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AMINATION OF 4-AZAFLUORENE UNDER CHICHIBABIN REACTION CONDITIONS. SOME CHEMICAL TRANSFORMATIONS OF 1-AMINO-4-AZAFLUORENE

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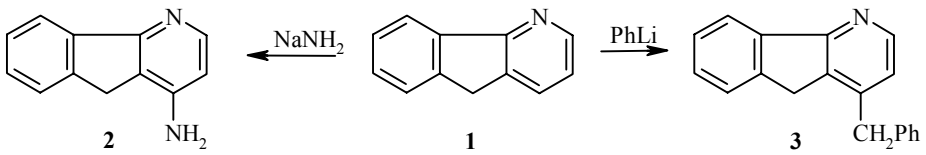
4-Azafluorene is aminated by sodium amide in dimethylaniline at $C_{(1)}$. The oxidation of 1-amino-4-azafluorene was studied along with the condensation of this compound with acetic anhydride and its diazotization.

Keywords: 1-amino-4-azafluorene, diazotization, nucleophilic substitution.

The electrophilic substitution reactions and transformations involving the methylene group at $C_{(9)}$ have been studied rather thoroughly for the azafluorene isomers [1]. On the other hand, nucleophilic substitution into the pyridine fragment has hardly been investigated. Only the phenylation of 3-methyl-2-azafluorene by phenyllithium in ether has been studied [2]. This reaction proceeds at the free α-carbon atom to give 3-methyl-1-phenyl-2-azafluorene.

We are the first to undertake a systematic study of nucleophilic substitution reactions in azafluorene **1** series. In the present work, sodium amide, butyllithium, phenyllithium, and triphenylsilyllithium were used as the nucleophiles. Toluene and dimethylaniline were used as the solvents in the Chichibabin amination of 4-azafluorene (**1**). The amination by sodium amide proceeds at a significant rate only in dimethylaniline at reflux at the γ-carbon atom of the pyridine fragment of the molecule. 1-Amino-4-azafluorene (**2**) was obtained in 62% yield.



2 **1** **3**

It proved impossible to show formation of the second expected Chichibabin amination product of 3-amino-4-azafluorene by either ^{1}H NMR spectroscopy or GC/MS.

4-Azafluorene **1** does not react with butyllithium, phenyllithium, or silyllithium in ether or THF. 1-Benzyl-4-azafluorene (**3**) was obtained in about 10% yield only by the action of phenyllithium in toluene at reflux. The formation of compound **3** is attributed to the formation of highly nucleophilic benzyllithium due to

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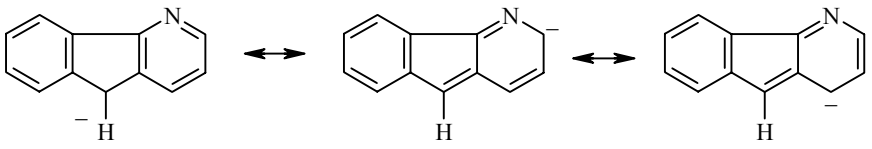
the metallation of toluene by phenyllithium [3]. The low reactivity of **1** in reactions with nucleophilic reagents and the formation of substitution products at $C_{(1)}$ (γ-substitution) may be explained assuming that the 4-azafluorenyl anion (**A**) with negative charge centered at $C_{(9)}$ is formed as an intermediate. This hypothesis is in good accord with the data of various workers [4-6] on the reaction of azafluorenes with nucleophiles.

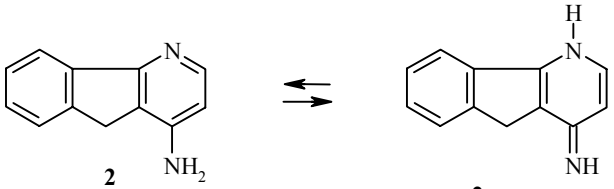


A **B** **C**

As the result of delocalization, the pyridine fragment in this anion (only two resonance forms **B** and **C** are given) would be deactivated relative to the action of nucleophiles. Resonance structure **B** with a *p*-quinoid fragment probably makes the greatest contribution to the electron density distribution. Thus, the $C_{(3)}$ position should be more deactivated than the $C_{(1)}$ position, which is in good accord with the experimental data.

