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14. ABSTRACT

A group of isostructural crystals has been identified for a series of 1,2-dihalotetrafluoroethanes X(CF2)2Y (X = Br, I; Y = Br, I). 1,2-Dibromotetrafluoroethane (BrCF2CF2Br), 1,2-diiodotetrafluoroethane (ICF2CF2I) and 1-bromo-2-iodotetrafluoroethane (BrCF2CF2I), have been in-situ pressure crystallized in a diamond-anvil cell and their structures determined by X-ray diffraction. All the crystals are monoclinic, space group P21/n, with the midpoint of the C–C bond located at the centre of inversion. The freezing pressures of these compounds have been determined to be 0.80(5) GPa, 0.30(5) GPa and 0.10(5) GPa for BrCF2CF2Br, BrCF2CF2I and CF2ICF2I, respectively. In the structure of ICF2CF2I, the –CF2–CF2– moiety is orientationally disordered about the intramolecular I···I axis at 0.16(5) GPa, but it becomes ordered at 0.86(5) GPa. The BrCF2CF2I crystal structure is disordered in a different way: the –CF2–CF2– is ordered but the Br and I atoms are substitutionally disordered with equal occupancies. The CF2BrCF2Br structure is completely ordered. The formation of isostructural crystals by these compounds and different types of molecular disorder can be rationalized by the intermolecular interactions at varied thermodynamical conditions. The cohesion forces in these structures are dominated by I···I, Br···Br and (Br/I)···(Br/I) contacts, but (Br/I)···F contacts are considerably shorter in BrCF2CF2I than in ICF2CF2I and BrCF2CF2Br.

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First high pressure crystallization and study of disorder modes in isostructural dihaloperfluoroethanes (Preprint)

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ABSTRACT

A group of isostructural crystals has been identified for a series of 1,2-dihalotetrafluoroethanes $X(CF_2)_2Y$ (X = Br, I; Y = Br, I). 1,2-Dibromotetrafluoroethane ($BrCF_2CF_2Br$), 1,2-diiodotetrafluoroethane (ICF_2CF_2I) and 1-bromo-2-iodotetrafluoroethane ($BrCF_2CF_2I$), have been *in-situ* pressure crystallized in a diamond-anvil cell and their structures determined by X-ray diffraction. All the crystals are monoclinic, space group $P2_1/n$, with the midpoint of the C–C bond located at the centre of inversion. The freezing pressures of these compounds have been determined to be 0.80(5) GPa, 0.30(5) GPa and 0.10(5) GPa for $BrCF_2CF_2Br$, $BrCF_2CF_2I$ and CF_2ICF_2I, respectively. In the structure of ICF_2CF_2I, the $–CF_2–CF_2–$ moiety is orientationally disordered about the intramolecular I···I axis at 0.16(5) GPa, but it becomes ordered at 0.86(5) GPa. The $BrCF_2CF_2I$ crystal structure is disordered in a different way: the $–CF_2–CF_2–$ is ordered but the Br and I atoms are substitutionally disordered with equal occupancies. The CF_2BrCF_2Br structure is completely ordered. The formation of isostructural crystals by these compounds and different types of molecular disorder can be rationalized by the intermolecular interactions at varied thermodynamical conditions. The cohesion forces in these

structures are dominated by I···I, Br···Br and (Br/I)···(Br/I) contacts, but (Br/I)···F contacts are considerably shorter in $BrCF_2CF_2I$ than in ICF_2CF_2I and $BrCF_2CF_2Br$.

INTRODUCTION

Haloperfluorocarbons find diverse applications in fields ranging from freezing technology to medicine. The pharmacological activity of two enantiomers of a racemic halothane, widely used as a highly volatile general anesthetic, is ascribed to their relative selective interactions with specific protein binding sites[1]. Although halogenated perfluorocarbons are generally considered inert, recently it has been evidenced that halogen atoms of bromo– or iodoperfluorocarbons strongly interact with nitrogen, oxygen and sulfur atoms of hydrocarbon Lewis bases[2-7]. Structures of complexes, containing ICF_2CF_2I, $BrCF_2CF_2Br$ or $BrCF_2CF_2Br$ moieties, have been determined[2-6], revealing a disordering of the ethane moieties and Br/I atoms. Meanwhile, the structures of the principal components, ICF_2CF_2I and $BrCF_2CF_2I$, have not been investigated. The only example of a structurally characterized HFC (halofluorocarbon) is $BrCF_2CF_2Br$ where a low-temperature neutron powder diffraction data have been investigated[8]. In principle, the structures of 1,2-dihaloperfluoroethanes should be governed by analogous halogen···halogen interactions, and we intended to investigate the types of molecular association, stability of the structures and compressibility of the intermolecular contacts in this series of prototypical compounds. It was hoped, that by applying high-pressure techniques new phases of these compounds could be obtained, which would be considerably different from those frozen by cooling.

