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Synthesis of new nitrogen-containing perfluoroalkyl iodides

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Abstract

Perfluoro(dimethylamino)-, perfluoro(diethylamino)-, perfluoro(1-pyrrolidinyl)-, perfluoromorpholino-, perfluoropiperidino- and perfluoropropoxy-substituted perfluoroalkyl iodides were synthesized directly by the reaction of the corresponding perfluoroacyl fluorides with lithium iodide in high yield. Under controlled reaction conditions, it was possible to synthesize either iodo-perfluoroacyl fluorides or perfluoroalkylidene diiodides by the reaction of perfluoro(alkanedioyl) difluorides with lithium iodide. Perfluoro(α-alkylamino-substituted alkyl) iodides may be good candidates for the media of solar-pumped lasers. © 1997 Elsevier Science S.A.

Keywords: Alkyl iodide; Lithium iodide; Solar-pumped laser

1. Introduction

Perfluoroalkyl groups give rise to unique properties such as excellent low surface energy and high electronegativity. Thus the introduction of a perfluoroalkyl group into a molecule often brings about a dramatic change in its properties. Perfluoroalkyl iodides are useful perfluoroalkylating reagents because they have a weak carbon–iodine bond [1]. Perfluoroalkyl iodides have generally been prepared either by the reaction of perfluoroolefins with "iodine fluoride" [2] or by the pyrolytic reaction of silver salts of perfluorocarboxylic acids in the presence of iodine [3]. The method involving the reaction of perfluoroacyl chloride with potassium iodide has also been reported [4].

We have found a new convenient method for the preparation of perfluoroalkyl iodides which consists of the direct conversion of acyl fluorides into alkyl iodides by the reaction with lithium iodide (Scheme 1) [5]. The requisite perfluoroacyl fluorides, which contain a perfluoroalkylamino group, are easily available by electrochemical fluorination [6] or oligomerization of hexafluoropropene oxide [7].

Perfluoroalkyl iodides can also be used as the media of solar-pumped iodine lasers [8]. Among them, the perfluoro-*t*-butyl iodide (PTBI) has been considered to be the best for two reasons [8c]: first, the absorption peak is shifted toward the red; second, the dimerization of perfluoroalkyl radicals formed is greatly inhibited. Here we report that some nitrogen-containing perfluoroalkyl iodides are suitable for the media of solar-pumped iodine lasers because they satisfy the two reasons mentioned above.

2. Results and discussion

Nitrogen-containing perfluoroalkyl iodides **1–5** were synthesized by the reaction of perfluoroacyl fluorides with lithium iodides in good yields (Table 1). Partially fluorinated alkyl iodide **6-I** was also obtained by the same method. Table 2 shows the results of the reaction of perfluoroacyl halides with various alkali iodides. Perfluoroalkyl iodides were obtained in excellent yields by the reaction of perfluoroacyl fluoride **1d-COF**, **3c-COF** and **3d-COF** with lithium iodide (runs 1, 4 and 7). The reactions of perfluoroacyl chlorides **3c-COCl** and **3d-COCl** with potassium iodide were also successful in moderate yields (runs 6 and 8), although those of perfluoroacyl fluorides **1d-COF** and **3c-COF** with sodium or potassium iodide failed (runs 2, 3 and 5). Thus perfluoroalkyl iodides were synthesized successfully from perfluoroacyl fluorides only with lithium iodide among the alkali metal iodides. This reaction proceeds via formation of perfluoroacyl iodide [9], in which the interaction between lithium and acid fluorine may be important in the halogen exchange process of acyl halides (Scheme 2).

Under controlled reaction conditions, it was possible to synthesize either perfluoro(iodoacyl) fluorides or perfluoroalkylidene diiodides by the reaction of perfluoro(alkanedioyl) difluorides with lithium iodide (Scheme 3). For example, by using an excess of lithium iodide perfluo-

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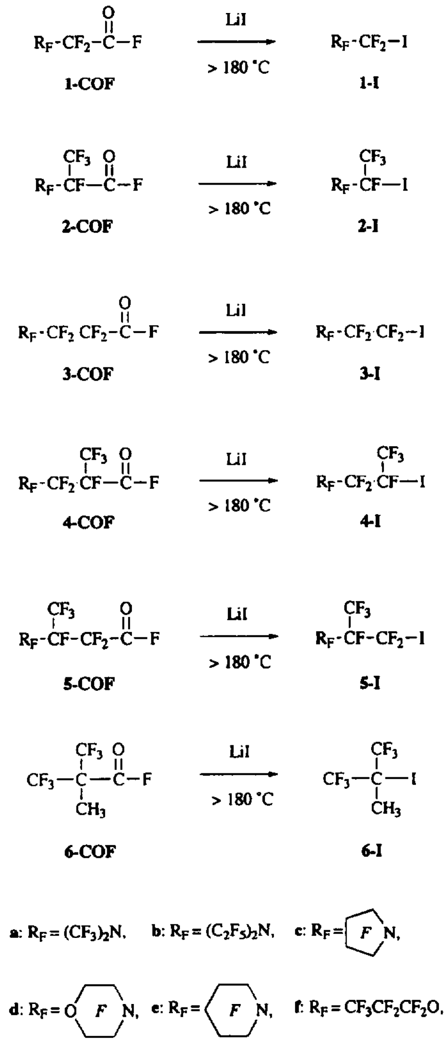
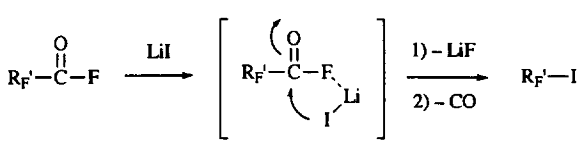


Scheme 1.



Scheme 2.

roalkylidene diiodide **7** was obtained in 72% yield, while by using an equimolar amount of lithium iodide iodo-perfluoroacyl fluoride **8** was obtained in 50% yield. Perfluoro-(iodoacyl) fluorides should be useful synthetic intermediates because they have two different functional groups. This acyl fluoride group can be further converted to another acyl halide group [9].

