

C1—C2—O23	118.2 (4)	C1—C10—C9	115.7 (5)
C3—C2—O23	104.8 (7)	C1—C10—C28	106.0 (5)
C2—C3—C4	99.9 (5)	C5—C10—C9	106.7 (5)
C2—C3—O21	105.3 (7)	C5—C10—C28	112.4 (5)
C4—C3—O21	116.1 (4)	C9—C10—C28	104.7 (4)
C3—C4—C5	109.8 (6)	C9—C11—C12	108.3 (4)
C3—C4—C18	115.4 (5)	C11—C12—C13	112.3 (6)
C3—C4—C19	98.1 (5)	C12—C13—C14	108.6 (5)
C5—C4—C18	111.6 (5)	C12—C13—C16	112.0 (6)
C5—C4—C19	108.8 (5)	C12—C13—O34	110.4 (5)
C18—C4—C19	112.2 (6)	C14—C13—C16	101.7 (5)
C4—C5—C6	110.1 (5)	C14—C13—O34	117.6 (6)
C4—C5—C10	115.7 (5)	C16—C13—O34	106.1 (4)
C6—C5—C10	107.6 (5)	C8—C14—C13	100.1 (5)
C5—C6—C7	112.6 (4)	C8—C15—C16	102.6 (4)
C5—C6—C8	107.5 (6)	C13—C16—C15	107.5 (5)
C7—C6—C8	114.0 (4)	C13—C16—C17	123.3 (6)
C6—C7—O25	111.2 (5)	C15—C16—C17	129.3 (5)
C6—C7—O27	125.8 (8)	C4—C19—O23	110.4 (6)
O25—C7—O27	123.0 (7)	C4—C19—O24	129.2 (8)
C6—C8—C9	107.6 (4)	O23—C19—O24	120.4 (6)
C6—C8—C14	112.7 (6)	C1—C20—O21	109.2 (5)
C6—C8—C15	119.1 (5)	C1—C20—O22	130.6 (7)
C9—C8—C14	110.3 (5)	O21—C20—O22	120.3 (6)
C9—C8—C15	108.0 (6)	C3—O21—C20	107.2 (5)
C14—C8—C15	98.8 (4)	C2—O23—C19	108.1 (5)

Data were collected to the maximum  $\theta$  possible for a Rigaku AFC-6R diffractometer equipped with an evacuated exit-beam collimator. The  $\theta$ -scan width was  $(1.6 + 0.3\tan\theta)^\circ$ , with a  $\theta$ -scan rate  $32^\circ \text{ min}^{-1}$  and up to four scans on weak reflections and background counts for one quarter of scan time on each end of every scan. H atoms were included at calculated positions and methyl groups were aligned to best match peaks observed in difference electron-density maps. The absolute structure was assigned to conform with the known chirality of the compound's precursors.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1992). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *Xtal DIFDAT ABSORB SORTRF ADDREF* (Hall & Stewart, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *Xtal CRYLSQ* (Hall, King & Stewart, 1995). Molecular graphics: *Xtal*. Software used to prepare material for publication: *Xtal BONDLA CIFIO*.

Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: TA1104). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Barton, D. H. R. & McCombie, S. W. (1975). *J. Chem. Soc. Perkin Trans.* pp. 1574–1585.
- Beale, M. H. (1985). *J. Chem. Soc. Perkin Trans.* pp. 1147–1156.
- Cambridge Structural Database (1995). Version of October 1995. Cambridge Data Centre, 12 Union Road, Cambridge, England.
- Haigh, C. W. & Mallion, R. B. (1972). *Org. Magn. Reson.* **4**, 203–228.
- Hall, S. R., King, G. S. D. & Stewart, J. M. (1995). Editors. *Xtal3.4 User's Manual*. University of Western Australia, Australia.
- Hall, S. R. & Stewart, J. M. (1990). Editors. *Xtal3.0 Reference Manual*. Universities of Western Australia, Australia, and Maryland, USA.
- Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.
- Mander, L. N. (1992). *Chem. Rev.* **92**, 573–612.
- Mander, L. N. & Owen, D. J. (1996). *Tetrahedron Lett.* **37**, 723–726.
- Mander, L. N. & Sherburn, M. S. (1996). *Tetrahedron Lett.* **37**, 4255–4258.
- Molecular Structure Corporation (1992). *MSCIAFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sternhell, S. (1975). *Dynamic Nuclear Magnetic Resonance Spectroscopy*, edited by L. M. Jackman & F. A. Cotton, pp. 163–201. New York: Academic Press.

