

Short communication

Perfluorocarbon–hydrocarbon self assembling. Thermal and vibrational analyses of one-dimensional networks formed by  $\alpha,\omega$ -diiodoperfluoroalkanes with K.2.2. and K.2.2.2.

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Abstract

When perfluorocarbon diiodides **1** and hydrocarbon diamines **2**, **3** are co-crystallised from chloroform a donor–acceptor interaction between the nitrogen atoms of **1** and the iodine atoms of **2**, **3** lead to the formation of infinite one-dimensional coordination networks **4** and **5**. Thermal and infrared analyses of these adducts are reported. Nitrogen–iodine interaction is proposed as a non-covalent bonding strong enough to drive the formation of co-crystals between fluorocarbon and hydrocarbon derivatives. © 1998 Elsevier Science S.A. All rights reserved.

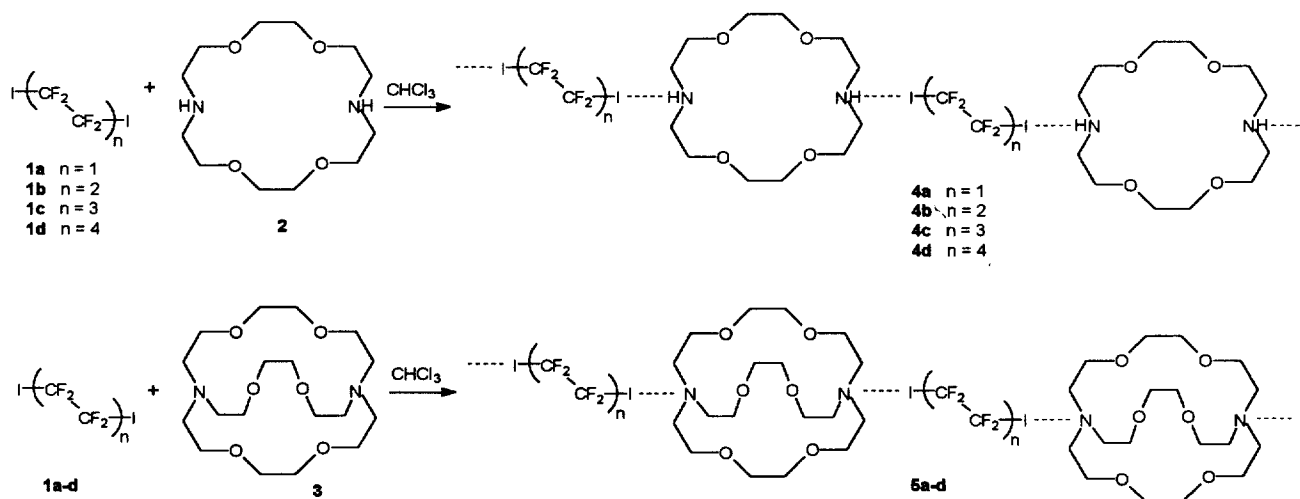
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1. Introduction

Numerous analytical techniques (microwave, infrared, and ultraviolet spectroscopy, nuclear magnetic resonance and nuclear quadrupolar resonance, X-ray analyses,...) consistently show that carbon-bound halogens (C–X, X = Cl, Br, I) can be involved in attractive interactions (C–X···El) with electronegative atoms (El = N, O, S) [1,2]. In general, the tendency to give short C–X···El contacts (namely deep interpenetration of van der Waals volumes) increases on moving from chlorine to bromine to iodine and tends to be highly directional on the extended C–X bond axis [3,4]. Moreover, if the environment around the halogen is sufficiently electron-withdrawing, the resulting attractive interaction can become strong enough not only to influence, but also to drive the crystal packing in the solid. For instance, in the case of the chloro-propylenitrile, a dimer is formed, the Cl···N distance is 2.984(0.90) Å, and the maximum energy gain is about 10 kJ/mol, which is about half the magnitude of an average hydrogen bond [5]. The term ‘halogen bonding’ has been suggested for this type of specific interaction in order to emphasize the parallel with the hydrogen bonding [1].

