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A Three-Dimensional Refinement of the Crystal Structure of 4-Nitroaniline

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The structure of 4–nitroaniline has been refined three-dimensionally with visually-estimated Cu $K\alpha$ data. Positional and thermal parameters for the carbon, nitrogen, and oxygen atoms, and positional parameters for the hydrogen atoms, were obtained by least squares. The standard errors in bond lengths not involving hydrogen are 0·006–0·007 Å; the corresponding errors in bond angles are about 0·4°. Intramolecular bond distances were corrected for the effects of thermal motion. These distances are discussed, and compared with those in related molecules. The molecular geometry supports the view that there is a small but significant contribution of a quinonoid resonance form to the structure of the molecule, although the amino group appears to interact with the aromatic ring to a greater extent than does the nitro group. The nitro group shows a pronounced torsional oscillation, the r.m.s. amplitude being about 14°; this sort of motion seems to be characteristic of nitro groups in aromatic compounds.

Introduction

A determination of the crystal structure of 4-nitroaniline by means of the three axial projections was reported earlier (Donohue & Trueblood, 1956; Abrahams & Robertson, 1948). However, the precision of that determination was low, the estimated standard deviations of the bond distances being of the order of 0·035 Å. Because of the importance of this molecule in discussions of the effects of electron-withdrawing and electron-attracting substituents in aromatic rings, a careful three-dimensional refinement of the structure was deemed worthwhile in order to provide greatly increased precision.

Experimental

Needle-like crystals of 4-nitroaniline were grown by controlled cooling of a hot aqueous solution. Sections cut from selected crystals of regular cross section and thickness 0·5 mm. or less were mounted on fibers or in thin-walled glass capillaries. Equi-inclination multiple-film Weissenberg photographs were taken with Cu $K\alpha$ radiation about the a and b axes, with $h=0$ to 4 and $k=0$ to 3 respectively. Intensities were estimated visually by comparison with calibrated intensity strips, with corrections made for spot extension on upper-layer photographs (Phillips, 1956); no corrections were made for absorption. About 75% of the reflections in the sphere of reflection were accessible for measurement; of these, 826 were observed while the intensities of an additional 274 were below the minimum observable limit. The intensities were multiplied by the Lorentz-polarization-Tunell correction factors to convert them to relative values of F^2; the corresponding F^2 values were then correlated to put data from different films on the same scale. An additional 9($hk0$) reflections with $h \geqq 5$ and $k \geqq 5$ observed by Abrahams and Robertson were also then included after the suitable correlations had been made.

Cell constants a_0, c_0, and β were determined from single-crystal oscillation photographs taken on the Weissenberg camera with the film in the Straumanis arrangement. The determination of b_0 was done with less precision from several high-angle reflections on an ($0kl$) Weissenberg photograph. The resulting values, with their e.s.d.'s, are:

$$a_0=12\cdot336\pm0\cdot008,\quad b_0=6\cdot07\pm0\cdot02,$$
$$c_0=8\cdot592\pm0\cdot005\ \text{Å},$$
and
$$\beta=91\cdot45^\circ\pm0\cdot05^\circ\quad(\cos\beta=-0\cdot0252)$$
$$(\text{Cu}\ K\alpha_1=1\cdot54051\ \text{Å},\ \text{Cu}\ K\alpha_2=1\cdot54433\ \text{Å}).$$

The space group is $P2_1/n-(C_{2h}^5)$.

Refinement of the structure

All calculations except some of those involved in analysis of the molecular vibrations were carried out on SWAC (Sparks *et al.*, 1956). The form factors used for oxygen, nitrogen, and hydrogen were those of McWeeny (1951), and that for carbon was taken from an average curve based on McWeeny's (1954) trigonal-carbon curves. Least squares refinement was started with the final position parameters from the two-dimensional study (Donohue & Trueblood, 1956), and with three averaged anisotropic temperature fac-

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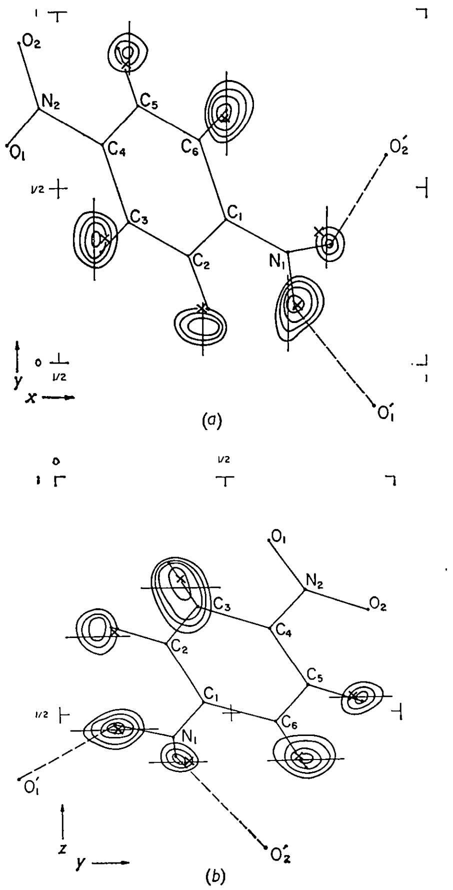

Fig. 1. Composite difference map, contributions of heavy atoms calculated with parameters from seventh least-squares. Contours drawn at intervals of 0·05 e.Å^{-3}, starting at 0·3 e.Å^{-3}. The lines through each atom in a given drawing indicate the position of the section used for this atom in the other drawing; (*a*) view along (100); (*b*) view along (001). The dots show the positions first assumed for the hydrogen atoms, as described in the text, and the crosses their positions as indicated by the least-squares calculations.

tors divined from that work; the hydrogen atoms were omitted. Because of the limitations of the computer, it was not possible to evaluate and solve the full matrix of the least squares equations. Consequently, the block-diagonal approximation (3 × 3 and 6 × 6 blocks for each atom, 1 × 1 for the scale factor) was used, with partial shift factors of 0·75, 0·375, and 0·20 for the x_i, B_{jk} and B_{jj}, and the scale factor, respectively, to insure convergence. The weighting system used was that of Hughes (1941), with $F_{\min} = 2·5$. Those reflections which were too weak to be observed were included with $F_0 = F'_{\min.}/\sqrt{3}$, and $F'_{\min.}$ varying over a factor of about ten in the different regions of reciprocal space; part of this variation was due to variation in exposure times.

