

in bond angle and torsional parameters. Fig. 4 illustrates a similar geometrical comparison of the X-ray crystal structures of all three substances and Fig. 5 is a stereographic view of the crystal packing.

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Structure of Pentafluorophenyl Isocyanide at 115 K

BY DIETER LENTZ AND DAGMAR PREUGSCHAT

Institut für Anorganische und Analytische Chemie der Freien Universität Berlin, Fabeckstrasse 34–36, W-1000 Berlin 33, Germany

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Abstract. C_7F_5N , $M_r = 193.08$, orthorhombic, $Cmca$, $a = 7.611(3)$, $b = 9.427(5)$, $c = 18.603(14)$ Å, $V = 1334$ Å³, $Z = 8$, $D_x = 1.92$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 1.56$ cm⁻¹, $F(000) = 752$, $T = 115(5)$ K, $R = 0.053$, $wR = 0.050$ for 67 variables and 863 unique reflections for which $F_o > 6\sigma(F_o)$. Pentafluorophenyl isocyanide is an almost planar molecule. The molecular plane made up of the six phenyl C atoms is perpendicular to the crystallographic mirror plane (at $x = 0$) which bisects the phenyl ring and the isocyano group. The C—C bond lengths in the aromatic ring are almost identical, as are the C—F bond lengths. The isocyano moiety is almost linear.

Introduction. In contrast to the extensive structural information available on isocyanide complexes there are only a few isocyanides which have been structurally characterized by X-ray crystallography, electron diffraction or microwave spectroscopy. The only fluorinated isocyanides known thus far are trifluoromethyl isocyanide (Lentz, 1984, and references therein) and pentafluorophenyl isocyanide (Lentz, Grasse & Preugschat, 1988), which tend to polymerize readily.

Experimental. Crystals of pentafluorophenyl isocyanide were prepared by reaction of dibromo-*N*-(pentafluorophenyl)methanimine with magnesium in tetrahydrofuran (Lentz, Grasse & Preugschat, 1988). Crystals were grown by sublimation at 253 K (melting point with decomposition 286 K), in an evacuated Schlenk tube. A colourless crystal, $0.4 \times 0.5 \times 0.4$ mm, was mounted on the end of a glass fibre using a procedure described by Veith & Bärnighausen (1974) modified by Schumann, Genthe, Hahn, Hossain & van der Helm (1986). Enraf-Nonius CAD-4 diffractometer, unit-cell data from 25 reflections with $9 < \theta < 17^\circ$, $2 \leq \theta \leq 30^\circ$, ω/θ scan, $\Delta\omega = (1.1 + 0.35\tan\theta)^\circ$, scan speed $1\text{--}5^\circ \text{ min}^{-1}$, with $0 \leq h \leq 10$, $0 \leq k \leq 12$, $0 \leq l \leq 25$ and $-22 \leq l \leq 25$ for $0kl$ reflections, 1224 measured reflections, 990 unique reflections ($R_{\text{int}} = 0.018$) of which 863 had $F_o > 6\sigma(F_o)$. Two intensity-control reflections (154, 248) were measured with F_o 80 (1), 74 (1) and showed no change during data collection. The data were not corrected for extinction or absorption and the structure was solved by direct methods (*SHELXS86*; Sheldrick, 1985). All atoms were refined with anisotropic displacement parameters by full-matrix least-squares techniques based on F . The refinement mini-

mized $\sum w(|F_o| - |F_c|)^2$, $w = [\sigma^2(F) + 0.0005F^2]^{-1}$ (SHELX76; Sheldrick, 1976). Final $R = 0.053$, $wR = 0.050$ for 67 parameters. Largest Δ/σ for the final cycle of refinement was 0.001. The final difference map was qualitatively featureless with $\Delta\rho_{\max}$, $\Delta\rho_{\min} = 0.34$, $-0.59 \text{ e } \text{Å}^{-3}$, respectively. Scattering factors for neutral atoms from Cromer & Mann (1968); corrections for f' and f'' applied for all atoms from *International Tables for X-ray Crystallography* (1974, Vol. IV). Table 1* contains the atomic parameters and Table 2 contains bond distances and angles. The molecular structure is shown in Fig. 1 and the crystal packing in Fig. 2.

