# 1-Chloro-2-nitrobenzene: N—O···Cl halogen bonds and aromatic π–π stacking, and thermal vibrations in the vicinity of the melting point

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The crystal structure of 1-chloro-2-nitrobenzene, $C_6H_4ClNO_2$, is made up of molecules which are linked by N—O···Cl halogen bonds. These molecular chains are involved in aromatic π–π stacking; the intermolecular O···Cl distance is 3.09 Å. Such short halogen bonds are not common. A rigid-body analysis including the non-rigidly attached rigid group provides the mean-square amplitudes of the molecular translations and librations, and of the internal torsional vibrations of the nitro group. The results reveal the driving role of the torsional vibrations of the nitro group in the phase transition to the liquid phase.

## Comment

The investigation of interactions in the crystal structure of the title compound, (I), is part of our studies concerning supramolecular aggregation in 1-substituted nitrobenzenes.
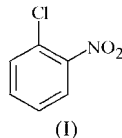


The molecule of (I) is not planar. Fig. 1 shows the molecule with the atom numbering. Table 1 reports selected geometric parameters. The dihedral angle between the planes of the benzene ring and the nitro group is 42.14°. This twist results from a steric effect. The intramolecular Cl···O distance is short, at 2.943 (5) Å.

Quantum-chemical calculations of the geometry of the molecule using *GAUSSIAN03* at the RHF/6-31g** basis level (Frisch *et al.*, 2004) indicate a similar geometry, with a dihedral angle of 40.26°. Similar Cl···O interactions have been reported, *e.g.* for a form of 1-chloro-2,4-dinitrobenzene (Wilkins *et al.*, 1990), 2-chloro-1,3,5-trinitrobezene (Willis *et al.*, 1971) and 1,2-dichloro-3-nitrobenzene (Sharma *et al.*,

1986). The intramolecular Cl···O distances in these crystals are 2.964 (2), 2.924 (2) and 2.999 (2) Å, respectively.

An interaction of a similar nature occurs between the molecules of (I). The intermolecular Cl···O distance from the crystal structure determination is 3.095 (5) Å (Fig. 2). Such an interaction involving a halogen atom and an electronegative heteroatom is called halogen bonding, by analogy with hydrogen bonding (Metrangolo & Resnati, 2001; Ouvrard *et al.*, 2003). In contrast with hydrogen bonding, halogen bonding, Y—halogen···X, is always linear, with the halogen atom pointing to an electron lone pair of a heteroatom. Halogen bonding is an important interaction leading to supramolecular synthons which most often involve I atoms (Saha *et al.*, 2005). In the title structure, the benzene ring, the Cl atom and the nearest O atom of a neighbouring molecule are coplanar. These interactions create a supramolecular synthon in which Cl···O is *cis* to C—N (Allen *et al.*, 1997). The scheme below illustrates this type of interaction.
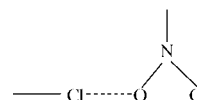


Halogen bonding has been observed in the crystal structure of the high-temperature polymorph of *p*-chloronitrobenzene (Mak & Trotter, 1962); in the crystal structure, the Cl···O distances are 3.183 and 3.080 Å at 300 and 100 K, respectively (Mossakowska & Wójcik, 2005). However, only O···O and Cl···Cl interactions occur in the crystal structure of *m*-chloronitrobenzene (Gopalakrishna, 1965) and in the low-temperature polymorph of *p*-chloronitrobenzene (Meriles *et al.*, 2000).

Translationally equivalent along the *a* crystallographic axis, the molecules of (I) are linked by π–π interactions; the interplanar spacing is 3.566 (5) Å and the centroid offset is 1.375 Å (Fig. 3). Thus, supramolecular tapes formed *via* halogen bonding are involved in molecular stacking *via* aromatic π–π interactions. Competition between these two types of specific intermolecular interactions results in a layered structure (Figs. 2 and 3), with additional short C—H···O intermolecular contacts (Fig. 3 and Table 2).
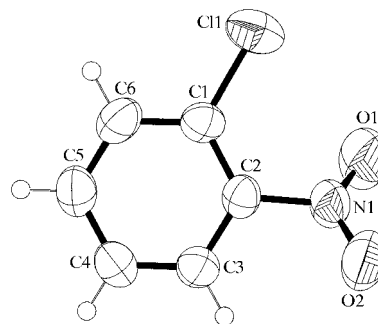


**Figure 1**
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability and H atoms are shown as small spheres of arbitrary radii.