Azafluorene **2** is oxidized by atmospheric oxygen under phase-transfer catalysis conditions to give 1-amino-4-aza-9-fluorenone (**4**).

4-Aminopyridine is known to exist largely in the amine form and is protonated at the ring nitrogen atom [7, 8]. The UV spectrum of this compound shows a bathochromic shift of the long-wavelength band relative to the spectrum of unsubstituted pyridine. We might have expected that the presence of an indene fragment condensed with 4-aminopyridine moiety in azafluorene **2** and azafluorenone **4** would affect the position of the amino–imino equilibrium and the direction of protonation.



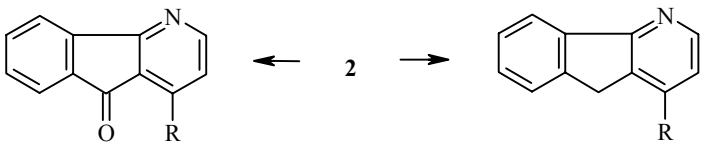
2 **2a**

A PPP quantum-chemical calculation was carried out for models of azafluorene **2**, its imine form **2a**, azafluorenone **4**, and their protonated forms (Table 1). The structure of the model molecules was assumed planar. The calculations show that the amine form is more stable than the imine form in the case of 1-amino-4-azafluorene. The atomization energy ΔH for the amino form is by 0.274 eV higher than for the imine form. Comparison of the calculated and experimental electronic absorption spectra for compound **2** (see Table 2) also indicates that this compound exists in the amine form in solution. The results of calculations suggest the preference for protonation of compounds **2** and **4** at the pyridinic nitrogen atom. The good correlation of the calculated and experimental electronic absorption spectra support these data. We should note that the calculated characteristics for amine form **2** protonated at the pyridinic nitrogen atom are similar to those for imino form **2a** protonated at the exocyclic imine nitrogen atom. The long-wavelength UV bands for compounds **2** and **4** due to π_0–π^* electronic transitions in the azafluorene system undergo bathochromic shifts by 14 and 16 nm upon protonation, respectively, which is in good accord with the results for 4-aminopyridine [9]. On the other hand, upon protonation, the band at 378 nm in the spectrum of azafluorenone **4** due to electronic transitions involving the carbonyl group undergoes a hypsochromic shift by 26 nm, which may indicate protonation of this group.

TABLE 1. Atomization Energies ΔH, Solvation Coefficients M and π-Electron Energies E_π for compounds **2**, **2a**, and **4** and Their Protonated Forms Calculated by the PPP Method

	2	**2** ()	**2** (NH; H^+)	**2a**	**2a** (=N^+H_2)	**4**	**4** ()
ΔH, eV	120.025	124.782	122.995	119.751	124.695	121.917	126.681
M, eV	0.981	1.915	0.533	2.515	4.200	2.417	3.354
E_π, eV	25.111	25.727	24.269	24.727	25.760	25.160	25.786

Some chemical transformations of aminoazafluorene **2** were studied. The diazotization of this compound under the Schiemann reaction conditions leads to 1-fluoro-4-azafluorene (**5**). Diazotization in concentrated hydrochloric acid or in the mixture of bromine and hydrobromic acid gave 1-chloro- (**6**) and 1-bromo-4-azafluorene (**7**), respectively, along with 1-hydroxy-4-azafluorene (**8**).



