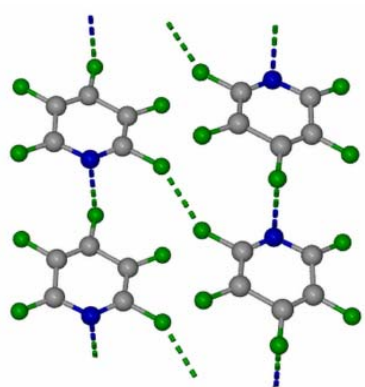


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SYNOPSIS



Subjecting pentafluoropyridine to high pressures inside a DAC (diamond anvil cell) results in the formation of molecular crystals with $F\cdots F$ and $N\cdots F$ contacts commensurate with sums of van der Waals radii of these atoms; the strongest of these interactions arrange the molecules into interpenetrating hexamers and double ribbons.

Intermolecular interactions in crystalline pentafluoropyridine under high pressure: Structure and compressibility at 0.3 and 1.1 GPa (PREPRINT)

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Abstract

Pentafluoropyridine has been *in-situ* pressure crystallized in a diamond-anvil cell (DAC) and its structure determined at 0.30(5) GPa and 1.10(5) GPa and at room temperature by single-crystal X-ray diffraction. The freezing pressure of pentafluoropyridine has been determined to be 0.10(5) GPa. The crystals are monoclinic, space group $P2_1/c$. The crystal packing is governed by F...F and C/N...F van der Waals contacts, but no ring stacking is observed. The intermolecular interactions are non-directional, and the crystal compresses nearly isotropically between 0.3 and 1.1 GPa.

Keywords: halogen...nitrogen interactions; pentafluoropyridine; high-pressure crystallization;

1. Introduction

Substitution of hydrogen with fluorine atoms in organic compounds drastically change their physical and chemical properties and the fluorine-containing compounds find wide applications in technology, agriculture and medicine. The fluorinated-pyridine derivatives are used as liquid crystals, herbicides and antibiotics [1]. Pentafluoropyridine (PFP) is an important substrate, because fluorine atoms are prone to nucleophilic substitution [2-4]. The structural studies of pentafluoropyridine were carried out only for co-crystals with other compounds, obtained when pentafluoropyridine was used as a solvent. The methyl-pentafluoropyridyl-tetramethylethylenediamine-platinum(II) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate [5], pentafluoropyridine-coordinated complex cis-tetracarbonyl-perfluoropyridinyl-tri-isopropylphosphine-rhenium tetrakis(3,5-bis(trifluoromethyl)phenyl)-borate [6] and bis(μ -2-hydroxo)-bis(1,2-

bis(dicyclohexylphosphino)ethane-P,P')-diplatinum(II) bis(tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) pentafluoropyridine solvate [7] were investigated. A survey of CSD reveals that no crystal structure is known for pure pentafluoropyridine. In the co-crystal structure of bis(μ 2-hydroxo)-bis(1,2-bis(dicyclohexylphosphino)ethane-P,P')-diplatinum(II) bis(tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) pentafluoropyridine [7] the pentafluoropyridine rings π -stack with the phenyl rings of bis(trifluoromethyl)phenyl)borate anion. Halogen atoms can form various types of intermolecular interactions, either with other halogen atoms or with other electronegative functional groups [8,9]. In haloperfluorocarbons $[X(CF_2)_nX]$; $X = \text{Br}$ or I], the bromine or iodine atoms acquire a partial positive charge and they favorably form short interactions with electron rich nitrogen or oxygen containing Lewis bases. In the crystal structures of 1,2-dibromo-, 1,2-diiodo-, 1-bromo-2-iodoperfluoroethanes, pure, and in co-crystals with 1,4-dioxane, we have observed short halogen $\cdots$ halogen and halogen $\cdots$ oxygen contacts [10,11].

This study on pressure-crystallized pentafluoropyridine was aimed at investigating the preferences of the nitrogen and fluorine atoms to form intermolecular contacts and molecular π -stacking association in the pure substance. We also intended to perform a similar study for pyridine:pentafluoropyridine mixture [12].

2. Results and discussion

Pentafluoropyridine (perfluoropyridine, C_5F_5N) crystallizes at 231.65 K [13] but no low temperature structural studies of this compound were reported. In our study the high-pressure technique has been applied for crystallizing perfluoropyridine and its structure determining at 0.3 GPa and 1.1 GPa. The crystal data and experimental details are listed in Table 1. Structural drawings were prepared using the X-Seed interface of POV-Ray [14,15].

