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Convenient syntheses and characterization of fluorophilic perfluorooctyl-propyl amines and ab initio calculations of proton affinities of related model compounds

Zoltán Szlávik[a], Gábor Tárkányi[b], Ágnes Gömöry[c], György Tarczay[d], József Rábai[a,*]

[a]*Department of Organic Chemistry, Eötvös University, P.O. Box 32, H-1518, Budapest 112, Hungary*
[b]*Chemical Works of Gedeon Richter, Spectroscopic Research Division, P.O. Box 27, H-1475, Budapest 10, Hungary*
[c]*Institute of Chemistry, Chemical Research Center, Hungarian Academy of Sciences, P.O. Box 17, H-1525, Budapest, Hungary*
[d]*Department of General and Inorganic Chemistry, Eötvös University, P.O. Box 32, H-1518, Budapest 112, Hungary*

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Abstract

A convenient and effective method for the preparation of perfluorooctyl-propyl amines ($[R_{f8}(CH_2)_3]_nNH_{3-n}$ (**1–3**), $n = 1, 2, 3$; $R_{f8}(CH_2)_3NHMe$ (**4**); $[R_{f8}(CH_2)_3]_2NMe$ (**5**); $R_{f8}(CH_2)_3NMe_2$ (**6**); $R_{f8} = F(CF_2)_8$) via a step by step alkylation with $R_{f8}(CH_2)_3I$ is described. The fluorophilicity values of **1–6** were determined by GC and range from 0.79 ± 0.07 (**1**) to 5.3 ± 0.2 (**3**). Systematic ab initio calculations of proton affinities of model compounds (**7a–j**) using Hartree–Fock and density functional theory imply that the inserted trimethylene spacer unit efficiently reduces the electron-withdrawing effect of the perfluorinated segment. All structures were verified by multinuclear one- and two-dimensional NMR experiments involving both homo- ($^{19}F-^{19}F$) and hetero-nuclear ($^{1}H-^{13}C$, $^{1}H-^{15}N$, $^{19}F-^{13}C$) correlations based on the GMQFCOPS and inverse ^{1}H and/or ^{19}F detected GHSQC, GHMQC sequences with broadband adiabatic ^{13}C-decoupling.

Keywords: Perfluorooctyl-propyl amines; Preparation; Fluorous biphase systems; Fluorophilicity; Ab initio calculations; Proton affinities; NMR spectroscopy

1. Introduction

The use of apparently non-toxic and environmentally friendly perfluorocarbon fluids, such as perfluoro-alkanes, amines and ethers, has emerged as a new powerful tool for synthetic organic chemistry. The concept of a new phase-separation and immobilization technique, known as fluorous biphase system (FBS) provides attractive alternatives for conventional homogeneous catalytic processes [1–4]. Another expanding field, known as fluorous synthesis, allows the easy separation of reactants and product molecules according to their phase preference by fluorous-organic liquid–liquid extraction or by filtration through a reverse phase fluorous silica gel [5,6]. The outstanding efficacy of these separation techniques relies on the purposeful design and tuning of the phase preference of the reaction components involving permanent or temporary attachments of fluorous phase labels to certain molecules. The application of this strategy in liquid-phase combinatorial chemistry provides high speed techniques for isolation of compound libraries [7]. The fluorophilicity of compounds depends on several factors, such as size, constitution and number of the appended perfluorinated ponytails ($F(CF_2)_n- = R_{fn}$). As fluorous partition coefficients [3,8–12] and fluorophilicity (f) values [13,14] have become preferred tools for the measurement of phase behavior, they facilitate the design of novel fluorophilic compounds.

In the present work we describe the synthesis of some perfluorooctyl-propyl amines ($[R_{f8}(CH_2)_3]_nNH_{3-n}$ (**1–3**), $n = 1, 2, 3$; $R_{f8}(CH_2)_3NHMe$ (**4**); $[R_{f8}(CH_2)_3]_2NMe$ (**5**); $R_{f8}(CH_2)_3NMe_2$ (**6**); $R_{f8} = F(CF_2)_8$), some of them having high potential in fluorous phase base and metal catalyzed reactions, as their multidentate analogues [15,16], and in semiconductor science [17] or as synthons for fluorophilic compounds. The variable number of fluorinated segments modifies both the fluorophilicity and steric hindrance of the

* Corresponding author. Tel.: +36-1-209-0555; fax: +36-1-372-2620.
E-mail address: rabai@szerves.chem.elte.hu (J. Rábai).

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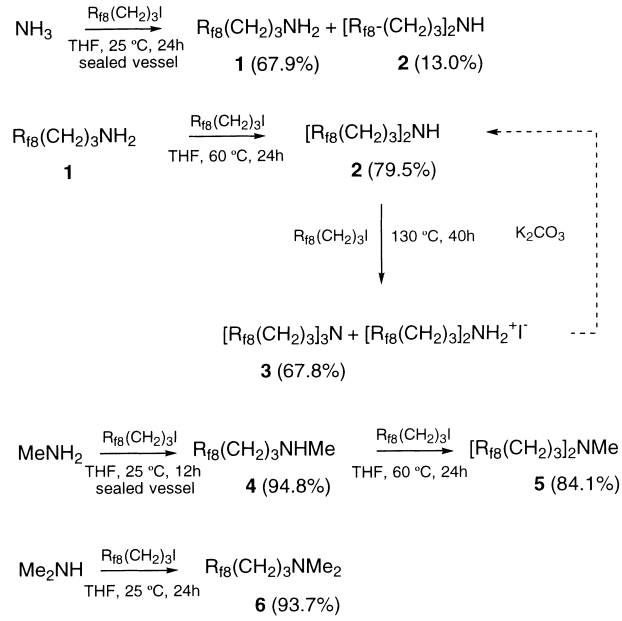
ligand, the small and compact methyl group(s) increase the electron density around the nitrogen atom without making a considerable spatial contribution. The size of the fluorous ponytail (R_{f8}) is a reasonable compromise between commercial price and the produced phase preference effect. The role of the trimethylene spacer unit inserted in between the amino group and the *F*-octyl segment is to insulate the electron-withdrawing effect and to ensure usual reactivity of the functional group [3,12]. Since the article [18] usually cited in connection with the role of the number of methylene units necessary to separate the perfluorinated unit and the functional group (in case of phosphine model compounds) applies a lower level of computational theory (PM3 semi-empirical method), so we aimed to calculate this effect for the amine equivalents using more reliable ab initio methods.

