

### 35. X-Ray Studies of Molecular Overcrowding. Part V.<sup>1</sup> The Crystal and Molecular Structure of 2-Chloro-4-nitroaniline.

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2-Chloro-4-nitroaniline crystallizes in the orthorhombic system, space group  $Pna2_1$ , with four molecules in the unit cell of dimensions  $a = 11.25$ ,  $b = 16.85$ ,  $c = 3.87$  Å. The atomic co-ordinates and anisotropic thermal parameters have been refined by least-squares calculations from three-dimensional intensity data. The final value of  $R$  is 0.103. The molecules are held together in the crystal by normal van der Waals forces and by a weak  $NH \cdots O$  hydrogen bond of length 3.05 Å. The nitro-group is twisted  $4^\circ 20'$  out of the plane of the benzene ring. The angle between the C-Cl and C-NH<sub>2</sub> bond directions is  $62^\circ 30'$ . The atomic thermal vibrations have been analysed in terms of rigid-body molecular vibrations and it has been established that the centre of oscillation of the molecule is displaced by about 1.2 Å from the centre of mass. The root-mean-square translational movement in the molecular plane (0.21 Å) is considerably greater than that normal to the plane (0.13 Å).

In a number of crystallographic studies of benzene derivatives it has been found that nitro-groups adjacent to hydrogen atoms buttressed by bulky substituents (nitro- and carboxyl groups) are rotated out of the benzene planes; thus in 2-chloro-5-nitrobenzoic

TABLE 1.

Atomic co-ordinates.

Atom	$x/a$	$y/b$	$z/c$	Atom	$x/a$	$y/b$	$z/c$
C(1) .....	0.1849	0.4534	0.1159	N(1) .....	0.1101	0.5147	0.0218
C(2) .....	0.2947	0.4641	0.2762	N(2) .....	0.4019	0.2573	0.4090
C(3) .....	0.3676	0.4014	0.3793	O(1) .....	0.4937	0.2714	0.5727
C(4) .....	0.3295	0.3247	0.2942	O(2) .....	0.3707	0.1895	0.3287
C(5) .....	0.2217	0.3095	0.1339	Cl .....	0.3396	0.5614	0.3790
C(6) .....	0.1513	0.3740	0.0414				

TABLE 2.

Standard deviations of the final atomic co-ordinates (Å).

Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C(1) .....	0.008	0.009	0.017	N(1) .....	0.008	0.008	0.012
C(2) .....	0.009	0.008	0.013	N(2) .....	0.008	0.007	0.016
C(3) .....	0.009	0.009	0.013	O(1) .....	0.009	0.008	0.012
C(4) .....	0.008	0.008	0.017	O(2) .....	0.009	0.007	0.019
C(5) .....	0.010	0.008	0.016	Cl .....	0.002	0.002	0.007
C(6) .....	0.008	0.009	0.015				

acid,<sup>1</sup> *m*-dinitrobenzene,<sup>2</sup> and 1-chloro-2,4-dinitrobenzene<sup>3</sup> such nitro-groups are inclined at  $7^\circ$ ,  $11^\circ$ , and  $15^\circ$ , respectively, to the benzene planes. We considered it possible that a substituent considerably smaller than nitro or carboxyl (*e.g.*, Br, Cl, or CH<sub>3</sub>) placed *meta* to a nitro-group might exert a small buttressing effect on the adjacent hydrogen atom and hence produce a measurable, though small, displacement of the nitro-group from the benzene plane. To test this we have determined the crystal structure of 2-chloro-4-nitroaniline and refined the atomic parameters extensively by Fourier and least-squares methods. The final atomic co-ordinates are given in Table 1 and the estimated standard deviations of these co-ordinates in Table 2. The final electron-density distribution is shown in Fig. 1 as superimposed contour sections drawn parallel to (001) and covering the region of one molecule. The arrangement of the molecules in the crystal as viewed in projection along the *c*-axis is illustrated in Fig. 2.

<sup>1</sup> Part IV, Ferguson and Sim, *J.*, 1962, 1767.

<sup>2</sup> Trotter, *Acta Cryst.*, 1961, **14**, 244.

<sup>3</sup> Watson, *Nature*, 1960, **188**, 1102.

TABLE 3.

Deviations ( $\text{\AA}$ ) of the atoms from various planes.

	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)
C(1) .....	-0.013	-0.005	-0.001	—	N(1) ...	-0.041	-0.023	-0.005
C(2) .....	0.038	0.028	0.024	—	N(2) ...	-0.016	-0.039	-0.077
C(3) .....	0.023	0.004	-0.015	—	O(1) .....	-0.070	-0.108	-0.153
C(4) .....	0.044	0.032	0.008	0.003	O(2) .....	0.032	0.016	-0.026
C(5) .....	0.000	0.005	-0.011	—	Cl .....	0.010	-0.009	-0.006
C(6) .....	-0.007	0.008	0.006	—				

The displacements of the atoms from the best plane through the chlorine, carbon, nitrogen, and oxygen atoms of the molecule, calculated by the method of Schomaker *et al.*,<sup>4</sup> are shown in Table 3. Application of the  $\chi^2$ -test<sup>5</sup> to these displacements indicated that the

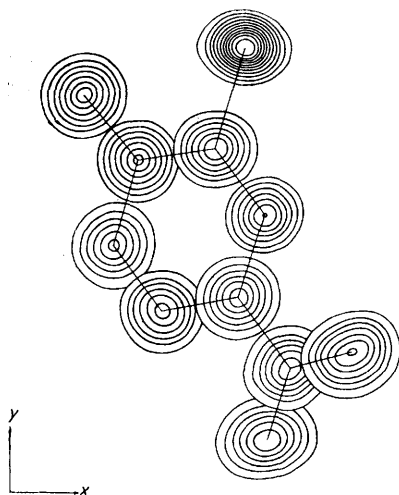


FIG. 1. Final three-dimensional electron-density distribution for 2-chloro-4-nitroaniline shown by means of superimposed contour sections drawn parallel to (001). Contour interval  $1 \text{ e}\text{\AA}^{-3}$ , except around the chlorine atom where it is  $2 \text{ e}\text{\AA}^{-3}$ .

