peri-Naphthylenediamines
36.* 5,6-Bis(dimethylamino)acenaphthylene in [4+2] cycloaddition reactions. Synthesis and characteristic features of protonation of "proton sponges" with the 8,9-diazafluoranthene structure

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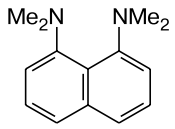
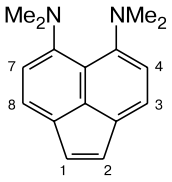
5,6-Bis(dimethylamino)acenaphthylene is readily involved in [4+2] cycloaddition reactions with *symm*-tetrazine derivatives to form new "proton sponges" with the diazafluoranthene skeleton. Under analogous condition, 1,8-bis(dimethylamino)-4-vinylnaphthalene gave 4-pyridazinyl derivatives. The relative reactivities of 5,6-bis(dimethylamino)acenaphthylene, 1,8-bis(dimethylamino)-4-vinylnaphthalene, 5-dimethylaminoacenaphthylene, and acenaphthylene in the reactions with 3,6-diphenyl-*symm*-tetrazine are in a ratio of 32 : 17 : 14 : 1. The site of protonation of 3,4-bis(dimethylamino)-7,10-diphenyl-8,9-diazafluoranthene is controlled by the basicity of the solvent. The reaction in acetonitrile afforded the cation stabilized by an intramolecular hydrogen bond, whereas the reaction in dimethyl sulfoxide gave rise to the resonance-stabilized cation. 6,7-Bis(dimethylamino)phenalen-1-one was protonated only at the carbonyl group.

Key words: acenaphthylenes, 8,9-diazafluoranthenes, α-vinylnaphthalene, pyridazines, 1,2,4,5-tetrazines, phenalen-1-one, [4+2] cycloaddition, relative reactivity, protonation, "proton sponges".

In our recent studies of the chemistry of 1,8-bis(dimethylamino)naphthalene ("proton sponge", **1**, see the review[2]), we have demonstrated that, in spite of large steric strains in this molecule, the *peri*-dimethylamino groups retain the exceptionally strong electron-donating effect toward the aromatic π-system. This is manifested in the unusually high reactivity of compound **1** in electrophilic substitution reactions[3] as well as in its involvement in new types of reactions, which have not been observed earlier for compounds of the naphthalene series.[4] In this connection, it was of interest to quantitatively estimate the electron-donating effects of two NMe_2 groups in molecule **1**, particularly, in the transformations requiring stabilization of the positive charge in the transition complex. Unfortunately, the solution of this problem presents difficulties because most of the reactions of "proton sponges" follow radically different pathways compared to their analogs containing other +M substituents or one NMe_2 group. In attempting to find transformations of "proton sponges" proceeding similarly to those of their electronic analogs, we studied the [4+2] cycloaddition of 5,6-bis(dimethylamino)acenaphthylene (**2**), which has been synthesized recently,[5] and a series of related compounds, *viz.*, acenaphthylenes **3** and **4** and 1,8-bis(dimethylamino)-4-vinylnaphthalene (**5**).



1



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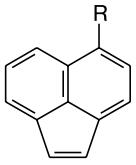
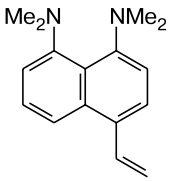


3: R = NMe_2
4: R = H



5

It is known that acenaphthylenes act as very active dienophiles in inverse electron demand cycloaddition reactions[6,7] in which the lowest unoccupied MO of the diene and the highest occupied MO of the dienophile are involved in the transition state of the reaction. In our study, we used readily available 3,6-diphenyl-*symm*-tetrazine (DPT) (**6**) as the diene.

* For Part 35, see Ref. 1.

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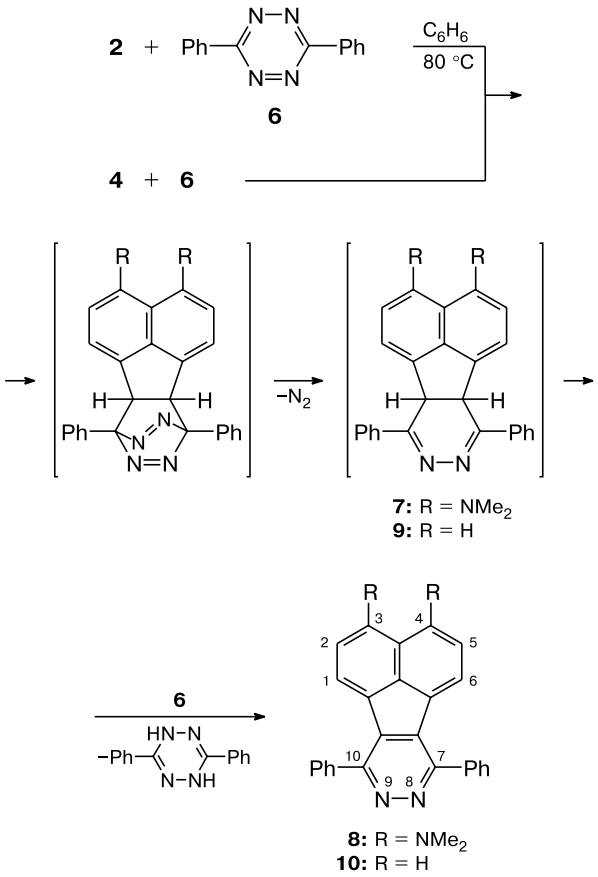
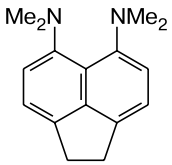
We found that up to one-half of the starting diamine **2** remained unconsumed upon heating of acenaphthylene **2** with DPT in benzene even if the diene and dienophile were taken in an equimolar ratio, and 8,9-diazafluoranthene (**8**) was the only isolated product (Table 1). This is consistent with the general scheme of transformations in which the second DPT molecule serves as an oxidant[8] with respect to the initially formed cycloadduct **7** (Scheme 1). Actually, refluxing of the starting components, which were taken in a **2** : **6** ratio of 1 : 2, over 30 h afforded dehydrogenation product **8** in 94% yield, and 3,6-diphenyl-1,4-dihydro-1,2,4,5-tetrazine was detected in the reaction mixture.

Scheme 1



Unlike the above-described reaction, the reaction of unsubstituted acenaphthylene **4** with tetrazine **6** (as was demonstrated in the study[7]) proceeded to completion even if the reagents were taken in a molar ratio of 1 : 1 because dehydrogenation of dihydrodiazafluoranthene **9** must proceed more difficultly and there are no reasons to expect that a portion of DPT would be consumed for its oxidation. Nevertheless, only aromatic heterocycle **10** was isolated in this case as well due, presumably, to autooxidation of form **9** with atmospheric oxygen (xylene, sealed tube, 180—200 °C, 1 h, 80%).[7] Evidently, the reaction of tetrazine **6** with diamine **2** proceeded much more readily than that with acenaphthylene **4**.

