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5,6-Bis(dimethylamino)acenaphthylene as an activated alkene and 'proton sponge' in halogenation reactions

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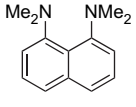
Abstract—It has been shown that 5,6-bis(dimethylamino)acenaphthylene in its reactions with X_2 (X=Cl, Br, I) and *N*-X-succinimides behaves simultaneously as an electron-rich alkene or arene and proton sponge. Thus, addition of bromine or iodine to the C(1)=C(2) bond is followed by immediate dehydrohalogenation leading to the formation of the corresponding 1(2)-(di)halogenoacenaphthylenes in good yields. Reaction with chlorine enables isolation of only 1,4,7-trichloro-5,6-bis(dimethylamino)acenaphthylene. With *N*-halosuccinimides, the halogenation is directed mainly by the steric bulk of the entering halogen and then by solvent polarity thus allowing the regioselective preparation of 1(2)- or 4(7)-(di)halides. Introduction of the third and fourth bromine atoms, but not chlorine, is accomplished by mono-N-demethylation. The pK_a values of some new derivatives of acenaphthene and acenaphthylene proton sponges were measured by competitive transprotonation ^{1}H NMR spectroscopy technique in DMSO. The X-ray molecular structures of 4,7-dichloro-5,6-bis(dimethylamino)acenaphthylene and its monoprotonated form are reported.

1. Introduction

It is well known that 1,8-bis(dimethylamino)naphthalene ('proton sponge', **1**) simultaneously displays properties of a strong neutral organic base[1] and a very weak *N*-nucleophile.[2] At the same time, due to the pronounced electron-donating effect of two NMe_2 groups, the proton sponge is a very active *C*-nucleophile easily reacting with many electrophiles at positions 4(5) or 2(7).[2] Recently, we have described 5,6-bis(dimethylamino)acenaphthylene (**2**),[3] which as an alkene exhibits enhanced activity in [4+2]-cycloaddition reactions with reverse electronic demands.[4] Aside from an activated alkene, acenaphthylene **2** could also be considered as an arene and a proton sponge derivative. In view of this, it seemed rather intriguing to study its behaviour toward typical electrophiles and the scope of the present work is to report on halogenation reactions of **2**.



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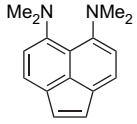

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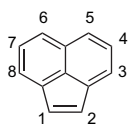

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Keywords: 5,6-Bis(dimethylamino)acenaphthylene; Activated alkenes; Proton sponge; Halogenation; N-demethylation; Basicity; Molecular structure.
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2. Results and discussion

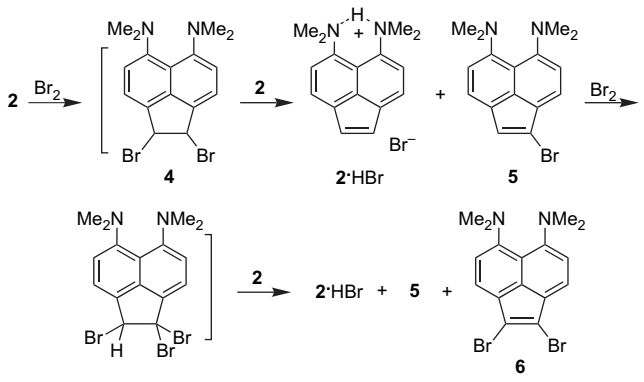
2.1. Bromination

It is known that parent acenaphthylene **3** readily adds 1 equiv of bromine to form 1,2-dibromide and derivatives of **3** with electron-releasing substituents in the naphthalene ring react even faster.[5–7] Though the reaction proceeds with low stereospecificity, it was noted that electron-withdrawing functions in the naphthalene moiety as well as polar solvents favour *trans*-addition.[7] From this, one can assume that reactivity of acenaphthylene sponge **2** toward Br_2 should be rather high. This is indeed the case but the results of bromination turned out to be quite specific.