Discussion. The asymmetric unit consists of half a pentafluorophenyl isocyanide molecule. The almost planar molecule possesses a crystallographic mirror plane (at $x = 0$) which is perpendicular to the plane of the phenyl ring and bisects the phenyl ring and the isocyano group. The C5 atom has the largest deviation of 0.078 (2) Å from the least-squares plane, [maximum deviation 0.0003 (12)] defined by C1, C2, C3 and C4. The different C—C and C—F bond lengths of the pentafluoroaromatic ring system are equal within e.s.d.'s. The isocyano moiety is found to be almost linear. The C—N bond length of the isocyano function is similar to those of 4-C₆H₄Br—NC, 4-C₆H₄I—NC (Britton, Konnerth & Lam, 1978) and 2,4,6-C₆H₂Br₃—NC (Carter, Britton & Gleason, 1977). A comparison of the C—N length to the aromatic ring is not useful owing to the large e.s.d.'s for 4-C₆H₄Br—NC, 4-C₆H₄I—NC and 2,4,6-C₆H₂Br₃—NC. Interestingly, the N—C bond of the only aliphatic isocyanide which has been characterized by X-ray crystallography, N(CH₂—CH₂—CH₂—NC)₃ (Hahn & Tamm, 1991), is significantly shorter. The C—N bond length of the isocyano function determined in the solid state is generally shorter than that determined in the gaseous state for H—NC (Pearson, Cresswell, Winnewisser & Winnewisser, 1976), CH₃NC (Halonen & Mills, 1978), CF₃NC (Christen, Ramme, Haas, Oberhammer & Lentz, 1984) and HC≡C—NC (Krüger, Dreizler, Preugschat & Lentz, 1991), by electron diffraction and/or microwave spectroscopy. The C—N bond distance of the coordinated CN—C₆F₅ of 1.178 (4) Å in Cp*Mn(CO)₂(CN—C₆F₅) (Lentz, Graske & Preugschat, 1988) is found to be 0.019 Å longer than in free isocyanide. The pentafluorophenyl isocyanide molecules are packed so that the F1 atom is located above the centre of the aromatic ring of another

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å² × 10²)

$$B_{\text{eq}} = (1/3)\sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	B_{eq}
C1	0.0000	0.1004 (2)	0.5710 (1)	1.45
C2	0.1573 (2)	0.0400 (1)	0.5918 (1)	1.40
C3	0.1568 (2)	-0.0803 (1)	0.6342 (1)	1.27
C4	0.0000	-0.1413 (2)	0.6562 (1)	1.14
C5	0.0000	-0.3575 (2)	0.7375 (1)	2.44
F1	0.0000	0.2149 (1)	0.5295 (1)	2.28
F2	0.3079 (1)	0.0979 (1)	0.5703 (1)	2.23
F3	0.3080 (1)	-0.1376 (1)	0.6549 (1)	2.05
N	0.0000	-0.2595 (2)	0.6999 (1)	1.58

Table 2. Bond lengths (Å), selected intermolecular distances (Å) and bond angles (°)

F1—C1	1.328 (2)	C2—C3	1.381 (2)
F2—C2	1.331 (1)	C3—C4	1.386 (1)
F3—C3	1.328 (1)	C4—N	1.380 (2)
C1—C2	1.381 (1)	C5—N	1.159 (3)
C1...C1'	3.251	C1...F1'	3.512
C1...C5''	3.584	C2...F1'	3.507
C2...C5''	3.528	C3...F1'	3.509
C3...C5''	3.395	C4...F1'	3.523
C4...C5''	3.327	F1...F2''	2.949
C2—C1—C2''	120.2 (2)	C2—C3—F3	119.8 (1)
C2—C1—F1	119.9 (1)	C4—C3—F3	119.5 (1)
C1—C2—C3	119.7 (1)	C3—C4—C3''	118.9 (1)
C1—C2—F2	119.5 (1)	C3—C4—N	120.5 (1)
C3—C2—F2	120.7 (1)	C4—N—C5	179.0 (2)
C2—C3—C4	120.7 (1)		

Symmetry code: (i) $-x, -y, -z$; (ii) $x, 0.5 + y, 0.5 - z$; (iii) $0.5 - x, 0.5 - y, -z$; (iv) $-x, y, z$.

