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Reaction, identification, and fluorescence of aminoperfluorophenazines

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A B S T R A C T

Perfluorophenazine regiospecifically reacted with monoalkyl-, dialkyl-, and arylamines to afford the corresponding 2-amino-substituted derivatives. 2-(Ethylamino)- and 2-(diethylamino)perfluorophenazine reacted with another molar amount of ethylamine and diethylamine to preferentially provide the 2,7-disubstituted derivatives, respectively. Perfluoro(2,7-dimethylphenazine) was allowed to react with ethylamine to give the 1-ethylamino derivative. These regiospecific reactions were explained by the density functional theory (DFT) calculations. Perfluorophenazine reacted with ethylenediamine to afford the 2,3-cyclized and *N*,*N*′-bis(2-perfluorophenazinyl) derivatives. These amino-substituted products showed UV–vis absorption (λ_{max}) and fluorescence maxima (F_{max}) in the range of 439–536 and 524–613 nm in hexane, respectively. Some of them exhibit intense fluorescence.

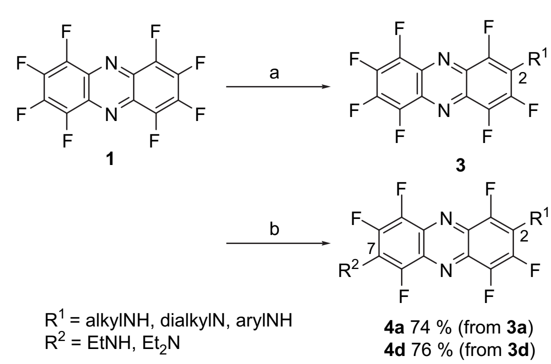
1. Introduction

Phenazines are important compounds due to their application to dyes and medicine. Fluoro- and perfluorophenazines are synthesized by the chemical[1] and electrochemical oxidation[2] of fluoroanilines. Perfluorophenazine has been reported to react with a hydroxide ion and dimethylamine to give the 2-hydroxy and 2-dimethyl-amino derivatives, respectively.[3] The photochemical reaction of perfluorophenazine in aqueous acetonitrile has been reported to produce the 2-hydroxy derivative.[4] However, it was pointed out that the thermal reaction of perfluorophenazine with a hydroxide ion might produce the 1-hydroxy derivative.[4] As fluorine atoms on the aromatic ring show complicated fluorine–fluorine coupling in the ^{19}F NMR spectroscopy, identification of perfluoroaromatic compounds is difficult. Thus, the reaction of perfluorophenazine with nucleophiles is not clearly understood. Therefore, it is of importance to clarify the reaction. Furthermore, as fluoro-, fluoroalkyl-, perfluoroalkyl-sulfonyl-, and fluoroalkanoyl-substituted compounds show unique properties, the properties of fluorine-containing dyes are also of interest from the viewpoint of their applications.[5] Though a few kinds of fluoroalkyl-substituted dyes such as coumarins and perylenediimides have been reported to show strong fluorescence, no perfluoroaromatic compounds showing intense fluorescence have been reported so far. We report herein the reaction, identification, and fluorescence properties of aminoperfluorophenazines.

2. Results and discussion

2.1. Reaction and identification

Perfluorophenazine (**1**) was allowed to react with a molar amount of amines **2** in the presence of triethylamine (TEA) to regiospecifically provide the 2-amino-substituted products **3** as shown in Scheme 1 and Table 1.



Scheme 1. Reaction of **1** with amines **2**. Reagents and conditions: (a) **2** (R^1H, 1.2 molar amounts), DMF, TEA, 0–25 °C, 3–24 h. (b) **2** (R^2H, 1.2 molar amounts), DMF, TEA, 0–25 °C, 24 h.

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Table 1
Reaction of **1** with amines **2**[a]

Run	Compd	R^1	Time (h)	Yield[b] of **3** (%)
1	**a**	EtNH	3	74
2	**b**	*c*-HexNH	3	92
3	**c**	Me_2N	3	96
4	**d**	Et_2N	3	75
5	**e**	$(CH_2)_4N$	3	91
6	**f**	PhNH	24	27
7	**g**	$4\text{-}MeOC_6H_4NH$	24	67
8	**h**	$4\text{-}Et_2NC_6H_4NH$	8	85

[a] A DMF solution (10 mL) of **1** (0.5 mmol) was reacted with amines **2** (0.6 mmol) in the presence of TEA (0.55 mmol) at 0–25 °C.
[b] Isolated yields.

The ^{19}F NMR spectrum of **3a**, obtained by the reaction of **1** with ethylamine (**2a**), showed seven signals at −157.34 (1F), −153.47 (1F), −152.94 (1F), −151.94 (1F), −151.16 (1F), −150.04 (1F), and −143.05 (1F) ppm. The EIMS spectrum showed the molecular ion peak at *m*/*z* 349. The elemental analysis data indicated the molecular formula of $C_{14}H_6F_7N_3$. It is clear that this compound is ethylamino-substituted perfluorophenazine. However, these data are not sufficient to identify whether the product is 1- or 2-ethylamino derivative. Therefore, the X-ray crystallography of **3a**, crystallized from a dichloromethane–hexane mixed solution, was performed. The ORTEP drawing is depicted in Figure 1. It is clear that only 2-(ethylamino)perfluorophenazine is isolated. The phenazine ring is planar and the other component atoms are located on the same plane.

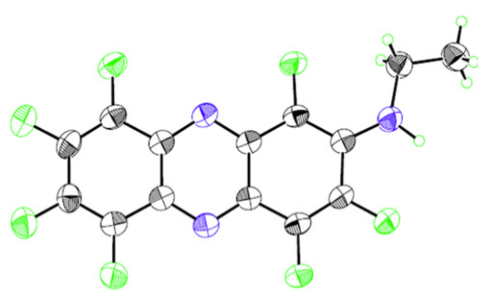


Figure 1. ORTEP drawing of **3a**.

Compound **1** smoothly reacted with alkylamines **2a**, **2b**, **2c**, **2d**, and **2e** to provide **3a**, **3b**, **3c**, **3d**, and **3e** in good yields, respectively. When compound **1** was allowed to react with aromatic amines **2f**, **2g**, and **2h**, longer reaction time was required to complete the reaction due to low nucleophilicity of the aromatic amines. The yield of **3f** was low because of the formation of unidentified products.

