

Isomorphism and pseudosymmetry in 2,6-dichloro- and 2,6-dibromobenzonitrile

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The title compounds are isomorphous, with two half-molecules in the asymmetric unit of a monoclinic unit cell in the space group $C2/m$. For the chloro compound: $a = 18.0525$ (8), $b = 20.7374$ (10), $c = 3.8334$ (2) Å, $\beta = 101.143$ (1)°; for the bromo compound: $a = 18.2269$ (15), $b = 21.349$ (2), $c = 3.9663$ (3) Å, $\beta = 101.446$ (2)°. The dominant intermolecular interactions are between halogen atoms rather than between halogen and nitrile, as is the case in the corresponding 2,4,6-trihalobenzonitriles. The molecules pack into layers with a fourfold pseudosymmetry. The pseudosymmetry appears to be the consequence of halogen–halogen intermolecular interactions.

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1. Introduction

We have previously determined the structures of several 2,4,6-trisubstituted benzonitriles, with iodine, bromine or chlorine as substituents, in a search for intermolecular interactions between the Lewis-basic N atoms in the nitrile group and the Lewis-acidic halogen atoms (see Britton, 1997, and references therein). In particular, in the trichloro and tribromo compounds (Carter & Britton, 1972) there are dimeric intermolecular interactions between the nitrogen and the *ortho*-halogen on one molecule with the corresponding atoms on the next. In the chloro compound this happens with one of the two *ortho*-chlorine atoms on each molecule; in the bromo compound it happens with both *ortho*-bromine atoms, with each nitrogen being involved in two such interactions. Desiraju & Harlow (1989) have discussed such interactions more generally and Reddy *et al.* (1993) have used the $CN \cdots Cl$ interaction as a motif to form intermolecular tapes.

We report here the structure of 2,6-dichloro- and 2,6-dibromobenzonitrile. These were undertaken to see if similar intermolecular interactions were present and also to see if similar differences occurred. The crystals proved to be isomorphous, the intermolecular interactions were quite different and, unexpectedly, the structures involved significant but understandable pseudosymmetry.

2. Experimental

The chloro compound was obtained from Alfa Products. The bromo compound was prepared from the corresponding aniline *via* the Sandmeyer reaction: m.p. 427–428 K; lit. m.p. 428 K (Cirigottis *et al.*, 1974); 1H NMR ($CDCl_3$, 300 MHz): d 7.30 (dd, $J = 8.6, 8.1$ Hz, 1H), 7.64 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): d 134.2, 131.9, 126.9, 115.9, 105.0; IR (CH_2Cl_2 , cm^{-1}): 2254 (s, sharp, nitrile), 1552 (s, Ar C=C).

Crystals of both, suitable for diffraction, were prepared by recrystallization from ethanol. For both compounds the crystals used were thick needles elongated along *c*.

The determination of the structures was straightforward. The experimental data are given in Table 1.¹ The absorption corrections were made using *SADABS* (Sheldrick, 1996; Blessing, 1995).

The two compounds are isomorphous, in space group *C2/m* with *Z* = 8. Although this appears to be a case with *Z'* (the number of molecules in the asymmetric unit) = 1, it is, in fact, a case with *Z'* = 2, with one molecule lying on a twofold axis and the other on a mirror plane with the plane of the molecule perpendicular to the mirror. Zorky and coworkers (Zorky *et al.*, 1967; Belsky *et al.*, 1995; Zorky, 1996) have suggested that a better description would be *C2/m*, *Z* = 8(*2,m*) to distinguish it from the case with all molecules in general positions, *C2/m*, *Z* = 8 (1), and that these two alternatives should be regarded as being two different structural classes. In the following discussion the molecule lying on the twofold axis will be referred to as molecule 1 and the molecule perpendicular to the mirror plane as molecule 2.