Taking into account the aforesaid, it seemed attractive to us to use directly 5,6-bis(dimethylamino)acenaphthene **11**[9] for the synthesis of "proton sponge" **8**. However, the experiment demonstrated that compound **11** was not dehydrogenated with DPT in refluxing benzene (*cf.* successful dehydrogenation of compound **11** with chloranil[5]).

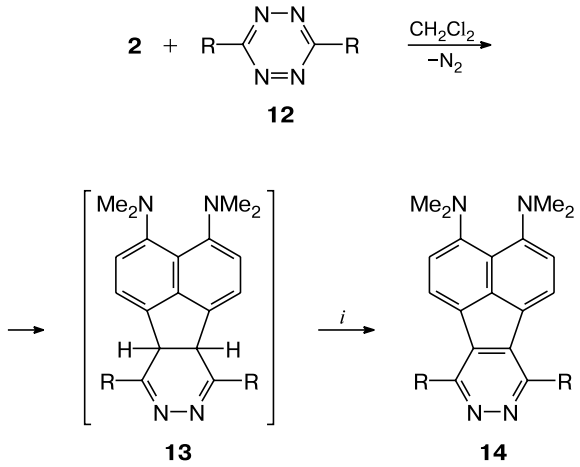


11

By contrast, acenaphthene **11** reacted with tetrazine **6** in refluxing dimethyl sulfoxide (189 °C). The dienophile : diene ratio of 1 : 3 was the ratio of choice in the reactions performed under an inert atmosphere, which corresponds to the series of the transformations **11** → **2** → **7** → **8**. In each step of this process, one equivalent of azadiene was consumed. After 6.5 h, the starting compounds disappeared but the yield of compound **8** was at most 27% due to competitive oligomerization processes.

As expected, the reaction of "proton sponge" **2** with dimethyl tetrazinedicarboxylate **12** proceeded even more readily (already at 20 °C) to form diazafluoranthene **14** as the final product in high yield (Scheme 2, see Table 1).

Scheme 2



R = CO_2Me

i. atmospheric O_2 or **12**.

In the reaction of equimolar amounts of **2** and **12**, like in the reaction with tetrazine **6**, diamine **2** remained partially unconsumed. The latter compound rapidly disappeared upon the addition of the second equivalent of tetrazine **12**. The ^1H NMR monitoring in $CDCl_3$ showed that dihydro adduct **13** was the primary reaction product, which was then oxidized to compound **14** (including with

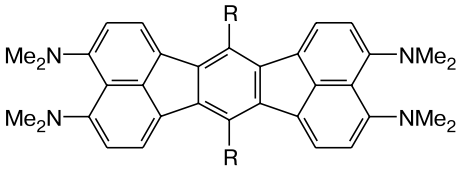
Table 1. Physicochemical characteristics of the compounds synthesized

Compound	M.p./°C (solvent)	Found / Calculated (%)			Molecular formula
		C	H	Cl (I)	
3	Oil	85.9 86.1	6.6 6.7	—	$C_{14}H_{13}N$
8	275—276 (benzene)	81.2 81.4	6.5 5.9	—	$C_{30}H_{26}N_4$
8*	242—245 (decomp., EtOH)	66.2 66.4	5.4 5.0	6.2 6.5	$C_{30}H_{27}ClN_4O_4$
10	309—310 ($CHCl_3$)	—	—	—	—
14	170—172 (toluene)	65.2 65.0	5.3 5.5	—	$C_{22}H_{22}N_4O_4$
16	Oil	84.9 85.2	7.6 7.7	—	$C_{14}H_{15}N$
17	184—185 (*n*-octane)	84.1 84.2	5.6 5.3	—	$C_{28}H_{21}N_3$
17*	103—104 169—170 (decomp., MeCN)	67.1 67.3	4.6 4.4	6.8 7.1	$C_{28}H_{22}ClN_3O_4$
18	199—201 (toluene)	80.6 80.7	6.7 6.8	—	$C_{30}H_{30}N_4$
19	161—162.5 (*n*-octane)	81.3 81.1	6.5 6.4	—	$C_{30}H_{28}N_4$
19*	>150 (darkened) 234—236 (decomp., MeCN)	66.2 66.1	5.5 5.4	6.7 6.5	$C_{30}H_{29}ClN_4O_4$
21	199 235 (decomp., MeOH)	63.4 63.7	5.4 5.0	(21.3) (21.7)	$C_{31}H_{29}IN_4$
22	215 (blackened) 236 (decomp., MeCN)	56.2 56.6	4.8 4.6	10.3 10.8	$C_{31}H_{30}Cl_2N_4O_8$
23*	260—262 (decomp., EtOH)	56.3 56.8	5.2 5.6	9.7 9.3	$C_{18}H_{21}ClN_2O_5$

* Perchlorate.

atmospheric oxygen). This fact indicates that dehydrogenation of dihydrodiazine **13** proceeded more difficultly than that of its analog containing the phenyl groups, which was even not detected in the reaction mixture. In spite of this fact, the isolation of compound **13** presented difficulties because this compound gradually underwent aromatization both in air and solutions (process was completed in 2—3 days).

We failed to use diazafluoranthenes **8** and **14** as the starting compounds in the [4π+2π] cycloaddition reactions for the construction of more complex polycyclic systems of type **15** containing two fragments of "proton sponge" **2**.

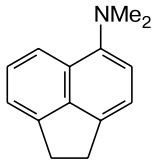


15

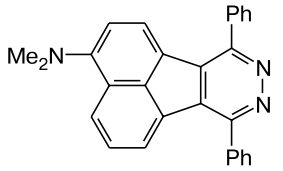
R = Ph, CO_2Me

Refluxing of compounds **8** or **14** in the presence of one equivalent of acenaphthylene **2** in *o*-xylene for 60 h revealed no evidence of their reaction. Under more drastic condition (*o*-xylene, sealed tube, 200 °C, 3 h), 80—90% of the starting compounds were recovered and the remaining portions decomposed. Evidently, the fact that azadienes **8** and **14**, unlike pyridazines containing electron-withdrawing groups,[10] are inactive in these reactions results from a substantial increase in the energy of LUMO because of an increase in the electron density in the pyridazine rings of **8** and **14** caused by the *peri*-dimethylamino groups.

The previously unknown model compound **3** was prepared by alkylation of 5-aminoacenaphthene in the KOH—DMF system to form 5-dimethylaminoacenaphthene (**16**) (yield was 95%) followed by dehydrogenation with chloranil upon heating in benzene (this compound was not dehydrogenated with DPT in refluxing DMSO). The transformation **16** → **3** was accompanied by a change in the color because acenaphthylene **3**, unlike virtually colorless compound **16**, is a dark-orange oil with λ_{max} 425 nm. The reaction of alkene **3** with DPT afforded aromatic product **17** (refluxing in benzene, 90 h, 74%).