2. Results and discussion

2.1. Synthesis and fluorophilicity

The literature of simple amines containing a $-(CH_2)_3-$ spacer adjacent to the nitrogen and a perfluoroalkyl unit is poor and contains two different approaches to their synthesis. An obvious method is the $LiAlH_4$ reduction of precursor amide derivatives [19]. This synthetic strategy was applied to produce *N*,*N*-dialkyl-perfluorooctyl-propyl amines, including the *N*,*N*-dimethyl derivative (**6**) [20]. Recently, Fish and coworkers applied direct alkylation successfully using *F*-octyl-propyl iodide [$R_{f8}(CH_2)_3I$] to prepare 1,4,7-triazacyclononane derivatives [21,22], while the corresponding tosylate [$R_{f8}(CH_2)_3OTs$] afforded some acyclic tri- and tetra-amines [15]. Since there exists an excellent method to obtain the required reactant $R_{f8}(CH_2)_3I$ [21,22] from the $R_{f8}(CH_2)_3OH$ alcohol precursor [14], we selected the latter pathway to the step-by-step synthesis of amines containing one or more perfluorinated segment (Scheme 1). At the same time as this work was in progress, a paper describing a reductive amination method based on fluorinated aldehydes appeared as an alternative synthesis of perfluorooctyl amines containing different $-(CH_2)_m-$ spacer units ($m = 3-5$) [23].

While the insertion of the first *F*-alkyl-propyl segment can be carried out under mild conditions, the reactivity of amines decreases considerably with the level of alkylation and the synthesis of the tertiary amine **3** proceeds with a reasonable rate only if it is heated for a long time (130°C, 40 h) in the absence of solvent. This difference in reactivity renders it possible to achieve large selectivity of the alkylation processes by suitably varying the experimental conditions. When mixed product formation is observable (parallel production of primary amine **1** and secondary derivative **2** happens even in the presence of a large excess of ammonia) or the conversion is not complete, the separation can be easily carried out by fractional distillation, since the addition



Scheme 1.

of a further *F*-octyl-propyl unit in a molecule results in a large boiling point enhancement.

The fluorophilicity value (f_a) of compound 'a' is defined by the partition coefficient (P_a) between perfluoro(methylcyclohexane) and toluene according to the following equation [13,14]:

$$f_a = \ln P_a = \ln\left[\frac{c_a(CF_3C_6F_{11})}{c_a(CH_3C_6H_5)}\right].$$

This is a practical measure of the phase preference as according to this definition a molecule is 'fluorophilic' if its *f* value is positive and this can be easily determined in the case of volatile compounds by gas chromatography simply from the integrated areas (A_a):

$$f_a = \ln\left[\frac{A_a(CF_3C_6F_{11})}{A_a(CH_3C_6H_5)}\right],$$

if the volumes of the two phases and the sampled and injected volumes are the same.

The fluorophilicity data of amines (Table 1) show that all of them are fluorophilic and the values increase dramatically

Table 1
Fluorophilicity values (25°C)

Compound	*f*
$R_{f8}CH_2CH_2CH_2NH_2$ (**1**)	0.79 ± 0.07[a]
$(R_{f8}CH_2CH_2CH_2)_2NH$ (**2**)	3.40 ± 0.06[a]
$(R_{f8}CH_2CH_2CH_2)_3N$ (**3**)	5.30 ± 0.20[a]
$R_{f8}CH_2CH_2CH_2NHMe$ (**4**)	0.89 ± 0.03
$(R_{f8}CH_2CH_2CH_2)_2NMe$ (**5**)	3.63 ± 0.05
$R_{f8}CH_2CH_2CH_2NMe_2$ (**6**)	1.37 ± 0.08

[a] These values closely agree with the partition coefficients measured by Gladysz and coworkers [23].

Table 2
Computed proton affinity values, charge and geometry effects of model compounds

Structure	Proton affinity (kcal mol^{-1})[a]		Natural charge[b]		Pyramidality[c] (°)	
	HF[d]	DFT[e]	HF[d]	DFT[e]	HF[d]	DFT[e]
$F(CF_2)_2CH_2NH_2$ (**7a**)	202.05	201.41	−0.151	−0.126	3.81	9.84
$F(CF_2)_2(CH_2)_2NH_2$ (**7b**)	209.30	207.73	−0.174	−0.151	5.17	10.54
$F(CF_2)_2(CH_2)_3NH_2$ (**7c**)	215.39	212.12	−0.180	−0.155	5.25	10.46
$F(CF_2)_2(CH_2)_4NH_2$ (**7d**)	218.06	214.14	−0.185	−0.159	5.52	10.56
$F(CF_2)_2(CH_2)_5NH_2$ (**7e**)	220.23	215.81	−0.187	−0.161	5.53	10.56
$F(CF_2)_2(CH_2)_3NHMe$ (**7f**)	224.88	219.49	−0.385	−0.344	6.55	9.31
$F(CF_2)_2(CH_2)_3NMe_2$ (**7g**)	231.06	223.75	−0.615	−0.560	7.46	8.93
$[F(CF_2)_2(CH_2)_3]_2NH$ (**7h**)	221.33	218.43	−0.384	−0.342	6.50	9.27
$[F(CF_2)_2(CH_2)_3]_2NMe$ (**7i**)	227.30	222.56	−0.617	−0.561	7.14	8.41
$[F(CF_2)_2(CH_2)_3]_3N$ (**7j**)	223.66	221.56	−0.625	−0.570	6.42	7.96

[a] Derived from total energy data including ZPE correction calculated at the HF/3-21G(d) level.
[b] With the contribution of hydrogens summed into the heavy atoms.
[c] Defined as $120^\circ - \sum$ (RNR bond angles)/3.
[d] HF/3-21G(d), with the basis set of 3-21 + G(d) for N atom and 3-21G(d′) for F atoms.
[e] B3LYP/6-31G(d), with the basis set of 6-31 + G(d) for N atom and 6-31G(d′) for F atoms.

with the number of perfluorinated groups as expected [9]. The *N*-methylation of an amine [10] also increases the *f* values, as the solvation forces through hydrogen bonding represent a factor for toluene phase preference and has negligible contribution to the interactions with the perfluorinated solvent.