4, 10, 12 **2** **5–9**, **11**

4 R = NH_2, **5** R = F; **6** R = Cl; **7**, **10** R = Br; **8** R = OH; **9** R = OAc; **11**, **12** R = NHAc

TABLE 2. Electronic Absorption Spectra of Compounds **2** and **4***

Compound	λ, nm (*f*)	λ, nm (log ε)	Compound	λ, nm (*f*)	λ, nm (log ε)
2	311 (0.06)	301 (3.86)	**2** ()	306 (0.21)	315 (4.05)
	280 (0.16)	285 (3.86)		281 (0.13)	305 (4.15)
	264 (9.45)	270 (3.88)		267 (0.62)	293 (4.11)
	245 (0.86)	249 (4.29)		244 (0.65)	279 (4.04)
	238 (0.24)	212 (4.20)		234 (0.28)	251 (4.13)
	213 (0.33)			218 (0.05)	208 (4.08)
	208 (0.21)			206 (0.31)	
	207 (0.44)			203 (0.64)	
4	443 (0.09)	378 (3.38)	**4** ()	442 (0.03)	352 (3.08)
	386 (0.09)			355 (0.13)	
	307 (0.06)			311 (0.07)	
	264 (0.20)	268 (4.28)		268 (0.54)	284 (4.44)
	258 (0.21)	259 (4.31)		261 (0.28)	234 (3.68)
	239 (0.55)	239 (4.10)		240 (0.67)	
	238 (0.97)			231 (0.49)	
	227 (0.01)			226 (0.05)	216 (3.93)
	203 (0.69)	209 (3.92)		212 (0.12)	203 (3.64)

* λ (ε) – experimental data, λ (*f*) – calculated by PPP method, *f* - oscillator strength.

TABLE 3. ^{1}H NMR Spectral Characteristics of 1-Substituted 4-Azafluorenes and 4-Azafluorenones **2-12**

Compound	Chemical shifts, δ, ppm. (*J*, Hz)							
	2-H	3-H, d	5-H	6-H	7-H	8-H	9-H, s	1-R
2	6.18 (d, *J* = 5.5)	8.05 (*J* = 5.5)	7.05 (m)	7.30-7.40 (m)		7.6 (m)	3.65	6.10 (br. s, NH_2)
3	7.13 (d, *J* = 5.5)	8.47 (*J* = 5.5)	8.44 (m)	7.27-7.67 (m)			3.83	4.19 (s, CH_2Ph)
4	6.50 (d, *J* = 6.10)	8.01 (*J* = 6.10)	7.57 (d, *J* = 7.3; *J* = 1.2)	7.45 (td, *J* = 7.3; *J* = 7.3; *J* = 0.9)	7.59 (td, *J* = 7.3; *J* = 7.3; *J* = 1.2)	7.69 (dd, *J* = 7.3; *J* = 1.1)	—	8.24 (s, NH_2)
5	6.93 (dd, *J* = 5.8; *J* = 8.9)	8.57 (*J* = 5.8; *J* = 7.9)	8.10 (m)	7.40-7.55 (m)		7.6 (m)	3.93	—
6	7.19 (d, *J* = 5.5)	8.48 (*J* = 5.5)	8.07 (m)	7.40-7.55 (m)			3.92	—
7	7.36 (d, *J* = 5.2)	8.40 (*J* = 5.2)	8.08 (m)	7.40-7.50 (m)		7.6 (m)	3.88	—
9	7.03 (d)	8.60	8.10 (m)	7.40 (m)	7.50 (m)	7.55 (m)	3.82	2.39 (s, CH_3CO)
10	7.35 (d, *J* = 5.2)	8.38 (*J* = 5.2)	7.87 (dt, *J* = 7.3; *J* = 0.9; *J* = 0.9)	7.63 (dt, *J* = 7.3; *J* = 7.3; *J* = 0.9)	7.48 (dt, *J* = 7.3; *J* = 0.9; *J* = 0.9)	7.27 (dt, *J* = 7.3; *J* = 0.9; *J* = 0.9)	—	—
11	8.01 (d, *J* = 5.5)	8.55 (*J* = 5.5)	8.09 (m)	7.35-7.45			3.78	2.29 (s, CH_3)
12	8.21 (d, *J* = 6.10)	8.47 (*J* = 6.10)	7.68 (dt, *J* = 7.6; *J* = 1.2; *J* = 1.2)	7.68 (td, *J* = 7.6; *J* = 1.2; *J* = 1.2)	7.60 (td, *J* = 7.6; *J* = 1.2; *J* = 1.2)	7.83 (td, *J* = 7.6; *J* = 1.2; *J* = 1.2)	—	2.30 (s, CH_3); 9.74 (br. s, NH)

