

The Crystal and Molecular Structure of 3-Nitroperchlorylbenzene*

BY GUS J. PALENIK†

U.S. Naval Ordnance Test Station, China Lake, California 93555, U.S.A.

JERRY DONOHUE‡

Department of Chemistry, University of Southern California, California 90007, U.S.A.

AND K. N. TRUEBLOOD

Department of Chemistry,§ University of California, Los Angeles, California 90024, U.S.A.

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3-Nitroperchlorylbenzene forms acicular crystals, with space group $Pbn2_1$ (No. 33). There are four molecules in the unit cell with $a=14.717$, $b=10.707$, and $c=5.032$ Å. The structure was solved from a sharpened three-dimensional Patterson function and refined by Fourier syntheses and full-matrix least-squares methods. The final residual, R , for the 745 observed reflections, measured with a scintillation counter, is 0.066. The benzene ring, with an average C–C distance of 1.380 ± 0.010 Å, is planar but the nitro group is twisted by 13° from this plane. Decreased resonance interaction between the nitro group and the aromatic ring contributes to the long C–N distance of 1.497 Å. The C–Cl distance of 1.786 Å is long compared with a C–Cl bond where the Cl atom is unsubstituted. Large thermal motions in both the nitro and perchloryl groups reduced the accuracy of the bond lengths of N–O, average 1.25 Å, and Cl–O, average 1.45 Å; however, the values in both cases are comparable to the distances found in similar compounds.

Introduction

The preparation of perchlorylaromatic compounds by Inman, Oesterling & Tyczkowski in 1958 provided the possibility of determining the geometry of the perchloryl group in an organic environment. At that time there had been few precise structure analyses of either organic or inorganic compounds containing the nitro or perchloryl group. The presence of both groups on the same aromatic nucleus prompted us to initiate a determination of the crystal structure of 3-nitroperchlorylbenzene (3-NPCB) late in 1958, but for various reasons the study was not completed for nearly 8 years.

Experimental

The preparation of 3-NPCB, $C_6H_4ClNO_5$, was carried out using a procedure similar to that given by Inman, Oesterling & Tyczkowski (1958). Transparent acicular crystals elongated in the c direction were grown by evaporation of an alcohol solution. The crystals have an appreciable vapor pressure and were coated with a thin layer of polystyrene to decrease losses by sublimation.

Equi-inclination Weissenberg photographs (Cu $K\alpha$, $\lambda=1.5418$ Å) were taken with the needle axis as the

rotation axis for crystal 1, $l=0$ to 2, and for crystal 2, $l=0$ to 3. A small fragment was cleaved from a larger crystal and mounted with [110] as the rotation axis; only the zero layer was recorded because this crystal was too small to give good intensity photographs. The intensities from the zero layer about [110] were used to correlate the data from the various layers about c . The resulting set of 659 observed reflections will be designated the visual data (VD).

The only systematic absences on the above photographs are:

$$0kl \text{ absent if } k=2n+1$$

$$h0l \text{ absent if } h+l=2n+1.$$

Thus, the space group is either $Pbn2_1$ (C_{2v}^9) or $Pbnm$ (D_{2h}^{16}). The unit-cell dimensions, determined from Weissenberg photographs calibrated with NaCl powder patterns, are $a=14.74$, $b=10.74$ and $c=5.04$ Å. These dimensions and the space group possibilities are similar to those of m -dinitrobenzene (Trotter & Williston, 1966). Consequently, the space group was initially assumed to be $Pbn2_1$ and the unconventional setting was retained for possible comparison with m -dinitrobenzene. The structure analysis confirmed this choice of space group; however, the two compounds are not closely related structurally.

Over a period of about 6 years crystals of 3-NPCB had grown on the sides of the sample tube by sublimation at room temperature. For reasons described below it appeared essential to obtain a more precise set of intensity data. One clear, well-developed crystal was selected and cleaved with a razor blade to give a fragment $0.12 \times 0.17 \times 0.22$ mm, which was sealed in a

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† Present address: Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada.

‡ Present address: Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, U.S.A.

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thin-walled capillary. The crystal was dipped in liquid nitrogen to minimize primary extinction, and then mounted on a General Electric single-crystal orienter. The long dimension of the crystal (the *c* axis) was parallel to the ϕ axis of the orienter. The unit-cell dimensions were determined by measuring the 2θ values that could be observed for the $h00$, $0k0$ and $00l$ reflections using a narrow beam of Mo $K\alpha$ radiation ($\alpha_1 = 0.70926$ and $\alpha_2 = 0.71354$ Å). The average dimensions, together with their e.s.d.'s, are

$$\begin{aligned} a &= 14.717 \pm 0.008 \text{ \AA} \\ b &= 10.707 \pm 0.006 \\ c &= 5.023 \pm 0.004 \end{aligned}$$

These dimensions are in reasonable agreement with the values measured from the Weissenberg photographs and were used in all calculations of geometry quoted below. The density calculated for four molecules per unit cell is 1.722 g.cm^{-3} ; that measured by flotation in a $\text{CCl}_4\text{-CBr}_4$ solution is 1.70 g.cm^{-3} .

The second set of intensities was measured with a General Electric Diffractometer which had been automated by the Datex Corporation. The stationary crystal-stationary counter technique was employed in measuring 2973 reflections of the type hkl and $h\bar{k}l$ with $2\theta < 60.0$ (Mo radiation). A 20-sec count was taken for each reflection with a Zr filter at the counter window. Four standard reflections were checked after each 75 intensity measurements. The largest and smallest numbers of counts differed by less than 10% in all four cases and there were no apparent trends with time.

