1	1	10.5	-10.3	6	1	11	<6.9	9.2
6	0	2	<6.0	7.1	4	0	$\overline{22}$	6.7	6.8	13	1	1	18.1	17.9	7	1	11	26.6	-25.7
6	0	4	22.4	-33.5	6	0	$\bar{2}$	48.6	-47.9	14	1	1	7.3	- 8.1	8	1	11	19.1	17.7
6	0	6	27.6	-29.2	6	0	$\bar{4}$	14.3	-15.7	15	1	1	9.5	- 9.4	9	1	11	20.0	21.0
6	0	8	19.1	-21.5	6	0	$\bar{6}$	63.9	68.9	3	1	3	2.9	- 2.6	10	1	11	20.0	-20.9
6	0	10	9.5	-11.3	6	0	$\bar{8}$	34.3	34.1	4	1	3	10.5	- 8.0	11	1	11	<6.2	0.1
6	0	12	19.1	-18.2	6	0	$\overline{10}$	<6.8	- 3.1	5	1	3	18.1	-15.4	12	1	11	<5.5	1.2
6	0	14	<8.0	4.0	6	0	$\overline{12}$	13.3	13.1	6	1	3	25.7	-25.9	1	1	13	<5.6	- 2.5
6	0	16	11.4	-13.9	6	0	$\overline{14}$	13.3	17.4	7	1	3	16.2	19.9	2	1	13	18.1	19.5
6	0	18	9.5	7.1	6	0	$\overline{16}$	7.4	0.1	8	1	3	24.8	20.1	3	1	13	29.6	31.9
6	0	20	15.3	-17.9	6	0	$\overline{18}$	10.5	12.1	9	1	3	51.5	44.6	4	1	13	8.6	10.1
6	0	22	14.3	-16.2	6	0	$\overline{20}$	<7.4	0.4	10	1	3	35.3	33.3	5	1	13	10.5	11.9
8	0	2	11.4	-13.2	6	0	$\overline{22}$	9.5	14.6	11	1	3	38.1	32.6	6	1	13	<6.5	- 6.2
8	0	4	28.6	-33.7	8	0	$\bar{2}$	39.1	-33.3	12	1	3	11.4	-13.8	7	1	13	10.5	-10.4
8	0	6	42.9	46.3	8	0	$\bar{4}$	82.9	83.9	13	1	3	<3.7	- 3.1	8	1	13	15.2	16.5
8	0	8	60.1	61.1	8	0	$\bar{6}$	9.5	8.2	14	1	3	<3.9	2.9	9	1	13	41.9	-38.5
8	0	10	14.3	-17.4	8	0	$\bar{8}$	45.8	+46.6	15	1	3	4.8	6.0	10	1	13	17.2	15.1
8	0	12	11.4	9.3	8	0	$\overline{10}$	16.2	13.7	2	1	5	29.6	-21.2	11	1	13	<5.8	- 0.1
8	0	14	<8.0	- 4.2	8	0	$\overline{12}$	13.3	12.2	3	1	5	62.0	-54.1	12	1	13	8.6	- 9.9
8	0	16	15.3	13.3	8	0	$\overline{14}$	<9.2	0.0	4	1	5	17.2	-17.8	1	1	15	41.0	36.5
8	0	18	14.3	-10.7	8	0	$\overline{16}$	36.2	35.4	5	1	5	<3.9	5.6	2	1	15	19.1	-21.7
8	0	20	<6.9	2.0	8	0	$\overline{18}$	9.5	- 8.9	6	1	5	11.4	-13.7	3	1	15	20.0	19.2
4	1	15	<7.0	- 5.8	12	1	$\bar{7}$	24.4	-11.0	0	2	2	6.7	- 8.5	6	2	8	13.3	-14.9
5	1	15	<7.0	- 6.2	13	1	$\bar{7}$	7.6	- 7.7	0	2	4	47.7	-44.4	7	2	2	7.6	- 9.8
6	1	15	<6.8	-12.2	1	1	$\bar{9}$	73.4	73.7	0	2	6	32.4	-26.9	7	2	4	24.8	-24.8
7	1	15	<6.5	- 1.9	2	1	$\bar{9}$	69.6	-67.1	0	2	8	6.6	- 4.6	7	2	6	21.0	-22.1
8	1	15	<6.4	- 1.2	3	1	$\bar{9}$	16.2	13.9	0	2	10	65.7	63.1	7	2	8	<6.0	- 3.2
1	1	17	9.5	-13.0	4	1	$\bar{9}$	<6.0	- 5.0	0	2	12	40.0	43.4	7	2	10	<6.2	- 3.9
2	1	17	<7.4	9.6	5	1	$\bar{9}$	43.9	-40.9	0	2	14	13.3	19.1	7	2	12	16.2	-20.2
3	1	17	21.9	23.1	6	1	$\bar{9}$	<6.4	7.8	0	2	16	40.0	38.4	7	2	14	23.8	26.3
4	1	17	<7.0	- 0.2	7	1	$\bar{9}$	<6.8	7.8	0	2	18	9.5	-12.2	7	2	16	14.3	-17.2
5	1	17	16.2	16.2	8	1	$\bar{9}$	28.6	25.4	1	2	0	95.3	88.3	8	2	2	4.8	12.6