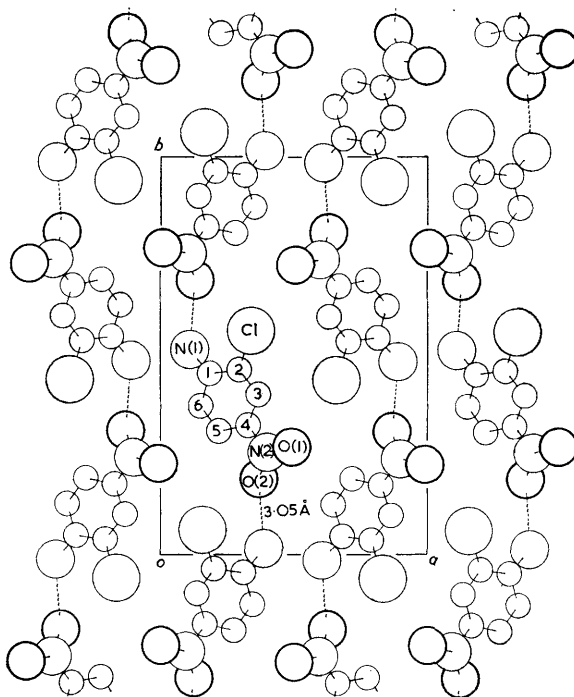


FIG. 2. The arrangement of molecules in the crystal as viewed along the  $c$ -axis.

molecule cannot be considered planar, for  $\Sigma\Delta^2 = 1.23 \times 10^{-2} \text{ \AA}^2$  and  $\chi^2 = \Sigma\Delta^2/\sigma^2 \approx 59$ . When the oxygen atoms were omitted from the calculation of a mean molecular plane the resultant atomic deviations (see Table 3) were still too large for the plane to be regarded as satisfactory, for  $\Sigma\Delta^2 = 4.1 \times 10^{-3} \text{ \AA}^2$  and  $\chi^2 \approx 20$ . Since the nitrogen atom of the nitro-group had the largest deviation we calculated the mean plane through the carbon atoms, the chlorine atom, and the nitrogen atom of the amino-group. The deviations of these atoms from the plane (see Table 3) are sufficiently small to be considered insignificant ( $\Sigma\Delta^2 = 1.1 \times 10^{-3} \text{ \AA}^2$  and  $\chi^2 \approx 5$ ).

<sup>4</sup> Schomaker, Waser, Marsh, and Bergman, *Acta Cryst.*, 1959, **12**, 600.

<sup>5</sup> Fisher and Yates, "Statistical Tables," Oliver and Boyd, Edinburgh, 1957.

The deviations of the atoms of the nitro-group and carbon atom C(4) of the benzene ring from a plane are not significant (see Table 3). The angle between this plane and that through C(1) ··· C(6), N(1), Cl is 4° 20', slightly greater than the corresponding angle in *p*-nitroaniline (1° 54').<sup>6</sup> The nitrogen atom of the nitro-group is displaced by 0.077 Å from the mean plane through C(1) ··· C(6), N(1), Cl, implying an out-of-plane deflection of the C(4)-N(2) bond of about 3°; this also is rather greater than the value reported for *p*-nitroaniline (0° 24').<sup>6</sup> If these differences can be attributed to the chlorine atom rather than to crystal packing forces, then the chlorine atom indeed appears to exert a measurable steric effect on the nitro-group in the 4-position. However, the effect is small and further crystal analyses of related compounds appear desirable.

TABLE 4.  
Anisotropic temperature factors ( $b_{ij} \times 10^5$ ).

	$b_{11}$	$b_{22}$	$b_{33}$	$b_{12}$	$b_{23}$	$b_{13}$
C(1) .....	1104	515	4382	6	600	527
C(2) .....	1258	387	5324	-272	-696	1067
C(3) .....	1206	492	5743	42	1135	772
C(4) .....	1477	462	2883	157	768	642
C(5) .....	1711	443	4047	-201	103	1741
C(6) .....	1258	520	8623	-175	-93	1524
N(1) .....	1198	580	8235	151	1129	238
N(2) .....	1712	531	10,475	504	2087	2860
O(1) .....	2364	844	10,260	1109	1027	-218
O(2) .....	2724	521	17,778	470	1112	856
Cl .....	1487	416	5491	-245	-996	239

TABLE 5.  
Interatomic distances (Å) and angles.

<i>Intramolecular bonded distances.</i>							
	Uncorrected	Corrected	e.s.d.		Uncorrected	Corrected	e.s.d.
C(1)-C(2)	1.394	1.400	0.014	C(1)-N(1)	1.382	1.386	0.012
C(2)-C(3)	1.396	1.401	0.012	C(2)-Cl	1.760	1.766	0.009
C(3)-C(4)	1.401	1.407	0.012	C(4)-N(2)	1.466	1.471	0.013
C(4)-C(5)	1.387	1.392	0.015	N(2)-O(1)	1.235	1.240	0.015
C(5)-C(6)	1.391	1.395	0.013	N(2)-O(2)	1.236	1.240	0.011
C(6)-C(1)	1.420	1.425	0.013				