The reflections of the type $0kl$ with $k = 2n + 1$ and $h0l$ with $h + l = 2n + 1$, which are required by the space group to be absent, were also surveyed and these 176 reflections were then used to calculate a background correction as a function of 2θ . Reflections which were greater than 1.2 times the appropriate background count were considered to be observed. The final set of counter data (CD) consisted of 745 observed reflections out of the 1274 independent reflections in the portion of the reciprocal lattice that was surveyed.

Determination and refinement of the trial structure

(a) The visual data

A sharpened three-dimensional Patterson synthesis with the origin peak removed was calculated. The Cl-Cl vectors were easily recognized, but the *y* parameter of the Cl atom was approximately zero so that the heavy atom method could not be easily applied. However, a consideration of the Cl-light atom vectors in a model of the molecule yielded a plausible trial structure. It was apparent that the molecule does not lie in a plane normal to *c* and thus the space group must be $Pbn2_1$.

The centrosymmetric projection down *c* is fairly well resolved and was refined first. Successive Fourier syntheses reduced the usual residual *R* to 0.20 for the 182 observed $hk0$ reflections (VD). The *z* coordinates were then estimated from the projected distances by a com-

parison with the expected values and a three-dimensional Fourier synthesis was calculated. At this point, *R* was 0.27 for the complete set of three-dimensional data.

Refinement was continued using least-squares methods, with 3×3 blocks for the positional parameters and 6×6 blocks for the anisotropic thermal parameters. Partial shifts of 3/4 for positional and 3/8 for thermal parameters were employed. The *z* coordinate for the Cl atom was fixed at 0.000 to define the origin in the polar space group. The value of *R* dropped to 0.11 and since there were no detectable trends in the various small shifts in the final cycles, the refinement was considered completed. Unfortunately, the geometry of the molecule as calculated with the final least-squares parameters was chemically unreasonable, although the crystal structure determination seemed acceptable by most standards. The three Cl-O distances varied from 1.35 to 1.45 Å, with an estimated standard deviation of 0.015 Å, and the C-C distances in the benzene ring varied from 1.33 to 1.42 Å.

When more powerful computing facilities became available, a full-matrix refinement of the data was carried out. The final parameters were not significantly different from those obtained by the block approximation. We felt that the inconsistencies might have resulted from inadequate interlayer scaling and so a refinement was carried out in which an individual scale factor for each layer was allowed to vary. The distances and angles in the molecule did not improve to any significant degree. Collection of a more precise set of intensities seemed essential to determine whether the apparent asymmetry of the molecule was indeed real.

(b) The counter data

The starting positional parameters for the full-matrix least-squares refinement based on the counter data were those from the three-dimensional Fourier synthesis calculated with the VD. Initially, the positions, one isotropic thermal parameter per atom and a single overall scale factor, 52 parameters in all, were refined. The function minimized was $\sum w(\Delta F)^2$, with the following weighting scheme:

$$\begin{aligned} w &= F_o/40 & \text{if } F_o < 40 \\ w &= 1 & \text{if } 40 < F_o < 200 \\ w &= 200/F_o & \text{if } F_o > 200 \end{aligned}$$

After four cycles, the residual *R* was 0.116. Anisotropic thermal parameters were then introduced giving a total of 117 parameters, and the full-matrix refinement was continued. After 5 cycles *R* had converged to 0.075 and a difference Fourier synthesis was calculated. The four hydrogen atoms were readily located and were included in the structure factor calculation, but their parameters were not refined. Three least-squares cycles reduced *R* to 0.066 and the refinement was terminated. The final shifts averaged less than 2% of the corresponding estimated standard deviations. The final positional parameters are given in Table 1 and the thermal

parameters in Table 2. A final difference electron density synthesis was calculated, omitting the hydrogen atoms. The hydrogen atom positions obtained from this synthesis are listed in Table 1. A difference synthesis through the plane of the benzene ring is illustrated in Fig. 1. The hydrogen atom peak heights are 0.5, 0.4, 0.4 and 0.5 $e.\text{\AA}^{-3}$ and the estimated standard deviation of the electron density is about 0.09 $e.\text{\AA}^{-3}$. The final structure factors calculated with the parameters given in Tables 1 and 2 are listed in Table 3. The scattering factors were taken from *International Tables for Crystallography* (1962), except for carbon, which was taken from McWeeny (1951). No correction was made for anomalous dispersion in the case of the chlorine atom in the polar space group, $Pbn2_1$. Cruickshank & McDonald (1967) estimated that for molybdenum

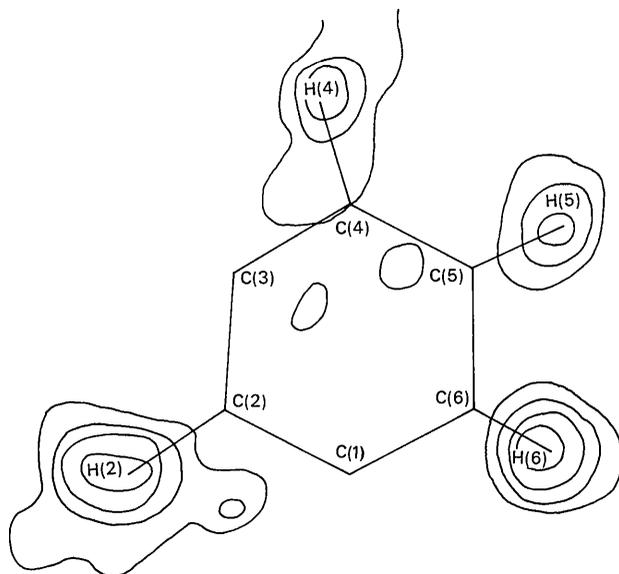


Fig. 1. A difference Fourier synthesis through the plane of the benzene ring which illustrates the probable positions of the hydrogen atoms. Contours are at approximately $0.1 e.\text{\AA}^{-3}$, with the lowest contour at $0.2 e.\text{\AA}^{-3}$.