3. Discussion

3.1. General

The atom labelling and anisotropic displacement ellipsoids for both molecules are shown in Fig. 1. The final coordinates are given in Tables 2 and 3. Bond lengths and angles are given in Table 4.

The bond lengths and angles are normal and in every case the corresponding values for the two independent molecules agree within experimental error. In aromatic compounds with substituents adjacent to each other it is common to find the substituents displaced in opposite directions from the mean plane of the ring. This effect shows up clearly in the chloro molecule 2, where both Cl atoms are 0.036 (2) Å above this plane and the nitrile C and N are both below it at 0.020 (3) and 0.021 (3) Å, respectively. In the chloro molecule 1 the effect is obscured by the symmetry of the site, since the average nitrile C and N positions must lie in the mean plane and the two Cl atoms must lie on opposite sides. Presumably, the expected distortions are averaged out over the entire structure. The results for the bromo compound are similar, but involve considerably larger standard uncertainties in the values.

3.2. Packing

The packing of the bromo compound is shown in Fig. 2. The chloro compound is virtually identical. The molecules lie in layers parallel to the (201) plane. Within the layers the strong (short) intermolecular contacts are *X*···*X* and *H*···*N*, which are described in detail in Tables 5 and 6. The *X*···*X* contacts are also compared to those in 4-methyl-2,6-dibromobenzonitrile (Gleason & Britton, 1976) and in elementary Cl₂ and

Br₂ (Donohue, 1974), where similar contacts occur. In the *X*···*X* contacts we would describe this as the Lewis acid *X* interacting with the Lewis base *X*; we would expect the angle at the acidic *X* to be 180° ideally and the angle at the basic *X* to be between 90 and 120°. Each *X* atom is involved in two interactions and acts both as an acid and as a base. As can be seen, the cyclic *X*₄ rings have close to these idealized values. The Cl···Cl distances in the aromatic compounds are about the usual van der Waals distances, but the Br···Br distances are significantly shorter, shorter in fact than the Cl···Cl distances. These shorter distances imply stronger interactions and this would appear to be confirmed in two ways. Inspection of Fig. 1 shows that the anisotropic displacement ellipsoids are smaller in the bromo than in the chloro compound, suggesting

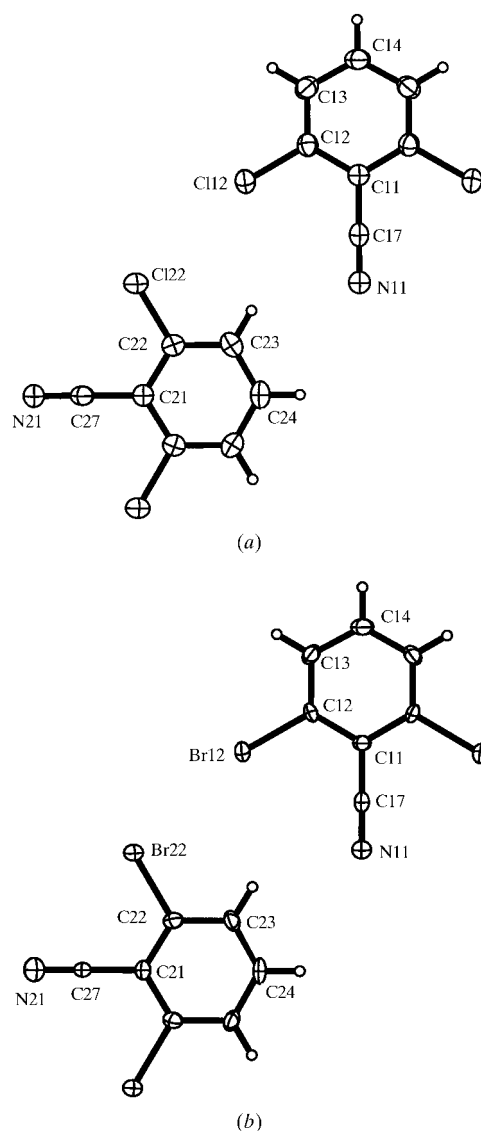


Figure 1
The structures of 2,6-dichloro- (above) and 2,6-dibromobenzonitrile (below). Displacement ellipsoids are shown at the 50% probability level. H atoms are shown with arbitrary radii. The molecules are oriented as in Fig. 2.

