

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 25-05-2007		2. REPORT TYPE Journal Article		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Interpenetrated structure and compressibility studies in pressure frozen pentafluoropyridine crystals at 0.3 and 1.1 GPa (Postprint)				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Anna Olejniczak & Andrzej Katrusiak (Adam Mickiewicz University, Poland); Ashwani Vij (AFRL/RZSP)				5d. PROJECT NUMBER	
				5e. TASK NUMBER 23030423	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RZSP 10 E. Saturn Blvd. Edwards AFB CA 93524-7680				8. PERFORMING ORGANIZATION REPORT NUMBER AFRL-PR-ED-JA-2007-290	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RZS 5 Pollux Drive Edwards AFB CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S NUMBER(S) AFRL-PR-ED-JA-2007-290	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited (PA #07268A).					
13. SUPPLEMENTARY NOTES Published in the Journal of Fluorine Chemistry 129 (2008) 173-177, ©2007 Elsevier B.V. All rights reserved.					
14. 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 P21/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.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 6	19a. NAME OF RESPONSIBLE PERSON Dr. Ashwani Vij
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code) N/A

Interpenetrated structure and compressibility studies in pressure frozen pentafluoropyridine crystals at 0.3 and 1.1 GPa

Anna Olejniczak^a, Andrzej Katrusiak^{a,*}, Ashwani Vij^{b,**}

^a Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland

^b Air Force Research Laboratory/RZSP, 10 E. Saturn Boulevard, Building 8451, Edwards AFB, CA 93524, USA

Received 28 September 2007; received in revised form 18 October 2007; accepted 21 October 2007

Abstract

Pentafluoropyridine has been pressure frozen *in situ* in a diamond-anvil cell (DAC) and its structure determined at 0.30(5) 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.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Halogen...nitrogen interactions; Pentafluoropyridine; High-pressure crystallization; Interpenetrated structures

1. Introduction

Substitution of hydrogen with fluorine atoms in organic compounds drastically changes their physical and chemical properties and the fluorine-containing compounds find wide applications in technology, agriculture and medicine. 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 methylpentafluoropyridyltetramethylethylenediamineplatinum(II) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate [5], pentafluoropyridine coordinated complex *cis*-tetracarbonylperfluoropyridinyltriisopropylphosphinerhenium 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 Cambridge Structural Database reveals that no crystal structure is known for pure pentafluoropyridine. In the co-crystal structure of the 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 the bis(trifluoromethyl)phenylborate 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 $[X(CF_2)_nX]$; $X = Br$ 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.

This study on pressure frozen 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 [10]. By applying high-pressure we aim to obtain quantitative information about intermolecular interactions in this compound. In principle, high-pressure can be transformed into forces squeezing the contacts between molecules, and thus the relation between the applied pressure and changes in intermolecular contacts can be used for deriving the force constants of the cohesion forces. However, such an analysis can

* Corresponding authors. Tel.: +48 61 8291443; fax: +48 61 8291505.

** Corresponding authors. Tel.: +1 661 2756278; fax: +1 661 2755471.

E-mail addresses: katran@amu.edu.pl (A. Katrusiak),
ashwani.vij@edwards.af.mil (A. Vij).

be conveniently performed only for simple structures, for which directions and components of the forces generated by pressure can be easily determined.

2. Results and discussion

Pentafluoropyridine (perfluoropyridine, C_5F_5N) crystallizes at 231.65 K [11] but no low-temperature structural studies of this compound have been reported. In our study the high-pressure technique has been applied for crystallizing perfluoropyridine and its structure determining at 0.3 and 1.1 GPa. The crystal data and experimental details are listed in Table 1.