# organic compounds

A search of the Cambridge Structural Database (Version of April 2006; Allen, 2002) resulted in 156 retrieved crystal structures of aromatic compounds with close intermolecular contacts between at least one Cl atom and a nitro group. Among these retrieved structures, 314 close contacts correspond to $Cl\cdots O-N$ interactions, *i.e.* to one O atom of a nitro group. Fig. 4 shows the distribution of the short $Cl\cdots O$ intermolecular distances in the retrieved structures. The asymmetric histogram reveals that very short $O\cdots Cl$ distances are not common.

The crystal structure of (I) is isostructural with that of 1-bromo-2-nitrobenzene (Fronczek, 2005). The crystal structure of (I) has been determined in this work at a temperature only a few degrees (about 7 K) below the melting point. Although the structure is reliable, the anisotropic displacement parameters show very large values due to pronounced molecular dynamics. In particular, the anisotropic displacement parameters of the nitro-group O atoms are large,
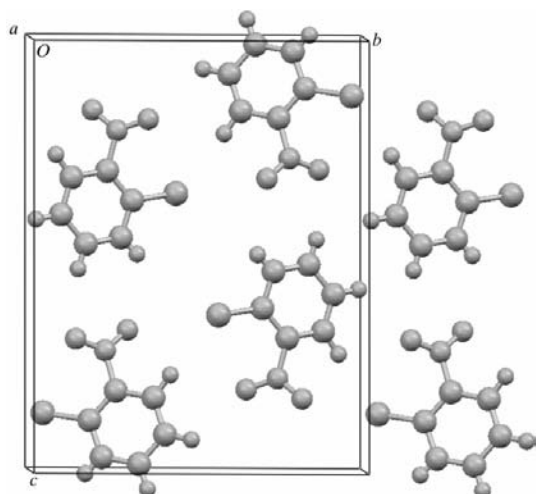
**Figure 4**
Histogram illustrating the distances between a Cl atom and a nitro-group O atom for 156 compounds in the Cambridge Structural Database. For details, see *Comment*.

**Figure 2**
A projection of the crystal structure of (I) on to (100), showing the intermolecular $O\cdots Cl$ contacts (dashed lines).
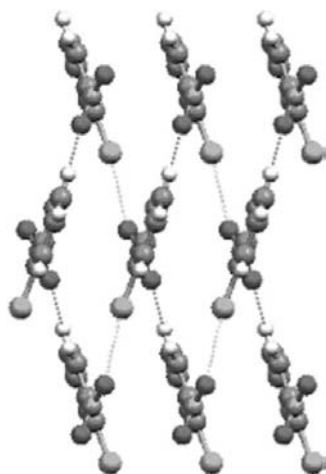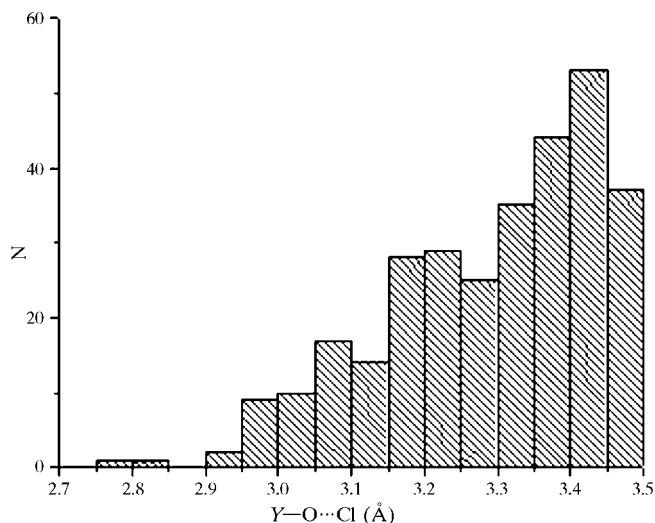
**Figure 3**
A projection of the crystal structure of (I) on to (010), showing the short $Cl\cdots O$ and $C-H\cdots O$ intermolecular interactions (dashed lines).

