Preparation of Dialkylamino-Substituted Benzenes and Naphthalenes by Nucleophilic Replacement of Fluorine in the Corresponding Perfluoroaromatic Compounds


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Z. Naturforsch. 61b, 615 – 625 (2006); received December 13, 2005

The reactions between hexafluorobenzene (HFB) and octafluoronaphthalene (OFN) with secondary aliphatic amines (pyrrolidine, dimethylamine and piperidine) and lithium amides (pyrrolidide, dimethylamide and piperidide) have been investigated both experimentally and (in part) theoretically. With amines HFB, depending on the selected conditions, gives either di-substituted products or a complex mixture of di-, tri- and tetrasubstituted compounds. Under similar conditions OFN produces almost exclusively the 2,3,6,7-tetrasubstituted compound. Interaction of HFB with the more nucleophilic lithium amides results in the replacement of four fluorines giving 1,2,4,5-tetrasubstituted di-fluorobenzenes, while OFN under similar conditions with lithium pyrrolidide produces an inseparable mixture of 1,2,4,5,6,8-hexa- and 1,2,3,4,5,6,8-hepta-substituted derivatives. With lithium dimethylamide, it is possible to substitute six (in dioxane) or seven (in THF) fluorines in OFN. Lithium piperidide in all employed solvents reacts with OFN to give only the 1,2,4,5,6,8-hexasubstituted derivative. Theoretical calculations indicate that with lithium dimethylamide the third fluorine is substituted at position 1, whereas with dimethylamine it is position 3. The basicities of selected hexa- and heptakis(dialkylamino)naphthalenes have been measured; they are all stronger bases than 1,8-bis(dimethylamino)naphthalene, although by less than expected.

Key words: Hexafluorobenzene, Octafluoronaphthalene, Nucleophilic Substitution, Dialkylamino-Substituted Arenes, Basicity

Introduction

It is possible to replace hydrogen by fluorine in a wide range of hydrocarbons without major structural changes [1]. The resulting fluorocarbon systems usually show high thermal stability and have volatilities similar to those of the corresponding hydrocarbon. Because fluorine is so electronegative there are of course major differences in the chemistry of hydro- and fluorocarbons; in particular whereas aromatic hydrocarbons (e.g., benzene) tend to undergo electrophilic substitution (with hydrogen formally leaving as a proton) the reactions of aromatic perfluorocarbons are dominated by nucleophilic substitution. Perfluoroaromatic compounds readily undergo nucleophilic replacement of fluorines, often giving rise to highly substituted derivatives [2, 3].

Although a great many papers have been published in this field, much remains to be done. For example, there is only limited data available concerning nucleophilic substitution by secondary amines. It is generally known that with HFB in excess secondary amine, 1,4-disubstitution typically take place [4, 5], whereas with OFN 2,6-disubstitution occurs [6]. With N-lithium amides, Koppang has shown that interaction of HFB with different lithium anilides allows preparation of mono-, 1,2- or 1,4-di- and 1,2,4,5-tetrasubstituted derivatives, depending on the conditions [7, 8]. We are aware of only one report on the replacement of more than one fluorine in OFN; reaction with lithium amides gave an inseparable mixture of 2,6- and 2,7-dialkylaminosubstituted derivatives (with relative abundance 2 : 1) [9]. Attempts to prepare more highly substituted products have appar-
Action of neutral amines on HFB and OFN

Standard reaction conditions include: 95 °C, 1,3-dimethylimidazolidin-2-one [dimethyl(ethylene)urea, DMEU] as solvent and a 4-fold excess of amine. At lower temperatures, as well as lower amine concentrations, monosubstitution is the main reaction pathway. Selection of the reaction conditions was based on preliminary experiments in which several dipolar aprotic solvents [including dimethylformamide (DMF), hexamethylphosphoric triamide (HMPTA) and dimethyl sulphoxide (DMSO)] were tested. In particular, DMF was rejected at an early stage of this work due to its decomposition, even at low temperatures, to form dimethylamine, which competes with the starting amine in nucleophilic substitution. HMPTA was rejected mainly because of its carcinogenicity and difficulties removing this solvent from the reaction products. DMSO would seem to be a good alternative for the more expensive DMEU, but its main disadvantage is thermal lability at elevated temperatures and slightly lower yields in comparison with DMEU.

