Reactions of 2-polyfluoroacylcyclohexanones with 1,2-diaminoarenes

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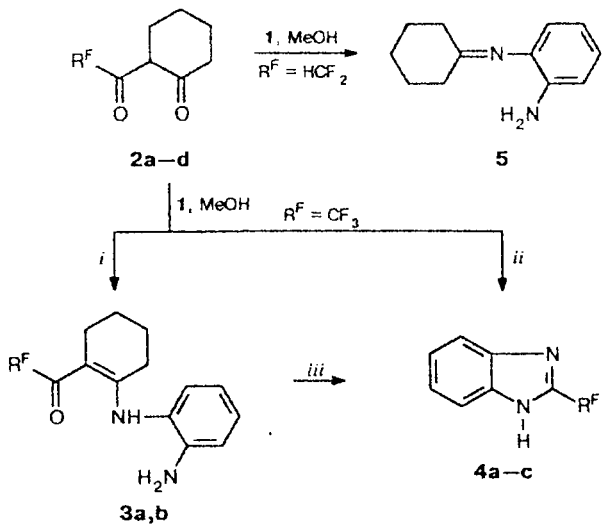
Reactions of 2-polyfluoroacylcyclohexanones with 1,2-diaminoarenes yield, depending on the reaction conditions, various 2-polyfluoroalkyl-substituted benzimidazoles.

Key words: 2-polyfluoroacylcyclohexanones, 1,2-phenylenediamine, 2,3-diaminonaphthalene, benzimidazoles, aminovinyl ketones.

As a rule, reactions of unsymmetrical polyfluoroalkyl-containing 1,3-diketones with 1,2-phenylenediamine (**1**) yield mixtures whose separation can give products of condensation involving either one (aminovinyl ketones and benzimidazoles) or both (3*H*-1,5-benzodiazepines) carbonyl groups, including products of their further intramolecular transformations.[1–3]

The present work studies the reaction of compound **1** with polyfluoroalkyl-containing 1,3-diketones, *viz.*, 2-polyfluoroacylcyclohexanones (**2a—d**) (Scheme 1).

Scheme 1



R^F = CF_3 (**2a, 3a, 4a**), $H(CF_2)_2$ (**2b, 3b, 4b**), HCF_2 (**2c**), n-C_6F_{13} (**2d, 4c**)
i. Without a catalyst or with AcOH (rapidly). *ii*. AcOH (72 h) or $BF_3 \cdot Et_2O$, toluene, Δ. *iii*. $MeNH_2$ or AcOH (72 h).

We showed that 2-polyfluoroacylcyclohexanones react with 1,2-phenylenediamine (**1**) to give, depending on the reaction conditions, various products. Thus, the reaction of diketones **2a,b** with **1** in MeOH without a catalyst results in immediate formation of 1-[(2-aminophenyl)amino]-2-polyfluoroacylcycloalk-1-enes (**3a,b**), products of condensation at one carbonyl group, aminovinyl ketone **3a** precipitating from the reaction mixture. In the presence of AcOH, the precipitate of **3a** is also formed (for R^F = CF_3), but its β-diketone carbon skeleton is split upon keeping of the reaction mixture for 72 h to give 2-trifluoromethylbenzimidazole (**4a**). More drastic reaction conditions, *viz.*, refluxing of a mixture of diketone and compound **1** in toluene in the presence of catalytic amounts of $BF_3 \cdot Et_2O$ with azeotropic removal of released water, afford 2-polyfluoroalkylbenzimidazoles in somewhat higher yields. Acyclic 1,3-diketones are transformed into 2-polyfluoroalkylbenzimidazoles only when they contain two fluoroalkyl groups, while unsymmetrical polyfluoroalkyl-containing 1,3-diketones react with **1** to give fluorine-free benzimidazoles.[3]

In the case of 2-difluoroacetylcyclohexanone **2c**, the reaction with compound **1** follows an unusual pathway to yield imine **5**, which is free of the fluoroalkyl substituent.