2.2. Theoretical investigations

The electronic properties of the functional group of the synthesized molecules containing perfluorinated segments together with steric factors around the nitrogen atom strongly influence their coordinating power. Charge and space occupancy together with proton affinity data of the quantum mechanical vacuum model are reasonable approximations of the basic strength and complexing ability of amines in fluorocarbon solvents having extremely low polarity values, for example $\varepsilon = 1.85$ for perfluoro-(methylcyclohexane) [24]. Computations were performed using the Gaussian-98 program system [25] on an IBM SP2 computer. Geometry optimizations followed by the vibrational zero point energy (ZPE) calculation of the model compounds, both in neutral and protonated forms, were first carried out at the HF/3-21G(d) level with diffuse functions on the N atom. The DFT calculations using the hybrid Becke3LYP (B3LYP, Becke's three-parameter exchange [26] and Lee et al. correlation [27]) method were performed at the 6-31G(d) basis set applying also diffuse functions on the N atom and in the case of F atoms 6-31G-dagger basis set was used according to Petersson et al., defined as part of the complete basis set methods [28,29]. The ZPE data of the HF/3-21G(d) calculations were used also in the case of larger basis set energy corrections to decrease the computational cost. This approximation was tested in the case of $R_{f2}(CH_2)_3NH_2$ (**7c**) as a model species and was found to predict the value of proton affinity within 1 kcal mol^{-1}. The spatial effects around the N atom were taken into account introducing 'pyramidality', measured in degrees and defined with the formula:

$$120^\circ - \sum\left(\frac{\text{RNR bond angles}}{3}\right).$$

For this definition a decreasing value of pyramidality corresponds to a more crowded atomic distribution around the functional group with a geometry closer to the complete planarity (Table 2). The DFT optimizations seem to provide the more reliable geometry parameters considered in further conclusions.

The calculated proton affinity and the charge population data for primary amines $R_{f2}(CH_2)_nNH_2$ (**7a–e**) show asymptotic increase with the number of inserted methylene groups. Both methods describe the tendencies similarly and differ only in the absolute values, however in the case of the low basis set HF calculations the increments of the proton affinities seem to be overestimated. The geometry around the N atom differs considerably from the completely pyramidal case only if the fluorinated segment is separated with a single methylene spacer unit (**7a**).

Introducing methyl and or $R_{f2}(CH_2)_3$– units into the model molecule $R_{f2}(CH_2)_3$–NH_2 (**7c**) increases the calculated basicity and decreases pyramidality, with a contribution slightly larger in the case of the CH_3 group (**7f–j**). The electron density around the N atom increases nearly linearly with the number of alkyl groups for both types confirming the correctness of the selection of the trimethylene spacer unit.

2.3. Structure elucidation with NMR spectroscopy

All structures were verified by multinuclear one- and two-dimensional NMR experiments that allowed a so-called ab initio structure determination. Two-dimensional experiments involved both homo- (^{19}F–^{19}F) and hetero-nuclear

(^{1}H–^{13}C, ^{1}H–^{15}N, ^{19}F–^{13}C) correlations based on the GMQFCOPS and inverse ^{1}H and/or ^{19}F detected GHSQC, GHMQC sequences employing broadband adiabatic ^{13}C-decoupling.

The ^{1}H, ^{13}C and ^{19}F chemical shift data for structures **1–6** showed many similarities. The ^{1}H spectra exhibited no spectral overlap and members of the *n*-propyl group could readily be identified on the basis of their characteristic shifts and coupling patterns as well as their correlations to the neighboring nitrogen and carbons. H-3 correlated through one bond to C-3, a carbon which gave triplet ($^{2}J_{(C,F)} = 22.2 \pm 0.3$ Hz) in the ^{1}H decoupled ^{13}C spectrum. H-2 gave largest correlation through three bonds to N-1.

The ^{13}C shifts of signals due to CH_2 and CF_2 carbons were determined by recording broadband ^{1}H and ^{19}F decoupled one-dimensional ^{13}C spectra. C-1 showed the largest chemical shift variation by the structures (from 48.3 to 58.5 ppm) therefore it was found to be the most characteristic ^{13}C signal. Identification of carbons bonded to fluorines could be obtained parallel with the assignment of fluorines in the perflouoroalkyl chain utilizing ^{19}F–^{19}F homo- (Fig. 1) and ^{19}F–^{13}C (Fig. 2) one-bond two-dimensional correlation experiments. $CF_2(11)$ and $CF_2(4)$ were good starting points for the sequential assignment of the CF_2 members due to their characteristic ^{13}C and ^{19}F chemical shifts. ^{19}F–^{19}F correlated spectroscopy gave largest cross-peaks between every even ($4 \leftrightarrow 6 \leftrightarrow 8 \leftrightarrow 10$) and every odd ($5 \leftrightarrow 7 \leftrightarrow 9 \leftrightarrow 11$) members in the chain because $^{4}J_{^{19}F-^{19}F} \approx 9$ Hz coupling constant between every second neighbor is larger than $^{3}J_{^{19}F-^{19}F} \approx 1$ Hz between adjacent neighbors [30] (Fig. 1). ^{13}C assignments were then made from the one-bond ^{19}F–^{13}C correlation experiment as seen on Fig. 2 (note the ^{13}C isotope shift observed on ^{19}F cross-peaks). The assignments of C-7 and C-8 were found to be ambiguous due to the spectral overlap of F-7 and F-8 at 470 MHz (interchangeable assignments are denoted by $*$).

