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A Nuclear Quadrupole Resonance and X-ray Study of the Crystal Structure of 2,5-Dichloroaniline

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The crystal structure of 2,5-dichloroaniline, $C_6H_3Cl_2NH_2$, has been determined by the combined application of nuclear quadrupole resonance and X-ray diffraction.

The molecule is planar, except for the nitrogen which deviates slightly, by 0·06 Å. The benzene ring is slightly deformed from the regular hexagon and the observed bond lengths agree well with the result of a simple molecular orbital calculation. There is no hydrogen bonding in the structure. The shortest intermolecular Cl...Cl distance, 3·37 Å, is shorter than the usually quoted van der Waals distance of 3·6 Å.

Introduction

This paper is a part of the series of investigations making use of nuclear quadrupole resonance (n.q.r.) and X-ray diffraction for studying the structures of chlorine-substituted aromatic compounds. In the previous work, (Dean, Pollak, Craven and Jeffrey, 1958; Chu, Jeffrey & Sakurai, 1962; Sakurai, 1962a, Sakurai, 1962b), the molecules had a centre of symmetry corresponding to that of the crystal. Therefore, once the molecular orientation was determined by studying the Zeeman splitting of the Cl^{35} n.q.r., the crystal structure could be solved directly. In the present work, the molecule occupies a general position and a direct solution from the n.q.r. measurements is not possible, since these do not provide information relating to the translational symmetry. The molecular structure factor was therefore calculated from the n.q.r. molecular orientation data and the position of the molecule was obtained using the modified Patterson function of Giglio, Liquori & Ripamonti, (1958). Excluding the NH_2 group, the molecule of 2,5-dichloroaniline has a pseudo-centre of symmetry and only the real part of the molecular structure factor had to be considered.

Crystal data

The crystals are monoclinic, with space group $P2_1/c$ from the systematic extinctions $h0l$ absent for l odd, $0k0$ absent for k odd. The cell dimensions measured with a G.E. XRD-5 diffractometer and single-crystal orienter are

$$a=13{\cdot}237\pm0{\cdot}007,\ b=3{\cdot}892\pm0{\cdot}006,\ c=18{\cdot}803\pm0{\cdot}02\ \text{Å}$$
$$\beta=135°13'\pm11'.\ V=682\pm3\ \text{Å}^3,$$
$$\text{with } Z=4,\ D_x=1{\cdot}577\pm0{\cdot}006\ \text{g.cm.}^3.$$

A suitable liquid for the density measurement by flotation was not obtained. However, the pure quadrupole Cl^{35} resonance spectrum consists of only two lines of frequencies 33·90 and 34·01 mc. sec.$^{-1}$ at room temperature. Since the molecule is non-centrosymmetric, these two frequencies must correspond to the two different chlorine atoms in a molecule and therefore the asymmetric unit in the cell must be one molecule.

Experimental

Eastman's highest purity grade material was purified by repeated zone refinements by using a Fisher's zone refiner. A single crystal for the n.q.r. measurements was grown by Bridgman's technique. The purified sample was sealed in a glass tube 1·4 cm diameter, at one end of which a capillary tube was attached. Since the direction of the crystallographic axes other than the symmetry axis cannot be determined by the n.q.r. technique for monoclinic crystals, a Weissenberg photograph was taken of the part of the crystal in the capillary to determine its orientation with respect to the scale attached to the n.q.r. spectrometer. This measurement could not be made to an accuracy of better than two degrees, since the crystal had to be transferred from the X-ray camera to the coil of the n.q.r. spectrometer. The n.q.r. measurements were made on a spectrometer described by Dean (1960).

For the X-ray analysis, single crystals elongated about the b axis and approximately cylindrical in diameter were obtained from alcoholic solution. The intensity measurements were made on a crystal sealed in a thin-walled glass capillary to avoid evaporation. The zero to third layers about the b axis were recorded on multiple-film Weissenberg photographs using Cu $K\alpha$ radiation. The intensities were estimated by eye and 907 independent reflections were obtained.

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This is about 60 per cent of the reflections in the limiting sphere. The correlation of the four layers was by means of the double-slit technique of Stadler (1950). No corrections were made for absorption. The effect of the α_1, α_2 resolution was corrected as previously described by Sakurai (1962*a*). The intensities were reduced to relative structure amplitudes using an IBM 650 data reduction program of Shiono (1960).

Determination of the structure

Since the two chlorine atoms are at the *para* positions of the benzene ring, the n.q.r. zero magnetic splitting loci of both frequencies almost coincide in orientation. The direction of the *b* axis, which was approximately along the polar axis of the spectrometer coordinates, could be determined accurately from the symmetrical arrangement of these loci. The centres of the loci were assigned to the σ bonds. The π bond directions were assumed to be the directions of the asymmetry of the loci. The resulting angular orientations obtained are shown in Table 1.

Table 1. *N.Q.R. and corresponding X-ray bond orientation data*

Angle between	n.q.r.	X-ray
b axis and $Cl_5\sigma$ bond	76·8 ± 0·4°	77·1 ± 0·4°
b axis and $Cl_2\sigma$ bond	76·5 ± 0·4	76·3 ± 0·4
$Cl_2\sigma$ bond and $Cl_5\sigma$ bond	0·8 ± 0·2	0·8 ± 0·8
$Cl_2\pi$ bond and $Cl_5\pi$ bond	5·3	

Asymmetry parameter η

Cl_2	0·069 ± 0·015
Cl_5	0·066 ± 0·015

At that stage it was impossible to distinguish the two C–Cl bonds, *i.e.* relative to the amino group. This was done later by comparison with the X-ray results.

Since η is small a few degrees of uncertainty is expected for the π bond orientations.

The orthogonal molecular axes *L*, *M* and *N* are defined as in Fig. 1. *M* bisects the two σ bonds and *N* bisects the two π bonds. The direction cosines between the molecular axes and the crystal axes were obtained from the determination of the approximate orientation of the crystal of the n.q.r. spectrometer. The coordinates of the atoms in the crystal with respect to the origin of the molecular axes were then calculated with the assumption of a planar hexagonal benzene ring and C–C and C–Cl bonds of 1·38 and 1·70 Å respectively. These parameters are given in Table 2.