Azafluorenes **5-8** were isolated chromatographically as pure compounds. 1-Hydroxy-4-azafluorene **8** was converted into its O-acetyl derivative **9** by the action of acetic anhydride. 1-Bromo-4-aza-9-fluorenone (**10**) was obtained in high yield in the oxidation of 1-bromo-4-azafluorene **7** by potassium permanganate. Aminoazafluorene **2** and aminoazafluorenone **4** were converted into the corresponding acetylamino derivatives **11** and **12**, respectively under the action of acetic anhydride.

The structures of compounds **2-12** were supported by spectral data. The IR spectra of amino-substituted compounds **2** and **4** show two stretching bands for the associated NH_2 group in the vicinity of 3460 and 3300 cm^{-1}. The IR spectrum of compound **2** taken in CCl_4 shows asymmetric and symmetric vibrations for the free NH_2 group at 3500 and 3420 cm^{-1}, respectively. The stretching band for the NH group in compound **12** is observed at 3343 cm^{-1} and the NH deformation band is seen at 1535-1580 cm^{-1}. The C=O stretching vibrations for compounds **4**, **10**, and **12** give rise to intense bands at 1785, 1712, and 1695 cm^{-1}, respectively. The ^1H NMR spectra of 1-substituted 4-azafluorenes and 4-azafluorenones (Table 3) show signals for all the protons in these molecules with the expected chemical shifts and coupling constants. The ^1H NMR spectrum of fluoro derivative **5** shows coupling constants of protons 2-H and 3-H with the fluorine atom (J_{2F} and J_{3F}).

Thus, methods were developed for the synthesis of 4-azafluorenes and 4-azafluorenones functionally substituted in the pyridine fragment, which may serve as synthones for the construction of polycyclic compounds holding interest for biological screening. The tautomeric and chemical transformations of 1-amino-4-azafluorene and 4-aminopyridine are similar.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer in KBr pellets. The ^1H NMR spectra were taken for ~2% solutions in $CDCl_3$ on a Bruker WP-200 spectrometer at 200 MHz at 30°C. The chemical shifts were measured relative to TMS as the internal standard. The mass spectra were taken on a Varian MAT-112 spectrometer with direct sample inlet into the ion source. The ionizing voltage was 70 eV. Silufol UV-254 plates were used for thin-layer chromatography, while Brockmann Grade 2 alumina (Ls 5/40) or Woelm silica gel (32-63 μm) was used for column chromatography. Iodine vapor was used as the developer.

1-Amino-4-azafluorene (2). Mixture of 4-azafluorene (5 g, 30 mmol), sodium amide (4.68 g, 120 mmol), and dimethylaniline (100 ml) was placed into a three-necked flask equipped with a stirrer, thermometer, air condenser, and bubble counter. The mixture was heated for 5 h at 190-195°C (hydrogen evolution was noted). A black insoluble precipitate formed at the bottom of the flask. Dimethylaniline was decanted off and the precipitate was carefully decomposed by adding of 96% aqueous ethanol (50 ml) under cooling. Then, alumina (20 g) was added and ethanol was distilled off until dryness. The residue was placed onto a column (40 × 4 cm) packed with alumina and eluted with ethyl acetate to give 3.2 g (62%) of compound **2** as pale yellow crystals; mp 204-206°C (ethanol–ethyl acetate), R_f 0.52 (3:1 ethyl acetate–ethanol). IR spectrum, ν, cm^{-1}: 3460, 3300 (NH_2). Mass spectrum, *m/z* (I_{rel}, %): 182 (M^+, 100), 181 (29), 155 (6), 154 (6), 144 (7), 127 (7), 115 (9), 108 (9), 106 (9), 105 (29), 104 (18), 91 (30), 78 (31). Found, %: C 79.12; H 5.42; N 15.38. $C_{12}H_{10}N_2$. Calculated, %: C 79.09; H 5.45; N 15.38. M 182.