Table 1. Crystal data and details of structure refinement for pentafluoropyridine.

Pressure (GPa)	0.30(5)	1.10(5)
Chemical formula	C_5F_5N	C_5F_5N
Temperature (K)	296(2)	296(2)
Formula weight	169.06	169.06
Radiation type	Mo $K\alpha$	Mo $K\alpha$
Wavelength ($\text{\AA}$)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions ($\text{\AA}$)	a 7.4390(15)	7.1269(15)

	<i>b</i> 5.1794(10)	5.0633(10)
	<i>c</i> 14.821(3)	14.527(3)
	β 103.41(3)	103.86(3)
Volume (Å ³)	555.48(19)	508.95(18)
<i>Z</i>	4	4
Calculated density (g/cm ³)	2.022	2.206
Crystal diameter and height (mm)	0.48 and 0.2	0.43 and 0.15
Absorption coefficient (mm ⁻¹)	0.241	0.263
<i>F</i> (000)	328	328
θ -range for data collection (°)	2.81 to 28.67	2.89 to 28.37
Limiting indices	$-9 \leq h \leq 9,$ $-5 \leq k \leq 6,$ $-11 \leq l \leq 11$	$-4 \leq h \leq 4,$ $-6 \leq k \leq 6,$ $-17 \leq l \leq 17$
Reflect. Collected/ unique (<i>R</i> _{int})	2247 / 374 (0.0735)	1991 / 324 (0.2819)
Completeness (to $\theta_{\max}$) (%)	26.2 (to 28.67)	25.3 (to 27.49)
Data/restraints/parameters	374 / 0 / 101	324 / 0 / 101
Goodness-of-fit on <i>F</i> ²	1.377	1.129
Final <i>R</i> ₁ / <i>wR</i> ₂ (<i>I</i> > 2 σ ₁)	0.0975 / 0.2877	0.1059 / 0.3026
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.1193 / 0.3260	0.1360 / 0.3026
Weighting scheme	$1/[\sigma^2(Fo^2)+(0.2000*P)^2+0.00*P],$ where $P=(\text{Max}(Fo^2,0)+2*Fc^2)/3$	
	$1/[\sigma^2(Fo^2)+(0.2000*P)^2+0.00*P],$ where $P=(\text{Max}(Fo^2,0)+2*Fc^2)/3$	
Largest diff. peak and hole (e.Å ⁻³)	0.214 and -0.202	0.258 and -0.227

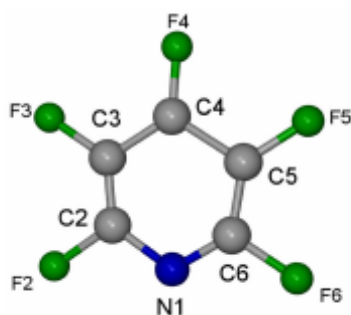


Fig. 1 The molecule of pentafluoropyridine at 0.3 GPa and 296 K.

Crystals of perfluoropyridine at 0.3 GPa/296 K and 1.1 GPa/296K crystallized in a monoclinic space group $P2_1/c$, with one symmetry-independent molecule. The shortest intermolecular interactions involve the fluorine atoms, so the structures of perfluoropyridine is mainly governed by $F\cdots F$ and $N\cdots F$ interactions. The $N\cdots F$ and the shortest $F\cdots F$ contacts link the molecules into motifs of interpenetrating hexamers and double ribbons (Fig. 2). The shortest of $F\cdots F$ contact at 0.3 GPa/296 K of 2.85(2) Å, which is slightly shorter than the sum of van der Waals radii for the F-atoms (2.94 Å) according to Bondi [16], is formed across a center of inversion, and the angle $C-F\cdots F$ is 166.5(15)°. Thus the $F\cdots F$ interactions between the perfluoropyridine molecules are very weak. At 1.1 GPa/296 K the closest $F\cdots F$ contact is 2.61(2)Å, which is considerably less than the sum of van der Waals radii (Fig. 2); the $C-F\cdots F$ angle becomes 149.1(9)°. These shortest $F\cdots F$ contacts assemble molecules into pairs, whereas together with the next shortest interactions of $F(3)\cdots F(5)$, hexamers are formed which interpenetrate mimicking links of a chain extending along crystal direction [011] as shown in Fig. 2a. The molecules interacting via $F(4)\cdots N(1)$ contacts form 1-dimentional step-like aggregates along [010] (Figure 2b), and the $N\cdots F$ distance is 3.07(2) Å at 0.3 GPa; and 2.85(2) Å at 1.1 GPa. In principle, halogen atoms (Lewis acids, electron acceptor) can interact with atoms possessing lone electron pairs (Lewis bases, electron donor) [8,9]. The intermolecular $N\cdots F$ contacts in perfluoropyridine can be classified in this way.