6	1	17	10.5	-12.8	9	1	$\bar{9}$	25.7	20.7	2	2	0	33.4	-34.9	8	2	4	<6.4	1.7
7	1	17	19.1	-17.7	10	1	$\bar{9}$	<8.0	3.9	3	2	0	27.6	-21.4	8	2	12	16.2	-20.0
8	1	17	14.3	-12.1	11	1	$\bar{9}$	19.1	-18.1	4	2	0	41.9	-41.5	8	2	14	12.4	-15.0
9	1	17	6.7	- 7.6	12	1	$\bar{9}$	<7.1	- 2.9	5	2	0	25.7	-23.3	11	2	2	17.2	-21.6
1	1	19	21.0	22.9	13	1	$\bar{9}$	15.3	-15.0	6	2	0	26.7	23.8	11	2	4	14.3	19.8
2	1	19	17.6	16.0	1	1	$\overline{11}$	15.3	18.2	7	2	0	30.5	-21.9	12	2	2	12.4	15.2
3	1	19	<7.6	- 0.8	2	1	$\overline{11}$	15.4	17.2	8	2	0	19.0	-20.2	1	2	$\bar{2}$	22.9	-26.1
4	1	19	<7.6	1.0	3	1	$\overline{11}$	21.9	-14.7	9	2	0	9.0	-10.6	2	2	$\bar{2}$	83.9	-70.1
5	1	19	<7.4	4.2	4	1	$\overline{11}$	21.0	21.1	10	2	0	26.7	26.2	3	2	$\bar{2}$	40.0	33.6
6	1	19	8.6	11.9	5	1	$\overline{11}$	6.7	7.2	11	2	0	19.1	20.9	4	2	$\bar{2}$	6.7	-11.5
7	1	19	<7.0	2.5	6	1	$\overline{11}$	<6.1	5.2	12	2	0	31.6	28.4	5	2	$\bar{2}$	<5.4	0.0
4	1	$\bar{1}$	9.5	-10.3	7	1	$\overline{11}$	<6.5	0.0	1	2	2	34.4	-29.7	6	2	$\bar{2}$	15.3	-14.9
5	1	$\bar{1}$	93.4	-99.4	8	1	$\overline{11}$	27.6	29.5	1	2	4	35.3	32.9	7	2	$\bar{2}$	<5.6	5.8
6	1	$\bar{1}$	35.3	25.0	9	1	$\overline{11}$	14.3	-14.3	1	2	6	<4.8	- 9.9	8	2	$\bar{2}$	21.9	20.2
7	1	$\bar{1}$	23.8	21.9	10	1	$\overline{11}$	<7.0	- 0.5	1	2	8	21.9	25.6	9	2	$\bar{2}$	15.3	16.4
8	1	$\bar{1}$	<6.7	- 1.3	11	1	$\overline{11}$	14.3	13.8	1	2	10	<5.7	- 1.8	10	2	$\bar{2}$	36.2	35.4
9	1	$\bar{1}$	15.3	-15.0	12	1	$\overline{11}$	15.3	-18.0	1	2	12	16.2	-19.3	11	2	$\bar{2}$	32.4	27.9
10	1	$\bar{1}$	10.5	-15.3	13	1	$\overline{11}$	10.5	- 7.5	1	2	14	20.0	19.6	1	2	$\bar{4}$	95.3	86.3
11	1	$\bar{1}$	13.3	15.9	14	1	$\overline{11}$	6.7	6.4	1	2	16	21.9	-21.9	2	2	$\bar{4}$	47.7	-44.0
12	1	$\bar{1}$	10.5	-11.1	15	1	$\overline{11}$	4.8	7.1	1	2	18	26.7	-28.4	3	2	$\bar{4}$	21.0	20.3
13	1	$\bar{1}$	16.2	-16.5	1	1	$\overline{13}$	16.2	-18.3	1	2	20	12.4	13.4	4	2	$\bar{4}$	9.5	6.9
4	1	$\bar{3}$	20.2	-20.2	2	1	$\overline{13}$	7.6	9.0	2	2	2	18.1	- 8.7	5	2	$\bar{4}$	26.7	-33.7
5	1	$\bar{3}$	20.2	-24.0	3	1	$\overline{13}$	7.7	-11.9	2	2	4	<5.5	- 7.9	6	2	$\bar{4}$	<5.4	- 4.3
6	1	$\bar{3}$	<6.0	7.3	4	1	$\overline{13}$	21.0	-25.9	2	2	6	19.1	24.3	7	2	$\bar{4}$	22.9	-27.9
7	1	$\bar{3}$	24.8	-25.1	5	1	$\overline{13}$	15.3	-18.5	2	2	8	<5.5	- 1.9	8	2	$\bar{4}$	<5.8	- 3.8
8	1	$\bar{3}$	11.4	14.7	6	1	$\overline{13}$	23.8	26.1	2	2	10	10.5	16.5	9	2	$\bar{4}$	15.3	20.0
9	1	$\bar{3}$	9.5	-10.2	7	1	$\overline{13}$	9.5	10.6	2	2	12	<5.7	1.1	10	2	$\bar{4}$	<6.2	8.3