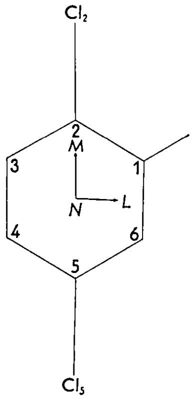

Fig. 1. The molecular axes.
N is perpendicular to the molecular plane.

Table 2. *Parameters deduced from n.q.r. data*

Direction cosines between molecular axes and crystal axes*

	a′	*b*	*c*
L	0·006	−0·480	0·878
M	0·966	0·233	0·122
N	−0·257	0·846	0·466

Approximate coordinates with respect to the origin of the molecule†

	x	*y*	*z*
Cl_2	0·317	0·187	0·179
C_1	0·070	0·142	−0·002
C_2	0·142	0·084	0·080
C_3	0·072	−0·058	0·074

* For convenience of calculation, the direction cosines are taken with respect to the *a′*, *b* and *c* axes, where *a′* is perpendicular to the *bc* plane.

† C_4, C_5, C_6 and Cl_5 are assumed to be the corresponding centrosymmetrical positions. The nitrogen atom coordinates are not determined.

In order to determine the position of the molecular centre in the crystal, the (010) plane projection was considered first. On this projection, the structure factor expression can be written as follows;

$$F_{hl}=4\Sigma' f_j \cos 2\pi(hx_{jo}+lz_{jo}) \\ \times \cos 2\pi(hX+lZ)+4f_{\rm N} \cos 2\pi(hx_{\rm N}+lz_{\rm N})$$

where X, Z are the coordinates of the molecular origin, x_{jo}, z_{jo} are the coordinates of atoms with respect to the centre of the molecule, and $x_{\rm N}, z_{\rm N}$ are the nitrogen coordinates. Σ' refers to the summation over the chlorine and carbon atoms only. If the contribution of the nitrogen is neglected,

$$(F_{hl/a_{hl}})^2 \approx \cos^2 2\pi(hX+lZ)$$

$$a_{hl} = 4\Sigma_j' f_j \cos 2\pi(hx_{jo}+lz_{jo})$$

Therefore a Fourier series

$$M(x, z) = \sum_{hl} (F_{hl}/a_{hl})^2 \cos 2\pi(hX+lZ) \\ = \tfrac{1}{2} \sum_{hl} [1+\cos 2\pi(h2X+l2Z)] \cos 2\pi(hx+lz)$$

will give a peak at $2X, 2Z$. This is the modified Patterson function derived by Giglio, Liquori & Ripamonti (1958). The values of a_{hl} were calculated from the coordinates in Table 2. Those values smaller than $4\sum_j f_j/10$ were rejected because a small error

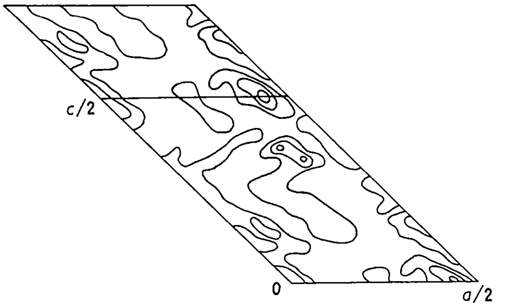

Fig. 2. A modified Patterson function on (010) projection.

in a_{hl} may introduce a large error in M. The resultant function is shown in Fig. 2. It has considerable structure, with the highest peak at $2X=0\cdot432$ and $2Z=0\cdot506$. Placing the molecular origin at X, Z, the structure factor signs were calculated and a Fourier synthesis projection was computed. As shown in Fig. 3, this clearly revealed the molecular shape and the position of the nitrogen atom. The atomic positions were then refined by successive Fourier and differential Fourier synthesis and structure factor calculations to a reliability factor for the ($h0l$) reflexions of 16·2%. To determine the Y coordinate of the molecular origin, a one-dimensional Patterson function was calculated along the line parallel to b axis through chlorine atoms. A value of $Y=0\cdot19$ was obtained, and the initial atomic coordinates thereby derived gave an overall structure factor agreement of 34%. Successive refinements by three-dimensional differential syntheses using isotropic temperature factors reduced this to 17%. A three-dimensional difference Fourier synthesis was then computed, a typical section of which is shown in Fig. 4. Since it indicated some anisotropic thermal motion of the chlorine atoms, an anisotropic least squares refinement was carried out. The Hughes (1941) weighting scheme was used and unobserved reflections were omitted. The hydrogen atoms were included as fixed atom contributions, at assumed positions coplanar with the ring with C–H = 1·07 Å, and N–H = 1·04 Å. The R factor was thereby reduced to 12·6 per cent, excluding non-observed reflections. Five strong low-order reflections for which the agreement was poor due to extinction were omitted

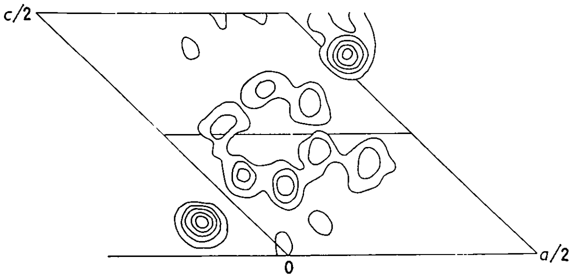

Fig. 3. The first Fourier map on (010) projection.

Table 3. *Atomic parameters and standard deviations*

Atom	x	y	z	$\sigma x 10^{-4}$	$\sigma y 10^{-3}$	$\sigma z 10^{-4}$
Cl_2	0·5367	0·3879	0·4148	2	0·8	2
Cl_5	−0·1084	0·0186	0·0672	3	0·9	2
C_1	0·2860	0·346	0·2173	8	3	6
C_2	0·3566	0·280	0·3182	10	3	7
C_3	0·2843	0·140	0·3376	11	3	7
C_4	0·1418	0·059	0·2631	9	3	8
C_5	0·0725	0·118	0·1639	10	3	7
C_6	0·1413	0·262	0·1402	10	3	7
N	0·3586	0·475	0·1943	10	3	7