EXPERIMENTAL

1,2-Dibromoperfluoroethane has been *in-situ* pressure crystallized in a Merrill-Bassett miniature diamond anvil cell (DAC)[9]. The freezing pressure of 0.8 GPa has been determined when the polycrystalline sample was in equilibrium with the liquid. Then the pressure was increased to 1.03 GPa and the DAC heated until one small grain was left. The single-crystal, grown from this seed by slowly cooling the DAC (Figure 1), filled whole the high-pressure chamber at 310(2) K. Diffraction data were measured for this single-crystal.

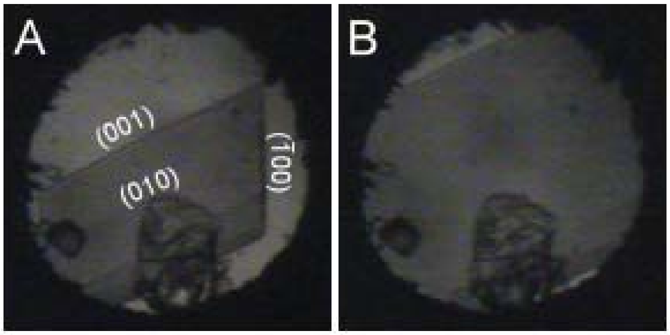

Figure 1. Two stages of the single-crystal growth of 1,2-dibromotetrafluoroethane: the plate-like crystal at 450 K (A), and the single-crystal covering almost all surface of the culet in the chamber at 330 K (B). Newton fringes can be observed for the very thin plate in photograph (A). Two ruby chips were placed in the chamber: the bigger one at the bottom of the photograph and the smaller to its left.

1,2-Diiodotetrafluoroethane froze at 0.10 GPa at 296 K. Then the pressure was increased to 0.16 GPa, and the single-crystal (Figure 2) was grown as explained above. The single-crystal diffraction data have been measured at 0.16 GPa.

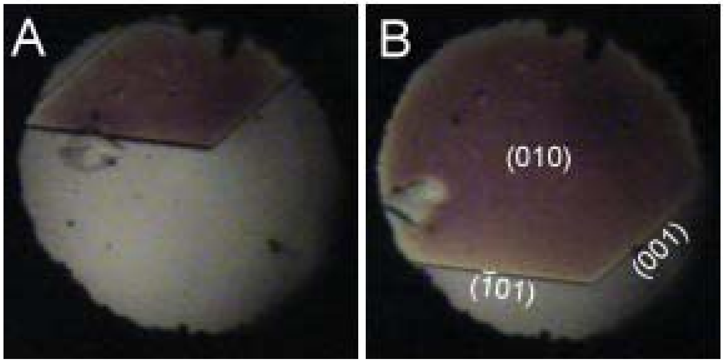

Figure 2. The pressure-crystallized single crystal of 1,2-diiodoperfluoroethane in the DAC chamber at 443 K (A) and 383 K (B).

After measurement the ICF_2CF_2I was loaded to the DAC again and then pressurized to 0.86 GPa, a single crystal was obtained by heating and cooling the DAC. However, during the cooling on the surface of single crystal some additional dendritic crystals appeared (Figure 3). The measurement was performed on this single crystal.

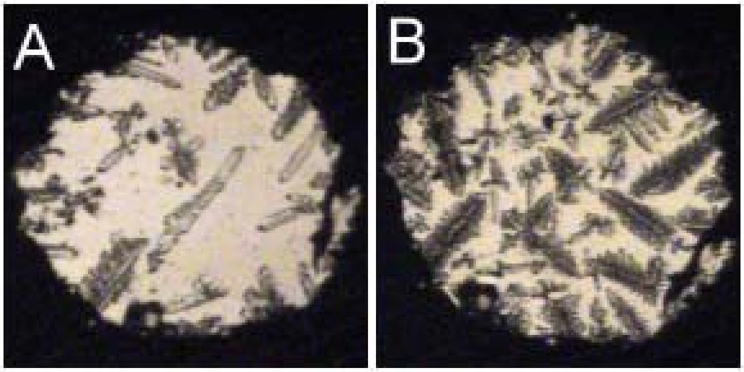

Figure 3. The pressure-crystallized single crystal of 1,2-diiodoperfluoroethane at 453 K (A); and at 296 K/0.86 GPa (B) with small dendritic forms developed on the upper crystal face.

1-Bromo-2-iodotetrafluoroethane froze at 0.30 GPa, then the pressure was increased to 0.60 GPa. The single-crystal was obtained by heating and cooling the DAC. The defects visible on the sample surface self-repaired while cooling the DAC till room temperature in the process of self-repair of the crystal morphology (Figure 4 A-D). This sample was used for the diffraction measurement, after which the DAC was heated again and the pressure increased to 1.10 GPa (Figure 4E). After the data collection pressure was further increased to 3.50 GPa (Figure 4F) and the x-ray data measured again.