10	1	$\bar{3}$	<7.2	1.8	8	1	$\overline{13}$	<8.0	- 2.8	2	2	14	12.4	17.7	11	2	$\bar{4}$	11.4	-13.0
11	1	$\bar{3}$	<7.4	8.5	9	1	$\overline{13}$	50.5	46.0	2	2	16	9.6	9.8	2	2	$\bar{6}$	38.1	-30.1
12	1	$\bar{3}$	14.3	16.0	10	1	$\overline{13}$	39.0	-34.2	2	2	18	29.6	-29.3	2	2	$\bar{6}$	<5.0	- 1.0
13	1	$\bar{3}$	9.5	- 9.7	11	1	$\overline{13}$	7.7	10.4	2	2	20	12.4	17.3	3	2	$\bar{6}$	66.7	-57.4
3	1	$\bar{5}$	30.1	-29.0	13	1	$\overline{13}$	7.6	8.4	3	2	2	28.6	24.8	4	2	$\bar{6}$	<6.1	9.5
4	1	$\bar{5}$	<5.8	- 5.8	1	1	$\overline{15}$	<7.0	1.4	3	2	4	53.4	50.1	5	2	$\bar{6}$	6.4	- 8.5
5	1	$\bar{5}$	<6.0	9.3	2	1	$\overline{15}$	11.4	16.4	3	2	6	19.1	22.2	6	2	$\bar{6}$	23.8	-24.5
6	1	$\bar{5}$	31.5	25.3	3	1	$\overline{15}$	11.6	-14.2	3	2	8	42.9	43.7	7	2	$\bar{6}$	15.0	-14.5
7	1	$\bar{5}$	21.0	-22.5	4	1	$\overline{15}$	<6.8	3.0	3	2	10	<6.4	- 9.3	8	2	$\bar{6}$	13.3	19.6
8	1	$\bar{5}$	<6.4	0.5	5	1	$\overline{15}$	7.6	5.0	3	2	12	23.8	26.9	9	2	$\bar{6}$	13.3	-16.2
9	1	$\bar{5}$	<6.6	- 1.4	6	1	$\overline{15}$	7.7	-10.9	3	2	14	6.7	12.7	10	2	$\bar{6}$	14.3	-20.4
10	1	$\bar{5}$	<7.0	1.4	7	1	$\overline{15}$	11.4	8.7	3	2	16	11.4	16.7	11	2	$\bar{6}$	9.5	9.1
11	1	$\bar{5}$	19.1	-20.6	8	1	$\overline{15}$	20.9	-19.8	3	2	18	13.3	-13.2	1	2	$\bar{8}$	<5.5	- 6.4
12	1	$\bar{5}$	<7.4	- 4.0	9	1	$\overline{15}$	20.0	22.4	4	2	2	3.8	- 7.3	2	2	$\bar{8}$	76.3	70.9
13	1	$\bar{5}$	11.4	-10.5	10	1	$\overline{15}$	<8.0	2.4	4	2	4	83.9	68.8	3	2	$\bar{8}$	81.0	81.1
1	1	$\bar{7}$	22.9	-17.8	11	1	$\overline{15}$	<7.5	3.5	4	2	6	18.1	-21.7	4	2	$\bar{8}$	19.1	22.0
2	1	$\bar{7}$	32.4	-26.1	12.	1	$\overline{15}$	<6.0	5.0	4	2	8	28.6	33.6	5	2	$\bar{8}$	33.4	-35.1
3	1	$\bar{7}$	95.3	93.0	13	1	$\overline{15}$	7.6	6.7	4	2	10	<6.2	4.9	6	2	$\bar{8}$	<5.8	7.0
4	1	$\bar{7}$	41.9	-42.9	1	1	$\overline{17}$	20.0	-20.2	4	2	12	13.3	17.3	7	2	$\bar{8}$	<6.0	- 2.5
5	1	$\bar{7}$	<7.2	- 3.0	2	1	$\overline{17}$	7.5	4.0	5	2	2	40.0	-37.5	8	2	$\bar{8}$	26.7	-31.4
6	1	$\bar{7}$	23.8	-23.4	3	1	$\overline{17}$	16.2	-20.0	5	2	4	29.6	-27.6	9	2	$\bar{8}$	46.7	46.9
7	1	$\bar{7}$	27.6	-27.5	4	1	$\overline{17}$	13.3	-17.4	5	2	6	26.7	30.3	10	2	$\bar{8}$	29.6	-29.0
8	1	$\bar{7}$	9.5	-10.4	5	1	$\overline{17}$	40.0	-41.3	5	2	8	11.4	10.3	1	2	$\overline{10}$	90.6	88.4
9	1	$\bar{7}$	16.2	-17.2	6	1	$\overline{17}$	7.4	9.6	6	2	2	11.4	-14.2	2	2	$\overline{10}$	58.1	57.2
10	1	$\bar{7}$	<7.4	9.1	7	1	$\overline{17}$	18.2	17.1	6	2	4	29.6	24.8	3	2	$\overline{10}$	13.3	-17.0
11	1	$\bar{7}$	<7.4	4.3	0	2	0	83.0	-93.9	6	2	6	29.6	33.4	4	2	$\overline{10}$	10.5	-15.2