Crystals of perfluoropyridine at 0.3 GPa/296 K and 1.1 GPa/296 K crystallized in a monoclinic space group $P2_1/c$, with one symmetry-independent molecule (Fig. 1). The shortest intermolecular interactions involve the fluorine atoms, so the structures of perfluoropyridine are governed mainly by $F \cdots F$ and $N \cdots F$ close-packing contacts. These $N \cdots F$ 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 [12], is formed across a center of inversion, and the angle $C-F \cdots F$ is 166.5(15)°. Thus, the $F \cdots F$ contacts 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);

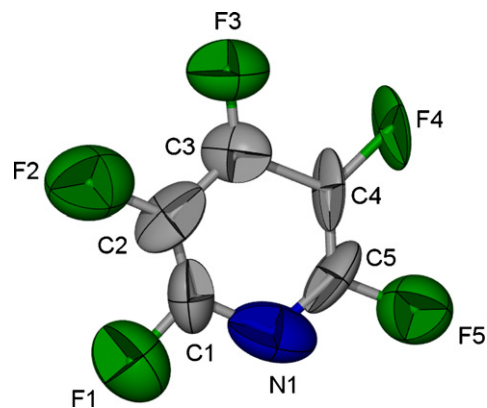


Fig. 1. ORTEP representation of pentafluoropyridine at 0.3 GPa and 296 K, with displacement ellipsoids at 30% probability.

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 $[0\ 1\ 1]$ as shown in Fig. 2a. Interestingly, the hexamer formation is engineered by interaction of ortho-fluorine atoms of one molecule with para-fluorine atoms of the neighboring molecule, which in turn employs the meta-fluorine atoms to complete the hexamer structure (following the molecules in a counter-clockwise manner). The molecules interacting via $F(4) \cdots N(1)$ contacts

Table 1
Crystal data and details of structure refinement for pentafluoropyridine at 0.3 and 1.1 GPa

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 (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions (Å)		
	a 7.4390(15)	7.1269(15)
	b 5.1794(10)	5.0633(10)
	c 14.821(3)	14.527(3)
	β 103.41(3)	103.86(3)
Volume (Å ³)	555.48(19)	508.95(18)
Z	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
$F(0\ 0\ 0)$	328	328
θ -range for data collection (°)	2.81–28.67	2.89–28.37
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 (R_{int})	2247/374 (0.0735)	1991/324 (0.2819)
Completeness (to θ_{max}) (%)	26.2 (to 28.67)	25.3 (to 27.49)
Data/restraints/parameters	374/0/101	324/0/101
Goodness-of-fit on F^2	1.377	1.129
Final R_1/wR_2 ($I > 2\sigma_1$)	0.0975/0.2877	0.1059/0.3026
R_1/wR_2 (all data)	0.1193/0.3260	0.1360/0.3026
Weighting scheme	$1/[\sigma^2(F_o^2) + (0.2000*P)^2 + 0.00*P]$, where $P = (\text{Max}(F_o^2, 0) + 2*F_c^2)/3$	$1/[\sigma^2(F_o^2) + (0.2000*P)^2 + 0.00*P]$, where $P = (\text{Max}(F_o^2, 0) + 2*F_c^2)/3$
Largest diff. peak and hole (e.Å ⁻³)	0.214 and -0.202	0.258 and -0.227

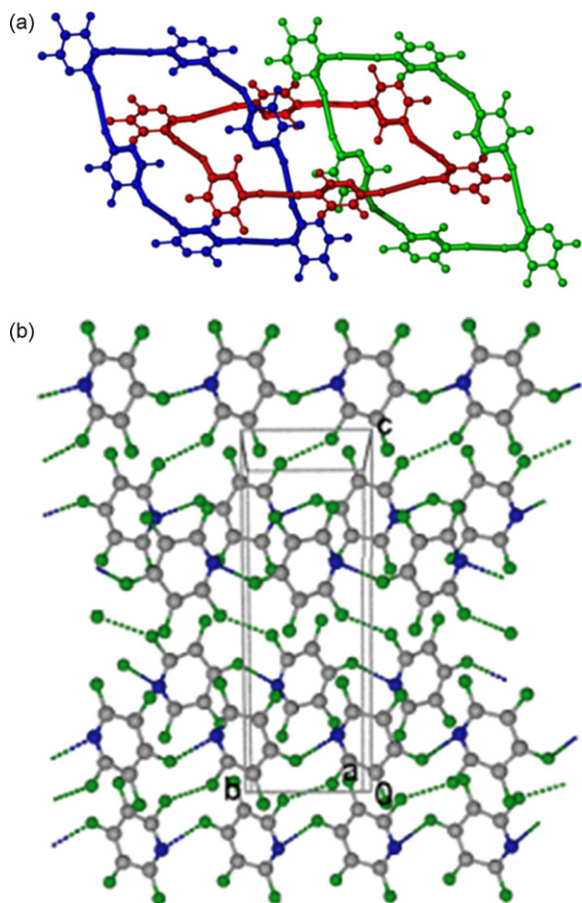


Fig. 2. The interpenetrating hexamers (in different colors for clarity) of molecules forming F...F contacts (a) and chains along [001] of F...N interactions, joined by F...F contacts (b).

form one-dimensional step-like aggregates along [010] (Fig. 2b), and the N...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...F contacts in perfluoropyridine can be classified in this way.