1-Benzyl-4-azafluorene (3). Solution of azafluorene **1** (2 g, 11.9 mmol) in toluene (70 ml) was added to phenyllithium obtained from lithium (0.84 g, 120 mmol) and bromobenzene (9.34 g, 59.5 mmol) in absolute ether (50 ml). Ether was distilled off. The reaction mixture was heated at reflux for 8 h and cooled. Then, water (20 ml) was added. The toluene layer was separated and the aqueous layer was extracted with two 30-ml toluene portions. The combined extract was dried over $MgSO_4$. Toluene was distilled off and the residue was subjected to chromatography on silica gel column (70 × 2 cm) using hexane, 1:10, 1:5, and 1:2 heptane–ethyl acetate as the eluent to give 1.1 g of compound **1**; mp 93-94°C (heptane). A mixed probe with an authentic sample gave an undepressed melting point. Then, compound **3** (0.3 g, 10%) was eluted as colorless crystals; mp 80-82°C (ethyl acetate–hexane), R_f 0.64 (1:2 ethyl acetate–ethanol). Mass spectrum, *m/z* (I_{rel}, %): 257 (M^+, 100), 256 (15), 254 (16),

227 (10), 180 (26), 179 (65), 178 (23), 167 (14), 166 (66), 152 (23), 151 (12), 150 (11), 139 (30), 138 (14), 127 (20), 125 (12), 113 (17), 91 (83), 89 (16), 87 (17), 78 (40), 65 (30), 51 (82), 43 (16). Found, %: C 88.61; H 5.62; N 5.70. $C_{19}H_{15}N$. Calculated, %: C 88.70; H 5.83; N 5.45. M 257.

1-Amino-4-aza-9-fluorenone (4). Mixture of azafluorene **2** (2 g, 11 mmol), TBAI (0.15 g), 50% aqueous NaOH (15 ml), and benzene (100 ml) was heated at 60°C with air bubbling for 15 h. The reaction was monitored by thin-layer chromatography. Then, water (30 ml) was added. The benzene layer was separated and the aqueous layer was extracted with three 100 ml ether portions. The combined extract was dried over $MgSO_4$. The solvents were distilled off. The residue was subjected to chromatography on a silica gel column (70 × 2 cm) with ethyl acetate as the eluent to give 1.1 g (51%) of aminoazafluorenone **4** as yellow needles; mp 205-207°C (ethyl acetate), R_f 0.58 (10:1 ethyl acetate–ethanol). IR spectrum, ν, cm^{-1}: 3400, 3300, 3200 (NH_2), 1695, 1680 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 196 (M^+, 100), 195 (93), 170 (45), 169 (53), 168 (20), 167 (7), 142 (5), 141 (18), 140 (26), 116 (3), 115 (8), 114 (12), 113 (7), 98 (7), 91 (5). Found, %: C 73.32; H 3.95; N 14.18. $C_{12}H_8N_2O$. Calculated, %: C 73.47; H 4.08; N 14.19. M 196.