The reaction of 2-ethylamino- and 2-(diethylamino)-perfluorophenazines **3a** and **3d** with another molar amount of amines **2a** and **2d** preferentially gave the 2,7-diamino derivatives **4a** and **4d**, respectively, as shown in Scheme 1. The ^{19}F NMR spectrum of **4d** showed three signals at −154.65 (2F), −141.62 (2F), and −136.01 (2F) ppm. The EIMS spectrum indicated the molecular ion peak at *m*/*z* 430. The elemental analysis data showed the component $C_{20}H_{20}F_6N_4$. Again, it is not clear whether the product is 2,7- or 2,8-disubstituted derivative. Figure 2 shows the ORTEP drawing of **4d**, crystallized from a dichloromethane–hexane mixed solution. Thus, the product **4d** was identified as 2,7-bis(diethylamino)perfluorophenazine. The phenazine ring is planar. The fluorine and nitrogen atoms are located on the same plane. The ethyl groups on the amino moieties are projected out of the plane. The reaction of **3a** with **2a** also gave 2,7-bis(ethylamino) derivative **4a**, whose ^{19}F NMR spectrum was similar to that of **4d**.

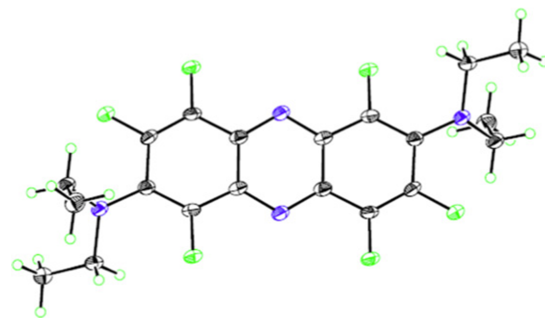
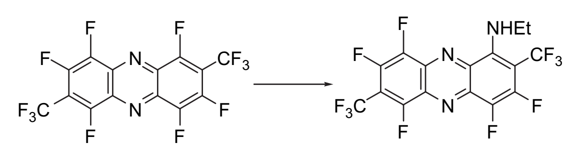


Figure 2. ORTEP drawing of **4d**.

Perfluoro(2,7-dimethylphenazine) (**5**) smoothly reacted with ethylamine (**2a**) to preferentially give 1-ethylamino derivative **6a** in a 47% yield as shown in Scheme 2. The ^{19}F NMR spectrum of **6a** showed seven signals at −166.48 (1F), −150.97 to −150.89 (1F), −136.29 to −136.14 (1F), −127.67 to −127.47 (1F), −119.87 to −119.65 (1F), −56.12 to −56.02 (3F), and −52.40 (3F) ppm. The EIMS spectrum showed the molecular ion peak at *m*/*z* 449. The elemental analysis showed the component $C_{16}H_6F_{11}N_3$. The ORTEP drawing of **6a** is shown in Figure 3. It is clear that the reaction of **5** with **2a** gave 1-ethylaminoperfluoro(2,7-dimethylphenazine) (**6a**). The phenazine ring is slightly distorted due to steric repulsion between the neighboring trifluoromethyl and ethylamino groups. The ethylamino group at the 1-position and trifluoromethyl group at the 2-position are slightly deviated toward the opposite direction from the phenazine ring.



5 **6a** 47 %

Scheme 2. Reaction of **5** with ethylamine (**2a**). Reagents and conditions: ethylamine (**2a**, 1.2 molar amounts), DMF, TEA, 0–25 °C, 1 h.

The reaction of **1** with diamines **7a** and **7b** is shown in Scheme 3. Compound **1** was allowed to react with ethylenediamine (**7a**) to provide both 2,3-cyclized and *N*,*N*′-bis(2-perfluorophenazinyl) derivatives **8a** and **9a**. The EIMS spectrum of **8a** revealed the molecular ion peak at *m*/*z* 344. The ^{19}F NMR spectrum showed only three signals at −163.76 (2F), −160.91 to −160.88 (2F), and −156.45 to −156.42 (2F) ppm. The elemental analysis data also supported the structure. Thus, the compound **8a** was identified as the 2,3-cyclized

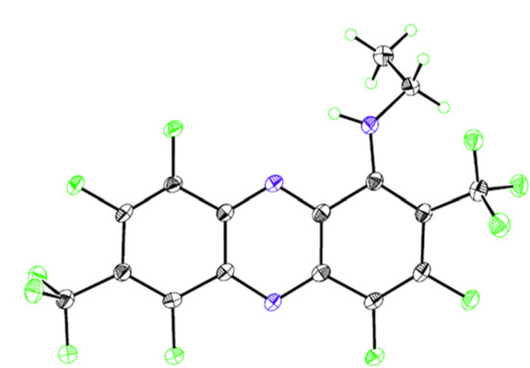
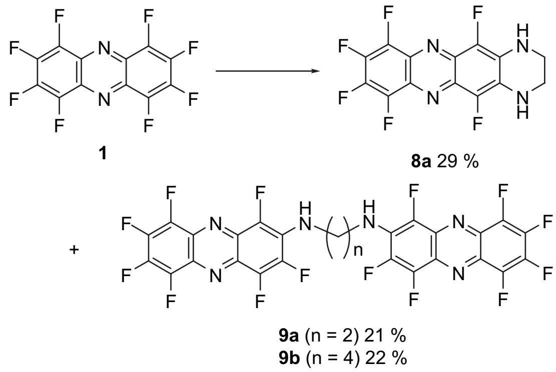


Figure 3. ORTEP drawing of **6a**.



Scheme 3. Reaction of **1** with diamines **7a** and **7b**. Reagents and conditions: ethylenediamine (**7a**, *n*=2, 1.2 molar amounts), DMF, TEA, 0–25 °C, 1.5 h, and 1,4-diaminobutane (**7b**, *n*=4, 1.2 molar amounts), DMF, 0–25 °C, 3 h.

derivative. The EIMS spectrum of **9a** showed the molecular ion peak at *m*/*z* 668. The ^{19}F NMR spectrum of **9a** showed seven signals at −156.95 (2F), −156.82 (2F), −156.74 to −156.66 (2F), −155.04 (2F), −154.37 (2F), −154.13 (2F), and −143.01 (2F) ppm. The reaction of **1** with butane-1,4-diamine (**7b**) afforded only *N*,*N*′-bis(2-perfluorophenazinyl) derivative **9b**.

2.2. DFT calculations for regiospecific reactions

To elucidate the regiospecific substitution reactions of perfluorophenazines with amines, the DFT calculations were performed with the Gaussian 03W program.[6] The structures were optimized at the B3LYP/6-31G* level.[7–9] All the energies include the zero-point energy corrections, which were scaled by a factor of 0.9804.[10] The calculated partial charge and fukui function (f^*), which did not reproduce the reaction, and cartesian coordinates of the optimized structures are shown in Supplementary data.