Atom	$B_{11}\times10^{-2}$	$B_{22}\times10^{-2}$	$B_{33}\times10^{-2}$	$\sigma B_{11}\times10^{-4}$	$\sigma B_{22}\times10^{-3}$	$\sigma B_{33}\times10^{-4}$
Cl_2	1·03	7·7	0·592	3	6	1·7
Cl_5	1·08	9·1	0·708	3	6	1·9
C_1	0·95	2·7	0·58	9	9	5
C_2	1·04	3·0	0·61	10	9	6
C_3	1·03	5·4	0·44	10	10	5
C_4	1·47	3·5	0·80	11	9	6
C_5	1·09	2·9	0·62	10	9	5
C_6	1·37	4·0	0·54	11	9	5
N	1·81	5·9	0·90	12	9	6

Atom	$B_{12}\times10^{-2}$	$B_{13}\times10^{-2}$	$B_{23}\times10^{-2}$	$\sigma B_{12}\times10^{-4}$	$\sigma B_{13}\times10^{-4}$	$\sigma B_{23}\times10^{-4}$
Cl_2	−0·56	0·49	−0·48	6	2	5
Cl_5	−0·50	0·56	−0·40	7	2	6
C_1	0·27	0·52	0·07	18	5	14
C_2	0·33	0·51	0·26	23	6	15
C_3	−0·14	0·46	−0·11	23	6	17
C_4	0·27	0·92	0·27	22	17	17
C_5	−0·08	0·61	−0·18	19	6	16
C_6	0·65	0·65	0·23	22	7	16
N	−0·01	1·05	0·09	24	8	19