Table 1. *Final positional parameters and their estimated deviations*

Values for all atoms $\times 10^4$ except for the hydrogen atoms, which are 10^3 . E.s.d.'s in parentheses. Hydrogen atom positions are from the final difference map (see text).

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	1411 (5)	1306 (7)	1906 (19)
C(2)	0580 (5)	1904 (7)	1893 (21)
C(3)	0543 (5)	2914 (7)	3546 (21)
C(4)	1253 (5)	3300 (7)	5119 (32)
C(5)	2069 (5)	2700 (8)	4960 (38)
C(6)	2155 (5)	1653 (8)	3345 (23)
O(1)	2428 (5)	-0281 (8)	-0520 (26)
O(2)	1119 (6)	-1045 (6)	1605 (23)
O(3)	0976 (6)	0103 (7)	-2299 (18)
O(4)	-0458 (5)	4307 (9)	5531 (26)
O(5)	-0911 (4)	3320 (7)	2073 (24)
N	-0354 (4)	3556 (7)	3745 (23)
Cl	1489 (1)	-0089 (2)	*
H(2)	006	161	052
H(4)	101	407	640
H(5)	265	290	571
H(6)	267	127	296

* Arbitrarily set equal to zero to fix the origin in the polar space group. The average correlation coefficient between the *z* parameters of different atoms was only *ca.* 0.1, because the chlorine atom is significantly heavier than the other atoms and its *z* parameter was fixed. The possible error in the *z* coordinate of the chlorine atom caused by neglect of anomalous dispersion is only about one-half of the e.s.d. in the *z* parameter of any of the other atoms.

radiation with a sulfur atom the maximum error would be 0.005 \AA . The large thermal motion in 3-NPCB at room temperature prohibits this precision.

Discussion

Libration corrections were estimated for the benzene ring and the bonds from the ring to the nitrogen and chlorine atoms by treating these eight atoms as a rigid body (Schomaker & Trueblood, 1968). The resulting libration tensor (Table 4) was used for making corrections to the intramolecular distances (Cruickshank, 1961a). The fit of these eight atoms to the rigid-body model was about as good as the data warranted, the

Table 2. *Final thermal parameters and their estimated standard deviations*

All values have been multiplied by 10^4 . The temperature factor for an atom is of the form

$$\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	37 (3)	82 (6)	242 (31)	-21 (8)	16 (21)	-74 (27)
C(2)	42 (3)	78 (7)	369 (40)	-11 (8)	-16 (24)	-4 (33)
C(3)	37 (3)	78 (7)	398 (43)	4 (8)	16 (23)	24 (34)
C(4)	42 (3)	94 (7)	542 (48)	-15 (8)	-6 (34)	-117 (54)
C(5)	41 (4)	122 (9)	687 (58)	-12 (9)	-76 (42)	-89 (64)
C(6)	32 (3)	93 (7)	512 (51)	23 (8)	-48 (24)	-52 (38)
O(1)	54 (3)	205 (10)	1136 (82)	-19 (10)	136 (32)	-488 (58)
O(2)	98 (5)	88 (6)	726 (54)	1 (9)	41 (32)	-50 (33)
O(3)	96 (5)	151 (9)	438 (34)	-44 (12)	-38 (24)	-127 (37)
O(4)	59 (4)	156 (8)	973 (81)	44 (9)	14 (30)	-232 (50)
O(5)	47 (3)	163 (9)	902 (58)	48 (9)	-159 (27)	-84 (47)
N	35 (3)	79 (6)	695 (56)	16 (7)	-17 (25)	10 (36)
Cl	46 (1)	100 (2)	503 (10)	-22 (2)	42 (9)	-117 (12)

Table 3. Observed and calculated structure factors

The five columns in each group contain the values, reading from left to right, of h , $10F_o$, $10F_c$, $10A_c$, and $10B_c$. A negative F_o indicates an unobserved reflection which was not included in the least-squares refinement.