Firstly, the reaction of **1** with amines **2** to produce the 2-amino derivatives **3** was examined. The reaction of **1** with **2d** was investigated in detail. The geometries of **1**, **2d**, transition-state structures, (diethylamino)perfluoro-phenazines, and hydrogen fluoride were optimized. The optimized transition-state structures at the 1- and 2-positions, **TS1** and **TS2**, respectively, are shown in Figure 4. The structures were characterized in two ways: (a) the frequency calculations yielded only one imaginary frequency of 193*i* and 127*i* cm^{-1} for **TS1** and **TS2** structures, respectively, and (b) the imaginary frequency vibrational mode for the transition states clearly showed that the mode leads to the reaction path direction. The **TS2** structure was calculated to be 1.50 kcal mol^{-1} more stable than **TS1** structure, indicating that the activation energy to produce the 2-substituted derivative is less than that to produce the 1-substituted product. In the **TS1** structure, the phenazine ring was distorted from planar structure due to steric and/or electronic repulsion between the diethylamino-nitrogen and the nitrogen atom at the 10-position. **TS2** structure could prevent such repulsion by distorting two fluorine atoms attaching to the 1- and 3-positions. Hence, it is reasonable that the planar **TS2** structure is more stable than the distorted **TS1** structure.

The potential energy profile along the intrinsic reaction coordinate (IRC) of the reaction at the 2-position is shown in Figure 5. The reaction was exothermic. The potential energy curve showed a plateau before reaching at **TS2**. The plateau edge is indicated as **PE2**. The structures at **PE2** and **TS2** together with selected bond length are shown in Figure 6. The **PE2** structure indicates that the nitrogen atom of **2d** is approaching the carbon atom at the

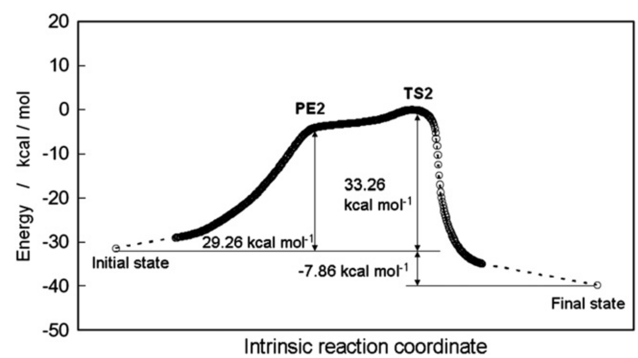


Figure 5. Calculated potential energy profile along the intrinsic coordination for reaction of **1** with **2d** at 2-position.

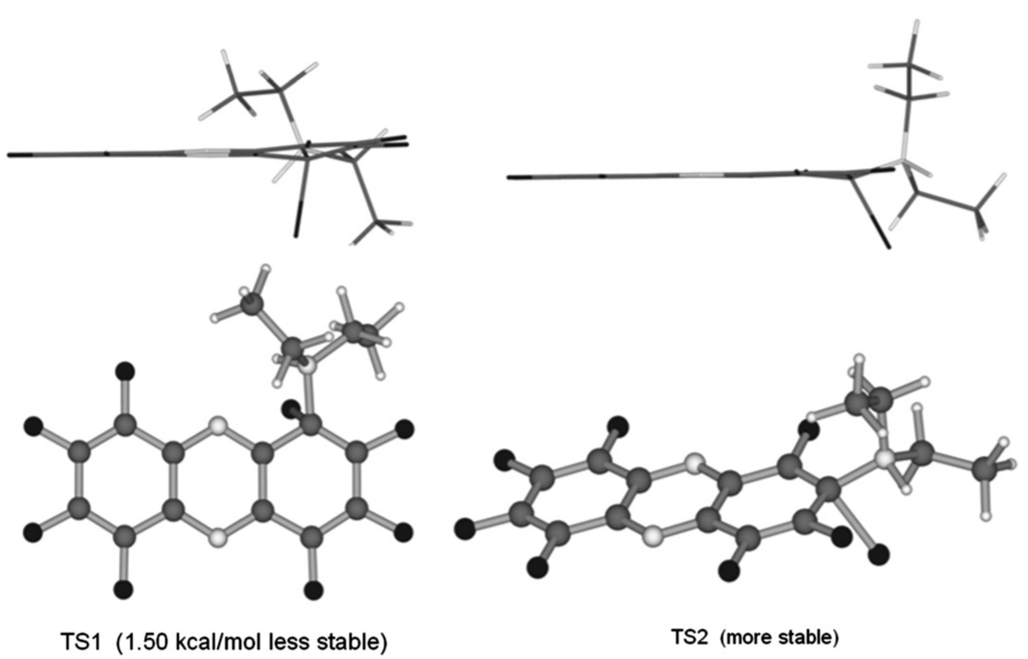


Figure 4. Optimized transition-state structures **TS1** and **TS2** leading to 1- and 2-diethylamino derivatives in reaction of **1** with **2d**.

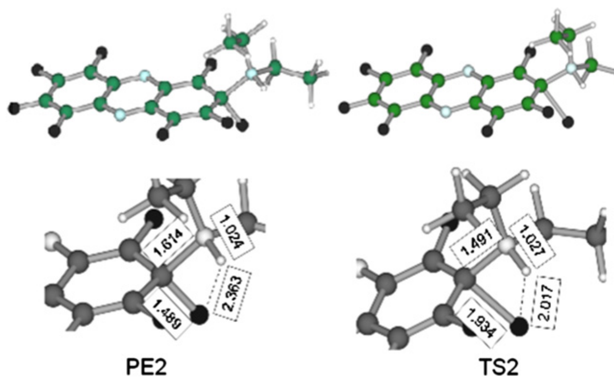


Figure 6. **SH2** and **TS2** structures and selected bond length (Å).

2-position of **1**. The **TS2** structure depicts that the C–N linkage is formed at the 2-position and, at the same time, hydrogen fluoride is eliminating. Thus, the regiospecific substitution reaction of **1** with amines **2** proceeds by way of four-centered transition state to produce the 2-amino derivatives **3**.

Next, the reaction of **3d** with **2d** to form 2,7-bis(diethylamino) derivative **4d** was examined. The calculated transition-state structures, **TS26**, **TS27**, **TS28**, and **TS29** are shown in Figure 7. The **TS27** structure was calculated to be most stable followed by **TS28**, **TS26**, and **TS29** structures. This result supports that 2-amino-perfluorophenazines **3** regiospecifically react with amines **2** to give the 2,7-disubstituted products **4**.