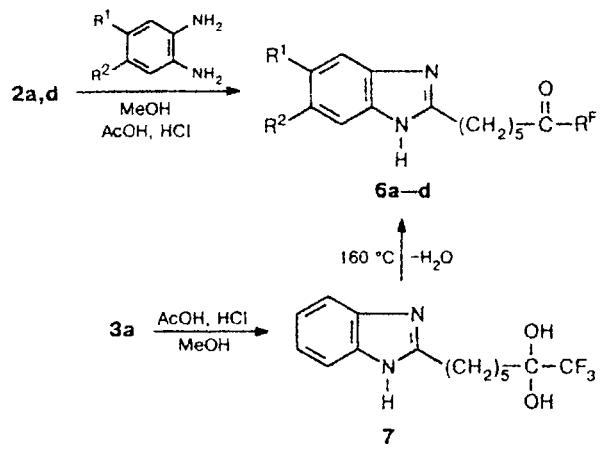
Another direction of splitting of the carbon skeleton of cyclic diketones **2** occurs in their reactions with **1** catalyzed simultaneously by hydrochloric and acetic acids. In this case, the condensation is accompanied by opening of the cyclohexanone ring (Scheme 2).

Thus, the reaction of 2-polyfluoroacylcyclohexanones **2a,d** with compound **1** in methanol in the presence of hydrochloric and acetic acids yields 2-(6-oxopolyfluoroalkyl)benzimidazoles (**6a,b**). These 1,3-diketones react in a similar manner with 2,3-diaminonaphthalene to give 2-(6-oxopolyfluoroalkyl)naphtho[2,3-*d*]imidazoles (**6c,d**). Cyclization of aminovinyl ketone **3a** in the presence of acetic and hydrochloric acids unexpectedly resulted in the formation of ketone hydrate (**7**) instead of ketone **6a**. It is known that ketone hydrates are quite stable only if they contain two fluoroalkyl substituents (as in hexafluoroacetone).[6] However, compound **7** was

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 3, pp. 562—565, March, 1999.

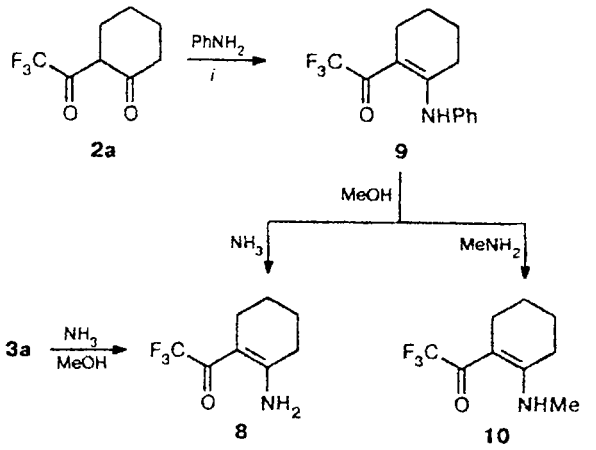
1066-5285/99/4803-0557 $22.00

Scheme 2



R^F = CF_3 (**2a**, **6a,c**), *n*-C_6F_{13} (**2d**, **6b,d**); R^1 = R^2 = H (**6a,b**), R^1, R^2 = $(CH_2{=}CH_2)_2$ (**6c,d**)

Scheme 3



i. $BF_3 \cdot Et_2O$, toluene, Δ.

found to be rather stable and can be recrystallized. This *gem*-diol releases water only upon heating to ~160 °C to give ketone **6a**.

It should be noted that aminovinyl ketones **3a,b** form only one structural isomer (of the two possible) that bears the carbonyl group at the fluoroalkyl substituent. Its structure was confirmed by an IR band at 1580 cm^{-1} characteristic of a chelated carbonyl group located near the polyfluoroalkyl fragment in aminovinyl ketones. This is also in agreement with the direction of reactions of acyclic 1,3-diketones with arylamines.[7] To prove more strictly the structure of these aminovinyl ketones, we attempted to transaminate compound **3a** by reacting it with methylamine. It is known that the ^1H NMR spectra of *N*-methyl-substituted aminovinyl ketones having a *gem*-amino group with respect to the fluoroalkyl substituent exhibit spin-spin coupling between the Me-protons and the fluorine atoms of the fluoroalkyl substituent through the five bonds ($^5J_{H-F}$ = 1.3—1.5 Hz), which is absent in the ^1H NMR spectra of isomeric aminovinyl ketones.[7] However, treatment of aminovinyl ketone **3a** with methylamine gave 2-trifluoromethylbenzimidazole (**4a**) rather than the expected *N*-methyl-substituted aminovinyl ketone. That is why we decided to follow a bypass route to prove the structure of compound **3** (Scheme 3).