h	$10F_o$	$10F_c$	$10A_c$	$10B_c$
0 0 0	0	0	0	0
1 0 0	127	128	128	128
2 0 0	254	256	256	256
3 0 0	381	382	382	382
4 0 0	508	510	510	510
5 0 0	635	636	636	636
6 0 0	762	764	764	764
7 0 0	889	890	890	890
8 0 0	1016	1018	1018	1018
9 0 0	1143	1144	1144	1144
10 0 0	1270	1272	1272	1272
11 0 0	1397	1400	1400	1400
12 0 0	1524	1528	1528	1528
13 0 0	1651	1656	1656	1656
14 0 0	1778	1784	1784	1784
15 0 0	1905	1912	1912	1912
16 0 0	2032	2040	2040	2040
17 0 0	2159	2168	2168	2168
18 0 0	2286	2296	2296	2296
19 0 0	2413	2424	2424	2424
20 0 0	2540	2552	2552	2552
21 0 0	2667	2680	2680	2680
22 0 0	2794	2808	2808	2808
23 0 0	2921	2940	2940	2940
24 0 0	3048	3068	3068	3068
25 0 0	3175	3196	3196	3196
26 0 0	3302	3324	3324	3324
27 0 0	3429	3456	3456	3456
28 0 0	3556	3588	3588	3588
29 0 0	3683	3720	3720	3720
30 0 0	3810	3852	3852	3852
31 0 0	3937	3984	3984	3984
32 0 0	4064	4116	4116	4116
33 0 0	4191	4248	4248	4248
34 0 0	4318	4380	4380	4380
35 0 0	4445	4512	4512	4512
36 0 0	4572	4644	4644	4644
37 0 0	4699	4776	4776	4776
38 0 0	4826	4908	4908	4908
39 0 0	4953	5040	5040	5040
40 0 0	5080	5172	5172	5172
41 0 0	5207	5304	5304	5304
42 0 0	5334	5436	5436	5436
43 0 0	5461	5568	5568	5568
44 0 0	5588	5700	5700	5700
45 0 0	5715	5832	5832	5832
46 0 0	5842	5964	5964	5964
47 0 0	5969	6096	6096	6096
48 0 0	6096	6228	6228	6228
49 0 0	6223	6360	6360	6360
50 0 0	6350	6492	6492	6492
51 0 0	6477	6624	6624	6624
52 0 0	6604	6756	6756	6756
53 0 0	6731	6888	6888	6888
54 0 0	6858	7020	7020	7020
55 0 0	6985	7152	7152	7152
56 0 0	7112	7284	7284	7284
57 0 0	7239	7416	7416	7416
58 0 0	7366	7548	7548	7548
59 0 0	7493	7680	7680	7680
60 0 0	7620	7812	7812	7812
61 0 0	7747	7944	7944	7944
62 0 0	7874	8076	8076	8076
63 0 0	8001	8208	8208	8208
64 0 0	8128	8340	8340	8340
65 0 0	8255	8472	8472	8472
66 0 0	8382	8604	8604	8604
67 0 0	8509	8736	8736	8736
68 0 0	8636	8868	8868	8868
69 0 0	8763	9000	9000	9000
70 0 0	8890	9132	9132	9132
71 0 0	9017	9264	9264	9264
72 0 0	9144	9396	9396	9396
73 0 0	9271	9528	9528	9528
74 0 0	9398	9660	9660	9660
75 0 0	9525	9792	9792	9792
76 0 0	9652	9924	9924	9924
77 0 0	9779	10056	10056	10056
78 0 0	9906	10188	10188	10188
79 0 0	10033	10320	10320	10320
80 0 0	10160	10452	10452	10452
81 0 0	10287	10584	10584	10584
82 0 0	10414	10716	10716	10716
83 0 0	10541	10848	10848	10848
84 0 0	10668	10980	10980	10980
85 0 0	10795	11112	11112	11112
86 0 0	10922	11244	11244	11244
87 0 0	11049	11376	11376	11376
88 0 0	11176	11508	11508	11508
89 0 0	11303	11640	11640	11640
90 0 0	11430	11772	11772	11772
91 0 0	11557	11904	11904	11904
92 0 0	11684	12036	12036	12036
93 0 0	11811	12168	12168	12168
94 0 0	11938	12300	12300	12300
95 0 0	12065	12432	12432	12432
96 0 0	12192	12564	12564	12564
97 0 0	12319	12696	12696	12696
98 0 0	12446	12828	12828	12828
99 0 0	12573	12960	12960	12960
100 0 0	12700	13092	13092	13092
101 0 0	12827	13224	13224	13224
102 0 0	12954	13356	13356	13356
103 0 0	13081	13488	13488	13488
104 0 0	13208	13620	13620	13620
105 0 0	13335	13752	13752	13752
106 0 0	13462	13884	13884	13884
107 0 0	13589	14016	14016	14016
108 0 0	13716	14148	14148	14148
109 0 0	13843	14280	14280	14280
110 0 0	13970	14412	14412	14412
111 0 0	14097	14544	14544	14544
112 0 0	14224	14676	14676	14676
113 0 0	14351	14808	14808	14808
114 0 0	14478	14940	14940	14940
115 0 0	14605	15072	15072	15072
116 0 0	14732	15204	15204	15204
117 0 0	14859	15336	15336	15336
118 0 0	14986	15468	15468	15468
119 0 0	15113	15600	15600	15600
120 0 0	15240	15732	15732	15732
121 0 0	15367	15864	15864	15864
122 0 0	15494	15996	15996	15996
123 0 0	15621	16128	16128	16128
124 0 0	15748	16260	16260	16260
125 0 0	15875	16392	16392	16392
126 0 0	16002	16524	16524	16524
127 0 0	16129	16656	16656	16656
128 0 0	16256	16788	16788	16788
129 0 0	16383	16920	16920	16920
130 0 0	16510	17052	17052	17052
131 0 0	16637	17184	17184	17184
132 0 0	16764	17316	17316	17316
133 0 0	16891	17448	17448	17448
134 0 0	17018	17580	17580	17580
135 0 0	17145	17712	17712	17712
136 0 0	17272	17844	17844	17844
137 0 0	17399	17976	17976	17976
138 0 0	17526	18108	18108	18108
139 0 0	17653	18240	18240	18240
140 0 0	17780	18372	18372	18372
141 0 0	17907	18504	18504	18504
142 0 0	18034	18636	18636	18636
143 0 0	18161	18768	18768	18768
144 0 0	18288	18900	18900	18900
145 0 0	18415	19032	19032	19032
146 0 0	18542	19164	19164	19164
147 0 0	18669	19296	19296	19296
148 0 0	18796	19428	19428	19428
149 0 0	18923	19560	19560	19560
150 0 0	19050	19692	19692	19692
151 0 0	19177	19824	19824	19824
152 0 0	19304	19956	19956	19956
153 0 0	19431	20088	20088	20088
154 0 0	19558	20220	20220	20220
155 0 0	19685	20352	20352	20352
156 0 0	19812	20484	20484	20484
157 0 0	19939	20616	20616	20616
158 0 0	20066	20748	20748	20748
159 0 0	20193	20880	20880	20880
160 0 0	20320	21012	21012	21012
161 0 0	20447	21144	21144	21144
162 0 0	20574	21276	21276	21276
163 0 0	20701	21408	21408	21408
164 0 0	20828	21540	21540	21540
165 0 0	20955	21672	21672	21672
166 0 0	21082	21804	21804	21804
167 0 0	21209	21936	21936	21936
168 0 0	21336	22068	22068	22068
169 0 0	21463	22200	22200	22200
170 0 0	21590	22332	22332	22332
171 0 0	21717	22464	22464	22464
172 0 0	21844	22596	22596	22596
173 0 0	21971	22728	22728	22728
174 0 0	22098	22860	22860	22860
175 0 0	22225	22992	22992	22992
176 0 0	22352	23124	23124	23124
177 0 0	22479	23256	23256	23256
178 0 0	22606	23388	23388	23388
179 0 0	22733	23520	23520	23520
180 0 0	22860	23652	23652	23652
181 0 0	22987	23784	23784	23784
182 0 0	23114	23916	23916	23916
183 0 0	23241	24048	24048	24048
184 0 0	23368	24180	24180	24180
185 0 0	23495	24312	24312	24312
186 0 0	23622	24444	24444	24444
187 0 0	23749	24576	24576	24576
188 0 0	23876	24708	24708	24708
189 0 0	24003	24840	24840	24840
190 0 0	24130	24972	24972	24972
191 0 0	24257	25104	25104	25104
192 0 0	24384	25236	25236	25236
193 0 0	24511	25368	25368	25368
194 0 0	24638	25500	25500	25500
195 0 0	24765	25632	25632	25632
196 0 0	24892	25764	25764	25764
197 0 0	25019	25896	25896	25896
198 0 0	25146	26028	26028	26028
199 0 0	25273	26160	26160	26160
200 0 0	25400	26292	26292	26292
201 0 0	25527	26424	26424	26424
202 0 0	25654	26556	26556	26556
203 0 0	25781	26688	26688	26688
204 0 0	25908	26820	26820	26820
205 0 0	26035	26952	26952	26952
206 0 0	26162	27084	27084	27084
207 0 0	26289	27216	27216	27216
208 0 0	26416	27348	27348	27348
209 0 0	26543	27480	27480	27480
210 0 0	26670	27612	27612	27612
211 0 0	26797	27744	27744	27744
212 0 0	26924	27876	27876	27876
213 0 0	27051	28008	28008	28008
214 0 0	27178	28140	28140	28140
215 0 0	27305	28272	28272	28272
216 0 0	27432	28404	28404	28404
217 0 0	27559	28536	28536	28536
218 0 0	27686	28668	28668	28668