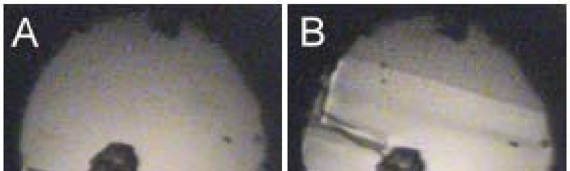

Figure 4. 1-Bromo-2-iodotetrafluoroethane single-crystal pressure freezing in the DAC chamber: 443 K (A); 393 K (B); 373 K (C); and at 296 K/0.6 GPa (D). Analogously obtained single crystals at 1.1GPa (E) and 3.5 GPa (F) at room temperature. Two ruby chips for pressure calibration are placed one below the chamber center and other at its upper edge.

Pressure in the DAC was calibrated by ruby-fluorescence method[10,11], using 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. The CrysAlis version 1.171.24 software[12] was used for the data collections[13] and the preliminary reduction of the data. After the intensities were corrected for the effects of DAC absorption, sample shadowing by the gasket, and the sample absorption[14], the diamond reflections have been eliminated. The systematic absences unequivocally showed that the crystals are monoclinic in space group $P2_1/n$. All structures were solved straightforwardly by direct methods[15], and refined by full-matrix least-squares[16]. Anisotropic temperature factors were generally applied, but where the anisotropic refinement resulted in non-positive definite ellipsoids, isotropic thermal parameters were retained. The crystal data and the structure refinement details are listed in Table 1. Structural drawings were prepared using the X-Seed interface of POV-Ray[17,18].

Table 1. Crystal data and details of structure refinement for $BrCF_2CF_2Br$, CF_2ICF_2I and $BrCF_2CF_2I$.

		$BrCF_2CF_2Br$	ICF_2CF_2I		$BrCF_2CF_2I$		
Pressure (GPa)		1.03(5)	0.16(5)	0.86(5)	0.60(5)	1.00(5)	3.50(5)
Temperature (K)		296(2)	296(2)	296(2)	296(2)	296(2)	296(2)
Formula weight		259.84	353.82	353.82	306.83	306.83	306.83
Wavelength (Å)		0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system		Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group		$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
Unit cell dimensions (Å,°)	*a*	5.768(1)	6.563(2)	6.4133(13)	6.1357(12)	5.9698(12)	5.7683(12)
	b	6.078(1)	6.293(4)	5.9350(12)	6.1449(12)	6.1503(12)	6.0823(12)
	c	8.080(1)	8.935(6)	8.4792(17)	8.3967(17)	8.2360(16)	8.0112(16)
	β	107.01(3)	106.47(5)	103.68(3)	108.30(3)	108.58(3)	109.92(3)
Volume ($Å^3$)		270.88(9)	353.8(3)	313.58(11)	300.57(10)	286.63(10)	264.26(9)
Z		2	2	2	2	2	2
Calculated density (g/cm^3)		3.186	3.321	3.747	3.390	3.555	3.856
Absorption coefficient (mm^{-1})		14.936	8.868	10.006	11.950	12.531	13.592
F(000)		236	308	308	272	272	272
Crystal diameter/height (mm)		0.36/0.07	0.39/0.07	0.46/0.06	0.41/0.09	0.37/0.09	0.36/0.08

θ-range for data collection (°)	4.27 to 29.53	3.43 to 30.08	3.60 to 28.63	3.63 to 28.66	3.71 to 29.39	3.81 to 29.66
Min/max indices: h, k, l	-6/6;-7/7;-7/8	-9/9, -5/5, -10/10	-8/8, -1/1, -11/11	-8/8,-8/8,-4/4	-8/8,-7/7,-8/8	-6/6,-7/7,-10/10
Reflect. Collected/ unique (R_{int})	2085/342 (0.0505)	2575/436 (0.0409)	1107/197 (0.1967)	2252/225 (0.0617)	2216/362 (0.0594)	1960/330 (0.0969)
Completeness (to $\theta_{\max}$) (%)	45.2 (to 29.53°)	42 (to 30.08°)	24.5 (to 28.63)	29.0 (to 28.66)	45.7 (to 29.39)	44.4 (to 29.66)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restrains/ parameters	342/0/38	436/9/47	197/0/32	225/1/18	362/0/38	330/0/38
Goodness-of-fit on F^2	1.139	1.238	1.429	1.082	1.192	1.171
Final R_1/wR_2 ($I>2\sigma_1$)	0.0495/0.1138	0.0569/0.1304	0.1302/0.3029	0.1166/0.2670	0.0618/0.1153	0.0596/0.1762
R_1/wR_2 (all data)	0.0564/0.1180	0.0844/0.1446	0.1335/0.3107	0.1240/0.2734	0.0722/0.1234	0.0692/0.1991
Weighting scheme	w=1/(sigma^2(Fo^2)+(0.0739*P)^2+0.24*P), where P=(Max(Fo^2,0)+2*Fc^2)/3	w=1/(sigma^2(Fo^2)+(0.0486*P)^2+1.11*P), where P=(Max(Fo^2,0)+2*Fc^2)/3	w=1/(sigma^2(Fo^2)+(0.2000*P)^2+1.11*P), where P=(Max(Fo^2,0)+2*Fc^2)/3	w=1/(σ^2(Fo^2)+(0.1087*P)^2+12*P), where P=(Max(Fo^2,0)+2*Fc^2)/3	w=1/(σ^2(Fo^2)+(0.0455*P)^2+2.48*P), where P=(Max(Fo^2,0)+2*Fc^2)/3	w=1/(σ^2(Fo^2)+(0.1199*P)^2+2.30*P), where P=(Max(Fo^2,0)+2*Fc^2)/3
Largest diff. peak and hole (e.Å^{-3})	0.322/-0.443	0.408/-0.318	1.680/-1.373	0.825/-0.959	0.620/-0.575	1.438/-1.361