Finally, the regiospecific reaction of **5** with ethylamine (**2a**) to produce the 1-ethylamino derivative **6a** was examined. **TS271** structure was calculated to be most stable followed by **TS274** and **TS273** structures as shown in Figure 8. This result clearly shows that the substitution reaction of **5** with **2a** regiospecifically proceeds at the 1-position.

2.3. UV–vis absorption and fluorescence spectra

The UV–vis absorption and fluorescence spectra of **3a** in various solvents are shown in Figure 9. Compound **3a** showed positive solvatochromism as normally observed for non-ionic dyes. The dipole moment of **3a** in the ground and excited states were calculated to be 5.32 and 9.19 D, respectively, supporting its positive

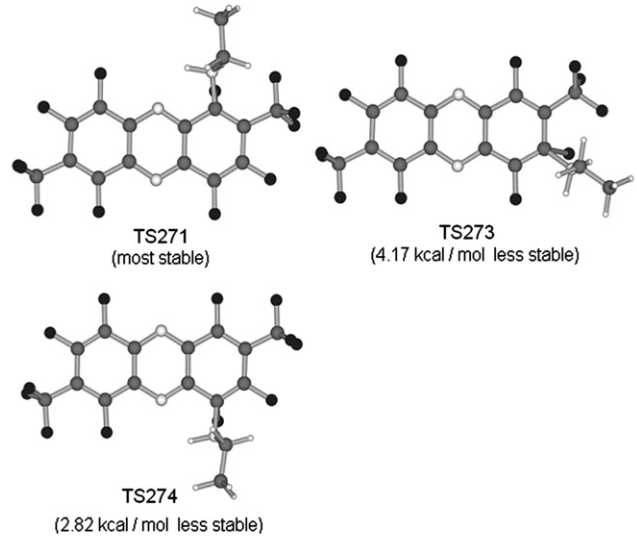


Figure 8. Optimized transition-state structures **TS271**, **TS273**, and **TS274** leading to 1-, 3-, and 4-ethylamino derivatives in the reaction of **5** with **2a**.

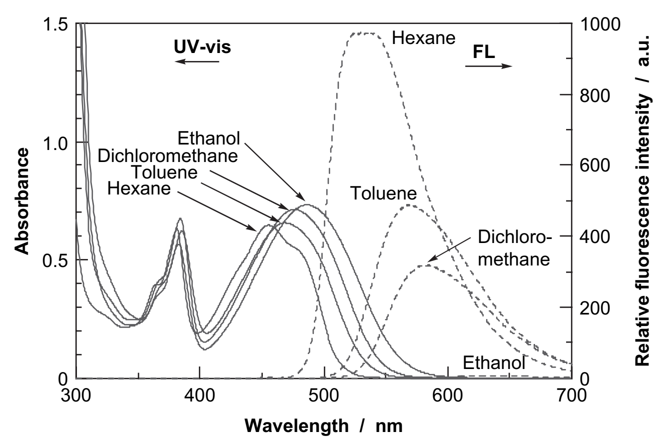


Figure 9. UV–vis absorption and fluorescence spectra of **3a** in various solvents. Solid and dotted lines represent UV–vis absorption and fluorescence spectra, respectively. Measured at the concentration of 1×10^{-4} mol dm^{-3} at 25 °C.

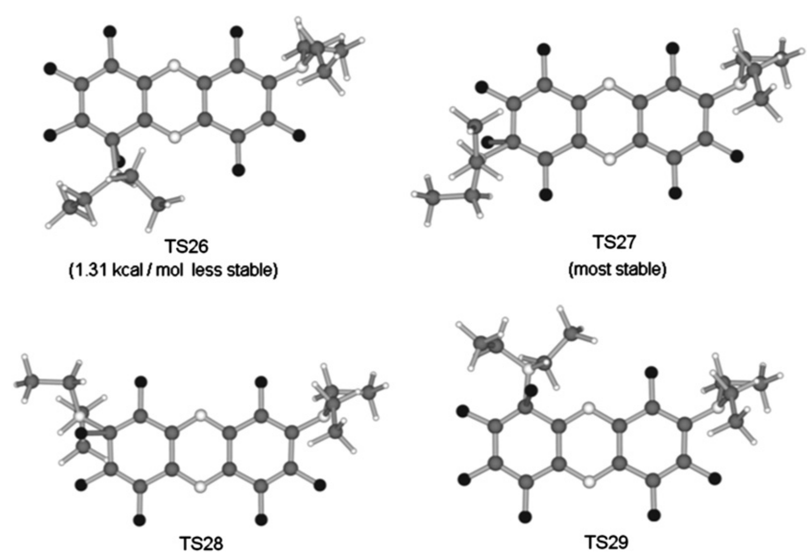


Figure 7. Optimized transition-state structures **TS26**, **TS27**, **TS28**, and **TS29** leading to 2,6-, 2,7-, 2,8-, and 2,9-bis(diethylamino) derivatives in the reaction of **3d** with **2d**.

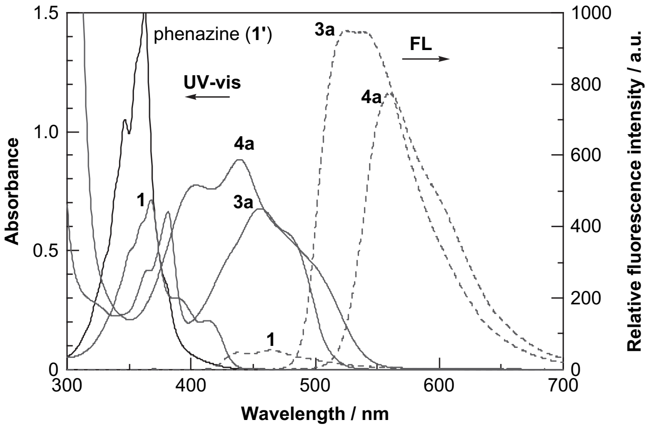


Figure 10. UV–vis absorption and fluorescence spectra of **1**, **1′**, **3a**, and **4a** in hexane. Solid and dotted lines represent UV–vis absorption and fluorescence spectra, respectively. Measured at the concentration of 1×10^{-4} mol dm^{-3} at 25 °C.

solvatochromism. The F_{max} of **3a** also showed positive solvatochromism. The fluorescence intensity drastically decreased in polar solvents.