HFB under standard conditions even after 24 h produces mainly 1,4-disubstituted products of type 5 (Scheme 1), along with minor amounts of 1,3- (6) and 1,2- (7) isomers. The product composition and structures were determined by a combination of GC/MS, and 1H and 19F NMR. Thus, for example, compounds 6 show the following characteristic 19F NMR signals: an unresolved multiplet at about δ = −140 ppm (2-F), a doublet at −159 ppm (4,6-F, 3J = 21 Hz) and a triplet of doublets at −169 ppm (5-F, 3J = 21 Hz, 5J = 2 Hz). These 19F signals resemble those observed earlier for products obtained by nucleophilic substitution in pentafluoroanilines [4].

Extending the reaction time for up to 7 days had no effect on the substitution pattern, and only with pyrrolidine were trace amounts of trisubstituted prod-
### Scheme 2

![Scheme 2](image)

<table>
<thead>
<tr>
<th>Amine</th>
<th>R</th>
<th>Time, days</th>
<th>Reaction mass composition, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>14</td>
<td>15</td>
<td>16</td>
</tr>
<tr>
<td>Dimethyamine</td>
<td>N(CH₃)₂</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Dimethyamine</td>
<td>N(CH₃)₂</td>
<td>7</td>
<td>0</td>
</tr>
<tr>
<td>Pyrrolidine</td>
<td>pyrrolidin-1-yl</td>
<td>3</td>
<td>0.3</td>
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<tr>
<td>Pyrrolidine</td>
<td>pyrrolidin-1-yl</td>
<td>7</td>
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<tr>
<td>Piperidine</td>
<td>piperidin-1-yl</td>
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<tr>
<td>Piperidine</td>
<td>piperidin-1-yl</td>
<td>7</td>
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</tbody>
</table>

Prolonged heating (up to 7 days) does not have a major effect on the product distribution, increasing somewhat the abundance of compounds 8 and 9.

OFN, having more sites for fluorine substitution along with a larger \( \pi \)-system, already after 3 days produces a mixture of di- 14, tri- 15, and tetr subst utituted 16 derivatives (Scheme 2). The characteristic feature is substitution of \( \beta \)-fluorines exclusively. Triamines 15 show the following set of \( ^{19} \text{F} \) NMR signals: a doublet of doublets at \( \delta = -133 \text{ ppm} \) (4-F, \( J_{\text{peri}} = 69 \text{ Hz} \), \( 5J = 15 \text{ Hz} \)), a doublet of doublets at \( -134 \text{ ppm} \) (5-F, \( J_{\text{peri}} = 69 \text{ Hz} \), \( 5J = 15 \text{ Hz} \)), a doublet of doublets at \( -135 \text{ ppm} \) (1-F, \( J_{\text{peri}} = 67 \text{ Hz} \), \( 5J = 16 \text{ Hz} \)), a doublet at \( -148 \text{ ppm} \) (7-F, \( 3J = 16 \text{ Hz} \)) and a doublet of multiplets at \(-152 \text{ ppm} \) (8-F, \( J_{\text{peri}} = 67 \text{ Hz} \)). The fluorines in compounds of type 16 give a singlet at about \(-135 \text{ ppm} \) (compare with the above-mentioned spectral data and [16]).

Compounds 16 become essentially the sole products in the reaction with dimethyamine and pyrrolidine at the end of 7 days. However, even under these conditions piperidine gave a mixture of 15 and 16, and in order to make the latter the main product, increasing the temperature to 190 °C was required. The substitution pattern for the two other amines at this temperature essentially does not change, although the product yields are lower. With dimethyamine about 20% of the penta substituted product 17 was detected, its \( ^{19} \text{F} \) NMR spectra contained a characteristic \( \text{peri} \)-coupling constant of about 80 Hz in agreement with the proposed structure.

The exclusive \( \beta \)-substitution observed in the reaction of OFN is again a result of maximizing the number of activating meta- and ortho-fluorines [15]. Thus only intermediate 13, and not 12, is produced on reaction of 6 with amines.
compounds 5 and 16 into more electron deficient N-oxides. However, in acidic media (H$_2$O$_2$/acetic or formic acid [3, 5]) even at low temperatures, only oxidation with tarring of all reaction mass takes place. On the other hand, in neutral conditions (H$_2$O$_2$ in methanol, similar to [17]; t-butyl hydroperoxide in the presence of transition metals [18]; H$_2$O$_2$-urea adduct/phthalic anhydride system [19]) the starting compounds remain unchanged even after prolonged reaction times.

