High-pressure study of halogen interactions in perfluorated haloethanes and their complexes with 1,4-dioxane

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GENERAL ABSTRACT

Owing to significant differences in physical and chemical properties between fluorine compounds and their hydrogen analogues, haloperfluorocarbons find wide applications in technology, agriculture, medicine and in other fields. The general anesthetics are mostly halogenated compounds. In haloperfluorocarbons $[X(CF_2)_nX$; X=Br or I], the bromine or iodine atoms acquire a partial positive charge and they favourably form short interactions with electron rich nitrogen or oxygen. High pressure studies can be used for measuring the compressibility of intermolecular contacts between halogen atoms, identifying the interactions governing the molecular association, eliminating the molecular disorder and determining the thermodynamical conditions favoring the cocrystallizaton. Pressure is an important thermodynamical parameter that can considerably modify properties of substances, and therefore should be taken into account in all processes where pressure change.

Figure 2. DAC on a goniometer head.

Figure 1. Merrill-Bassett diamond-anvil cell[1] (DAC).

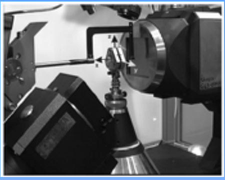

Figure 3. The diamond anvil cell mounted on the diffractometer with indicated x, y and z directions.

TECHNICAL ABSTRACT

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 ($BrCF_2CF_2I$) and their complexes with 1,4-dioxane have been studied using high-pressure technique. Each of the investigated compound has been in-situ pressure frozen in a Merrill-Bassett miniature diamond anvil cell (DAC)[1](Fig.1-3). The freezing pressure of particular compounds and mixture has been determined when the polycrystalline sample was in equilibrium with the liquid. Single-crystal of each compound or mixture was obtained by heating polycrystalline mass in the DAC, till one seed was left, which was then grown by slowly lowering its temperature. Pressure in the DAC was calibrated by ruby-fluorescence method[2,3], 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 process of growing single-crystals of some of the substances investigated has been illustrated by the photographs in Figs. 4-6.

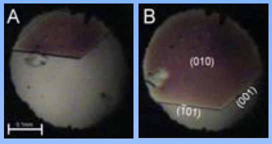

Figure 4. The pressure-frozen single crystal of 1,2-diiodoperfluoroethane in the DAC chamber at 443 K (A) and 383 K (B) and at 0.16GPa.

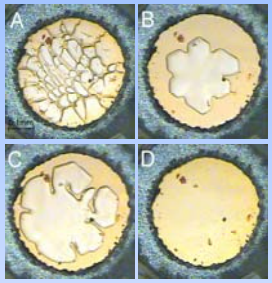

Figure 5. Isochoric growth of the 1,2-diiodoperfluoroethane:1,4-dioxane 1:1 cocrystal: (A) the melting process of the polycrystal sample at 400 K; (B) one single-crystal at 433 K and (C) at 395K; (D) the single-crystal filling the whole volume of the DAC chamber at 296 K and 0.3GPa.

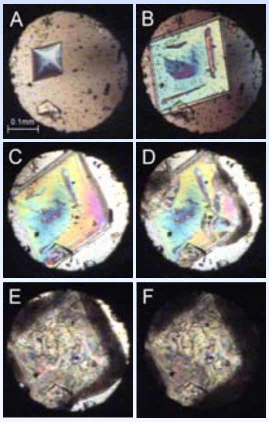

Figure 6. Separation of 1,4-dioxane from 1,2-dibromoperfluoroethane:1,4-dioxane mixture by pressure-freezing. (A) One 1,4-dioxane crystal grain left in the DAC chamber at 503 K; (B) this crystal at 483 K with clearly visible faults on its surfaces; (C) the self-repair process of the crystal at 473 K; (D) polycrystalline 1,2-dibromoperfluoroethane appearing at the upper left edge of the chamber at 443 K; and (E, F) the single-crystal of 1,4-dioxane and the polycrystals of 1,2-dibromoperfluoroethane filling the whole volume of the DAC.

MOLECULAR PACKING AND INTERMOLECULAR NTERACTIONS

Disorder modes in isostructural dihaloperfluoroethanes

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). All the crystals are monoclinic, space group $P2_1/n$, with the midpoint of the C–C bond located at the centre of inversion (Fig. 7). 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 $BrCF_2CF_2Br$ 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.