Results and Discussion

Structure of 1,2-dibromoperfluoroethane. The pressure-crystallized $BrCF_2CF_2Br$ is isostructural with the crystal obtained by cooling[8]. At 1.03 GPa/296 K the molecules each forming two shortest Br···Br contacts of 3.872(2) Å are arranged into endless chains along the [100] direction and the next four short contacts arrange molecules into layers along the (101) crystal plane. The Br···Br interaction in low-temperature phases are longer and the shortest distance between Br atoms is of 4.04 Å[8]. According to Nyburg & Faerman[19] the van der Waals radius of Br is anisotropic, and it is shorter along C-Br bond than perpendicular to it. The shorter radius of Br is 1.54 Å, and the longer radius is 1.84 Å. Thus the Br-atoms in CF_2BrCF_2Br interact along their longer radii. These chains interact *via* Br···F contacts of 3.221(8) Å along the (101) plane. The $BrCF_2CF_2Br$ molecules in both low-temperature and high-pressure structures are ordered.

1,2-Diiodoperfluoroethane: in its crystal structure at 0.16 GPa and 296K the molecules are disordered in this way, that the positions of iodine atoms are well defined and the $–CF_2–CF_2–$ group rotating about the I···I intramolecular axis. In this structure the shortest I···I contacts of 4.212(2) Å are formed between molecules arranged into layers along (101) planes and the next short contact arranges molecules into chains along the $[\bar{1}10]$ direction, as shown in Figure 5. In the terms of anisotropic van der Waals radii[19], the I-atoms form the I···I contacts of 4.212(2) Å along their major and minor radii, *i.e.*, the C–I···I angles are between 68 ° and 96 °on one side, and between 139 ° and 168 °on the other, respectively (for disordered $–CF_2–CF_2–$ moiety).

Figure 5. The molecular packing and short I···I interaction patterns in 1,2-diiodotetrafluoroethane at 0.16 GPa/296 K (A) and 0.86 GPa/296 K (B). The I···I short contacts along (101) plane are indicated as blue dashed lines and these along $[\bar{1}10]$ direction as the orange dashed lines. In drawing (A) all the sites of disordered C and F atoms have been shown.

At 0.86 GPa the orientation of the ICF_2CF_2I molecules becomes ordered. The pattern of intermolecular short contacts is almost the same as at 0.16 GPa, but the intermolecular distances between I atoms are 3.890(2) Å along the (101) plane and 4.552(11) Å along $[\bar{1}10]$ direction. Also another I···I contact of 4.287(11) Å along [010] direction, squeezed by about 0.5 Å compared to that at 0.16 GPa becomes shorter than the sum of van der Waals radii. Surprisingly, the I···F and F···F distances become slightly longer at 0.86 GPa than at 0.16 GPa. The molecular packing and I···I interaction pattern are shown in Figure 5.

Crystal structure of 1-bromo-2-iodoperfluoroethane. In the structure of BrCF2CF2I the I- and Br-atoms are substitutionally disordered both with equal occupancies. This monoclinic phase, with the I- and Br-atoms disordered, in all the range investigated remains stable till 3.4 GPa.

The molecular packing in the pressure-crystallized structures of $BrCF_2CF_2I$ is governed by the intermolecular interactions of (Br/I)-atoms. The molecules, each forming four short (Br/I)···(Br/I) contacts of 4.088(11) Å at 0.6 GPa, are arranged into corrugated layers along the (101) crystal plane, and the next two shortest contact of 4.257(8) Å bind the molecules into endless chains along the [100] direction. At 1.10 GPa these distances are squeezed to 4.059(2) Å and 4.067(2) Å, and at 3.4 GPa to 3.964(2) Å and 3.876(3) Å, respectively. However the three-dimensional pattern of intermolecular interactions, presented in Figure 6, remains unchanged in this pressure range.