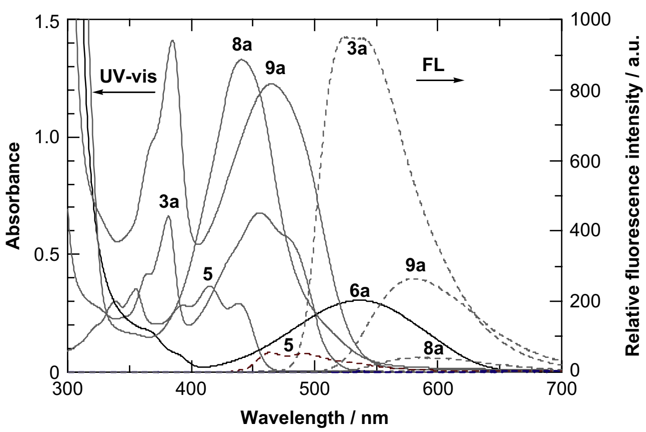


Figure 11. UV–vis absorption and fluorescence spectra of **3a**, **5**, **6a**, **8a**, and **9a**. Solid and dotted lines represent UV–vis absorption and fluorescence spectra, respectively. Compounds **3a**, **5**, and **6a** were measured in hexane at the concentration of 1×10^{-4} mol dm^{-3} at 25 °C. Compounds **8a** and **9a** were measured in dichloromethane at the concentration of 1×10^{-4} mol dm^{-3} at 25 °C.

The UV–vis absorption and fluorescence spectra of selected phenazine derivatives are indicated in Figures 10 and 11. Their spectral data are listed in Table 2. The λ_{max} of phenazines **1′** and **1** were observed at 362 and 367 nm in hexane, respectively, there being no remarkable difference between the fluorine-free and perfluoro derivatives. The molar absorption coefficient (ε) of **1′** (15,200) was larger than that of **1** (7460). The λ_{max} of 2-amino derivatives **3a**–**h** (456–509 nm) were more bathochromic than **1** (367 nm). 2,7-Disubstituted derivatives **4a** and **4d** (439 and 476 nm, respectively) were more bathochromic than **1** (362 nm). 1-Ethylamino derivative **6a** (536 nm) was more bathochromic than **5** (414 nm). The λ_{max} of **8a**, **9a**, and **9b** were observed at 441, 465, and 473 nm in dichloromethane, respectively. Thus, the introduction of alkylamino and arylamino group(s) into perfluorophenazines caused bathochromic shift. The λ_{max} of **3h** in ethanol shifted from 550 to 468 nm by addition of a drop of diluted hydrochloric acid. These results indicate that the 2-amino-substituted perfluorophenazines have intramolecular charge-transfer chromophoric system from the amino substituent(s) to pyrazine moiety.

No fluorescence was observed for fluorine-free **1′**. Non-amino-substituted perfluorophenazines **1** and **5** showed weak fluorescence. Interestingly, amino-substituted perfluorophenazines **3a**, **3b**, **3c**, **3d**, **3e**, **3f**, **4a**, **4d**, **8a**, **9a**, and **9b** were fluorescent compounds, showing F_{max} in the range of 524–583 nm. In a series of 2-(4-substituted anilino) derivatives **3f**, **3g**, and **3h**, the fluorescence intensity decreased with increasing electron-donating ability of the substituent at the 4-position. This result is opposite to the known information that fluorescence intensity increases by introducing electron-donating substituents. *N*,*N′*-Bis[perfluoro(2-phenazinyl)] derivatives **9a** and **9b** were less fluorescent than alkylamino derivatives **3a**, **3b**, **3c**, **3d**, and **3e**. Though no fluorescence was observed for **3h** and **6a**, compounds **3a**, **3b**, **3c**, **3d**, **3e**, **3f**, and **4d** were intensely fluorescent compounds (Φ_f>0.88). No such intensely fluorescent perfluoroaromatic compounds have been reported so far. These new materials have potential applications for emitters in OLED and solid-state organic dye laser.

3. Conclusions

Some novel aminoperfluorophenazines were synthesized and identified by X-ray crystallography. The regiospecific reactions of perfluorophenazines with amines were elucidated by DFT

Table 2
UV–vis absorption and fluorescence spectra of phenazines

Run	Compd	R^1	R^2	λ_{max}[a] (nm)	ε	F_{max}[a] (nm)	Φ_f[b]
1	**1′**	—		362	15,200	—[c]	—[c]
2	**1**	F	F	367	7460	466	0.06
3	**3a**	EtNH	F	456	7070	524	0.94
4	**3b**	*c*-HexNH	F	460	7200	545	0.92
5	**3c**	Me_2N	F	467	7000	546	0.97
6	**3d**	Et_2N	F	470	7230	551	0.98
7	**3e**	$(CH_2)_4N$	F	491	8000	560	0.88
8	**3f**	C_6H_5NH	F	460	8100	537	0.97
9	**3g**	$4\text{-}MeOC_6H_4NH$	F	479	7700	613	<0.01
10	**3h**	$4\text{-}Et_2NC_6H_4NH$	F	509	7400	—[c]	—[c]
11	**4a**	EtNH	EtNH	439	8800	560	0.47
12	**4d**	Et_2N	Et_2N	476	10,400	559	0.92
13	**5**	CF_3	CF_3	414	3360	465	0.09
14	**6a**	—	—	536	3000	—[c]	—[c]
15	**8a**	—	—	441[d]	13,300	583[d]	0.04[d]
16	**9a**	—	—	465[d]	12,300	579[d]	0.33[d]
17	**9b**	—	—	473[d]	14,400	583[d]	0.26[d]

[a] Measured in hexane at the concentration of 1×10^{-4} mol dm^{-3} at 25 °C otherwise cited.
[b] Determined using quinine sulfate in 0.1 mol dm^{-3} of sulfuric acid (Φ_f=0.55, λ_{ex}=366 nm).
[c] No fluorescence.
[d] Measured in dichloromethane at the concentration of 1×10^{-4} mol dm^{-3} at 25 °C.

calculations. Perfluorophenazine reacted with ethylenediamine to provide 2,3-cyclized and *N*,*N*′-bis(2-phenazinyl) derivatives. The amino-substituted products were fluorescent compounds, the F_{max} being in the range of 524–613 nm. Some of the products were intensely fluorescent compounds showing Φ_f higher than 0.88. This is the first report that perfluoroaromatic compounds show highly intense fluorescence.