^{15}N chemical shifts determined from ^{1}H–^{15}N multiple bond correlation experiments correspond to highly shielded

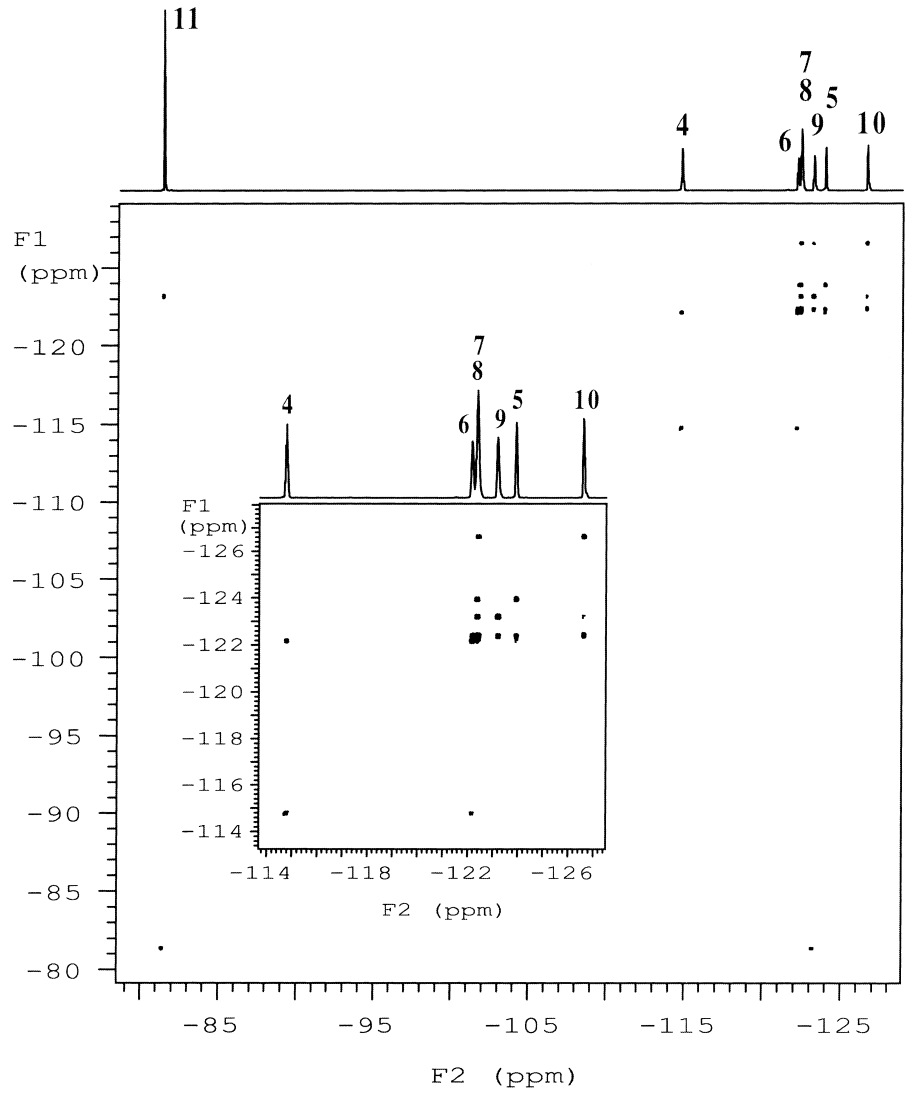


Fig. 1. ^{19}F–^{19}F-GMQFCOPS experiment for compound **4**.

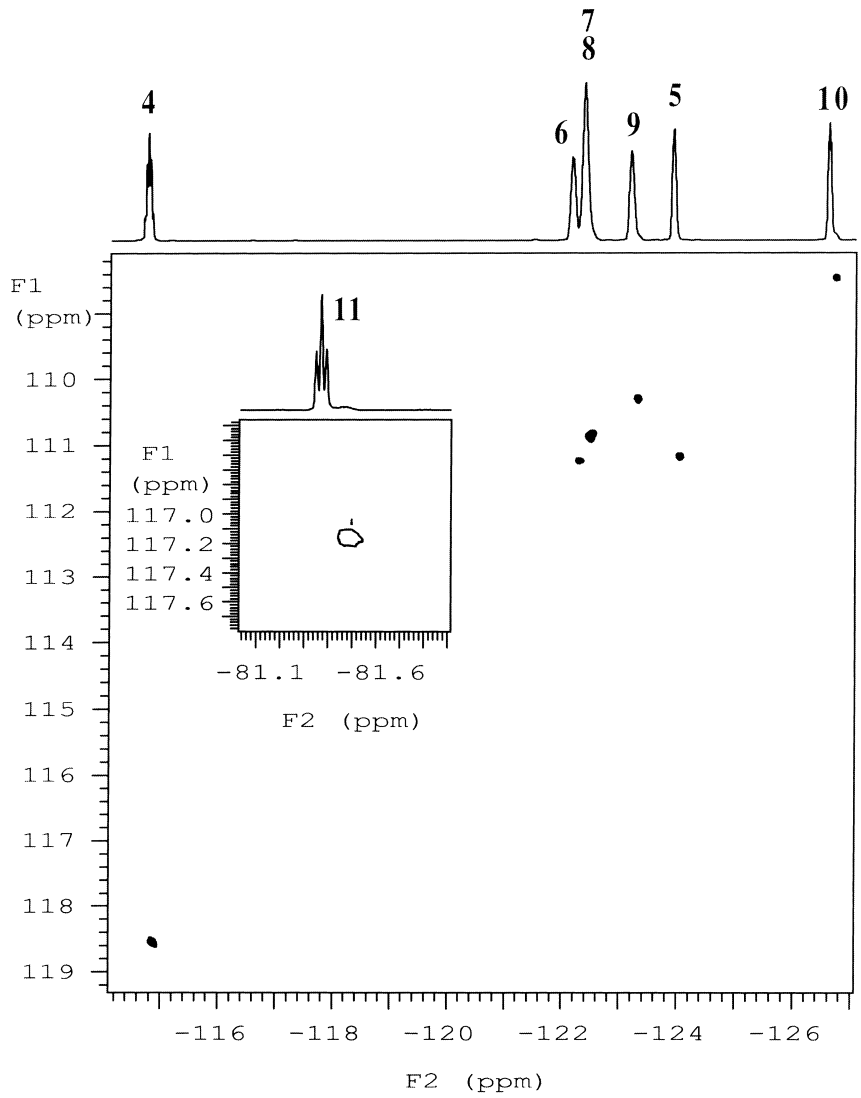


Fig. 2. Broadband ^{13}C-decoupled ^{19}F-detected ^{19}F–^{13}C-GHSQC experiment for compound **4**. Note the ^{13}C vs. ^{12}C isotope shift detected on ^{19}F.