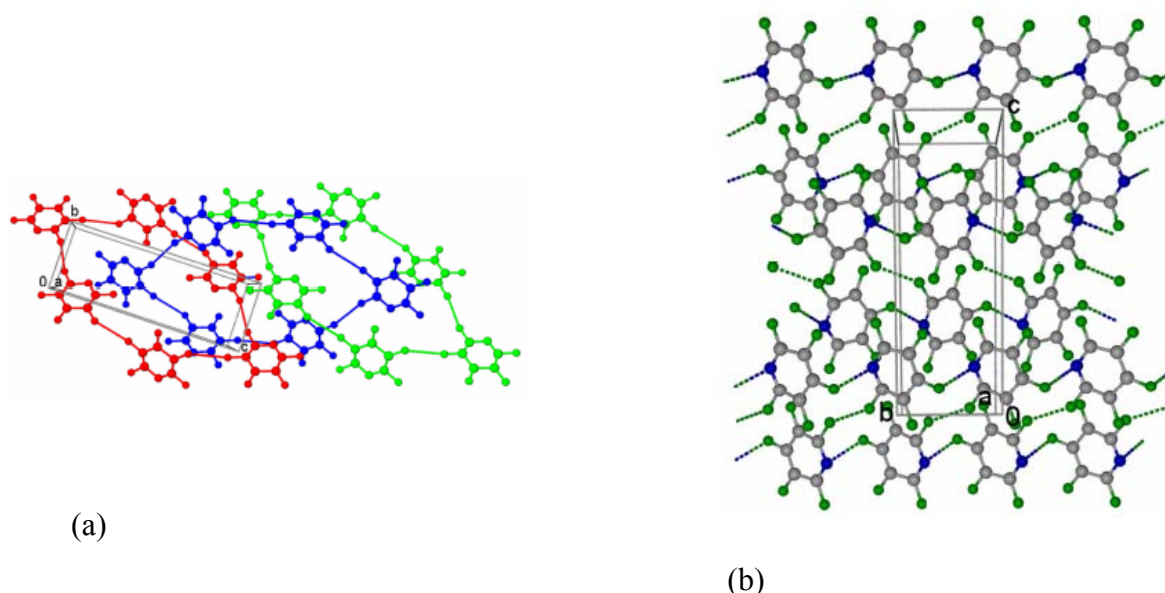


Fig. 2 The interpenetrating hexamers (in different colors for clarity) of molecules forming $F\cdots F$ contacts (a); and chains along [001] of $F\cdots N$ interactions, joined by $F\cdots F$ contacts (b).

The intermolecular contacts of perfluoropyridine molecules have been illustrated on the Hirshfeld surface [17,18] in Figure 3. It can be observed that the pattern of molecular arrangements remain unchanged between 0.3 GPa and 1.1 GPa, and only the intermolecular contacts, all involving the F atoms, become squeezed. The N $\cdots$ F contact is inclined to the molecular plane by nearly 90°, and the C-F $\cdots$ N angle is close to 90° too. Thus, the direction of the N $\cdots$ F contacts indicates that the lone electron pair of N-atom is not essential for this interaction.