It came to light that, instead of the expected dibromide **4**, proton sponge **2** yields only unsaturated monobromide **5** and dibromide **6** along with noticeable amounts of regenerated starting material (Scheme 1; Table 1).

Evidently, monobromide **5** is formed as a consequence of dehydrobromination of the initial addition product **4** by means of the starting compound **2** or **4** (cf. data on dehydrohalogenation of 1,2-dihalogenoacenaphthenes by alkali metal alcoholates or pyridine[8,9]). Repeated addition of Br_2 to **5** followed by dehydrobromination results in dibromide **6**.

As seen in Table 1, dibromide **6** predominates in polar protic media (AcOH), which promotes HBr loss. In contrast, monobromide **5** is accumulated in nonpolar solvent (CCl_4 or benzene), presumably because of the heterogeneous conditions.

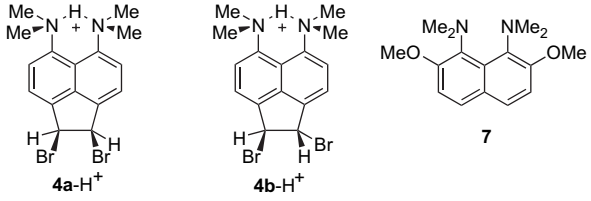


Scheme 1.

Table 1. Interaction of acenaphthylene **2** with molecular bromine

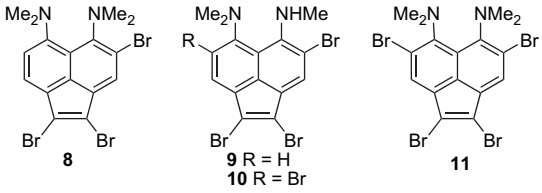
Br_2 (equiv)	T (°C)	Solvent	Reaction time (h)	Mode of addition	Isolated yields (%)			
					2	**5**	**6**	Tarring
0.5	22	CCl_4	1	$Br_2 \rightarrow$ **2**	55	29	4	12
1	22	CCl_4	1	$Br_2 \rightarrow$ **2**	31	37	16	16
1	22	CCl_4	1	**2** $\rightarrow Br_2$	40	30	20	10
1	0	C_6H_6	0.3	$Br_2 \rightarrow$ **2**	30	38	17	15
1	22	AcOH	1	$Br_2 \rightarrow$ **2**	30	20	40	10

To avoid the dehydrobromination reaction, we used the protonated form of compound **2** as starting material. As expected, action of 1 equiv of Br_2 on perchlorate **2**·$HClO_4$ in MeCN after work-up yielded monobromide **5** nearly in quantitative yield. Obviously, the primary addition product in this case is the salt **4**·$HClO_4$, which can be isolated after careful evaporation of acetonitrile. The ^{1}H NMR spectrum of **4**·$HClO_4$ is generally typical for symmetrical 4,5-disubstituted proton sponges and contains two doublets for the aromatic protons at δ 7.85 and 8.00 ppm along with two-proton singlet for the CH(Br)–CH(Br) bridge at 6.16 ppm. At the same time, at δ 3.13 and 3.15 ppm two doublets of equal intensity with $J_{NMe,NH}$=2.6 Hz are observed, indicating magnetic non-equivalence of two pairs of *N*-methyl groups. Clearly, in cations either *cis*-**4a** or *trans*-dibromide **4b**, two CH_3 groups are opposite to the bromine atoms, while the other two are closer to the bridge CH-protons. Unfortunately, these data cannot be assigned to certain isomers.