nitrogens typically characteristic for amines. In $CDCl_3$ the upfield shift of N-1 was found to be roughly proportional to the number of hydrogens > methyl groups > alkyl groups bonded to the nitrogen (in this order), giving the smallest shift for compound **1** and largest for compound **2**. Recently, Deelman and coworkers applied a similar approach for the assignment of the ^{19}F and ^{13}C NMR signals of some perfluoroalkylated triphenylphosphine derivatives [31].

3. Conclusions

The step-by-step synthesis of amines ($[R_{f8}(CH_2)_3]_nNH_{3-n}$ (**1–3**), $n = 1, 2, 3$; $R_{f8}(CH_2)_3NHMe$ (**4**); $[R_{f8}(CH_2)_3]_2NMe$ (**5**); $R_{f8}(CH_2)_3NMe_2$ (**6**); $R_{f8} = F(CF_2)_8$) using perfluorooctyl-propyl iodide provides a simple access to highly fluorocarbon soluble ligands for FBS applications. Ab initio computations of model compounds support the validity of the concept, that the trimethylene block is an efficient spacer unit to insulate the strong electron-withdrawing effect of the perfluorinated segment from the reaction center (N atom). The fluorophilicity values obtained in this study increase the number of experimentally determined fluorous partition coefficients for a nascent databank and thus are expected to facilitate the understanding of the correlations between molecular parameters and fluorous phase preference.

4. Experimental details

Melting points were determined on a Boetius micro melting point apparatus and are uncorrected. The reagent $R_{f8}(CH_2)_3I$ was prepared from the corresponding alcohol precursor molecule [21,22]. The applied THF solvent was analytical grade and used without further purification. The ammonia and methylamine gases were analytical grade (Merck), the 20% stock solution of dimethylamine in THF was generated from an aqueous solution of its hydrochloride

with KOH and was occluded in the solvent at −80°C. Caution: sealed tube experiments were performed using an appropriate safety shield.

^{1}H-, ^{13}C- and ^{19}F-NMR measurements were carried out at 30°C in $CDCl_3$ and CD_3COCD_3 on a Varian INOVA-500 spectrometer (operating at 500 MHz for ^{1}H) equipped with a waveform generator, using a $^{1}H\{^{13}C, ^{15}N\}$ PFG-triple resonance 5 mm probe tunable for ^{19}F. Samples were prepared and measured in ca. 50 mmol/l concentration. ^{1}H, ^{19}F and ^{15}N chemical shifts are given relative to $\delta(\mathrm{TMS}) = 0.00$ ppm, $\delta(CFCl_3) = 0.00$ ppm and $\delta(CH_3NO_2) = 0.00$ ppm, respectively, where TMS, $CFCl_3$ and CH_3NO_2 were used as internal standards. ^{13}C chemical shifts are referenced relative to the solvent ^{13}C-shifts $\delta(CDCl_3) = 77.00$ ppm and $\delta(CD_3COCD_3) = 29.92$ ppm. For the assignments we utilized two-dimensional correlation experiments which were run according to the proper set-up of coupling and gradient parameters based on the GMQFCOPS and inverse ^{1}H and/or ^{19}F detected GHSQC, GHMQC sequences provided by the manufacturer. Broadband ^{19}F- and ^{13}C-decoupling and bandselective ^{19}F decoupling was performed by adiabatic decoupling using the WURST [32] decoupling sequence. Amine nitrogen shifts were determined from ^{1}H–^{15}N multiple bond correlation experiments using inverse detection, with an accuracy of ±0.6 ppm due to the relatively poor (55 Hz) digital resolution in the F1 dimension. The experiment was set up to give maximum signal for ^{1}H–^{15}N long range coupling constant of 5 Hz.

The FT-IR measurements were carried out on a BRUKER IFS 55 spectrometer. Mass spectra were determined on a VG ZAB2-SEQ tandem mass spectrometer using electron impact (70 eV) for ionization; direct probe sample introduction (for **2**, **3**, **5**) or septum inlet (for **1**, **4**, **6**) were used at a source temperature of 200°C. Mass range (*m/z*) from 25 to 1500 (for **2**, **3**, **5**) and from 25 to 520 (for **1**, **4**, **6**) were considered. The accuracy of the HRMS measurements is described by the formula: $(M(\mathrm{found}) - M(\mathrm{calculated}))/M(\mathrm{calculated}) \leq 10^{-6}$. All the reaction steps were monitored by gas chromatography (Hewlett Packard 5890 Series II, PONA 50 m to 0.2 mm, 0.5 μm column, H_2 carrier gas, FID).

Partition coefficients were determined in the following way. In a 2.00 ml volumetric flask the given compounds (10 mg) were extracted in a 1.00 ml to 1.00 ml mixture of pre-equilibrated perfluoro(methylcyclohexane) and toluene. The closed vessel was first immersed in a water bath (50°C) for 30 min with frequent shaking, then allowed to cool to 25°C. After standing overnight or longer at this temperature 300 ± 3 μl aliquots of the separated upper and lower phases were withdrawn and diluted with 300 ± 3 μl benzotrifluoride, which served as an internal standard during GC analysis. An average of 7–11 injections for each run of three independent determinations resulted in the listed *f* values with the corresponding standard deviations (Table 1).