4. Experimental

4.1. Instruments

Melting points were measured with a Yanagimoto MP-S2 micromelting-point apparatus. NMR spectra were recorded on JEOL ECA500 and Varian Inova 400 and 500 spectrometers. Mass spectra were taken on a Shimadzu QP-1000 spectrometer. UV–vis absorption and fluorescence spectra were measured with Shimadzu UV-160A and Hitachi F-4500 spectrometers, respectively. Elemental analysis was performed with a Yanaco MT-6 CHN corder.

4.2. Materials

Ethylamine (**2a**), dimethylamine (**2c**), diethylamine (**2d**), 4-methoxyaniline (**2g**), and butane-1,4-diamine (**7b**) were purchased from Nakarai Tesque Co., Ltd. Phenazine (**1**′), cyclohexylamine (**2b**), pyrrolidine (**2e**), aniline (**2f**), *N*,*N*-diethyl-*p*-phenylenediamine (**2h**), and ethylenediamine (**7a**) were purchased from Tokyo Kasei Co., Ltd. Perfluorophenazine (**1**) and perfluoro(2,7-dimethylphenazine) (**5**) were prepared as described in the literature.[11]

4.3. Reaction of phenazines with amines

To a DMF solution (10 mL) of phenazines **1**, **3**, or **5** (0.5 mmol) and triethylamine (0.55 mmol) was added an amine **2** or **7** (0.6 mmol). Then, the mixture was stirred. After the reaction was completed, the reaction mixture was poured into water (100 mL). The product was extracted with ethyl acetate, purified by column chromatography (SiO_2, **3a**, **3b**, **3c**, **3d**, **3e**, **3f**, **3g**, **3h**, and **9b**: chloroform; **4a**, and **4d,** and **6a**: toluene; **8a** and **9a**: chloroform–ethyl acetate=1:1), and recrystallized (**3a** and **4d**: hexane; **3b**, **3c**, **3d**, **3e**, **3f**, **3g**, **3h**, **4a**, **6a**, **8a**, **9a**, and **9b**: benzene). The physical and spectral data are shown below.

4.3.1. *2-Ethylamino-1,3,4,6,7,8,9-heptafluorophenazine (**3a**)*

Mp 143.0–143.5 °C; ^{1}H NMR ($CDCl_3$) δ=1.41 (t, *J*=7.1 Hz, 3H), 3.79 (quin d, *J*=7.1 and 3.8 Hz, 2H), 4.63 (br s, 1H); ^{19}F NMR ($CDCl_3$, ext. $CFCl_3$) δ=−157.34 (d, *J*=14.4 Hz, 1F), −153.47 (t, *J*=14.4 Hz, 1F), −152.94 (t, *J*=16.4 Hz, 1F), −151.94 (t, *J*=16.4 Hz, 1F), −151.16 (t, *J*=16.4 Hz, 1F), −150.04 (t, *J*=16.4 Hz, 1F), −143.05 (d, *J*=14.4 Hz, 1F); EIMS (70 eV) *m*/*z* (rel intensity) 349 (M^+; 44), 334 (100). Anal. Calcd for $C_{14}H_6F_7N_3$: C, 48.15; H, 1.73; N, 12.03%. Found: C, 47.76; H, 1.92; N, 12.02%.

4.3.2. *2-Cyclohexylamino-1,3,4,6,7,8,9-heptafluorophenazine (**3b**)*

Mp 129.0–130.0 °C; ^{1}H NMR ($CDCl_3$) δ=1.23–1.84 (m, 8H), 2.20 (d, *J*=9.2 Hz, 2H), 3.97 (br s, 1H), 4.55 (s, 1H); ^{19}F NMR ($CDCl_3$, ext. $CFCl_3$) δ=−156.26 (d, *J*=13.5 Hz, 1F), −153.42 (t, *J*=13.5 Hz, 1F), −153.13 (t, *J*=16.7 Hz, 1F), −152.04 (t, *J*=16.7 Hz, 1F), −151.20 (t, *J*=16.7 Hz, 1F), −150.15 (t, *J*=16.7 Hz, 1F), −142.80 (d, *J*=13.5 Hz, 1F); EIMS (70 eV) *m*/*z* (rel intensity) 403 (M^+; 51), 360 (23), 340 (25), 321 (100). Anal. Calcd for $C_{18}H_{12}F_7N_3$: C, 53.61; H, 3.00; N, 10.42%. Found: C, 53.41; H, 2.96; N, 10.24%.

4.3.3. *2-Dimethylamino-1,3,4,6,7,8,9-heptafluorophenazine (**3c**)*

Mp 152.0–153.0 °C; ^{1}H NMR ($CDCl_3$) δ=3.26 (s, 6H); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ=−76.62 (t, *J*=13.8 Hz, 1F), −74.83 (t, *J*=16.3 Hz, 1F), −74.78 (t, *J*=16.3 Hz, 1F), −74.25 (t, *J*=16.3 Hz, 1F), −73.08 (t, *J*=16.3 Hz, 1F), −68.83 (br s, 1F), −57.02 (br s, 1F); EIMS (70 eV) *m*/*z* (rel intensity) 349 (M^+; 100), 348 (80), 333 (26), 306 (32), 174 (25). Anal. Calcd for $C_{16}H_6F_7N_3$: C, 48.15; H, 1.73; N, 12.03%. Found: C, 47.93; H, 1.76; N, 11.91%.

4.3.4. *2-Diethylamino-1,3,4,6,7,8,9-heptafluorophenazine (**3d**)*

Mp 132.0–132.5 °C; ^{1}H NMR ($CDCl_3$) δ=1.26 (t, *J*=7.1 Hz, 6H), 3.54 (q, *J*=7.1 Hz, 4H); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ=−75.88 (t, *J*=14.9 Hz, 1F), −74.00 (t, *J*=14.9 Hz, 1F), −73.86 (t, *J*=15.8 Hz, 1F), −73.48 (t, *J*=15.8 Hz, 1F), −72.39 (t, *J*=15.8 Hz, 1F), −65.52 (d, *J*=15.8 Hz, 1F), −56.00 (d, *J*=14.9 Hz, 1F); EIMS (70 eV) *m*/*z* (rel intensity) 377 (M^+; 39), 362 (100), 334 (71). Anal. Calcd for $C_{16}H_{10}F_7N_3$: C, 50.93; H, 2.67; N, 11.14%. Found: C, 50.98; H, 2.62; N, 11.15%.

