The Crystal and Molecular Structure of 3,4-Dichloronitrobenzene

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(Received October 5, 1982)

Synopsis. $C_6H_3Cl_2NO_2$, F. W. = 192.0, tetragonal, $I4_1/a$, $a = 28.094(12)$, $c = 3.838(6)$ Å, $V = 3030$ Å^3, $Z = 16$, $D_x = 1.68$ Mg m^{-3}, μ(Mo $K\alpha$) = 0.8 mm^{-1}. Refinement with 1093 diffractometer data gave a final R value of 0.07. The molecule is practically planar except for the nitro group, the plane of which is inclined at 8.8° to the benzene plane. The two C–Cl bond distances are approximately equal to each other. The intermolecular Cl(2)···O(2^{ii}) contact of 3.095 Å is remarkably short.

Our previous NQR study showed the equivalent character of the two C–Cl bonds in the title compound (abbreviated hereafter as DCNB), which are not equivalent with respect to the nitro substituent.[1] The crystal-structure analysis and a CNDO/2 calculation of DCNB have been carried out in order to clarify the C–Cl bond character in this compound.

Experimental

Commercial material was purified by recrystallization from a benzene solution. The crystals of DCNB are colorless needles. A crystal with dimensions of $0.3 \times 0.3 \times 0.4$ mm^3, obtained by cutting off a part of the specimen used for the NQR measurement and sealed in a Lindemann glass capillary, was used for the intensity measurement. The intensities of 1183 independent reflections were measured on a Rigaku automated four-circle diffractometer in $\omega/2\theta$ scan mode, using Mo $K\alpha$ radiation monochromated by a graphite crystal. Three standard reflections, monitored every 50 reflections, showed a steady decline in intensity; at the end of the data collection, the maximum reduction reached 13%. The intensity data were then put on a common scale with reference to the standard reflections. 1093 reflections with $|F_o| \geq 3\sigma(|F_o|)$ were used for the analysis. No correction was made for absorption or extinction.

The positions of the Cl atoms were located from a sharpened Patterson map, and the remaining non-H atoms, by Fourier methods. A block-diagonal least-squares refinement using anisotropic temperature factors reduced the R value to 0.09. At this stage, a difference synthesis revealed all the hydrogen atoms in plausible positions. Further refinement was carried out including the isotropic H atoms. The final R value was 0.07 for 1093 observed reflections. A weighting scheme of $w = 1$ if $|F_o| \geq 5.5$ and $w = 0.3$ otherwise was employed. The final atomic parameters and their standard deviations are listed in Table 1.[2] The atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*.[3] The calculations were carried out on HITAC 5020E and 8800/8700 computers at the Computer Center of the University of Tokyo and on TOSBAC 3400 and HITAC 8250 computers at Saitama University.

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent thermal parameters (B_{eq}) for the non-hydrogen atoms, with e.s.d.'s in parentheses

Atom	x	y	z	B_{eq}/Å^2
O(1)	1748(2)	398(2)	4162(19)	8.27
O(2)	1098(2)	627(2)	6619(16)	6.88
N	1463(2)	697(2)	4933(17)	5.21
Cl(1)	833(1)	2397(1)	3572(6)	5.72
Cl(2)	1822(1)	2668(1)	186(6)	5.48
C(1)	1543(2)	1192(2)	3707(16)	3.82
C(2)	1192(2)	1517(2)	4159(16)	3.85
C(3)	1276(2)	1978(2)	3036(17)	4.04
C(4)	1712(2)	2091(2)	1623(15)	3.63
C(5)	2058(2)	1756(2)	1141(17)	4.17
C(6)	1976(2)	1292(2)	2234(18)	4.17

Results and Discussion

The bond lengths and angles of DCNB are shown in Fig. 1, together with the atomic numbering scheme. All the atoms of DCNB are practically coplanar except for those of the nitro group, the plane of which is inclined at 8.8° to the benzene plane. The geometry of the nitro group in DCNB seems to be normal as compared with those of unhindered nitro groups in other aromatic nitro compounds.[4–6] The C(2)–C(1)–C(6) bond angle is 124.1(5)°. Such an increase in the internal angle at the nitro-substituted carbon is commonly observed for other aromatic nitro compounds.[5,6] The C–C bond distances in the benzene ring vary from 1.358 Å to 1.390 Å. The C–Cl bond distances are 1.728(6) Å and 1.739(6) Å. A CNDO/2 calculation based upon the molecular geometry observed was carried out in order to gain a better understanding of the ground-state electronic distribution of the π orbitals.[7] The π characters of the C–C bonds in the benzene ring are essentially equivalent; those of the two C–Cl bonds are also equivalent (4%). These results reveal that the nitro group in DCNB exerts no influence on the electronic distribution of the π orbitals of the C–Cl bonds and are consistent with the conclusion derived from the NQR data.