*4.1. 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoro-undecyl-amine (**1**) and bis(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-undecyl)-amine (**2**)*

In a thick-walled glass tube (with an internal volume of 200 ml) $R_{f8}(CH_2)_3I$ (30.0 g, 51.0 mmol) was dissolved in 70 ml THF, cooled to −80°C and approximately 15 ml liquid ammonia was condensed to it. The tube was sealed and the mixture was continuously stirred at room temperature for 24 h. The mixture of products was analyzed by GC and complete conversion of $R_{f8}(CH_2)_3I$ was found into the corresponding primary and secondary amines (69.9% **1**, 30.1% **2**). The crude mixture was diluted with diethyl ether and treated with a 1 M solution of K_2CO_3. The organic phase was washed twice with distilled water, separated, dried over Na_2SO_4 and the solvent was removed by rotary evaporation. Finally, the products were separated by fractional distillation under reduced pressure. The main fraction containing GC pure **1** (16.5 g, 67.9%) was collected at a bath temperature of 80–110°C (20 mmHg). The analysis of the second fraction (150–170°C bath temperature, 0.1 mmHg) indicated that complete separation of products had been achieved (6.21 g, 13.0% **2**, 100% purity by GC). Analytical data for **1**: NMR ($CDCl_3$) ^{1}H-NMR: 1.19 s, br (2H) [NH_2]; 1.71–1.78 m (2H) [H-2]; 2.09–2.21 m (2H) [H-3]; 2.80 t (2H) [H-1]. ^{19}F-NMR: −81.3 [F-11]; −114.6 [F-4]; −122.1 [F-6]; −122.4 [F-7 and F-8]; −123.2 [F-9]; −123.9 [F-5]; −126.6 [F-10]. ^{13}C-NMR: 24.2 [C-2]; 28.5 [C-3]; 41.3 [C-1]; 108.4 [C-10]; 110.3 [C-9]; 110.8 [C-7]*; 110.9 [C-8]*; 111.1 [C-5]; 111.2 [C-6]; 117.2 [C-11]; 118.6 [C-4]. ^{15}N-NMR: −360.7 [C_1–N]. FT-IR (liquid film) υ (cm^{-1}): 3378 (NH_{as}); 3297 (NH_s); 2952 (CH_{as}); 2876 (CH_s); 1242, 1206 (CF). MS (*m/z*, I%, $M - X$): 477, 0.1, *M*; 476, 10, $M - H$; 458, 5.7, $M - F$; 438, 0.5, $M - HF_2$; 30, 100, CH_2NH_2. HRMS (*m/z*) calculated for $C_{11}H_7F_{17}N$, $[M - H]^+ = 476.0307$, found $[M - H]^+ = 476.0302$.

*4.2. Bis(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-undecyl)-amine (**2**) from **1***

In a 100 ml reaction flask fitted with a reflux condenser **1** (11.2 g, 23.5 mmol) and $R_{f8}(CH_2)_3I$ (6.94 g, 11.8 mmol) dissolved in 50 ml THF were stirred at 60°C for 24 h applying by-pass nitrogen flow during the entire reaction. The crude mixture was diluted with diethyl ether and treated with a 1 M solution of K_2CO_3, washed with distilled water and dried as in case of the preparation of compound **1**. The crude product (GC composition: 35.3% **1**, 10.8% $R_{f8}(CH_2)_3I$, 52.3% **2** and 0.83% **3**, assigned later) was purified by fractional distillation. From the first fraction unreacted **1** was regenerated (bath temperature raised to 140°C at 20 mmHg, 4.55 g, 9.54 mmol, 95.1% purity by GC), the main fraction contained the secondary amine **2** (bath temperature raised to 180°C at 0.1 mmHg, 10.4 g, 79.5%, 94.4% purity by GC, mp 37–40°C). NMR ($CDCl_3$) ^{1}H-NMR: 1.03 s, br (1H) [NH]; 1.72–1.79 m (2H) [H-2];

2.10–2.24 m (2H) [H-3]; 2.70 t (2H) [H-1]. ^{19}F-NMR: −81.4 [F-11]; −114.8 [F-4]; −122.2 [F-6]; −122.4 [F-7 and F-8]; −123.2 [F-9]; −124.1 [F-5]; −126.6 [F-10]. ^{13}C-NMR: 20.8 [C-2]; 28.7 [C-3]; 48.3 [C-1]; 108.5 [C-10]; 110.3 [C-9]; 110.8 [C-7]*; 110.9 [C-8]*; 111.1 [C-5]; 111.2 [C-6]; 117.2 [C-11]; 118.6 [C-4]. ^{15}N-NMR: −345.2 [C_1–N]. FT-IR (KBr) υ (cm^{-1}): 3352 (NH); 2953 (CH_{as}); 2888, 2831 (CH_s); 1243, 1205 (CF). MS (*m/z*, I%, $M-X$): 937, 0.6, *M*; 936, 4.7, $M-H$; 918, 14, $M-F$; 568, 3.1, $M-369$; 490, 100, $R_{f8}(CH_2)_3NH–CH_2$. HRMS (*m/z*) calculated for $C_{22}H_{12}F_{34}N$, $[M-H]^+ = 936.0427$, found $[M-H]^+ = 936.0479$.