The relative reaction rates and product distributions allows the nucleophilicity order for amines to be established: pyrrolidine > dimethylamine > piperidine. This sequence is in agreement with data for other nucleophilic substitution reactions [20].

**Reaction with lithium dialkylamides**

The amides were prepared in situ by reaction of n-butyllithium with amines at −10 °C. We used two equivalents of amide for each fluorine atom with reactions carried out at 20 °C for a period of 24 h.

Tetrasubstituted derivatives 9 were the main products in the case of HFB, with overall yields ranging from 80 to 90%. Whereas in THF and refluxing diethyl ether only compound 9 formed, the same reaction in dioxane leads to a mixture of tri- (8) and tetrasubstituted (9) products; for example, with lithium piperidide the ratio was 42:58. Lithium dimethylamide was an exception giving in diethyl ether a mixture of 5, 8 and 9. This probably arises due to the lower solubility of dimethylamide in ether in comparison with lithium piperidide and pyrrolidine. The addition of excess amide or “disaggregating” agents, such as N,N,N',N'-tetramethylethylenediamine (TMEDA) and HMPTA, to THF solutions does not increase the number of fluorines replaced.

Confirmation of the functional group arrangement in tetrasubstituted benzenes was confirmed by X-ray analysis for the product of the reaction between HFB and lithium piperidide, namely 3,6-difluoro-1,2,4,5-tetrakis(piperidin-1-yl)benzene (Fig. 1). Its distinctive feature, along with considerable twisting (by 60°) of the piperidino groups relative to the benzene ring (c.f. 55° for 1,4,5,8-tetrafluoro-2,3,6,7-tetrakis(piperidin-1-yl)naphthalene), is the significant deviation of fluorines from the least-squares plane of the aromatic ring, 0.22 Å in comparison with 0.054 Å in a similar naphthalene derivative of type 16 [13]. Despite the presence
of sterically demanding substituents, the benzene ring is almost planar; atoms C(1) and C(1A) (Fig. 1) deviate from the least-squares plane by only around 0.5°, showing some tendency to adopt a boat form.

With OFN, the addition of HMPTA to ethereal solvents is necessary in order to prevent contamination with less substituted derivatives. The nature of the solvent, along with nucleophile strength, are the major factors determining the number of fluorines substituted.

Reaction with lithium piperidide in all solvents used leads to the formation of the hexasubstituted product 19 exclusively; its structure was confirmed by X-ray analysis [14].

Lithium dimethylamide give compound 20 only in dioxane; in THF the substitution pattern changes, leading to the heptasubstituted derivative 21. With the more nucleophilic lithium pyrrolidide in dioxane produced an inseparable mixture of 22 and 23 (45 and 55%, respectively), while in THF only 23 formed.

All efforts to achieve octasubstitution, by varying the reaction conditions and the concentration of amide, were unsuccessful.

Attempts to substitute the remaining fluorines in tetrakis(dialkylamino)naphthalenes 16 were also made. Neither lithium piperidide nor pyrrolidide gave any new products, possibly due to repulsion between the amino groups in the corresponding σ-complexes. With lithium dimethylamide in THF, the amine 24 is formed in about 42% yield. Its 19F NMR spectrum showed a number of complicated multiplets, indicating a “through space” interaction with the methyl protons of the peri-dimethylamino group [21].

In general reaction of OFN with neutral amines results primarily in the tetrasubstituted product 16 whereas reaction with lithium amides readily gives the hexasubstituted product 19 and even heptasubstituted products such as 21 and 23. Why do the substitution patterns differ?

Despite the fact that we have not identified the products of mono- and disubstitution in the reaction of OFN with lithium amides, the course of nucleophilic substitution begins similarly to that with neutral amines, with initial replacement of fluoride at position 2 and then positions 6 or 7. This assumption is based on previous observations of the reaction of OFN and lithium diisopropylamide [9]. Thereafter, the substitution pattern differs, as with neutral amines positions 2, 3, 6 and 7 are substituted (see 16), whereas with amides fluorines at positions 3 and 7 are typically not substituted in the final product, although all other fluorines are (see 19). Thus the difference in substitution seems to occur during replacement of the third fluoride.