Table 2 (*cont.*)

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
5	2	$\overline{10}$	10.5	12.0	1	3	13	19.0	-17.8	0	4	8	6.7	- 9.2	10	4	12	16.2	9.3
6	2	$\overline{10}$	<6.6	0.9	2	3	13	49.5	-52.1	0	4	10	9.6	- 8.5	11	4	2	<6.4	1.1
7	2	$\overline{10}$	34.3	34.0	3	3	13	29.5	-27.7	0	4	12	9.6	- 9.3	11	4	4	12.4	- 9.5
8	2	$\overline{10}$	41.0	-42.9	1	3	$\bar{1}$	11.4	-12.9	1	4	0	6.7	- 7.3	1	4	$\bar{2}$	15.2	18.4
1	2	$\overline{12}$	<6.6	- 6.6	2	3	$\bar{1}$	47.7	51.4	2	4	0	6.7	7.7	1	4	$\bar{4}$	19.1	-18.8
2	2	$\overline{12}$	<5.6	1.4	3	3	$\bar{1}$	11.4	-11.3	3	4	0	<6.4	0.6	1	4	$\bar{6}$	<6.4	- 1.7
3	2	$\overline{12}$	<5.8	4.4	4	3	$\bar{1}$	41.9	41.0	4	4	0	9.5	12.2	1	4	$\bar{8}$	9.5	-13.3
4	2	$\overline{12}$	32.4	33.3	5	3	$\bar{1}$	24.8	25.8	5	4	0	9.6	12.1	1	4	$\overline{10}$	6.7	- 7.1
5	2	$\overline{12}$	21.0	-25.5	6	3	$\bar{1}$	<6.2	- 3.9	6	4	0	22.9	-22.9	1	4	$\overline{12}$	<6.5	- 4.7
6	2	$\overline{12}$	17.2	-22.0	7	3	$\bar{1}$	16.3	-18.8	7	4	0	36.2	36.7	1	4	$\overline{14}$	<6.6	3.0
7	2	$\overline{12}$	9.5	-12.5	1	3	$\bar{3}$	33.4	-37.7	8	4	0	19.1	-21.3	1	4	$\overline{16}$	19.1	-17.7
1	2	$\overline{14}$	14.8	-16.3	2	3	$\bar{3}$	14.3	-14.7	9	4	0	11.4	-10.8	2	4	$\bar{2}$	8.6	10.8
2	2	$\overline{14}$	<6.0	2.4	3	3	$\bar{3}$	13.3	17.8	1	4	2	<4.5	1.8	2	4	$\bar{4}$	11.4	9.2
3	2	$\overline{14}$	11.4	6.3	4	3	$\bar{3}$	8.6	10.9	1	4	4	10.5	-10.9	2	4	$\bar{6}$	7.6	7.3
0	3	1	47.7	-45.4	5	3	$\bar{3}$	22.9	-25.7	1	4	6	18.1	-19.7	2	4	$\bar{8}$	6.7	- 7.5
0	3	3	17.2	17.0	6	3	$\bar{3}$	<6.2	- 1.3	1	4	8	4.8	- 5.8	2	4	$\overline{16}$	9.5	-12.0
0	3	5	35.9	-36.6	7	3	$\bar{3}$	<6.4	4.5	1	4	10	8.6	12.6	2	4	$\overline{18}$	7.6	7.5
0	3	7	9.5	13.8	8	3	$\bar{3}$	35.3	-33.0	1	4	18	12.4	9.1	2	4	$\overline{20}$	28.6	25.4
0	3	9	4.8	- 3.9	9	3	$\bar{3}$	38.1	32.8	2	4	2	<4.8	3.8	3	4	$\bar{2}$	9.5	- 7.7
0	3	11	45.8	-48.7	10	3	$\bar{3}$	25.7	-28.8	2	4	4	29.6	35.1	3	4	$\bar{4}$	5.5	- 7.4
0	3	13	9.5	11.9	1	3	$\bar{5}$	<5.5	- 7.4	2	4	6	18.1	-22.7	3	4	$\bar{6}$	9.5	11.1
1	3	1	26.7	22.9	2	3	$\bar{5}$	24.8	25.6	2	4	8	43.9	-46.1	3	4	$\bar{8}$	<6.2	0.6
2	3	1	20.0	24.5	3	3	$\bar{5}$	14.3	-16.3	3	4	2	4.8	4.1	3	4	$\overline{10}$	<6.4	- 4.3
3	3	1	12.4	18.0	4	3	$\bar{5}$	20.0	-22.2	3	4	4	9.5	- 9.8	3	4	$\overline{12}$	13.3	-13.7
4	3	1	12.4	14.2	5	3	$\bar{5}$	15.3	-15.7	3	4	6	9.6	10.0	3	4	$\overline{16}$	9.5	- 9.6
5	3	1	31.5	32.7	6	3	$\bar{5}$	29.6	-29.1	3	4	8	41.0	-43.7	3	4	$\overline{18}$	11.4	11.5
7	3	1	9.5	8.9	7	3	$\bar{5}$	41.0	41.1	3	4	10	<6.4	2.4	4	4	$\bar{2}$	12.4	12.9
1	3	3	25.7	29.8	8.	3	$\bar{5}$	31.1	-42.6	3	4	12	10.6	-12.9	4	4	$\bar{4}$	14.3	16.6
2	3	3	12.4	-12.5	9	3	$\bar{5}$	<6.4	- 6.4	3	4	16	9.5	10.7	4	4	$\bar{6}$	3.8	5.0