*Acta Cryst.* (1997). **C53**, 225–227

## 4-Bromo-2,6-dichlorobenzonitrile

DOYLE BRITTON

*Department of Chemistry, University of Minnesota, Minneapolis, MN 55455-0431, USA. E-mail: britton@chemsun.chem.umn.edu*

(Received 31 October 1995; accepted 9 October 1996)

## Abstract

The molecular structure of 4-bromo-2,6-dichlorobenzonitrile,  $\text{C}_7\text{H}_2\text{BrCl}_2\text{N}$ , is normal. The most striking feature of the crystal packing is a short distance of  $3.102(5) \text{ \AA}$  between the N and Br atoms of adjacent molecules, which can be thought of as an interaction between the Lewis base, CN, and the Lewis acid, Br.

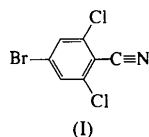
## Comment

We have previously determined the structures of several 2,4,6-trisubstituted benzonitriles, with iodo, bromo, chloro or methyl groups as substituents, in the search for intermolecular interactions between the Lewis-basic N atoms in the nitrile group and the Lewis-acidic halogen atoms; the methyl group was used as a non-acidic comparison group of about the same size as the halogens. The occurrence of  $\text{N}\cdots\text{X}$  distances shorter than the sum of the van der Waals radii was taken as evidence for such interactions.

In the tribromo and trichloro compounds (Carter & Britton, 1972), such short distances are found. In the tribromo compound, both *ortho*-Br atoms are  $3.06 \text{ \AA}$  from the N atoms in adjacent molecules. In the trichloro compound, only one *ortho*-Cl atom is close to an N atom, at a distance of  $3.22 \text{ \AA}$ , consistent with chlorine being a weaker Lewis base than bromine. In the trimethyl compound (Britton, 1979), there are no short  $\text{N}\cdots\text{CH}_3$  distances, as was expected.

In the tribromo compound, the *para*-Br atom is not involved in any short intermolecular distances and we have studied the consequences of replacing the Br atom with chloro, methyl and iodo groups. The 2,6-dibromo-4-chloro compound (Gleason & Britton, 1978) is isomorphous with the tribromo compound and must have similar distances. Since chlorine is a weaker acid than bromine, this was not unexpected. The 2,6-dibromo-4-methyl compound (Gleason & Britton, 1976) packs in a completely different fashion, with no short N···Br distances; the dominant interaction appears to be Br···Br, which was unexpected. The 2,6-dibromo-4-iodo compound (Gleason & Britton, 1978) has an N···I distance of 3.15 Å and only one of the Br atoms is involved in a short N···Br distance of 3.28 Å. Since iodine is a stronger acid than bromine, this change from the tribromo structure is quite understandable.

We report here the structure of 4-bromo-2,6-dichlorobenzonitrile, (I). The bond lengths and angles are normal. The molecule deviates slightly from planarity. The C<sub>6</sub> ring is planar within experimental error, but the substituents are not, with the Br4 [0.071 (4) Å], Cl2 [0.042 (4) Å] and Cl6 [0.075 (4) Å] atoms out of the plane of the ring on one side, and the C7 [0.036 (5) Å] and N1 [0.068 (5) Å] atoms out of the plane on the other.



Using the van der Waals radii suggested by Pauling (1960), there are only four intermolecular distances shorter than normal. The Cl2 atom is 3.480 (2) Å from the Cl6 atom in the molecule at  $(2-x, \frac{1}{2}+y, \frac{3}{2}-z)$  and 3.519 (2) Å from the Cl6 atom in the molecule at  $(1-x, \frac{1}{2}+y, \frac{3}{2}-z)$ , both of which can be compared to the suggested distance of 3.60 Å. Cl···Cl contacts of this sort in structures with 4 Å axes are common and have been discussed by Sarma & Desiraju (1986) who