The intermolecular contacts of perfluoropyridine molecules have been illustrated on the Hirschfeld surface [13,14] in Fig. 3. The pattern of molecular arrangements remains unchanged between 0.3 and 1.1 GPa, and only the intermolecular contacts, all involving the F atoms, become squeezed. The N...F contact is inclined to the molecular plane by nearly 90°, and the C–F...N angle is close to 90°. Thus, the direction of the N...F contacts indicates that the lone electron pair of N is not essential for this interaction.

The shortest N...F and F...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

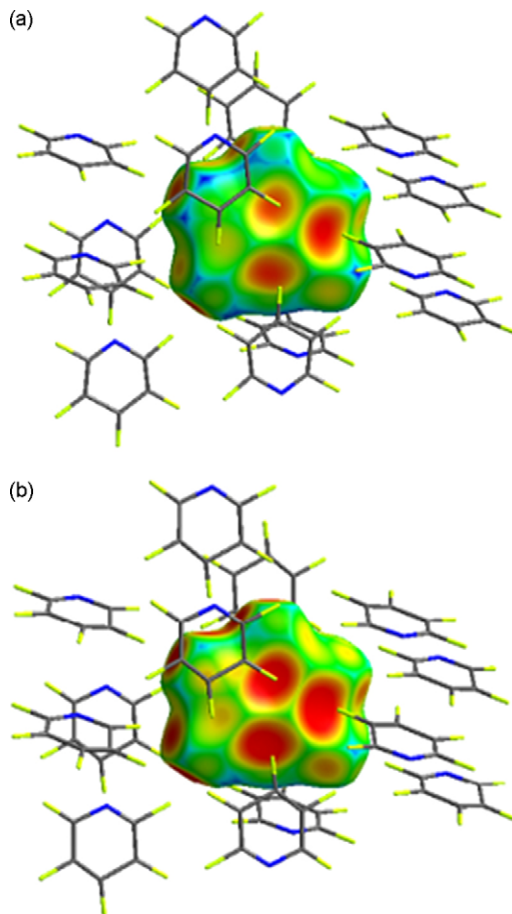


Fig. 3. Intermolecular interactions of pentafluoropyridine at 0.30 GPa (a) and at 1.10 GPa (b) at room temperature represented by a color scale on the Hirschfeld surface [13,14]. The property mapped onto the surface is the distance from its element to the nearest exterior and it ranges from 1.40 Å (red) to 2.25 Å (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

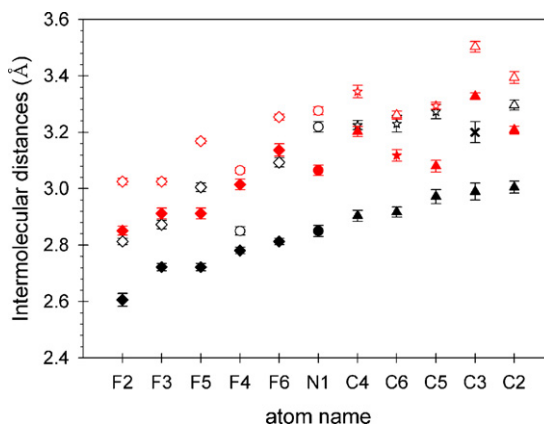


Fig. 4. Two shortest intermolecular contacts of all atoms at 0.3 GPa/296 K (gray symbols, filled for the shortest contact and empty for the next; the color version of the plot is available online) and at 1.1 GPa/296 K (black). N...F contacts have been marked with circles, F...F with diamonds, C...F with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