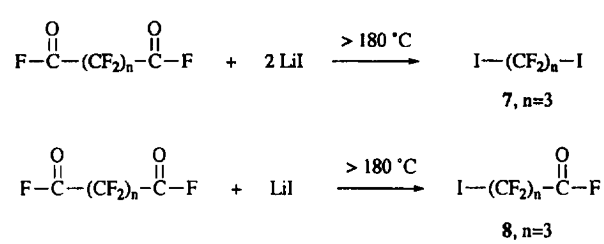
Table 3 shows the UV data of nitrogen-containing perfluoroalkyl iodides **1** and **2** together with that of PTBI. It is generally found that the wavelength of maximum absorbance is in the following increasing order: primary < secondary < tertiary iodide. However, those of N-containing perfluoroalkyl iodides, in spite of being primary or secondary iodides, are comparable to that reported for the tertiary iodides [8e]. Moreover, their molar absorption coefficients are larger than that of PTBI, which means that N-containing perfluoroalkyl

Table 1
Synthesis of perfluoroalkyl iodides

R_FCOF		LiI (mmol)	T (°C)	t (h)	Conv. (%)	Yield (%)
	mmol					
1a-COF	23.6	34.7	180	7.25	80	74
1c-COF	13.8	15.8	180	6.5	~100	38
1d-COF	12.9	15.0	180	6.5	~100	69
1e-COF	6.39	11.0	180	6.5	~100	59
2a-COF	12.6	24.8	180	7.25	77	63
2c-COF	8.89	13.1	200	6.0	~100	64
2d-COF	8.07	13.6	180	6.5	~100	50
2e-COF	9.19	12.2	180	6.5	75	59
2f-COF	5.42	7.3	180	6.5	~100	79
3a-COF	12.5	25.1	200	6.0	~100	90
3b-COF	7.95	12.7	180	17.75	~100	72
3c-COF	11.4	13.8	180	5.5	~100	73
3d-COF	12.0	13.4	180	6.5	~100	86
3f-COF	4.76	7.17	180	7.25	91	71
4b-COF	7.89	11.4	180	6.5	~100	63
4c-COF	9.07	12.2	180	6.5	~100	67
4d-COF	9.11	12.0	180	6.5	~100	76
5d-COF	6.67	12.0	180	6.5	~100	34
6-COF	9.57	12.0	180	7.0	~100	78

Table 2
Reaction of perfluoroacyl halides with alkali iodides

Run	Acyl halides		Alkali iodides		Yields (%)
		mmol		mmol	
1	**1d-COF**	12.9	LiI	15.0	69
2	**1d-COF**	0.780	NaI	3.47	0
3	**1d-COF**	0.737	KI	2.91	0
4	**3c-COF**	11.4	LiI	13.8	73
5	**3c-COF**	22.2	NaI	27.7	6
6	**3c-COCl**	26.5	KI	24.1	50
7	**3d-COF**	12.0	LiI	13.4	86
8	**3d-COCl**	25.4	KI	25.4	59



Scheme 3.

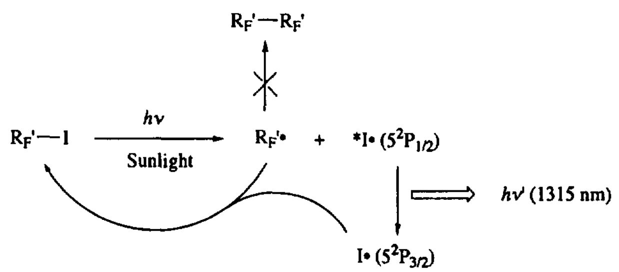
iodides are more effective in photo-absorption than PTBI for use in solar-pumped lasers.

The photolytic dissociation of perfluoroalkyl iodides leads to substantial formation of electronically excited iodine [I* ($5^2P_{1/2}$)], which brings an inversion of the population to the ground-state iodine [I ($5^2P_{3/2}$)] (Scheme 4). And then laser action occurs on the transition,

$$I^* \rightarrow I + h\nu \ (1315 \text{ nm})$$

Table 3
UV data of perfluoroalkyl iodides

Iodides	λ_{max} (nm)	ϵ_{max} ($dm^3mol^{-1}cm^{-1}$)
1c-I	282	268
1d-I	283	270
1e-I	282	273
2a-I	284	276
2c-I	284	301
2d-I	288	265
2e-I	293	251
$(CF_3)_3CI$	287	199



Scheme 4.

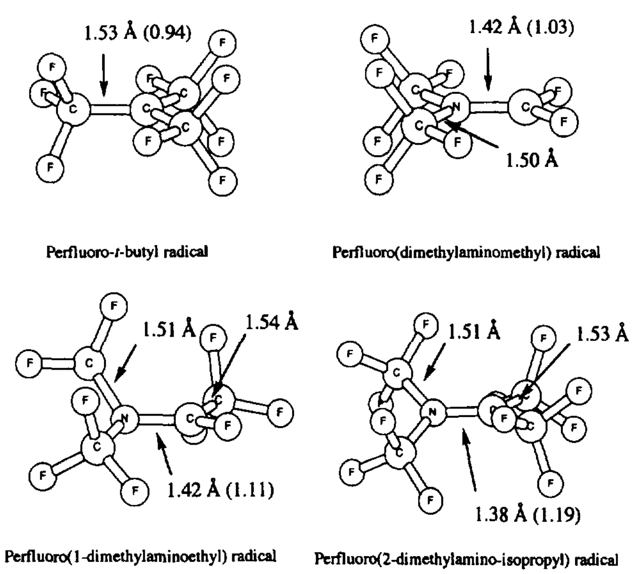


Fig. 1. Optimized structures of perfluoroalkyl radicals by MOPAC [10]. The values in parentheses are bond orders.

