2,4,6-Trichlorophenylisonitrile and 2,4,6-trichlorobenzonitrile

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The molecular structures of the title compounds, 2,4,6-trichlorophenylisonitrile (IUPAC name: 2,4,6-trichlorophenyl isocyanide), $C_7H_2Cl_3N$, and 2,4,6-trichlorobenzonitrile, $C_7H_2Cl_3N$, are normal. The two structures are not isomorphous, but do contain similar two-dimensional layers in which pairs of molecules are held together by pairs of Cl···CN [3.245 (3) Å] or Cl···NC [3.153 (2) Å] interactions. The two-dimensional isomorphism is lost through different layer-stacking modes.

Comment

In the January 2000 version of the Cambridge Structural Database (207567 entries), the structures of five aromatic isonitriles are reported for which the structures of the corresponding nitriles are also known. In two of these pairs, 4-aminophenylisonitrile (Britton, 1993) and 4-aminobenzonitrile (Merlino & Sartori, 1982), and 4-iodophenylisonitrile (Britton *et al.*, 1978) and 4-iodobenzonitrile (Schlemper & Britton, 1965; Desiraju & Harlow, 1989), the isomers are isomorphous. In the other three, 1,4-phenylenediisonitrile (Hulme, 1952; Colapietro, Domenicano, Portalone, Torrini *et al.*, 1984) and terephthalonitrile (van Rij & Britton, 1977; Drueck & Littke, 1978; Colapietro, Domenicano, Portalone, Schultz & Hargittai, 1984), 4-bromophenylisonitrile (Britton *et al.*, 1978) and 4-bromobenzonitrile (Britton *et al.*, 1977), and 2,4,6-tribromophenylisonitrile (Carter *et al.*, 1977) and 2,4,6-tribromobenzonitrile (Carter & Britton, 1972), the isomers are not isomorphous. The latter three results are surprising in that these pairs of molecules are as close to isosteric (having the same size and shape) as is imaginable. To look for another example of such pairs, the structure of 2,4,6-trichlorophenylisonitrile, (I), has been determined to compare it with the structure of the corresponding nitrile (Carter & Britton, 1972). Also, to improve the comparison, the latter structure, (II), was redetermined.

The anisotropic displacement ellipsoids and the atom-labeling schemes for both title molecules are shown in Fig. 1. The bond lengths and angles are normal except for the pattern of the ring angles; see Table 1. In both molecules, the ring angles at C6 are about 1° larger than those at C2, although in an isolated molecule these would be expected to be equal. Likewise, the ring angles at C5 are about 0.8° smaller than those at C3. This would appear to be a case where packing forces (see Fig. 2) have distorted the basic molecular geometry.

(I)   (II)
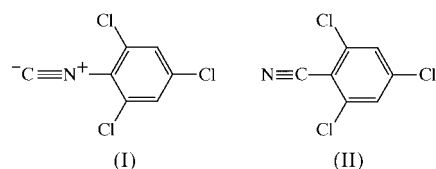
The packing in the isonitrile is related to that in the nitrile, but they are not identical. In both structures, there are two dimensional layers parallel to the (102) plane that are very similar. Fig. 2 shows the layer in the isonitrile; the picture of the layer in the nitrile is indistinguishable. Each molecule is involved in three kinds of close contacts: C2—Cl2···X—Y, where X is C7 and Y is N1 (both at $2 - x$, $-y$, $-z$) in the
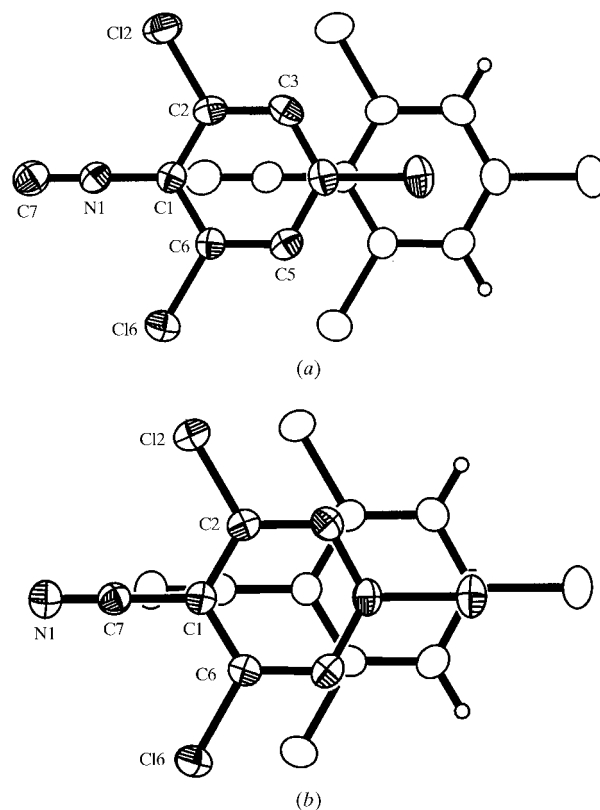