1-Fluoro-4-azafluorene (5). Sodium nitrite (0.5 g, 7.2 mmol) was added in portions over 1 h to solution of amine **2** (1.2 g, 7 mmol) in HBF_4 (10 ml) at 0°C. The mixture was stirred for 1 h at 0°C, then gradually heated to 50°C, and maintained at this temperature for 20 min. The mixture was cooled and water (10 ml) was added. The mixture was extracted with three 50 ml chloroform portions. The extract was dried over $MgSO_4$. Chloroform was distilled off and the residue was subjected to chromatography on a silica gel column (70 × 2 cm) with 1:10 ethyl acetate–hexane as the eluent to give 0.2 g (18%) of compound **5** as colorless crystals; mp 94-96°C (ethyl acetate–hexane), R_f 0.83 (1:1 ethyl acetate–ethanol). IR spectrum, ν, cm^{-1}: 1266 (Ar–F). Mass spectrum, *m/z* (I_{rel}, %): 187 (M^+, 60), 185 (65), 166 (100). Found, %: C 77.92; H 4.55; N 7.40. $C_{12}H_{10}FN$. Calculated, %: C 77.83; H 4.32; N 7.56. M 187.

1-Chloro- (6) and 1-Hydroxy-4-azafluorene (8). Solution of aminoazafluorene **2** (0.5 g, 2.7 mmol) in concentrated hydrochloric acid (2 ml) was cooled to 0°C and solution of $NaNO_2$ (0.29 g, 4 mmol) in water (1 ml) was added dropwise over 30 min. The rate of addition was controlled such that the temperature of the reaction mixture did not exceed 5°C. The mixture was stirred for 1 h at 0-5°C and then heated to 90°C. The mixture was cooled and brought to pH 8 by adding potassium carbonate to give 60 mg of compound **8** as a precipitate, which was filtered off, washed, and dried. The filtrate was extracted with chloroform and dried over $MgSO_4$. Chloroform was distilled off. The residue was subjected to chromatography on a silica gel column with 1:10 ethyl acetate–hexane as the eluent to give 0.21 g (42%) of compound **6** as white crystals; mp 86-88°C (hexane), R_f 0.79 (ethyl acetate). IR spectrum, ν, cm^{-1}: 1127 (Ar–Cl). Mass spectrum, *m/z* (I_{rel}, %): 203 (M^+, 14), 201 (M^+, 42), 166 (100), 151 (35), 141 (27), 140 (15). Found, %: C 70.90; H 4.90; N 6.93. $C_{12}H_{10}ClN$. Calculated, %: C 70.93; H 4.93; N 6.94. M 201.5.

1-Bromo-4-azafluorene (7). Amine **2** (2 g, 10.1 mmol) was added to concentrated hydrobromic acid (10 ml) at -10°C. Then, bromine (6.28 g, 39 mmol) and solution of sodium nitrite (2.56 g, 37.1 mmol) in water (5 ml) were added dropwise consecutively maintaining the temperature below 0°C. The mixture was maintained for 30 min at 0°C, neutralized by adding 10% aqueous sodium hydroxide, and extracted with chloroform. The extract was dried over $MgSO_4$. Chloroform was distilled off and the residue was subjected to chromatography on a silica gel column (70 × 1.5 cm) with 1:10 ethyl acetate–hexane as the eluent to give 1.46 g (54%) of bromoazafluorene **7** as pale yellow crystals; mp 120-122°C (ethyl acetate–hexane), R_f 0.59 (1:3 ethyl acetate–hexane). IR spectrum, ν, cm^{-1}: 761 (Ar–Br). Mass spectrum, *m/z* (I_{rel}, %): 247 (M^+, 40), 245 (M^+, 40), 244 (6), 166 (100), 165 (12), 164 (8), 139 (20), 138 (12), 137 (6), 131 (5), 114 (4), 113 (6), 112 (5), 111 (5). Found, %: C 58.41; H 5.10; N 5.63. $C_{12}H_{10}BrN$. Calculated, %: C 58.78; H 4.90; N 5.71. M 246.