r.m.s. difference of the observed and calculated U_{ij} being 0.0040 \AA^2 , about 7% of the average mean square amplitude, which is comparable to the e.s.d.'s of the B_{ij} in Table 2. The principal libration axis is essentially parallel to the Cl-N vector, deviating from it by only 3° . The effective screw motion is very small. The corrected bond distances are given in Table 5 and are illustrated in Fig. 2. The apparent inconsistencies of the structure obtained from the visual data were clearly specious.

Table 4. Parameters for the eight-atom rigid body*

Libration tensor†, L ($^\circ$)²

$$\begin{pmatrix} 26 & -10 & -10 \\ & 34 & 10 \\ & & 9 \end{pmatrix} \begin{matrix} (4) \\ (5) \\ (4) \\ (6) \\ (4) \\ (4) \end{matrix}$$

Principal axis representations

L	Eigenvalue	Direction cosines ($\times 10^3$)		
		a	b	c
	46 ($^\circ$) ²	558	-751	-352
	19	765	630	-131
	3	320	-196	927
Reduced T	0.0436 \AA^2	330	-902	-279
	0.0380	231	364	-902
	0.0356	915	233	328

Displacement of libration axes from intersecting

$$2e_1 - 3e_2 = 0.21 \text{ \AA}; \quad 3e_2 - 1e_3 = -1.25 \text{ \AA}; \quad 1e_3 - 2e_3 = -0.29 \text{ \AA}.$$

* Calculated from the thermal parameters by the method of Schomaker & Trueblood (1968). The eight atoms are the six carbon atoms, the nitrogen, and the chlorine (see text). Standard deviations for the components of L are in parentheses.

† Expressed in the crystal axial system.

The average (corrected) C-C distance in the benzene ring is $1.380 \pm 0.010 \text{ \AA}$, not significantly different from the distances reported for benzene [1.392 \AA (Cox, Cruickshank & Smith, 1958) and 1.397 \AA (Stoicheff, 1954)]. The ring is effectively planar; the deviations

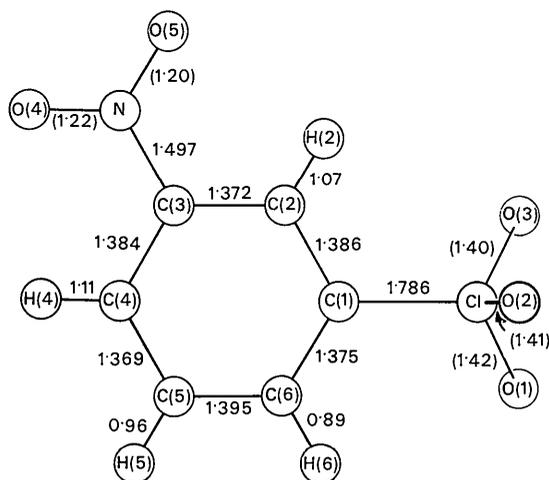


Fig. 2. Libration-corrected bond distances (\AA). Those in parentheses have not been corrected for thermal motion; the corrections vary from 0.03 to 0.06 \AA (see text).