<i>Intermolecular distances.*</i>							
O(2) ··· N(1) <sub>I</sub>	3.047	O(1) ··· C(6) <sub>V</sub>	3.526	C(2) ··· N(1) <sub>IV</sub>	3.656	N(2) ··· O(2) <sub>IV</sub>	3.755
N(1) ··· N(1) <sub>II</sub>	3.182	C(3) ··· C(6) <sub>IV</sub>	3.564	O(1) ··· Cl <sub>III</sub>	3.656	C(5) ··· C(6) <sub>IV</sub>	3.761
O(1) ··· C(5) <sub>III</sub>	3.365	N(2) ··· C(5) <sub>IV</sub>	3.571	Cl ··· N(1) <sub>IV</sub>	3.671	C(3) ··· C(4) <sub>IV</sub>	3.794
O(1) ··· N(2) <sub>IV</sub>	3.406	O(1) ··· Cl <sub>VI</sub>	3.587	C(3) ··· C(5) <sub>IV</sub>	3.691	Cl ··· C(1) <sub>IV</sub>	3.804
O(1) ··· C(4) <sub>IV</sub>	3.466	C(4) ··· C(6) <sub>IV</sub>	3.615	C(2) ··· C(6) <sub>IV</sub>	3.699	O(1) ··· C(5) <sub>IV</sub>	3.807
C(4) ··· C(5) <sub>IV</sub>	3.478	C(3) ··· C(1) <sub>IV</sub>	3.621	N(2) ··· C(4) <sub>IV</sub>	3.700	C(1) ··· C(6) <sub>IV</sub>	3.842
C(2) ··· C(1) <sub>IV</sub>	3.481	O(1) ··· C(5) <sub>V</sub>	3.627	C(1) ··· N(1) <sub>II</sub>	3.711	N(2) ··· C(6) <sub>III</sub>	3.846
O(2) ··· C(6) <sub>III</sub>	3.514	Cl ··· O(2) <sub>VII</sub>	3.645	C(3) ··· C(2) <sub>IV</sub>	3.720	O(2) ··· Cl <sub>I</sub>	3.846
O(1) ··· O(2) <sub>IV</sub>	3.519			C(1) ··· N(1) <sub>IV</sub>	3.751		

\* The subscripts refer to the following positions:

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

*Valency angles.*

C(1)C(2)C(3)	123.3°	C(5)C(6)C(1)	122.2	C(1)C(2)Cl	118.4	C(4)N(2)O(1)	118.1
C(2)C(3)C(4)	116.9	C(6)C(1)C(2)	116.7	C(3)C(2)Cl	118.2	C(4)N(2)O(2)	118.9
C(3)C(4)C(5)	122.9	C(2)C(1)N(1)	124.0	C(3)C(4)N(2)	118.3	O(1)N(2)O(2)	123.0
C(4)C(5)C(6)	118.0	C(6)C(1)N(1)	119.3	C(5)C(4)N(2)	118.6		

The anisotropic thermal parameters shown in Table 4 were analysed to yield the two symmetric tensors  $T$  and  $\omega$  (Table 11) which describe the translational vibrations and angular

<sup>6</sup> Trueblood, Goldish, and Donohue, *Acta Cryst.*, 1961, **14**, 1009.

oscillations of the molecule about axes parallel to the molecular inertial axes (see Experimental section). The centre of oscillation of the molecule is displaced from the centre of mass by 1.2 Å; the positions of these centres and of the molecular axes are shown in Fig. 3. The values of the  $T$  and  $\omega$  tensors are rather similar to those of naphthalene,<sup>7</sup> though in the present case the r.m.s. translational vibration perpendicular to the molecular plane (0.13 Å) is distinctly smaller than the r.m.s. translational vibrations parallel to the axes in the molecular plane (0.22, 0.21 Å), whereas in naphthalene the r.m.s. translational vibrations are considerably more isotropic (0.19, 0.20, 0.22 Å).

The various interatomic distances and valency angles derived from the final atomic co-ordinates, are listed in Table 5; the bond-lengths in the column headed "corrected" have been adjusted to allow for the effect of the angular oscillations of the molecule. The estimated standard deviations of the bond-lengths range from 0.009 to 0.015 Å. The average e.s.d. of a valency angle is about 1°.

The carbon-amino-nitrogen distance of 1.386 Å is in good agreement with the values of  $sp^2$ -carbon-nitrogen bonds in 2-amino-3-methylbenzoic acid (1.367 Å, uncorrected for librational effects),<sup>8</sup> *p*-nitroaniline (1.371 Å),<sup>6</sup> byssochlamic acid bis-*p*-bromophenylhydrazide (1.39 Å),<sup>9</sup> and various indole alkaloids, *e.g.*, echitamine (1.38 Å).<sup>10</sup> The dimensions of the nitro-group do not differ significantly from those reported for *p*-nitroaniline,<sup>6</sup> nitrobenzene,<sup>11</sup> and *m*-dinitrobenzene.<sup>2</sup> In each molecule the angles CNO are less than 120° while the angle ONO exceeds 120°; these angular variations can be interpreted qualitatively in terms of inter-electron repulsion between pairs of non-bonding electrons on the oxygen atoms. The carbon-chlorine distance of 1.766 Å is not significantly different from the values in 2-chloro-5-nitrobenzoic acid (1.753 Å),<sup>1</sup> *o*-chlorobenzoic acid (1.737 Å),<sup>12</sup> and 4,4'-dichlorodiphenyl sulphone (1.736 Å).<sup>13</sup> As the average carbon-chlorine distance in alkyl halides is 1.767 Å,<sup>14</sup> and the radius of an  $sp^2$ -hybridized carbon atom is 0.02–0.03 Å smaller than that of an  $sp^3$ -hybridized carbon atom, there appears to be little, if any, double-bond character associated with the carbon-chlorine bond in 2-chloro-4-nitroaniline.

The shortest intermolecular contact, 3.047 Å, occurs between oxygen atom O(2) of the nitro-group and the amino-nitrogen atom of a neighbouring molecule (see Fig. 2). This distance is indicative of weak hydrogen-bonding of the type NH...O. The other intermolecular approach distances (see Table 5) correspond to normal van der Waals interactions.

#### EXPERIMENTAL

*Crystal Data.*—2-Chloro-4-nitroaniline,  $C_6H_5ClN_2O_2$ ;  $M = 172.6$ ; m. p. 105–106°. Orthorhombic,  $a = 11.25$ ,  $b = 16.85$ ,  $c = 3.87$  Å,  $U = 734.0$  Å<sup>3</sup>,  $D_m = 1.545$  g. cm.<sup>-3</sup>,  $Z = 4$ ,  $D_c = 1.562$  g. cm.<sup>-3</sup>,  $F(000) = 352$ . Space group,  $Pna2_1$  ( $C^9_{2v}$ ). Absorption coefficient for X-rays ( $\lambda = 1.542$  Å),  $\mu = 42.6$  cm.<sup>-1</sup>. Crystallization from aqueous ethanol gave single crystals in the form of thin, narrow laths elongated along  $c$ .