After seven cycles of least squares, *R* (observed reflections only) had dropped from 0·227 to 0·119. At this juncture a three-dimensional difference synthesis was calculated, revealing the positions of the six hydrogen atoms of the molecule unambiguously (Fig. 1). These were the six highest peaks in the map, between 0·4 and 0·5 e.Å^{-3}; the only other two peaks above about 0·3 e.Å^{-3} were clearly spurious, one being about 0·5 Å from C2 and inside the aromatic ring and the other being about 0·3 Å from C5 on a line toward C6. The six hydrogen atoms were then inserted in the structure factor calculations. The positions of the four ring-hydrogens were so chosen that they were about 1·0 Å from the nearest carbon atom, with bond angles of about 120°; the two amino-hydrogens were placed at the positions found for them in the difference map. Isotropic temperature factors of 4·5 Å^2 for the four ring hydrogens and 6·0 Å^2 for the two amino hydrogens were assigned. Inclusion of these hydrogen atoms, with no other changes, led to a pronounced improvement both in R and in the weighted sum of the squares of the residuals (Fig. 2). Four more least squares cycles then completed the refinement. The positions of all sixteen atoms were refined, but the temperature factors of the hydrogen atoms were held constant; the course of the refinement to the point of convergence ($R = 9·5\%$) is indicated in Fig. 2. Each of the hydrogen atoms moved somewhat closer to the atom to which it is bonded (Table 7), although none of the individual changes can be considered significant, since none was more than about 2σ. At the end, the average C–H and N–H distance was 0·85 Å, with an e.s.d. of about 0·08 Å. Bond angles involving the ring

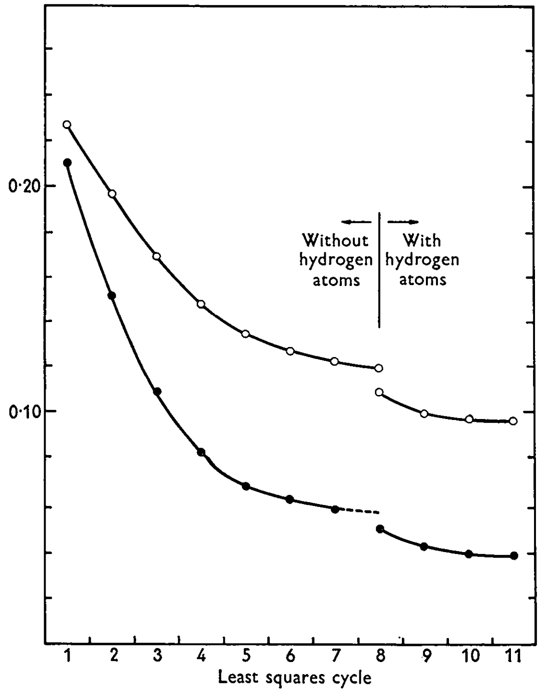

Fig. 2. Progress of refinement. Open circles: *R* (observed reflections only); filled circles: the weighted sum of the squares of the residuals (arbitrary scale).

Table 1. *Observed and calculated structure factors*

The running index is l; values of h and k for each group immediately precede that group. The central column is $10|F_o|$, the right-hand column $10F_c$. A minus sign after a value of F_o indicates that the reflection was not observed and that the value listed is $10F_{\text{min.}}/\sqrt{3}$.