16



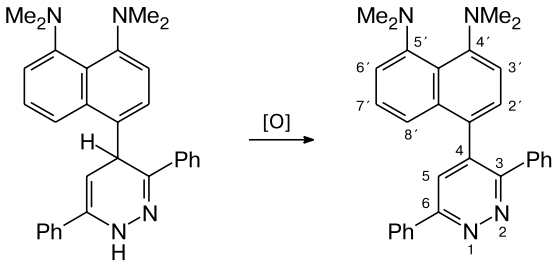
17

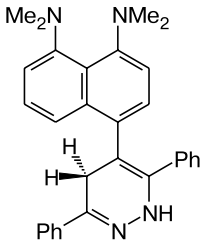
As can be seen from the reaction conditions, the reactivity of amine **3** appeared to be somewhat lower due to the presence of only one electron-donating group (see below).

In our opinion, 1,8-bis(dimethylamino)-4-vinylnaphthalene (**5**)[11] can be considered as an acyclic analog of acenaphthylene **2** in which the ethylene fragment would be expected to be less activated because it is remote from the 8-NMe_2 group. We found that heating of "proton sponge" **5** with one equivalent of tetrazine **6** (benzene, 30 h; *o*-xylene, 10 min) afforded 1,4-dihydropyrid-

azine **18**, which was isolated in individual form. The ^{1}H NMR spectrum of compound **18** has a broadened singlet at δ 9.3 belonging to the NH group as well as a doublet for the H(4) proton and a doublet of doublets for the H(5) proton at δ 5.4 (due to its coupling with the proton of the NH group). After the addition of D_2O, the signal at δ_H 9.3 disappeared and the signal at δ_H 5.4 degenerated into a doublet, which confirms structure **18** and is inconsistent with alternative structure **18a**. The transformation of compound **18** into aromatic pyridazine **19** required heating with chloranil (toluene, 100 °C, 10 min) or with one more equivalent of DPT (*o*-xylene, 2 h) (Scheme 3, see Table 1).

Scheme 3





Therefore, the reactions of compound **5** differ from those of acenaphthylenes **2—4**, which either immediately afford aromatic products or give dihydro forms (for example, **13**) that are readily oxidized. This behavior is typical of many insufficiently activated alkenes whose cycloadducts with tetrazines require additional aromatization (for example, with $K_2Cr_2O_7$—AcOH).[12] Even the reaction of *p*-methoxystyrene with ester **12** gave 1,4-dihydropyridazine with the structure of type **18** resistant to atmospheric oxygen.[13]

The relative reactivities of compounds **2—5** were estimated by ^{1}H NMR spectroscopic studies of their reactions with DPT in deuterated chloroform or 1,2-dichloroethane. A series of spectra were recorded with the use of all reagents taken at the initial concentrations of $6.78 \cdot 10^{-2}$ mol L^{-1}. The course of the reactions was followed from a decrease in the concentration of alkene until its conversion reached 25%. The ratio of the reactivities of the dienophiles in the series 5,6-bis(dimethylamino)acenaphthylene (**2**), 1,8-bis(dimethylamino)-4-vinylnaphthalene (**5**), 5-dimethylaminoacenaphthylene (**3**), and acenaphthylene (**4**) is 32 : 17 : 14 : 1 (Table 2). The reactivities of these compounds to DPT in benzene are comparable with those in xylene (**2** : **3** : **4** — 68 : 23 : 1; for the reaction conditions, see the Experimental section).

Table 2. Rate constants and relative rates (k_{rel}) of the reactions of compounds **2—5** with *symm*-diphenyltetrazine (**6**) at 21 °C

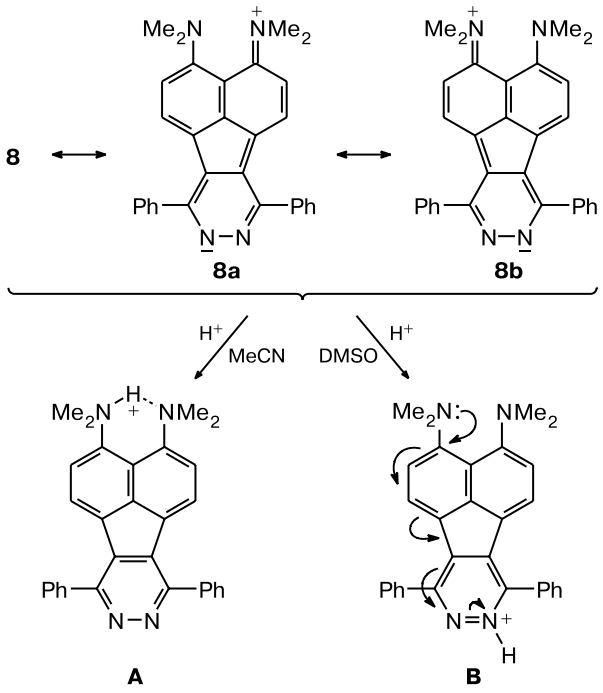
Compound	Solvent	$k \cdot 10^3$ [a] /L mol^{-1} s^{-1}	k_{rel} [b]
2	$CDCl_3$	2.34	32
2	$CDCl_2CDCl_2$	1.93	26
3	$CDCl_3$	1.02	14
4	$CDCl_3$	$7.32 \cdot 10^{-2}$	1
5	$CDCl_3$	1.26	17

[a] The accuracy of determination was ±5%.
[b] k(**4**) = 1.

Therefore, the introduction of one NMe_2 group at position 5 leads to an increase in the reactivity of the acenaphthylene system by more than an order of magnitude, and the introduction of the second NMe_2 group at the *peri* position causes a further approximately twofold increase in the reactivity. The reactivity of vinylnaphthalene **5** is intermediate between those of acenaphthylenes **2** and **3**. The fact that the largest increase in the reactivity occurs upon the insertion of the first NMe_2 group is, apparently, associated with steric hindrances in "proton sponge" **2**, which decrease the efficiency of conjugation of each dimethylamino group with the π system of the ring. At the same time, these results are inconsistent with other data, which are indicative of dramatic changes in the reactivities on going from 1-dimethylaminonaphthalene to 1,8-bis(dimethylamino)naphthalene (**1**).[1] Apparently, this is attributed to the fact that the transition state of the cycloaddition reaction under study is characterized by low polarity and, consequently, it is poorly sensitive to the resonance effect of the substituents.