Table 4(*a*). *Crystal structure factors*

F_o and F_c are multiplied by 10

h	l	F_o	F_c
k=	0		
0	2	258	-264
0	4	345	-394
0	6	388	-343
0	8	475	-428
0	10	29	-19
0	12	219	210
0	14	123	105
0	16	20	-19
1	0	9	-47
1	2	115	101
1	4	374	340
1	6	185	166
1	8	112	117
1	10	368	-340
1	12	119	-102
1	14	25	24
1	16	12	21
-1	2	9	3
-1	4	176	-183
-1	6	18	3
-1	8	22	-39
-1	10	191	-156
-1	12	30	-25
-1	14	30	45
-1	16	121	112
-1	18	12	13
2	0	305	237
2	2	661	760
2	4	335	308
2	6	25	-26
2	8	365	-353
2	10	30	-28
2	12	28	27
2	14	19	18
-2	2	296	342
-2	4	809	-1235
-2	6	848	-1097
-2	8	407	393
-2	10	230	255
-2	12	375	288
-2	14	30	40
-2	16	76	-70
-2	18	104	-93
3	0	337	-338
3	2	493	-548
3	4	341	299
3	6	540	521
3	8	30	-32
3	10	29	34
3	12	72	-106
-3	2	302	-363
-3	4	156	-126
-3	6	393	413
-3	8	52	44
-3	10	23	24
-3	12	28	-6
-3	14	30	23
-3	16	29	21
4	0	447	-422
4	2	365	330
4	4	258	243
4	6	29	-39
4	8	30	9
4	10	27	-37
4	12	17	16
-4	2	309	-337
-4	4	584	-751
-4	6	98	86
-4	8	429	393
-4	10	554	546
-4	12	105	97
-4	14	143	-122
-4	16	273	-271
-4	18	27	-11
-4	20	20	34
5	0	586	-637
5	2	368	-341
5	4	119	-86
5	6	99	72
5	8	217	211
5	10	26	162
-5	2	236	192
-5	4	493	561
-5	6	549	564
-5	8	87	-58
-5	10	125	-101
-5	12	237	-249
-5	14	29	29
-5	16	30	19
6	0	74	-43
6	2	29	-32
6	4	30	23
6	6	29	-27
6	8	24	-48
-6	2	227	-220
-6	4	56	-12
-6	6	304	282
-6	8	455	461
-6	10	98	72
-6	12	218	-214
-6	14	209	-204
-6	16	121	-111
-6	18	0	-16
-6	20	145	123
7	0	40	64
7	2	265	-270
7	4	234	-209
7	6	102	-72
7	8	113	94
-7	2	388	365
-7	4	543	564
-7	6	70	-67
-7	8	39	-40
-7	10	601	-631
-7	12	173	-169
-7	14	256	252
-7	16	53	53
-7	18	37	68
8	0	101	96
8	2	69	66
8	4	27	27
8	6	61	-60
-8	2	29	-47
-8	4	27	48
-8	6	25	25
-8	8	24	-13
-8	10	98	59
-8	12	274	-242
-8	14	206	-191
-8	16	177	181
-8	18	82	32
-8	20	33	70
9	0	157	117
9	2	28	37
9	4	114	-108
-9	2	386	329
-9	4	149	139
-9	6	364	-368
-9	8	373	-383
-9	10	131	-131
-9	12	152	136
-9	14	119	111
-9	16	351	363
-9	18	172	-141
-9	20	107	-97
10	0	28	-17
10	2	27	103
-10	2	82	-72
-10	4	111	-93
-10	6	167	-140
-10	8	129	128
-10	10	29	7
-10	12	29	-2
-10	14	74	21
-10	16	54	-29
-10	18	149	135
-10	20	28	-14
-10	22	55	-60
11	0	125	122
11	2	0	38
-11	2	28	-8
-11	4	119	-101
-11	6	136	-108
-11	8	372	-369
-11	10	272	267
-11	12	259	262
-11	14	137	124
-11	16	30	-31
-11	18	76	-74
-11	20	155	-138
-12	2	177	-133
-12	4	67	-53
-12	6	128	118
-12	8	44	52
-12	10	167	149
-12	12	30	-3
-12	14	141	-123
-12	16	30	-16
-12	18	29	30
-12	20	39	-18
-13	2	9	-15
-13	4	67	-65
-13	6	59	-65
-13	8	116	97
-13	10	29	48
-13	12	177	159
-13	14	69	60
-13	16	230	-233
-13	18	61	-65
-13	20	31	-27
-13	22	64	56
-14	6	166	160
-14	8	84	76
-14	10	38	-50
-14	12	89	-88
-14	14	99	-92
-14	16	28	-29
-14	18	54	66
-14	20	42	40
-14	22	28	4
-15	8	42	25
-15	10	20	22
-15	12	23	15
-15	14	81	-77
-15	16	43	-43
-15	18	50	-45
-15	20	64	48
-15	22	35	48
-16	12	97	-78
-16	14	23	-19
-16	16	107	86
-16	18	23	46
K=	1		
0	1	0	717
0	2	129	150
0	3	273	308
0	4	176	178
0	5	542	-610
0	6	18	23
0	7	292	-282
0	8	127	-112
0	9	232	-173
0	10	190	-172
0	11	153	128
0	12	79	70
0	13	116	99
0	14	66	66
0	15	43	38
1	0	324	-540
1	1	197	211
1	2	146	-106
1	3	95	82
1	4	53	-58
1	5	317	323
1	6	178	-152
1	7	74	58
1	8	24	14
1	9	283	-241
1	10	177	149
1	11	79	-72
1	12	0	10
1	13	116	-78
1	14	53	-39
-1	1	0	33
-1	2	489	-1040
-1	3	179	-224
-1	4	182	-172
-1	5	14	24
-1	6	267	302
-1	7	136	-140
-1	8	21	13
-1	9	74	-63
-1	10	159	121
-1	11	120	-98
-1	12	27	13
-1	13	74	82
-1	14	54	-49
-1	15	71	74
-1	16	53	-51
2	0	95	-90
2	1	286	320
2	2	15	30
2	3	463	431
2	4	354	313
2	5	96	99
2	6	129	105
2	7	214	-172
2	8	265	-233
2	9	161	-125
2	10	0	7
2	11	0	-31
2	12	49	-31
-2	1	456	652
-2	2	211	243
-2	3	547	-1125
-2	4	86	95
-2	5	433	-486
-2	6	61	-64
-2	7	200	-184
-2	8	125	-128
-2	9	154	131
-2	10	74	-55
-2	11	314	291
-2	12	46	30
-2	13	178	179
-2	14	43	79
-2	15	76	-78
-2	16	42	35
-2	17	67	-71
3	0	129	147
3	1	384	-379
3	2	118	106
3	3	206	178
3	4	174	-140
3	5	261	203
3	6	201	-163
3	7	301	253
3	8	109	82
3	9	0	15
3	10	0	33
3	11	109	-102
3	12	110	22
-3	1	390	-429
-3	2	41	-83
-3	3	134	-140
-3	4	269	-290
-3	5	54	39
-3	6	170	164
-3	7	132	133
-3	8	360	410
-3	9	159	151
-3	10	71	-52
-3	11	63	-54
-3	12	36	-50
-3	13	61	63
-3	14	154	-121
4	0	370	-358
4	1	28	34
4	2	211	176
4	3	127	99
4	4	194	175
4	5	223	187
4	6	0	-20
4	7	63	-39
4	8	78	76
4	9	0	-5
4	10	62	-54
4	11	127	20
-4	1	320	-337
-4	2	196	173
-4	3	368	-395
-4	4	95	89
-4	5	286	-327
-4	6	232	-224
-4	7	187	233
-4	8	143	-129
-4	9	519	568
-4	10	21	-10
-4	11	127	120
-4	12	61	75
-4	13	26	-46
-4	14	55	54
-4	15	188	-135
-4	16	27	-3
-4	17	134	-122
5	0	271	226
5	1	462	-439
5	2	23	26
5	3	313	-269
5	4	122	-112
5	5	126	124
5	6	0	-31
5	7	116	110
5	8	0	-18
5	9	71	126
-5	1	155	-126
-5	2	18	-28
-5	3	244	258
-5	4	54	50
-5	5	230	249
-5	6	268	244
-5	7	436	490
-5	8	26	52
-5	9	0	-143
-5	10	0	9
-5	11	178	-180
-5	12	155	-129
-5	13	36	-30
-5	14	85	-90
-5	15	0	-32
-5	16	0	-25
-5	17	0	14
-5	18	129	101
6	0	108	-90
6	1	0	-24
6	2	60	-78
6	3	0	-2
6	4	0	22
6	5	0	-51
6	6	119	99
6	7	0	-13
6	8	66	47
-6	1	262	-222
-6	2	243	213
-6	3	130	100
-6	4	126	-139
-6	5	106	75
-6	6	85	-87
-6	7	260	274
-6	8	308	-277
-6	9	249	227
-6	10	68	74
-6	11	51	-45
-6	12	188	180
-6	13	269	-279
-6	14	0	-3
-6	15	107	-99
-6	16	0	-7
-6	17	0	-43
-6	18	0	-40
-6	19	91	94
7	0	119	104
7	1	175	-151
7	2	0	19
7	3	209	-164
7	4	0	-25
7	5	67	-128
-7	1	140	121
-7	2	85	-75
-7	3	508	479
-7	4	142	124
-7	5	298	258
-7	6	117	100
-7	7	135	-122
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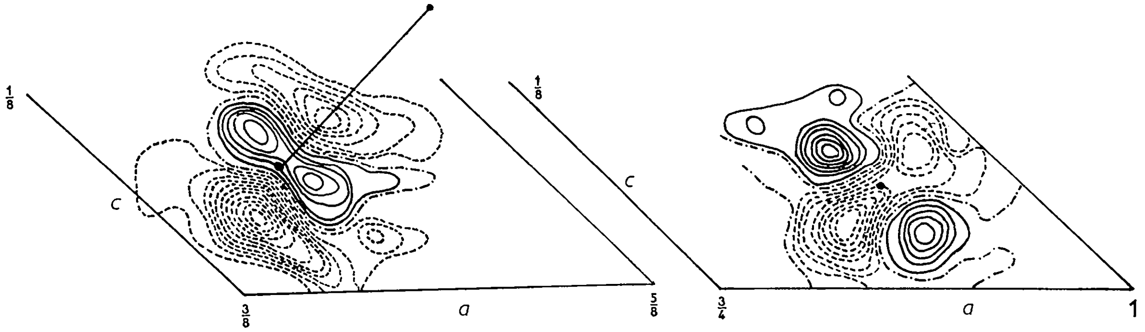


Fig. 4. ($F_o - F_c$) synthesis showing anisotropic thermal motion of the chlorine atoms. Left Cl_2, right Cl_5.

from the refinement. These reflections are shown in Table 4(*b*).