0 0		
2	166	145-
4	344	295
6	36	14
8	30	26
10	51	50-
1 0		
11-	6-	6-
9-	22	20-
7-	54	54-
5-	158	140
3-	136	128-
1-	291	282
1	102	88
3	14	14
5	278	268
7	108	109-
9	16	18-
2 0		
10-	12	12-
8-	49	46
6-	99	109-
4-	56	69
2-	260	276-
	205	212
2	1444	1459-
4	5-	
6	164	150-
8	30	30-
10	6-	1
3 0		
11-	6-	9
9-	95	90-
7-	8-	8
5-	80	82
3-	115	115
1-	352	330-
1	89	72-
3	59	56-
5	101	101-
7	124	131-
9	32	33
4 0		
10-	18	16
8-	61	56
6-	50	55-
4-	67	79
2-	33	19
	17	15
2	104	109-
4	184	188
6	13	6
8	64	61
10	10	11
5 0		
9-	14	16-
7-	264	317
5-	7-	8-
3-	104	99
1-	252	277-
1	268	284
3	125	129-
5	26	22-
7	47	53
9	30	32
6 0		
10-	22	23-
8-	76	64
6-	76	77-
4-	15	17
2-	225	212
	196	171-
2	11	3
4	34	33
6	43	39
8	8-	7
7 0		
9-	75	68-
7-	60	53
5-	405	460-
3-	7-	3
1-	277	262-
1	100	117
3	44	45-
5	105	112
7	22	17
9	23	17
8 0		
8-	13	12-
6-	122	134-
4-	20	18
2-	7-	2
	327	309-
2	99	100
4	75	67
6	21	17-
8	7-	6-
9 0		
9-	15	15
7-	77	65
5-	71	67-
3-	280	285
1-	7-	1
1	198	182
3	8-	2-
5	21	18-
7	76	70-
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8-	24	24-
6-	59	50
4-	93	92
2-	22	19
	46	41
2	151	144
4	24	26-
6	85	69-
8	9	5
11 0		
7-	6-	7-
5-	42	37-
3-	33	26
1-	34	40-
1	8-	17
3	66	71-
5	8-	12-
7	10	10
12 0		
6-	58	53
4-	34	30-
2-	8-	2-
	8-	
2	30	25-
4	33	29-
6	10	9
13 0		
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3-	33	28
1-	8-	1
1	33	26-
3	7-	9-
5	6-	8
14 0		
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2-	12	8-
	46	44-
2	6-	4-
4	22	24-
15 0		
3-	9	12-
1-	37	38-
1	5-	1-
3	10	6-
0 1		
1	432	363
2	86	69-
3	270	252
4	166	150
5	139	111
6	145	125
7	14	6
8	16	16-
9	18	11-
10	70	75-
11	3-	5
1 1		
10-	7-	4
9-	8-	
8-	8-	11
7-	35	34
6-	86	80
5-	95	78-
4-	236	228-
3-	186	171
2-	120	115
1-	484	531-
	434	358
1	313	336
2	212	185-
3	56	69-
4	29	23
5	36	36
6	42	51
7	30	28-
8	9-	6
9	8-	2-
10	20	20-
2 1		
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9-	48	44-
8-	135	137-
7-	26	19-
6-	34	40-
5-	39	52
4-	172	147
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2-	458	456
1-	97	84-
	39	37-
1	580	654-
2	508	560
3	52	55
4	14	13
5	135	132-
6	38	29
7	54	52-
8	30	24-
9	8-	5-
10	7-	5-
3 1		
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9-	109	115-
8-	69	61-
7-	20	15
6-	18	18
5-	130	136-
4-	350	294-
3-	22	7-
2-	283	280
1-	137	145-
	139	130-
1	682	805
2	308	284-
3	56	52-
4	78	69
5	20	15
6	68	56-
7	26	21
8	16	5
9	8-	1-
10	6-	1-
4 1		
10-	6-	1-
9-	48	43-
8-	50	45-
7-	65	72
6-	146	151
5-	86	93
4-	42	40-
3-	184	179-
2-	92	82
1-	261	238
	338	366-
1	75	77-
2	35	31-
3	308	306
4	287	271-
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6	20	15
7	20	24
8	64	64-
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8-	34	34
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5-	36	39-
4-	7-	10-
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	67	66-
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2	24	28-
3	438	426-
4	100	99
5	22	20-
6	20	16-
7	63	73-
8	9-	9
9	28	30-
10	5-	4-
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	162	161-
1	20	17-
2	73	81
3	7-	10
4	36	37
5	42	45-
6	40	50
7	8-	2
8	34	34-
9	7-	3
7 1		
9-	36	36
8-	40	36-
7-	9-	4
6-	105	119-
5-	38	44-
4-	53	47-
3-	7-	1-
2-	46	46-
1-	63	45-
	178	159-
1	139	136-
2	38	40-
3	7-	9
4	73	62
5	141	146
6	8-	1
7	8-	3-
8	8-	4
9	67	69
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7-	9-	7-
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4-	65	68-
3-	18	23-
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	81	82-
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4	18	13
5	32	30
6	8-	7-
7	16	10-
8	20	21
9	22	23
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5-	24	20-
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8	10	7-
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7	24	24-
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	30	26
1	16	16-
2	8-	6
3	46	42
4	7-	2-
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3-	18	14
2-	12	5-
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	65	61-
1	12	6-
2	7-	3
3	6-	7-
4	53	64-
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2-	8	3-
1-	20	17-
	6-	6-
1	6-	1
2	5-	2
0 2		
	244	334-
1	62	38-
2	108	87-
3	239	209
4	34	21
5	146	137-
6	66	58
7	13	6-
8	14	17
9	45	42-
10	38	38
1 2		
10-	80	87
9-	48	52
8-	46	44-
7-	34	33-
6-	32	30
5-	152	139
4-	34	24
3-	53	49-
2-	188	188
1-	96	81-
	212	209-
1	12-	11-
2	245	252-
3	28	27-
4	86	91
5	20	6-
6	9-	3
7	30	27-
8	10-	7
9	35	38
10	36	34-
2 2		
10-	11	3
9-	71	73-
8-	45	34-
7-	33	39-
6-	9-	2-
5-	104	112
4-	192	177-
3-	200	208-
2-	145	134-
1-	200	208
	42	33
1	330	332
2	174	164
3	92	90
4	8-	9-
5	37	35-
6	70	70
7	62	64
8	10-	4-
9	25	19
3 2		
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9-	9-	9
8-	140	135-
7-	58	62-
6-	22	22-
5-	46	43-
4-	34	32
3-	294	256-
2-	94	90-
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1	28	15
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3	18	11
4	108	123
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10	9	12
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5-	24	22
4-	52	45-
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2-	268	245
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	42	34
1	86	88
2	92	91
3	383	393-
4	16	5-
5	16	5-
6	51	62
7	25	20-
8	65	61-
9	39	43-
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6-	58	68
5-	27	24
4-	134	158
3-	118	110
2-	120	123-
1-	190	189
	40	39
1	45	45
2	178	174-
3	94	93
4	118	113-
5	9-	8-
6	25	22-
7	45	43-
8	114	110-
9	40	37-
6 2		
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8-	9-	4-
7-	10-	2-
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5-	76	82-
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2	74	79
3	152	157-
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5	174	182
6	25	26-
7	49	39-
8	54	52-
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7 2		