For effective cyclic laser action, it is important that the recombination of perfluoroalkyl radical ($R_F'\cdot$) and ground-state iodine occur selectively. For this to happen, the dimerization of $R_F'\cdot$ must be greatly inhibited. Fig. 1 shows the optimized structures of the perfluoro-*t*-butyl radical and nitrogen-containing perfluoroalkyl radicals by PM3 method using the MOPAC program [10]. The bond length between the radical carbon and nitrogen (1.38–1.42 Å) is shortened as compared with the CF_3–N bond (1.50–1.51 Å), which would be caused by the interaction between the lone pair of nitrogen and the singly occupied orbital of the radical carbon (Fig. 2). This interaction results in a doubly occupied π orbital and a singly occupied $\pi*$ orbital, which is a totally bonding interaction between the radical carbon and nitrogen. Furthermore, in the

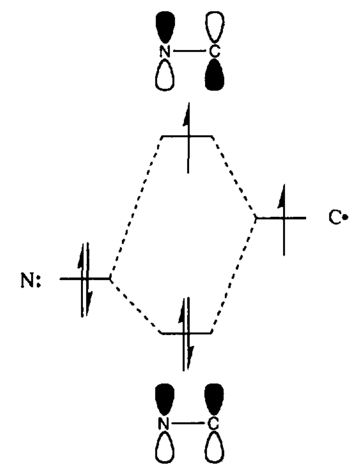


Fig. 2. The interaction between lone pairs of nitrogen and singly occupied orbitals of radical carbon.

perfluorodimethylamino ethyl or isopropyl radicals, the groups are out of plane to avoid repulsion between trifluoromethyl groups attached to the nitrogen and to the radical carbon (Fig. 1). Thus, the dimerizations of these two radicals are greatly inhibited relative to that of the perfluoro-*t*-butyl radical because the perfluoroalkylamino groups shield the radical center. We believe that perfluoro(α-alkylamino-substituted alkyl) iodides, which are close to the ideal medium for a solar-pumped laser, will stimulate a further development in this field.

3. Experimental

3.1. Reagents

All nitrogen-containing perfluoroacyl fluorides used were synthesized by electrochemical fluorination of corresponding methyl esters of alkylamino-substituted carboxylic acids [6], and fractionally distilled from dry sodium fluoride. Anhydrous lithium iodide (Aldrich) was handled in a dry nitrogen atmosphere and dried further by heating under vacuum before use.

3.2. General procedures

A conventional vacuum system, consisting of a Pyrex glass vacuum line equipped with Heise Bourdon tube, was used to handle gases and volatile liquids. Standard PVT techniques or direct weighing were used for quantitative starting materials or products. Fractional condensation (trap-to-trap distillation) or gas chromatography was used for the purification of products. Analytical GLC work was carried out with a Gasukuro LL-75 modified gas chromatograph using 3 mm diameter stainless steel columns packed with 25% Kel-F 90 on chromosorb PAW. The carrier gas was helium in all cases. Infrared spectra were recorded on a Hitachi EPI-G3 spectrometer with a 7 cm glass cell equipped with KBr windows. ^1H and ^{19}F NMR spectra were obtained on a Hitachi R-90H spectrometer using $CDCl_3$ as a solvent. Chemical shifts for ^1H and ^{19}F NMR spectra are reported with respect to $(CH_3)_4Si$ and $CFCl_3$, respectively, J values being given in Hz.

3.3. Perfluoro(dimethylaminomethyl) iodide **1a-I** [5]

A mixture of lithium iodide (4.64 g, 34.7 mmol) and perfluoro(dimethylaminoacetyl) fluoride **1a-COF** (23.6 mmol) was heated at 180 °C for 7.25 h in a stainless steel reactor. 74% yield (80% conversion); b.p. 56.5–57.0 °C; n_D^{20} 1.3310; d_4^{20} 2.0685 g cm^{-3} (Found: C, 11.16. Calc. for C_3F_8IN: C, 10.96%); δ_F(85 MHz; $CDCl_3$) −19.8 (2F, sept., J 13.4, CF_2), −54.6 (6F, t, J 13.4, CF_3); ν_{max}(gas)/cm^{-1} 1349vs, 1317s, 1266, 1216s, 1156w, 1052, 996, 843, 761, 731; m/z 310 (0.4%, M^+–F), 202 (94%, M^+–I), 177 (51%, CF_2I^+), 127 (34%, I^+), 114 (31%, $C_2F_4N^+$), 69 (100%, CF_3^+).

3.4. Perfluoro(1-pyrrolidinylmethyl) iodide **1c-I** (nc)

A mixture of lithium iodide (2.11 g, 15.8 mmol) and perfluoro(1-pyrrolidinylacetyl) fluoride **1c-COF** (13.8 mmol) was heated at 180 °C for 6.5 h in a stainless steel reactor. 38% yield; b.p. 99.5–100.5 °C; n_D^{20} 1.3500; d_4^{20} 2.0946 g cm^{-3} (Found: C, 15.61. Calc. for $C_5F_{10}IN$: C, 15.36%); δ_F(85 MHz; $CDCl_3$) −20.3 (2F, quint., J 9.1, CF_2), −93.3 (4F, t, J 9.1, –CF_2–$\underline{CF_2}$–N–), −133.4 (4F, s, –$\underline{CF_2}$–CF_2–N–); ν_{max}(liq)/cm^{-1} 1344s, 1332s, 1299, 1247s, 1215s, 1170, 1130, 1037, 970vs, 872w, 775; λ_{max}(hexane)/nm 282 (ϵ/dm^3 mol^{-1} cm^{-1} 268); m/z 372 (10%, M^+ − F), 264 (19%, M^+–I), 177 (64%, CF_2I^+), 127 (37%, I^+), 114 (78%, $C_2F_4N^+$), 69 (100%, CF_3^+).

3.5. Perfluoro(morpholinomethyl) iodide **1d-I** [5]

A mixture of lithium iodide (2.01 g, 15.0 mmol) and perfluoro(morpholinoacetyl) fluoride **1d-COF** (12.9 mmol) was heated at 180 °C for 6.5 h in a stainless steel reactor. 69% yield; b.p. 108.0–109.0 °C; n_D^{20} 1.3522; d_4^{20} 2.1211 g cm^{-3} (Found: C, 14.51. Calc. for $C_5F_{10}INO$: C, 14.76%); δ_F(85 MHz; $CDCl_3$) −17.9 (2F, quint., J 15.9, CF_2), −92.3 (4F, t, J 15.9, –O–CF_2–$\underline{CF_2}$–N–), −85.4 (4F, s, –O–$\underline{CF_2}$–CF_2–N–); ν_{max}(liq)/cm^{-1} 1332, 1293s, 1220vs, 1186s, 1167s, 1140s, 1085, 997, 930, 772; λ_{max}(hexane)/nm 283 (ϵ/dm^3 mol^{-1} cm^{-1} 270); m/z 388 (1.4%, M^+–F), 280 (70%, M^+–I), 177 (41%, CF_2I^+), 127 (23%, I^+), 114 (100%, $C_2F_4N^+$), 69 (37%, CF_3^+).