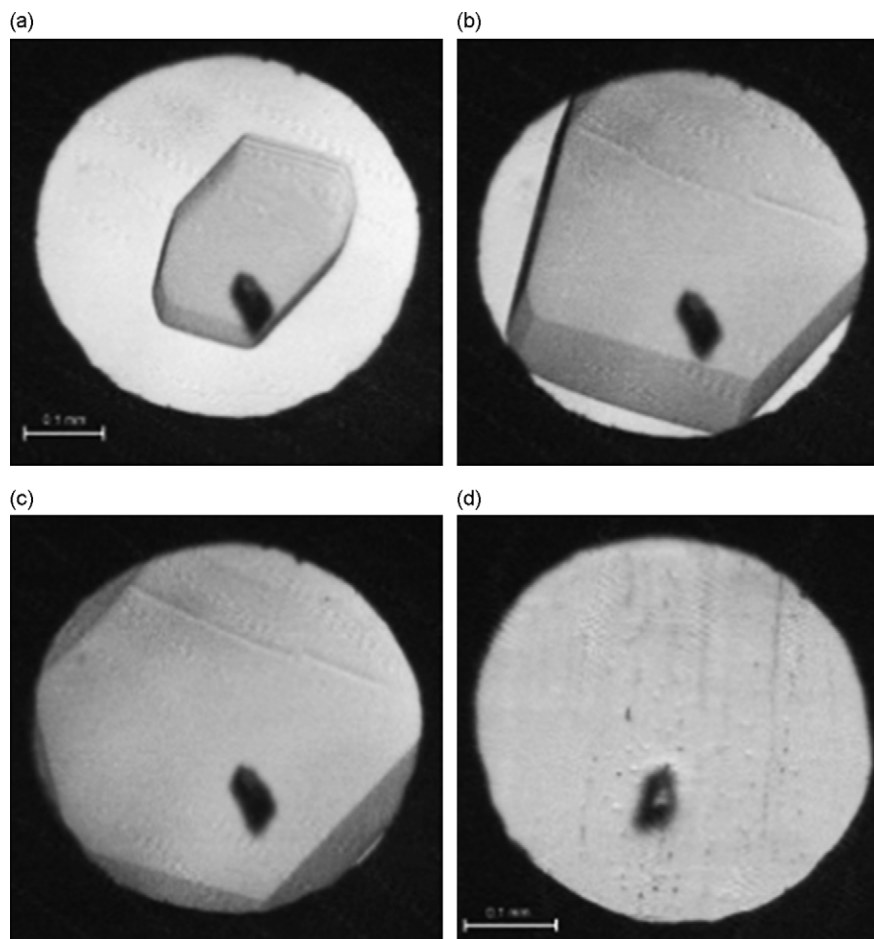


Fig. 5. The growth stages of a single-crystal of perfluoropyridine at 1.1 GPa: (a) a single crystal seed at 433 K; (b) at 413 K; (c) at 403 K and (d) the final form of the crystal at 1.1 GPa and 296 K. Newton fringes are visible on the upper edge of the seed in photograph (a). The vertical cracks in 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.

contacts considerably increased compared to the structure at 0.3 GPa (Fig. 4).

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

Pentafluoropyridine, 99% purity from Sigma–Aldrich, was used without further purification.

Experiments were carried out using a miniature diamond-anvil cell (DAC) [15]. The pressure inside the DAC was calibrated by the ruby-fluorescence method [16,17] 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 [15]. 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 (Fig. 5).

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 [18]. The CrysAlis version 1.171.24 [19] 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 [20,21], 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 [22], refined by full-matrix least squares on F^2 [23] with anisotropic temperature factors for all atoms, and structural drawings were prepared using the X-Seed interface of POV-ray [24,25].

The single crystal of pentafluoropyridine obtained at 1.1 GPa was strongly strained, which resulted in broadened reflection profiles and a higher high R_{int} value (Table 1). This sample strain was generated in the process of crystallization, when except for one seed the substance was melted and then slowly cooled down. So obtained single crystal fully filled the high-pressure chamber at ~ 400 K. The further cooling of this highly anisotropic single crystal in the practically undeformable pressure chamber led to the strains in the sample. We tried to improve the quality of the crystal by annealing it at 370 K, however, all strains could not be eliminated due to subsequent cooling process of the sample. The details of the experiments, refinements and crystal structures have been deposited in the form of CIF files CCDC 655825 and 655826 in the Cambridge Structural Database.