Table 4(*b*). *Observed reflections omitted in the least-square refinement*

	F_o	F_c
$\bar{2}04$	89·2	−126·1
$\bar{2}06$	93·4	−112·8
$\bar{1}12$	52·4	−102·5
$\bar{2}11$	48·8	63·6
$\bar{2}13$	58·5	−113·3

The atomic coordinates, temperature factors, and their standard errors are shown in Table 3. The observed and calculated structure factors from the final cycle of calculations are shown in Table 4(*a*). The IBM 650 and 7070 computers were used for the computations, using programs written by Shiono (1957, 1959, 1960). The least-squares refinements were computed on an IBM 704 using the full matrix program of Busing & Levy (1959).

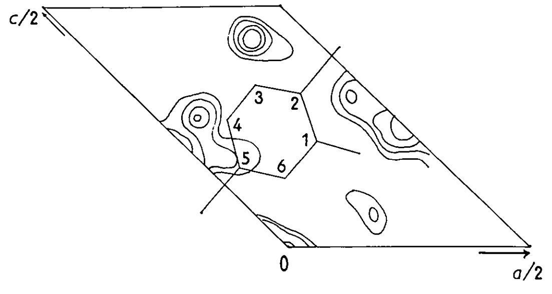


Fig. 5. Final ($F_o - F_c$) synthesis on (010) projection. The interval of the contours is 0·05 e.Å^{-2} beginning from 0·05 e.Å^{-2}.

Fig. 5 shows a difference Fourier projection on (010) using the final anisotropic coordinates, excluding the hydrogen atoms, for the reflections with sin $\theta \leq 0·5$. Two of the larger peaks can be associated with hydrogen atoms but the data did not permit location of the other three atoms.

The determination of the thermal vibrations

The individual atomic temperature factors in Table 3 were transformed into the mean square displacements U_{ij}, along the principal axes of the moment of inertia of the molecule shown in Fig. 6 and Table 5. The tensors of translational and rotational motion were obtained by the least-squares formula derived by Cruickshank (1956*a*), and these values and their standard errors are shown in Table 6. The calculated U_{ij} are compared with observed values in Table 7,

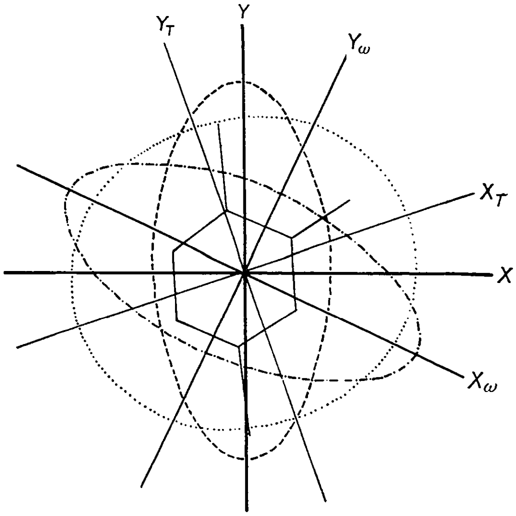


Fig. 6. Section of the ellipsoids of thermal motion on the molecular plane.

— — — — — — Moment of inertia.
·············· Translational motion.
—·—·—·—·— Rotational motion.

Table 5. *Direction cosines between the principal axes of the molecule and the crystal axes*

	a'	b	c	(Atomic weight Å^2) Moment of inertia
J_1	0·092	−0·301	0·949	702·5
J_2	0·966	0·259	−0·011	172·4
J_3	−0·242	0·918	0·315	964·9

Table 6. *Tensors of molecular vibration*

Translation $T \times 10^{-2}$ Å^2

$$\begin{pmatrix} 4\cdot05 & -0\cdot29 & 0\cdot52 \\ & 4\cdot74 & 0\cdot32 \\ & & 1\cdot48 \end{pmatrix}$$

Rotation ω deg.^{2}

$$\begin{pmatrix} 15\cdot0 & 7\cdot8 & 2\cdot4 \\ & 27\cdot5 & 3\cdot3 \\ & & 14\cdot6 \end{pmatrix}$$

$\sigma(T)$

$$\begin{pmatrix} 0\cdot32 & 0\cdot26 & 0\cdot21 \\ & 0\cdot25 & 0\cdot19 \\ & & 0\cdot32 \end{pmatrix}$$

$\sigma(\omega)$

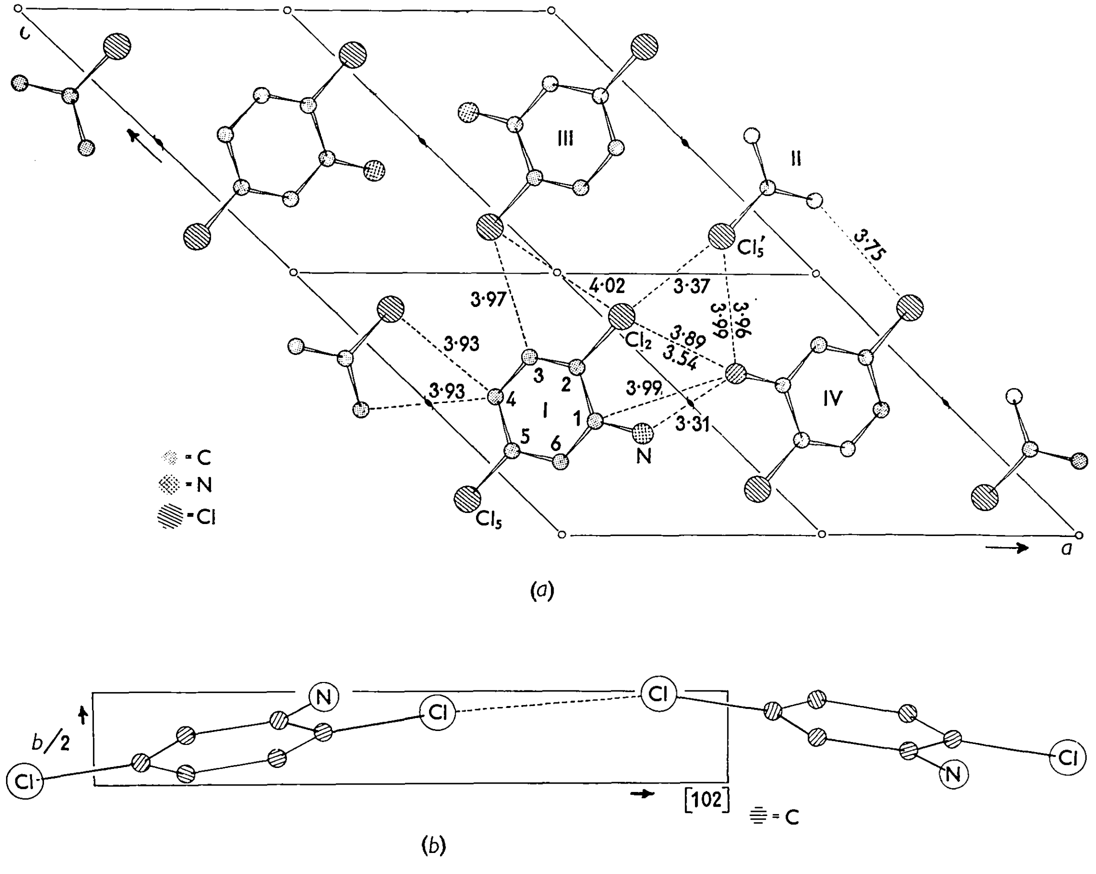
$$\begin{pmatrix} 1\cdot6 & 3\cdot2 & 1\cdot4 \\ & 6\cdot4 & 2\cdot9 \\ & & 2\cdot1 \end{pmatrix}$$