3	3	3	26.7	27.5	10	3	$\bar{5}$	12.0	13.0	4	4	2	4.8	4.6	4	4	$\bar{8}$	12.4	14.8
4	3	3	31.5	34.2	11	3	$\bar{5}$	19.1	17.0	4	4	4	7.6	8.4	4	4	$\overline{10}$	4.8	- 3.5
5	3	3	14.3	14.8	1	3	$\bar{7}$	15.3	-18.9	4	4	6	12.4	11.1	4	4	$\overline{12}$	<6.6	0.2
6	3	3	15.3	-16.0	2	3	$\bar{7}$	21.0	-24.7	4	4	8	7.6	- 7.5	4	4	$\overline{14}$	16.2	-13.4
1	3	5	25.7	32.3	3	3	$\bar{7}$	24.8	-23.9	4	4	10	13.3	-14.1	4	4	$\overline{18}$	13.3	14.5
2	3	5	13.2	- 8.4	4	3	$\bar{7}$	28.6	25.8	5	4	2	<5.2	- 3.2	5	4	$\bar{2}$	21.9	22.1
3	3	5	14.3	17.4	5	3	$\bar{7}$	6.8	8.2	5	4	4	7.6	7.1	5	4	$\bar{4}$	<6.4	4.1
4	3	5	<5.4	- 2.4	6	3	$\bar{7}$	<6.2	- 6.3	5	4	6	7.6	- 7.2	5	4	$\bar{6}$	17.2	19.2
5	3	5	<5.6	- 5.8	7	3	$\bar{7}$	<6.4	- 6.9	5	4	8	9.6	9.1	5	4	$\bar{8}$	6.0	- 6.1
6	3	5	18.1	22.2	8	3	$\bar{7}$	13.3	14.1	5	4	10	16.2	-16.1	5	4	$\overline{10}$	25.7	-22.3
7	3	5	<6.2	- 7.9	9	3	$\bar{7}$	7.0	6.3	5	4	12	<6.4	1.1	5	4	$\overline{12}$	23.8	18.4
9	3	5	16.2	-15.4	10	3	$\bar{7}$	15.0	14.2	5	4	14	17.6	-15.1	5	4	$\overline{16}$	9.1	9.1
1	3	7	15.3	17.6	11	3	$\bar{7}$	23.8	22.7	5	4	18	18.1	11.6	5	4	$\overline{18}$	3.8	4.6
2	3	7	<6.0	1.9	1	3	$\bar{9}$	<6.0	7.1	6	4	2	5.0	4.3	6	4	$\bar{2}$	<6.6	- 3.4
3	3	7	<6.2	- 0.5	2	3	$\bar{9}$	18.4	21.7	6	4	4	11.4	13.1	6	4	$\bar{4}$	15.3	16.4
4	3	7	26.7	24.2	3	3	$\bar{9}$	22.9	-19.4	6	4	6	4.9	- 3.4	6	4	$\bar{6}$	5.7	7.3
5	3	7	<6.4	6.2	9	3	$\bar{9}$	7.6	8.8	6	4	8	<5.5	- 0.4	6	4	$\overline{12}$	4.8	- 4.2
6	3	7	<6.8	0.0	10	3	$\bar{9}$	15.3	12.4	6	4	10	<6.0	4.9	7	4	$\bar{2}$	18.1	-16.3
7	3	7	16.2	-16.6	2	3	$\overline{11}$	21.0	-23.4	6	4	12	11.4	6.8	7	4	$\bar{4}$	16.2	15.0
8	3	7	21.9	19.7	3	3	$\overline{11}$	14.3	-14.5	7	4	2	7.6	8.4	7	4	$\bar{6}$	10.5	- 8.9
9	3	7	13.3	-11.8	1	3	$\overline{13}$	7.6	- 6.8	7	4	4	7.6	7.5	7	4	$\bar{8}$	7.6	- 7.2
10	3	7	<6.6	4.6	2	3	$\overline{13}$	22.9	25.6	7	4	12	10.4	6.5	8	4	$\bar{2}$	9.5	10.8
11	3	7	13.3	-11.7	3	3	$\overline{13}$	32.4	-36.8	8	4	2	40.0	-35.0	8	4	$\bar{4}$	3.8	- 3.3
1	3	9	31.5	31.6	4	3	$\overline{13}$	20.0	24.0	8	4	4	5.7	4.2	9	4	$\bar{2}$	<6.6	- 2.2
2	3	9	<6.2	1.1	1	3	$\overline{15}$	35.3	34.5	8	4	10	7.6	5.9	9	4	$\bar{4}$	8.6	- 6.4
3	3	9	<6.4	5.9	2	3	$\overline{15}$	32.3	31.9	9	4	2	9.5	9.3	9	4	$\bar{6}$	<6.6	3.0
4	3	9	17.2	19.7	6	3	$\overline{15}$	16.2	14.8	9	4	10	4.8	- 5.6	9	4	$\bar{8}$	9.5	- 7.4
5	3	9	12.4	-15.6	9	3	$\overline{15}$	13.3	-10.4	10	4	2	9.5	-10.9	9	4	$\overline{10}$	16.2	-11.9
6	3	9	30.6	29.4	0	4	0	5.7	- 6.3	10	4	4	18.1	-14.6	9	4	$\overline{14}$	9.6	- 6.7
10	3	9	25.7	-19.9	0	4	2	31.4	32.5	10	4	6	4.7	4.4	10	4	$\overline{12}$	23.8	18.2
1	3	11	43.7	-37.7	0	4	4	8.6	-11.6	10	4	8	6.8	- 3.7	11	4	$\bar{8}$	20.0	-14.4
3	3	11	31.5	26.7	0	4	6	30.5	-34.8	10	4	10	13.4	10.1					