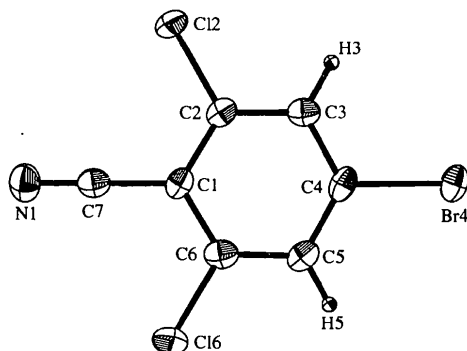


Fig. 1. The molecule of C<sub>7</sub>H<sub>2</sub>BrCl<sub>2</sub>N. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as spheres of arbitrary size.

call them  $\beta$  structures following Schmidt (1964). The same two molecules that have the Cl2···Cl6 contact of 3.519 Å also have an N1···H5 contact (based on the idealized H-atom position) of 2.625 Å, which can be compared to the suggested distance of 2.7 Å.

The shortest intermolecular distance (relative to normal) is an N···Br interaction between adjacent molecules related to each other by the *c* glide operation [the Br atom interacts with the N atom on the molecule at  $(-1+x, \frac{1}{2}-y, -\frac{1}{2}+z)$ ]. The C—N···Br—C atoms involved in the interaction have C—N···Br angles of 130.2 (4)°, N···Br distances of 3.102 (5) Å and N···Br—C angles of 173.2 (4)°. The distance is shorter than the van der Waals distance (3.45 Å) between the N and Br atoms, the angle at the Br atom is consistent with the Br atom starting to expand its octet and the angle at the N atom is similar to that found in the other compounds described above. N···Br interactions have also been discussed extensively by Desiraju & Harlow (1989). These N···Br interactions lead to chains of molecules parallel to the [201] direction.

The packing, as a whole, can be described more easily by starting with the Cl···Cl contacts mentioned earlier. These Cl···Cl contacts occur in zigzag chains parallel to the *a* axis. Since each molecule is involved in two such chains, one at each Cl atom, the Cl···Cl interactions can be thought of as leading to a two-dimensional layer of molecules parallel to the (001) plane. These two-dimensional layers are bound into a three-dimensional structure by the N···Br interactions which occur between molecules in adjacent two-dimensional layers.

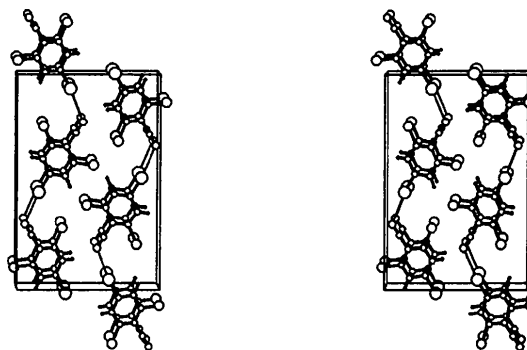


Fig. 2. The packing of C<sub>7</sub>H<sub>2</sub>BrCl<sub>2</sub>N viewed perpendicular to the *bc* plane. The intermolecular N···Br contact is shown as a light line.

## Experimental

A sample of the title compound was obtained from the chemical collection of the Department of Chemistry, University of Minnesota, USA.

### Crystal data

C<sub>7</sub>H<sub>2</sub>BrCl<sub>2</sub>N  
M<sub>r</sub> = 250.91

Mo K $\alpha$  radiation  
 $\lambda$  = 0.71069 Å

Monoclinic  
 $P2_1/c$   
 $a = 3.9237 (1) \text{ \AA}$   
 $b = 11.9223 (2) \text{ \AA}$   
 $c = 17.7519 (3) \text{ \AA}$   
 $\beta = 97.034 (2)^\circ$   
 $V = 824.18 (3) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 2.022 (1) \text{ Mg m}^{-3}$   
 $D_m$  not measured

Cell parameters from 2682 reflections  
 $\theta = 2-25^\circ$   
 $\mu = 5.56 \text{ mm}^{-1}$   
 $T = 173 (2) \text{ K}$   
 Plate  
 $0.50 \times 0.28 \times 0.08 \text{ mm}$   
 Colorless

#### Data collection

Siemens SMART area-detector diffractometer  
 $\omega$  scans  
 Absorption correction:  $\psi$  scans (XPREP in SHELXTL; Sheldrick, 1994)  
 $T_{\min} = 0.259$ ,  $T_{\max} = 0.641$   
 4108 measured reflections  
 1519 independent reflections