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2	47	42
3	25	18-
4	65	68-
5	71	70
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7	45	44-
8	9-	11
9 2		
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7-	27	24
6-	12-	8
5-	12-	4
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3-	40	44-
2-	69	76-
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	22	18
1	49	51-
2	22	27-
3	10-	
4	25	19-
5	12-	16
6	54	59-
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7-	13	11-
6-	18	16-
5-	58	57-
4-	13	8
3-	13	18-
2-	25	27-
1-	40	44-
	56	60-
1	94	101-
2	45	47-
3	10-	3-
4	10-	
5	20	22-
6	20	15
7	18	18-
11 2		
7-	36	33-
6-	29	24
5-	10-	3-
4-	49	46-
3-	36	30-
2-	105	109
1-	10-	1-
	10-	1
1	47	51-
2	27	26
3	56	49
4	18	22
5	10-	5-
6	8-	
7	6-	3
12 2		
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5-	9-	
4-	9-	6-
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2-	45	44-
1-	33	43
	10-	12
1	10-	12
2	40	41
3	105	104
4	38	34
5	9-	1-
6	5-	1
13 2		
5-	25	21
4-	29	24-
3-	33	30-
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	65	67-
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2	42	43
3	45	41
4	16	17-
5	16	15-
14 2		
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3-	8-	2
2-	13	13
1-	71	76-
	42	45
1	18	24-
2	6-	
3	8-	8-
4	5-	9-
15 2		
2-	5-	1-
1-	31	30
	25	30-
1	16	14-
0 3		
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2	54	47-
3	70	72-
4	187	186-
5	52	51-
6	44	32-
7	8-	5
8	46	44-
9	38	31
10	30	35-
1 3		
10-	18	17
9-	8-	2
8-	24	14-
7-	27	28
6-	36	40
5-	119	115
4-	108	104
3-	70	73-
2-	30	26
1-	100	102-
	244	226-
1	63	66
2	150	134
3	52	54-
4	73	79-
5	168	169-
6	50	43-
7	97	94
8	29	17-
9	42	33-
10	5-	3
2 3		
10-	5-	6-
9-	29	24
8-	10-	2-
7-	29	26-
6-	51	49-
5-	24	27-
4-	34	21-
3-	18	12-
2-	20	24
1-	69	82
	178	190-
1	238	235
2	67	70
3	44	37
4	52	54-
5	8-	2-
6	166	165
7	69	68
8	33	22
9	8-	11-
10	24	30
3 3		
9-	27	29-
8-	10-	7
7-	55	60
6-	31	24
5-	52	62-
4-	35	26-
3-	60	51-
2-	94	100-
1-	18	18-
	24	33-
1	58	48
2	174	164
3	22	18
4	44	42-
5	13	10
6	98	93
7	134	134
8	13	10
9	33	28-
4 3		
9-	29	32
8-	13	15
7-	55	58-
6-	27	21-
5-	8-	3-
4-	44	42
3-	88	83
2-	6-	14
1-	81	82
	160	173-
1	30	33-
2	99	103
3	76	73-
4	39	32-
5	28	19
6	43	43
7	28	28
8	65	65-
9	30	31-
5 3		
9-	15	17-
8-	35	36-
7-	51	51
6-	51	44-
5-	97	94-
4-	31	26-
3-	80	67-
2-	8-	9-
1-	18	7-
	13	9
1	27	18-
2	73	79
3	38	30-
4	35	29-
5	27	27-
6	10-	2
7	10-	8-
8	42	45-
9	46	50-
6 3		
9-	20	19
8-	20	18-
7-	75	71-
6-	10-	8-
5-	51	46
4-	8-	5-
3-	9	1
2-	82	82-
1-	80	78-
	46	35
1	88	97-
2	42	42
3	27	19
4	27	26
5	11	30-
6	10-	8
7	15	23-
8	11	16-
9	15	19-
7 3		
9-	29	33-
8-	20	15
7-	9-	8
6-	91	89
5-	38	36-
4-	40	41
3-	20	20
2-	9-	9
1-	177	211
	31	34
1	27	20
2	22	13
3	51	49
4	84	78-
5	60	65
6	22	26-
7	9-	6
8 3		
8-	6-	1-
7-	8-	2
6-	23	23
5-	84	86
4-	10-	11
3-	13	14-
2-	22	28
1-	62	68
	126	141
1	33	30
2	53	53-
3	33	33
4	73	76
5	13	10-
6	46	44-
7	31	28
8	6-	4-
9 3		
8-	9	6
7-	8-	4-
6-	9-	4-
5-	9-	4
4-	95	92-
3-	10-	4-
2-	10-	12-
1-	51	52
	22	18
1	161	168-
2	42	43-
3	8-	7-
4	8-	6
5	42	42-
6	46	47
7	51	56-
10 3		
7-	6-	6
6-	29	28
5-	9-	2
4-	15	13-
3-	57	57-
2-	27	29-
1-	10-	
	29	24-
1	86	89-
2	104	109-
3	8-	7-
4	20	13
5	9-	7
6	71	80-
11 3		
7-	4-	1-
6-	31	26-
5-	31	23
4-	9-	7-
3-	9-	6
2-	27	31
1-	18	13
	10-	11-
1	49	46-
2	27	25-
3	64	62
4	22	23
5	13	17-
12 3		
6-	11	14
5-	6-	8
4-	8-	8-
3-	38	27-
2-	18	16
1-	12-	8
	22	21
1	11	2
2	13	15
3	40	41
4	38	38
13 3		
4-	22	21
3-	8-	10
2-	8-	
1-	29	27-
	22	17
1	8-	6-
2	8-	11
3	15	15
4	13	13
14 3		
3-	9	8-
2-	18	17-
1-	42	37
	27	30-
1	11	14
0 4		
	289	233-
1	139	112-
2	32	22
3	53	54
4	21	14-
5	197	190-
6	82	82-
7	11	16
8	8-	2-
9	21	21-
1 4		
9-	29	15-
8-	21-	25-
7-	43	47
6-	36	43
5-	100	112-
4-	64	67-
3-	107	111
2-	21-	38-
1-	28	33
	28	34
1	21-	4
2	43	41-
3	25-	13-
4	50	43-
5	121	120-
6	36	42-
7	28	29
8	21-	17
9	36	37-
2 4		
7-	22	19-
6-	25-	6
5-	25-	13
4-	122	141
3-	173	193-
2-	50	58
1-	50	57
	25-	17-
1	144	145-
2	129	131
3	25-	5
4	29-	22
5	29-	11-
6	43	45-
7	108	95
8	21-	14
9	17-	13-
3 4		
6-	32-	3
5-	32-	1-
4-	32-	23
3-	146	144
2-	27-	34
1-	27-	15
	27-	26
1	27-	6
2	73	73-
3	36	31-
4	46	50
5	32-	4-
6	36	34
7	36	36
8	21-	7
4 4		
8-	21-	5-
7-	24-	12-
6-	21-	15
5-	30	36
4-	48	48
3-	24	12
2-	158	152-
1-	79	74
	24	18
1	17-	4
2	36	36-
3	73	64
4	24	23-
5	36	31
6	36	24-
7	21-	7-
8	48	43
9	10-	17-
0 5		
1	26	31
2	24	19
3	37	44-
4	24	31
5	66	53-
6	16	19-
7	8-	6
8	6-	9
1 5		
8-	28	23
7-	28	27-
6-	57	75-
5-	71	77-
4-	43	42
3-	25-	9-
2-	25-	27-
1-	36	35-
	25-	10
1	25-	19
2	25-	10-
3	25-	31-
4	25-	16
5	25-	19
6	21-	5-
7	28	28-
8	12-	7-
2 5		
6-	21-	5
5-	25-	7-
4-	65	85-
3-	137	154
	29-	17-
1	50	59
2	29	12
3	43	55-
4	29-	21-
5	29	34
6	29	18-
3 5		
6-	26-	32-
5-	32-	12
4-	210	197
3-	109	103
2-	55	49-
1-	32-	20
	36	33
1	32-	32
2	32-	45
3	32-	16-
4	32-	19-
5	32-	18
6	46	28-
7	36	26-
4 5		
6-	21-	31
5-	17-	19-
4-	21-	
3-	21-	26
2-	97	111
1-	170	163-
	24	28
1	67	66
2	61	63
3	85	81-
4	24	14-
5	24	10
6	21-	2
7	17-	4-
5 5		
	36	13
6 5		
	91	78-
7 5		
	78	73
8 5		
	24	25-
9 5		
	24	17-
10 5		
	18	7-
0 6		
	76	80-
1	8-	
2	47	46
3	16	6-
4	63	54-
5	105	82
6	21	17
1 6		
7-	8-	11
6-	36	42-
5-	50	50-
4-	36	30-
3-	21-	17-
2-	25-	15-
1-	28	28-
	28	35-
1	25-	19-
2	25-	10
3	21-	24
4	21-	17
5	21-	22
6	16-	16-
7	8-	36
2 6		
4-	25-	6-
3-	50	61
2-	35	48
	43	54-
1	29-	
2	50	55
3	25-	12
4	25-	6-
5	29	11-
6	29	28
3 6		
6-	21-	28
5-	21-	5
4-	27-	9
	32-	29
1	32-	15
2	55	49
3	27-	31
4	27-	16-
5	21-	4-
6	36	31-
4 6		
5-	14-	11
4-	36	3-
3-	36	42
2-	17-	38-
1-	17-	14
	30	9-
1	21-	16
2	24-	20
3	30	16
4	21-	14-
5	17-	6-
6	18	15-
6 6		
	72	69
7 6		
	91	76-
0 7		
1	29	26-
2	16	13-
3	6-	1-
4	24	21
1 7		
4-	28	18-
3-	16-	11
2-	16-	22-
1-	21-	7
	21-	16-
1	57	52-
2	16-	18
3	16-	2-
4	12-	4
2 7		
	21-	2
3 7		
4-	16-	20-
	27-	18
1	27-	12-
2	27-	2-
3	27	15
4 7		
	12	21
6 7		
	12	2