*Experimental Measurements.*—Rotation, oscillation, and Weissenberg photographs were taken with Cu- $K_\alpha$  radiation ( $\lambda = 1.542$  Å); precession photographs were taken with  $M\alpha$ - $K_\alpha$  radiation ( $\lambda = 0.7107$  Å). The systematic absences are consistent with two space groups,  $Pna2_1$  and  $Pnam$ . The centrosymmetric space group  $Pnam$  requires two mirror planes  $c/2$  apart, each plane containing two molecules flat within it. Examination of the  $c$ -axis projection showed that the molecular plane is only approximately, not exactly, parallel to (001) and the space group is therefore  $Pna2_1$ . The intensity data, consisting of the layers  $hk0$ — $hk2$ , were

<sup>7</sup> Cruickshank, *Acta Cryst.*, 1957, **10**, 504.

<sup>8</sup> Brown and Marsh, *Acta Cryst.*, 1960, **13**, 1037.

<sup>9</sup> Paul, Sim, Hamor, and Robertson, *J.*, 1963, 5502.

<sup>10</sup> Hamilton, Hamor, Robertson, and Sim, *J.*, 1962, 5061.

<sup>11</sup> Trotter, *Acta Cryst.*, 1959, **12**, 884.

<sup>12</sup> Ferguson and Sim, *Acta Cryst.*, 1961, **14**, 1262.

<sup>13</sup> Sime and Abrahams, *Acta Cryst.*, 1960, **13**, 1.

<sup>14</sup> Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Spec. Publ.* No. 11, 1958.

TABLE 6.

Measured and calculated values of the structure factors.

<i>h</i>	<i>k</i>	<i>l</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	$\alpha^\circ$	<i>h</i>	<i>k</i>	<i>l</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	$\alpha^\circ$	<i>h</i>	<i>k</i>	<i>l</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	$\alpha^\circ$	<i>h</i>	<i>k</i>	<i>l</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	$\alpha^\circ$			
0	1	1	53	56	202				7	6	67	3	10	0	4	4	0				1	33	27	205		
0	2	0	14	13	0	2	0	0	38	52	180	3	11	1	16	16	23				1	14	13	262		
0	3	1	19	17	279				107	141	60				5	5	239				5	2	0	0		
0	4	0	65	69	74				21	25	24				12	13	261				1	10	8	319		
0	5	1	49	50	0	2	1	0	28	37	0				13	12	180				2	12	13	254		
0	6	2	14	15	39				47	52	302				21	20	50				5	3	0	0		
0	7	1	25	25	351				27	26	240				4	5	258				1	11	11	213		
0	8	0	22	22	180	2	2	0	39	45	180				7	8	180				2	5	5	348		
0	9	1	31	28	117				27	23	103				8	8	5				5	4	0	0		
0	10	2	36	32	43				8	8	126				2	2	100				1	12	14	48		
0	11	1	41	36	180	2	3	0	58	63	180				10	9	0				2	18	22	269		
0	12	0	36	32	43				12	12	147				15	16	8				5	5	0	0		
0	13	1	9	9	270				24	23	108				4	3	248				1	16	19	24		
0	14	0	20	16	180	2	4	0	20	22	0				4	4	180				2	3	3	287		
0	15	1	13	13	101				15	13	93				5	4	256				5	6	0	0		
0	16	2	27	25	214				13	13	18				6	5	113				1	15	16	275		
0	17	0	5	4	180	2	5	0	18	14	180				4	4	180				2	15	15	287		
0	18	1	12	10	261				32	31	268				4	4	203				5	7	0	0		
0	19	2	42	37	232				24	22	59				3	3	181				1	18	21	61		
0	20	0	7	8	180	2	6	0	15	14	180				7	7	180				2	8	7	53		
0	21	1	9	8	337				17	18	234				3	3	51				5	8	0	0		
0	22	2	18	16	309				12	11	280				10	10	85				1	12	12	218		
0	23	0	18	20	0	2	7	0	4	4	180				7	8	222				2	6	6	303		
0	24	1	13	10	281				17	18	2				6	6	180				5	9	1	16	20	54
0	25	2	3	3	41				14	14	139				3	3	4				2	18	18	66		
0	26	0	3	4	0	2	8	0	42	42	0				5	5	129				5	10	0	13	13	180
0	27	1	9	7	295				29	27	195				9	8	235				1	7	8	266		
0	28	2	14	12	23				5	4	262				56	68	180				2	6	6	104		
0	29	0	1	2	0	2	9	0	5	5	337				52	38	233				5	11	1	5	6	352
0	30	1	6	7	25				3	3	321				50	46	99				5	12	0	14	13	180
1	1	0	9	7	0	2	10	0	10	9	0				22	27	0				1	10	10	221		
1	1	1	82	72	1				11	11	246				23	20	4				2	15	16	91		
1	2	0	35	32	248				6	6	261				16	14	12				5	13	0	4	3	0
1	2	1	25	31	0	2	11	0	22	20	0				26	30	180				1	6	6	208		
1	3	0	19	18	310				12	13	22				26	26	233				2	6	7	55		
1	3	1	25	26	92				15	15	266				18	21	208				5	14	0	10	9	180
1	4	0	5	6	180	2	12	0	9	9	0				19	20	0				2	10	12	80		
1	4	1	22	19	44				6	7	350				25	26	208				5	15	0	3	3	0
1	4	2	15	17	239				5	3	58				9	9	290				5	15	1	5	5	235
1	5	0	33	30	180				38	40	0				12	13	0				5	15	2	7	7	296
1	5	1	24	21	95				10	9	47				12	13	84				5	16	0	2	2	0
1	5	2	20	17	107				19	18	283				7	7	112				5	17	1	7	8	207
1	6	0	23	23	180	2	14	0	5	5	0				40	41	0				2	3	2	2	289	
1	6	1	33	28	262				3	3	204				15	17	212				5	18	0	6	6	0
1	6	2	17	16	86				8	7	123				15	16	289				2	4	4	259		
1	7	0	22	19	180				6	6	0				5	6	0				5	19	0	2	1	180
1	7	1	30	25	30				6	5	127				6	4	63				1	7	6	6	233	
1	7	2	37	33	117				10	10	16				16	16	256				5	20	0	3	4	0
1	8	0	45	44	180	2	16	0	8	8	180				6	5	180				6	0	0	37	45	0
1	8	1	37	33	231				15	15	55				14	14	167				1	23	22	225		
1	8	2	17	16	156				2	2	168				11	10	38				2	15	13	258		
1	9	0	5	5	0	2	17	1	4	4	219				10	9	0				6	1	0	16	17	180
1	9	1	18	19	103				2	5	4	3			29	31	57				1	9	8	48		
1	9	2	15	14	166				4	5	52				17	17	245				2	4	4	60		
1	10	0	7	5	180	2	18	1	6	5	106				2	2	0				6	2	0	19	17	0
1	10	1	27	27	215				8	9	180				5	4	244				1	15	14	325		
1	10	2	14	13	86				6	5	207				9	9	36				2	16	15	269		
1	11	0	20	21	0	2	19	0	9	9	85				3	3	0				6	3	0	9	8	0
1	11	1	17	15	249				2	3	76				11	11	51				1	24	24	83		
1	11	2	15	14	264				4	5	180				2	2	282				2	7	7	240		
1	12	0	10	10	217	3	1	0	22	26	180				16	15	180				6	4	0	11	11	180
1	12	1	6	5	149				13	9	211				10	11	63				1	2	1	9		
1	12	2	21	20	0				53	50	72				12	14	84				2	6	7	111		
1	13	0	10	10	164	3	2	0	12	15	180				4	5	180				6	5	0	4	2	0
1	13	1	19	15	245				15	14	176				9	9	109				1	25	27	43		
1	13	2	13	14	0				11	10	321				6	5	35				2	9	9	219		
1	14	0	13	12	108	3	3	0	29	31	180				14	16	180				6	6	0	15	14	180
1	14	1	3	3	1				15	14	308				19	21	61				1	7	5	2		
1	14	2	7	7	0				8	7	114				9	9	74				2	4	6	148		
1	15	0	13	12	218	3	4	0	5	5	0				3	3	242				6	7	0	3	2	180
1	15	1	22	20	265				25	22	208				7	7	180				1	5	6	131		
1	15	2	6	6	180				4	4	163				3	4	95				2	16	17	247		
1	16	0	4	3	222	3	5	0	36	37	0				5	5	194				6	8	0	25	25	180
1	16	1	8	8	180				25	24	204				12	12	180				1	7	8	315		
1	16	2	7	6	74				10	10	302				8	8	249				2	18	21	84		
1	17	0	2	2	3	24	3	6	0	46	42	180			7	7	87				6	9	0	12	11	0
1	17	1	6	6	7	0			38	34	245				7	7	0				1	6				