and the agreement justifies the assumption of rigid body vibration.

Of the off-diagonal elements of the tensors only ω_{12} is significant. Therefore, as would be expected, the principal axes of the rotational vibration in the plane of the molecule are slightly different from the principal axes of the molecule. A section of the ellipse of the thermal motion of the molecular plane is shown in Fig. 6. The translational motion in the plane of the molecule is greater than that normal to it. The root mean square displacements of the translational motion along the principal axes of the molecule are 0·20, 0·22 and 0·12 Å respectively and the amplitudes of the rotation are 3·9, 5·2 and 3·8 degrees. The largest amplitude corresponds to the axis of smallest moment of inertia.

Table 7. *Mean square displacement along the principal axes of the molecule*

	U_{11}		U_{22}		U_{33}		U_{12}		U_{13}		U_{23}	
Atom	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
Cl_2	6·8	7·9	4·1	4·8	5·8	6·3	0·2	1·1	−0·4	−0·3	0·7	0·2
Cl_5	7·8	8·7	4·5	4·7	6·8	6·3	−0·1	0·5	−0·3	−0·3	0·3	0·3
C_1	5·2	4·2	4·3	5·1	2·0	2·1	−0·4	−0·7	0·7	0·6	0·0	0·3
C_2	5·7	4·7	4·7	4·8	2·7	2·5	−0·1	0·6	1·6	0·4	0·1	0·3
C_3	4·3	4·1	4·4	5·7	4·2	3·6	0·4	0·7	0·0	0·4	0·5	0·1
C_4	4·1	4·4	6·5	5·6	2·9	2·9	−1·8	−1·0	0·5	0·6	−0·5	0·2
C_5	5·1	5·1	4·6	4·8	2·3	2·4	−0·7	−0·5	0·3	0·4	0·6	0·3
C_6	4·2	4·3	6·4	5·2	2·6	3·0	0·5	0·8	0·3	0·4	−0·2	0·2
N	5·3	4·9	7·8	6·7	4·6	4·7	−1·5	−0·8	0·3	0·7	0·5	0·1



(*a*)

(*b*)

Fig. 7. The molecular arrangement in the crystal. (*a*) The projection on (010) showing the shorter intermolecular distances. (*b*) The projection showing the shortest chlorine separation.

Discussion of the crystal structure

The arrangement of the molecules in the crystal is shown in Fig. 7. The molecular plane makes an angle of 23·4° with the *ac* plane. The direction cosines of the molecular axes defined in Fig. 1 are shown in Table 8. The difference between these values and those given in Table 2 is mainly due to the uncertainty in relating the *a* and *c* axial directions to the n.q.r. observations.

Table 8. *Direction cosines between the molecular axes and crystal axes*

	a'	b	c
L	−0·015	−0·327	0·941
M	0·966	0·225	0·094
N	−0·242	0·918	0·315

Table 9. *The intermolecular chlorine–nitrogen distances shorter than* 4·1 Å

Cl_2(I) –Cl_5(II)	3·369
Cl_2(I) –Cl_2(I$^-$)	3·892
Cl_2(I) –Cl_2(III)	4·020
Cl_5(I) –Cl_5(I$^-$)	3·892
Cl_2(I) –N(IV$^-$)	3·540
Cl_2(I) –N(IV)	3·886
Cl_5(II)–N(IV)	3·963
Cl_5(II)–N(IV$^-$)	3·987
N(I) –N(IV)	3·313
N(I) –N(I$^-$)	3·892

Roman figures in the parentheses correspond to the molecules in Fig. 7(*a*) and their coordinates are deduced from those in Table 3 by following relations.

(I) x, y, z (II) $1+x, \frac{1}{2}-y, \frac{1}{2}+z$ (III) $1-x, 1-y, 1-z$
(IV) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$ (IV$^-$) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$.

The intermolecular chlorine to nitrogen distances shorter than 4·1 Å are listed in Table 9. The shortest N · · · Cl distance is 3·54 Å. There is no evidence of a N–H · · · Cl hydrogen bond. The shortest chlorine–chlorine distance is 3·37 Å, which is considerably less than the usually quoted Van der Waals distance of 3·6 Å. This is compared with some similar values for other structures in Table 10.

These results suggest that there is an orientation factor associated with the occurrence of these shorter distances, since they satisfy the condition that either both angles between C–Cl and Cl · · · Cl are 160 ± 10°, or one is about 175° and the other about 80°, as shown in Figure 8. A similar arrangement has been found in molecular chlorine (Collin, 1952), and in 2,4-dibromomenthone (Wunderlich and Lipscomb, 1960).