The three-dimensional data were collected from zero to fourth layer equi-inclination Weissenberg photographs taken with Cu radiation and the crystal oscillated along the b axis. The crystal had the cross-section $0{\cdot}3\times0{\cdot}4$ mm^2 and the length 0·7 mm. Intensities of 589 reflexions out of the 1394 possible for these layers were estimated visually, using extended spots in higher layer photographs; intensities were corrected for the Lorentz–polarization–Tunell factor (Cochran, 1948) as well as for the effect of spot extension (Phillips, 1956); absorption was neglected.

Refinement of the structure

The refinement was started with the atomic parameters and the overall temperature factor (3·2 Å^2) obtained from the preliminary analysis (Sakore & Pant, 1965). All calculations were carried out on the CDC 3600-160A computer of the Tata Institute of Fundamental Research, Bombay. The atomic scattering factors were obtained from the analytical constants given in Moore's (1963) tables. The atomic parameters and the individual isotropic temperature factors of the atoms were refined by four cycles of least squares. The 620 structure factors used for the refinement as well as for estimating R included those unobserved reflexions for which F_c was initially greater than the minimum observable value; 202 appears to be subject to extinction and was excluded from all calculations. To start with, R was 0·151. After the third cycle of refinement, the changes in atomic parameters were less than 0·0001 and R was 0·114. A (010) difference Fourier map at this stage revealed the hydrogen atom of the carboxylic group clearly. The hydrogen atom was then included in the

calculations and one more cycle of least squares refinement was performed. The final R was 0·112. The final atomic and thermal parameters are given in Table 1 and F_o and F_c in Table 2.

The standard deviations of atomic parameters and the interatomic distances were estimated (Lipson & Cochran, 1953) assuming $p=5$ Å^2 and $\sigma(F)/|F|$ to be equal to R (0·112); the deviations in bond angles were estimated by the method of Darlow (1960).

Description of the structure and discussion

The intramolecular bond lengths and angles are shown in Fig. 1(*a*) and listed in Table 3. The equations of the various planes referred to the a', b, c orthogonal axes, the angles between them and the deviations of the atoms from the different planes are shown in Table 4. The best plane through the benzene ring was obtained by the method of Schomaker, Waser, Marsh & Bergman (1959).

The average C–C bond length in the benzene ring is 1·396 Å, which is not significantly different from the value (1·393 Å) found in crystalline benzene (Cox, Cruickshank & Smith, 1958). The different bond lengths in the ring are not significantly different from the average value, except probably the C(1)–C(2) bond length (1·411 Å), which differs from the average by about 2σ. It thus appears that the general picture in

Table 3. *Intramolecular bond lengths and angles*

	Bond lengths		Bond angles
C(1)–C(2)	1·411 ± 0·008 Å	O(1)–C(7)–O(2)	123·9 ± 0·5°
C(2)–C(3)	1·396 ± 0·008	C(1)–C(7)–O(2)	115·0 ± 0·5
C(3)–C(4)	1·388 ± 0·008	C(1)–C(7)–O(1)	121·1 ± 0·5
C(4)–C(5)	1·397 ± 0·008	C(7)–C(1)–C(2)	118·2 ± 0·5
C(5)–C(6)	1·389 ± 0·008	C(7)–C(1)–C(6)	120·2 ± 0·5
C(6)–C(1)	1·393 ± 0·008	C(6)–C(1)–C(2)	121·2 ± 0·5
C(1)–C(7)	1·501 ± 0·008	C(1)–C(2)–C(3)	120·2 ± 0·5
C(4)–N	1·480 ± 0·007	C(2)–C(3)–C(4)	117·3 ± 0·5
N–O(3)	1·228 ± 0·006	C(3)–C(4)–C(5)	122·8 ± 0·5
N–O(4)	1·203 ± 0·006	C(4)–C(5)–C(6)	119·7 ± 0·5
C(7)–O(1)	1·222 ± 0·007	C(1)–C(6)–C(5)	118·6 ± 0·5
C(7)–O(2)	1·319 ± 0·007	C(3)–C(4)–N	117·7 ± 0·4
O(2)–H(1)	0·969 ± 0·034	C(5)–C(4)–N	119·3 ± 0·4
O(1)–O(2)	2·653 ± 0·006	C(4)–N–O(3)	118·3 ± 0·4
$(x,y,z)(1-x,\bar{y},\bar{z})$		C(4)–N–O(4)	117·3 ± 0·4
		O(3)–N–O(4)	124·1 ± 0·4
		C(7)–O(2)–H(1)	105·2 ± 2·1
		C(7)–O(2)–O(1)	113·4 ± 0·5