hydrogen atoms did not change by as much as one e.s.d. (about 5°) but there were more significant changes in two of the angles involving the amino hydrogens, both in a reasonable direction. The C–N–H angles changed from 148° and 97° to 130° and 118°.

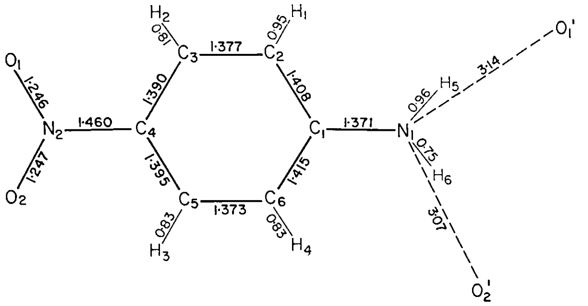

Fig. 3. Bond distances. The intramolecular distances include the corrections arising from vibrational anisotropy.

The final calculated structure factors are compared in Table 1 with the observed values. The calculated amplitude is greater than the estimated minimum observable $|F|$ for ten of the 274 unobserved reflections, but it is larger than 1·5 F_{min} for only one of these, (167), for which F_c is twice F_{min}. Table 2 gives the final positional parameters of all the atoms with their estimated standard deviations, evaluated in the least squares calculations. The atoms may be identified with the help of Fig. 3. (The numbering of the atoms has been changed from that used earlier so that the nitro group is bonded to C4.) The final temperature factors are listed in Table 3, together with the components of the corresponding vibration tensor **U** (Cruickshank, 1956a) referred to the orthogonal axial system **a***, **b**, **c**.

The direction cosines and distances from the origin of the best planes through various groups of atoms in the structure are presented in Table 4, together with the angles between these planes. These planes were evaluated by a least-squares procedure (Schomaker, Waser, Marsh, & Bergman, 1959). The direction cosines were then used with the U_{ij} of Table 3 to calculate the mean square displacements of the atoms in different directions in the structure, and were also used to calculate the displacements of the principal axes of the individual atomic vibration ellipsoids from various significant molecular directions. All of the results of these calculations will not be reproduced here, but the most significant values are given in Table 5. Examination of these values indicates that there is a considerable torsional oscillation of the

Table 2. *Final position parameters and their standard deviations**

	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C1	7293	4158	5251	0003	0009	0005
C2	6781	3063	6472	0003	0008	0005
C3	5946	4044	7243	0003	0008	0005
C4	5608	6136	6800	0003	0008	0004
C5	6087	7240	5575	0003	0008	0004
C6	6927	6279	4813	0003	0008	0005
N1	8127	3219	4502	0003	0008	0005
N2	4730	7217	7600	0003	0007	0004
O1	4295	6199	8649	0003	0006	0004
O2	4466	9093	7209	0003	0006	0004
H1	695	158	673	005	010	007
H2	564	353	798	005	010	007
H3	591	853	535	005	010	007
H4	724	695	411	005	010	007
H5	825	168	466	006	012	008
H6	855	374	401	006	012	008

* Decimal point at the left omitted.

Table 3. *Thermal vibration parameters** (×10⁴)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C1	56	301	112	−6	2	−77
C2	63	242	129	−41	−9	−8
C3	61	258	109	−13	3	89
C4	50	283	97	−5	7	57
C5	58	226	104	−15	5	46
C6	61	293	103	−1	19	39
N1	90	404	196	90	91	3
N2	63	327	117	−11	39	85
O1	98	448	181	23	140	166
O2	109	292	197	126	124	146
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	431	562	419	−11	−5	−101
C2	485	452	484	−18	−36	−9
C3	470	482	408	−25	−4	118
C4	385	528	362	−9	9	76
C5	447	422	389	−28	2	61
C6	470	547	383	−4	39	53
N1	693	754	721	171	227	0
N2	485	610	433	−21	93	113
O1	755	836	659	44	357	218
O2	840	545	721	239	312	187

* The B_{ij} are the coefficients of h_ih_j in the temperature factor expression. The U_{ij} are in $(\text{Å})^2$ and are referred to the orthogonal axes a^*, b and c. The e.s.d.'s of the B_{ii} and U_{ii} average about 5%; those of the U_{ij} $(i \neq j)$ are comparable to those of the U_{ii} in absolute magnitude, while $\sigma(B_{ij})$ for $i \neq j$ is about twice $[\sigma(B_{ii})\sigma(B_{jj})]^{\frac{1}{2}}$ because of the way in which the B_{ij} are defined.

Table 4. *Least-squares planes*†

	Direction cosines with respect to **a***	**b**	**c**	Distance from origin (Å)	Description of plane
I. Planes					
1	0·6563	0·4077	0·6348	9·648	Aromatic ring
2	0·6609	0·3791	0·6477	9·653	C4 and nitro group
3	0·5910	0·1829	0·7857	9·139	C1 and amino group
4	0·6656	0·1774	0·7249	9·578	C1, N1 and hydrogen-bonded oxygen atoms

II. Angles between normals

	2	3	4
1	1·9°	16°	14·2°
2	—	14°	(32·6°)‡
3	—	—	5·5°

† For molecule whose coordinates are given in Table 2.

‡ The angle between planes 2 and 4 involves the C–NO_2 plane in the two molecules containing O1′ and O2′ (these molecules are parallel to each other).

nitro group about the C–N bond, with a small additional wagging of the entire nitro group. The amino nitrogen atom, N1, has a considerable vibration normal to the C–N bond, with the chief motion normal to the molecular plane; since the thermal parameters for the hydrogen atoms cannot be determined from our data, it is not possible to say whether there is additional tosional motion here as well.

Table 5. *Some approximate mean-square displacements* (Å^2 × 10^3)

	Approximate direction of displacement*		
Atom	Normal to molecular plane	In plane, normal to bond	Parallel to bond
O1	116	074	035
O2	123	046	041
N2	061	(*a*) 059 (O1) (*b*) 038 (O2) (*c*) 042 (C4)	(*a*) 033 (O1) (*b*) 056 (O2) (*c*) 048 (C4)
C4	044	039 (N2)	044 (N2)
N1	100	074	043
C1	039	060 (N1)	042 (N1)

* Values parallel and normal to bonds for C1 and C4 are given only for the C–N bonds. The atoms listed beside certain values in this table indicate the direction of the bond in question.

It is clear from Table 5 that the molecule as a whole cannot be considered as a rigid body, but it seemed possible that the aromatic ring itself could be so regarded, at least to a first approximation.

Consequently the thermal parameters of the six carbon atoms were used in the determination by least squares of overall translational and librational tensors (Cruickshank, 1956b); the center of mass was taken as the (unweighted) average of the atomic positions (excluding the hydrogen atoms). The results are presented in Table 6. The translational motion is nearly isotropic, with the r.m.s. displacements varying only by about 10%, and the libration is small, the r.m.s. amplitude being slightly less than 4° about **a*** and appreciably less about the other axes. The r.m.s. amplitude of libration of the aromatic ring about the normal to the molecular plane is somewhat less than 4°, and the consequent corrections to the C–C bond distances are very small, about 0·003 Å. That this analysis was not unreasonable was indicated by the fact that of the 36 calculated U_{ij} evaluated for the six carbon atoms from the tensors of Table 6, only 2 differed by as much as twice the e.s.d. from the observed value.

Table 6. *Translational and librational tensors for aromatic ring considered as a rigid body*†

$$\mathbf{T} = \begin{array}{ccc} 0·0430 & -0·0018 & 0·0012\ \text{Å}^2 \\ & 0·0448 & 0·0043 \\ & & 0·0358 \end{array} \qquad \boldsymbol{\omega} = \begin{array}{ccc} 15 & -1 & 5\ (^\circ)^2 \\ & 4 & 5 \\ & & 2 \end{array}$$

† $\bar{\sigma}(T_{ij}) \sim 0·002$ Å^2 and $\bar{\sigma}(\omega_{ij}) \sim 4$ (°)^2. The axes here are **a***, **b**, and **c**.