3.6. Perfluoro(piperidinomethyl) iodide **1e-I** [5]

A mixture of lithium iodide (1.47 g, 11.0 mmol) and perfluoro(piperidinoacetyl) fluoride **1e-COF** (6.39 mmol) was heated at 180 °C for 6.5 h in a stainless steel reactor. 59% yield; b.p. 121.5–122.5 °C; n_D^{20} 1.3501; d_4^{20} 2.1112 g cm^{-3} (Found: C, 16.23. Calc. for $C_6F_{12}IN$: C, 16.34%); δ_F(85 MHz; $CDCl_3$) −17.8 (2F, quint., J 19.0, CF_2), −91.4 (4F, t, J 19.0, –CF_2–CF_2–$\underline{CF_2}$–N–), −132.2 (4F, s, –CF_2–$\underline{CF_2}$–CF_2–N–), −134.6 (2F, s, –$\underline{CF_2}$–CF_2–CF_2–N–); ν_{max}(liq)/cm^{-1} 1369, 1348, 1310s, 1264, 1232, 1201s, 1186s, 1148, 1097, 1066, 1024, 970s, 763; λ_{max}(hexane)/nm 282 (ϵ/dm^3 mol^{-1} cm^{-1} 273); m/z 422 (6%, M^+–F), 314 (93%, M^+–I), 177 (63%, CF_2I^+), 114 (56%, $C_2F_4N^+$), 69 (100%, CF_3^+).

3.7. Perfluoro(1-dimethylaminoethyl) iodide **2a-I** [5]

A mixture of lithium iodide (3.32 g, 24.8 mmol) and perfluoro(2-dimethylaminopropionyl) fluoride **2a-COF** (12.6 mmol) was heated at 180 °C for 7.25 h in a stainless steel reactor. 63% yield (77% conversion); b.p. 79.5–80.5 °C; n_D^{20} 1.3365; d_4^{20} 2.1023 g cm^{-3} (Found: C, 12.37. Calc. for $C_4F_{10}IN$: C, 12.68%); δ_F(85 MHz; $CDCl_3$) −52.1 {6F, m, $(CF_3)_2N$}, −80.3 (3F, m, $\underline{CF_3}$–CFI), −112.4 (1F, m, CF_3–$\underline{CF}$I); ν_{max}(gas)/cm^{-1} 1346vs, 1310vs, 1273s, 1242s, 1213s, 1170w, 1135w, 993, 893, 832, 760, 730, 714; λ_{max}(hexane)/nm 284 (ϵ/dm^3 mol^{-1} cm^{-1} 276); m/z 379 (5%, M^+), 252 (28%, M^+–I), 227 (30%, $C_2F_4I^+$), 164 (28%, $C_3F_6N^+$), 114 (39%, $C_2F_4N^+$), 69 (100%, CF_3^+).

3.8. Perfluoro[1-(1-pyrrolidinyl)ethyl] iodide **2c-I** [5]

A mixture of lithium iodide (1.76 g, 13.1 mmol) and perfluoro[(2-(1-pyrrolidinyl)propionyl] fluoride **2c-COF** (8.89 mmol) was heated at 200 °C for 6.0 h in a stainless steel reactor. 64% yield; b.p. 115.0–116.0 °C; n_D^{20} 1.3508; d_4^{20} 2.1111 g cm^{-3} (Found: C, 16.13. Calc. for $C_6F_{12}IN$: C, 16.34%); δ_F(85 MHz; $CDCl_3$) −80.7 (3F, m, $\underline{CF_3}$–CFI), −90.6 (2F, J_{AB} 171.2, –CF_2–$\underline{CF_2}$–N–), −93.0 (2F, J_{AB} 171.2, –CF_2–$\underline{CF_2}$–N–), −112.2 (1F, m, CF_3–$\underline{CF}$I), −133.5 (4F, s, –$\underline{CF_2}$–CF_2–N–); ν_{max}(liq)/cm^{-1} 1335, 1307, 1264, 1217vs, 1165, 1126, 1067, 1013, 971s, 884, 758, 709, 670; λ_{max}(hexane)/nm 284 (ϵ/dm^3 mol^{-1} cm^{-1} 301); m/z 422 (0.2%, M^+–F), 314 (39%, M^+–I), 227 (16%, $C_2F_4I^+$), 164 (12%, $C_3F_6N^+$), 145 (60%, $C_3F_5N^+$), 131 (14%, $C_3F_5^+$), 127 (100%, I^+), 126 (36%, $C_3F_4N^+$), 119 (20%, $C_2F_5^+$), 114 (13%, $C_2F_4N^+$), 100 (22%, $C_2F_4^+$), 69 (52%, CF_3^+).

3.9. Perfluoro(1-morpholinoethyl) iodide **2d-I** [5]

A mixture of lithium iodide (1.82 g, 13.6 mmol) and perfluoro(2-morpholinopropionyl) fluoride **2d-COF** (8.07 mmol) was heated at 180 °C for 6.5 h in a stainless steel reactor. 50% yield; b.p. 128.0–129.0 °C; n_D^{20} 1.3524; d_4^{20} 2.1264 g cm^{-3} (Found: C, 15.51. Calc. for $C_6F_{12}INO$: C, 15.77%); δ_F(85 MHz; $CDCl_3$) −81.7 (3F, m, $\underline{CF_3}$–CFI), −85.7 (4F, s, –O–$\underline{CF_2}$–CF_2–N–), −87.3 (2F, J_{AB} 193.5, –O–CF_2–$\underline{CF_2}$–N–), −92.8 (2F, J_{AB} 193.5, –O–CF_2–$\underline{CF_2}$–N–), −111.1 (1F, m, CF_3–$\underline{CF}$I); ν_{max}(liq)/cm^{-1} 1329, 1303, 1287, 1260, 1210br, 1174, 1134, 1119, 1080, 1018, 930, 875, 758, 719; λ_{max}(hexane)/nm 288 (ϵ/dm^3 mol^{-1} cm^{-1} 265);

m/z 457 (0.2%, M^+), 438 (0.1%, M^+–F), 388 (0.2%, M^+–CF_3), 330 (38%, M^+–I), 227 (21%, $C_2F_4I^+$), 164 (46%, $C_3F_6N^+$), 145 (21%, $C_3F_5N^+$), 127 (11%, I^+), 126 (4%, $C_3F_4N^+$), 119 (100%, $C_2F_5^+$), 114 (24%, $C_2F_4N^+$), 100 (44%, $C_2F_4^+$), 69 (37%, CF_3^+).