We further attempted to record the spectrum of the free base **4** immediately in the NMR ampoule after addition of strong base **7**[10] (1 equiv) to a solution of salt **4**·$HClO_4$ (1 equiv) in CD_3CN. However, as a result of very fast dehydrobromination, the final solution contained nothing but cations **5**-H^+ and **7**-H^+. The mechanism of this transformation deserves special investigation since the process may theoretically begin either with elimination of the NH-proton from cation **4**-H^+ followed by dehydrobromination of dibromide **4** (Scheme 2) or, alternatively, with E2-elimination inside the cation **4**-H^+ mediated by the base **7**.[10]

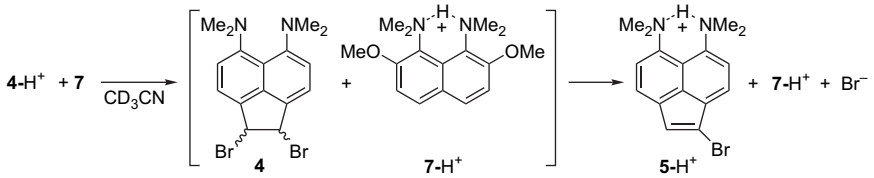
It is known that the proton sponge **1** is brominated selectively by NBS at positions 2 and 7.[11] We found that, unlike **1**, the acenaphthylene **2** under treatment with NBS in chloroform gives a complex mixture of inseparable products. On going from $CHCl_3$ to DMF, the process becomes more controllable and, apart from bromides **5** and **6**, allows the preparation of tri- and tetrabromo derivatives **8**–**10**. Some results of these experiments are collected in Table 2.



As can be seen (Table 2), the five-membered cycle is brominated first and the introduction of the third bromine atom into the naphthalene ring is accomplished by N-demethylation. In parallel with the bromination of acenaphthene, which proceeds in the NBS/DMF system at position 5 (in $CHCl_3$ or CCl_4, only the bridge protons are substituted[12]), we believe that the bromination of **2** under these conditions is realized via an electrophilic substitution pathway. The mechanism for the N-demethylation has been considered previously.[13] Lowering the temperature to −57 °C has practically no effect on the yields (see Table 2). All reactions

Table 2. Interaction of acenaphthylene **2** with NBS in DMF

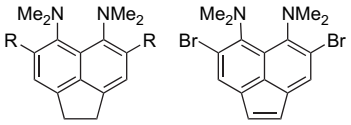
NBS (equiv)	Isolated products (%)					
	T (°C)	**5**	**6**	**8**	**9**	**10**
1	−15	10	9	—	—	—
2	−15	—	12	—	—	—
3	−15	—	4	5	4	—
4	−15	—	—	—	22	—
4	−57	—	—	—	24	—
5	−15	—	—	—	10	10
6	−15	—	—	—	8	13
10	−15	—	—	—	—	1



Scheme 2.

with NBS are characterized by strong tarring, and the compounds obtained are rather labile and prone to decompose when subjected to chromatography. Previously, we have managed to crystallize tribromide **9**, X-ray studies of which proved the functional group arrangement and revealed a very weak intramolecular hydrogen bond (IHB) of the NHN type.[14,15]

Prolonged heating of *N*-trimethyl substituted bromides **9** and **10** with excess of iodomethane followed by treatment with sodium carbonate leads to tetramethyl derivatives **8** and **11** in good yields.



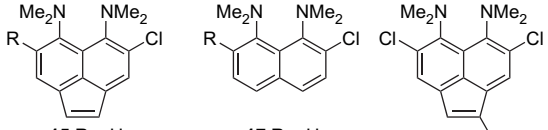
12 R = H
13 R = Br
14

Unlike acenaphthylene **2**, acenaphthene proton sponge **12**[3] under the action of NBS in $CHCl_3$ (even at low temperature) is almost completely turned into tar, which makes impossible the direct synthesis of *ortho*-bromides **13** and **14**. However, in DMF the tarring is hampered and apart from unreacted acenaphthene **12** (64%), the mono-**5** (14%) and dibromoacenaphthylenes **6** (22%) are formed with 2 equiv of NBS at −15 °C as judged by NMR spectroscopic analysis.

Interestingly, bromination of an equimolar mixture of acenaphthylenes **2** and **3** with 1 equiv of bromine in CCl_4 at room temperature gives no chance for the parent acenaphthylene **3**, which remains practically intact and the NMR spectroscopy (in DMSO-d_6) indicates that **2** turns into a mixture of **2** and **5** as hydrobromides.