The crystal structure viewed along the c axis is

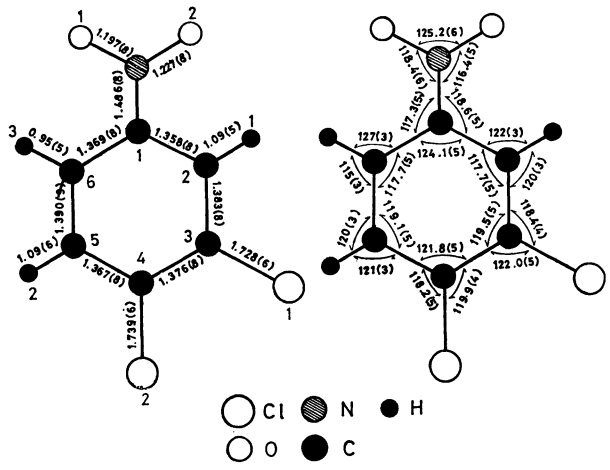

Fig. 1. Bond lengths (l/Å) and angles (ϕ/°) with their e.s.d.'s in parentheses.

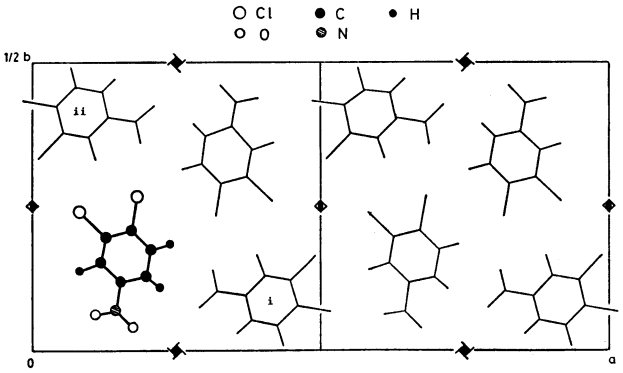

Fig. 2. A projection of the crystal structure along the c axis.

Table 2. Short C-Cl···O intermolecular distances

	C-Cl···O angle ϕ/°	Cl···O distance l/Å
2,5-Dichloro-1,4-benzoquinone	164	3.10
2,3-Dichloro-1,4-benzoquinone	164	3.01
2,3-Dichloro-1,4-naphthoquinone	164	3.10
3,4-Dichloronitrobenzene	164.8	3.095

presented in Fig. 2. The DCNB molecules are stacked in infinite columns along the c axis, with the mean interplanar distance of 3.601 Å. The intermolecular contacts between molecular stacks are normal except for Cl(2)···O(2^{ii}) (3.095 Å) and H(2)···O(2^{i}) (2.43 Å), which are shorter than the usually quoted van der Waals distances. The C(4)–Cl(2)···O(2^{ii}) angle is 164.8°. Similar short intermolecular contacts were observed in the crystals of some benzoquinone and naphthoquinone derivatives, which are listed in Table 2.[8] Gaultier, Hauw, and Schvoerer observed a red shift of the absorption maxima of the C=O stretching bands of these compounds in their crystalline and solution states, and proposed that the unusual contacts are attributable to charge-transfer interaction between the Cl atom and the carbonyl oxygen.[8] The absorption maxima of the symmetric and antisymmetric NO_2 stretching bands in the crystalline DCNB were observed at 1347.7 cm^{-1} and 1538.2 cm^{-1} respectively, and those in a CCl_4 solution, at 1345.2 cm^{-1} and 1534.6 cm^{-1}. Seemingly, these deviations are too small to be significant.

The authors are grateful to Professor Yoshihiko Saito for the use of the Rigaku four-circle diffractometer at the Institute of Solid State Physics, the University of Tokyo. Thanks are also due to Professor Takashi Shimozawa, Saitama University, for his keen interest and valuable discussion.

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