¹Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK0072). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details.

	Chloro compound	Bromo compound
Crystal data		
Chemical formula	C ₇ H ₃ Cl ₂ N	C ₇ H ₃ Br ₂ N
Chemical formula weight	172	260.92
Cell setting	Monoclinic	Monoclinic
Space group	<i>C2/m</i>	<i>C2/m</i>
<i>a</i> (Å)	18.0525 (8)	18.2269 (15)
<i>b</i> (Å)	20.7374 (10)	21.349 (2)
<i>c</i> (Å)	3.8334 (2)	3.9663 (3)
β (°)	101.143 (1)	101.446 (2)
<i>V</i> (Å ³)	1408.02 (12)	1512.7 (2)
<i>Z</i>	8	8
<i>D_x</i> (Mg m ⁻³)	1.623	2.291
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
Wavelength (Å)	0.71073	0.71073
No. of reflections for cell parameters	2740	2694
θ range (°)	1.5–25.0	1.5–25.0
μ (mm ⁻¹)	0.828	10.631
Temperature (K)	172 (2)	174 (2)
Crystal form	Thick needle	Thick needle
Crystal size (mm)	0.45 × 0.15 × 0.15	0.50 × 0.21 × 0.16
Crystal color	Colorless	Colorless
Data collection		
Diffractionmeter	Siemens SMART area detector	Siemens SMART area detector
Data collection method	ω scans	ω scans
Absorption correction	Multi-scan	Multi-scan
<i>T</i> _{min}	0.69	0.086
<i>T</i> _{max}	0.88	0.183
No. of measured reflections	3625	3985
No. of independent reflections	1289	1378
No. of observed reflections	1114	1148
Criterion for observed reflections	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)
<i>R</i> _{int}	0.021	0.033
θ _{max} (°)	25.03	25.05
Range of <i>h</i> , <i>k</i> , <i>l</i>	–21 → <i>h</i> → 18 –24 → <i>k</i> → 24 –4 → <i>l</i> → 4	–14 → <i>h</i> → 21 –23 → <i>k</i> → 25 –4 → <i>l</i> → 4
No. of standard reflections	125	131
Refinement		
Refinement on	<i>F</i> ²	<i>F</i> ²
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)]	0.030	0.036
<i>wR</i> (<i>F</i> ²)	0.077	0.100
<i>S</i>	1.05	1.19
No. of reflections used in refinement	1289	1378
No. of parameters used	100	100
H-atom treatment	Riding	Riding
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0450P)^2 + 0.9200P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0560P)^2 + 1.9400P]$, where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ) _{max}	0.001	–0.001
$\Delta\rho$ _{max} (e Å ⁻³)	0.246	0.991
$\Delta\rho$ _{min} (e Å ⁻³)	–0.240	–1.069
Extinction method	<i>SHELXTL</i> (Sheldrick, 1994)	<i>SHELXTL</i> (Sheldrick, 1994)
Extinction coefficient	0.0077 (7)	0.0014 (2)
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs		
Data collection	<i>SAINT</i> (Siemens, 1995)	<i>SAINT</i> (Siemens, 1995)
Cell refinement	<i>SAINT</i> (Siemens, 1995)	<i>SAINT</i> (Siemens, 1995)
Data reduction	<i>SAINT</i> (Siemens, 1995)	<i>SAINT</i> (Siemens, 1995)
Structure solution	<i>SHELXTL</i> (Sheldrick, 1994)	<i>SHELXTL</i> (Sheldrick, 1994)
Structure refinement	<i>SHELXTL</i> (Sheldrick, 1994)	<i>SHELXTL</i> (Sheldrick, 1994)
Preparation of material for publication	<i>SHELXTL</i> (Sheldrick, 1994)	<i>SHELXTL</i> (Sheldrick, 1994)