It can be readily seen that cycloadducts **8**, **14**, **17**, and **19** prepared by us are pronounced push-pull systems in which the dimethylamino groups are efficiently conjugated with the pyridazine ring. This must lead to a substantial contribution of bipolar structures of types **8a** and **8b** to the resonance hybrid and, as a consequence, to a decrease in the basicity of the NMe_2 groups and an increase in the basicity of the pyridazine system (Scheme 4). In this situation, in spite of high basicity typical of "proton sponges",[2] it cannot be predicted with certainty that the resulting cycloadducts would be protonated at the dimethylamino groups rather than at the heterocycle. This conclusion was confirmed by our studies performed with the use of electronic absorption and ^{1}H NMR spectroscopy.

Scheme 4



It appeared that diazafluoranthene **8** in acetonitrile (CD_3CN) was protonated with one equiv. of $HClO_4$ to form the cation **A** in which the NMe_2 groups are linked through an intramolecular hydrogen bond (see Scheme 4). The chemical shift of the proton of the NH group in this cation is >16 ppm, and the signal of the dimethylamino groups is observed as a doublet with the spin-spin coupling constant ^3J = 2.6 Hz (Table 3), which is also characteristic of cations of other "proton sponges" containing the five-membered ring at the *peri* positions of the naphthalene ring.[5]

It should be noted that protonation of compound **8** in acetonitrile (MeCN) was not visually accompanied by a change in the color of the solution, although the UV spectrum of salt **8** · $HClO_4$ substantially changed and became similar to the spectrum of diazafluoranthene **10** (Table 4). This is attributable to the presence of a low concentration of unprotonated base **8**, which masked the color of the solution. Actually, the spectrum of salt **8** · $HClO_4$ has a low-intensity long-wavelength band in the visible region, which is observed as a shoulder in virtually the same region as that of the corresponding band of compound **8** (see Table 4). When the concentration of perchlorate **8** · $HClO_4$ was $3 \cdot 10^{-5}$ mol L^{-1}, the

Table 3. Spectroscopic characteristics of the compounds synthesized

Compound	^{1}H NMR spectrum		Other spectroscopic properties[a]
	Conditions	δ, *J*/Hz	
3	CD_3CN	3.09 (s, 6 H, NMe_2); 6.89 (d, 1 H, H(4)); 6.94 (d, 1 H, H(2)); 7.52 (dd, 1 H, H(7)); 7.58 (d,1 H, H(3)); 7.69 (d, 1 H, H(8)); 7.01 (d, 1 H, H(1)); 8.10 (d, 1 H, H(6)); $J_{1,2}$ = 5.2, $J_{3,4}$ = 7.5, $J_{6,7}$ = 8.4, $J_{7,8}$ = 6.9, $J_{6,8}$ = 1.4	UV: 238 (sh, 4.18), 287 (3.59), 310 (3.56), 324 (3.62), 359 (3.54), 375 (sh, 3.49), 425 (3.43)
8	$CDCl_3$	2.95 (s, 12 H, NMe_2); 6.89 (d, 2 H, H(2), H(5)); 7.57 (m, 6 H, Ph); 7.67 (d, 2 H, H(1), H(6)); 7.92 (m, 4 H, Ph); $J_{1,2}$ = 8.2	UV[b] Fluorescence: 483 (excit.), 536 (fluor.)
8*[c]	CD_3CN	3.21 (d, 12 H, NMe_2); 7.90 (m, 10 H, 2 Ph); 8.06, 8.12 (both d, 2 H each, H(1), H(2), H(5), H(6)); 16.10 (m, 1 H, NH); $J_{1,2}$ = 8.0, $J_{NH,NMe}$ = 2.6	UV[b]
	DMSO-d_6 70 °C	3.09 (br.s, 12 H, NMe_2); 3.40 (br.s, $H_2O + H^+$); 7.27, 7.64 (both d, 2 H each, H(1), H(2), H(5), H(6)); 7.78 (m, 6 H, Ph); 7.96 (m, 4 H, Ph); $J_{1,2}$ = 9.0	
10	DMSO-d_6	7.74 (m, 10 H); 7.95 (m, 4 H); 8.26 (m, 2 H)	UV[b]
14	DMSO-d_6	3.03 (s, 12 H, NMe_2); 4.12 (s, 6 H, OMe); 7.22 (d, 2 H, H(2), H(5)); 8.55 (d, 2 H, H(1), H(6)); $J_{1,2}$ = 8.7	UV: 262 (4.19), 304 (4.00), 368 (4.14), 476 (sh, 429), 499 (4.45); (MeCN + $HClO_4$) 238 (sh, 4.27), 313 (4.17), 333 (sh, 4.08), 411 (4.05), 513 (sh, 3.40) IR: 1720 (CO); 1580, 1570, 1550, 1500 (ring)
16	$CDCl_3$	2.97 (s, 6 H, NMe_2); 3.40 (m, 4 H, H(1), H(2)); 7.04 (d, 1 H, H(4)); 7.23, 7.32 (both br.d, 1 H each, H(3), H(8)); 7.50, 7.88 (both dd, 1 H each, H(6), H(7)); $J_{3,4}$ = 7.4, $J_{6,7}$ = 8.3, $J_{7,8}$ = 7.0, $J_{6,8}$ = 1.4	—

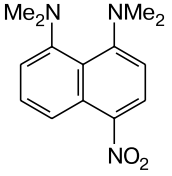
(*to be continued*)

Table 3 (*continued*)