1282 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.203$  (before absorption correction and 0.081 (after)  
 $\theta_{\max} = 25.1^\circ$   
 $h = -4 \rightarrow 4$   
 $k = -14 \rightarrow 14$   
 $l = -20 \rightarrow 20$   
 Intensity decay:  $< 1\%$

#### Refinement

Refinement on  $F$   
 $R = 0.046$   
 $\omega R = 0.056$   
 $S = 1.74$   
 1282 reflections  
 100 parameters  
 H atoms not refined  
 $w = 4F^2/[\sigma^2(F^2) + (0.05F^2)^2]$

$(\Delta/\sigma)_{\max} = 0.02$   
 $\Delta\rho_{\max} = 1.02 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -1.35 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Br4—C4	1.894 (5)	C1—C7	1.449 (7)
Cl2—C2	1.729 (5)	C2—C3	1.394 (7)
Cl6—C6	1.723 (5)	C3—C4	1.384 (7)
N1—C7	1.154 (7)	C4—C5	1.392 (8)
C1—C2	1.391 (7)	C5—C6	1.390 (8)
C1—C6	1.399 (7)		
C2—C1—C6	118.5 (5)	C4—C5—C6	117.7 (5)
C1—C2—C3	121.1 (5)	C1—C6—C5	121.8 (5)
C2—C3—C4	118.6 (5)	N1—C7—C1	179.4 (5)
C3—C4—C5	122.4 (5)		

The data collection nominally covered more than a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different  $\varphi$  angle for the crystal and each exposure covered  $0.3^\circ$  in  $\omega$ . The crystal-to-detector distance was 4.94 cm. Coverage of the unique set was approximately 98% complete to at least  $25^\circ$  in  $\theta$ . Crystal decay was monitored by repeating the initial frames at the end of the data collection and analyzing the duplicate reflections.

Data collection: *ASTRO* (Siemens, 1995a). Cell refinement: *SAINT* (Siemens, 1995b). Data reduction: *SAINT*. Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984) and *DIRDIF* (Buerskens, 1984). Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1985). Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

The author would like to thank Dr Victor G. Young Jr of the University of Minnesota X-ray Diffraction Laboratory for collecting the data on the SMART system.

Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: BK1210). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

#### References

- Beurskens, P. T. (1984). *DIRDIF. Direct Methods for Difference Structures – an Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors*. Technical Report 1984/1. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.
- Britton, D. (1979). *Cryst. Struct. Commun.* **8**, 667–670.
- Carter, V. R. & Britton, D. (1972). *Acta Cryst.* **B28**, 945–950.
- Desiraju, G. R. & Harlow, R. L. (1989). *J. Am. Chem. Soc.* **111**, 6757–6764.
- Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.
- Gleason, W. B. & Britton, D. (1976). *Cryst. Struct. Commun.* **5**, 229–232.
- Gleason, W. B. & Britton, D. (1978). *Cryst. Struct. Commun.* **7**, 365–370.
- Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Pauling, L. (1960). In *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell University Press.
- Sarma, J. A. R. P. & Desiraju, G. R. (1986). *Acc. Chem. Res.* **19**, 222–228.
- Schmidt, G. M. J. (1964). *J. Chem. Soc.* pp. 2014–2021.
- Sheldrick, G. M. (1994). *SHELXTL*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1995a). *ASTRO. Data Collection Software for the SMART System*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1995b). *SAINT. Data Processing Software for the SMART System*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

*Acta Cryst.* (1997). **C53**, 227–229

### 2,4-Dinitro-*trans*-cinnamic Acid

VENKAT R. THALLADI, C. V. KRISHNAMOHAN SHARMA AND GAUTAM R. DESIRAJU

*School of Chemistry, University of Hyderabad, Hyderabad 500 046, India. E-mail: grdch@uohyd.ernet.in*

(Received 19 March 1996; accepted 3 October 1996)

#### Abstract

2,4-Dinitrocinnamic acid [3-(2,4-dinitrophenyl)prop-2-enoic acid],  $\text{C}_9\text{H}_6\text{N}_2\text{O}_6$ , crystallizes as a normal centrosymmetric carboxy dimer. Both  $\text{O} \cdots \text{H}$  and  $\text{C} \cdots \text{H} \cdots \text{O}$  hydrogen bonds are found in the structure.