The mechanism of nucleophilic aromatic substitution (S_NAr) is generally held to proceed via a two-stage process involving the covalent addition of a nucleophile to a substituted (or unsubstituted) carbon ring atom, followed by departure of the leaving group (fluoride in this case) to form the substituted product (Scheme 3). The usually negatively charged intermediate, containing both the nucleophile and the leaving group, is known as a Meisenheimer complex [22], and is the anionic equivalent of the Wheland intermediate in electrophilic substitution [23]. The negative charge in the Meisenheimer complex is delocalized into the aromatic π-system which, like the Wheland intermediate, can be considered as a resonance hybrid of multiple canonical forms.

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thermodynamic argument, i.e., the thermodynamically most stable Meisenheimer complex is the one most likely to form, and the substitution pattern follows directly from that.

Despite its simplicity, and the fact that it cannot possibly account for all the different nucleophiles, solvents and reaction conditions found experimentally, this model proved to be remarkably reliable, successfully predicting the principal substitution site in 16 different aromatic perfluorocarbons, including OFN [24].

The general consensus among experimentalists appears to be that for strong nucleophiles the rate-limiting step in nucleophilic substitution reactions is Meisenheimer complex formation, whereas for weak nucleophiles (such as amines) the rate-limiting step is decomposition of the Meisenheimer complex into the products [2, 27]. The simple model presented in ref. [24] ought to be applicable to the latter case, as any initially formed Meisenheimer complex can decompose several times back into the reactants before forming products, which favors formation of the most thermodynamically stable complex. On the other hand, if the Meisenheimer complex decomposes readily to products, then the thermodynamics is of much less importance and the quantity that really needs to be computed is the barrier height. In this situation, one would not expect the model in ref. [24] to work at all.

We have carried out B3LYP/6-31G* calculations on all distinct Meisenheimer complexes derived from 14 using dimethylamine as the nucleophile (R = N(CH$_3$)$_2$). All calculations used the PQS program [28]. Such calculations are clearly in the spirit of the model in ref. [24]. The lowest energy Meisenheimer complex corresponds to substitution at posi-
Fig. 3. Transition state for decomposition of the Meisenheimer complex derived from 14 by attachment of dimethylamine at position 3. The arrows indicate the atomic displacements in the imaginary mode. The hydrogen atom directly attached to the nitrogen in the dimethylamine ligand is leaving (arrow down) and forming a bond with the leaving fluorine atom formerly attached to the ring carbon at position 3. The ring carbon – leaving fluorine atom distance in the transition state is 1.97 Å. According to Weinhold’s NBO analysis [29], this fluorine is well on the way to being a fluoride ion, with a calculated atomic charge of $-0.64$ e.

Additionally we have located transition states for the reaction of LiN(CH$_3$)$_2$ with 14, with substitution at positions 1, 3 and 4. We have not incorporated any solvent effects, and thus the transition states we have located formally correspond to reaction in the gas phase. Nevertheless, the lowest energy transition state corresponds to nucleophilic attack at position 1, not position 3 which is actually the least favorable. The estimated barrier height for attack at position 1 is only 7.4 kcal/mol, indicating – as is found experimentally – that lithium dimethylamide is very reactive. All transition states were verified as such by vibrational analysis. A schematic of the transition structure for 1-substitution with arrows showing the atomic displacements in the imaginary mode is shown in Fig. 2. The transitions states for 3- and 4-substitution are similar.

Additionally we have calculated transition states for the loss of HF from the various Meisenheimer complexes in the reactions with dimethylamine. As expected, computed barrier heights are noticeably greater than those for the reaction with amide, being around 35 kcal/mol (gas phase), but the lowest barrier is for loss of HF from position 3. Note that in addition to the corresponding Meisenheimer complex being the most stable energetically, the 3-substituted product is also the most stable of the possible products. The transition state for loss of HF from position 3 is shown in Fig. 3.