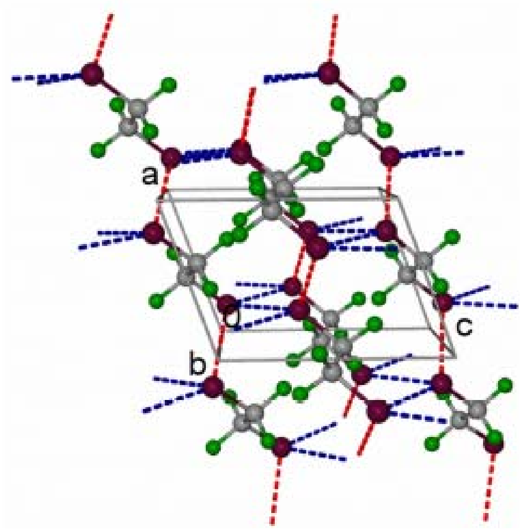

Figure 6. The (Br/I)···(Br/I) interactions in the structure of 1-bromo-2-iodoperfluoroethane at 3.4 GPa. The Br(I)···Br(I) short contacts along [100] chains have been indicated by red dashed lines, those along the (101) planes by blue dashed lines.

Pressure only slightly affects the C-(Br/I)···(Br/I) angles, they all become smaller with increasing pressure. The directions of interactions can be referred to the concept of anisotropic van der Waals radii of halogen atoms[19], the interaction forming chains are inclined by about 90° to the (Br/I)-C bond *i.e.*

along the major van der Waals radius, and the C-(Br/I)···(Br/I) angles within the (101) planes are of about 95° and 140°, thus along the major and along an intermediate between minor and major radii. The (Br/I)···F contacts are all longer than the sum of van der Waals radii of Br and F[20] at 0.6 GPa (Table 3), but above 1.1 GPa these contacts become shorter than this sum. This confirms that this structure of $BrCF_2CF_2I$ is tightly packed, and that there are no spaces left for the $-CF_2$-CF_2- disordering. The shortest (Br/I)···F contacts arrange the molecules into layers along the (101) planes, and the next shortest contacts into run along the [010] direction.

The intermolecular contacts of the $BrCF_2CF_2Br$, ICF_2CF_2I and $BrCF_2CF_2I$ molecules have been illustrated on their Hirshfeld surfaces[21,22] in Figure 7. The molecular arrangements and interactions, illustrated by these drawings are very similar for the $BrCF_2CF_2Br$, ICF_2CF_2I and $BrCF_2CF_2I$ crystals, which is consistent with their isostructurality. It can be observed, that the molecules interact most strongly with the terminal Br and I atoms, and that the interactions of the F atoms are considerably weaker.

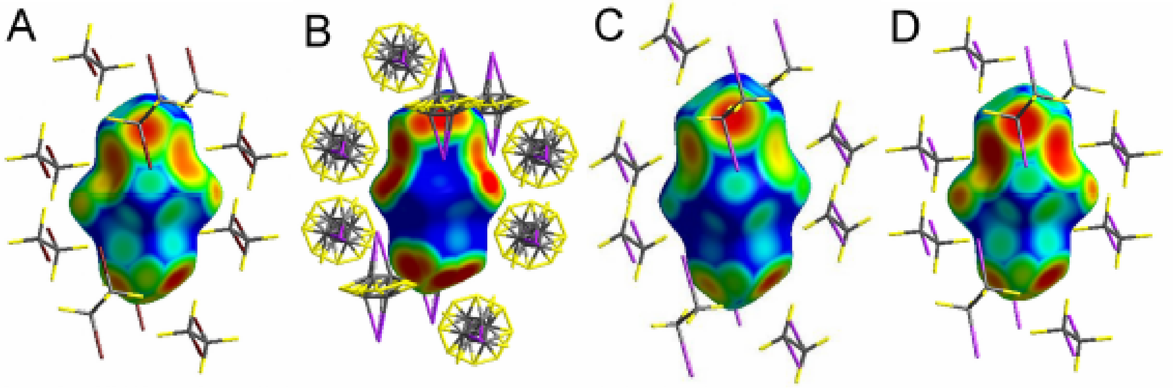

Figure 7. Intermolecular interactions of $BrCF_2CF_2Br$ at 1.03 GPa(A), ICF_2CF_2I at 0.16 GPa (B) and $BrCF_2CF_2I$ at 0.60 GPa (C) and at 3.40 GPa (B) at room temperature represented by a color scale on the Hirshfeld surface[21,22]. The property mapped onto the surface is the distance from its element to the nearest exterior and it ranges from 1.40 Å (red) to 2.25 Å (blue) in the pictures. In drawing (B) all the sites of disordered atoms have been included.