Iodotrifluoromethane has been reported to form discrete molecular complexes (1:1 stoichiometry) with various monoamines [6,7]. These complexes have been studied in the gas phase at room temperature and in the solid phase in the cold (80 K) [8]. The interaction has been rationalised as a  $n \rightarrow \sigma^*$  donation [9] and a similar behaviour has been described for perfluoroethyl- and *n*-perfluoropropyl iodides [10]. While no energy data are available for this nitrogen–iodine interaction, we expect it to be strong due to the powerful electron withdrawing ability of perfluoroalkyl groups. We thus anticipated that the nitrogen–iodine interactions between perfluorocarbon  $\alpha,\omega$ -diiodides and hydrocarbon  $\alpha,\omega$ -diamines would drive a spontaneous self-assembling of the fluorocarbon and hydrocarbon parts according to a recognition pattern involving either end of both the donor (nitrogen atom) and the acceptor (iodine atom). The formation of infinite one-dimensional networks, hopefully solid and crystalline at room temperature, was thus expected. In this paper we report that this is the case when  $\alpha,\omega$ -diiodoperfluoroalkanes **1a–d** interact with 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (kryptofix 2.2., K.2.2., **2**) or with 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacosane (kryptofix 2.2.2., K.2.2.2., **3**). Infinite one-dimensional

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Scheme 1. Infinite one-dimensional networks **4a–d** and **5a–d** formed by  $\alpha,\omega$ -diiodoperfluoroalkanes (**1a–d**) with kryptofix 2.2. (2) and kryptofix 2.2.2. (3).

coordination networks **4a–d** and **5a–d** are formed as white crystals and their infrared spectra and differential scanning calorimetry analyses are outlined in this preliminary note.

## 2. Results and discussion

When equimolar amounts of perfluorinated  $\alpha,\omega$ -diiodoalkanes **1a–d** and hydrocarbon diamines **2, 3** are co-crystallized from chloroform, white solids **4a–d** and **5a–d** are formed (Scheme 1). These materials are stable and crystalline at room temperature and can be handled in the air without particular precautions. Elemental analyses (Table 1) show that diiodoperfluoroalkanes **1** and diamines **2, 3** are present in a

1:1 ratio in solids **4a–d** and **5a–d**. To now the stoichiometry of the adducts formed by perfluoroalkyl iodides and organic bases had been proven only by vapour pressure measurements [6,7].

In  $^{19}\text{F}$  NMR spectra of concentrated solutions of **4a–d** and **5a–d**, the difluoromethylene geminal to iodine is shifted to high-fields compared to pure precursors **1**.<sup>1</sup> On diluting these samples, the chemical shift of the  $\text{CF}_2\text{I}$  group moves back to the frequencies shown by pure iodides **1** and both  $^1\text{H}$  and

Table 1  
Elemental analyses of infinite one-dimensional networks **4a–d** and **5a–d**

Compound	C (%)	H (%)	N (%)	I (%)	F (%)
<b>4a</b>	27.01	4.48	4.71	41.56	11.89
	(27.29)	(4.25)	(4.54)	(41.19)	(12.33)
<b>4b</b>	26.52	3.97	4.11	35.14	20.81
	(26.83)	(3.66)	(3.91)	(35.44)	(21.22)
<b>4c</b>	26.22	3.37	3.51	30.86	27.31
	(26.48)	(3.21)	(3.43)	(31.09)	(27.93)
<b>4d</b>	25.89	3.08	3.21	28.00	32.86
	(26.22)	(2.86)	(3.06)	(27.70)	(33.18)
<b>5a</b>	32.96	5.09	3.99	34.40	10.04
	(32.89)	(4.97)	(3.84)	(34.75)	(10.41)
<b>5b</b>	31.53	4.59	3.60	30.24	18.71
	(31.82)	(4.37)	(3.37)	(30.57)	(18.30)
<b>5c</b>	30.68	4.03	2.76	27.52	24.07
	(30.98)	(3.90)	(3.01)	(27.28)	(24.50)
<b>5d</b>	30.01	3.72	2.48	24.95	29.06
	(30.31)	(3.52)	(2.72)	(24.63)	(29.50)

Data in parenthesis are referred to values calculated for a 1:1 ratio between diiodides **1** and diamines **2, 3**.