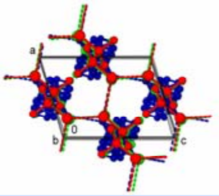

Figure 7. ICF_2CF_2I (blue), $BrCF_2CF_2I$ (green) and $BrCF_2CF_2Br$ (red) unit cells and structures projected along [010] and superimposed. The unit-cell dimensions of ICF_2CF_2I have been adjusted to possibly precisely overlay unit-cell edges. The applied scaling factors for *a* and *c* were: 0.88:1.00, respectively.

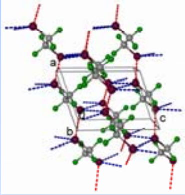

Figure 8. The (Br/I)···(Br/I) interactions in the structure of $BrCF_2CF_2I$ at 3.4 GPa. The Br(I)···Br(I) short contacts along [100] chains have been indicated by red dashed lines, those along the (101) planes by blue dashed lines.

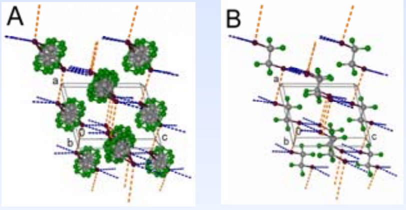

Figure 10. The molecular packing and short I···I interaction patterns in ICF_2CF_2I at 0.16 GPa/296 K (A) and 0.86 GPa/296 K (B).. In drawing (A) all the sites of disordered C and F atoms have been shown.

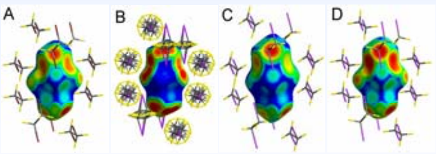

Figure 9. Intermolecular interactions of $BrCF_2CF_2Br$ at 1.03 GPa(A), ICF_2CF_2I at 0.16 GPa (B) and $BrCF_2CF_2I$ at 0.60 GPa (C) and at 3.40 GPa (B) at room temperature represented by a colour scale on the Hirshfeld surface[4,5]. The property mapped onto the surface is the distance from its element to the nearest exterior and it ranges from 1.40 Å (red) to 2.25 Å (blue) in the pictures.

	CF_2ICF_2I	CF_2ICF_2I	CF_2BrCF_2Br	CF_2BrCF_2I	CF_2BrCF_2I	CF_2BrCF_2I	CF_2ICF_2I: $C_4H_8O_2$	$C_4H_8O_2$	CF_2BrCF_2I: $C_4H_8O_2$
p [GPa]	0.16(5)	0.86(5)	1.03(5)	0.60(5)	1.10(5)	3.40(5)	0.30(5)	0.42(5)	0.62(5)
T [K]	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)
Sp. gr.	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$R\bar{3}$	$P2_1/n$	$P2_1/c$
a *b* *c* *β*	6.563(2) 6.293(4) 8.935(6) 106.47(5)	6.4133(13) 5.9350(12) 8.4792(17) 103.68(3)	5.768(1) 6.078(1) 8.444(2) 113.78(3)	6.1357(12) 6.1449(12) 8.3967(17) 108.30(3)	5.9698(12) 6.1503(12) 8.2360(16) 108.58(3)	5.7683(12) 6.0823(12) 8.0112(16) 109.92(3)	8.838(1) 13.532(3) 8.838(1)	5.6590(10) 6.4100(10) 5.8920(10) 98.36(3)	9.5983(19) 5.9716(12) 9.784(2) 107.41(3)
V [Å^3]	353.8(3)	313.58(11)	270.90(9)	300.57(10)	286.63(10)	264.26(9)	915.4(3)	211.46(6)	535.13(19)
R_1/wR_2 ($I>2\sigma_1$)	0.0569/ 0.1304	0.1302/ 0.3029	0.0477/ 0.0683	0.1166/ 0.2670	0.0618/ 0.1153	0.0596/ 0.1762	0.1335/ 0.3502	0.1784/ 0.3250	0.0700/ 0.1584
R_1/wR_2 (all data)	0.0844/ 0.1446	0.1335/ 0.3107	0.0547/ 0.0704	0.1240/ 0.2734	0.0722/ 0.1234	0.0692/ 0.1991	0.1451/ 0.3668	0.2073/ 0.3400	0.0814/ 0.1651

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Halogen···oxygen interactions and disorder modes in pressure frozen complexes of 1,2-dihaloperfluoroethanes with 1,4-dioxane