**Basicity of hexa- and heptakis(dialkylamino)fluoronaphthalenes**

The basicity of the poly(dialkylamino)naphthalenes 19 – 24 is of particular interest, inasmuch as compounds producing Hb of type 2 following protonation are currently among the most intensively studied of all organic bases [10]. These derivatives furthermore contain strongly electron donating β-amino groups, which should significantly increase the resulting basicity.
Since the pyrrolidino substituted products \(22 \) and \(23\) readily oxidize upon exposure to air, we measured the basicity for piperidino \(19\) and dimethylamino \(20, 21, 24\) substituted derivatives. pKa values were determined in 80\% aq. dioxane along with values for the parent compounds \(25\) and \(26\) (Table 1).

During our measurements derivatives \(19 - 21\) gave mono- \(27\) and then diprotonated \(28\) salts, while hexaamine \(24\) gave only the monocation \(29\). As can be seen from Table 1, all compounds synthesized, except the piperidino substituted compound \(19\), are stronger bases than \(25\) and \(26\), although the increase in basicity is not as great as we anticipated based on the number of amino groups. This is most likely due to the strongly strained structures of compounds \(19 - 24\) and their protonated cations, which lead to IHB destabilization and accordingly decrease the basicity.

**Conclusions**

A series of dialkylaminosubstituted benzenes and naphthalenes have been synthesized by nucleophilic substitution in the corresponding perfluoroaromatic compounds using secondary amines and secondary lithium amides. With hexafluorobenzene (HFB) the same substitution pattern is observed with both amines and amides, but with octafluoronapthalene (OFN) the substitution pattern differs after the first two fluorines have been replaced. Theoretical calculations indicate that with lithium dimethylamide the third fluorine is substituted at position 1, whereas with dimethylamine it is position 3. The maximum number of fluorines that can be replaced under our reaction conditions is four for HFB and six (with lithium piperidide) or seven (with dimethylamide and pyrrolidide) for OFN. The hexa- and heptasubstituted naphthalenes are stronger bases than the parent 1,8-bis(dimethylamino)naphthalene \(25\), although the increase in basicity is smaller than expected.

**Experimental Section**

Hexafluorobenzene, octafluoronaphthalene, pyrrolidine and DMEU were purchased from Lancaster; HMPTA and
1.6 M n-butyllithium in hexane from Fluka. \(^{1}H\) and \(^{19}F\) NMR spectra were recorded on a Varian Unity-300 spectrometer with (CH\(_3\))\(_4\)Si as the internal standard for \(^{1}H\) and CFC\(_3\) for \(^{19}F\). GC/MS were performed on Perkin Elmer PE-5MS RX apparatus. A 25 m fused silica (methylphenylsilicone) capillary column was used with UHP grade helium as the carrier gas. pK\(_a\) values were measured by potentiometric titration of corresponding conjugated acids with 0.1 M aq KOH in 80% aqueous dioxiane according to the method described in ref. [31]. 0.05 M aq KCl was used as stock electrolyte. Hydrogen ion activity was measured using an electric cell containing glass and Ag/AgCl (reference) electrodes.

To the amine (2 equivalents per each fluorine atom) in anhydrous THF (or other solvent, 3 ml) 1.6 M n-ButLi in hexane (2 equivalents per each fluorine atom) were added dropwise at −10 °C under argon. The reaction mixture was stirred at −10 °C for 20 min and then a solution of the perfluoroaromatic (0.1 mmol) in THF (or other solvent, 2 ml) was added. The solution was allowed to warm up to room temperature, stirred for 24 h and then quenched with MeOH (1 ml). The reaction mixture was then poured into 30% aq. KOH (15 ml) and the products were extracted with hexane (5 × 3 ml). The extract was washed with water (3 × 15 ml), dried over Na\(_2\)SO\(_4\), evaporated to dryness and crystallized from a suitable solvent or separated by column chromatography on alumina.

3.6-Difluoro-1,2,4,5-tetakis(dimethylamino)benzene

THF as solvent, yield 80%; colourless needles with m. p. 123 − 124 °C (from MeOH). \(^{1}H\) NMR (300 MHz, CDCl\(_3\)): \(\delta = 2.79\) (24 H, m, N(CH\(_2\))\(_2\)), \(^{19}F\) NMR (272 MHz, CDCl\(_3\)): \(\delta = -137.46\) (s) − MS (El, 70 eV); \(m/z\) (%) = 268 (100) \([M]^{+}\), 256 (14) \([M-CH_2NH_2]^{+}\), 255 (17) \([M-2CH_2NH_2]^{+}\), 58 (39) \([C_6H_4N]^{+}\), 44 (71) \([C_6H_4]^{+}\). – C\(_{14}\)H\(_{22}\)F\(_2\)N\(_4\) (286.4): calcd. C 57.8, H 8.3, N 19.6; found C 57.9, H 8.3, N 18.9.