Aminovinyl ketone **3a** was successfully transaminated with ammonia into *N*-unsubstituted aminovinyl ketone **8**. The reaction of aniline with 2-trifluoroacetylcyclohexanone (**2a**) in toluene yielded 1-(phenylamino)-2-trifluoroacetylcyclohex-1-ene (**9**), which was transaminated with methylamine into 1-(methylamino)-2-trifluoroacetylcyclohex-1-ene (**10**) and with ammonia into an unsubstituted aminovinyl ketone. The latter proved to be identical with compound **8** directly obtained from aminovinyl ketone **3a**. Inasmuch as the ^1H NMR spectrum of *N*-methyl-substituted aminovinyl ketone **10** exhibits a doublet for the CH_3 group (*i.e.*, $H_{CH_3}-F_{CF_3}$ spin-spin coupling is not observed), its carbonyl group is located at the polyfluoroalkyl substituent. The transamination is not accompanied by structural isomerization,[8] which suggests similar structures for aminovinyl ketones **3a**, **8**, and **9** (as regards the position of the carbonyl group).

Experimental

IR spectra were recorded on a Specord 75 IR spectrophotometer. ^1H NMR spectra were recorded on a Tesla BS-567A spectrometer (100 MHz) with $SiMe_4$ as the internal standard. The starting β-diketones **2a,c,d** were obtained according to the known procedure,[4,5] and **2b** was obtained in a similar way.

2-(2,2,3,3-Tetrafluoropropanoyl)cyclohexanone (2b). M.p. 88—89 °C (10 Torr). Found (%): C, 47.56; H, 4.37; F, 33.47. $C_9H_{10}F_4O_2$. Calculated (%): C, 47.79; H, 4.46; F, 33.60. IR (thin film), ν/cm^{-1}: 1570 (C=O); 2400—3500 (OH). ^1H NMR ($CDCl_3$), δ: 1.63—1.90 (m, 4 H, 2 CH_2); 2.30—2.57 (m, 4 H, 2 CH_2); 6.20 (tt, 1 H, HCF_2, $^2J_{H-F}$ = 52.67 Hz, $^3J_{H-F}$ = 5.61 Hz); 15.42 (br.s, 1 H, OH).

Reaction of 2-trifluoroacetylcyclohexanone (2a) with 1,2-phenylenediamine (1) in the presence of $BF_3 \cdot Et_2O$. A solution of **2a** (15.5 g, 80 mmol) and **1** (8.6 g, 80 mmol) in 100 mL of toluene was refluxed with three drops of $BF_3 \cdot Et_2O$ in a flask equipped with a Dean—Stark adapter until water ceased to evolve (~4 h). The reaction mixture was then cooled and filtered through a silica gel layer, and the toluene was removed (oil bath). The residue was suspended in 100 mL of water and heated to boiling. The suspension was diluted with EtOH to complete dissolution of the solid product and cooled. The precipitate that formed was filtered off to give 2-trifluoromethylbenzimidazole (**4a**) (its characteristics correlate with those cited in Ref. 3). Yield 12.3 g (83%).

Reaction of 2-(2,2,3,3-tetrafluoropropanoyl)cyclohexanone (2b) with compound 1 in the presence of $BF_3 \cdot Et_2O$. By analogy, 2-(1,1,2,2-tetrafluoroethyl)benzimidazole **4b** was ob-

tained from **2b** (10 g, 44 mmol) and **1** (4.8 g, 44 mmol). Yield 2.5 g (26%) (recrystallized from EtOH—water (1 : 3)). The characteristics of **4b** correlate with those cited in Ref. 3.