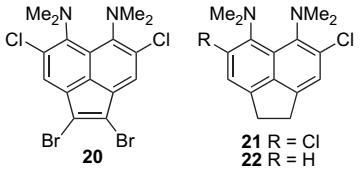
2.2. Chlorination

We have investigated the interaction of acenaphthylene **2** with either *N*-chlorosuccinimide (NCS) or 1-chlorobenzotriazole (CBT). The latter was used earlier for selective *ortho*-chlorination of compound **1**.[16] In contrast to **1**, acenaphthylene **2** reacts with CBT in chloroform giving complex mixture of products. However, in the case of NCS ($CHCl_3$ or DMF, −15 °C), depending on the amount of chlorinating agent (1 or 2 equiv), it is possible to prepare both mono-**15** and dichloride **16**. By analogy, proton sponge **1** reacts with NCS to form mono-**17** and dichlorides **18**. Using for the chlorination molecular chlorine in $CHCl_3$ at 20 °C or −15 °C resulted only in tarrification while on going from chloroform to acetic acid enabled us to isolate trichloride **19** as a single product (5–16% depending on the amount of Cl_2).



15 R = H
16 R = Cl
17 R = H
18 R = Cl
19

Similar to other 2,7-disubstituted derivatives of **1**,[10] dichloride **16** is very inert toward electrophiles that is caused by an almost perpendicular orientation of the NMe_2 group planes relatively the naphthalene π-system and, hence, low activation of the latter (see X-ray data below). For example, **16** does not undergo halogenation with NCS and NBS in chloroform at wide temperature conditions whereas sterically less hindered dibromide **6** reacts with 2 equiv of NCS in $CHCl_3$ to form mixed tetrahalide **20** in 89% yield.



20
21 R = Cl
22 R = H

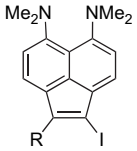
The only products, though in low yield (3–6%), that could be isolated after interaction of acenaphthene **12** with 2 equiv of NCS in $CHCl_3$ turned out to be chloroacenaphthylenes **15** and **16**.

Catalytic hydrogenation (Pd/C, H_2) of dichloride **16** in ethanol gave in near quantitative yield acenaphthene **21** with both the chlorine atoms intact. At the same time, monochloride **15**, taken as free base or perchlorate, readily undergoes protodechlorination (in MeOH, EtOH, EtOAc or THF), giving as a sole product acenaphthene **12**, but not the compound **22**. The reason for the lability of C–Cl bond is not clear in this case.

In contrast to the behaviour of **16**, catalytic hydrogenation of dibromide **6** in the presence of sodium carbonate quantitatively leads to acenaphthene **12**, and the reduction of polyhalide **20** ends up with dichloride **21** in high yield. Therefore, taking into account the possibility of easy oxidation of acenaphthene **12** back into acenaphthylene **2**,[3] the bromine atoms at position(s) 1(2) of **6**, **20** can be selectively removed.

2.3. Iodination

We have found that action of 2 equiv of *N*-iodosuccinimide (NIS) on acenaphthylene **2** even at low temperature ends up with strong tarring along with small fractions (4–8% depending on the solvent) of diiodide **23**. This can be isolated as a labile (especially on sorbents) orange crystalline compound.



23 R = I
24 R = H

Attempted synthesis of monoiodide **24** with 1 equiv of NIS in $CHCl_3$ failed; the only products that could be detected were diiodide **23** (2%) and the starting compound **2** (15%). Also, it was not possible to perform polyiodination of diamine **2** using 3 equiv of NIS in chloroform. However, employing molecular iodine as halogenating agent in AcOH allowed us to prepare iodides **23** and **24** in reasonable yield (Table 3).[17]