4.3. Tris(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-undecyl)-amine (3) from 2

In a sealed tube a mixture of **2** (10.4 g, 11.1 mmol) and $R_{f8}(CH_2)_3I$ (6.53 g, 11.1 mmol) was heated for 40 h at 130°C. Then 100 ml diethyl ether was added to the crude product cooled to room temperature. The ether insoluble precipitate was filtered off and washed several times with diethyl ether. The colorless solid was treated with a 1 M solution of K_2CO_3 and extracted with diethyl ether (100 ml). The organic phase was washed twice with distilled water, separated, dried over Na_2SO_4 and the solvent was removed (5.25 g, 5.60 mmol unreacted **2**, GC pure). The ether soluble components of the mother liquor were analyzed directly by GC (19.5% R_{f8}–$(CH_2)_3$–I, 9.43% **2** and 67.9% **3**). The solvent was removed by rotary evaporation (10.1 g) and the product was purified first by flash chromatography (Kieselgel 40, 19 cm long column with a diameter of 2 cm, 200 ml chloroform eluent; GC 26.0% $R_{f8}(CH_2)_3I$, 71.0% **3** and 0.00% **2**) and finally by fractional distillation. The main fraction containing **3** (5.21 g, 67.8%, 97.5% purity by GC, mp 32–37°C) was collected at a bath temperature of 210–230°C (0.1 mmHg). NMR (acetone-d_6) ^{1}H-NMR: 1.76–1.83 m (2H) [H-2]; 2.25–2.37 m (2H) [H-3]; 2.59 t (2H) [H-1]. ^{19}F-NMR: −80.8 [F-11]; −113.9 [F-4]; −121.2 [F-6]; −122.5 [F-7 and F-8]; −122.3 [F-9]; −123.5 [F-5]; −125.8 [F-10]. ^{13}C-NMR: 19.0-2]; 29.4 [C-3]; 53.5 [C-1]; 109.5 [C-10]; 111.3 [C-9]; 111.8 [C-7]*; 111.9 [C-8]*; 112.2 [C-5]; 112.3 [C-6]; 118.1 [C-11]; 120.3 [C-4]. ^{15}N-NMR: −345.6 [C_1–N]. FT-IR (KBr) υ (cm^{-1}): 2962 (CH_{as}); 2827 (CH_s); 1245, 1205 (CF). MS (*m/z*, I%, $M-X$): 1397, 0.6, *M*; 1396, 4.6, $M-H$; 1378, 17, $M-F$; 1028, 3.0, $M-369$; 950, 100, M–$R_{f8}(CH_2)_2$. HRMS (*m/z*) calculated for $C_{33}H1_7F_{51}N$, $[M-H]^+ = 1396.0547$, found $[M-H]^+ = 1396.0569$.

4.4. (4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoro-undecyl)-methyl-amine (4)

In a thick-walled glass tube (with an internal volume of 100 ml) $R_{f8}(CH_2)_3I$ (3.50 g, 5.95 mmol) was dissolved in 25 ml THF and cooled to −80°C to condense approximately 10 ml liquid methylamine at this mixture. The tube was sealed and the solution was stirred overnight at room temperature. The crude mixture was worked up as in the case of compound **1** and finally purified by distillation to produce **4** (100–120°C bath temperature at 20 mmHg, 2.77 g, 94.8%, 98.3% purity by GC). NMR ($CDCl_3$) ^{1}H-NMR: 1.16 s, br (1H) [NH]; 1.74–1.82 m (2H) [H-2]; 2.09–2.21 m (2H) [H-3]; 2.44 s (3H) [N–Me]; 2.67 t (2H) [H-1]. ^{19}F-NMR: −81.4 [F-11]; −114.7 [F-4]; −122.1 [F-6]; −122.4 [F-7 and F-8]; −123.2 [F-9]; −123.9 [F-5]; −126.6 [F-10]. ^{13}C-NMR: 20.5 [C-2]; 28.8 [C-3]; 36.2 [N–Me]; 50.9 [C-1]; 108.5 [C-10]; 110.3 [C-9]; 110.8 [C-7]*; 110.9 [C-8]*; 111.1 [C-5]; 111.2 [C-6]; 117.2 [C-11]; 118.6 [C-4]. ^{15}N-NMR: −351.8 [C_1–N]. FT-IR (liquid film) υ (cm^{-1}): 3298 (NH); 2956 (CH_{as}); 2883, 2855 (CH_s); 1243, 1208 (CF). MS (*m/z*, I%, $M-X$): 0.1, 491, *M*; 490, 7.2, $M-H$; 472, 7.6, $M-F$; 452, 0.1, $M-HF_2$; 44, 100, CH_2NHMe. HRMS (*m/z*) calculated for $C_{12}H_9F_{17}N$, $[M-H]^+ = 490.0463$, found $[M-H]^+ = 490.0459$.

4.5. Bis(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-undecyl)-methyl-amine (5) from 4

In a 25 ml reaction flask fitted with a reflux condenser a mixture of **4** (1.23 g, 2. 50 mmol) and $R_{f8}(CH_2)_3I$ (0.882 g, 1.50 mmol) dissolved in 10 ml THF was intensively stirred for 24 h at 60°C applying by-pass nitrogen flow. The crude mixture of products cooled to room temperature was treated with a 1 M solution of KOH and extracted with diethyl ether. The ether phase was washed twice with distilled water, separated, dried over Na_2SO_4 and finally the volatile components were removed. The crude product **5** was purified by fractional distillation under reduced pressure (main fraction collected at a bath temperature of 160–170°C, 0.1 mmHg, 1.27 g, 94.6% purity by GC). Second distillation under the same conditions resulted in compound **5** with appropriate purity (1.20 g, 84.1%, 98.1% purity by GC). NMR ($CDCl_3$) ^{1}H-NMR: 1.71–1.78 m (2H) [H-2]; 2.07–2.19 m (2H) [H-3]; 2.18 s (3H) [N–Me]; 2.40 t (2H) [H-1]. ^{19}F-NMR: −81.5 [F-11]; −114.9 [F-4]; −122.3 [F-6]; −122.5 [F-7 and F-8]; −123.3 [F-9]; −124.3 [F-5]; −126.7 [F-10]. ^{13}C-NMR: 18.2 [C-2]; 28.4 [C-3]; 41.3 [N–Me]; 56.2 [C-1]; 108.5 [C-10]; 110.3 [C-9]; 110.8 [C-7]*; 110.9 [C-8]*; 111.2 [C-5]; 111.3 [C-6]; 117.2 [C-11]; 118.7 [C-4]. ^{15}N-NMR: −347.3 [C_1–N]. FT-IR (liquid film) υ (cm^{-1}): 2962 (CH_{as}); 2853 (CH_s); 1245, 1205 (CF). MS (*m/z*, I%, $M-X$): 951, 2.5, *M*; 950, 6.2, $M-H$; 932, 22, $M-F$; 582, 3.4, $M-369$; 504, 100, $R_{f8}(CH_2)_3NMe–CH_2$. HRMS (*m/z*) calculated for $C_{23}H_{14}F_{34}N$, $[M-H]^+ = 950.0662$, found $[M-H]^+ = 950.0652$.