Compound	^{1}H NMR spectrum		Other spectroscopic properties[a]
	Conditions	δ, *J*/Hz	
17	$CDCl_3$	3.16 (s, 6 H, NMe_2); 6.81 (d, 1 H, H(2)); 7.48 (dd, 1 H, H(5)); 7.60 (m, 6 H, Ph); 7.65 (d, 1 H, H(1)); 7.77 (br.d, 1 H, H(6)); 7.95 (m, 4 H, Ph); 8.25 (br.d, 1 H, H(4)); $J_{1,2}$ = 8.0, $J_{4,5}$ = 8.5, $J_{5,6}$ = 7.2, $J_{4,6}$ = 0.9	UV: 248 (sh, 4.44), 278 (sh, 4.18), 328 (3.97), 468 (4.01) Fluorescence: 481 (excit.), 546 (fluor.)
17*[c]	CD_3CN	3.55 (s, 6 H, NMe_2); 6.50 (br.s, H_2O + H^+); 7.89 (m, 6 H); 8.02 (m, 5 H); 8.10 (m, 3 H); 8.63 (d.d, 1 H, H(4)), $J_{4,5}$ = 7.9, $J_{4,6}$ = 0.9	UV: 272 (4.30), 343 (4.05), 387 (4.04), 534 (3.25)
18	Acetone-d_6	2.71, 2.78 (both s, 6 H each, 4′- and 5′-NMe_2); 5.44 (d.d, 1 H, H(5)); 5.59 (d, 1 H, H(4)); 6.81 (d, 1 H, H(3′)); 7.06, 7.20—7.36, 7.50, 7.74 (all m, 2 H, 6 H, 3 H, 2 H, 2 Ph + H(2′), H(6′), H(7′)); 8.06 (br.d, 1 H, H(8′)); 9.25 (br.s, 1 H, NH); $J_{2',3'}$ = 7.9, $J_{6',7'}$ = 7.6, $J_{7',8'}$ = 8.3, $J_{4,5}$ = 5.7, $J_{NH,5}$ = 2.3	IR: 3305 (NH); 1605, 1590, 1500 (ring)
19	$CDCl_3$	2.80 (s, 12 H, 4′- and 5′-NMe_2); 6.81 (d, 1 H, H(3′)); 6.88 (br.d, 1 H, H(6′)); 6.98—7.20, 7.47, 8.17 (all m, 6 H, 5 H, 2 H, 2 Ph + + H(2′), H(7′), H(8′)); 7.90 (s, 1 H, H(5)); $J_{2',3'}$ = 7.8, $J_{6',7'}$ = 7.4	UV: 250 (4.55), 278 (sh, 4.41), 358 (4.03)
19*[c]	CD_3CN	3.11, 3.15 (both d, 6 H each, 4′- and 5′-NMe_2); 7.36, 7.48, 7.79, 8.22 (all m, 4 H, 1 H, 5 H, 2 H); 7.61 (t, 1 H, H(7′)); 7.94 (br.d, 1 H, H(6′)); 8.03 (d, 1 H, H(3′)); 8.93 (s, 1 H, H(5)); 18.72 (br.s, 1 H, NH); $J_{2',3'}$ = 7.9, $J_{6',7'}$ = 7.6, $J_{NH,4'\text{-}NMe}$ = 2.0, $J_{NH,5'\text{-}NMe}$ = 2.8	—
	DMSO-d_6	3.12 (m, 12 H, NMe_2); 7.23, 7.36, 7.60, 8.29 (all m, 3 H, 2 H, 5 H, 3 H); 7.83, 8.18 (both d, 1 H each, H(2′), H(3′)); 8.09 (br.d, 1 H, H(6′)); 18.47 (br.s, 1 H, NH); $J_{2',3'}$ = 7.9	
21	CD_3CN, 70 °C	3.06, 3.14 (both s, 6 H each, 3- and 4-NMe_2); 4.28 (s, 3 H, N(8)Me); 6.98, 7.10, 7.23 (all d, 1 H each, H(1), H(2), H(5)); 7.70—8.00 (m, 11 H, H(6) + 2 Ph); $J_{1,2}$ = 8.9, $J_{5,6}$ = 9.1	UV: 263 (sh, 4.20), 343 (4.11), 502 (sh, 4.19), 530 (4.38) Fluorescence: 527 (excit.), 563 (fluor.)
	DMSO-d_6, 100 °C	3.05, 3.14 (both s, 6 H each, 3- and 4-NMe_2); 4.28 (s, 3 H, N(8)Me); 6.90, 7.14, 7.29 (all d, 1 H each, H(1), H(2), H(5)); 7.70—8.00 (m, 11 H, H(6) + 2 Ph); $J_{1,2}$ = 8.9, $J_{5,6}$ = 9.0	
22	CD_3CN	3.18 (m, 12 H, NMe_2); 4.45 (s, 3 H, N(8)Me); 7.11 (d, 1 H, H(6)); 7.90 (m, 11 H, H(5) + 2 Ph); 8.10, 8.19 (both d, 1 H each, H(1), H(2)); 16.07 (br.s, 1 H, NH); $J_{5,6}$ = 7.9, $J_{1,2}$ = 8.0	UV: 270 (sh, 4.24), 339 (4.00), 391 (3.79), 485 (sh, 3.72), 519 (3.74)
23*[c]	CD_3CN	2.65, 2.66, 3.59, 3.61 (all s, 3 H each, NMe); 2.30 (br.s, OH + H_2O); 2.81 (s, 3 H, C(3)Me); 7.09 (s, 1 H, H(2)); 7.48, 7.52, 8.35, 8.49 (all d, 1 H each, H(4), H(5), H(8), H(9)); $J_{4,5}$ = $J_{8,9}$ = 9.1	IR: 3400—3280 (OH); 1625, 1600, 1590, 1560, 1540, 1530 (ring)
	DMSO-d_6	2.62, 3.59 (both br.s, 6 H each, 6- and 7-NMe_2); 2.75 (s, 3 H, C(3)Me); 7.03 (s, 1 H, H(2)); 7.51, 7.59, 8.32, 8.42 (all d, 1 H each, H(4), H(5), H(8), H(9)); 11.70 (br.s, 1 H, OH); $J_{4,5}$ = $J_{8,9}$ = 9.7	

[a] UV (MeCN, λ/nm), IR (Nujol mulls, ν/cm^{-1}), and fluorescence (MeCN, λ/nm) spectra.
[b] The UV spectrum is given in Table 4.
[c] Perchlorate.

degree of its deprotonation in acetonitrile reached 6% (for 1,8-bis(dimethylamino)-4-nitronaphthalene perchlorate (**20**), ≤ 1%).[14] The above-considered data indicate that the basicity of "proton sponge" **8** is at least an order of magnitude lower than the basicity of push-pull system **20** whose pK_a in MeCN is 14.1.[2] Interestingly, the solvatochromism which reflects the contribution of the polarized structures of types **8a** and **8b** to neutral molecules **8** and **20** and is calculated as the difference $\Delta\lambda_{max}$ between the long-wavelength absorption bands on going, for example, from highly polar DMSO to weakly polar $CHCl_3$ (dipole moments are given in Table 4), is identical for both compounds (20 nm for **8** and 21 nm for **20**).[14]



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Since concentrations generally used in ^{1}H NMR spectroscopic studies are more than 1000 times higher than those used in electronic absorption spectroscopy, the NMR spectrum in acetonitrile detected nothing but the cation **A**.