Table 7. *Intramolecular distances and angles**

	Distance (Å)		
Atoms	Uncorr.	Corr.†	E.s.d.
C1–C2	1·405	1·408	0·006
C2–C3	1·374	1·377	0·007
C3–C4	1·387	1·390	0·006
C4–C5	1·392	1·395	0·006
C5–C6	1·370	1·373	0·007
C6–C1	1·412	1·415	0·007
C1–N1	1·353	1·371	0·007‡
C4–N2	1·454	1·460	0·007‡
N2–O1	1·227	1·246	0·007‡
N2–O2	1·229	1·247	0·007‡
C2–H1	0·95		0·06
C3–H2	0·81		0·06
C5–H3	0·83		0·06
C6–H4	0·83		0·06
N1–H5	0·96		0·07
N1–H6	0·75		0·07
O1 . . . H2	2·40	(2·34)§	
O2 . . . H3	2·45	(2·42)	
H1 . . . H5	2·4	(2·5)	
H4 . . . H6	2·5	(2·6)	

Atoms	Angle
C6–C1–C2	118·9°
C1–C2–C3	120·8
C2–C3–C4	119·2
C3–C4–C5	121·2
C4–C5–C6	119·8
C5–C6–C1	120·1
C2–C1–N1	121·2
C6–C1–N1	119·9
C3–C4–N2	120·4
C5–C4–N2	118·4
C4–N2–O1	117·7
C4–N2–O2	119·0
O1–N2–O2	123·3

* The atoms are identified in Fig. 3; the numbering has been changed from that of the two-dimensional study in order to conform more with chemical convention. The e.s.d.'s of the bond angles at carbon atoms are about 0·4°, those at N are about 0·35°. Bond angles involving hydrogen atoms are given in Fig. 4; their e.s.d. is about 5°.

† Corrected for librational and torsional effects (see text).

‡ Including an arbitrary uncertainty of 0·005 Å in the correction for thermal motion.

§ For some distances involving hydrogen atoms, two values are given. The first is that found if one accepts the hydrogen positions of Table 2; the second (in parentheses) is that corresponding to the same bond angles for the hydrogen atoms, but a C–H distance of 1·09 Å and an N–H distance of 1·02 Å.

Table 8. *Deviation of atoms* (Å) *from least-squares planes**

	Plane			
Atom	1	2	3	4
C1	+**0·005**		+**0·005**	−**0·038**
C2	−**0·005**			
C3	−**0·001**			
C4	+**0·008**	+**0·001**		
C5	−**0·008**			
C6	+**0·002**			
N1	+0·022		−**0·018**	+**0·061**
N2	+0·019	−**0·002**		
O1	−0·004	+**0·001**		
O2	+0·061	+**0·001**		
O1′	+0·494		−0·034	−**0·009**
O2′	−0·614		−0·324	−**0.014**
H1	−0·10			
H2	+0·04			
H3	+0·05			
H4	+0·03			
H5	+0·22		+**0·01**	+0·09
H6	−0·17		**0·00**	+0·02

* Bold face type indicates atom was used to define the plane. O1′ and O2′ are the atoms hydrogen-bonded to the amino group. The planes are identified in Table 4.

Corrections to the N–O and C–N distances arising from the motions implied by the displacements of Table 5 are more significant. These corrections were evaluated by standard methods (Cruickshank, 1956c) and amounted to 0·006 Å for the C4–N2 bond, 0·018 Å for the C1–N1 bond, and 0·019 and 0·018 Å for the N2–O1 and N2–O2 bonds respectively. Table 7 gives the uncorrected and corrected bond distances, and the bond angles (for which the corrections were small and were assumed negligible), together with the e.s.d.'s of these quantities. The corrected values of these molecular parameters are given also in Fig. 3. The displacements of various atoms from the least-squares planes of Table 4 are given in Table 8.

Discussion

The molecular structure

The molecule very nearly has a two-fold axis collinear with the C–N bonds. The two nitrogen atoms are just significantly out of the plane of the aromatic ring, by about 0·02 Å (in the same direction); the angle of the C1–N1 bond with the ring plane is 0·7°, that of the C4–N2 bond is 0·4°. The symmetry would be *mm*2 were it not for these small distortions and the tip of the nitro and amino groups relative to the plane of the aromatic ring (Table 4). These groups are twisted about the C–N bonds respectively 1·9° and 16°; viewed from outside the molecule, these twists are in the same direction. The aromatic ring is itself planar, although the deviations of C4 and C5, each 0·008 Å and in opposite directions, approach the limit of 2σ, accepted as the criterion of 'possible significance'. The nitro group is planar with the attached carbon, as is the amino group with its attached carbon. Although the precision of location of the hydrogen atoms is low, the amino group is clearly not pyramidal with angles near tetrahedral, for that configuration requires one hydrogen atom to be moved about 0·8 Å (some 10σ) from its observed position, or both to be moved about 0·4 Å in the same direction. It is suggestive that the principal motion of the amino-nitrogen atom, corresponding to the rather high r.m.s. amplitude of vibration of 0·32 Å, is roughly normal to the plane of the amino group (the direction differs by about 22° from the normal but the precision of location of the principal axes of thermal motion is low with these visual data, and the data of Tables 3 and 4 may be used to calculate that the r.m.s. amplitude in the direction strictly normal to the plane is 0·31 Å, not significantly different). To the extent that the attached hydrogen and carbon atoms do not move with the nitrogen in this motion, the configuration approaches the tetrahedral at the nitrogen atom when this atom is at the extremes of its principal vibration, for in the pyramidal structure with about 110° angles it should be about 0·35 Å from the plane of the other three atoms. However, since the phenol oxygen atom of β-4-nitrophenol (Coppens, 1960) is also 'wagging' appreciably at room temperature with the principal motion also normal to the aromatic ring plane, the motion of N1 in the present study is probably not directly related to the trigonal hybridization of the atom.

The average C–C distance is 1·393 Å, identical to the value found in crystalline benzene (Cox, Cruickshank, & Smith, 1958). However, the bonds parallel to the long axis of the molecule are significantly shorter than the average, in accord with the predictions of resonance theory which would suggest minor contributions from quinonoid valence bond structures. Of the other four bonds, the pair near the nitro group have the average value, while those near the amino group are significantly longer than the average. It seems more than coincidence that this same general picture, with however smaller departures from the average, has been found by Coppens (1960) in his careful study of both the α- and β-forms of 4-nitrophenol. It does not seem worthwhile to speculate quantitatively about bond orders or the relative contributions of different valence bond forms in view of the arbitrariness of the standards used in such a discussion. However, in both 4-nitroaniline and 4-nitrophenol, one expects cooperative electronic interaction of the *p*-substituents, with a greater effect anticipated in the former compound. It is noteworthy that the distribution of bond distances in the aromatic ring in these two compounds is just the opposite of that pointed out by Trotter (1960; see especially his Table 3) for many monosubstituted benzenes and alkylbenzenes. In all of his examples, which invariably involved electron-withdrawing substituents, the 2–3 and 5–6 bonds were *longer* than the other four, with the average discrepancy for ten compounds being 0·04 Å, equal in magnitude (but opposite in sign) to the variation found in the present structure. Although the precision of most of the determinations cited by Trotter is rather low, with an optimistic average e.s.d. in a bond length being perhaps 0·015 to 0·02 Å, the average values for all ten compounds are probably significant.