The –CF_2–CF_2– disorder in ICF_2CF_2I. The different types of disorder can be explained by the intermolecular interactions. In all structures the patterns formed by short contacts are very similar. The unit-cell dimensions and intermolecular distances are listed in Tables 2 and 3. The two of three shortest contacts of each Br, I and (Br/I) atoms form in all structures the same patterns, and the next short contact in ICF_2CF_2I at 0.16 GPa runs along [$\bar{1}$10] direction, at 0.86 GPa along [010], in $BrCF_2CF_2Br$ and $BrCF_2CF_2I$ along [100]. At pressure of 0.86 GPa in ICF_2CF_2I the shortest I···I contacts are significantly squeezed. However, the differences between the three shortest contacts are much smaller in $BrCF_2CF_2Br$ and $BrCF_2CF_2I$, than in ICF_2CF_2I. The interactions along [100] in $BrCF_2CF_2Br$ and $BrCF_2CF_2I$, and these along [010] in ICF_2CF_2I at 0.86 GPa, which are absent in the ICF_2CF_2I at 0.16 GPa, can be responsible for ordering the -CF_2-CF_2- groups. A similar role can be played by the Br···F and (Br/I)···F interactions, which are about 0.2 Å shorter than the shortest of I···F in ICF_2CF_2I.

The (Br/I) disorder in $BrCF_2CF_2I$. The differences between van der Waals radii of Br and I atoms[23] are of about 0.2 Å (1.95 Å for Br vs. 2.15 Å for I), and the differences between C-Br (1.91 Å) and C-I (2.16 Å) bond length is of about 0.25 Å[21]. It is reasonable to assume, that the $BrCF_2CF_2I$ molecule disordered in two orientations (*i.e.* $BrCF_2CF_2I$ and ICF_2CF_2Br) occupies the space limited by the midpoints of the shortest (Br/I) contacts, as shown in Figure 8A. This assumption would imply that in the averaged structure the C and F atoms should be shifted by approximately 0.45 Å along the (Br/I)···(Br/I) molecular axis. Indeed, these thermal ellipsoids are elongated along the (Br/I)···(Br/I) molecular axis, as illustrated in Figure 8. However, the ellipsoids of C and F atoms are also significantly elongated in the direction approximately perpendicular to molecular plane (Figure 8C). It can be deducted that the two disordered sites of the molecule are not coplanar, but they are inclined by about 50° (as assessed from the amplitudes of the thermal ellipsoids) one to the other in the way indicated in Figure 8C.

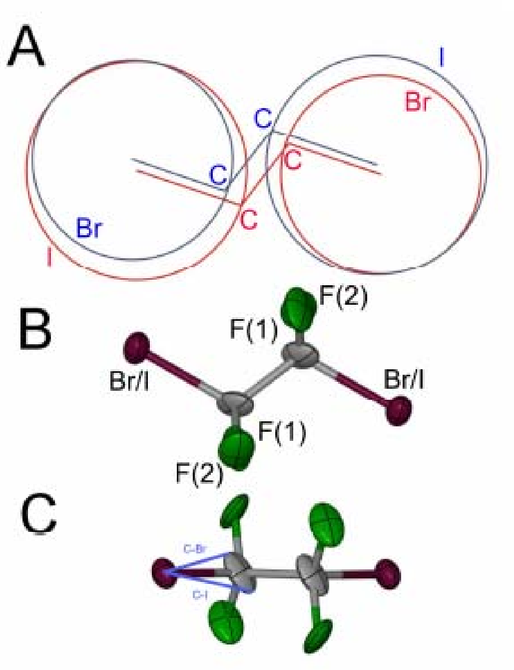

Figure 8.(A)The geometric reconstruction of the shifts of C atoms two $BrCF_2CF_2I$ molecules (viewed along their molecular plane) orientationally disordered in this way that they fill the space between the midpoints of the shortest contacts to their neighbors, (the F atoms are omitted for clarity), based on the van der Waals radii and C-C, C-Br and C-I bond lengths; (B) the of thermal ellipsoids along the molecular plane, drawn at 50% probability level, observed at 3.4 GPa/296K; and (C) the ORTEP view of the molecule drawn perpendicular to its plane. The two positions of the disordered molecule in drawing (A) have been indicated one by red color and the other by blue.

Isostructural crystallization of $BrCF_2CF_2Br$, $BrCF_2CF_2I$ and ICF_2CF_2I. 1-Bromo-2-iodoperfluoroetane, 1,2-dibromoperfluoroethane and 1,2-diiodoperfluoroethane all crystallize in monoclinic space group $P2_1/n$, with the molecules in *s*-trans conformation located at the inversion centres (Figure 9). It is surprising that despite their isostructurality the molecules behave differently. The $BrCF_2CF_2Br$ structure is completely ordered, in ICF_2CF_2I the $-CF_2-CF_2-$ moiety rotate about I···I molecular axis at 0.16 GPa, but it is ordered at 0.86 GPa, and in the $BrCF_2CF_2I$ structure the Br and I atoms are disordered and occupy the same site. It has been shown for ICF_2CF_2I, that the disorder of $–CF_2–CF_2–$ moieties can be eliminated by increasing pressures. $BrCF_2CF_2I$ is the only structure in this series with two different halogen atoms substitutes at the 1,2-sites. A similar type of disorder was recently found in the crystals of CH_2BrCl[24] and CH_2ClI[25]. It should be still clarified if this substitutional disorder in the perfluoroethanes can be controlled by thermodynamical conditions.