that the bromo molecules are held together more tightly. The layers are not exactly planar (see below), but the molecules in the bromo compound are slightly closer to planar than those in the chloro compound, again suggesting that the Br···Br interaction is stronger. The H···N distances are about the usual van der Waals distances, but the interactions are surely attractive and presumably contribute to the near planarity of the overall arrangement.

The layers are 3.244 Å apart in the chloro compound and 3.331 Å in the bromo compound. The molecules are slightly tilted with respect to the mean layer: chloro molecules 1 and 2 are tilted 7.7 (1) and 5.7 (2)°, respectively, out of the plane and bromo 1 and 2 are tilted 5.5 (2) and 5.2 (2)°, respectively. This results in average intermolecular distances of 3.487 (1) and 3.431 (4) Å, respectively, for the chloro molecules 1 and 2, and 3.520 (3) and 3.512 (6) Å, respectively, for bromo 1 and 2. In Fig. 3 the overlaps between molecules in adjacent layers are shown.

As was stated in §1, this work was begun with the expectation that CN···X interactions would be found. They were not. We conclude that CN···X and X···X interactions are comparable in energy and that it is not possible to predict which will predominate. Nevertheless, as Reddy *et al.* (1993) have shown, CN···X interactions are useful supramolecular synthons that should still be considered in trying to design new solid-state materials.

2,6-Dimethylbenzonitrile, which has a similar size and shape, also crystallizes in a layered structure (Drew & Willey, 1991), but the packing arrangement is quite different and the layer symmetry is *pg*.

Table 2

Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2).

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a'_i a'_j \mathbf{a}_i \cdot \mathbf{a}_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Cl12	0.36135 (3)	0.24609 (2)	0.16576 (13)	0.0335 (2)
N11	1/2	0.12857 (11)	0	0.0393 (6)
C11	1/2	0.25326 (11)	0	0.0252 (6)
C12	0.43829 (9)	0.28813 (8)	0.0742 (4)	0.0270 (4)
C13	0.43795 (10)	0.35460 (9)	0.0742 (5)	0.0320 (4)
C14	1/2	0.38722 (13)	0	0.0345 (6)
C17	1/2	0.18391 (13)	0	0.0288 (6)
Cl22	0.24617 (2)	0.13011 (2)	0.51158 (12)	0.0350 (2)
N21	0.12163 (13)	0	0.6686 (7)	0.0378 (6)
C21	0.25257 (12)	0	0.4900 (6)	0.0245 (5)
C22	0.28927 (9)	0.05788 (8)	0.4425 (4)	0.0265 (4)
C23	0.35903 (10)	0.05818 (9)	0.3443 (5)	0.0314 (4)
C24	0.39295 (14)	0	0.2954 (7)	0.0319 (6)
C27	0.17964 (14)	0	0.5879 (6)	0.0276 (6)

Table 3

Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2).

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a'_i a'_j \mathbf{a}_i \cdot \mathbf{a}_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Br12	0.35939 (3)	0.24585 (2)	0.19831 (13)	0.0243 (2)
N11	1/2	0.1362 (3)	0	0.038 (2)
C11	1/2	0.2567 (3)	0	0.0182 (14)
C12	0.4402 (2)	0.2904 (2)	0.0864 (11)	0.0188 (10)
C13	0.4401 (3)	0.3559 (2)	0.0843 (12)	0.0245 (11)
C14	1/2	0.3874 (3)	0	0.030 (2)
C17	1/2	0.1901 (3)	0	0.024 (2)
Br22	0.24603 (3)	0.13240 (2)	0.51581 (12)	0.0267 (2)
N21	0.1297 (4)	0	0.6772 (18)	0.037 (2)
C21	0.2566 (3)	0	0.4871 (14)	0.0184 (14)
C22	0.2923 (3)	0.0560 (2)	0.4366 (11)	0.0196 (10)
C23	0.3616 (2)	0.0562 (2)	0.3386 (11)	0.0221 (11)
C24	0.3936 (4)	0	0.2856 (18)	0.029 (2)
C27	0.1857 (4)	0	0.5918 (17)	0.0211 (14)