4.3.5. *1,3,4,6,7,8,9-Heptafluoro-2-pyrrolidinophenazine (**3e**)*

Mp 278.5–279.0 °C; ^{1}H NMR ($CDCl_3$) δ=2.04–2.07 (m, 4H), 3.93–3.97 (m, 4H); ^{19}F NMR ($CDCl_3$, ext. $CFCl_3$) δ=−155.72 (t, *J*=16.6 Hz, 1F), −153.65 (t, *J*=14.0 Hz, 1F), −152.31 (t, *J*=16.6 Hz, 1F), −151.59 (br s, 1F), −151.48 (t, *J*=16.6 Hz, 1F), −150.63 (t, *J*=16.6 Hz, 1F), −133.89 (br s, 1F); EIMS (70 eV) *m*/*z* (rel intensity) 375 (M^+; 100), 374 (80), 332 (32), 319 (49), 305 (23). Anal. Calcd for $C_{16}H_8F_7N_3$: C, 51.21; H, 2.15; N, 11.20%. Found: C, 51.23; H, 2.42; N, 11.19%.

4.3.6. *2-Anilino-1,3,4,6,7,8,9-heptafluorophenazine (**3f**)*

Mp 207.0–208.0 °C; ^{1}H NMR ($CDCl_3$) δ=6.44 (br s, 1H), 7.14–7.20 (m, 3H), 7.35–7.39 (m, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ=−76.25 (t, *J*=15.9 Hz, 1F), −75.08 (t, *J*=15.9 Hz, 1F), −74.74 (t, *J*=15.9 Hz, 1F), −74.65 (t, *J*=15.9 Hz, 1F), −73.06 (t, *J*=15.9 Hz, 1F), −64.46 (d, *J*=15.9 Hz, 1F), −62.21 (d, *J*=15.9 Hz, 1F); EIMS (70 eV) *m*/*z* (rel intensity) 397 (M^+; 100), 378 (65), 377 (94). Anal. Calcd for $C_{18}H_6F_7N_4$: C, 54.42; H, 1.52; N, 10.58%. Found: C, 54.24; H, 1.60; N, 10.34%.

4.3.7. *1,3,4,6,7,8,9-Heptafluoro-2-(4-methoxyanilino)-phenazine (**3g**)*

Mp 195.0–196.0 °C; ^{1}H NMR ($CDCl_3$) δ=3.84 (s, 3H), 6.36 (br, 1H), 6.92 (d, *J*=9.7 Hz, 2H), 7.16 (d, *J*=9.7 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ=−74.83 (t, *J*=15.3 Hz, 1F), −73.73 (t, *J*=16.6 Hz, 1F), −73.63 (t, *J*=16.6 Hz, 1F), −73.09 (t, *J*=16.6 Hz, 1F), −71.63 (t, *J*=16.6 Hz, 1F), −66.68 (d, *J*=15.3 Hz, 1F), −61.69 (d, *J*=15.3 Hz, 1F); EIMS (70 eV) *m*/*z* (rel intensity) 427 (M^+; 100), 412 (75), 364 (18), 344 (27). Anal. Calcd for $C_{19}H_4F_7N_3O$: C, 53.41; H, 1.89; N, 9.83%. Found: C, 53.34; H, 2.13; N, 9.80%.

4.3.8. *2-[4-(Diethylamino)anilino]-1,3,4,6,7,8,9-heptafluorophenazine (**3h**)*

Mp 171.0–171.5 °C; ^{1}H NMR ($CDCl_3$) δ=1.18 (t, *J*=7.3 Hz, 6H), 3.37 (q, *J*=7.3 Hz, 4H), 6.32 (br, 1H), 6.66 (d, *J*=8.3 Hz, 2H), 7.10 (d, *J*=8.3 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext. $CFCl_3$) δ=−153.08 to −153.02 (m, 1F), −152.45 to −152.38 (m, 1F), −151.69 to −151.61 (m, 1F), −151.10 to −151.02 (m, 1F), −149.97 to −149.90 (m, 1F), −146.72 to −146.64 (m, 1F), −139.68 to −139.60 (m, 1F); EIMS (70 eV) *m*/*z* (rel intensity) 468 (M^+; 76), 453 (100), 424 (23), 377 (23), 376 (20). Anal. Calcd for $C_{22}H_{15}F_7N_4$: C, 56.42; H, 3.23; N, 11.96%. Found: C, 56.29; H, 3.23; N, 11.91%.

4.3.9. *2,7-Bis(ethylamino)-1,3,4,6,8,9-hexafluorophenazine (**4a**)*

Mp 159.5–160.0 °C; ^{1}H NMR ($CDCl_3$) δ=1.34 (t, *J*=7.1 Hz, 6H), 3.51 (br, 4H), 4.39 (br, 2H); ^{19}F NMR ($CDCl_3$, ext. $CFCl_3$) δ=−154.02 to −153.98 (m, 2F), −153.60 (br s, 2F), −152.62 to −152.59 (m, 2F); EIMS (70 eV) *m*/*z* (rel intensity) 374 (M^+; 86), 359 (58), 329 (100). Anal. Calcd for $C_{16}H_{12}F_6N_4$: C, 51.34; H, 3.23; N, 14.97%. Found: C, 51.55; H, 3.61; N, 15.07%.

*4.3.10. 2,7-Bis(diethylamino)-1,3,4,6,8,9-hexafluorophenazine (**4d**)*

Mp 190.5–191.0 °C; ^{1}H NMR ($CDCl_3$) δ=1.21 (t, J=7.2 Hz, 6H), 3.47 (q, J=7.2 Hz, 4H); ^{19}F NMR ($CDCl_3$, ext. $CFCl_3$) δ=−154.65 (t, J=15.5 Hz, 2F), −141.62 (d, J=15.5 Hz, 2F), −136.01 (d, J=15.5 Hz, 2F); EIMS (70 eV) m/z (rel intensity) 430 (M^+; 38), 415 (100), 371 (22), 343 (24). Anal. Calcd for $C_{20}H_{20}F_6N_4$: C, 55.81; H, 4.68; N, 13.02%. Found: C, 55.74; H, 4.71; N, 12.95%.