Reaction of 2-trifluoroacetylcyclohexanone (2a) with compound 1 without a catalyst. A solution of **2a** (1 g, 5 mmol) in 3 mL of MeOH was agitated with compound **1** (0.6 g, 5 mmol) for 10 min. The precipitate that formed was filtered off and recrystallized from a MeOH—water (3 : 1) mixture to give 1-[(2-aminophenyl)amino]-2-trifluoroacetylcyclohex-1-ene **3a**. Yield 0.3 g (20%), colorless needles, m.p. 145—146 °C. Found (%): C, 58.92; H, 5.14; N, 9.92. $C_{14}H_{15}F_3N_2O$. Calculated (%): C, 59.15; H, 5.32; N, 9.85. IR (Vaseline oil), ν/cm^{-1}: 1580 (C=O); 3350, 3445 (N—H). ^1H NMR ($CDCl_3$), δ: 1.60—2.56 (m, 8 H, 4 CH_2); 3.9 (br.s, 2 H, NH_2); 6.66—7.75 (m, 4 H, Ar); 12.7 (s, 1 H, NH).

Reaction of 2-trifluoroacetylcyclohexanone (2a) with compound 1 in the presence of AcOH. *A.* Compound **1** (0.9 g, 8 mmol) and 1 mL of glacial AcOH were added to a solution of **2a** (1.5 g, 8 mmol) in 6 mL of MeOH. After one hour, the crystals that formed were filtered off and recrystallized from a MeOH—water (3 : 1) mixture to give 1-[(2-aminophenyl)amino]-2-trifluoroacetylcyclohex-1-ene (**3a**). Yield 1 g (44%).

B. Compound **1** (0.9 g, 8 mmol) and 1 mL of glacial AcOH were added to a solution of **2a** (1.5 g, 8 mmol) in 10 mL of MeOH, and the reaction mixture was left for 72 h. The methanol was removed, and the solid residue was recrystallized from an EtOH—water (1 : 3) mixture to give 2-trifluoromethylbenzimidazole (**4a**). Yield 0.2 g (13%).

Reaction of 2-(2,2,3,3-tetrafluoropropanoyl)cyclohexanone (2b) with compound 1 in the presence of AcOH. *A.* 1-[(2-Aminophenyl)amino]-2-(1,1,2,2-tetrafluoropropanoyl)cyclohex-1-ene (**3b**) was obtained from **2b** (1 g, 0.45 mmol) and **1** (0.5 g, 0.45 mmol). Yield 0.5 g (35%), yellowish crystals (MeOH—water (4 : 1)), m.p. 121—122 °C. Found (%): C, 57.00; H, 5.03; F, 24.24; N, 8.88. $C_{15}H_{16}F_4N_2O$. Calculated (%): C, 56.96; H, 5.10; F, 24.03; N, 8.86. IR (Vaseline oil), ν/cm^{-1}: 1570 (C=O); 3360, 3450 (NH). ^1H NMR ($CDCl_3$), δ: 1.37—1.78 (m, 4 H, 2 CH_2); 2.32 (br.s, 2 H, CH_2); 2.64—2.77 (m, 2 H, CH_2); 3.76 (br.s, 2 H, NH_2); 6.31 (tt, 1 H, HCF_2, $^2J_{H-F}$ = 53.0 Hz, $^3J_{H-F}$ = 5.7 Hz); 6.71—7.36 (m, 4 H, Ar); 12.88 (s, 1 H, NH).

B. 2-(1,1,2,2-Tetrafluoroethyl)benzimidazole (**4b**) was obtained from **2b** (2 g, 8.8 mmol) and **1** (0.95 g, 8.8 mmol). Yield 0.45 g (24%) (recrystallized from EtOH—water (1 : 3)).