4.6. Dimethyl-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-undecyl)-amine (6)

In a 50 ml reaction flask $R_{f8}(CH_2)_3I$ (7.06 g, 12.0 mmol) mixed with a 20% solution of dimethylamine in THF (13 g, 58 mmol) was stirred at room temperature for 24 h. The

product was treated with a 1 M solution of NaOH and extracted with ether (25 ml). The ether phase was washed with distilled water, separated and dried over $MgSO_4$. The solvent was removed and the crude product **6** was distilled under reduced pressure (0.1 mmHg, bath temperature raised to 100°C, bp 45°C/0.1 mmHg [20]) in a short path distillation apparatus (5.68 g, 93.7%, 96.1% purity by GC). NMR ($CDCl_3$) ^{1}H-NMR: 1.72–1.79 m (2H) [H-2]; 2.07–2.20 m (2H) [H-3]; 2.22 s (6H) [N–Me]; 2.33 t (2H) [H-1]. ^{19}F-NMR: −81.4 [F-11]; −114.7 [F-4]; −122.2 [F-6]; −122.4 [F-7 and F-8]; −123.2 [F-9]; −123.9 [F-5]; −126.6 [F-10]. ^{13}C-NMR: 18.4 [C-2]; 28.8 [C-3]; 45.2 [N–Me]; 58.5 [C-1]; 108.5 [C-10]; 110.3 [C-9]; 110.8 [C-7]*; 110.9 [C-8]*; 111.2 [C-5]; 111.3 [C-6]; 117.2 [C-11]; 118.7 [C-4]. ^{15}N-NMR: −351.4 [C_1–N]. FT-IR (liquid film) υ (cm^{-1}): 2980, 2954 (CH_{as}); 2866, 2824 (CH_s); 1243, 1208 (CF). MS (*m/z*, I%, $M-X$): 505, 4.0, M; 504, 6.4, $M-H$; 487, 4.8, $M-F$; 486, 8.0, $M-HF$; 58, 100, CH_2NMe_2. HRMS (*m/z*) calculated for $C_{13}H_{11}F_{17}N$, $[M-H]^+ = 504.0620$, found $[M-H]^+ = 504.0625$.

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References

[1] I.T. Horváth, J. Rábai, Science 266 (1994) 72.
[2] B. Cornils, Angew. Chem. Int. Ed. Engl. 36 (1997) 2057.
[3] I.T. Horváth, Acc. Chem. Res. 31 (1998) 641.
[4] M. Cavazzini, F. Montanari, G. Pozzi, S. Quici, J. Fluorine Chem. 94 (1999) 183.
[5] D.P. Curran, Angew. Chem. Int. Ed. Engl. 37 (1998) 1175.
[6] A. Studer, S. Hadida, R. Ferritto, S.Y. Kim, P. Jeger, P. Wipf, D.P. Curran, Science 275 (1997) 823.
[7] A. Studer, D.P. Curran, Tetrahedron 53 (1997) 6681.
[8] D.P. Curran, M. Hoshino, J. Org. Chem. 61 (1996) 6480.
[9] V. Herrera, P.J.F. de Rege, I.T. Horváth, T.L. Husebo, R.P. Hughes, Inorg. Chem. Commun. 1 (1998) 197.
[10] B. Linclau, A.K. Singh, D.P. Curran, J. Org. Chem. 64 (1999) 2835.
[11] J.J.J. Juliette, D. Rutherford, I.T. Horváth, J.A. Gladysz, J. Am. Chem. Soc. 121 (1999) 2696.
[12] L.P. Barthel-Rosa, J.A. Gladysz, Coord. Chem. Rev. 190–192 (1999) 587.
[13] L.E. Kiss, J. Rábai, L. Varga, I. Kövesdi, Synlett (1998) 1243.
[14] Z. Szlávik, G. Tárkányi, Gy. Tarczay, Á. Gömöry, J. Rábai, J. Fluorine Chem. 98 (1999) 83–87.
[15] F. De Campo, D. Lastécouéres, J.M. Vincent, J.B. Verlhac, J. Org. Chem. 64 (1999) 4969.
[16] D.M. Haddleton, S.G. Jackson, S.A.F. Bon, J. Am. Chem. Soc. 122 (2000) 1542.
[17] H.E. Katz, A.J. Lovinger, J. Johnson, C. Kloc, T. Siegrist, W. Li, Y.-Y. Lin, A. Dodabalapur, Nature 404 (2000) 478.
[18] I.T. Horváth, G. Kiss, R.A. Cook, J.A. Bond, P.A. Stevens, J. Rábai, E.J. Mozeleski, J. Am. Chem. Soc. 120 (1998) 3133.
[19] S. Shinkai, K. Torigoe, O. Manabe, T. Kajiyama, J. Chem. Soc., Chem. Commun. 12 (1986) 933.
[20] J.B. Nivet, R. Bernelin, M. Blanc, J.G. Riess, Eur. J. Med. Chem., Chim. Ther. 27 (1992) 891.
[21] J.M. Vincent, A. Rabion, V.K. Yachandra, R.H. Fish, Angew. Chem. 109 (1997) 2438.
[22] J.M. Vincent, A. Rabion, V.K. Yachandra, R.H. Fish, Angew. Chem., Int. Ed. Engl. 36 (1997) 2346.
[23] C. Rocaboy, W. Bauer, J.A. Gladysz, Eur. J. Chem. (2000) 2621.
[24] N.V. Lifanova, T.M. Usacheva, V.I. Zhuravlev, Russ. J. Phys. Chem. (Engl. Transl.) 66 (1992) 125.
[25] Gaussian Inc., release A.7, Pittsburgh, PA, 1999.
[26] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[27] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[28] G.A. Petersson, A. Bennett, T.G. Tensfeldt, M.A. Al-Laham, W.A. Shirley, J. Mantzaris, J. Chem. Phys. 89 (1988) 2193.
[29] G.A. Petersson, M.A. Al-Laham, J. Chem. Phys. 94 (1991) 6081.
[30] E.F. Mooney, An Introduction to 19F NMR Spectroscopy, Heyden/Sadtler, 1970, ISBN 08550100808.
[31] B. Richter, E. de Wolf, G. van Koten, B.-J. Deelman, J. Org. Chem. 65 (2000) 3885.
[32] E. Kupce, R.J. Freeman, Mag. Reson. A 115 (1995) 273.