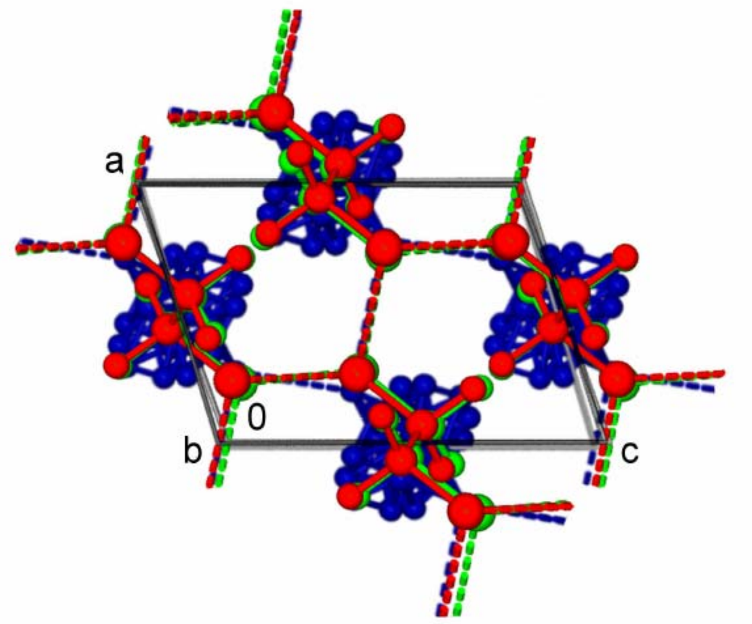

Figure 9. ICF_2CF_2I (blue), $BrCF_2CF_2I$ (green) and $BrCF_2CF_2Br$ (red) unit cells and structures projected along [010] and superimposed. The unit-cell dimensions of ICF_2CF_2I have been adjusted to possibly precisely overlay the adjust of the unit cell. The applied scaling factor was: 0.88:1.00, respectively.

Table 2. Comparison of unit-cell dimensions of high-pressure structures of haloperfluoroethanes.

	$BrCF_2CF_2I$			ICF_2CF_2I		$BrCF_2CF_2Br$
P (GPa)/T (K)	0.6/296	1.1/296	3.4/296	0.16/296	0.86/296	1.03/296
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	6.1357(12)	5.9698(12)	5.7683(12)	6.563(2)	6.4133(13)	5.768(1)
b (Å)	6.1449(12)	6.1503(12)	6.0823(12)	6.293(2)	5.9350(12)	6.078(1)
c (Å)	8.3967(17)	8.2360(16)	8.0112(16)	8.935(6)	8.4792(17)	8.080(1)
β (deg)	108.30(3)	108.58(3)	109.92(3)	106.47(5)	103.68(3)	107.01(3)

Table 3. Comparison of halogen···halogen interaction geometry in high-pressure structures of haloperfluoroethanes (X=Br, I or Br/I).

	$BrCF_2CF_2I$			ICF_2CF_2I		$BrCF_2CF_2Br$
p (GPa)/T (K)	0.6/296	1.1/296	3.4/296	0.16/296	0.86/296	1.03/296
$X\cdots X^{i}$(Å)				4.716(3)	4.552(11)	
$X\cdots X^{ii}$(Å)	4.257(8)	4.067(2)	3.876(3)			3.872(2)
$X\cdots X^{iii}$(Å)	4.088(11)	4.059(2)	3.964(2)	4.212(2)	3.890(2)	4.014(2)
$X\cdots X^{iv}$(Å)	4.088(11)	4.059(2)	3.964(2)	4.212(2)	3.890(2)	4.014(2)
$X\cdots X^{vi}$(Å)					4.287(11)	
$X\cdots F^{v}$(Å)	3.339(80)	3.288(12)	3.163(13)	3.441(3)	3.564(16)	3.221(8)
$X\cdots F^{iv}$(Å)				3.458(51)		
$X\cdots F^{vi}$(Å)	3.400(27)	3.343(7)	3.294(7)			3.328(4)
$X\cdots F^{vii}$(Å)				3.513(52)	3.594(77)	
$X\cdots F^{ii}$(Å)					3.554(30)	
$F\cdots F^{viii}$(Å)	3.47(11)	3.171(24)	2.924(24)	2.628(51)	2.663(54)	3.010(9)
$C-X\cdots X^{i}$ (°)				136.0(1) 149.55(79) 121.53(29)	115 (1)	
$C-X\cdots X^{ii}$ (°)	90(1)	87.2(6)	86.9(5)			89.5(2)
$C-X\cdots X^{iii}$ (°)	101.1(4)	97.5(6)	95.6(4)	96.29 (73) 68.00 (32) 89.35 (77)	85(2)	98.8(2)
$C-X\cdots X^{iv}$ (°)	142(1)	141.5(6)	138.0(5)	139.41(43) 146.62(77) 168.30(61)	174(2)	139.0(2)
$C-X\cdots X^{vi}$ (°)					82 (2)	
$C-X\cdots F^{v}$ (°)	149(1)	147.6(8)	146.4(5)	153(1)	133(2)	148.4(2)