*3.10. Perfluoro(1-piperidinoethyl) iodide **2e-I** [5]*

A mixture of lithium iodide (1.63 g, 12.2 mmol) and perfluoro(2-piperidinopropionyl) fluoride **2e-COF** (9.19 mmol) was heated at 180 °C for 6.5 h in a stainless steel reactor. 59% yield (75% conversion); b.p. 140.0–142.0 °C; n_D^{20} 1.3527; d_4^{20} 2.1313 g cm^{-3} (Found: C, 16.72. Calc. for $C_7F_{14}IN$: C, 17.13%); δ_F(85 MHz; $CDCl_3$) −82.3 (3F, m, $C\underline{F}_3$–CFI), −84.9 (2F, J_{AB} 206.5, –CF_2–CF_2–$C\underline{F}_2$–N–), −93.4 (2F, J_{AB} 206.5, –CF_2–CF_2–$C\underline{F}_2$–N–), −108.4 (1F, m, CF_3–$C\underline{F}$I), −131.5 (4F, s, –CF_2–$C\underline{F}_2$–CF_2–N–), −134.6 (2F, s, –$C\underline{F}_2$–CF_2–CF_2–N–); ν_{max}(liq)/cm^{-1} 1351, 1299, 1266s, 1232s, 1212s, 1206s, 1193vs, 1173, 1144s, 1127, 1096, 1063, 1044, 996, 970s, 889, 848, 758, 712, 655, 636; λ_{max}(hexane)/nm 293 (ϵ/dm^3 mol^{-1} cm^{-1} 251); m/z 472 (0.2%, M^+–F), 422 (0.4%, M^+–CF_3), 364 (42%, M^+–I), 227 (25%, $C_2F_4I^+$), 164 (31%, $C_3F_6N^+$), 131 (57%, $C_3F_5^+$), 127 (11%, I^+), 126 (8%, $C_3F_4N^+$), 119 (33%, $C_2F_5^+$), 114 (24%, $C_2F_4N^+$), 100 (35%, $C_2F_4^+$), 69 (100%, CF_3^+).

*3.11. Perfluoro(1-propoxyethyl) iodide **2f-I** [11]*

A mixture of lithium iodide (0.98 g, 7.3 mmol) and perfluoro(2-propoxypropionyl) fluoride **2f-COF** (5.42 mmol) was heated at 180 °C for 6.5 h in a Pyrex tube. 79% yield; b.p. 84.0–85.0 °C; n_D^{20} 1.3153; d_4^{20} 1.9859 g cm^{-3} (Found: C, 14.56. Calc. for $C_5F_{11}IO$: C, 14.58%); δ_F(85 MHz; $CDCl_3$) −84.5 (3F, d, J 7.5, $C\underline{F}_3$–CFI), ~ −83 (2F, AA'BB', CF_3–CF_2–$C\underline{F}_2$–O–), ~ −90 (2F, AA'BB', CF_3–CF_2–$C\underline{F}_2$–O–), −75.8 (1F, m, CF_3–$C\underline{F}$I), −81.8 (3F, m, $C\underline{F}_3$–CF_2–CF_2–O–), −130.5 (2F, s, CF_3–$C\underline{F}_2$–CF_2–O–); ν_{max}(gas)/cm^{-1} 1342, 1309, 1244vs, 1228, 1209, 1154s, 1109, 1081, 997, 927, 911, 808, 755, 741.

*3.12. Perfluoro(2-dimethylaminoethyl) iodide **3a-I** [5]*

A mixture of lithium iodide (3.36 g, 25.1 mmol) and perfluoro(3-dimethylaminopropionyl) fluoride **3a-COF** (12.5 mmol) was heated at 200 °C for 6.0 h in a stainless steel reactor. 90% yield; b.p. 81.0–82.5 °C; n_D^{20} 1.3317; d_4^{20} 2.0809 g cm^{-3} (Found: C, 12.79. Calc. for $C_4F_{10}IN$: C, 12.68%); δ_F(85 MHz; $CDCl_3$) −52.7 (6F, m, CF_3), −61.2 (2F, m, –CF_2–$C\underline{F}_2$–I), −88.4 (2F, m, –$C\underline{F}_2$–CF_2–I); ν_{max}(liq)/cm^{-1} 1351vs, 1271, 1219vs, 1155, 1104, 994, 955w, 857w, 806, 754s, 730, 684w; m/z 379 (7%, M^+), 360 (0.1%, M^+–F), 252 (30%, M^+–I), 227 (39%, $C_2F_4I^+$), 202 {54%, $(CF_3)_2NCF_2^+$}, 177 (15%, CF_2I^+), 164 (27%, $C_3F_6N^+$), 127 (17%, I^+), 114 (41%, $C_2F_4N^+$), 100 (21%, $C_2F_4^+$), 69 (100%, CF_3^+).