*4.3.11. 1-Ethylamino-3,4,6,8,9-pentafluoro-2,7-bis(trifluoromethyl)-phenazine (**6a**)*

Mp 110.5–111.0 °C; ^{1}H NMR ($CDCl_3$) δ=1.43 (t, J=7.1 Hz, 3H), 3.63–3.67 (m, 2H), 6.87 (br s, 1H); ^{19}F NMR ($CDCl_3$, ext. $CFCl_3$) δ=−166.48 (d, J=17.1 Hz, 1F), −150.97 to −150.89 (m, 1F), −136.29 to −136.14 (m, 1F), −127.67 to −127.47 (m, 1F), −119.87 to −119.65 (m, 1F), −56.12 to −56.02 (m, 3F), −52.40 (s, 3F); EIMS (70 eV) m/z (rel intensity) 449 (M^+; 92), 434 (34), 430 (31), 429 (50), 414 (100), 408 (35), 388 (34), 387 (29). Anal. Calcd for $C_{16}H_6F_{11}N_3$: C, 42.78; H, 1.35; N, 9.35%. Found: C, 43.78; H, 1.72; N, 9.39%.

*4.3.12. Pyridazino[2,3-b]-1,2,3,4,6,11-hexafluorophenazine (**8a**)*

Mp>300 °C; ^{1}H NMR (acetone-d_6) δ=3.71 (br s, 2H), 6.94 (s, 4H); ^{19}F NMR (acetone-d_6, ext. $CFCl_3$) δ=−163.76 (s, 2F), −160.91 to −160.88 (m, 2F), −156.45 to −156.42 (m, 2F); EIMS (70 eV) m/z (rel intensity) 344 (M^+; 93), 343 (100), 328 (26), 207 (35). Anal. Calcd for $C_{14}H_6F_6N_4$: C, 48.85; H, 1.76; N, 16.28%. Found: C, 48.61; H, 2.10; N, 15.98%.

*4.3.13 . N,N′-Bis(1,3,4,6,7,8,9-heptafluoro-2-phenazinyl)-ethane-1,2-diamine (**9a**)*

Mp 297.0–297.5 °C (dec); ^{1}H NMR (acetone-d_6) δ=2.78 (s, 4H), 4.17 (br s, 2H); ^{19}F NMR (acetone-d_6, ext. $CFCl_3$) δ=−156.95 (t, J=16.5 Hz, 2F), −156.82 (br, 2F), −156.74 to −156.66 (m 2F), −155.04 (t, J=16.5 Hz, 2F), −154.37 (t, J=16.5 Hz, 2F), −154.13 (t, J=16.5 Hz, 2F), −143.01 (br s, 2F); EIMS (70 eV) m/z (rel intensity) 668 (M^+; 20), 335 (100), 334 (95). Anal. Calcd for $C_{26}H_6F_{14}N_6$: C, 46.72; H, 0.90; N, 12.57%. Found: C, 46.97; H, 0.69; N, 12.61%.

*4.3.14 . N,N′-Bis(1,3,4,6,7,8,9-heptafluoro-2-phenazinyl)-butane-1,4-diamine (**9b**)*

Mp 295.0–295.5 °C (dec); ^{1}H NMR ($CDCl_3$) δ=2.78 (s, 4H), 3.83 (s, 4H), 6.62 (br s, 2H); ^{19}F NMR (acetone-d_6, ext. $CFCl_3$) δ=−158.96 (br, 2F), −157.33 (t, J=16.0 Hz, 2F), −156.74 to −156.66 (m, 2F), −155.05 (t, J=16.0 Hz, 2F), −154.46 (t, J=16.0 Hz, 2F), −154.27 (t, J=16.0 Hz, 2F), −143.37 (br s, 2F); EIMS (70 eV) m/z (rel intensity) 696 (M^+; 20), 376 (32), 375 (28), 374 (37), 356 (47), 334 (100). Anal. Calcd for $C_{28}H_{10}F_{14}N_6$: C, 48.29; H, 1.45; N, 12.07%. Found: C, 48.54; H 1.76; N, 12.05%.

5. X-ray crystallography

The single crystals of compounds **3a**, **4d**, and **6a** were obtained by a solvent diffusion method using hexane and dichloromethane. Crystal data for **3a**: $C_{14}H_6F_7N_3$, M_W=349.21, monoclinic, $P2_1/n$, Z=4, a=5.391(3), b=12.168(7), c=19.82(1) Å, β=86.99(3)°, D_{calcd}=1.786 g cm^{-3}, 10,700 reflections were collected, 2207 unique (R_{int}=0.062), 1558 observed ($I>2\sigma(I)$), 229 parameters, R_1=0.052, wR_2=0.133, GOF=1.152, refinement on F^2. Crystal data for **4d**: $C_{20}H_{20}F_6N_4$, M_W=430.40, triclinic, P-1, Z=1, a=5.194(1), b=9.331(2), c=10.250(2) Å, α=108.02(1), β=92.71(1), γ=94.34(1)°, D_{calcd}=1.521 g/cm^3, 4883 reflections were collected, 1662 unique (R_{int}=0.086), 978 observed ($I>2\sigma(I)$), 137 parameters, R_1=0.0626, wR_2=0.1713, GOF=0.956, refinement on F^2. Crystal data for **6a**: $C_{16}H_6F_{11}N_3$, M_W=449.23, monoclinic, $P2_1/c$, Z=4, a=10.6161(8), b=12.2022(9), c=13.328(1) Å, β=111.433(5)°, D_{calcd}=1.853 g/cm^3, 15,540 reflections were collected, 2893 unique (R_{int}=0.080), 2093 observed ($I>2\sigma(I)$), 275 parameters, R_1=0.0455, wR_2=0.1298, GOF=0.994, refinement on F^2. The measurement was performed on a Rigaku Raxis-RAPID imaging plate diffractometer with a graphite-monochromated Cu Kα radiation. The data were collected to a maximum 2θ value of 136.5° at room temperature for **3a** and to a maximum 2θ value of 136.4° at −180(1) °C under cold N_2 gas flow for **4d** and **6a**. 24, 30, and 26 ($\Delta\varphi$=30°) images were measured using an oscillation technique for **3a**, **4d**, and **6a**, respectively. An absorption correction was applied for **4d** and **6a**, but not applied for **3a**. The structures were solved by the direct method (*SHELX97*[12]) and refined by least-squares calculations using the *Crystal Structure* program package.[13] All non-hydrogen atoms for these compounds were refined anisotropically. The hydrogen atoms for **3a** and **4d** were located on the calculated positions and not refined. For **6a**, the hydrogen atom of the amino group was found in the difference Fourier map and only the positional parameters were refined. The other hydrogen atoms were located on the calculated positions and not refined.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers for **3a** (CCDC297182), **4d** (CCDC297183), and **6a** (CCDC297184), respectively.

Supplementary data

The calculated partial charge, fukui function ($f*$), and the cartesian coordinates of the optimized structures are provided. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.06.079.

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