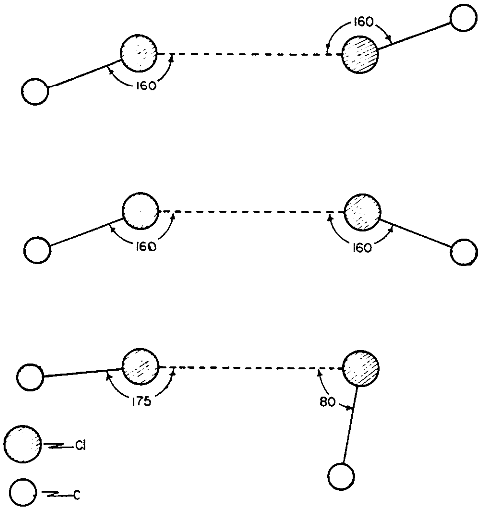


Fig. 8. The short Cl · · · Cl intermolecular distances.

From the n.q.r. studies of molecular iodine (Robinson, Dehmelt & Gordy, 1955) and of the cyanogen halides (Gellar & Schawlow, 1955) there is evidence that the short intermolecular distances between halogen atoms in these structures are caused by some covalent bond character in the cohesive forces between the molecules. In tetrachlorohydroquinone, pentachlorophenol and solid chlorine, however, the Cl^{35} quadrupole coupling constants appear to be unaffected by these intermolecular approaches. This suggests that they are normal van der Waals interactions, and that the results shown in Table 10 indicate that the van der Waals radius is not necessarily constant for all directions relative to the C–Cl bond.

Discussion of the molecular structure and bond character

The bond lengths and the valence angles are shown in Table 11 and Fig. 9. The bond lengths are corrected

Table 10. *Short* C–Cl. . .Cl–C *intermolecular distances*

Distance	Angles between C–Cl bond and Cl · · · Cl distance		Molecule	Reference
	1	2		
3·27 Å	154°	154°	2,2′-Dichlorobenzidene	Smare (1948)
3·37	166	157	2,5-Dichloroaniline	This work
3·37	168	168	Tetrachlorohydroquinone	Sakurai (1962*a*)
3·43	175	78	Pentachlorophenol	Sakurai (1962*b*)
3·43	176	80	Tetrachlorohydroquinone	Sakurai (1962*a*)
3·43	148	155	2-Amino-4,6-dichloropyrimidine	Clews & Cochran (1948)
3·47	174	79	Pentachlorophenol	Sakurai (1962*b*)
3·49	165	165	Pentachlorophenol	Sakurai (1962*b*)

for the effect of rotational vibration (Cruickshank, 1956b). The least-square plane through six carbon atoms of the benzene ring was calculated and the deviations of the atomic positions from the plane are shown in Table 12. All carbon and chlorine atoms are in a plane within experimental error, and the nitrogen atom deviates from it by 0·063 Å.

Table 11. *Bond lengths and bond angles*

	Without rotational correction	With rotational correction
C_2–Cl_2	1·737 Å	1·744 Å
C_5–Cl_5	1·736	1·743
C_1–C_2	1·417	1·423
C_2–C_3	1·353	1·360
C_3–C_4	1·368	1·378
C_4–C_5	1·391	1·400
C_5–C_6	1·382	1·388
C_6–C_1	1·392	1·398
C_1–N	1·395	1·407

Bond angles

C_1–C_2–C_3	120·4°
C_2–C_3–C_4	122·9
C_3–C_4–C_5	116·9
C_4–C_5–C_6	122·4
C_5–C_6–C_1	119·6
C_6–C_1–C_2	117·8
C_1–C_2–Cl_2	117·9
C_3–C_2–Cl_2	121·7
C_4–C_5–Cl_5	118·3
C_6–C_5–Cl_5	119·3
C_6–C_1–N	120·2
C_2–C_1–N	121·9

Standard errors

In bonds		In bond angles	
C–Cl	0·012 Å	Cl–C–C	0·9°
C–C	0·017	C–C–C	1·1
C–N	0·016	C–C–N	1·0

Table 12. *Deviation of the atoms from the plane of the benzene ring*

C_1	−0·009 Å
C_2	0·007
C_3	−0·010
C_4	−0·002
C_5	0·006
C_6	0·008
Cl_2	−0·007
Cl_5	−0·005
N	−0·063

The carbon–carbon bond distances deviate slightly from the regular benzene ring, especially, C_1–C_2 is longer and C_2–C_3 is shorter than the ordinary benzene C–C distance. A simple molecular orbital calculation was carried out using the Hückel approximation with the following parameters,

Carbon coulomb integral	α
Carbon carbon resonance integral	β
Nitrogen coulomb integral	$H_{NN}=\alpha+(X_N-X_C)\beta$
Nitrogen carbon resonance integral	$H_{NC}=\beta$
Chlorine coulomb integral	$H_{ClCl}=\alpha+1\cdot1\beta$
Chlorine carbon resonance integral	$H_{ClC}=0\cdot6\beta$

where X_N, and X_C are electronegativities of the corresponding atoms. The parameters for the chlorine atoms were those used by I'haya (1959), for the best agreement with the observed dipole moment of

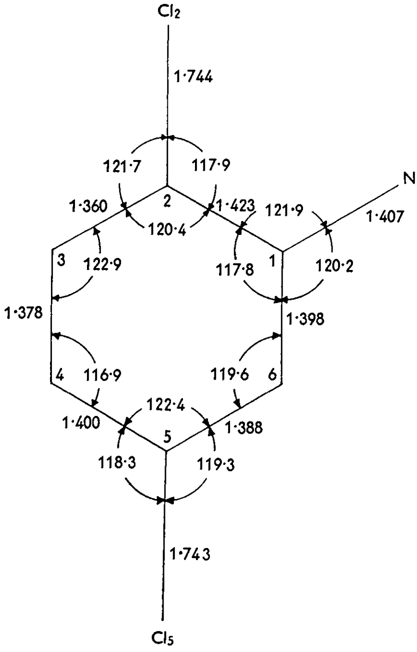


Fig. 9. The bond lengths and valence angles.