Table 3. Iodination of acenaphthylene **2** in different conditions

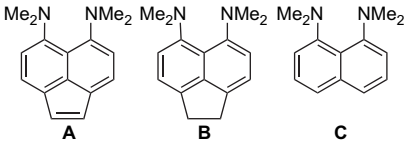
Reagent	Solvent	Equiv	T (°C)	Isolated products (%)	
				23	**24**
NIS	$CHCl_3$	1	−15	2	Traces
		2	−15	4	—
	THF	2	−15	6	—
	DMF	2	−15	8	—
I_2	AcOH	1	20	36	15
		2	20	40	—

As can be seen, acenaphthylene **2** reacts with iodinating agents both via electrophilic substitution and through electrophilic addition–elimination. The very fact of substitution in the five-membered core of acenaphthylene is of principal importance since only single cases of such transformations are known in the literature. Among them are radical nitration of acenaphthylene with dinitrogen tetroxide, leading to 1-nitro- and 1,2-dinitroacenaphthylenes in moderate yield,[18] and electrophilic substitution of trimethylsilyl groups in 1(2)-(bis)trimethylsilyl-acenaphthylenes.[19] The latter approach, in particular, gives 1-iodo- and 1,2-diiodoacenaphthylenes in good yield, although the trimethylsilyl-acenaphthylenes can be prepared from acenaphthylene in at least two steps.[20] The vast majority of other methods to synthesize 1(2)-(di)substituted acenaphthylenes in either case is based on addition–elimination or addition–oxidation sequence (see e.g., preparation of 1-fluoro-[21] and 1-methylthioacenaphthylenes[22]).

2.4. Basicity

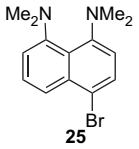
By the competitive transprotonation technique using ^1H NMR spectroscopy,[10] we have measured pK_a values of some synthesized halides and model bases (**1**, **2**, **12**, **18**, **25**) in DMSO. Evidently, the results collected in Table 4 provide not as much information as expected due to the absence of compounds with Cl and Br substituents at the same positions. Even so, it is noticeable that the Br atoms at positions 1 and 2 of the acenaphthylene system (compounds **5** and **6**, cf. also **1** and **25**) lower the basicity to a marked degree, and for the second substituent it is less expressed. On the other hand, the influence of Cl atoms at positions 4 and 7 is much less clear (compounds **15** and **16**). If the first substituent increases the basicity by 0.7 pK_a, the second one lowers it, although the overall basicity is slightly higher than that of unsubstituted **2**. The basicity of tetrahalide **20** (pK_a=3.0) seems to reflect superposition of the above tendencies and is similar to pyridine (pK_a=3.4, DMSO[26]). Interestingly, the influence of chlorine atoms placed in *ortho*-positions to the NMe_2 groups in naphthalene and acenaphthene systems is strictly opposite and decreases the basicity correspondingly by 0.7 and 1.0 pK_a (Table 4). The reason for these differences (repeatedly checked by us) is still unclear.

Table 4. Basicity constants, pK_a, of some synthesized and model compounds (DMSO, 22 °C)



Compound	Structure type	Substituents	pK_a[a]	Refs.
2	**A**	—	4.2	[b,c]
5	**A**	1-Br	2.4	[b]
6	**A**	1,2-Br_2	2.1	[b]
15	**A**	4-Cl	4.9	[b]
16	**A**	4,7-Cl_2	4.4	[b]
20	**A**	1,2-Br_2-4,7-Cl_2	3.0	[b]
12	**B**	—	7.4	[b,d]
21	**B**	4,7-Cl_2	6.4	[b]
1	**C**	—	7.5	23
25	**C**	4-Br	6.5	24
18	**C**	2,7-Cl_2	6.8	25

[a] Accuracy is ±0.05 pK_a.
[b] This work.
[c] This value was corrected in this work; previously reported value is 5.7, Ref. 3.
[d] Corrected in this work; 7.7 in Ref. 3.