3.6-Difluoro-1,2,4,5-tetakis(pyrrolidin-1-yl)benzene

THF as solvent, yield 90%; colourless needles with m. p. 197 − 198 °C (from MeOH). \(^{1}H\) NMR (300 MHz, CDCl\(_3\)): \(\delta = 1.86\) (16 H, m, CH\(_2\)CH\(_2\)), 3.23 (16 H, m, N(CH\(_2\))\(_2\)), \(^{19}F\) NMR (272 MHz, CDCl\(_3\)): \(\delta = -137.17\) (s) − MS (El, 70 eV); \(m/z\) (%) = 390 (100) \([M]^{+}\), 195 (16) \([M-195]^{+}\), 70 (55) \([C_6H_5N]^{+}\), 55 (20) \([C_6H_4]^{+}\), 41 (38) \([C_6H_7-CH_3]^{+}\). – C\(_{22}\)H\(_{32}\)F\(_2\)N\(_4\) (390.5): calcd. C 67.7, H 8.3, N 14.35; found C 67.6, H 8.1, N 14.2.

3.6-Difluoro-1,2,4,5-tetras(piperidin-1-yl)naphthalene

THF as solvent, yield 79%; colourless needles with m. p. 224 − 225 °C (from MeOH). \(^{1}H\) NMR (300 MHz, CDCl\(_3\)): \(\delta = 1.55\) (8 H, m, CH\(_2\)), 1.61 (16 H, m, CH\(_2\)CH\(_2\)), 3.03 (16 H, m, N(CH\(_2\))\(_2\)), \(^{19}F\) NMR (272 MHz, CDCl\(_3\)): \(\delta = -136.46\) (s) − MS (El, 70 eV); \(m/z\) (%) = 446 (100) \([M]^{+}\), 378 (12) \([M-C_6H_5]^{+}\), 295 (10) \([M-C_6H_5-C_6H_4N]^{+}\), 83 (15) \([C_6H_4N]^{+}\), 43 (28) \([C_6H_2N]^{+}\). – C\(_{26}\)H\(_{40}\)F\(_2\)N\(_4\) (446.6): calcd. C 69.9, H 9.0, N 12.5; found C 70.1, H 9.1, N 12.3.

3.6-Difluoro-1,2,4,5,7,8-hexakis(piperidin-1-yl)naphthalene

THF as solvent, yield 46%; yellow powder with m. p. 247 − 248 °C (from CH\(_2\)Cl\(_2\)). – UV/vis (n-hexane): 10 = 224 (4.46), 259 (4.43), 368 nm (4.07). –
$^1$H NMR (300 MHz, CDC$_3$): $\delta = 1.59$ (36 H, m, CH$_3$CH$_2$CH$_2$), 3.03 (16 H, s, N(CH$_2$)$_2$), 3.16 (8 H, m, N(CH$_2$)$_2$). $^1$F NMR (272 MHz, CDC$_3$): $\delta = -134.54$ (s). $^{13}$C NMR (75 MHz, CDCl$_3$): 58 (100) [C$_3$H$_8$N]+, 374 (12) [M-C$_3$H$_8$N]+, 58 (100) [C$_3$H$_8$N]+. 

7-Fluoro-1,2,3,4,5,6,8-heptakis(dimethylamino)naphthalene

THF as solvent, yield 43%; yellow needles with m.p. 148–149 °C (from MeOH/hexane). – UV/vis (n-hexane): $\lambda_{max}$ (log $\varepsilon$) = 213 (4.54), 236 (4.50), 311 (3.41), 355 nm (shoulder). – $^1$H NMR (300 MHz, CDC$_3$): $\delta = 2.75$ (12 H, m, N(CH$_2$)$_2$), 2.77 (12 H, s, N(CH$_2$)$_2$), 2.78 (12 H, m, N(CH$_2$)$_2$), 2.81 (24 H, m, N(CH$_2$)$_2$), 2.82 (12 H, s, N(CH$_2$)$_2$). $^19$F NMR (272 MHz, CDC$_3$): $\delta = -134.0$ (s). – MS (EI, 70 eV): m/z (%) = 447 (14) [M]+, 389 (11) [M-C$_3$H$_8$N]+. 