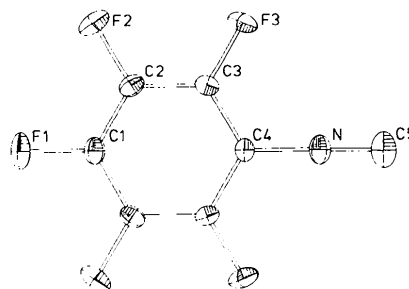


Fig. 1. Molecular structure and crystallographic numbering scheme adopted (ORTEP; Johnson, 1971).

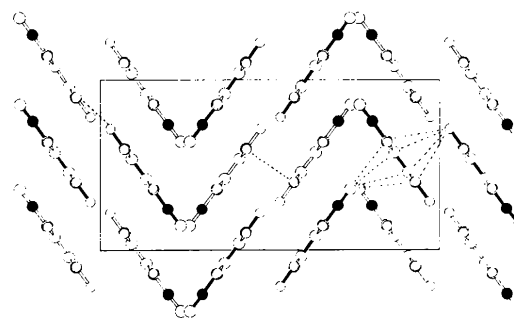


Fig. 2. Packing diagram (SCHAKAL; Keller, 1988). Projection along the a axis. Molecules around $x = 0$ are symbolized by filled bonds, molecules around $x = 0.5$ by open bonds. N atoms are symbolized by filled circles.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55526 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1000]

molecule, thus it has very similar non-bonding distances to the aromatic C1–C4 atoms. As a consequence, C1...C1 is the shortest intermolecular distance (3.251 Å). The isocyanide C5 atom of another molecule points toward the free side of the aromatic ring and has its shortest contact to C4. This kind of packing differs from that of 4-C₆H₄Br—NC, 4-C₆H₄I—NC and 2,4,6-C₆H₂Br₃—NC which have shortest intermolecular distances of 3.25, 3.22 and 3.18 Å, respectively, between the isocyanide C atom and the halogen atom. The shortest intermolecular distance is found between the F1 and F2 atoms.

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Structures of Two Diastereomers of 1-(α -Hydroxy-*m*-methoxybenzyl)-1-(phenylsulfinyl)cyclopropane

BY PONGCHAN THINAPONG† AND MANAT POHMAKOTR

Department of Chemistry, Mahidol University, Bangkok 10400, Thailand

AND BRIAN SKELTON AND ALLAN H. WHITE

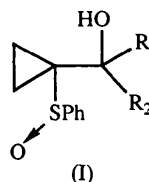
School of Chemistry, University of Western Australia, Nedlands, WA 6009, Australia

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Abstract. C₁₇H₁₈O₃S, *S***R** diastereomer, *M*_r = 302.4, orthorhombic, *Pbca*, *a* = 23.073 (1), *b* = 17.340 (3), *c* = 7.299 (1) Å, *V* = 2920 Å³, *Z* = 8, *D*_x = 1.375 g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $\mu = 1.8 \text{ cm}^{-1}$, *F*(000) = 1280, *T* = 295 K, *R* = 0.039 for 1149 observed [*I* ≥ 3 σ (*I*)] reflections. *R***R** diastereomer, triclinic, *P* $\bar{1}$, *a* = 9.873 (9), *b* = 10.009 (5), *c* = 11.024 (7) Å, $\alpha = 56.67$ (3), $\beta = 55.68$ (5), $\gamma = 69.65$ (5)°, *V* = 750 Å³, *Z* = 2, *D*_x = 1.34 g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $\mu = 1.8 \text{ cm}^{-1}$, *F*(000) = 320, *T* = 295 K, *R* = 0.041 for 1231 observed [*I* ≥ 3 σ (*I*)] reflections. Structure determinations of the two title

compounds enable assignment of relative stereochemistries at the chiral centres, inaccessible by other chemical means.

Introduction. Compounds of formula (I) have been shown to be versatile intermediates for the preparation of cyclobutanone derivatives (Hiroi, Nakamura & Anzai, 1987). Recently, compounds of this type



† Author to whom correspondence should be addressed.