C-X···F^{iv} (°)				125.34(85) 141(1) 138(1) 117.40(91) 143(1)		
C-X···F^{vi} (°)	99(1)	98.4(5)	96.0(4)			96.7(3)
C-X···F^{vii} (°)				104.26(82) 133(1) 120(1)	94(1)	
C-X···F^{ii} (°)					164(3)	

Symmetry codes: i: 2-x,2-y,-z; ii: 2-x,1-y,-z; iii: 1.5-x,y-0.5,-z-0.5; iv: 1.5-x,y+0.5,-z-0.5; v: 0.5+x,1.5-y,z-0.5; vi: 1-x,2-y,-z; vii: x,y+1,z; viii1.5-x,0.5+y,0.5-z

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REFERENCES

(1) Bertaccini, J. R.; Trudell, J. R. *Br.J. Anaesth.* **2002**, *89*, 32.

(2) Amico, V.; Meille, S. V.; Corradi, M.T.; Resnati, G. *J. Am. Chem. Soc.* **1998**, *120***,** 8261.

(3) Cardillo, P.; Corradi, E.; Lunghi, A.; Meille, S. V.; Messina, M. T.; Metrangolo, P.; Resnati, G. *Tetrahedron* **2000**, *56*, 5535.

(4) Chu, Q.; Wang, Z.; Huang, Q.; Yan, C.; Zhu, S. *J. Am. Chem. Soc.* **2001**, *123*, 11069.

(5) Chu, Q.; Wang, Z.; Huang, Q.; Yan, C.; Zhu, S. *New J. Chem.* **2003**, *27*, 1522.

(6) Kuhn, N.; Abu-Rayyan, A.; Steimann, M. *Z. Anorg. Allg. Chem.* **2003**, *629*, 2066.

(7) Metrangolo, P.;. Pilati, T.; Resnati, G.; Stevenazzi, A. *Chem. Comm.* **2004**, 1492.

(8) Pawley, G.S.; Whitley, E. *Acta Cryst. C* **1988**, *44*, 1249.

(9) Merrill, L.; Bassett, W. A. *Rev. Sci. Instrum.* **1974**, *45*, 290.

(10) Piermarini, G. J.; Mighell, A. D.; Weir, C. E.; Block, S. *Science* **1969**, *165*, 1250.

(11) Mao, H. K.; Xu, J.; Bell, P. M. *J. Geophys. Res.* **1985**, *91*, 4673.

(12) Oxford Diffraction Limited. User Manual Xcalibur series Single Crystal Diffractometers, Version 1.3. Oxford Diffraction Poland, Wrocław,2002.

(13) Budzianowski, A.; Katrusiak, A. High-pressure crystallographic experiments with a CCD-detector in High-Pressure Crystallography (Eds.: Katrusiak, A.; McMillan, P. F.). Kluwer Academic Publisher, Dordrecht, **2004,** 157.

(14) Katrusiak, A. REDSHAD. Program for the correcting reflections intensities for DAC absorption, gasket shadowing and sample crystal absorption. Adam Mickiewicz University, Poznań, 2003.

(15) Sheldrick, G. M. *Acta Cryst A.* **1990**, *46*, 467.

(16) Sheldrick, G.M. The SHELX-97 manual. Univ. of Götingen, Germany, 1997.

(17) Barbour, L. J. *J. Supramol. Chem.* **2001**, *1* , 189.

(18) Persistence of Vision Pty. Ltd. *Persistence of Vision (TM) Raytracer*, Version 2.6. Williamstown, Victoria, Australia, **2004**.

(19) Nyburg, S. C.; Faerman, C. H. *Acta Cryst. B*, **1985**, *41*, 274.

(20) Batsanov, S. S. *Inorg. Matt.* **2001**, *37*, 1031.

(21) McKinnon, J. J.; Spackman, M. A.; Mitchell, A. S. *Acta Cryst. B* **2004**, *60*, 627.

(22) Wolff, S. K.; Grimwood, D. J.; McKinnon, J. J.; Jayatilaka, D.; Spackman, M. A. CrystalExplorer, Version 1.5.0, University of Western Australia, **2005**.

(23) Allen, F. H.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. International Tables for Crystallography *C* (Eds.Prince, E.)**.** Kluwer Academic Publisher, Dordrecht, Boston, London **2004**, 790.

(24) Podsiadło, M.; Katrusiak, A. (**2007**) – in preparation.

(25) Podsiadło, M.; Katrusiak, A. (**2007**) – in preparation.