Reaction of 2-(perfluoroheptanoyl)cyclohexanone (2d) with compound 1 in the presence of AcOH (procedure *B*). 2-(Perfluorohexyl)benzimidazole (**4d**) was obtained from **2d** (2 g, 4.5 mmol) and **1** (0.5 g, 4.5 mmol). Yield 1.5 g (77%), colorless crystals (EtOH—water (4 : 1)), m.p. 160 °C (sublim.). Found (%): C, 35.79; H, 1.25; F, 56.78; N, 6.29. $C_{13}H_5F_{13}N_2$. Calculated (%): C, 35.80; H, 1.16; F, 56.62; N, 6.42. IR (Vaseline oil), ν/cm^{-1}: 3060—3500 (N—H). ^1H NMR ($CDCl_3$), δ: 7.26—7.46 (m, 4 H, Ar); 7.70 (br.s, 1 H, NH).

Cyclization of 1-[(2-aminophenyl)amino]-2-trifluoroacetylcyclohex-1-ene (3a) in the presence of AcOH. Glacial AcOH (1 mL) was added to a solution of **3a** (0.7 g, 2.5 mmol) in 20 mL of MeOH. The reaction mixture was left for 72 h and then poured into 100 mL of water. The reaction products were extracted with $CHCl_3$. The extracts were combined and dried with $MgSO_4$. The solvent was removed, and the residue was recrystallized from toluene to give **4a**. Yield 0.3 g (65%).

Transamination of 1-[(2-aminophenyl)amino]-2-trifluoroacetylcyclohex-1-ene (3a) with methylamine. A flow of $MeNH_2$ was passed through a solution of **3a** (1.5 g, 5.3 mmol) in 20 mL of MeOH until the reaction mixture stopped heating up. The methanol was removed, and the residue was eluted with $CHCl_3$ on a silica gel layer and recrystallized from toluene to give **4a**. Yield 0.9 g (91%).

Transamination of 1-[(2-aminophenyl)amino]-2-trifluoroacetylcyclohex-1-ene (3a) with ammonia. By analogy, compound **8** was obtained from **3a** (0.5 g, 1.8 mmol) and ammonia. Yield 0.24 g (70%), colorless needles, m.p. 135—136 °C (from *n*-hexane). Found (%): C, 49.80; H, 5.48; F, 29.40; N, 7.21. $C_8H_{10}F_3NO$. Calculated (%): C, 49.74; H, 5.22; F, 29.51; N, 7.25. IR (Vaseline oil), ν/cm^{-1}: 1600 (C=O); 3160, 3295 (N—H). ^1H NMR ($CDCl_3$), δ: 1.52—1.93 (m, 4 H, 2 CH_2); 2.23—2.71 (m, 4 H, 2 CH_2); 5.49 (br.s, 1 H, NH); 10.29 (br.s, 1 H, NH).

1-(Phenylamino)-2-trifluoroacetylcyclohex-1-ene (9). A solution of **2a** (15.8 g, 80 mmol) and aniline (8.1 g, 80 mmol) in 150 mL of toluene was refluxed with three drops of $BF_3 \cdot Et_2O$ in a flask equipped with a Dean—Stark adapter until water ceased to evolve (~4 h). Then, the reaction mixture was cooled and filtered through a silica gel layer. The toluene was removed (oil bath), and the residue was recrystallized from *n*-hexane to give compound **9**. Yield 16.8 g (78%), yellow crystals, m.p. 70—71 °C. Found (%): C, 62.38; H, 5.24; F, 21.04; N, 5.18. $C_{14}H_{14}F_3NO$. Calculated (%): C, 62.45; H, 5.24; F, 21.17; N, 5.20. IR (Vaseline oil), ν/cm^{-1}: 1590 (C=O). ^1H NMR ($CDCl_3$), δ: 1.43—1.94 (m, 4 H, 2 CH_2); 2.22—2.79 (m, 4 H, 2 CH_2); 6.96—7.55 (m, 5 H, Ph); 13.26 (s, 1 H, NH).

Transamination of 1-(phenylamino)-2-trifluoroacetylcyclohex-1-ene 9 with ammonia. By analogy with the transamination of compound **3a**, 1-amino-2-trifluoroacetylcyclohex-1-ene was obtained from **9** (5 g, 19 mmol) and ammonia. Yield 3.1 g (85%). The product is identical with compound **8**.