<sup>1</sup> For instance, the following shifts were observed in deuteriochloroform solution:  $\Delta\delta_{\text{F}}$  (ppm) =  $\delta_{\text{pure iodide 1}} - \delta_{\text{adduct 4 or 5}}$ : **4a**, 0.04 M solution:  $\Delta\delta_{\text{CF}_2\text{I}} = 0.55$ ; 0.09 M solution:  $\Delta\delta_{\text{CF}_2\text{I}} = 0.97$ ; 0.13 M solution:  $\Delta\delta_{\text{CF}_2\text{I}} = 1.24$ . **4b**, 0.04 M solution:  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{I}} = 0.68$ ,  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{I}} = 0.08$ ; 0.07 M solution:  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{I}} = 1.05$ ,  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{I}} = 0.13$ ; 0.12 M solution:  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{I}} = 1.38$ ,  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{I}} = 0.16$ . **4c**, 0.03 M solution:  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.65$ ,  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.06$ ;  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.01$ ; 0.07 M solution:  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 1.05$ ,  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.11$ ;  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.06$ ; 0.10 M solution:  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 1.52$ ,  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.17$ ;  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.08$ . **4d**, 0.03 M solution:  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.59$ ,  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.07$ ;  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.05$ ,  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.04$ ; 0.06 M solution:  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 1.05$ ,  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.13$ ;  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.08$ ,  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.06$ ; 0.10 M solution:  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 1.59$ ,  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.20$ ;  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.11$ ,  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.09$ . **5a**, 0.03 M solution:  $\Delta\delta_{\text{CF}_2\text{I}} = 0.11$ ; 0.13 M solution:  $\Delta\delta_{\text{CF}_2\text{I}} = 0.51$ . **5b**, 0.03 M solution:  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{I}} = 0.10$ ,  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{I}} = 0.01$ ; 0.08 M solution:  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{I}} = 0.27$ ,  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{I}} = 0.03$ . **5c**, 0.02 M solution:  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.10$ ,  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = \Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.00$ ; 0.07 M solution:  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.26$ ,  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.03$ ;  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.02$ . **5d**, 0.02 M solution:  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.03$ ,  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = \Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = \Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.00$ ; 0.03 M solution:  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.10$ ,  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.01$ ;  $\Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = \Delta\delta_{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}} = 0.00$ . It is interesting to observe that at the same molar concentrations, infinite networks **4** derived from secondary amine **2** gives definitely greater  $\Delta\delta$  values than infinite networks **5** derived from tertiary amine **3**. Moreover, in adducts **4b–d** and **5b–d** the shifts of the difluoromethylene groups were progressively decreasing away from the iodine atom, namely the highest shifts were observed for the  $\text{CF}_2\text{I}$  group. This supports the hypothesis that, also in solution, the changes observed in physical and spectral properties of adducts **4** and **5**, compared to pure precursors **1–3**, are not due to 'generic' effects (e.g., those which may be explained in term of non-specific solute–solvent interactions) but can be ascribed to specific  $\text{N}\cdots\text{I}$  interactions.

$^{19}\text{F}$  NMR spectra of highly diluted adducts **4** and **5** cannot be distinguished from those shown by pure precursors **1**, **2**, and **3**. Moreover, on evaporating deuteriochloroform, solids **4** and **5** are re-formed. These observations prove that, on being dissolved, linear non-covalent co-polymers **4** and **5** give rise to the starting free species **1–3**. The irreversible adduct formation reported by Haszeldine between trifluoroiodomethane and trimethylamine was not taking place under our experimental conditions [11]. The interaction existing in the solid state between perfluorinated diiodides **1** and diamines **2**, **3** is reversible and similar in nature to the non-covalent binding described by Cheetham and Pullin [6], Cheetham et al. [7,8], McNaught and Pullin [10], and Larsen and Allred [12]. In solution, perfluorinated diiodides **1** and diamines **2**, **3** enter a rapid association process (driven by the same  $n \rightarrow \sigma^*$  donation from nitrogen to iodine which allows solid co-polymers **4a–d** and **5a–d** to be formed) and dimeric, trimeric, ... adducts are generated reversibly. It thus follows that crystalline materials **4a–d** and **5a–d**, isolated from equimolar mixtures of  $\alpha,\omega$ -diiodoperfluoroalkanes **1** and diamines **2**, **3**, have the structure of the infinite one-dimensional coordination networks reported in Scheme 1.<sup>2</sup>