(*a*)

(*b*)

Figure 1
The molecular structures of (*a*) 2,4,6-trichlorophenylisonitrile and (*b*) 2,4,6-trichlorobenzonitrile, viewed normal to the plane of the phenyl rings. C4 and Cl4 in (*a*) and C3, C4, C5, and C14 in (*b*) are unlabeled to avoid crowding the figures; the ring numbering is sequential in both cases. Displacement ellipsoids are shown at the 50% probability level; H atoms are shown as spheres of arbitrary size. Also shown (see the comments on packing) are the molecules in the next layer below.

isonitrile and the opposite in the nitrile; C4—Cl4···Cl6—C6 (at $-1 + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$); C5—H5···X—Y (also at $-1 + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$). The metrical data for these interactions in the isonitrile (with the corresponding value in the nitrile in brackets) are: C2—Cl2···X 170.0 (3)° [176.1 (2)°]; Cl2···X 3.245 (3) Å [3.153 (2) Å]; Cl2···X—Y 127.4 (3)° [119.2 (2)°]; C4—Cl4···Cl6 152.8 (3)° [149.9 (2)°]; Cl4···Cl6 3.573 (2) Å [3.633 (2) Å]; Cl4···Cl6—C6 133.4 (3)° [132.2 (2)°]; C5—H5···X 155° (149°); H5···X 2.74 Å (2.61 Å); H5···X—Y 156° (153°). As can be seen from Fig. 2, the H3 atoms point towards Cl atoms in adjacent molecules, but the distances are over 3.00 Å in each case. The vertical repeat distance in Fig. 2 is b, 15.975 Å (15.890 Å); the horizontal repeat distance is the vector sum $c - 2a$, 15.324 Å (15.166 Å).

The Cl4···Cl6 distance is shorter in the isonitrile than in the nitrile, but the Cl2···N7 and H5···N7 distances in the nitrile are shorter than the corresponding Cl2···C7 and H5···C7 distances in the isonitrile. If we compare the molecular volume, 203.3 Å^3, the melting point, 325–326 K, and the average U_{iso} for all the heavy atoms in the isonitrile, 0.034 Å^2, with the corresponding values for the nitrile, 198.6 Å^3, 353–354 K, and 0.032 Å^2, respectively, we conclude that the inter-molecular interactions, taken as a whole, are stronger in the nitrile than in the isonitrile, and that the nitrile group is a stronger Lewis base than the isonitrile group for these types of interactions.

The layers are only approximately planar. The benzene rings are tilted 6.3° (8.8°) away from the (102) plane. The centers of the benzene rings are 0.43 Å (0.47 Å) on either side of the mean plane.

The difference between the structures comes in the stacking of the layers. The face-to-face interactions are included in Fig. 1, which shows the two overlapping molecules related by translation along **a**. In the isonitrile, the NC group is directly under a benzene ring in one direction and the Cl4 atom is directly over a benzene ring in the other direction. In the nitrile, the overlap is partially between the benzene rings themselves. The average distance between the layers is slightly greater in the isonitrile, 3.321 (1) Å, than in the nitrile, 3.296 (1) Å, but, owing to the different tilts and sideways displacements, the perpendicular distance between the benzene rings is slightly less in the isonitrile, 3.387 (2) Å, than in the nitrile, 3.459 (2) Å.

The differences between the two packings could be described by saying that there is a π–π interaction between the isonitrile group and the adjacent benzene ring, an interaction that is absent in the nitrile. This difference also occurs in the packings of 1,4-phenylenediisonitrile and terephthalonitrile. In the former, the stacking of the layers puts isonitrile groups above and below benzene rings in adjacent layers. In the latter, the nitrile groups do not lie above or below any part of the molecules in the adjacent layers. In 2,4,6-tribromophenyliso-nitrile and the corresponding benzonitrile, the effect shows up as a smaller –NC···ring distance in the isonitrile compared with a similar arrangement, but longer –CN···ring distance, in the nitrile.

Experimental

The nitrile (m.p. 353–354 K) was available from the earlier structure determination. The isonitrile (m.p. 325.2–325.7 K) was synthesized from the corresponding aniline (30 mg), chloroform (0.050 ml), methylene chloride (0.10 ml), aqueous sodium hydroxide (0.15 ml, 20% w/v), and the phase-transfer catalyst tetrabutylammonium hydrogen sulfate (18 mg). The mixture was stirred at room temperature for 120 h. Water (4 ml) and methylene chloride (4 ml) were added, and the organic layer was collected and dried (MgSO$_4$). The solvent was evaporated under a stream of dry nitrogen. A ^{1}H NMR spectrum showed it to be a 1:1 mixture of product and starting aniline. The mixture was chromatographed on silica gel (20:1 hexane–EtOAc) and the resulting solid was sublimed to give a small amount of white crystals; ^{1}H NMR (acetone-d_6, 300 MHz) δ 7.82 (s) p.p.m.