Table 5. Intramolecular distances and angles*

(a) Bond distances and angles

	Uncorrected	Corrected for libration†
C(1)-C(2)	1.380 \AA	1.386 \AA
C(2)-C(3)	1.366	1.372
C(3)-C(4)	1.374	1.384
C(4)-C(5)	1.365	1.369
C(5)-C(6)	1.390	1.395
C(6)-C(1)	1.364	1.375
C(1)-Cl	1.779	1.786
C(3)-N	1.492	1.497
N-O(4)	1.215	1.26
N-O(5)	1.201	1.24
C1-O(1)	1.421	1.48
C1-O(2)	1.413	1.45
C1-O(3)	1.397	1.43
C(1)-C(2)-C(3)	113.6 $^\circ$	113.3 $^\circ$
C(2)-C(3)-C(4)	123.9	124.1
C(3)-C(4)-C(5)	119.6	119.7
C(4)-C(5)-C(6)	119.6	119.5
C(5)-C(6)-C(1)	117.2	117.2
C(6)-C(1)-C(2)	126.0	126.1
C(2)-C(1)-Cl	116.3	116.1
C(6)-C(1)-Cl	117.6	117.7
C(2)-C(3)-N	116.2	115.9
C(4)-C(3)-N	119.7	119.9
C(3)-N-O(4)	118	
C(3)-N-O(5)	117	
O(4)-N-O(5)	125	
C(1)-Cl-O(1)	106	
C(1)-Cl-O(2)	107	
C(1)-Cl-O(3)	107	
O(1)-Cl-O(2)	112	
O(1)-Cl-O(3)	113	
O(2)-Cl-O(3)	112	

* The e.s.d.'s of the bond distances average about 0.010 \AA and those of the bond angles about 0.6° .

† Bond distances involving the oxygen atoms were corrected by assuming a riding motion; see text.

(b) Nonbonded distances (uncorrected for thermal motion)

C(1)-O(1)	2.57 \AA	O(1)-O(2)	2.35 \AA
C(1)-O(2)	2.56	O(1)-O(3)	2.35
C(1)-O(3)	2.56	O(2)-O(3)	2.33
C(2)-O(1)	3.79	C(6)-O(1)	2.87
C(2)-O(2)	3.26	C(6)-O(2)	3.38
C(2)-O(3)	2.92	C(6)-O(3)	3.72
H(2)-O(2)	3.3	H(6)-O(1)	2.4
H(2)-O(3)	2.5	H(6)-O(2)	3.4
H(2)-O(5)	2.5	H(4)-O(4)	2.2
C(2)-O(5)	2.67	C(4)-O(4)	2.75
O(4)-O(5)	2.14		

from the least-squares plane are given in Table 6. The C(2)-C(1)-C(6) and C(2)-C(3)-C(4) angles are both significantly greater than 120° . Bailey & Prout (1965) and Carter, McPhail & Sim (1966) have both noted that the C-C-C angle at a trigonal carbon atom attached to a nitro group is always appreciably larger than 120° . In 3-NPCB the effect of the ClO_3 group is

similar to that of a nitro group, as was expected. Carter, McPhail & Sim (1966) have suggested that the strong electron-withdrawing power of the NO₂ group leads to less than $\frac{1}{3}$ *s* character in the C–N bond. The corresponding increase in *s* character in the C–C bonds to the *ortho* carbon atoms leads to an opening of the C–C–C angle.

The C–Cl distance of 1.786 ± 0.008 Å is one of the longest C(aromatic)–Cl distances reported to date. The twenty-six C–Cl distances tabulated in Table 7 average 1.737 ± 0.016 Å, significantly shorter than the C–Cl distance found in this study. Indeed, the longest of the distances tabulated in Table 7, all of which involve a chlorine atom bonded to only one other atom, is 0.02 Å shorter than the distance found in 3-NPCB. It is reasonable that the single-bond radius for a chlorine atom increases with increasing substitution on the atom; a similar effect is well known for carbon.

The perchloryl and nitro groups are both librating appreciably, as is usually the case with nitro groups. Approximate corrections for the thermal motion were calculated by the procedure suggested by Leung & Marsh (1958) which is equivalent to the 'riding motion' of Busing & Levy (1964). Clearly, the Cl–O distances (Table 5), which average 1.45 Å, have not been determined with a great deal of precision. Nevertheless, the average Cl–O distance is in good agreement with the 1.46 ± 0.01 Å reported by Truter, Cruickshank & Jeffrey (1960) in NO₂⁺ClO₄[−]. The fact that the Cl–O bond length is slightly (although not significantly) shorter in 3-NPCB is in line with arguments given by Cruickshank (1961*b*) in a general discussion of MO₄[−] ions and related species. Essentially the π -bonding is

divided among the three Cl–O bonds in 3-NPCB but is distributed over all four Cl–O bonds in the perchlorate ion. The plane defined by the three oxygen atoms of the ClO₃ group is perpendicular to the C–Cl bond, but makes an angle of 85° with respect to the benzene ring. The tilting of the plane of the ClO₃ oxygen atoms increases the C(2)–O(3) and C(6)–O(1) non-bonded distances to 2.92 and 2.87 Å respectively. The orientation of the ClO₃ group with respect to the benzene ring also minimizes the nonbonded repulsions.