pointing to strong torsional vibrations of the nitro group. Aromatic molecules fulfil well the exigencies of the rigid-body approximation (Cruickshank, 1956; Dunitz *et al.*, 1988; Schomaker & Trueblood, 1998), especially at elevated temperatures. Calculations within the **TLS** formalism, with the correlation of the internal vibration of the non-rigidly attached rigid group performed with *THMA11* (Farrugia, 1999), enabled the monitoring of molecular motions in the vicinity of the melting point. The mean-square amplitudes of the molecular translations and librations are large (0.035–0.057 $Å^2$ and 16–45$°^2$, respectively). The largest libration occurs about the axis close to the $C-Cl$ bond. The internal torsional vibration of the nitro group occurs about the $C-N$ bond. The mean-square amplitude of the overall nitro group rotation is about 227$°^2$ and may be compared with the librational contribution to the motion (from the molecular libration), which is about 31$°^2$. The results of the rigid-body analysis of the crystal structure of (I) reveal the driving role of the torsional vibrations of the nitro group in the phase transition to the liquid phase.

## Experimental

Commercially available (POCH Poland) *o*-chloronitrobenzene, (I), was not purified further and was not recrystallized. The crystals sublime on exposure to the atmosphere (m.p. 304–306 K) and had to be enclosed and sealed within thin-walled glass capillaries in order to use them for collecting X-ray intensity data.

*Crystal data*

| | |
|---|---|
| $C_6H_4ClNO_2$ | $Z = 4$ |
| $M_r = 157.55$ | $D_x = 1.555$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation |
| $a = 3.8210$ (10) Å | $\mu = 0.50$ mm$^{-1}$ |
| $b = 11.725$ (2) Å | $T = 298$ (2) K |
| $c = 15.118$ (3) Å | Block, pale yellow |
| $\beta = 96.55$ (3)° | $0.89 \times 0.55 \times 0.55$ mm |
| $V = 672.9$ (2) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Kuma KM-4 CCD area-detector diffractometer | 1214 independent reflections |
| $\omega$ scans | 975 reflections with $I > 2\sigma(I)$ |
| 2711 measured reflections | $R_{int} = 0.083$ |
| | $\theta_{max} = 25.8°$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0867P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.075$ | $+ 0.8782P]$ |
| $wR(F^2) = 0.205$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.09$ | $(\Delta/\sigma)_{max} = 0.019$ |
| 1214 reflections | $\Delta\rho_{max} = 0.52$ e Å$^{-3}$ |
| 91 parameters | $\Delta\rho_{min} = -0.45$ e Å$^{-3}$ |
| H-atom parameters constrained | |

All H atoms were treated as riding atoms, with C—H = 0.93 Å, and were refined isotropically, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *KM-4 CCD Software* (Kuma, 1999); cell refinement: *KM-4 CCD Software*; data reduction: *KM-4 CCD Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *MERCURY* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

## Table 1
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cl1—C1 | 1.717 (4) | N1—C2 | 1.468 (5) |
| N1—O1 | 1.194 (5) | C2—C3 | 1.380 (5) |
| N1—O2 | 1.199 (5) | | |
| | | | |
| O1—N1—O2 | 123.0 (4) | C2—C1—Cl1 | 122.6 (3) |
| O1—N1—C2 | 118.7 (4) | C3—C2—C1 | 121.1 (3) |
| C6—C1—C2 | 118.7 (4) | C3—C2—N1 | 116.8 (3) |
| C6—C1—Cl1 | 118.7 (3) | C1—C2—N1 | 122.1 (4) |

## Table 2
Short intermolecular contacts (Å) in (I).

| | | | |
|---|---|---|---|
| O2···Cl1$^i$ | 3.095 (5) | O1···C4$^{ii}$ | 3.266 (4) |
| O1···H4$^{ii}$ | 2.62 | | |

Symmetry codes: (i) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

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