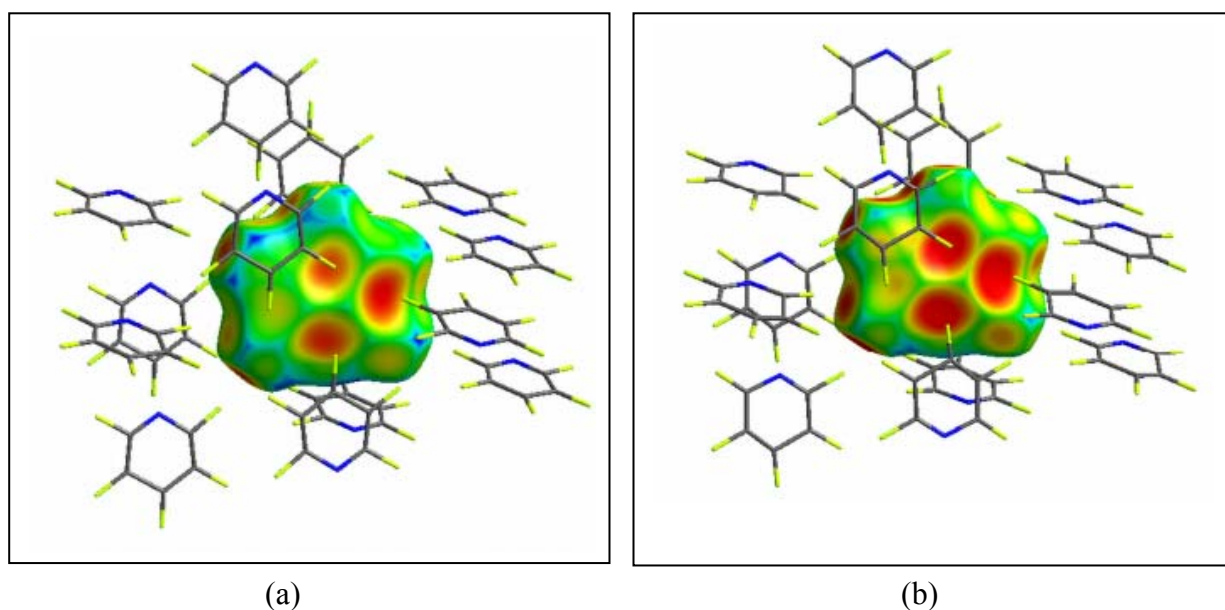


Fig.3 Intermolecular interactions of pentafluoropyridine at 0.30 GPa (a) and at 1.10 GPa (b) at room temperature represented by a color scale on the Hirshfeld surface [17,18]. The property mapped onto the surface is the distance from its element to the nearest exterior and it ranges from 1.40 Å (red) to 2.25 Å (blue).

The shortest N $\cdots$ F and F $\cdots$ F distances are squeezed on average by 0.2 Å with increasing pressure. The unit-cell *a* parameter is the most compressible and it compresses twice more than *b* and *c* parameters, which compress in a similar rate. This is consistent with the absence of strong directional interactions in pentafluoropyridine structure along [100] direction. It can be also observed, that in 1.1 GPa differences between the shortest and second shortest contacts considerably increased compared to the structure at 0.3 GPa.

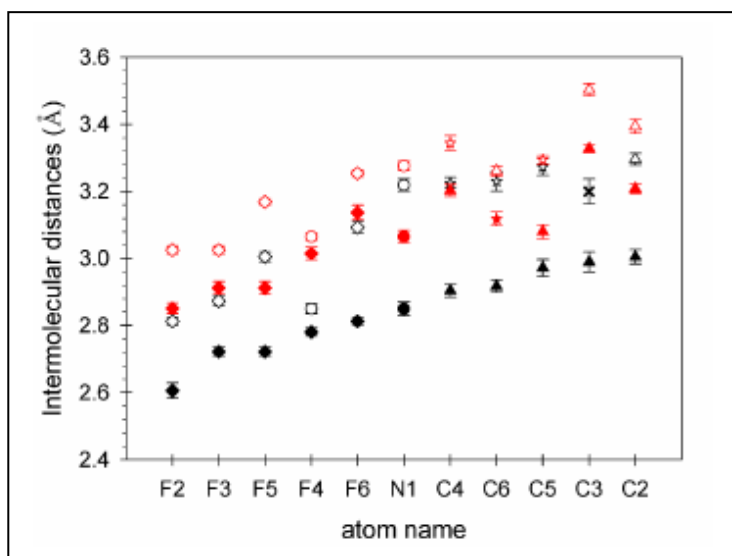


Fig. 4 Two shortest intermolecular contacts of all atoms at 0.3 GPa/296 K (red symbols, filled for the shortest contact and empty for the next) and at 1.1 GPa/296 K (black). N...F contacts have been marked with circles, F...F with diamonds, C...F with triangles, C...N with stars and C...C with cross.