3.3. Symmetry versus pseudosymmetry

The space group for both crystals is $C2/m$. This means that the projection of the structure down the *c* axis has plane-group symmetry pmm with molecules 1 and 2 crystallographically unrelated. However, inspection of Fig. 2 strongly suggests an approximate fourfold symmetry. If a transformation of the unit cell by the matrix $1, 0, -2/0, 1, 0/0, 0, 1$ is made, so that the layers are now parallel to the *ab* face, the new unit-cell dimensions are: $a = 20.933$ (1) and $b = 20.737$ (1) \AA for the chloro compound and $a = 21.273$ (2) and $b = 21.349$ (2) \AA for the bromo compound, much closer to the equality that would be required for fourfold symmetry. Since the $X \cdots X$ distances are about the same in both structures, the increase in unit-cell dimensions in the bromo compound arises almost entirely from the increase in the C—Br bond length compared with the C—Cl bond length.

The *x* and *y* coordinates are not changed by the matrix transformation of the cells. If molecule 1 were related to

Table 4

Selected geometric parameters (\AA , $^\circ$).

	$\text{Cl}_2\text{C}_6\text{H}_3\text{CN}$	$\text{Br}_2\text{C}_6\text{H}_3\text{CN}$
X12—C12	1.732 (2)	1.879 (4)
N11—C17	1.148 (3)	1.150 (9)
C11—C17	1.438 (3)	1.423 (9)
C11—C12	1.403 (2)	1.404 (5)
C12—C13	1.378 (3)	1.398 (7)
C13—C14	1.384 (2)	1.379 (6)
X22—C22	1.732 (2)	1.892 (4)
N21—C27	1.148 (3)	1.138 (9)
C21—C27	1.437 (3)	1.434 (8)
C21—C22	1.400 (2)	1.394 (5)
C22—C23	1.382 (2)	1.393 (6)
C23—C24	1.382 (2)	1.369 (6)
C12—C11—C12 ⁱ	117.9 (2)	118.3 (5)
C13—C12—C11	121.3 (2)	120.8 (4)
C12—C13—C14	119.0 (2)	119.2 (5)
C13—C14—C13 ⁱ	121.5 (2)	121.6 (6)
C22—C21—C22 ⁱⁱ	118.1 (2)	118.0 (5)
C23—C22—C21	121.2 (2)	121.2 (4)
C24—C23—C22	118.9 (2)	118.5 (5)
C23—C24—C23 ⁱⁱ	121.6 (2)	122.5 (6)

Symmetry codes: (i) $1 - x, y, -z$; (ii) $x, -y, z$.