The C–NH_2 distance of 1·371 Å agrees well with that found by Brown and Marsh (1960) in 2-amino-3-methylbenzoic acid (which is not a zwitterion), 1·367 ± 0·003 Å without correction for librational effects. There are no other precise values of aromatic C–NH_2 distances with which to compare that found here. Some related distances have been summarized elsewhere (Trotter, 1960; Brown, 1949; *Tables of Interatomic Distances*, 1958) but most of these are imprecise (with e.s.d.'s of at least 0·02 Å and usually more) or involve amide nitrogens, –NH_3^+, or a heterocyclic ring. The distance found is significantly longer than that suggested by Truter (1960) for a single bond between a trigonal nitrogen and a trigonal carbon, about 1·32–1·33 Å as found in many amides and related species, but is more nearly comparable to that actually found for C–N bonds in many unsubstituted heteroaromatic rings, reported values varying from 1·334 to 1·36 Å (Bak, Hansen, & Rastrup-Andersen, 1954; Wheatley, 1957 and 1960). We estimate that a sigma bond between a trigonal nitrogen and a trigonal carbon should be about 1·41 ± 0·02 Å, if one accepts a singlebond radius for trigonal carbon of about 0·735 ± 0·010 Å and for trigonal nitrogen of about 0·675 ± 0·015 Å; careful measurements of bond distances in a N-methyl pyridinium salt or a related species might give a better value for the latter radius. If these values are accepted, then there is a significant degree of double-bond character in the C–NH$_2$ bond, as indeed is expected if the configuration at the nitrogen atom is planar.

The C–N bond length of 1·460 Å at the nitro group is slightly shorter than the average of 1·48 Å found for a number of nitro aromatic hydrocarbons (Trotter, 1960), but the difference can barely be considered significant. Similarly it is slightly longer than the values reported for the two forms of 4-nitrophenol (Coppens, 1960), 1·442 ± 0·006 and 1·445 ± 0·003. None of these quoted values has been corrected for oscillational effects, although the shortest of them was measured at about 90 °K. where the effect would be small. The variation of distance with angle of twist of the nitro group in the compounds studied by Trotter is so small that he concludes that in these compounds resonance interaction across the C–N bond even in a planar molecule such as nitrobenzene is insufficient to cause any measurable shortening of the bond distance. To the extent that the C–NO$_2$ bond length in 4-nitroaniline is shorter than these values, the shortening might well be attributed to the same electronic interaction which gives importance to quinonoid resonance forms and shortens slightly the C1–N1, C2–C3 and C5–C6 bonds. The effect, on the C4–N2 bond is, however, very small. It is striking that although the nitrogen is undoubtedly trigonally hybridized in the nitro group, its single-bond radius here is not significantly smaller than that for a trigonally hybridized carbon. There seems a simple explanation for this in terms of the sort of intramolecular nonbonded repulsions discussed by Bartell (1960). If one uses his radii for oxygen (1·13 Å) and carbon (1·25 Å), one would predict, for various possible nitrogen positions, the following sets of values for the C–N and N–O distances (in Å) and the O–N–O angle: 1·40, 1·33, 117°; 1·45, 1·30, 121°; 1·50, 1·27, 125°. In terms of this remarkably simple and useful model, then, the significant amount of π-bonding (or double bond character) in the N–O bonds which makes the N–O bonds shorter than 1·30 Å, draws the oxygen atoms in sufficiently far that the C–N bond is lengthened by O...C repulsion. Conversely, if one takes the parameters to be 1·46, 1·25 and 123°, as found in the present study, one can get a perfect fit with carbon and oxygen radii each about 0·02 Å smaller than Bartell's values. The fact that the radii must be chosen slightly smaller here may reflect a tendency toward double-bond character in the N–C bond, balanced by increased O...C repulsion. This sort of effect may also be responsible for the fact that the single-bond radius of trigonally hybridized carbon atoms in carboxyl groups and carboxylate ions, which are isoelectronic with nitro groups, is slightly greater in some environments than the usual trigonal radius of carbon. This is particularly noticeable in oxalic acid and its derivatives (Robertson, 1960; Ayerst & Duke, 1954; Ahmed & Cruickshank, 1953; and *Tables of Interatomic Distances*, 1958) but is not unique to them.

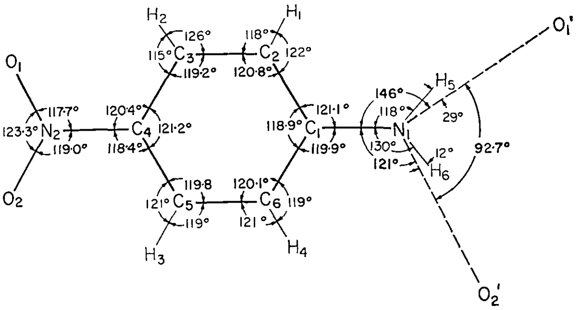

Fig. 4. Bond angles.

The pronounced torsional oscillation of the nitro group in 4-nitroaniline about the C–N bond corresponds to a r.m.s. amplitude of oscillation of nearly 14°. A straightforward calculation employing the classical approximation for the relation between the average amplitude and the average frequency for an angular oscillation (sec e.g. Cruickshank, 1956d) indicates that the corresponding frequency of this motion should be about 57 cm.$^{-1}$; a more rigorous calculation by summing appropriately weighted squares of amplitudes for different energy levels gives essentially the same result and indicates that the classical approximation is a very good one here (since $h\nu \sim 0{\cdot}28kT$). This frequency might be observable in the far infrared, or, by combination, in more accessible regions.

Few of the reported structural studies of aromatic nitro compounds have been carried out with anisotropic or even individual isotropic temperature factors, so it is not possible to check whether there is this sort of torsional oscillation in most of these structures. However, for all of those for which data are available, the motion of the nitro group seems remarkably similar. Thus for β-4-nitrophenol (Coppens, 1960), the published U_{ij} indicate that at room temperature the two oxygens of the nitro group have a mean square amplitude normal to the plane nearly twice that of the nitrogen atom, the absolute amounts being very similar to those in 4-nitroaniline. In the α-form, studied at 90 °K. (Coppens, 1960) the mean square amplitudes are of course much smaller, but again the two oxygens are moving significantly more than the nitrogen. In 2-nitrobenzaldehyde (Coppens, 1960), the oxygen atoms of the nitro group are both vibrating considerably more than is the nitrogen atom, although here the motion is complicated by the fact that the nitro group is tipped about $27\frac{1}{2}$° from the plane of the benzene ring and the C–N bond is also tipped out of the plane, presumably because of the close contact of one nitro group oxygen with the adjacent aldehyde group, which is tipped in the opposite direction. For nitrobenzene, studied by Trotter (1959) at −30 °C., only individual isotropic temperature factors are available, but those for the two oxygens of the nitro group are 7·5 Å^2, that for the nitrogen only 5·3 Å^2. If one makes the reasonable assumption that the motions of the oxygen and nitrogen atoms in directions parallel to the N–O bonds are about equal, then the average mean square amplitude of each oxygen atom in directions normal to the bond is about $8{\cdot}6/8\pi^2=0{\cdot}11$ Å^2. Presumably this high amplitude motion is concentrated in directions normal to the plane, for the close contact of the two oxygen atoms would prevent high amplitude oscillations in the plane. Finally, in an unpublished study of 3-nitroperchlorylbenzene (Palenik, Trueblood, & Donohue) we have found, even before refinement is complete, that the mean square amplitudes normal to the molecular plane containing the aromatic ring and the nitro group are about 0·038, 0·115, and 0·107 Å^2 for the nitrogen and the two oxygens respectively. Thus in all of these examples the pattern is very similar to that revealed in Table 5, and it would seem that high-amplitude torsional oscillations of the nitro group are common to all nitroaromatic compounds. It is suggestive that the contacts of the oxygen atoms with the ortho hydrogen atoms (Table 7) are somewhat below the sum (about 2·6 Å) of the usual van der Waals radii when the nitro group is planar with the aromatic ring.