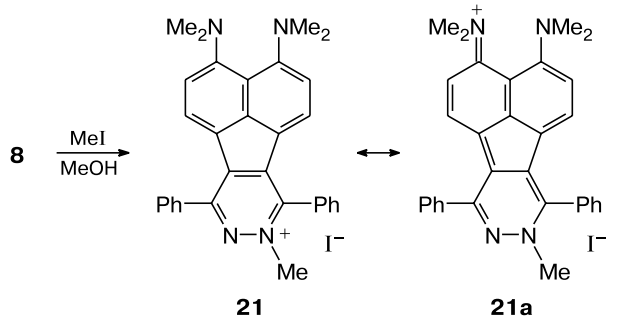
Table 4. Electronic absorption spectra of compounds **8**, **8**·$HClO_4$, and **10** in different solvents

Compound	Solvent	μ[a] /D	Color of solution	λ_{max}/nm (logε)[b]					
8	$CHCl_3$	1.1	Orange	259 (4.48),	302[c] (4.04),	332 (3.98),		**481 (4.25)**,	523[c] (3.04)
	EtOH	1.7	Orange	258 (4.41),	301[c] (3.98),	333 (4.00),	477[c] (4.23),	**495 (4.27)**	
	MeCN	3.5	Orange	258 (4.46),	299[c] (4.06),	333 (4.05),	472[c] (4.29),	**490 (4.34)**,	525[c] (3.68)
	DMSO	3.9	Orange		304[c] (4.07),	336 (4.06),	482[c] (4.31),	**501 (4.37)**	
8·$HClO_4$	MeCN	3.5	Orange		273 (4.31),		340 (4.01),	**397 (4.04)**,	482[c] (3.18)
	MeOH	1.7	Crimson	244 (4.22),	269 (4.23),	350 (3.98),	490[c] (3.94),	**560 (4.25)**	
10	EtOH [d]	1.7	Yellow	242 (4.65),	267[c] (4.24),	309 (4.00),	325 (3.99),	**371 (4.06)**	
	MeCN	3.5	Yellow	240 (4.74),	265[c] (4.26),	307 (4.00),	323 (3.99),	**368 (4.03)**	

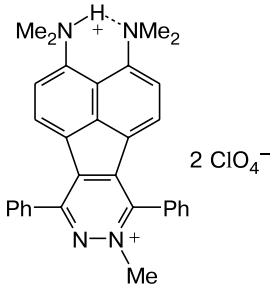
[a] The dipole moments of the solvents (benzene, 25 °C) were taken from the study.[15]
[b] The charge-transfer band (*para* band) is printed in bold type.
[c] Shoulder.
[d] This spectrum is somewhat different from that reported in the study[7] for the same solvent (240 (4.71), 265 (4.30), 310 (4.00), 325 (4.00), 370 (3.07)).

The use of a substantially more basic dimethyl sulfoxide instead of MeCN for protonation of diazafluoranthene **8** led to the appearance of a bright-crimson color, which was also observed in alcohol (λ_{max} 560 nm, see Table 4) and in the solid state. The ^1H NMR spectrum in DMSO-d_6 does not show a signal of the NH group at δ 16; instead, the spectrum has a signal common to the proton of the NH group and water at δ 3.6, whereas the dimethylamino groups are manifested as a broad hump, which is indicative of their weak involvement in the proton transfer (δ 3.1 compared to δ 3.2 in CD_3CN). At +70 °C, the above-mentioned hump is transformed into a narrow singlet.

With the aim of determining the position of the proton in the spectrum of a solution of perchlorate **8**·$HClO_4$ in DMSO, we prepared model compound **21**. In the solid state and in solutions (DMSO, EtOH, H_2O, and MeCN), this compound is bright red-crimson in color (λ_{max} 530 nm, see Table 3) and is similar in color to a solution of cation H^+-**8** in DMSO. In addition, solutions of compound **21** exhibit greenish-yellow fluorescence (see Table 3). In the ^1H NMR spectrum of compound **21**, the dimethylamino groups are manifested as a hump, which assumes a shape of two singlets only upon heating to 100 °C (DMSO-d_6). Conceivably, such a behavior of the NMe_2 groups in salt **21** is associated with their involvement in delocalization of the positive charge (see, for example, structure **21a**). Apparently, this fact is also responsible for a deep color of compound **21**. From this standpoint, cation H^+-**8** in DMSO and other basic solvents is best described by the tautomeric form **B** (see Scheme 4).



^1H NMR spectroscopic study demonstrated that cation H^+-**8** did not undergo secondary protonation in acetonitrile and DMSO (up to 10 equiv. of $HClO_4$ were added). By contrast, salt **21** in acetonitrile was protonated with perchloric acid to form orange diperchlorate **22** (λ_{max} 485 nm, δ_{NH} 16.1). In this case, the hypsochromic shift is, apparently, associated with the fact that the NMe_2 groups cannot be involved in delocalization of the positive charge, like in structure **21a**.



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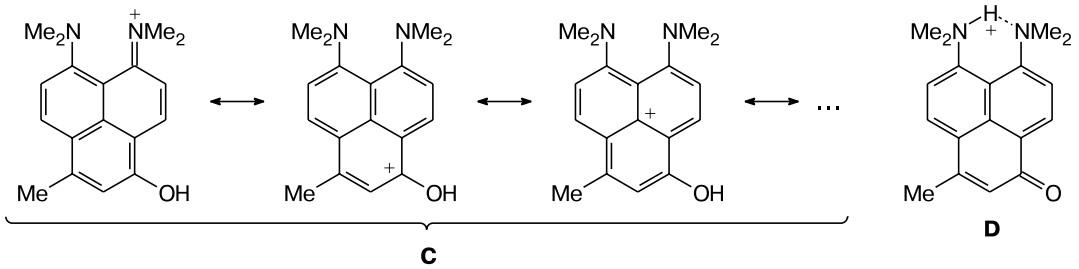
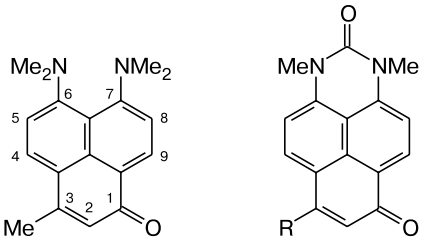
Therefore, in protic and/or basic solvents as well as in the solid state, cycloadduct **8** adds a proton at the heterocycle (**B**), whereas cations H^+-**8** in acetonitrile occur in the form **A**. Unfortunately, we failed to grow crystals of salt **8**·$HClO_4$ suitable for X-ray diffraction analysis because this salt is characterized by hygroscopicity and low hydrolytic stability.

Compound **8** is the first example of "proton sponges" capable of adding a proton at positions other than the NMe_2 groups. In searching for other analogous systems,



we examined phenalenone (**23**), which has been described earlier.[16] It is known[17] that both phenalenone and its heterocyclic derivatives of type **24** are protonated exclusively at the carbocyclic carbonyl group to give resonance-stabilized cations.



23 **24**

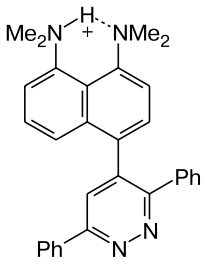
We found that "proton sponge" **23** adds a proton at the carbonyl group both in DMSO and MeCN with the only difference that the OH group generated in DMSO is involved in hydrogen bonding with the solvent (δ(OH) 11.7), whereas this group does not form hydrogen bonds with MeCN (δ(OH) 2.3). As a result, the resonance interactions of the NMe_2 groups with the phenalenium system are stronger in acetonitrile than in DMSO. Actually, due to the unsymmetrical structure of the cation **C** as a whole and because of flattening of the positively charged dimethylamino groups, the ^{1}H NMR spectrum of salt **23** · $HClO_4$ in MeCN shows individual signals for all NMe groups, whereas only broadening of the peaks of the NMe_2 groups is observed in the spectrum in DMSO at 20 °C (by analogy with compounds **8** · $HClO_4$ and **21**, see Table 3).