Acknowledgments

This study was supported by the European Office of Aerospace Research and Development, Grant no. FA8655-06-1-3039. Dr. A. Vij gratefully acknowledges AFOSR for a Window on Europe (WOE) grant and thanks Drs. Alan Garscadden, Robert Corley, Ronald Channell and Mr. Michael Huggins of AFRL/PR for their support. The authors also wish to thank Col. Matthew Morgan of EOARD for his generous and enthusiastic support of the AMU-AFRL joint High-Pressure Crystallography project.

References

- [1] R.E. Banks, B.E. Smart, J.C. Tatlow (Eds.), *Organofluorine Chemistry. Principles and Commercial Applications*, Plenum Press, New York, 1994.
- [2] M.S. Toy, R.S. Stringham, *Am. Chem. Soc. Div. Polym. Chem. Prepr.* 20 (1979) 866–869.
- [3] R.D. Chambers, P.R. Hoskin, G. Sandford, D.S. Yufit, J.A.K. Howard, *J. Chem. Soc. Perkin. Trans. 1* (2001) 2788–2795.
- [4] C.B. Murray, G. Sandford, S.R. Korn, D.S. Yufit, J.A.K. Howard, *J. Fluorine Chem.* 126 (2005) 571–576.
- [5] M.W. Holtcamp, L.M. Henling, M.W. Day, J.A. Labinger, J.E. Bercaw, *Inorg. Chim. Act.* 270 (1998) 467–478.
- [6] J. Huhmann-Vincent, B.L. Scott, G.J. Kubas, *Inorg. Chem.* 38 (1999) 115–124.
- [7] W.V. Konze, B.L. Scott, G.J. Kubas, *J. Am. Chem. Soc.* 124 (2002) 12550–12556.
- [8] P. Metrangolo, G. Resnati, *Chem. Eur. J.* 7 (2001) 2511–2519.
- [9] P. Metrangolo, H. Neukirch, T. Pilati, G. Resnati, *Acc. Chem. Res.* 38 (2005) 386–395.
- [10] An initial experiment of mixing pyridine and pentafluoropyridine resulted in the formation of a black amorphous mass, which did not show any diffraction reflections.
- [11] R.E. Banks, A.E. Ginsberg, R.N. Haszeldine, *J. Chem. Soc.* (1961) 1740–1743.
- [12] A. Bondi, *J. Phys. Chem.* 70 (1966) 3006–3007.
- [13] J.J. McKinnon, M.A. Spackman, A.S. Mitchell, *Acta Cryst. B60* (2004) 627–668.
- [14] S.K. Wolff, D.J. Grimwood, J.J. McKinnon, D. Jayatilaka, M.A. Spackman, *CrystalExplorer*, Version 1.5.0, University of Western Australia, 2005.
- [15] L. Merrill, W.A. Bassett, *Rev. Sci. Instrum.* 45 (1974) 290–294.
- [16] G.J. Piermarini, A.D. Mighell, C.E. Weir, S. Block, *Science* 165 (1969) 1250–1255.
- [17] H.K. Mao, J. Xu, P.M. Bell, *J. Geophys. Res.* 91 (1985) 4673–4676.
- [18] A. Budzianowski, A. Katrusiak, in: A. Katrusiak, P.F. McMillan (Eds.), *High-Pressure Crystallography*, Kluwer Academic Publisher, Dordrecht, 2004, pp. 157–168.
- [19] Oxford Diffraction Limited, *User Manual Xcalibur series Single Crystal Diffractometers*, Version 1.3. Wrocław: Oxford Diffraction Poland, 2002.
- [20] A. Katrusiak, REDSHAD. Program for the correcting reflections intensities for DAC absorption, gasket shadowing and sample crystal absorption, Adam Mickiewicz University, Poznań, 2003.
- [21] A. Katrusiak, *Z. Kristallogr.* 219 (2004) 461–467.
- [22] G.M. Sheldrick, *Acta Cryst. A46* (1990) 467–473.
- [23] G.M. Sheldrick, *The SHELX-97 manual*, University of Göttingen, Germany, 1997.
- [24] L.J. Barbour, *J. Supramol. Chem.* 1 (2001) 189–191.
- [25] Persistence of Vision Pty. Ltd. Persistence of Vision (TM) Raytracer, Version 2.6. Williamstown, Victoria, Australia, 2004.