Transamination of compound 9 with methylamine. By analogy with the transamination of compound **3a**, 1-(methylamino)-2-trifluoroacetylcyclohex-1-ene (**10**) was obtained from **9** (3 g, 10 mmol) and $MeNH_2$. Yield 1.8 g (77%), colorless needles, m.p. 56—57 °C. Found (%): C, 52.28; H, 5.73; F, 27.62; N, 6.73. $C_9H_{12}F_3NO$. Calculated (%): C, 52.17; H, 5.84; F, 27.51; N, 6.76. IR (Vaseline oil), ν/cm^{-1}: 1600 (C=O). ^1H NMR ($CDCl_3$), δ: 1.47—1.84 (m, 4 H, 2 CH_2); 2.30—2.60 (m, 4 H, 2 CH_2); 2.99 (d, 3 H, CH_3, $^3J_{H-H}$ = 5.3 Hz); 11.95 (s, 1 H, NH).

Reaction of 2-difluoroacetylcyclohexanone (2c) with compound 1. Compound **2c** (1.4 g, 8 mmol) was added to a solution of **1** (1.08 g, 10 mmol) in 4 mL of MeOH. The crystals that formed were filtered off to give imine **5**. Yield 0.5 g (33%), colorless needles, m.p. 124—125 °C. Found (%): C, 76.05; H, 9.08; N, 14.92. $C_{12}H_{16}N_2$. Calculated (%): C, 76.55; H, 8.57; N, 14.88. IR (Vaseline oil), ν/cm^{-1}: 3230, 3325 (NH). ^1H NMR (acetone-d_6), δ: 1.50—1.69 (m, 10 H, 5 CH_2); 4.80 (br.s, 2 H, NH_2); 6.28—6.48 (m, 4 H, Ar).

2-(6-Oxo-7,7,7-trifluoroheptyl)benzimidazole (6a). A solution of **2a** (5 g, 26 mmol) and **1** (3 g, 28 mmol) in 30 mL of MeOH was shaken with 1 mL of AcOH for 5 min and allowed to stand with 5 mL of conc. HCl for one day. Then, the reaction mixture was neutralized with a saturated solution of Na_2CO_3 and diluted with 50 mL of water. The crystals that formed were filtered off and recrystallized from a petroleum ether—*o*-xylene (3 : 1) mixture to give compound **6a**. Yield 2.5 g (34%), colorless crystals, m.p. 159—160 °C (sublim.). Found (%): C, 59.15; H, 5.11; F, 20.12; N, 9.76. $C_{14}H_{15}F_3N_2O$. Calculated (%): C, 59.15; H, 5.32; F, 20.05; N, 9.85. IR (Vaseline oil), ν/cm^{-1}: 1760 (C=O). ^1H NMR ($CDCl_3$), δ: 1.34—1.94 (m, 6 H, 3 CH_2); 2.74—2.87 (m, 4 H, 2 CH_2); 7.05—7.51 (m, 4 H, Ar); 12.10 (br.s, 1 H, NH).

2-(6-Oxo-7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluorododecyl)benzimidazole (6b). By analogy with **6a**, compound **6b** was obtained from **2d** (2 g, 4.5 mmol) and **1** (0.5 g, 4.5 mmol). Yield 1.2 g (51%), colorless crystals (from toluene), m.p. 160 °C. Found (%): C, 42.63; H, 2.79; F, 45.81; N, 5.35. $C_{19}H_{15}F_{13}N_2O$. Calculated (%): C, 42.71; H, 2.83; F, 46.22; N, 5.24. IR (Vaseline oil), ν/cm^{-1}: 1740 (C=O). ^1H NMR ($CDCl_3$), δ: 1.49—1.82 (m, 4 H, 2 CH_2); 2.03—2.33 (m, 2 H, CH_2); 2.75 (t, 2 H, CH_2, $^3J_{H-H}$ = 6.3 Hz); 3.42 (t, 2 H, CH_2, $^3J_{H-H}$ = 7.2 Hz); 7.40—7.87 (m, 4 H, Ar); 14.40 (br.s, 1 H, NH).