TABLE 6. (Continued.)

<i>h</i>	<i>k</i>	<i>l</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	$\alpha^\circ$	<i>h</i>	<i>k</i>	<i>l</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	$\alpha^\circ$	<i>h</i>	<i>k</i>	<i>l</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	$\alpha^\circ$	
6	13	0	8	9	180	8	1	0	6	5	180	9	10	2	7	8	264	
		1	11	13	225			1	10	8	261			1	2	2	0	
		2	6	7	114			2	9	9	125			1	5	6	94	
6	14	0	5	5	0	8	2	0	11	10	180			2	2	1	12	
		2	4	5	286	8	2	1	11	9	68	9	11	0	7	6	180	
6	15	0	2	1	180			2	4	4	338			2	5	5	279	
		1	4	5	275	8	3	0	20	19	180	9	12	0	4	4	0	
		2	3	4	140			1	4	3	276			1	7	9	48	
6	16	0	7	8	0			2	4	4	97			2	3	4	293	
		1	4	5	192	8	4	0	3	3	0	9	13	0	2	2	180	
		2	7	7	273			1	11	11	243			2	2	3	71	
6	17	0	4	4	180			2	4	3	33	9	14	0	5	4	0	
		1	5	5	37	8	5	0	24	22	180			1	3	3	54	
6	18	0	8	9	0			1	10	10	289			2	1	2	252	
6	19	0	2	2	0			2	16	16	79	9	15	0	8	8	180	
		1	3	4	53	8	6	1	8	8	263			1	2	2	348	
		2	11	11	0			2	3	2	35	9	16	0	4	3	0	
7	1	0	11	19	36	8	7	0	4	3	180			1	1	2	104	
		1	21	19	280			1	7	7	350	10	0	0	2	1	180	
		2	2	0	0			2	5	4	97			1	4	3	203	
7	2	0	7	6	21	8	8	0	12	11	0			2	8	9	89	
		1	12	10	101			1	15	17	209	10	1	0	3	3	0	
		2	8	8	84			2	2	2	331			1	6	6	254	
7	3	1	7	8	306	8	9	0	9	9	180			2	3	4	290	
		2	12	11	180			1	6	6	2	10	2	0	4	4	180	
7	4	0	12	12	38			2	2	3	256			1	4	4	292	
		1	18	20	79	8	10	0	13	11	0	10	3	0	7	7	110	
		2	4	4	180			1	7	8	271			2	14	12	0	
7	5	0	6	6	83	8	11	0	6	6	0			1	6	6	210	
		1	14	15	72			2	8	9	267			2	3	4	278	
		2	20	19	54	8	12	1	4	4	304	10	4	0	14	13	0	
7	6	0	3	2	0	8	13	0	10	11	0			2	2	3	0	
		1	19	19	180			2	6	6	272	10	5	0	13	12	0	
		2	7	7	109	8	14	1	4	4	39			1	11	12	214	
7	7	0	8	9	197			2	5	4	106			2	2	2	251	
		1	14	15	144	8	15	0	2	2	0	10	6	0	5	4	0	
		2	13	13	0			1	2	2	219			1	3	3	88	
7	8	0	7	8	61			2	4	5	293			2	2	3	282	
		1	10	9	180	8	16	0	1	1	180	10	7	1	5	5	178	
		2	12	14	199			1	6	7	36			2	2	2	22	
7	9	0	6	7	116	8	17	0	2	2	180	10	8	0	7	7	0	
		1	9	9	0			1	3	3	190			1	6	7	46	
		2	7	8	281	9	1	0	12	12	180			2	7	8	274	
7	10	0	3	3	337			1	6	5	99	10	9	0	2	2	0	
		1	3	4	129			2	9	10	103			1	4	5	243	
		2	13	11	0	9	2	0	4	3	180			2	5	6	93	
7	11	0	7	8	207			1	6	6	223	10	10	0	2	2	0	
		1	8	9	274			2	3	3	4			1	6	6	77	
		2	4	5	0	9	3	0	4	3	180			2	2	3	315	
7	13	0	3	3	113			1	5	5	100	10	11	0	3	2	180	
		1	3	3	238			2	9	9	163			1	3	4	24	
		2	3	3	0	9	4	0	5	4	180	10	12	1	3	3	150	
7	14	0	3	7	238			1	18	18	195			2	4	4	346	
		1	3	3	293	9	5	0	5	5	180	10	13	0	2	2	180	
		2	3	4	0			1	7	7	196			1	4	5	46	
7	15	0	5	6	55	9	6	0	2	5	4	241	10	14	0	4	3	180
		1	4	4	232			1	18	16	180			1	3	3	230	
		2	2	2	180			2	7	8	242	11	1	0	2	2	180	
7	16	0	2	1	234			1	3	3	98			1	6	7	247	
		1	4	4	341	9	7	0	8	7	0			2	4	4	0	
		2	5	5	0			1	3	4	259			1	2	2	66	
7	17	0	5	5	37			2	7	8	252			2	4	5	257	
		1	2	2	180	9	8	0	9	8	180	11	3	0	7	7	180	
		2	2	2	33			1	6	6	109			1	5	5	290	
8	0	0	5	6	0	9	8	2	2	3	36			2	3	3	269	
		1	18	14	37	9	9	0	13	11	0	11	4	0	12	11	0	
		2	8	7	349			1	5	5	295			1	5	6	5	