1-Acetoxy-4-azafluorene (9). Suspension of hydroxyazafluorene **8** (0.2 g, 12 mmol) in acetic anhydride (1 ml) was heated at reflux for 15 min and then neutralized by adding sodium carbonate. The mixture was extracted with chloroform. The extract was dried over $MgSO_4$. Chloroform was distilled off and the residue was crystallized from hexane to give 60 mg (24%) of compound **9** as white crystals; mp 110-112°C (hexane), R_f 0.48

(1:1 ethyl acetate–hexane). IR spectrum, ν, cm^{-1}: 1741 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 225 (M^+, 67), 183 (100), 154 (18), 127 (13). Found, %: C 74.6; H 4.88; N 6.22. $C_{14}H_{11}NO_2$. Calculated, %: C 74.67; H 4.90; N 6.23. M 225.

1-Bromo-4-aza-9-fluorenone (10). Mixture of compound **6** (1 g, 40 mmol), 50% aqueous NaOH (15 ml), and benzene (30 ml) was heated to 60°C and air was bubbled through for 5 h. The reaction was monitored by thin-layer chromatography. Then, water (50 ml) was added. The benzene layer was separated and dried over $MgSO_4$. Benzene was distilled off. The residue was subjected to chromatography on alumina column (7 × 4 cm) with ether as the eluent to give 0.82 g (82%) of ketone **10** as yellow crystals; mp 162-164°C (ethyl acetate–hexane), R_f 0.5 (2:1 ethyl acetate–hexane). IR spectrum, ν, cm^{-1}: 1710 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 261 (M^+, 100), 259 (M^+, 100), 230 (28), 226 (54), 202 (60), 201 (62), 195 (20), 190 (30), 180 (30). Found, %: C 55.62; H 3.08; N 5.40. $C_{12}H_8BrNO$. Calculated, %: C 55.38; H 3.07; N 5.38. M 260.

1-Acetylamino-4-azafluorene (11). Aminoazafluorene **2** (1 g, 5.5 mmol) in acetic anhydride (5 ml) was heated at reflux for 2 h. The reaction was monitored by thin-layer chromatography. Excess acetic anhydride was distilled off in vacuum. The residue was made basic by adding saturated sodium carbonate solution and extracted with three 50 ml ether portions. Ether was distilled off and the residue was subjected to chromatography on silica gel column (40 × 2 cm) using 1:1 ethyl acetate–hexane as the eluent to give 0.61 g (49.6%) of compound **11** as white crystals; mp 224-225°C (ethyl acetate–hexane), R_f 0.19 (ethyl acetate). IR spectrum, ν, cm^{-1}: 3343 (NH), 1687 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 224 (M^+, 96), 202 (12), 200 (44), 195 (54), 186 (60), 182 (100), 181 (11), 145 (70), 115 (64), 105 (40), 100 (20), 92 (30). Found, %: C 74.81; H 5.28; N 12.40. $C_{14}H_{12}N_2O$. Calculated, %: C 75.00; H 5.36; N 12.50. M 224.

1-Acetylamino-4-aza-9-fluorenone (12). Aminoazafluorenone **4** (0.5 g, 2.55 mmol) in acetic anhydride (5 ml) was heated at reflux for 2 h. Excess acetic anhydride was distilled off. The residue was made basic by adding saturated sodium carbonate solution. The mixture was extracted with three 30 ml ether portions. The extract was dried over $MgSO_4$. Ether was distilled off and the residue was subjected to chromatography on alumina column (20 × 1.5 cm) with 1:1 ethyl acetate–hexane as the eluent to give 0.41 g (82%) of compound **12** as light yellow crystals; mp 195-196°C (ethyl acetate–hexane), R_f 0.14 (1:1 ethyl acetate–hexane). IR spectrum, ν, cm^{-1}: 1690 (C=O), 3343 (NH), 1619 (C=O amide). Mass spectrum, *m/z* (I_{rel}, %): 238 (M^+, 83), 207 (95), 201 (62), 200 (10), 197 (86), 196 (100), 182 (56). Found, %: C 70.61; H 5.12; N 11.62. $C_{14}H_{10}N_2O_2$. Calculated, %: C 70.58; H 5.04; N 11.66. M 238.

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