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p-Isocyanobenzonitrile

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.002 Å
Disorder in main residue
R factor = 0.049
wR factor = 0.133
Data-to-parameter ratio = 13.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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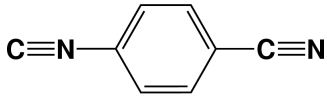
p-Dicyanobenzene and *p*-diisocyanobenzene are not isomorphous. The title compound, $C_8H_4N_2$, is isomorphous with *p*-dicyanobenzene. The molecule lies on a center of symmetry and is end-for-end disordered. The bond lengths and angles lie within normal ranges, but the precise values are obscured by the disorder.

Comment

Although *p*-dicyanobenzene and *p*-diisocyanobenzene have very similar shapes and volumes, they crystallize in quite different packing arrangements. The cyano compound (van Rij & Britton, 1977; Drück & Littke, 1978; Colapietro, Domenicano, Portalone, Schultz & Hargittai, 1984) packs with adjacent antiparallel cyano groups, while the isocyano compound (Hulme, 1952; Colapietro, Domenicano, Portalone, Torrini *et al.*, 1984) packs with the isocyano groups parallel to, and in contact with, benzene rings in adjacent molecules. A second, high-temperature polymorph of the cyano compound (Kubiak & Janczak, 1996) has a quite different packing arrangement from the low-temperature polymorph, but still involves antiparallel cyano groups. In view of the different intermolecular interactions in these two isomeric compounds, it seemed possible that the third isosteric isomer, *p*-isocyanobenzonitrile, might pack with a different environment at each end of the molecule. Accordingly, the structure of this isomer, (I), has been determined.



(I)

The structure was found to be isomorphous with the low-temperature form of the dicyanide, with complete end-for-end disorder of the molecules. The atom labelling and anisotropic displacement ellipsoids are shown in Fig. 1. The bond lengths and angles are consistent with those of the other two isomers, but the expected small differences are obscured by the disorder.

The unit-cell dimensions of *p*-dicyanobenzene and *p*-isocyanobenzonitrile are compared in Table 1. Although the two compounds are isomorphous, the differences in cell constants are larger than might be expected. It should also be noted that the molecular volume of *p*-diisocyanobenzene at 297 K is 168.8 $Å^3$ (Colapietro, Domenicano, Portalone, Torrini *et al.*, 1984), which is smaller than the corresponding volume for *p*-isocyanobenzonitrile. It appears that the isonitrile group packs more efficiently when it is parallel to a benzene ring and less efficiently when it is antiparallel to –CN and –NC.

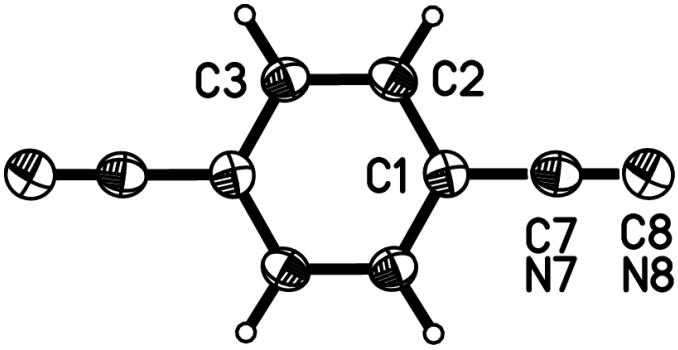


Figure 1
A view of the $C_6H_4(NC)(CN)$ molecule. Displacement ellipsoids are shown at the 50% probability level.

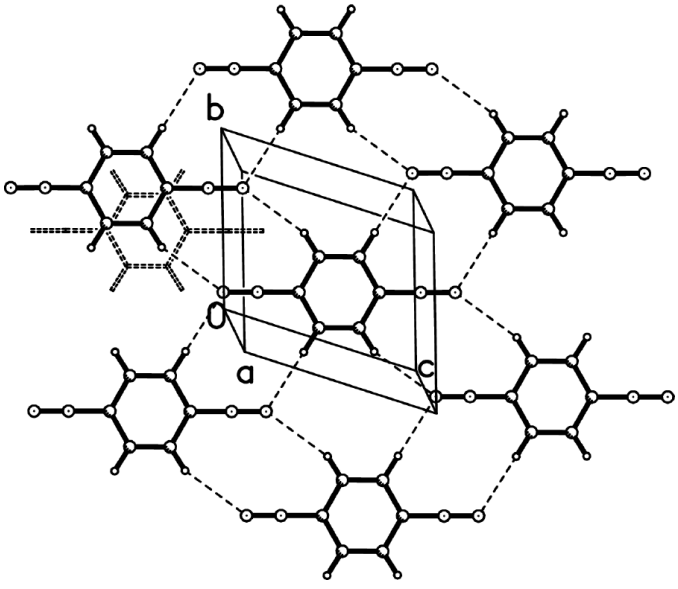


Figure 2
The packing of isocyanobenzonitrile. The view is normal to the molecular plane. The layer shown is parallel to $(11\bar{1})$. The molecule is tilted by 11.1° with respect to the layer. The dashed lines show contacts between H atoms and the disordered CN groups. One molecule from the next layer is shown with a dashed outline.