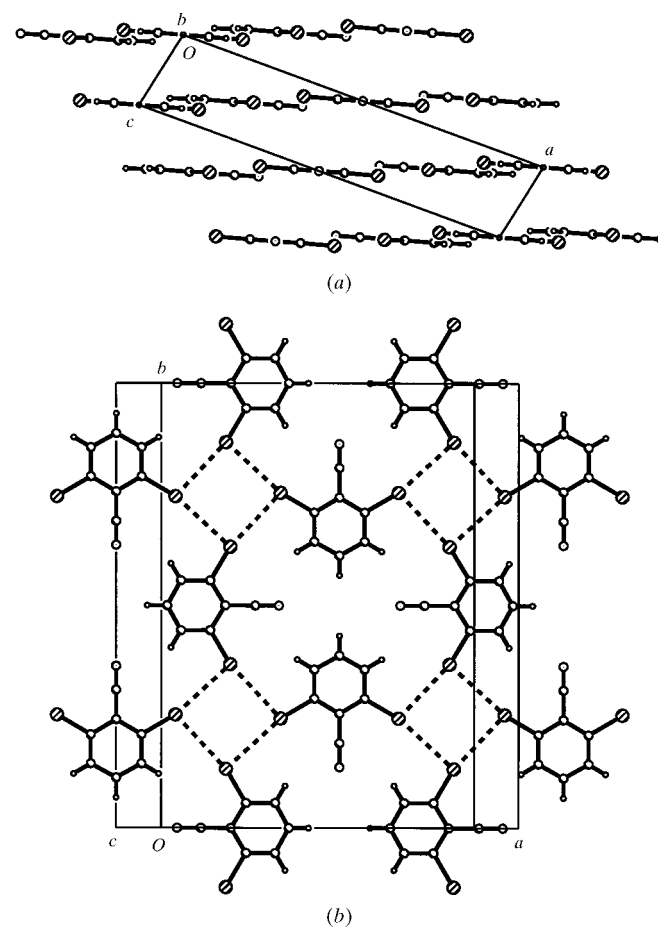


Figure 2

Packing of $\text{Br}_2\text{C}_6\text{H}_3\text{CN}$. Above: view along the *b* axis. Below: view perpendicular to (201). The layer shown in the lower view is the second layer from the top in the upper view. Short intermolecular contacts are shown as dashed lines.

Table 5

The intermolecular interactions $C-X \cdots X'-C'$ and $X-X \cdots X-X$ ($^\circ$, \AA).

C	X	X'	C'	C-X...X'	X...X'	X...X'-C'	Reference
Cl₂C₆H₃CN							
C12	Cl12	Cl22	C22	163	3.60	102	This work
C22	Cl22	Cl12 ⁱ	Cl2 ⁱ	164	3.58	103	This work
Br₂C₆H₃CN							
C12	Br12	Br22	C22	164	3.57	103	This work
C22	Br22	Br12 ⁱ	Cl2 ⁱ	166	3.55	102	This work
Br₂(CH₃)C₆H₂CN							
C3	Br	Br'	C3'	176	3.63	97	Gleason & Britton (1976)
Cl₂							
Cl'	Cl	Cl''	Cl'''	170	3.32	106	Donohue (1974)
Br₂							
Br'	Br	Br''	Br'''	170	3.32	105	Donohue (1974)

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.

molecule 2 by a fourfold rotation, then for each atom at x, y in molecule 1 there should be a similar atom at $y, \frac{1}{2} - x$ in molecule 2. Inspection of Tables 2 and 3 shows this relationship to be approximately satisfied for every pair of atoms in both structures.

The geometric part of the structure factor for space group $C2/m$ is $\cos 2\pi(hx + lz) \cos 2\pi ky$ for each atom in the asymmetric unit. If the atoms in these structures are taken in pairs, related as described in the previous paragraph, then this becomes $\cos 2\pi(hx + lz_1) \cos 2\pi ky + \cos 2\pi(hy + lz_2) \cos 2\pi kx \cos 2\pi(k/2)$. For $l = 0$ the z coordinates do not matter and the absolute value of this expression is the same for $kh0$ as for $hk0$. The $hk0$ layer of the reciprocal lattice is shown in Fig. 4. The approximate fourfold symmetry is apparent.