obtained from equatorial and equi-inclination multiple-film Weissenberg photographs. The intensities were estimated visually and were corrected for Lorentz, polarization, and the rotation factors<sup>15</sup> appropriate to upper layers. The absolute scale of each layer of reflexions was obtained during the analysis by correlation of the  $|F_o|$  values with the calculated structure amplitudes,  $|F_c|$ . In all 614 independent structure amplitudes were measured (Table 6). The crystal density was determined by flotation in aqueous zinc chloride.

*Structure Analysis.*—The initial *x* and *y* co-ordinates of the atoms other than hydrogen were derived from the *c*-axis projection of the isomorphous 2-bromo-4-nitroaniline crystal structure.<sup>16</sup>

<sup>15</sup> Tunell, *Amer. Min.*, 1939, **24**, 448.

<sup>16</sup> McPhail, Ph.D. Thesis, 1963, University of Glasgow.

Preliminary refinement of the crystal structure in the *c*-axis projection was then carried out by Fourier and least-squares methods and the value of *R*, the usual discrepancy factor, fell from 0.410 to 0.142 for the *hk*0 reflexions.

The initial *z* co-ordinates of the various atoms were derived by assuming that the molecule was planar and that the benzene ring was a regular hexagon of side 1.40 Å. An overall isotropic temperature factor *B* of 4.0 Å<sup>2</sup> was adopted and structure factors for the *hk*1 and *hk*2 reflexions were calculated; the values of *R* were 0.206 and 0.272, respectively.

The good agreement between measured and calculated structure amplitudes prompted us to proceed immediately to a least-squares refinement of positional and anisotropic temperature-factor parameters for all atoms other than hydrogen. The programme was that devised by Rollett.<sup>17</sup> After five rounds of calculations the parameter changes became small and the values of *R* were reduced to 0.137 for the *hk*0, 0.107 for the *hk*1, and 0.097 for the *hk*2 reflexions. The overall value of *R* for the 614 reflexions was 0.115.

At this stage we decided to allow for the hydrogen atoms of the benzene ring. Co-ordinates were calculated by placing the atoms radially at a distance of 1.08 Å from the carbon atoms to

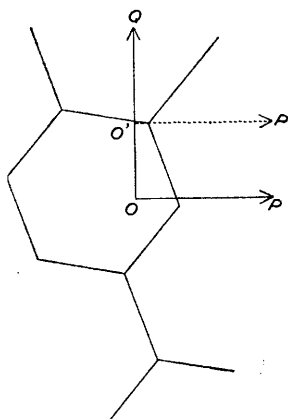


FIG. 3. The centre of mass, the centre of oscillation, and the molecular axes.

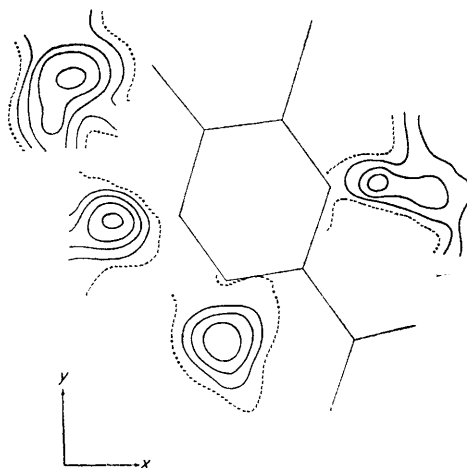


FIG. 4. Sections through the three-dimensional difference electron-density distribution at the positions of the hydrogen atoms. Contour interval 0.1 eÅ<sup>-3</sup>, zero contour broken.

which they are covalently bonded. The temperature factor for the hydrogen atoms was assigned the value  $B = 4.2 \text{ \AA}^2$ . Three further rounds of least-squares calculations were then carried out; hydrogen contributions were included in the structure-factor calculations, but only the parameters of the other atoms were adjusted by the programme. The overall value of *R* fell to 0.105.

