

***p*-Decylphenyl isocyanide and
p-decylbenzotrile: isomorphous
isonitrile/nitrile isomers**

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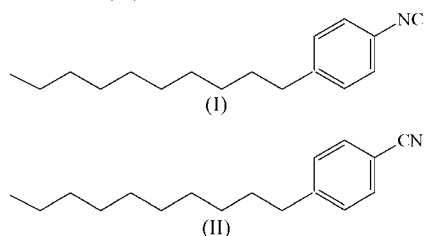
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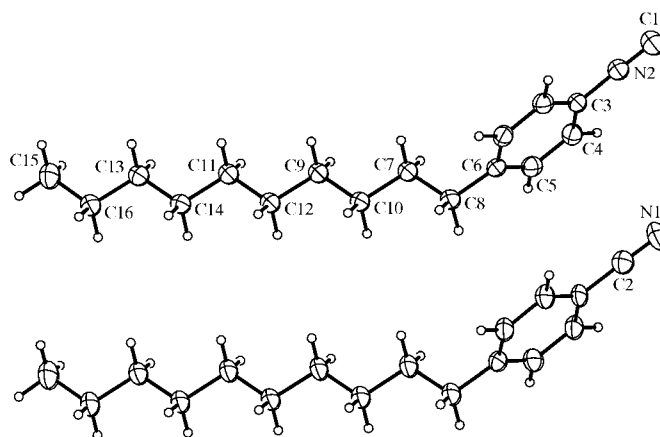
p-Decylphenyl isocyanide, $p\text{-C}_{10}\text{H}_{21}\text{-C}_6\text{H}_4\text{-NC}$ or $\text{C}_{17}\text{H}_{25}\text{N}$, and *p*-decylbenzotrile, $p\text{-C}_{10}\text{H}_{21}\text{-C}_6\text{H}_4\text{-CN}$ or $\text{C}_{17}\text{H}_{25}\text{N}$, are isomorphous. The molecules lie in mirror planes, with the C_6 rings perpendicular to the mirror. The packing of both molecules includes an aliphatic region, with close to ideal packing of the $\text{C}_{10}\text{H}_{21}$ chains, and an aromatic region, with phenyl ring–CN interactions. In addition, the CN ends of the molecules are also involved in a $\text{CN}\cdots\text{NC}$ dipolar interaction.

Comment

In the course of a study of the structures and properties of a series of $[\text{Pt}(\text{arylisonitrile})_4][\text{Pt}(\text{CN})_4]$ compounds (Daws *et al.*, 1997), it was felt useful to determine the structure of one of the aryl isonitrile ligands, namely *p*-decylphenyl isocyanide, (I); this structure is reported here. Corresponding nitriles and isocyanides sometimes have different packing arrangements, even though the pairs of molecules are very closely isosteric (Pink *et al.*, 2000, and references therein). In view of this fact, it also seemed worthwhile to determine the structure of *p*-decylbenzotrile, (II).



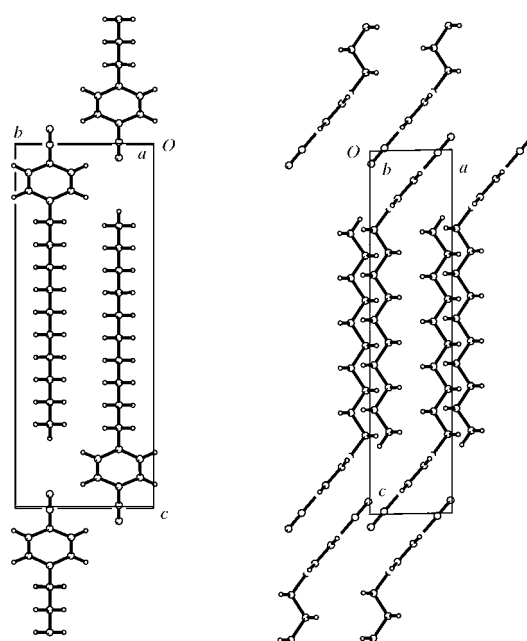
The two compounds are isomorphous. The anisotropic displacement ellipsoids and atom labelling are shown in Fig. 1. The bond lengths and angles in the two molecules agree within experimental error. The C3-N2 and N2-C1 distances in (I) are 1.407 (2) and 1.162 (2) Å, respectively, and the corresponding distances in (II), C3-C2 and C2-N1 , are 1.446 (3) and 1.153 (3) Å, respectively.