Therefore, the resonance stabilization ensures a larger gain in energy compared to that provided by the intramolecular hydrogen bond in the cation **D** whose formation was not detected (^{1}H NMR spectra have no signals at δ_H >15 and the IR spectrum shows no C=O stretching bands).

Due to the lower basicity of compound **14** (compared to **8**), it does not form stable salts with acids and, hence, its protonation was not studied. However, its UV spectrum in acetonitrile with an addition of perchloric acid showed (see Table 2) that protonation in this case also proceeded with the involvement of the NMe_2 groups (transformation **14** → H^+-**14** led to a substantial hypsochromic shift of the long-wavelength absorption band, λ_{max} 499 (log ε 4.45) → 411 (4.05) nm).

Under the action of one equiv. of $HClO_4$, diazafluoranthene **17** forms cation H^+-**17** even in acetonitrile. In this cation, the proton is located at the azine moiety of the molecule (like in the structure **B**). The formation of this cation is evidenced by a change in the color of the compound from orange to crimson-violet (λ_{max} 534 nm) and the fact that the signals for all protons in its ^{1}H NMR spectrum are shifted downfield by ~0.5 ppm compared to those observed in the spectrum of base **17** (see Table 3). Solutions of pyridazine **17** exhibit yellow-green fluorescence (λ_{max} of fluorescence is 546 nm; the Stokes shift is 65 nm). It should be noted that fluorescence of diamine **8** is observed at a somewhat lower wavelength (536 nm; the Stokes shift is 53 nm) due to spatial *peri*-interactions between the dimethylamino groups.

Interestingly, yellow diazafluoranthene **10** devoid of the alkylamino groups is insoluble in HCl (20%) or H_2SO_4 (50%) but is soluble in concentrated H_2SO_4, the solution developing a brown color.



H^+-**19**

Protonation of compound **19** both in MeCN and DMSO proceeded exclusively at the 1,8-bis(dimethylamino)naphthalene fragment to give cation H^+-**19** (δ_{NH} >18.5). Apparently, this direction of protonation is to a large extent determined by acoplanarity of the naphthalene and pyridazine rings, which reduces their mesomeric interaction.*

To summarize, we demonstrated that 5,6-bis(dimethylamino)acenaphthylene can be used as a building

* In the case of 1,8-bis(dimethylamino)-4-picrylnaphthalene trifluoroacetate containing a slightly asymmetrical intramolecular hydrogen bond, the acoplanarity of the trinitrophenyl group and the naphthalene ring is so high (~70°) that virtually only the inductive component of the electron-withdrawing effect of this group persists.[18]

block for the construction of new molecular systems, synthesized "proton sponges" with the diazafluoranthene skeleton, and showed that these compounds can change the site of protonation depending on the solvent. The quantitative data on the reactivities of "proton sponges" were obtained for the first time and these data were compared with the corresponding data for a series of their close analogs.

Experimental

The ^{1}H NMR spectra were recorded on Bruker DPX-250 (250 MHz) and Unity-300 (300 MHz) instruments with $SiMe_4$ as the internal standard. The kinetic measurements were carried out by ^{1}H NMR spectroscopy in $CDCl_3$; the initial concentrations of all reagents were $6.78 \cdot 10^{-2}$ mol L^{-1}. The UV spectra were measured on a Specord M-40 spectrophotometer. The fluorescence spectra were recorded on a Shimadzu RF 5001 PC instrument. The IR spectra were measured on a Specord IR-75 spectrometer. Chromatography was carried out on columns with Al_2O_3 (for activity grade according to Brockmann, see below) and on silica gel L40/100 μm (Chemapol). The course of the reactions and purities of the resulting compounds were monitored by TLC on Al_2O_3 and Silufol plates; visualization was carried out with iodine vapor. The melting points were measured in sealed glass tubes and were not corrected. The physicochemical characteristics of the resulting compounds are given in Tables 1, 3, and 4.

5,6-Bis(dimethylamino)acenaphthylene (2),[5] 3,6-diphenyl-1,2,4,5-tetrazine (6),[19] dimethyl *symm*-tetrazine-3,6-dicarboxylate (12),[13] and phenalenone 23 [16] were prepared according to procedures published earlier. Acenaphthylene **4** was prepared according to a modified procedure.[20] Benzene and xylene were dried with sodium metal and distilled. Acetonitrile and dimethyl sulfoxide were purified and dried according to standard procedures. Their deuterated analogs (CD_3CN and DMSO-d_6), $CDCl_3$, and $CDCl_2CDCl_2$ were used without additional purification (the contents of the major components were no lower 98%, the deuterium content was no lower than 99.7%, Izotop, St. Petersburg).

3,4-Bis(dimethylamino)-7,10-diphenyl-8,9-diazafluoranthene (8). ***A.*** A solution of *symm*-diphenyltetrazine (0.096 g, 0.4 mmol) in C_6H_6 (5 mL) was mixed with a solution of acenaphthylene **2** (0.048 g, 0.2 mmol) in benzene (5 mL). The resulting mixture was refluxed for 30 h, concentrated to a minimum volume, and chromatographed (Al_2O_3 (V), $CHCl_3$), the bright-orange zone being collected (R_f 0.20, $CHCl_3$). Compound **8** was obtained as brown crystals with a green tint in a yield of 0.084 g (94%).

B. A mixture of acenaphthene **11** (0.048 g, 0.2 mmol),[9] diphenyltetrazine **6** (0.14 g, 0.6 mmol), and DMSO (6 mL) was refluxed under argon for 6.5 h. Then the hot reaction mixture was diluted with water (10 mL) and extracted with benzene (3×6 mL). The extract was concentrated to a minimum volume and then treated as described in the method *A*. Diazafluoranthene **8** was isolated in a yield of 0.024 g (27%). The physicochemical properties of compound **8** were identical with those of the sample prepared according to the method *A*.

3,4-Bis(dimethylamino)-8-methyl-7,10-diphenyl-8,9-diazafluoranthenium iodide (21). Compound **8** (0.032 g, 0.072 mmol) was dissolved in MeOH (2 mL) and then iodomethane (0.015 mL, 0.24 mmol) was added with a microsampler. The resulting solution was kept at 22 °C for 7 days. The alcohol was distilled off. Compound **21** was obtained as dark-claret crystals in a yield of 0.04 g (94%).