The packing is shown in Fig. 2. The molecules lie in layers parallel to $(11\bar{1})$; the molecules are tilted by 11.1° with respect to the layers. The layers are held together by C—H···*X* contacts, where *X* is the terminal atom of the CN group. This same arrangement is present in the dicyanobenzene and has been discussed by Colapietro *et al.* (1984). In the isocyanobenzonitrile, the H···*X* distances are 2.67 and 2.66 Å. In the dicyanobenzene at the same temperature (unpublished work, this laboratory), the H···N distances are 2.66 and 2.61 Å and the molecules are tilted by 12.4° with respect to the plane of the layer.

Experimental

A crude sample, supplied by Professor S. W. Fenton, was purified by sublimation and then recrystallized from acetone to provide crystals for the X-ray study. The ^{1}H NMR spectrum showed the expected A_2B_2 pattern with no observable lines from either of the other two isomers. The IR spectrum showed peaks at 2120 (*s*) and 2220 cm^{-1} (*m*). On heating, the crystals began to sublime at *ca* 385 K, began to darken at *ca* 435 K, and melted with further decomposition at 453–458 K.

Crystal data

$C_8H_4N_2$
M_r = 128.13
Triclinic, $P\bar{1}$
a = 3.7923 (11) Å
b = 6.4680 (18) Å
c = 7.504 (2) Å
α = 113.099 (10)°
β = 94.412 (10)°
γ = 97.128 (10)°
V = 166.41 (8) Å^3
Z = 1
D_x = 1.279 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1186 reflections
θ = 3.0–27.5°
μ = 0.08 mm^{-1}
T = 173 (2) K
Needle, colorless
0.50 × 0.15 × 0.10 mm

Data collection

Siemens SMART area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996; Blessing, 1995)
T_{min} = 0.97, T_{max} = 0.99
1941 measured reflections
747 independent reflections
610 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 27.5°
$h = -4 \rightarrow 4$
$k = -8 \rightarrow 8$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.133
S = 1.07
747 reflections
54 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.079P)^2 + 0.0192P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Cell constants (Å, °).

	p-Dicyanobenzene		*p*-Isocyanobenzonitrile	
	297 K[i]	173 K[ii]	297 K[ii]	173 K[iii]
a	3.843 (1)	3.795 (1)	3.836 (1)	3.792 (1)
b	6.575 (2)	6.494 (2)	6.483 (2)	6.468 (2)
c	7.313 (2)	7.302 (2)	7.618 (2)	7.504 (2)
α	114.50 (2)	114.15 (1)	112.96 (1)	113.10 (1)
β	93.53 (3)	92.87 (1)	97.08 (1)	94.41 (1)
γ	96.99 (3)	97.77 (1)	95.88 (1)	97.13 (1)
V	165.6 (1)	161.6 (1)	170.7 (1)	166.4 (1)

References: (i) Colapietro *et al.* (1984); (ii) SMART CCD measurements, this lab; (iii) this work.

The reported solution and refinement were straightforward. Two possible ordered alternative arrangements were considered and ruled out. When the structure was refined assuming that the molecules were ordered and parallel, that is, in $P1$ rather than $P\bar{1}$, the final R value was lower, as a consequence of the larger number of parameters. However, the anisotropic displacement ellipsoids of the atoms in the CN groups were unreasonable in directions that indicated disorder. The structure was also refined assuming that the molecules were ordered and antiparallel in layers, in the fashion found in *p*-fluorobenzonitrile (Britton & Gleason, 1977), where the unit cell contains two molecules related by a center of symmetry. The SMART frames were reintegrated assuming such a doubled cell. The intensities of the reflections that should have arisen from the doubling were all on the order of the background noise, while structure-factor calculations for

this ordered double cell showed that about 10% of the new reflections should have had intensities well above background.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); 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*.

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References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Britton, D. & Gleason, W. B. (1977). *Acta Cryst.* B**33**, 3926–3928.
Colapietro, M., Domenicano, A., Portalone, G., Schultz, G., & Hargittai, I. (1984). *J. Mol. Struct.* **112**, 141–157.
Colapietro, M., Domenicano, A., Portalone, G., Torrini, I., Hargittai, I. & Schultz, G. (1984). *J. Mol. Struct.* **125**, 19–32.
Drück, U. & Littke, W. (1978). *Acta Cryst.* B**34**, 3095–3096.
Hulme, R. (1952). *Acta Cryst.* **5**, 144.
Kubiak, R. & Janczak, J. (1996). *Acta Chem. Scand.* **50**, 1164–1167.
Rij, C. van & Britton, D. (1977). *Acta Cryst.* B**33**, 1301–1303.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1995). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.