*3.13. Perfluoro(2-diethylaminoethyl) iodide **3b-I** [5]*

A mixture of lithium iodide (1.70 g, 12.7 mmol) and perfluoro(3-diethylaminopropionyl) fluoride **3b-COF** (7.95 mmol) was heated at 180 °C for 17.75 h in a stainless steel reactor. 72% yield; b.p. 125.5–126.5 °C; n_D^{20} 1.3344; d_4^{20} 2.0914 g cm^{-3} (Found: C, 14.56. Calc. for $C_6F_{14}IN$: C, 15.05%); δ_F(85 MHz; $CDCl_3$) −58.3 (–CF_2–$C\underline{F}_2$–I), −80.7 {$(C\underline{F}_3CF_2)_2N$}, −80.8 (–$C\underline{F}_2$–$CF_2$–I), −88.8 {$(CF_3C\underline{F}_2)_2N$}; ν_{max}(liq)/cm^{-1} 1282, 1228, 1148, 1102, 1059, 876, 780, 746; λ_{max}(hexane)/nm 272 (ϵ/dm^3 mol^{-1} cm^{-1} 257); m/z 479 (0.2%, M^+), 352 (3%, M^+–I), 227 (24%, $C_2F_4I^+$), 214 (25%, $C_4F_8N^+$), 177 (9%, CF_2I^+), 164 (9%, $C_3F_6N^+$), 127 (6%, I^+), 119 (100%, $C_2F_5^+$), 114 (7%, $C_2F_4N^+$), 100 (19%, $C_2F_4^+$), 69 (24%, CF_3^+).

*3.14. Perfluoro[(2-(1-pyrrolidinyl)ethyl] iodide **3c-I** [5]*

A mixture of lithium iodide (1.85 g, 13.8 mmol) and perfluoro[(3-(1-pyrrolidinyl)propionyl] fluoride **3c-COF** (11.4 mmol) was heated at 180 °C for 5.5 h in a stainless steel reactor. 73% yield; b.p. 116.0–117.5 °C; n_D^{20} 1.3461; d_4^{20} 2.0920 g cm^{-3} (Found: C, 16.36. Calc. for $C_6F_{12}IN$: C, 16.34%); δ_F(85 MHz; $CDCl_3$) −62.3 (2F, m, –CF_2–$C\underline{F}_2$–I), −89.5 (2F, m, –$C\underline{F}_2$–CF_2–I), −90.8 (4F, m, –CF_2–$C\underline{F}_2$–N–), −133.2 (4F, s, –$C\underline{F}_2$–CF_2–N–); ν_{max}(liq)/cm^{-1} 1343vs, 1308, 1268, 1217s, 1164s, 1123, 1091, 1031, 974s, 910, 871, 788, 751s; λ_{max}(hexane)/nm 272 (ϵ/dm^3 mol^{-1} cm^{-1} 246); m/z 441 (11%, M^+), 422 (0.8%, M^+–F), 314 (83%, M^+–I), 264 (50%, M^+–CF_2I), 227 (69%, $C_2F_4I^+$), 214 (26%, M^+–C_2F_4I), 177 (29%, CF_2I^+), 176 (41%, $C_4F_6N^+$), 127 (23%, I^+), 119 (100%, $C_2F_5^+$), 114 (41%, $C_2F_4N^+$), 100 (62%, $C_2F_4^+$), 69 (87%, CF_3^+).

*3.15. Perfluoro(2-morpholinoethyl) iodide **3d-I** [5]*

A mixture of lithium iodide (1.80 g, 13.4 mmol) and perfluoro(3-morpholinopropionyl) fluoride **3d-COF** (12.0 mmol) was heated at 180 °C for 6.5 h in a stainless steel reactor. 86% yield; b.p. 131.0–132.0 °C; n_D^{20} 1.3474; d_4^{20} 2.1085 g cm^{-3} (Found: C, 15.35. Calc. for $C_6F_{12}INO$: C, 15.77%); δ_F(85 MHz; $CDCl_3$) −62.7 (2F, m, –CF_2–$C\underline{F}_2$–I), −87.5 (4F, s, –O–$C\underline{F}_2$–CF_2–N–), −87.9 (2F, m, –$C\underline{F}_2$–CF_2–I), −92.6 (4F, m, –O–CF_2–$C\underline{F}_2$–N–); ν_{max}(liq)/cm^{-1} 1346, 1306, 1294, 1261, 1218s, 1188, 1162s, 1141, 1079, 930, 909, 757, 661, 627; λ_{max}(hexane)/nm 268 (ϵ/dm^3 mol^{-1} cm^{-1} 259); m/z 457 (3%, M^+), 438 (0.1%, M^+–F), 388 (0.1%, M^+–CF_3), 330 (24%, M^+–I), 280 (5%, M^+–CF_2I), 227 (33%, $C_2F_4I^+$), 164 (19%, $C_3F_6N^+$), 119 (100%, $C_2F_5^+$), 114 (42%, $C_2F_4N^+$), 100 (38%, $C_2F_4^+$), 69 (25%, CF_3^+).

*3.16. Perfluoro(2-piperidinoethyl) iodide **3e-I** (nc)*

B.p. 143.0–144.0 °C; n_D^{20} 1.3459; d_4^{20} 2.1071 g cm^{-3} (Found: C, 16.46. Calc. for $C_7F_{14}IN$: C, 17.13%); δ_F(85

MHz; $CDCl_3$) −62.6 (2F, $-CF_2-\underline{CF_2}-I$), −86.7 (2F, $-\underline{CF_2}-CF_2-I$), −91.4 (4F, $-CF_2-CF_2-\underline{CF_2}-N-$), −132.3 (4F, $-CF_2-\underline{CF_2}-CF_2-N-$), −134.6 (2F, $-\underline{CF_2}-CF_2-CF_2-N-$); ν_{max}(liq)/cm^{-1} 1368, 1346, 1324s, 1271s, 1232, 1207s, 1187s, 1161s, 1126, 1084, 1067, 1020, 970, 906, 748, 648, 634; λ_{max}(hexane)/nm 270 (ϵ/dm^3 mol^{-1} cm^{-1} 261); m/z 491 (46%, M^+), 472 (0.2%, M^+–F), 422 (0.3%, M^+-CF_3), 364 (37%, M^+–I), 314 (12%, M^+-CF_2I), 264 (8%, $M^+-C_2F_4I$), 227 (65%, $C_2F_4I^+$), 226 (30%, $C_5F_8N^+$), 177 (20%, CF_2I^+), 176 (10%, $C_4F_6N^+$), 131 (13%, $C_3F_5^+$), 127 (13%, I^+), 119 (100%, $C_2F_5^+$), 114 (25%, $C_2F_4N^+$), 100 (48%, $C_2F_4^+$), 69 (58%, CF_3^+).