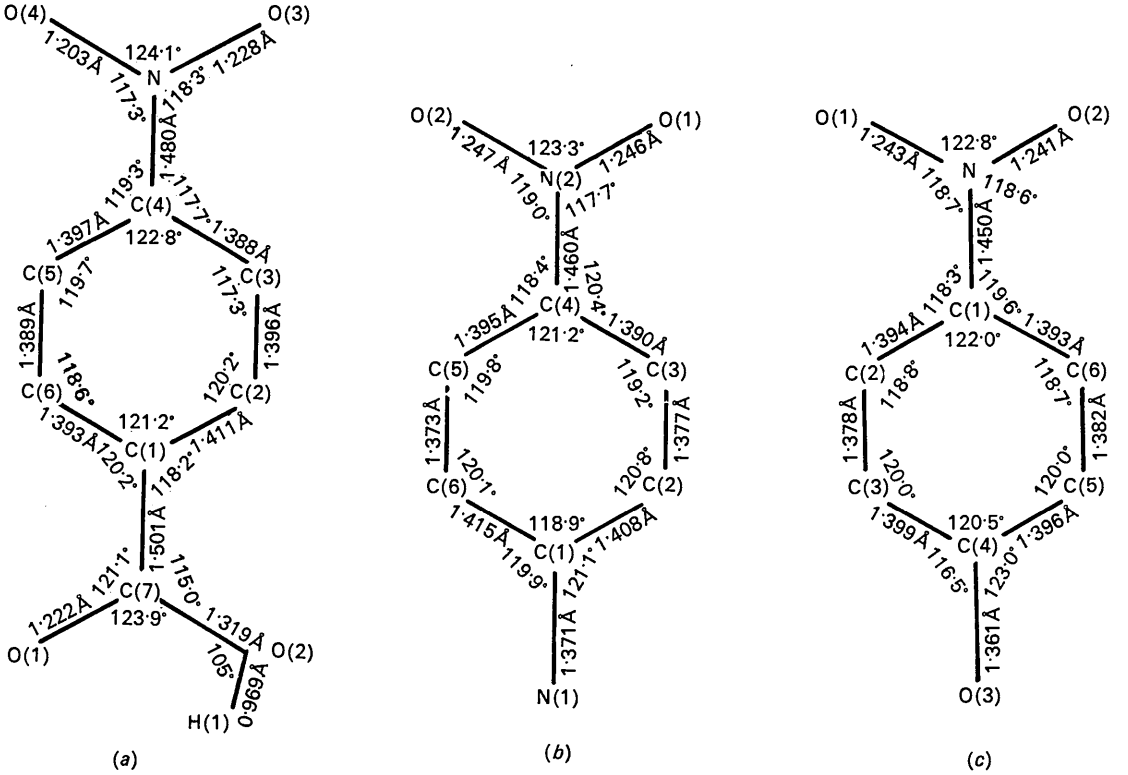

Fig. 1. Bond lengths and angles in (*a*) *p*-nitrobenzoic acid, (*b*) *p*-nitroaniline and (*c*) *β-p*-nitrophenol.

the case of *p*-nitrobenzoic acid is different from what is found in the cases of *p*-nitroaniline (Trueblood *et al.*, 1961) and *p*-nitrophenol (Coppens *et al.*, 1965*a*,*b*). The molecular dimensions of *p*-nitroaniline and *β*-*p*-nitrophenol are shown in Fig. 1(*b*) and (*c*) respectively along with the molecular dimensions of *p*-nitrobenzoic acid for comparison. In these compounds, the bonds parallel to the long axes of the molecules are significantly shorter than the other bonds of the benzene ring. These conclusions are in accord with the predictions of the resonance theory. In both *p*-nitroaniline and *p*-nitrophenol, one expects cooperative electronic interaction of the *para* substituents; this implies minor contributions from quinonoid valence bond structures. However, no such contribution is expected in the case of *p*-nitrobenzoic acid since the *para* substituents in this case are both electron withdrawing groups.

It may be of interest to compare the distribution of bond distances in the benzene ring in *p*-nitrobenzoic acid with that in the case of mono-substituted benzenes having electron withdrawing substituents (Trotter, 1960). Unlike the case of *p*-nitrobenzoic acid, the bonds parallel to the long axis in the benzene ring are larger than the other four bonds in monosubstituted benzenes; Trotter (1960) suggests that the bond length variations in mono-substituted benzenes can be explained by differences in hybridization of the carbon *σ* orbitals.

The carbon atom C(7) is not significantly out of the plane of the benzene ring (Table 4). However, the oxygen atoms O(1) and O(2) of the carboxylic group are

Table 4. *Equations of planes*

(1) Benzene ring	$-0{\cdot}0690x-0{\cdot}6738y+0{\cdot}7357z+1{\cdot}0945=0$
(2) Nitro group	$-0{\cdot}3012x-0{\cdot}6681y+0{\cdot}6802z+2{\cdot}1913=0$
(3) Carboxylic group	$-0{\cdot}0461x-0{\cdot}6352y+0{\cdot}7708z+0{\cdot}9015=0$
(4) Plane through O(1), O(2) and centre of the dimer	$-0{\cdot}0568x-0{\cdot}6087y+0{\cdot}7913z+0{\cdot}9384=0$

Angles between different planes

	(2)	(3)	(4)
(1)	13·7°	3·3°	5·0°
(2)	—	—	—
(3)	—	—	2·4°

Deviations of atoms from different planes (Å)

	Planes			
Atom	(1)	(2)	(3)	(4)
C(1)	0·007		−0·067	
C(2)	−0·000			
C(3)	−0·020			
C(4)	0·018	0·121		
C(5)	−0·001			
C(6)	−0·003			
C(7)	0·011			−0·021
N	0·049			
O(1)	0·024			
O(2)	−0·060			
O(3)	−0·282			
O(4)	0·221			
H	—			−0·081
Dimer centre	−0·118		−0·047	