When the hydrogen atoms were omitted from the calculation of structure factors,  $F_c$ , the value of *R* was 0.111. A three-dimensional Fourier synthesis with coefficients ( $F_o - F_c$ ) was evaluated, and sections through this electron-density distribution in the regions of the hydrogen atoms are shown in Fig. 4. Small peaks of height 0.3–0.4 eÅ<sup>-3</sup> appear in the expected positions for the hydrogen atoms of the benzene ring and one of the hydrogen atoms of the amino-group. Residual anisotropic thermal motion of the chlorine atom obscured the other hydrogen atom of the amino-group.

In the calculation of the final set of structure factors we allowed for all five hydrogen atoms of the molecule. The co-ordinates of those of the amino-group were obtained by assuming that the system C–NH<sub>2</sub> is planar with CNH angles of 120°, and that the N–H bond-length is 1 Å. The final calculated structure amplitudes and phase angles are shown with the measured

<sup>17</sup> Rollett, "Computing Methods and the Phase Problem in X-ray Crystal Analysis," ed. Pepinsky, Robertson, and Speakman, Pergamon Press, Oxford, 1961, p. 87.

structure amplitudes in Table 6. The final value of  $R$  is 0.103. The theoretical atomic scattering factors used in the structure-factor calculations were those of Berghuis *et al.*, for carbon, nitrogen, and oxygen,<sup>18</sup> that of McWeeny for hydrogen,<sup>19</sup> and that of Tomiie and Stam for chlorine.<sup>20</sup>

The phase constants and measured structure amplitudes shown in Table 6 were used to evaluate the three-dimensional electron-density distribution shown in Fig. 1 as superimposed contour sections drawn parallel to (001).

The standard deviations of the final atomic co-ordinates were derived from the least-squares residuals by means of the equation

$$\sigma^2(x_i) = \sum_j w_j (\Delta F_j)^2 / [(n - s) \sum_j w_j (\partial F_j / \partial x_i)^2]$$

The results are listed in Table 2.

The parameters defining the anisotropic thermal vibrations are given in Table 4; they are values of  $b_{ij}$  in the equation

$$\exp(-B \sin^2 \theta / \lambda^2) = 2^{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)}$$

*Analysis of the Thermal Motion.*—The anisotropic vibrations of each atom can be described by a symmetric tensor  $U$ . The mean-square amplitude of vibration in the direction of the unit vector  $l$  with components  $l_i$  is given by:

$$\bar{u}^2 = \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} l_i l_j$$

The six  $U_{ij}$  values for each atom, apart from hydrogen, referred to the molecular inertial axes (see Fig. 3 and Tables 7 and 8) were calculated from the anisotropic temperature factors of

TABLE 7.

Direction cosines of the molecular axes with respect to the crystallographic axes.

Axis	$a$	$b$	$c$
$OP$ .....	0.8255	0.3436	0.4477
$OQ$ .....	-0.3302	0.9374	-0.1107
$OR$ .....	0.4577	0.0564	-0.8873

TABLE 8.

Co-ordinates of the centre of mass,  $O$ , and the centre of oscillation,  $O'$ , of the molecule.

	$x/a$	$y/b$	$z/c$
$O$ .....	0.3082	0.3942	0.2839
$O'$ .....	0.2730	0.4610	0.2499

Table 4 and are shown in Table 9 in the columns headed "obs." The rigid-body vibrations of the molecule can be described by two symmetric tensors  $T$  and  $\omega$ , where  $T$  represents the translational vibrations of the mass centre and  $\omega$  the angular oscillations about the centre.<sup>21</sup> The  $U_{ij}^{\text{obs.}}$  values were used to calculate the  $T$  and  $\omega$  tensors, and these tensors were then used to derive values of  $U_{ij}^{\text{calc.}}$  for each atom; these values are given in Table 9 in the columns headed "calc. (i)." The discrepancies between the  $U_{11}^{\text{obs.}}$  and  $U_{11}^{\text{calc. (i)}}$  values indicated that, when the same axial directions are retained, the centre of oscillation of the molecule required to be moved along the  $Q$ -axis away from the centre of mass and towards the amino-group. Similar shifts of the centre of oscillation away from the mass centre have been encountered in monofluoroacetamide,<sup>22</sup> benzo[*c*]phenanthrene, and 1,12-dimethylbenzo[*c*]phenanthrene.<sup>23</sup>

Several calculations of the values of  $T$ ,  $\omega$ , and  $U_{ij}^{\text{calc.}}$  were carried out for different shifts ( $\Delta Q$ ) of the centre of oscillation. The results (see Table 10) show that a minimum value of  $\Sigma |U_{ij}^{\text{obs.}} - U_{ij}^{\text{calc.}}|$  is obtained when  $\Delta Q$  is about 1.2 Å. The  $T$  and  $\omega$  tensors obtained when the

<sup>18</sup> Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

<sup>19</sup> McWeeny, *Acta Cryst.*, 1951, **4**, 513.

<sup>20</sup> Tomiie and Stam, *Acta Cryst.*, 1958, **11**, 126.

<sup>21</sup> Cruickshank, *Acta Cryst.*, 1956, **9**, 757.

<sup>22</sup> Hughes and Small, *Acta Cryst.*, 1962, **15**, 933.

<sup>23</sup> Hirshfeld, Sandler, and Schmidt, *J.*, 1963, 2108.



TABLE 9.  
Observed and calculated values of  $U_{ij}$  (in units of  $10^{-2} \text{ \AA}^2$ ).