25

2.5. General remarks on halogenation of 6

As in the case of other aromatic compounds with the double bond C=C in the side chain, acenaphthylene **2** reacts with molecular bromine, iodine and in known degrees with chlorine, forming addition products to the C(1)=C(2) bond. The cause of this is obvious: substitution in the naphthalene ring is energetically less favourable due to violation of the aromaticity in the intermediate σ-complex. Calculated heats of formation for model protic complexes illustrate this statement (Fig. 1). However, when acenaphthylene **2** is treated by less polarizable and more hard electrophiles such as *N*-halosuccinimides, the factors connected with steric influence and charge control seem to prevail. As shown in Figure 1, maximal negative charge in molecule **2** is localized at the C(4) and C(7) atoms. With this in mind, it is clear that the relatively small chlorine atom enters these sterically hindered positions much readily than more voluminous bromine and iodine do.

2.6. Molecular structure

Preceding X-ray studies of 2,7-disubstituted proton sponges, including dichloride **18**, have revealed that the buttressing effect of *ortho*-substituents causes a decrease in the N···N distance, flattening of the NMe_2 groups and rotating them strongly out of the naphthalene ring plane. To obtain information on how the C(1)=C(2) bridge in the acenaphthylene proton sponge influences the buttressing effect of the *ortho*-chlorine atoms, we have grown crystals of dichloride **16** and its perchlorate **16**·$HClO_4$ suitable for X-ray diffraction analysis. The results, presented in Fig. 2 and in Table 5, clearly demonstrate that in acenaphthylene proton sponge series, the buttressing effect is much more pronounced than in their naphthalene counterparts. Thus, the nitrogen pyramids in **16**, if compared with other proton sponge bases, are planarized to the largest extent (ΣN=355.0°). Furthermore, if at transition from compound **2** to **16** the N···N distance is decreased by 0.078 Å, in the pair of compounds **1**

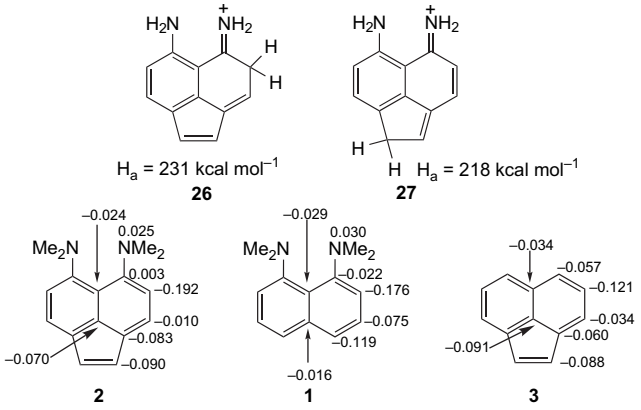


Figure 1. Heats of formation for proton σ-complexes **26** and **27** and distribution of (σ+π)-electron charges at the ring atoms of compounds **2**, **1** and **3** (PM3 method).

and **18** the same difference is equal only to 0.024 Å. Thus, the *ortho*-chlorine atoms make molecule **16** more rigid and flat if compared with **2** (cf. Δ*N* indices, Table 5). The reason for all this is obvious: in the parent proton sponge **1** the NMe_2 groups are already close to each other and only restricted possibilities for their additional approach exist. In contrast, in the acenaphthylene series owing to a tightening effect of the C(1)═C(2) bridge the amino groups are markedly separated and this provides more freedom for geometry changes. The same explanation can be applied to regularities of changing the N···N distance in the protonated forms of proton sponges. Thus, shortening of the N···N distance (given in brackets) for the following base-cation pairs **2**→**2**·H^+ (0.284 Å), **16**→**16**·H^+ (0.279), **1**→**1**·H^+ (0.238),[27] **18**→**18**·H^+ (0.207) moves in accord with the N···N distance in the corresponding bases: **2** (2.955 Å), **16** (2.877), **1** (2.792) and **18** (2.768).