The changes in atomic position from the structure reported on the basis of the two-dimensional analysis (Donohue & Trueblood, 1956) average about 0·05 Å, with the changes in y nearly three times as great as those in x and z. The largest changes were in the positions of C2 and C5, each of which moved about 0·08 Å. The C–NO$_2$ bond and two of the C–C bonds changed in length by 0·05 Å, and one of the N–O bonds changed by 0·04 Å. These changes are not unexpected inasmuch as the e.s.d. of a bond distance in the two-dimensional refinement was about 0·035 Å.

Table 9. *The hydrogen bonding system**

Atoms†	Angle	Atoms	Distance
C1–N1 ... O1′	146·1°	N1 ... O1′	3·14 Å
C1–N1 ... O2′	120·6	N1 ... O2′	3·07
O1′ ... N1 ... O2′	92·7		
N1–H5 ... O1′	140 (139)		
N1–H6 ... O2′	164 (162)		
H5–N1 ... O1′	29		
H6–N1 ... O2′	12		

* Angles in parentheses are for idealized N–H distance of 1·02 Å. See footnote § to Table 7. No corrections for librational effects have been calculated.

† Atoms O1′ and O2′ are in molecules $D_{00\bar{1}}$ and $D_{01\bar{1}}$ respectively. See footnote * of Table 10.

Table 10. *Intermolecular distances**

From atom X in molecule A	To atom Y in molecule		Distance†
C2	C5	$B_{1\bar{1}1}$	3·64 Å
C2	C6	$B_{1\bar{1}1}$	3·69
C2	C1	$B_{1\bar{1}1}$	3·83
C2	C2	$B_{1\bar{1}1}$	3·91
C2	C3	$B_{1\bar{1}1}$	3·86
C2	C4	$B_{1\bar{1}1}$	3·70
O2	C5	C_{010}	3·33
O2	C6	C_{010}	3·70
O1	O1	C_{001}	3·21
N1	O1	$D_{01\bar{1}}$	3·76
O1	N1	B_{101}	3·73
N2	N1	B_{101}	3·64
C3	N1	B_{101}	3·92
C4	N1	B_{101}	3·73
H5	O1	$D_{00\bar{1}}$	2·35 (2·29)‡
H6	O2	$D_{01\bar{1}}$	2·34 (2·09)
H1	C5	$B_{1\bar{1}1}$	3·34 (3·31)
H1	C6	$B_{1\bar{1}1}$	3·25 (3·20)
H1	C1	$B_{1\bar{1}1}$	3·11 (3·00)
H1	C2	$B_{1\bar{1}1}$	3·05 (2·92)
H1	C3	$B_{1\bar{1}1}$	3·13 (3·02)
H1	C4	$B_{1\bar{1}1}$	3·25 (3·20)

* Note that the atom numbering has been changed from the two-dimensional study. Molecule A is at x, y, z (Table 2), B at $(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$, C at $(1-x, 1-y, 1-z)$, and D at $(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$. Molecules equivalent by lattice translation are identified by subscripts.

† Uncorrected for libration effects.

‡ See footnote § of Table 7.

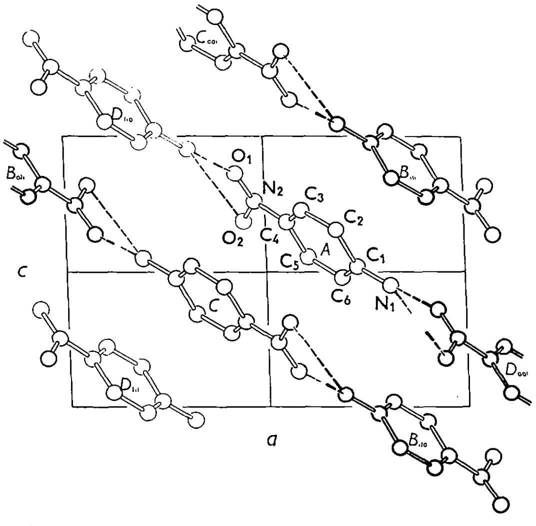

Fig. 5. The structure projected along the b axis.

The crystal structure

The arrangement of the molecules in the unit cell is indicated in Figs. 5 and 6. The changes from the two-dimensional results do not materially affect the discussion of the hydrogen-bonding (Table 9) or other intermolecular contacts (Table 10). Although one of the hydrogen bonds is about 0·11 Å longer than reported earlier, the other is essentially unaltered, and the corresponding C–N...O angles are changed but little. The angle between the plane of the aromatic ring and the plane defined by C1, N1, and the hydrogen-bonded oxygen atoms (planes 1 and 4 of Table 4) remains 14° as it was in the earlier structure. These hydrogen bonds are very typical of those between amino and nitro groups (Fuller, 1959).

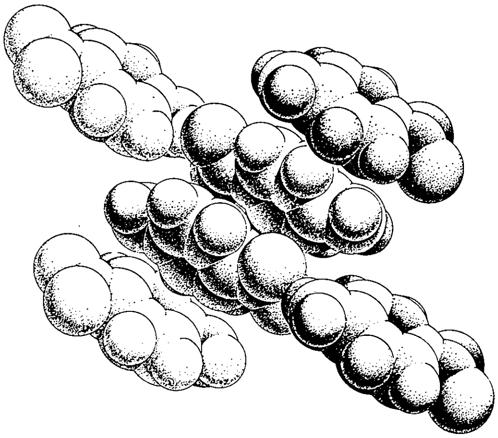

Fig. 6. Packing drawing of the structure, as viewed along the *b* axis.

Other intermolecular distances are given in Table 10, where, for convenience of comparison, the distances are listed in the same order as in Table 6 of the earlier report (Donohue & Trueblood, 1956). All distances less than 3·8 Å which involve 'heavy' atoms and all distances less than 3·3 Å which involve hydrogen atoms are listed. As noted before, the hydrogen atom on C2 lies nearly on the axis of the benzene ring of molecule $B_{1\bar{1}1}$, essentially in contact with atoms C1, C2 and C3 ('Contact' here assumes that the half-thickness of the aromatic ring is 1·7 Å and the van der Waals radius of the hydrogen atom is about 1·2 Å). No other features of the packing appear to merit special comment.

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