Atom	$U_{11}$			$U_{22}$			$U_{33}$		
	obs.	calc. (i)	calc. (ii)	obs.	calc. (i)	calc. (ii)	obs.	calc. (i)	calc. (ii)
C(1) ...	4.94	6.22	4.90	4.95	4.83	4.92	2.46	2.96	2.30
C(2) ...	4.66	5.83	4.86	4.82	4.29	4.50	2.76	2.42	1.81
C(3) ...	5.75	5.18	5.55	4.63	4.53	4.69	2.91	1.88	2.52
C(4) ...	6.25	5.85	6.97	4.32	4.26	4.48	2.12	2.44	3.28
C(5) ...	6.78	5.62	6.60	5.22	5.41	5.37	2.16	2.61	3.94
C(6) ...	5.83	5.25	5.13	5.68	6.16	5.95	3.79	2.48	3.59
N(1) ...	6.00	8.84	5.77	5.15	5.48	5.44	4.29	5.69	3.52
N(2) ...	10.22	8.41	10.21	4.17	4.29	4.50	4.02	4.86	5.56
O(1) ...	11.57	8.91	10.83	6.06	5.35	5.32	6.67	5.65	6.95
O(2) ...	12.51	11.08	13.07	4.83	4.39	4.57	9.34	7.52	7.64
Cl .....	4.89	8.16	5.49	5.15	5.21	5.22	3.60	5.04	3.02

Atom	$U_{12}$			$U_{23}$			$U_{13}$		
	obs.	calc. (i)	calc. (ii)	obs.	calc. (i)	calc. (ii)	obs.	calc. (i)	calc. (ii)
C(1) ...	0.38	0.51	0.00	-0.71	-0.55	-0.55	0.64	0.82	0.69
C(2) ...	-1.52	-0.41	-0.19	0.13	-0.65	-0.68	0.68	0.67	0.65
C(3) ...	0.42	-0.21	0.28	-1.14	-0.60	-0.63	0.27	0.70	0.78
C(4) ...	0.19	-0.37	-0.28	-1.00	-0.64	-0.69	1.57	0.69	0.66
C(5) ...	-1.47	-0.98	-1.36	-0.76	-0.47	-0.49	1.24	0.58	0.36
C(6) ...	-0.78	0.09	-0.73	0.00	-0.36	-0.31	-0.29	0.74	0.50
N(1) ...	0.98	1.84	0.81	-0.91	-0.45	-0.42	0.05	1.00	0.92
N(2) ...	0.85	0.10	0.30	-1.12	-0.73	-0.75	-0.69	0.74	0.90
O(1) ...	2.50	1.75	2.14	-0.13	0.69	-0.58	2.51	1.02	1.48
O(2) ...	-0.73	-1.15	-1.38	-0.90	0.66	-0.72	0.58	0.55	0.59
Cl .....	-1.63	-1.95	-0.79	0.17	-0.49	-0.51	1.49	0.43	0.49

TABLE 10.  
Values of  $\Sigma |\Delta U_{ij}| = \Sigma |U_{ij}^{obs.} - U_{ij}^{calc.}|$  (in units of  $10^{-2} \text{ \AA}^2$ ) for various shifts  $\Delta Q$  (in  $\text{\AA}$ ) of the centre of oscillation along  $OQ$  away from the mass centre.

$\Delta Q$ .....	0.0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8
$\Sigma  \Delta U_{ij} $ ...	50.56	45.01	39.26	35.85	34.34	33.39	33.32	33.67	34.30	34.84

TABLE 11.  
Values of  $T_{ij}$  (in  $10^{-2} \text{ \AA}^2$ ) and  $\omega_{ij}$  (in  $\text{deg.}^2$ ).

$$T = \begin{bmatrix} 4.87 & -0.11 & 0.66 \\ & 4.47 & -0.69 \\ & & 1.78 \end{bmatrix} \quad \omega = \begin{bmatrix} 8.64 & 0.29 & -0.27 \\ & 13.63 & -3.26 \\ & & 12.23 \end{bmatrix}$$

origin of the molecular axes was shifted by 1.2  $\text{\AA}$  to  $O'$  (see Fig. 3 and Table 8) are listed in Table 11; from the square roots of the diagonal terms the r.m.s. amplitudes of translational vibration in the directions of the molecular axes and the r.m.s. amplitudes of angular oscillation about the molecular axes are:

- along  $O'P$  0.22  $\text{\AA}$ ; about  $O'P$  2.9°;
- along  $O'Q$  0.21  $\text{\AA}$ ; about  $O'Q$  3.7°;
- along  $O'R$  0.13  $\text{\AA}$ ; about  $O'R$  3.5°.

The values of  $U_{ij}$  for the various atoms were calculated from the  $T$  and  $\omega$  tensors of Table 11 and are listed in Table 9 in the columns headed "calc. (ii)." The r.m.s. difference between

TABLE 12.  
Values of  $\sigma(T_{ij})$  (in  $10^{-2} \text{ \AA}^2$ ) and  $\sigma(\omega_{ij})$  (in  $\text{deg.}^2$ ).

$$\sigma(T) = \begin{bmatrix} 0.29 & 0.22 & 0.29 \\ & 0.23 & 0.25 \\ & & 0.44 \end{bmatrix} \quad \sigma(\omega) = \begin{bmatrix} 1.08 & 1.49 & 0.97 \\ & 6.03 & 2.62 \\ & & 0.95 \end{bmatrix}$$

the  $U_{ij}^{obs.}$  and  $U_{ij}^{calc. (ii)}$  values is 0.0066  $\text{\AA}^2$ , corresponding to an estimated standard deviation for the  $U_{ij}^{obs.}$  of 0.0073  $\text{\AA}^2$ . The estimated standard deviations of the  $T_{ij}$  and  $\omega_{ij}$  values are shown in Table 12.

Corrections<sup>21</sup> for the errors introduced into the atomic co-ordinates, and hence the bond-lengths, by the angular oscillations of the molecule were calculated from the  $\omega_{ij}$  values shown in Table 11. The corrected bond-lengths are listed in Table 5.

The calculations were carried out on the Glasgow University DEUCE computer with programmes devised by Dr. J. S. Rollett and Dr. J. G. Sime.

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[Received, March 5th, 1964.]

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