On going from base **16** to perchlorate **16**·$HClO_4$, the compound demonstrates an especially strong contraction (about 10%) of the N···N distance on protonation. This shortening, as it is evident for significant molecular relaxation, along with dimethylamino groups already preorganized for proton abstraction, could be ascribed also for the high basicity of **16**, which is larger than that of **2**. The IHB in cation **16**·H^+ is asymmetric with two unequal asymmetric positions for the bridged proton (disordered H-bonding), though

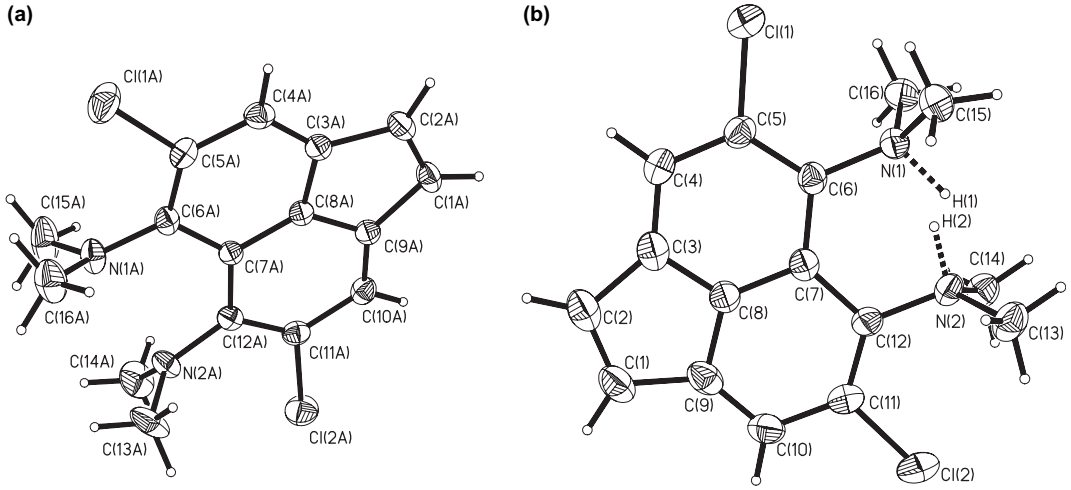


Figure 2. General view and atom numbering scheme for one of the two independent molecules **16** (a) and one independent cation of salt **16**·$HClO_4$ (b); perchlorate-anion is not shown. The ellipsoids for thermal motion are drawn at 30% probability level.

Table 5. Selected structural parametres for investigated and model compounds (lengths in Å, angles in deg)

Compound[a]	**2**	**2**·HBr	**16**[b]	**16**·$HClO_4$	**18**	**18**·HBr
N···N	2.955	2.671	2.877	2.598	2.768	2.561
N–H	—	0.98	—	0.90/0.90[c]	—	1.29
H···N	—	1.75	—	1.82/1.71[c]	—	1.29
∠NHN	—	156	—	144/168[c]	—	165
∠NMe_2-ring[d]	36	84	67	88	71	89
C_{ar}–N[d]	1.395	1.460	1.397	1.452	1.404	1.458
Σ*N*[d,e]	348.3	336.9	355.0	343.2	353.0	342.7
∠C(6)–C(7)–C(12)	129.8	129.1	129.7	127.5	124.5	124.9
C(1)═C(2)	1.339	1.332	1.338	1.361	—	—
Δ*N*[d,f]	0.360	0.041	0.066	0.058	0.051	0.022

[a] Data for compounds **2**, **2**·HBr, **18** and **18**·HBr were accepted from Refs. 27 and 28.
[b] Average data for two independent molecules.
[c] Values for each unequal position of the chelated proton.
[d] Average values.
[e] Sum of CNC angles at the N atoms.
[f] Deviations of N atoms from the mean ring plane.

of 50% occupancy. In summary, the steric influence of the *ortho*-chlorine substituents is opposite to the tightening effect of the CH═CH bridge, which favours weakening of IHB in the corresponding cation.[3,27] Such contradictory tendencies in cation **16**·H^+ result in small but distinct stretching of the C(1)═C(2) bond, which can be considered as a *reversed tightening effect*.