Rather than regard these relationships as fortuitous, we suggest the following interpretation. The basic structural motif is a two-dimensional sheet with fourfold symmetry in plane

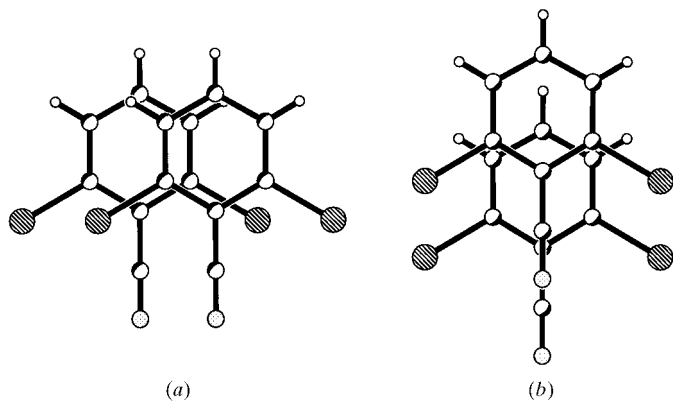


Figure 3

Layer-to-layer overlap in $\text{Br}_2\text{C}_6\text{H}_3\text{CN}$ viewed perpendicular to the molecular planes. (a) Molecule 1; (b) molecule 2. The overlaps in $\text{Cl}_2\text{C}_6\text{H}_3\text{CN}$ look essentially the same.

Table 6

The intermolecular interactions $C-H \cdots N-C'$ ($^\circ$, \AA).

C	H	N	C'	C-H...N	H...N	H...N-C'	C...N
Cl₂C₆H₃CN							
C13	H13	N21 ⁱ	C27 ⁱ	133	2.69	104	3.41
C23	H23	N11	C17	133	2.69	104	3.41
Br₂C₆H₃CN							
C13	H13	N21 ⁱ	C27 ⁱ	137	2.77	108	3.53
C23	H23	N11	C17	138	2.76	109	3.53

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$.

group $p4g$. The $p4g$ unit cell is rotated 45° to the unit cell shown in Fig. 2 and has half the area. These two-dimensional layers stack to form a three-dimensional structure. However, the fourfold axes are lost, since to keep them would require that the molecules stack directly over each other, something that does not occur in any of the hundreds of known aromatic compounds. As the sheets slip relative to each other to improve the layer-to-layer overlap the interactions in the axial directions become different from each other, giving rise to small differences in the axial lengths. Similarly, there is no mirror in the plane of the layer and the molecules tilt slightly out of the plane, again to improve the face-to-face interactions. The net result is a monoclinic structure that owes its basic arrangement to a tetragonal motif.

For a more general discussion of symmetry questions of this sort, see Zorky (1996).

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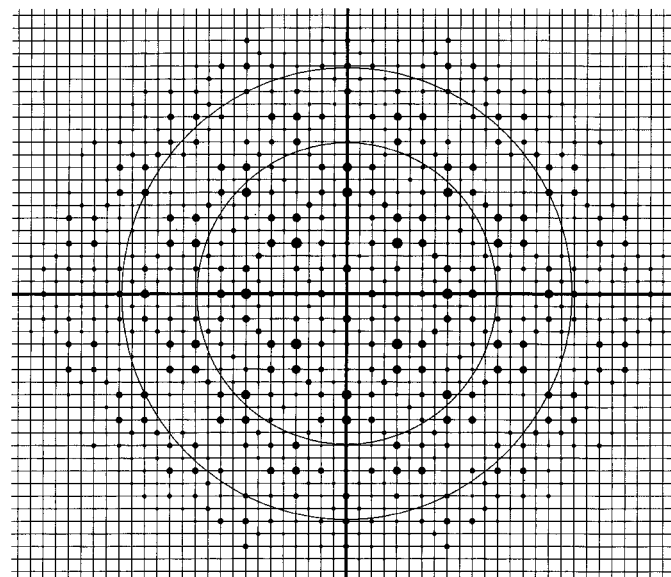


Figure 4

The $hk0$ reciprocal lattice layer. Spot sizes are based on the observed intensities of the reflections. In order to emphasize the intensity relationships in the pattern, the reciprocal lattice has been distorted so that the axes have equal lengths.

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