595 (36 H, m, N(CH$_2$)$_2$). -1H NMR (300 MHz, CDCl$_3$): $\delta = 2.77$ (12 H, m, N(CH$_2$)$_2$), 2.81 (24 H, s, N(CH$_2$)$_2$), 2.83 (12 H, m, N(CH$_2$)$_2$). $^19$F NMR (272 MHz, CDC$_3$): $\delta = -134.5$ (m). – MS (EI, 70 eV): m/z (%) = 447 (30) [M]+, 389 (17) [M-C$_3$H$_8$N]+, 382 (12) [M-C$_3$H$_8$N-H]+, 374 (12) [M-C$_3$H$_8$N-CH$_3$]+, 58 (100) [C$_3$H$_8$N]+. – $^{13}$C NMR (75 MHz, CDCl$_3$): 56 (90) [M-C$_3$H$_8$N]+, 80 (100) [M-C$_3$H$_8$N]+, 58 (100) [C$_3$H$_8$N]+. 

8-Fluoro-1,2,3,4,5,6,7-heptakis(dimethylamino)naphthalene

Obtained by reaction of 1,4,5,8-tetrafluoro-2,3,6,7-tetra-kis(dimethylamino)naphthalene (0.1 mmol) with lithium dimethylamide (0.8 mmol) in THF according to the general procedure. Yield 42%; yellow crystals with m.p. 176–177 °C (from MeOH/hexane). – UV/vis (n-hexane): $\lambda_{max}$ (log $\varepsilon$) = 220 (4.27), 303 (3.99), 360 nm (shoulder). – $^1$H NMR (300 MHz, CDC$_3$): $\delta = 2.77$ (12 H, m, N(CH$_2$)$_2$), 2.81 (24 H, s, N(CH$_2$)$_2$), 2.83 (12 H, m, N(CH$_2$)$_2$), 2.82 (12 H, s, N(CH$_2$)$_2$). $^19$F NMR (272 MHz, CDC$_3$): $\delta = -134.0$ (s). – MS (EI, 70 eV): m/z (%) = 447 (30) [M]+, 389 (17) [M-C$_3$H$_8$N]+, 382 (12) [M-C$_3$H$_8$N-H]+, 374 (12) [M-C$_3$H$_8$N-CH$_3$]+, 58 (100) [C$_3$H$_8$N]+. – $^{13}$C NMR (75 MHz, CDCl$_3$): 56 (90) [M-C$_3$H$_8$N]+, 80 (100) [M-C$_3$H$_8$N]+, 58 (100) [M-C$_3$H$_8$N]+. 

Crystal structure determination of 3,6-difluoro-1,2,4,5-tetra- kis(piperidin-1-yl)benzene

Single crystals suitable for X-ray diffraction were selected directly from the analytical sample.

Crystal data: C$_{24}$H$_{42}$F$_1$N$_7$, $M = 446.62$, triclinic space group $P1$, $a = 6.5655$ (11), $b = 8.8550$ (15), $c = 10.8553$ (19) $\AA$, $\alpha = 77.8934$ (3), $\beta = 88.4545$ (3), $\gamma = 79.2845$ (3). $Z = 1$, $D_{calc} = 1.223$ g cm$^{-3}$. Diffractometer: Bruker SMART 1000 CCD, $\mu$(Mo K$_\alpha$) = 0.098 mm$^{-1}$. Graphite monochromator, crystal size 0.25 x 0.35 x 0.50 mm, $T = 120(2)$ K. 4357 reflection measured, 2858 unique ($R_{int} = 0.0246$) which were used in all calculations, cut-off criterion $I > 2 \sigma(I)$, $\mu = 0.083$ mm$^{-1}$, solution and refinement with SHELXL-97 [32]. The final $R$ and $wR(F^2)$ values were 0.0608 and 0.1182 (all data), the residual electron density was between 0.24 and $-0.27$ e Å$^{-3}$. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre, CCDC-272720. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code +(1223)336-033; e-mail for inquiry: file-serv@ccdc.cam.ac.uk).