3. Conclusions

The crystal structure of perfluoropyridine revealed only weak intermolecular interactions and contacts commensurate with the sums of atomic van der Waals radii. The isotropic compression of F...F and N...F contacts suggests that directional forces markedly stronger than others are formed to 1.1 GPa.

4. Experimental

4.1 General experimental procedures

Experiments were carried out using a miniature diamond-anvil cell (DAC) [19]. The pressure inside the DAC was calibrated by the ruby-fluorescence method [20,21] and a Betsa PRL spectrometer, with an accuracy of 0.05 GPa. The single-crystal X-ray diffraction studies have been carried out with a KUMA KM4-CCD diffractometer.

4.2 Crystallization of pentafluoropyridine

Pentafluoropyridine was loaded in a diamond anvil cell [19]. The pressure in the DAC was increased to 0.1 GPa when the liquid crystallized and liquid and crystals coexisted in the chamber. Then the chamber was squeezed until the polycrystalline sample filled all the chamber volume. Following this, the DAC was heated until all crystals melted, except one, which was allowed to grow slowly when the DAC was cooled to 296 K. Because of the instability of the crystal at the melting pressure, the pressure was increased to 0.3 GPa, the DAC was heated and cooled slowly again to allow the single crystal to fill the chamber. After the diffraction measurement, the DAC chamber was heated and when one small grain was left at 433 K, the pressure was increased, and the entire procedure was repeated – at 296 K the pressure inside the cell was 1.1 GPa (Figure 5).

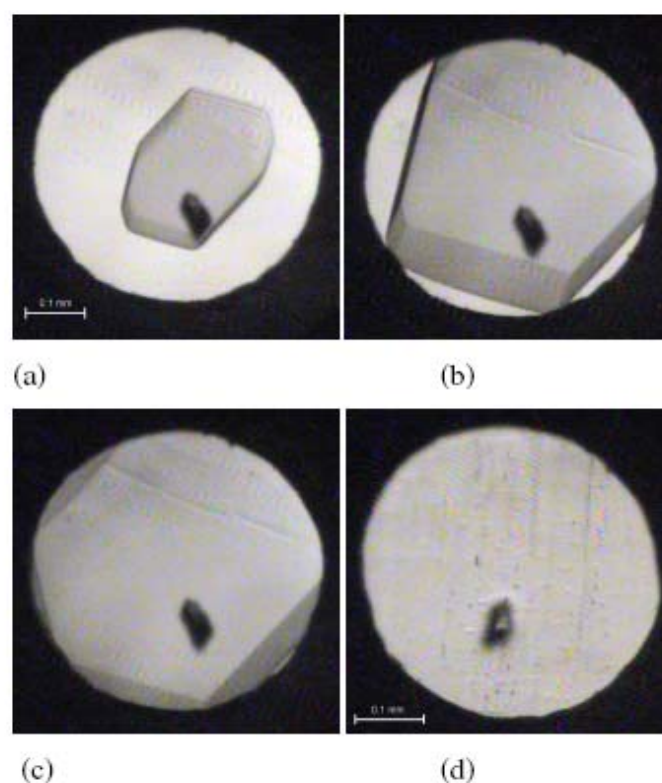


Fig. 5. The growth stages of a single-crystal of perfluoropyridine at 1.1 GPa: (a) a single crystal seed at 433 K; (b) at 413 K (b); (c) at 403 K; and (d) the final form of the crystal at 1.1 GPa and 296 K. Newton fringes are visible on the upper edge of the seed in photograph (a). The vertical cracks in the crystal in photograph (d) are due to strains of the anisotropic sample cooled in the rigid chamber. The ruby chip for pressure calibration is visible below the chamber center.

4.3 Crystal structure determinations

The X-ray diffraction data collections for perfluoropyridine single crystals were carried out with the exposures of 30 s and the 0.8 ° ω -scan frames [22]. The CrysAlis version 1.171.24 [23] was used for the data collections and preliminary data reduction. After the intensities were corrected for the effects of DAC absorption and sample shadowing by the gasket [24,25], the diamond reflections have been eliminated. The systematic absences unequivocally showed that the crystal is monoclinic in space group $P2_1/c$. All structures were solved straightforwardly by direct methods [26], and refined by full-matrix least-squares on F^2 [27] with anisotropic temperature factors for all atoms. The details of the experiments, refinements and crystal structures have been deposited in the form of CIF files CCDC..... and CCDC.... in the Cambridge Structural Database.

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