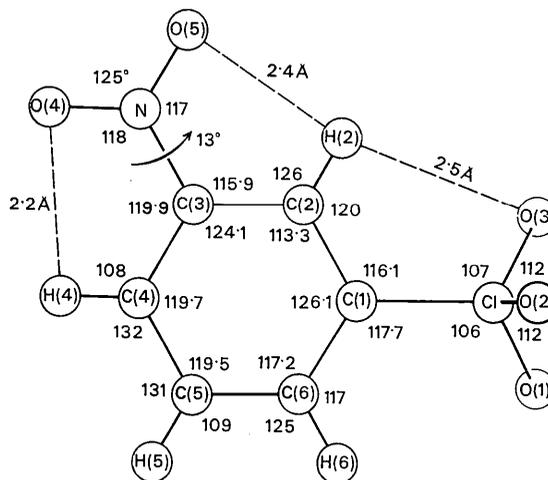


Fig. 3. Bond angles (°), torsion angle of the nitro group, and some intramolecular non-bonded O...H distances. The two angles not shown are C(1)–Cl–O(2), 107 and O(1)–Cl–O(3), 113.

Table 6. *Least-squares planes*

Deviations in boldface type indicate atoms which were used to define the plane.
Planes and deviations from plane (Å × 10³)

	I	II	III	IV	V
C(1)	−11	−14	35		
C(2)	6	17	34		
C(3)	10	28	0	3	
C(4)	−22	−11	−52		
C(5)	18	15	8		
C(6)	−2	−13	27		
Cl	−146	−159	−50		
O(1)	343	316	452		0
O(2)	−1520	−1533	−1416		0
O(3)	613	607	721		0
N	−54	−21	−86	−12	
O(4)	−294	−255	−360	4	
O(5)	178	217	163	4	
Parameters of the plane*					
A × 10 ⁴	3006	2915	3035	3498	−0614
B × 10 ⁴	5931	5984	5703	7352	8432
C × 10 ⁴	−7469	−7463	−7633	−5806	5341
D (Å)	−0.748	−0.741	−0.661	−1.534	0.613

* Equation of the plane in the form

$$\text{Deviation (Å)} = AX + BY + CZ + D$$

with X, Y, Z the coordinates of the atom in Å.

Table 7. Carbon-chlorine bond distances in various aromatic molecules

Compound	Distance	Reference
Bis-(5-chlorosalicylaldoximate)copper(II)	1.76	1
<i>N</i> -Methyl- <i>p</i> -chlorobenzaldoxime	1.768	2
<i>syn-p</i> -Chlorobenzaldoxime	1.728	2
2-Chloro-4-nitroaniline	1.766	3
<i>o</i> -Chlorobenzoic acid	1.737	4
2-Chloro-5-nitrobenzoic acid	1.753	5
<i>p</i> -Dichlorobenzene	1.74	6
9,10-Dichloroanthracene	1.74	7
4,4'-Dichlorodiphenyl sulfone	1.736	8
Di- <i>p</i> -chlorodiphenyltellurium diiodide	1.75	9
1,4,5,8-Tetrachloronaphthalene	1.74	10
Tetrachloro- <i>p</i> -benzoquinone	1.714	11
2,5-Dichloroaniline	1.744	12
Tetrachlorohydroquinone	1.73	13
Pentachlorophenol	1.71	13
<i>N</i> -5-Chlorosalicylideneaniline	1.752	14
	1.755	
2-Chloro- <i>N</i> -salicylideneaniline	1.737	15
Di- <i>p</i> -chlorophenyl hydrogen phosphate	1.735	16
2-Chloro-3-hydroxy-1,4-naphthoquinone	1.72	17
2-Chloro-3-amino-1,4-naphthoquinone	1.71	18
1-(4-Chlorobenzyl)-1-nitroso-2-(4,5-dihydro-2-imidazolyl)hydrazine monohydrate	1.732	19
<i>o</i> -Chlorobenzoylacetylene	1.734	20
Chloranilic acid	1.717	21
Chloranilic acid monohydrate	1.720	22
Ammonium chloranilate monohydrate	1.741	23

References: 1, Orioli, Lingafelter & Brown (1964); 2, Folting, Lipscomb & Jerslev (1964); 3, McPhail & Sim (1965); 4, Ferguson & Sim (1961); 5, Ferguson & Sim (1962); 6, Frasson, Garbuglio & Bezzi (1959); 7, Trotter (1959); 8, Sime & Abrahams (1960); 9, Chao & McCullough (1962); 10, Gafner & Herbstein (1962); 11, Chu, Jeffrey & Sakurai (1962); 12, Sakurai, Sundaralingam & Jeffrey (1963); 13, Table 15 of reference 12; 14, Bregman, Leiserowitz & Schmidt (1964); 15, Bregman, Leiserowitz & Osaki (1964); 16, Calleri & Speakman (1964); 17, Gaultier & Hauw (1965*a*); 18, Gaultier & Hauw (1965*b*); 19, Palenik (1965); 20, Ferguson & Islam (1966); 21, Andersen (1967*a*); 22, Andersen (1967*b*); 23, Andersen (1967*c*).