Structures of cocrystal of 1,2-diiodoperfluoroethane:1,4-dioxane at 0.30(5) GPa/296(2) K and of 1-bromo-2-iodoperfluoroethane:1,4-dioxane at 0.62(5) GPa/296 K were determined by single-crystal X-ray diffraction. Also the single-crystal of 1,4-dioxane separated from 1,2-dibromoperfluoroethane, which reminded liquid, was investigated at 0.42 GPa/296 K. In the structure of $ICF_2CF_2I{:}C_4H_8O_2$ the $-CF_2-CF_2-$ moiety is disordered about the I···I molecular axis and the $C_4H_8O_2$ molecule rotates about the O···O molecular axis too; and in $BrCF_2CF_2I{:}C_4H_8O_2$ the Br and I atoms are disordered in this way that they possess the same position with half occupancy; the molecule of $C_4H_8O_2$ is ordered in this complex, and it is also ordered in the structure of the dioxane crystal obtained from the $BrCF_2CF_2Br{:}C_4H_8O_2$ mixture.

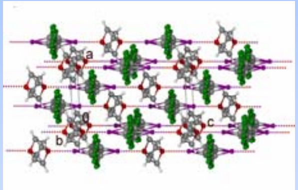


Figure 11. The molecular packing of 1,2-diiodoperfluoroethane:1,4-dioxane cocrystal at 0.30GPa/296K. The shortest I···O contacts have been indicated as dashed lines, and the disordered sites of the $-CF_2-CF_2-$ and $-CH_2-CH_2-$ moieties have been shown.

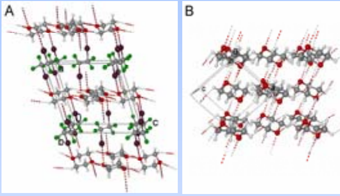


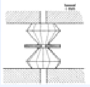
Figure 12. The molecular packing of (A) 1,2-dibromoperfluoro:1,4-dioxane cocrystal with the shortest Br/I···O interactions of 2.93(2) Å and O···H of 2.592 Å at 0.62 GPa/296 K; and (B) 1,4-dioxane with two shortest O···H contacts of 2.655 Å and 2.672 Å at 0.42 GPa/296 K.

CONCLUSIONS

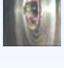
- The high-pressure studies on 1,2-dihaloperfluoroethanes and their complexes with 1,4-dioxane, 1:1 mol, revealed the molecular disorder, the patterns of intermolecular interactions and the ability of I and Br/I atoms to form short contacts with oxygen. However, the Br···O contacts have not been observed as pure $BrCF_2CF_2Br$ does not cocrystallize with $C_4H_8O_2$. The pressure freezing of $BrCF_2CF_2Br{:}C_4H_8O_2$, 1:1 mixture, resulted in a single crystal of $C_4H_8O_2$. At these conditions $BrCF_2CF_2Br$ remains liquid.
- It has been shown also for ICF_2CF_2I, that the disorder of $–CF_2–CF_2–$ moieties can be eliminated by increasing pressure, althought the crystal does not change symmetry.
- The studies performed showed that the pressure crystallization is very convenient for obtaining single crystals of molecular substances, even when it was very difficult to obtain these crystals by lowering temperature.

GLOSSARY

- **Miniature diamond anvil-cell (DAC)** – a device which can generate high pressure (500 GPa) and it is used for crystallization process and study the influence of pressure on substances; it consists of two diamonds, beryllium discs and steel elements (frame + screws + pins).



- **Diamond anvil** – a part of DAC; diamonds are used as anvils because they are very strong and hard, and therefore can be used for squeezing the hardest metal gaskets (for example made of tungsten or rhenium), and also they are transparent to many radiations including X-rays.



- **Perfluorated compounds** – the compounds, in which all the hydrogen atoms are substituted by fluorine atoms, which causes big changes in their electronic structure and properties.
- **Molecular disorder** – in **substitutional** disorder the same site in is occupied by different types of atoms; in **positional** disorder one atom occupies more than a single site.
- **Crystallization process** – a process of forming a solid from a liquid by lowering temperature or increasing pressure

- **Intermolecular interactions** – the non-covalent forces occurring between two or more molecules
- **Diffractometer** – an instrument for carrying out measurements and analysis of crystal structures by applying X-ray diffraction

- **Hirshfeld surface** – this surface is defined by the portion of space where the promolecule electron density contributes more than half of the total procrystal electron density; the simplest property to map onto the surface is the distance from the surface to the nearest nucleus external to the surface (d_e); which provides a picture of the nature of intermolecular contacts in the crystal.