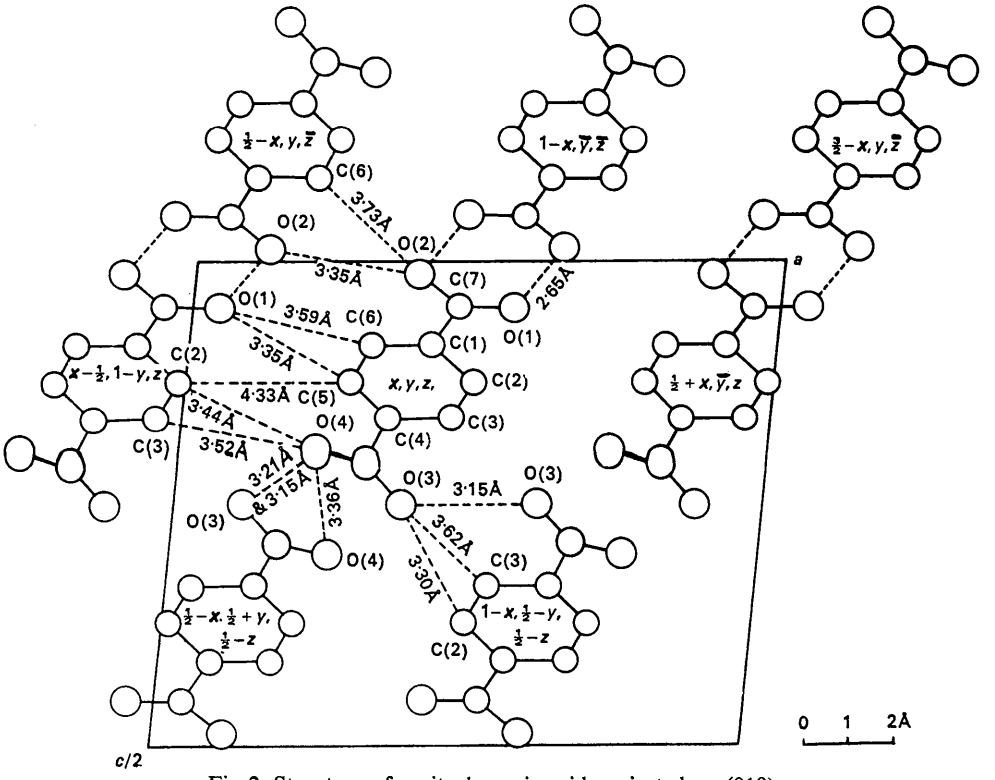

Fig. 2. Structure of *p*-nitrobenzoic acid projected on (010).

respectively 0·024 Å and −0·060 Å out of this plane; this is partly because the carboxylic group makes a small angle of 3·3° with the benzene ring plane and may partly be due to the fact that the oxygen atoms are drawn towards the centre of the dimer, presumably because of the force exerted by the hydrogen bonds. This is indicated by the unequal distances of the two oxygen atoms from the benzene ring plane and by the fact that the distance of the centre of the dimer from the plane of the carboxylic group (−0·047 Å) is less than its distance from the benzene ring plane (−0·118 Å).

The observed value of 1·501 Å for the exocyclic C–C bond length is the expected single bond distance between the carbon atoms in sp^2 states of hybridization. This indicates that there is no appreciable degree of conjugation across this bond; this fact again suggests that as expected, there is no contribution from quinonoid valence bond structure in *p*-nitrobenzoic acid.

The nitrogen atom N is −0·047 Å out of the plane of the benzene ring. The atom C(4) is 0·121 Å away from the plane of the nitro group; the angle between this and the benzene ring plane is 13·7°. The C–N bond length of 1·480 Å is significantly longer than the corresponding bond lengths in *p*-nitroaniline (1·460 Å), *α-p*-nitrophenol (1·442 Å) and *β-p*-nitrophenol (1·450 Å). The mean of the two N–O bond lengths in *p*-nitrobenzoic acid is 1·216 Å. In *p*-nitroaniline and *β-p*-nitrophenol, the corresponding lengths after correction for thermal motion are 1·247 Å and 1·242 Å respectively. There is pronounced torsional oscillation of the nitro group in these latter structures and the correction for torsional effects in N–O distances is about 0·018 Å. In the present study, anisotropic thermal parameters have not been obtained; however, the individual isotropic temperature factors for the oxygen atoms of the nitro group (Table 1) are not much larger than the values for other atoms; there is thus no suggestion of pronounced torsional oscillation of the nitro group. It thus appears that the N–O bonds in *p*-nitrobenzoic acid are significantly shorter than those in *p*-nitroaniline and *p*-nitrophenol. The shortening of the N–O bonds and the elongation of the C–N bond in *p*-nitrobenzoic acid from the corresponding values in *p*-nitroaniline and *p*-nitrophenol further supports the view that the bond length variations are due to minor contributions from quinonoid valence bond structures in the latter compounds.

The arrangement of molecules in the unit cell is shown in Fig. 2, in which the principal intermolecular distances are also shown.

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Refinement of the Structure of $Cd(NO_3)_2.4H_2O$

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The crystal structure of $Cd(NO_3)_2.4H_2O$ has been refined by least-squares calculations to a final *R* index of 8·4%. The estimated standard deviations of atomic coordinates ranged from 0·0005 to 0·0042. The essential features of the original structure are confirmed. Cadmium–oxygen distances (from water molecules) have values of 2·26 and 2·33 Å, and cadmium–oxygen distances (from nitrate groups) are 2·44 and 2·59 Å. The structure consists of tetra-aquocadmium nitrate groups joined by hydrogen bonds.

Introduction

This structure was first solved from Patterson and electron density projections (Matković & Ribar, 1963). The results obtained may be summarized as follows: The cadmium–oxygen (water) distances are smaller than cadmium–oxygen (nitrate group) distances and the compound was described as tetra-aquocadmium nitrate. Two of the three oxygen atoms from the nitrate group are much closer to the cadmium atom than the

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