3.17. *Perfluoro(2-propoxyethyl) iodide* ***3f-I*** *[12]*

A mixture of lithium iodide (0.96 g, 7.17 mmol) and perfluoro(3-propoxypropionyl) fluoride **3f-COF** (4.76 mmol) was heated at 180 °C for 7.25 h in a Pyrex tube. 71% yield (91% conversion); b.p. 84.5–85.5 °C; n_D^{20} 1.3120; d_4^{20} 1.9759 g cm^{-3} (Found: C, 14.42. Calc. for $C_5F_{11}IO$: C, 14.58%); δ_F(85 MHz; $CDCl_3$) −65.6 (2F, t, J 5.6, $-CF_2-\underline{CF_2}-I$), −85.1 (2F, m, $-\underline{CF_2}-O-$), −86.1 (2F, m, $-\underline{CF_2}-O-$), −81.7 (3F, t, J 7.2, CF_3), −130.3 (2F, s, $CF_3-\underline{CF_2}$); ν_{max}(liq)/cm^{-1} 1352, 1308s, 1250vs, 1211s, 1164s, 1129s, 1104, 1004s, 919, 780w, 740, 714; m/z 412 (16%, M^+), 285 (0.2%, M^+–I), 227 (48%, $C_2F_4I^+$), 177 (25%, CF_2I^+), 169 (36%, $C_3F_7^+$), 147 (25%, $C_3F_5O^+$), 127 (19%, I^+), 119 (97%, $C_2F_5^+$), 100 (37%, $C_2F_4^+$), 69 (100%, CF_3^+).

3.18. *Perfluoro(2-diethylamino-1-methylethyl) iodide* ***4b-I*** *[5]*

A mixture of lithium iodide (1.53 g, 11.4 mmol) and perfluoro(3-diethylamino-2-methylpropionyl) fluoride **4b-COF** (7.89 mmol) was heated at 180 °C for 6.5 h in a stainless steel reactor. 63% yield; b.p. 138.5–140.5 °C; n_D^{20} 1.3351; d_4^{20} 2.1230 g cm^{-3} (Found: C, 15.20. Calc. for $C_7F_{16}IN$: C, 15.90%); δ_F(85 MHz; $CDCl_3$) −71.5 {1F, J_{AB} 240.6, $-\underline{CF_2}-CF(CF_3)-I$}, −73.7 (3F, $\underline{CF_3}-CFI$), −78.7 {1F, J_{AB} 240.6, $-\underline{CF_2}-CF(CF_3)-I$}, −80.0 {6F, $(\underline{CF_3}CF_2)_2N-$}, −88.2 {4F, $(CF_3\underline{CF_2})_2N-$}, −139.5 (1F, $CF_3-\underline{CF}I$); ν_{max}(liq)/cm^{-1} 1283, 1228, 1140, 1094, 1062, 892, 875, 745; λ_{max}(hexane)/nm 278 (ϵ/dm^3 mol^{-1} cm^{-1} 220); m/z 529 (2%, M^+), 402 (0.2%, M^+-I), 277 (17%, $C_3F_6I^+$), 227 (3%, $C_2F_4I^+$), 214 (28%, $C_4F_8N^+$), 195 (22%, $C_4F_7N^+$), 177 (5%, CF_2I^+), 164 (26%, $C_3F_6N^+$), 150 (26%, $C_3F_6^+$), 131 (30%, $C_3F_5^+$), 127 (10%, I^+), 119 (100%, $C_2F_5^+$), 114 (13%, $C_2F_4N^+$), 100 (16%, $C_2F_4^+$), 69 (61%, CF_3^+).

3.19. *Perfluoro[1-methyl-2-(1-pyrrolidinyl)ethyl] iodide* ***4c-I*** *[5]*

A mixture of lithium iodide (1.63 g, 12.2 mmol) and perfluoro[2-methyl-3-(1-pyrrolidinyl)propionyl] fluoride **4c-COF** (9.07 mmol) was heated at 180 °C for 6.5 h in a stainless steel reactor. 67% yield; b.p. 126.5–128.5 °C; n_D^{20} 1.3446; d_4^{20} 2.1216 g cm^{-3} (Found: C, 16.83. Calc. for $C_7F_{14}IN$: C, 17.13%); δ_F(85 MHz; $CDCl_3$) −73.7 (3F, q, J 11.6, $\underline{CF_3}-CFI$), −82.0 {1F, J_{AB} 237.5, $-\underline{CF_2}-CF(CF_3)-I$}, −84.4 {1F, J_{AB} 237.5, $-\underline{CF_2}-CF(CF_3)-I$}, −90.9 (4F, t, J = 13.2 Hz, $-CF_2\underline{CF_2}-N-$), −133.6 (4F, s, $-\underline{CF_2}CF_2-N-$), −148.1 (1F, m, $CF_3-\underline{CF}I$); ν_{max}(liq)/cm^{-1} 1343s, 1307, 1276, 1220s, 1161, 1126, 1118, 1035, 975s, 947, 897, 871, 782, 760, 731, 714; λ_{max}(hexane)/nm 276 (ϵ/dm^3 mol^{-1} cm^{-1} 213); m/z 491 (9%, M^+), 472 (1%, M^+–F), 364 (7%, M^+–I), 345 (13%, M^+–I–F), 277 (29%, $C_3F_6I^+$), 264 (95%, $M^+-C_2F_4I$), 214 (16%, $M^+-C_3F_6I$), 177 (9%, CF_2I^+), 176 (13%, $C_4F_6N^+$), 169 (12%, $C_3F_7^+$), 164 (9%, $C_3F_6N^+$), 150 (14%, $C_3F_6^+$), 131 (26%, $C_3F_5^+$), 127 (21%, I^+), 119 (12%, $C_2F_5^+$), 114 (23%, $C_2F_4N^+$), 100 (31%, $C_2F_4^+$), 69 (100%, CF_3^+).