**Figure 1**

The molecules of (I) (top) and (II). Displacement ellipsoids are shown at the 50% probability level.

There are three major components to the packing, *viz.* the interactions of the aliphatic portions, the π interactions of the aromatic portions, and the dipolar interactions of the nitrile and isonitrile groups (see Fig. 2 for two orthogonal views of the packing).

The aliphatic $\text{C}_{10}\text{H}_{21}$ fragments pack parallel to each other, forming a two-dimensional layer containing hexagonal close-packed rods. This arrangement is similar to that found in *n*-decane (Bond & Davies, 2002). While the packing in *n*-decane is not identical to that in either of the CN compounds, since the planar C_{10} groups are oriented differently to one another in the two basically different structures, the cross-sectional areas of the rods in the CN compounds [18.26 (2) Å² for –NC and 18.25 (2) Å² for –CN] are only

**Figure 2**

The packing of (I); that of (II) is essentially the same. Left: view along *a*; right: view along *b*.

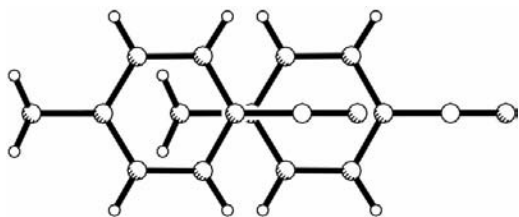


Figure 3

A view normal to the plane of the C_6 ring in the molecule of (I). Only atoms C7 in the decyl side chains are shown.

slightly larger than that in *n*-decane [$17.94(2) \text{ \AA}^2$], indicating that this aspect of the packing is only slightly affected by the terminal groups.

The overlap of the aromatic fragments is shown in Fig. 3. There is no overlap between the rings, but the $-CN$ and $-NC$ groups lie directly over the ring in the next layer. The perpendicular distances in (I) are $3.467(1)$ (between rings), $3.474(2)$ (between atoms N2) and $3.494(2) \text{ \AA}$ (between atoms C1). The distances in (II) are $3.474(2)$ (ring), $3.506(4)$ (C2) and $3.552(3) \text{ \AA}$ (N1). In each case, the $-NC$ or $-CN$ group is bent slightly out of the plane of the ring and away from the ring in the next molecule.

There are two pairs of dipolar interactions between each $-NC$ or $-CN$ group and its neighbors. One pair is attractive, involving groups related across a center of symmetry. In these interactions, the perpendicular distance between the parallel groups is $4.052(2) \text{ \AA}$ for (I) and $4.055(3) \text{ \AA}$ for (II). The dipoles are slightly displaced along the C—N bond direction from the positions of maximum attraction, assuming equal and opposite charges localized on the C and N atoms; the displacement is $0.149(2) \text{ \AA}$ for (I) and $0.184(3) \text{ \AA}$ for (II). The other pair of interactions is repulsive, involving groups related by translation along the *a* direction. In these interactions, the perpendicular distances between the parallel groups are shorter, *viz.* $3.525(2) \text{ \AA}$ for (I) and $3.557(3) \text{ \AA}$ for (II). However, the dipoles are considerably displaced along the C—N bond direction from the positions of maximum repulsion; the displacements are $3.054(2) \text{ \AA}$ for (I) and $3.017(3) \text{ \AA}$ for (II). The net result is that, for this simple model, the magnitude of the attractive interaction is about three times that of the repulsive interaction.