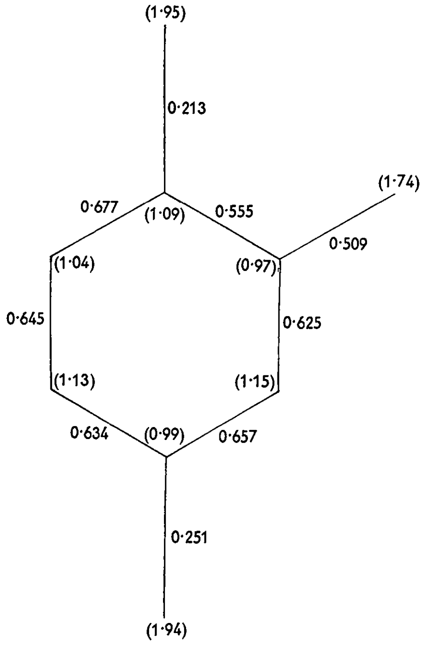


Fig. 10. Bond order and charge distribution from molecular orbital calculation.

monochlorobenzene. The resultant bond orders and charge distributions are shown in Fig. 10. The bond lengths obtained from these values by using the experimental relations between the bond order and the bond length of Daudel, Lefebvre & Moser (1959), are shown in Table 13.

Table 13. *Observed and calculated bond lengths*

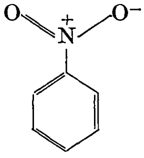
Bond	Observed	Molecular orbital	Hybridization by Trotter's graph
C_1–C_2	1·42 Å	1·42 (0)	1·42 (0)
C_2–C_3	1·36	1·38(−2)	1·35 (1)
C_3–C_4	1·38	1·39(−1)	1·40(−2)
C_4–C_5	1·40	1·40 (0)	1·40 (0)
C_5–C_6	1·39	1·39 (0)	1·37 (2)
C_6–C_1	1·40	1·40 (0)	1·43(−3)
T_0^2		1·5	5·5

(The values in parentheses are the differences between observed and calculated values with units of 10^{-2} Å.)

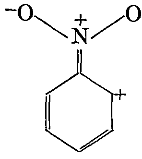
The agreement with the observed value is excellent. Recently Trotter (1960) showed that the observed C–C bond lengths in nitrobenzene are better explained by the state of hybridization than by the simple molecular orbital theory and he derived an experimental relation between the C–C bond length and C–C–C bond angle. The bond lengths for the present molecule were calculated from Trotter's relationship and shown in Table 13. Although the agreement is apparently worse than for the molecular orbital calculation, the difference from the observed values is not significant from the standpoint of a multi-parameter significance test (Cruickshank & Robertson, 1953). T_0^2 values calculated from Cruickshank & Robertson's formula (1953) are also shown in Table 13. Clearly in order to distinguish between these two interpretations, more accurate observation is necessary.

The C–N bond of 1·407 Å, is significantly shorter than the sum of the single-bond covalent radii, 1·47 Å, in contrast to the results found for nitrobenzene and some other nitro derivatives (Table 14). Trotter (1960) concluded that in these nitro compounds resonance is either unimportant across the C–N bond or that any resonance interaction is insufficient to cause any measurable shortening.

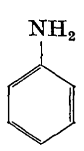
The difference between the C–N bond lengths in the nitro and aniline derivatives can be explained in terms of valence bond diagrams if it is assumed that the 'sacrificial' structures are relatively unimportant. Thus II is a 'sacrificial' structure relative to I since it contains one less bond, whereas, by the same criterion, IV would be comparable in importance to III.



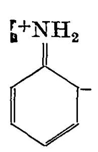
I



II



III



IV

In the toluidine hydrochlorides, the C–N bonds have the single-bond value, since the NH_3^+ cannot be conjugated with the benzene ring.

From the quadrupole data the ionicity and the double-bond character of the C–Cl bonds were calculated to be 22% and 2·7% respectively using

Table 14. C–N *bond lengths*

Molecule	Distance	Substituent	References
Nitrobenzene	1·49 Å	NO_2	Trotter (1960)
1,5-Dinitronaphthalene	1·49	NO_2	
9,10-Dinitroanthracene	1·45	NO_2	
Nitromesitylene	1·48	NO_2	
9-Nitroanthracene	1·48	NO_2	
m-Tolidinehydrochloride	1·45	$NH_3{}^+$	Fowweather & Hargreaves (1950)
p-Toluidinehydrochloride	1·45	$NH_3{}^+$	Von Eller (1955)
p-Nitroaniline	1·37	NH_2	Trueblood, Goldish & Donohue (1961)
	1·46	NO_2	
2,2′-Dichlorobenzidine	1·40	NH_2	Smare (1948)
2,5-Dichloroaniline	1·41	NH_2	This work

Table 15. C–Cl *bond lengths and the asymmetry parameters*

Compound	Mean value of C–Cl	Mean value of η	References
2,5-Dichloroaniline	1·744 Å	0·07	Present work
Tetrachlorohydroquinone	1·73(*a*)(*b*)	0·13	Sakurai (1962*a*)
Tetrachloroparaquinone	1·714	0·21	Chu, Jeffrey & Sakurai (1962)
Pentachlorophenol	1·71(*a*)(*b*)	0·17	Sakurai (1962*b*)
1,3,5-Trichlorobenzene	1·72(*b*)	0·11	Morino & Toyama (1960), Milledge & Pant (1960)
Paradichlorobenzene	1·65(*b*)	0·08	Dean (1952), Croatto, Bezzi & Bua (1952)
		0·06	Ogawa & Ohi (1959)

(*a*) A chlorine which is affected by the hydrogen bond is omitted.

(*b*) Original values for these compounds were not corrected for molecular vibration. In order to take into account this effect, 0·007 Å is added and the value is rounded at the third decimal place.

Bershons (1954) relations. In this calculation the temperature effect on the frequency was estimated to be 0·5 mc. The C–Cl bond lengths and the asymmetry parameters of some chlorobenzene derivatives are shown in Table 15.

These values are consistent with the assumption that the asymmetry parameter is proportional to the double bond character.

Recently Giardino (1961) has obtained more precise values of $\eta = 0{\cdot}0588 \pm 0{\cdot}0024$ and $0{\cdot}0789 \pm 0{\cdot}0042$ for the 34·01 and 33·90 mc. frequencies of 2,5-dichloroaniline.

It was pointed out by Bershon (1954) that the π electron density from the nitrogen is located more in the *ortho* and *para* positions than in the *meta* position and in consequence the asymmetry parameter of the *meta* chlorine will be larger than that at the *ortho* or *para*. This is in agreement with Giardino's result with the lower asymmetry parameter corresponding to Cl_2 and higher to Cl_5.

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