3.20. *Perfluoro(1-methyl-2-morpholinoethyl) iodide* ***4d-I*** *[5]*

A mixture of lithium iodide (1.60 g, 12.0 mmol) and perfluoro(2-methyl-3-morpholinopropionyl) fluoride **4d-COF** (9.11 mmol) was heated at 180 °C for 6.5 h in a stainless steel reactor. 76% yield; b.p. 144.0–145.0 °C; n_D^{20} 1.3482; d_4^{20} 2.1357 g cm^{-3} (Found: C, 16.15. Calc. for $C_7F_{14}INO$: C, 16.58%); δ_F(85 MHz; $CDCl_3$) −74.1 (3F, s, $\underline{CF_3}-CFI$), −77.1 {1F, J_{AB} 236.9, $-\underline{CF_2}-CF(CF_3)-I$}, −83.5 {1F, J_{AB} 236.9, $-\underline{CF_2}-CF(CF_3)-I$}, −87.7 (4F, s, $-O-\underline{CF_2}CF_2-N-$), −92.7 (4F, m, $-O-CF_2\underline{CF_2}-N-$), −145.3 (1F, m, $CF_3-\underline{CF}I$); ν_{max}(liq)/cm^{-1} 1345, 1303s, 1273, 1215s, 1178, 1140s, 1114, 1082, 948, 929, 896, 781, 762, 733, 660; λ_{max}(hexane)/nm 276 (ϵ/dm^3 mol^{-1} cm^{-1} 219); m/z 507 (9%, M^+), 380 (5%, M^+–I), 280 (66%, $M^+-C_2F_4I$), 277 (35%, $C_3F_6I^+$), 169 (17%, $C_3F_7^+$), 164 (20%, $C_3F_6N^+$), 150 (15%, $C_3F_6^+$), 131 (23%, $C_3F_5^+$), 127 (28%, I^+), 119 (100%, $C_2F_5^+$), 114 (62%, $C_2F_4N^+$), 100 (43%, $C_2F_4^+$), 69 (69%, CF_3^+).

3.21. *Perfluoro(2-morpholinopropyl) iodide* ***5d-I*** *(nc)*

A mixture of lithium iodide (1.60 g, 12.0 mmol) and perfluoro(3-morpholinobutanoyl) fluoride **5d-COF** (6.67 mmol) was heated at 180 °C for 6.5 h in a stainless steel reactor. 34% yield; b.p. 151.5–152.5 °C; n_D^{20} 1.3502; d_4^{20} 2.1366 g cm^{-3} (Found: C, 16.22. Calc. for $C_7F_{14}INO$: C, 16.58%); δ_F(85 MHz; $CDCl_3$) −54.3 (2F, s, $-CF_2I$), −72.4 (3F, s, $\underline{CF_3}-CF-$), −80– −93 (8F, m, $-O-\underline{CF_2}\underline{CF_2}-N-$), −143.1 (1F, s, $CF_3-\underline{CF}-$); ν_{max}(liq)/cm^{-1} 1330, 1215, 1205, 1171, 1116, 1081, 1057, 1004, 930, 816, 806, 777, 731, 715; λ_{max}(hexane)/nm 274 (ϵ/dm^3 mol^{-1} cm^{-1} 244); m/z 507 (0.6%, M^+), 380 (38%, M^+–I), 277 (26%, $C_3F_6I^+$), 213 (18%), 176 (26%), 164 (22%, $C_3F_6N^+$), 127 (20%, I^+), 119 (100%, $C_2F_5^+$), 114 (18%, $C_2F_4N^+$), 100 (35%, $C_2F_4^+$), 69 (66%, CF_3^+).

3.22. *1,1,1-Trifluoro-2-(trifluoromethyl)-2-iodopropane* **6-I** *(nc)*

A mixture of lithium iodide (1.60 g, 12.0 mmol) and 3,3,3-trifluoro-2-methyl-2-(trifluoromethyl)propanoyl fluoride **6-COF** (9.57 mmol) was heated at 180 °C for 7.0 h in a Pyrex tube. 78% yield (Found: C, 16.68; H, 0.52. Calc. for $C_4H_3F_6I$: C, 16.46; H, 1.04%); δ_H(90 MHz; $CDCl_3$) 2.19 (s); δ_F(85 MHz; $CDCl_3$) −70.6 (s); ν_{max}(gas)/cm^{-1} 1461w, 1398w, 1286vs, 1228, 1210s, 1148w, 1091, 1069; *m/z* 292 (78%, M^+), 273 (7%, M^+–F), 165 (3%, M^+–I), 146 (22%, M^+–I–F), 145 (57%, M^+–I–F–H), 127 (40%, I^+), 69 (100%, CF_3^+).

3.23. *Perfluoro(1,2-diiodopropane)* **7**

A mixture of lithium iodide (1.68 g, 12.6 mmol) and hexafluoropentane-1,5-dioyl difluoride (6.15 mmol) was heated at 180 °C for 7.0 h in a stainless steel reactor. 72% yield; b.p. 130.0–131.0 °C (lit. 131 °C [13]); n_D^{20} 1.4517 (lit. 1.4516 [13]); d_4^{20} 2.5795 g cm^{-3} (lit. 2.5812 [13]) (Found: C, 8.71. Calc. for $C_3F_6I_2$: C, 8.92%).

3.24. *Perfluoro(4-iodobutanoyl) fluoride* **8** *[14]*

A mixture of lithium iodide (0.78 g, 5.83 mmol) and hexafluoropentane-1,5-dioyl difluoride (6.15 mmol) was heated at 180 °C for 7.0 h in a stainless steel reactor. Monoiodide **8** (50% yield) was obtained with diiodide **7** (21% yield). ν_{max}(gas)/cm^{-1} 1888 (C=O), 1208, 1139, 1096, 804. The methyl ester from **8** had; b.p. 159.5–160.5 °C; n_D^{20} 1.3902; d_4^{20} 1.9460 g/cm^3 (Found: C, 18.27; H, 0.48. Calc. for $C_5H_3F_6IO_2$: C, 17.88; H, 0.90%); ν_{max}(gas)/cm^{-1} 1785 (C=O), 1441, 1330, 1186, 1142, 1095, 776.

3.25. *Molecular orbital calculations*

Molecular orbital calculations were conducted by the MOPAC program [10], and CAChe system (Sony Tektronix) was also used. The optimized structures of perfluoroalkyl radicals were calculated using DOUBLET-keyword by PM3 hamiltonian.

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