Experimental

The preparation of (I) has been reported previously (Daws *et al.*, 1997). Crystals suitable for diffraction were prepared by recrystallization from ethanol. Compound (II) was obtained according to the method of Casanova *et al.* (1966). A 0.23 g sample of neat *p*- $C_{10}H_{21}-C_6H_4-NC$ was heated to 473 K for 24 h under an argon atmosphere. After cooling overnight, the IR spectrum showed a single band at 2232.5 cm^{-1} due to the nitrile stretch. No isocyanide was present. The crude nitrile was purified by chromatography on silica gel using a 1:20 mixture of ethyl acetate and hexanes. Recrystallization from a variety of solvents gave crystals inferior to those of (I). The crystals used for the X-ray structure determination were obtained from acetone.

Compound (I)

Crystal data

$C_{17}H_{25}N$
 $M_r = 243.38$
 Monoclinic, $P2_1/m$
 $a = 4.6642(12) \text{ \AA}$
 $b = 7.831(2) \text{ \AA}$
 $c = 20.607(5) \text{ \AA}$
 $\beta = 91.13(1)^\circ$
 $V = 752.5(3) \text{ \AA}^3$
 $Z = 2$

$D_x = 1.074 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 985 reflections
 $\theta = 2.6\text{--}27.4^\circ$
 $\mu = 0.06 \text{ mm}^{-1}$
 $T = 173(2) \text{ K}$
 Plate, colorless
 $0.50 \times 0.25 \times 0.10 \text{ mm}$

Data collection

Siemens SMART area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2002; Blessing, 1995)
 $T_{\min} = 0.83$, $T_{\max} = 0.99$
 6459 measured reflections

1827 independent reflections
 1190 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -6 \rightarrow 6$
 $k = -10 \rightarrow 10$
 $l = -26 \rightarrow 26$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.106$
 $S = 1.04$
 1827 reflections
 154 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.054P)^2 + 0.023P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.17 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.18 \text{ e \AA}^{-3}$

Compound (II)

Crystal data

$C_{17}H_{25}N$
 $M_r = 243.38$
 Monoclinic, $P2_1/m$
 $a = 4.6526(12) \text{ \AA}$
 $b = 7.801(2) \text{ \AA}$
 $c = 20.466(5) \text{ \AA}$
 $\beta = 90.50(1)^\circ$
 $V = 742.8(3) \text{ \AA}^3$
 $Z = 2$

$D_x = 1.088 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 1019 reflections
 $\theta = 2.8\text{--}24.5^\circ$
 $\mu = 0.06 \text{ mm}^{-1}$
 $T = 173(2) \text{ K}$
 Plate, colorless
 $0.40 \times 0.20 \times 0.07 \text{ mm}$

Data collection

Siemens SMART area-detector diffractometer
 ω scans
 8715 measured reflections
 1812 independent reflections
 918 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.070$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -6 \rightarrow 6$
 $k = -10 \rightarrow 10$
 $l = -26 \rightarrow 26$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.107$
 $S = 0.74$
 1812 reflections
 104 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.104P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$
 Extinction correction: SHELXTL
 Extinction coefficient: 0.053(7)

For (I), the positions and isotropic displacement parameters for all of the H atoms were refined. For (II), given the lower quality of the data, the H atoms were placed in idealized positions, with C—H distances of 0.95 \AA for the aromatic H atoms, 0.99 \AA for the CH_2 H atoms and 0.98 \AA for the CH_3 H atoms. The U_{iso} values were set at $1.2U_{\text{eq}}$ of the attached C atoms for the aromatic and CH_2 H atoms, and at $1.5U_{\text{eq}}$ for the CH_3 H atoms.

For both *p*-decylphenyl isocyanide, (I), and *p*-decylbenzotrile, (II), data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1469). Services for accessing these data are described at the back of the journal.

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