3,4-Bis(dimethylamino)-7,10-bis(methoxycarbonyl)-8,9-diazafluoranthene (14). A solution of tetrazine **12** (0.08 g, 0.4 mmol) in CH_2Cl_2 (4 mL) was added portionwise to a solution of acenaphthylene **2** (0.048 g, 0.2 mmol) in CH_2Cl_2 (4 mL) (gas evolution). After 5 min, the solvent was evaporated and the residue was dissolved in $CHCl_3$. The solution was kept at 15 °C for 3 days, the solvent being slowly evaporated until aromatization of the dihydro form was completed. The residue was crystallized from toluene. Compound **14** was obtained in a yield of 0.07 g (85%) as dark-brown crystals with a green tint.

5-Aminoacenaphthene was prepared according to a known procedure.[21] ^{1}H NMR ($CDCl_3$), δ: 3.35 (m, 4 H, H(1), H(2)); 4.15 (br.s, 2 H, NH_2); 6.81 (d, 1 H, H(4)); 7.08 (br.d, 1 H, H(3)); 7.25 (br.d, 1 H, H(8)); 7.40 (t, 1 H, H(7)); 7.54 (br.d, 1 H, H(6)); $J_{3,4}$ = 7.3 Hz, $J_{6,7}$ = 8.2 Hz, $J_{7,8}$ = 6.8 Hz.

5-Dimethylaminoacenaphthene (16). Dimethylformamide (20 mL) was added to 5-aminoacenaphthene (1.5 g, 0.01 mol) and the reaction mixture was stirred under nitrogen until the compound was dissolved (5 min). Then finely dispersed KOH (1.3 g, 0.023 mol) was added. After 5 min, MeI (2.2 mL, 0.035 mol), which was cooled to 0 °C, was added portionwise. The reaction mixture was stirred at ~20 °C for 1 h and then at 70 °C for 1 h, cooled to 20 °C, and diluted with water (100 mL). Then a 10% KOH solution (5 mL) was added. Acenaphthene **16** that formed was extracted with light petroleum (6×50 mL) and the solvent was removed. A pale-brown oil was obtained in a yield of 1.46 g (74%).

5-Dimethylaminoacenaphthylene (3). A solution of compound **16** (0.5 g, 2.4 mmol) in benzene (10 mL) was mixed with a solution of chloranil (0.66 g, 2.7 mmol) in benzene (10 mL). The resulting solution was refluxed for 30 min and the benzene was distilled off. The residue was chromatographed (Al_2O_3 (II), $CHCl_3$), and the first bright-orange fraction was collected (R_f 0.93, $CHCl_3$). Compound **3** was obtained as a dark-orange oil in a yield of 0.22 g (44%).

3-Dimethylamino-7,10-diphenyl-8,9-diazafluoranthene (17). A solution of tetrazine **6** (0.082 g, 0.4 mmol) and acenaphthylene **3** (0.04 g, 0.2 mmol) in benzene (10 mL) was refluxed for 90 h. The solvent was removed, the residue was chromatographed (Al_2O_3 (III), $CHCl_3$), and the bright-orange fraction was collected (R_f 0.15, $CHCl_3$). Compound **17** was obtained as a red-orange substance in a yield of 0.06 g (74%).

7,10-Diphenyl-8,9-diazafluoranthene (10) was obtained from acenaphthylene **4** and tetrazine **6** as described earlier.[7] This compound was obtained as yellow crystals. Its m.p. and ^{1}H NMR spectrum were measured in the present study for the first time (see Table 4).

4-[4,5-Bis(dimethylamino)naphthalen-1-yl]-3,6-diphenyl-1,4-dihydropyridazine (18). 1,8-Bis(dimethylamino)-4-vinylnaphthalene (**5**)[11] (816 mg, 3.4 mmol) and tetrazine **6** (796 mg, 3.4 mmol) were fused together at 120 °C for 10 min (gas evolution). Then *o*-xylene (4 mL) was added and the reaction mixture was refluxed for 10 min until the pink color of the tetrazine disappeared. The solution was cooled to 20 °C and kept for 12 h. Then the pale-yellow crystals of 3,6-diphenyl-1,4-dihydro-1,2,4,5-tetrazine[19] that formed (220 mg, 27%) were filtered off.

The filtrate was concentrated at 20 °C to the volume of 1.5 mL and a heavy white precipitate was separated by washing with cold toluene (1 mL) and cold CCl_4 (2 mL). A white finely crystalline powder of compound **18** was obtained in a yield of 210 mg (13%). After isolation of the products, the residue was not separated and analyzed.

4-[4,5-Bis(dimethylamino)naphthalen-1-yl]-3,6-diphenylpyridazine (19). ***A.*** Vinylnaphthalene **5** (0.096 g, 0.4 mmol) and tetrazine **6** (0.187 g, 0.8 mmol) were fused together at 120 °C for 10 min (gas evolution). Then *o*-xylene (3 mL) was added and the reaction mixture was refluxed for 2 h until the pink color of the tetrazine disappeared. The solution was kept at 5 °C for 12 h. 3,6-Diphenyl-1,4-dihydro-1,2,4,5-tetrazine was separated in a yield of 0.092 g (97%). The xylene was removed from the filtrate, and the residue was mixed with chloroform (2 mL) and Al_2O_3 (1 g). Then the mixture was kept for 5 h to achieve complete oxidation of the traces of diphenyldihydrotetrazine (its chromatographic mobility is identical with that of product **19**) to tetrazine **6**. The resulting mixture was chromatographed (Al_2O_3 (II), $CHCl_3$), and the pale-yellow fraction was collected (R_f 0.33, $CHCl_3$). Yellow pyridazine **19** was obtained in a yield of 0.162 g (88%). This compound crystallized by concentration of its solution in *n*-octane.

B. A mixture of dihydrodiazine **18** (45 mg, 0.1 mmol), chloranil (25 mg, 0.1 mmol), and toluene (1 mL) was heated at 100 °C for 10 min. After cooling, the reaction mixture was chromatographed as described above. Aromatic product **19** was obtained in a yield of 35 mg (79%). The physicochemical properties of the aromatic product were identical with those of the sample prepared according to the procedure *A*.

Synthesis of perchlorates (general procedure). An equimolar amount of 70% $HClO_4$ was added with the use of a microsampler to a solution of the corresponding compound (0.1 mmol) in MeCN (2 mL). The solvent was removed *in vacuo*. The residue was washed with ether and crystallized if necessary. Salts **8**·$HClO_4$ (small dark-claret crystals), **17**·$HClO_4$ (brown-red crystals), **19**·$HClO_4$ (pale-yellow crystals), and **23**·$HClO_4$ (dark-claret crystals) were obtained in quantitative yields. An orange powder of compound **22** as diperchlorate was prepared by the reaction of iodide **21** with a fivefold excess of 70% $HClO_4$.

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