Isonitrile (I)

Crystal data

C$_7$H$_2$Cl$_3$N	D_x = 1.687 Mg m^{-3}
M_r = 206.45	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 1642
a = 4.5907 (6) Å	reflections
b = 15.975 (2) Å	θ = 2.2–25.1°
c = 11.1730 (13) Å	μ = 1.051 mm^{-1}
β = 97.187 (2)°	T = 173 (2) K
V = 813.0 (2) Å^3	Needles, colorless
Z = 4	0.15 × 0.05 × 0.05 mm

Data collection

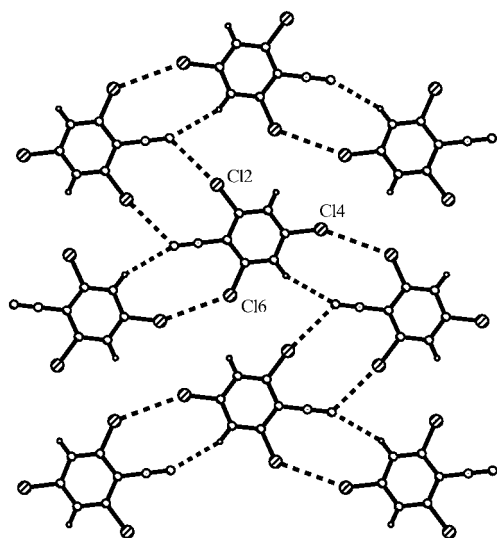|	
Siemens SMART area-detector diffractometer	R_{int} = 0.054
	θ_{max} = 27.5°
ω scans	$h = -5 \rightarrow 5$
Absorption correction: multi-scan	$k = -20 \rightarrow 18$
(SADABS; Sheldrick, 1996;	$l = -13 \rightarrow 14$
Blessing, 1995)	207 standard reflections
T_{min} = 0.90, T_{max} = 0.95	the first 207 reflections were
6423 measured reflections	remeasured at the end of the data
1855 independent reflections	collection 20 h later
1163 reflections with $I > 2\sigma(I)$	intensity decay: <1%

Figure 2
One layer of the structure of 2,4,6-trichlorophenylisonitrile viewed normal to the (102) plane. The corresponding view of the nitrile is indistinguishable to the eye. Short intermolecular contacts are shown with dashed lines.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.095$
$S = 0.93$
1855 reflections
100 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.049P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}

Nitrile (II)

Crystal data

$C_7H_2Cl_3N$
$M_r = 206.45$
Monoclinic, $P2_1/c$
$a = 3.8742\ (3)$ Å
$b = 15.8897\ (13)$ Å
$c = 12.9067\ (11)$ Å
$\beta = 90.975\ (2)°$
$V = 794.42\ (11)$ Å^3
$Z = 4$

$D_x = 1.726$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4571
  reflections
$\theta = 3.0–27.5°$
$\mu = 1.075$ mm^{-1}
$T = 173\ (2)$ K
Needle, colorless
$0.45 \times 0.25 \times 0.15$ mm

Data collection

Siemens SMART area-detector
  diffractometer
ω scans
Absorption correction: multi-scan
  (SADABS; Sheldrick, 1996;
  Blessing, 1995)
  $T_{min} = 0.70$, $T_{max} = 0.85$
8166 measured reflections
1811 independent reflections
1542 reflections with $I > 2\sigma(I)$

$R_{int} = 0.028$
$\theta_{max} = 27.49°$
$h = -4 \rightarrow 5$
$k = -20 \rightarrow 20$
$l = -16 \rightarrow 16$
181 standard reflections
  the first 181 reflections were
  remeasured at the end of the data
  collection 6 h later
  intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.068$
$S = 1.08$
1811 reflections
100 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.038P)^2 + 0.12P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994); program(s) used to refine structure: *SHELXLTL*; molecular graphics: *SHELXLTL*; software used to prepare material for publication: *SHELXLTL*.

Table 1
Selected bond angles for both compounds (°).

	Isonitrile (I)	Nitrile (II)
C2—C1—C6	119.3 (3)	118.1 (2)
C3—C2—C1	120.1 (3)	121.0 (2)
C2—C3—C4	119.3 (3)	118.5 (2)
C3—C4—C5	121.9 (3)	122.5 (2)
C4—C5—C6	118.4 (3)	117.9 (2)
C5—C6—C1	121.1 (3)	122.1 (2)

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