In general, the  $\text{C}\cdots\text{X}\cdots\text{E}$  interactions have been studied both in the solid, and liquid, and gas phase [1–4]. This is the case also for the dimeric molecular complexes formed by perfluoroalkyl iodides and amines, the strongest interaction being found, as expected, in the solid state [6–8,10]. For this reason we started our detailed study of the infinite networks **4** and **5** performing thermal analyses by differential scanning calorimetry and studying their vibrational spectra (500–3500  $\text{cm}^{-1}$  region, KBr pellet).

Heating curves of iodides **1a–d** and of K.2.2.2. **3** (pure compounds, temperature range 40–270°C, heating rate 10°C·min<sup>-1</sup>) are reported in Fig. 1 and heating curves of infinite networks **5a–d** in the same temperature range and with the same heating rate are reported in Fig. 2.<sup>3</sup> The sharp endotherm with a peak at 73°C shown by the amine **3** and associated with its melting is not present in any network **5** and the same holds for the melting endotherm of diiodoperfluorooctane **1d** (peak at 77°C) which is missing in the curve of **5d**. The curves of infinite networks **5a–d** show a similar trend: on heating the sample, an endotherm is first observed and it is rapidly followed by an exotherm. The two processes are probably associated with the melting of the sample and the successive reaction/decomposition of the melted systems, respectively. It is interesting to observe that infinite networks **5a–d** all melt at temperatures higher than starting amine **3**. For instance, when **3** (m.p. peak 73°C) interacts in

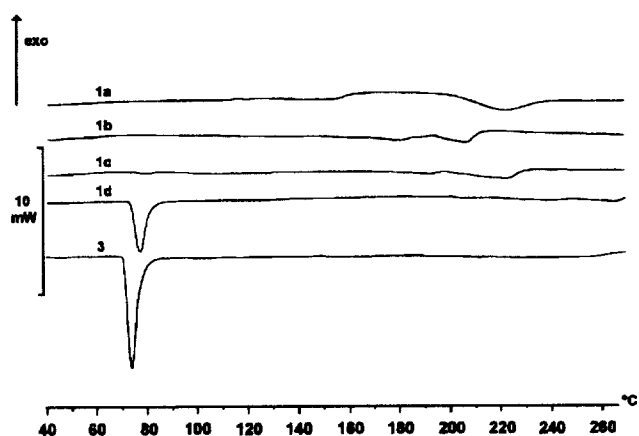


Fig. 1. Heating curves of perfluorodiiodoalkanes **1a–d** and cryptofix 2.2.2., **3**.

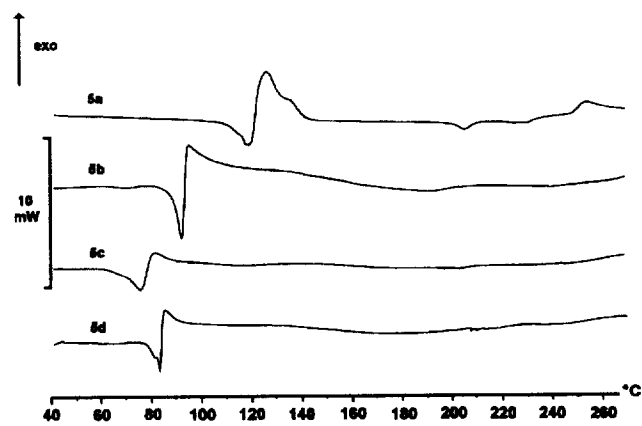


Fig. 2. Heating curves of one-dimensional infinite networks **5a–d**.