The angle between the planes defined by C(1)–Cl–O(3) and C(2)–C(1)–Cl is 37° and that between C(6)–C(1)–Cl and C(1)–Cl–O(1) is 24°, close to the ideal value of 30°. The angle between the planes C(1)–Cl–O(2) and C(2)–C(1)–Cl is 81° and between C(1)–Cl–O(2) and C(6)–C(1)–Cl is 95°, which is close to the ideal value of 90°. The three O–Cl–O angles are all greater than the tetrahedral value of 109°28', while the corresponding C–Cl–O angles are all smaller than the tetrahedral value. The increase in the O–Y–O angle is common in X₂YO₂ and XYO₃ species, and presumably results from the O...O nonbonded repulsions, which are decreased by increasing the average O...O distance, in this case to 2.34 Å.

The nitro group is twisted by 13° from the plane of the benzene ring; this twist angle is the same as that found by Trotter & Williston (1966) for the nitro groups in *m*-dinitrobenzene. The nitro group in 3-NPCB is wagging and the corrections to the N–O bond lengths are 0.03 and 0.03 Å. The two N–O distances of 1.24 and 1.26 Å are not significantly different. The average N–O distance is 1.247 Å in *p*-nitroaniline

(Trueblood, Goldish & Donohue, 1961), 1.242 Å in *β-p*-nitrophenol (Coppens & Schmidt, 1965*a,b*) and 1.248 Å in *m*-dinitrobenzene (Trotter & Williston, 1966), in good agreement with our average value of 1.25 Å.

The C–N distance of 1.497 Å is a long C(aromatic)–N(nitro group) bond, but compares favorably with the values 1.493 Å found for *m*-dinitrobenzene and 1.490 Å reported for *N*-methyl-*N*,2,4,6-tetranitroaniline by Cady (1967). However, in compounds where the resonance interaction of the nitro group and the ring is strong, the C–N bond lengths appear shorter. For example, the C–N distance is 1.460 Å in *p*-nitroaniline, 1.450 Å in *β-p*-nitrophenol and 1.450 Å in potassium picrate (Palenik, Bettman & Hughes, 1967). Although this interpretation is not completely unambiguous because the large librations of the NO₂ group reduce somewhat the accuracy of the C–N distances, it is consistent with the available data. The fact that the uncorrected C–NO₂ bond length in 4-nitrophenol is essentially the same at 90°K as at room temperature (Coppens & Schmidt, 1965*a,b*) indicates that the effect of thermal motion on the apparent length of this bond is not normally so large as to vitiate the above discussion.

All the interatomic distances less than 4.0 Å were calculated. The intermolecular heavy atom-heavy atom distances less than 3.3 Å and the hydrogen atom-heavy atom distances less than 2.8 Å are listed in Table 8. These distances are not unusually short and can be considered as van der Waals contacts. There are only two contacts involving O(1) which are shorter than 3.3 Å. The mean square displacement of O(1) is the largest of any atom in the structure and presumably results from the lack of restraining non-bonded contacts.

We gratefully acknowledge the help of Professor K. Conrow in preparing the sample of perchlorylbenzene and 3-nitroperchlorylbenzene and of Maryellin Rei-

Table 8. Intermolecular distances

The distance given is from atom *i* in the molecule specified by the parameters in Tables 1 and 2 to the atom *j* in the molecule specified by the letters *A–F*. Molecules *A–F* are located as follows:

<i>A</i>	$x, y, 1+z$	<i>D</i>	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$
<i>B</i>	$-x, -y, \frac{1}{2}+z$	<i>E</i>	$-x, 1-y, \frac{1}{2}+z$
<i>C</i>	$\frac{1}{2}-x, \frac{1}{2}+y, 1+z$	<i>F</i>	$-x, -1-y, -\frac{1}{2}+z$

Atom <i>i</i>	Atom <i>j</i>	Molecule	Distance
C(1)	O(3)	<i>A</i>	3.25 Å
C(2)	O(3)	<i>B</i>	3.17
C(5)	O(1)	<i>C</i>	3.22
C(6)	O(3)	<i>A</i>	3.25
O(4)	N	<i>E</i>	3.05
N	O(2)	<i>B</i>	3.25
O(2)	O(3)	<i>B</i>	3.29
O(4)	O(4)	<i>F</i>	3.22
O(2)	H(2)	<i>B</i>	2.7
H(2)	O(3)	<i>B</i>	2.6
H(5)	O(1)	<i>C</i>	2.7
H(5)	O(5)	<i>D</i>	2.6

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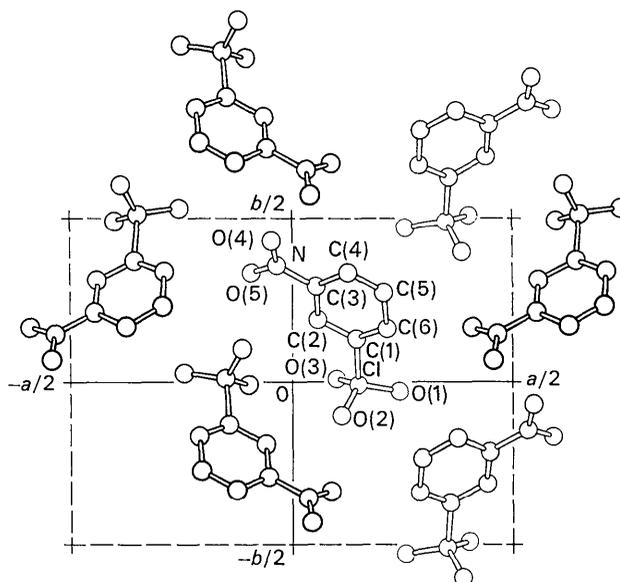


Fig.4. A view of the structure illustrating the molecular packing. The positive direction of *c* is toward the viewer.

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