2-(6-Oxo-7,7,7-trifluoroheptyl)naphtho[2,3-*d*]imidazole (6c). By analogy with **6a**, compound **6c** was obtained from **2a** (3.0 g, 15 mmol) and 2,3-diaminonaphthalene (2.4 g, 15 mmol). Yield 3.5 g (70%), colorless crystals (from *o*-xylene), m.p. 163—164 °C. Found (%): C, 64.60; H, 5.17; F, 16.94; N, 8.35. $C_{18}H_{17}F_3N_2O$. Calculated (%): C, 64.66; H, 5.13; F, 17.05; N, 8.38. IR (Vaseline oil), ν/cm^{-1}: 1750 (C=O). ^1H NMR (acetone-d_6), δ: 1.41—1.97 (m, 6 H, 3 CH_2); 2.84—3.08 (m, 4 H, 2 CH_2); 7.29—7.42 (m, 2 H, Ar); 7.87—8.02 (m, 4 H, Ar).

2-(6-Oxo-7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluorododecyl)naphtho[2,3-*d*]imidazole (6d). By analogy with **6a**, compound **6d** was obtained from **2d** (3.5 g, 7.9 mmol) and 2,3-diaminonaphthalene (1.25 g, 7.9 mmol). Yield 3.2 g (69%), colorless crystals (from *o*-xylene), m.p. 140—141 °C. Found (%): C, 47.04; H, 3.00; F, 41.97; N, 4.78. $C_{23}H_{17}F_{13}N_2O$. Calculated (%): C, 47.27; H, 2.93; F, 42.26; N, 4.79. IR (Vaseline oil), ν/cm^{-1}: 1740 (C=O); 3600 (NH). ^1H NMR ($CDCl_3$), δ: 1.26—2.09 (m, 6 H, 3 CH_2); 2.63—2.76 (m, 2 H, CH_2); 2.89—3.04 (m, 2 H, CH_2); 7.25—7.46 (m, 2 H, Ar); 7.86—7.96 (m, 4 H, Ar); 10.2 (br.s, 1 H, NH).

Cyclization of 1-[(2-aminophenyl)amino]-2-trifluoroacetylcyclohex-1-ene (3a) in the presence of AcOH and HCl. A solution of **3a** (0.4 g, 1.4 mmol) in 25 mL of MeOH was shaken with 0.5 mL of glacial AcOH for 5 min and allowed to stand with 2.5 mL of conc. HCl for one day. The reaction mixture was poured into 50 mL of water and neutralized with a saturated solution of Na_2CO_3. The precipitate that formed was filtered off, dried, and recrystallized from a water—EtOH (2 : 1) mixture to give 2-(6,6-dihydroxy-7,7,7-trifluoroheptyl)benzimidazole (7). Yield 0.3 g (71%), colorless crystals, m.p. 156—157 °C (decomp.). Found (%): C, 55.61; H, 5.57; N, 9.11. $C_{14}H_{17}F_3N_2O_2$. Calculated (%): C, 55.63; H, 5.67; N, 9.27. IR (Vaseline oil), ν/cm^{-1}: 3300 (O—H). ^1H NMR (DMSO-d_6), δ: 1.10—2.04 (m, 8 H, 4 CH_2); 2.66—2.98 (m, 2 H, CH_2); 6.59 (s, 2 H, 2 OH); 7.00—7.50 (m, 4 H, Ar); 12.11 (br.s, 1 H, NH).

Dehydration of 2-(6,6-dihydroxy-7,7,7-trifluoroheptyl)benzimidazole (7). Compound 7 (0.5 g, 1.7 mmol) was heated on a piece of watch glass to the melting point, kept at this temperature for one minute, and cooled. The residue was recrystallized from a petroleum ether—*o*-xylene (3 : 1) mixture to give 2-(6-oxo-7,7,7-trifluoroheptyl)benzimidazole (**6a**). Yield 0.39 g (83%).

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Received July 7, 1998