a 1:1 ratio with 1,2-diiodotetrafluoroethane **1a**, a liquid which boils at 112–113°C, the formed non-covalent co-polymer **5a** melts showing a peak at 118°C. These thermal behaviours are consistent with the formation of well defined molecular aggregates on interaction of iodides **1** with amine **3**. They also confirm that such an interaction occurs through specific and relatively strong bindings and is not a non-specific association of solvent–solute type.

Finally, it is worth noting that in **5a–c** the melting temperatures decrease with increased length of the fluorinated chain. In contrast, **5d** melts slightly higher than **5c**, but for this copolymer it has to be remembered that **1d** is a solid while **1c** is a liquid.

Because the central  $\text{N}\cdots\text{I}$  interaction is weaker than covalent or ionic bonds, it is reasonable to discuss vibrational spectra of infinite networks **4** and **5** in terms of modified modes of starting iodides **1** and amines **2**, **3**. The validity of the adopted approach is supported by the fact that similar changes of the absorption bands of a given iodide, or amine, were observed on interaction with different amines, or iodides, respectively. In Table 2 we list some of the absorp-

<sup>2</sup> Preliminary results from the X-ray analyses of **5a** definitively support this structural assignment and will be reported shortly.

<sup>3</sup> A heat flux calorimeter DSC 820 Mettler (silver furnace, ceramic sensor with 14 Au–AuPd thermocouples) was used. Samples (2–10 mg) were closed under nitrogen in a steel (CrNi 18 9) crucible. It had been observed that different thermograms were obtained in the presence or absence of air. Probably, oxygen at high temperatures was reacting with the samples. Reported curves have been obtained in the absence of air.

Table 2  
Selected infrared absorption bands of precursors **1–3** which underwent a shift on formation of infinite networks **4 and 5**

<b>2</b>	1353																			
<b>3</b>		2878																		
<b>1a</b>			1159	709	575															
<b>4a</b>	1351		<1152	699	563															
<b>5a</b>		2884	<1124	694																
<b>1b</b>						1196	718	560												
<b>4b</b>	1351					1183	<sup>a</sup>	556												
<b>5b</b>		2884				1183	713	556												
<b>1c</b>									1211	784	697									
<b>4c</b>	1351								1192	783	692									
<b>5c</b>		2886							1206	782	693									
<b>1d</b>																		1207	836	641
<b>4d</b>	1351																	1199	831	627
<b>5d</b>		2887																	831	634

<sup>a</sup> Intensity of the band strongly decreases.

tion bands of  $\alpha,\omega$ -diiodoalkanes **1a–d** and of diamines **2, 3** which underwent a systematic shift on adduct formation. Related bands in infinite networks **4a–d** and **5a–d** are also reported. As to the donor amine, the C–H stretching mode in the 2770–2940  $\text{cm}^{-1}$  region shifts to high frequencies for network **4** and **5** formation. Similar upward shifts on formation of other donor–acceptor adducts have been noticed [13,14], for instance of the dimers given by trimethylamine with  $\text{I}_2$ ,  $\text{Br}_2$ , and  $\text{IBr}$  [15], or of the trimers formed by 1,4-diazabicyclo[2.2.2]octane with boron trihalides [16]. As to the acceptor iodides **1**, among other absorptions, the C–F stretching modes in the 1150–1220  $\text{cm}^{-1}$  region move to lower frequencies. Similarly, it has been described that the complex formation between iodotrifluoromethane and various trialkylamines caused a downward shift of the C–F band at 1170 ca. both in the solid phase (80 K) and solution ( $\text{CCl}_4$ ) [8].

The formation of one-dimensional coordination networks between perfluorinated diiodides **1** and other hydrocarbon diamines and the ability of  $\alpha,\omega$ -dibromoperfluorocarbons to behave in a way similar to diiodides **1** is under active study.

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