3. Conclusions

It has been shown that the halogenation of the acenaphthylene proton sponge **2** proceeds in a more complex and ambiguous way compared to its naphthalene counterpart **1**. The reaction of **2** with bromine or iodine gives the C(1)═C(2) adduct, which as a result of high basicity of the substrate rapidly undergo E2-elimination, leading to 1-halogeno or 1,2-dihalogeno derivatives. The interaction of **2** with NBS, unlike proton sponge **1**, also proceeds preferentially at the C(1)═C(2) bond. In contrast, the chlorination of **2** with NCS is directed at the *ortho*-positions to the NMe_2 groups, giving 4-chloro- or 4,7-dichlorosubstituted derivatives in excellent yields. In summary, we have at our disposal both 1(2)- and 4(7)-halogeno derivatives of compound **2**, which can be further used in cross-coupling reactions and organometallic syntheses as well as building blocks for supramolecular structures. The existing possibility of fast and reverse change of their high basicity at once by 2–3 orders of magnitude gives them special attractiveness.

4. Experimental

4.1. General

The NMR spectra were recorded on Varian Unity-300 (300 MHz for ^{1}H, 75 MHz for ^{13}C) and Brucker DPX-250 (250 MHz for ^{1}H) instruments with $SiMe_4$ as the internal standard. The UV–vis spectra were registered on a Specord M-40 spectrophotometer and the IR spectra were measured on Specord IR-75 spectrometer. Chromatography was carried out on Al_2O_3 with different Brockmann activities and on silica gel L 40/100 μm (Chemapol). The progress of reactions and the purity of products were monitored by TLC on Al_2O_3 and Silufol plates; development with iodine vapour. The melting points were measured in sealed capillaries and are uncorrected. The solvents were purified and dried by standard methods. Commercial NBS (99%, Acros Organics), NCS (99%, Lancaster) and Pd/C (5%, Lancaster) were used. Acenaphthylene **2** was prepared as described earlier,[3] and NIS was synthesized from NBS.[29]

Red plates of dichloride **16** suitable for X-ray diffraction analysis were obtained by isothermic evaporation of its saturated solution in MeOH/$CHCl_3$ (2:1, v/v) at 20 °C. Orange prisms of perchlorate **16**·$HClO_4$ were prepared by the same way using saturated solution of the salt in MeOH. The X-ray diffraction studies were performed at room temperature. The atomic coordinates, bond lengths, bond angles and torsion angles for the structures of **16** and **16**·$HClO_4$ were deposited with the Cambridge Structural Database (CCDC nos. 611178 and 611179, respectively).

4.2. Bromination of 5,6-bis(dimethylamino)acenaphthylene (2) in acetic acid

A solution of Br_2 (0.052 mL, 1 mmol) in AcOH (15 mL) was added for 15 min with stirring to a solution of compound **2** (0.24 g, 1 mmol) in AcOH (15 mL). Then the resulting solution was stirred for 30 min more and the main part of AcOH was distilled off. The residue was diluted with H_2O (20 mL) and neutralized with concd NH_4OH (10 mL). The products were extracted with CCl_4, the extract was concentrated to a minimum volume and chromatographed on silica gel with $CHCl_3$ elution. The first yellow-orange zone with R_f 0.63 gave dark red-brown crystals of 1,2-dibromo-5,6-bis-(dimethylamino)acenaphthylene (**6**), 160 mg (40%), mp 140–141 °C (from MeOH). Found: C, 48.30; H, 4.00; Br, 39.95%. Calcd for $C_{16}H_{16}Br_2N_2$: C, 48.52; H, 4.07; Br, 40.34%. ^{1}H NMR ($CDCl_3$) δ ppm: 2.91 (12H, s, NMe_2), 6.86 (2H, d, *J* 7.8 Hz, H-4, H-7), 7.49 (2H, d, *J* 7.8 Hz, H-3, H-8). ^{13}C NMR ($CDCl_3$, ^1J/Hz) δ ppm: 44.2 (135.8, NMe), 113.3 (157.4, C-4, C-7), 115.5 (C-1, C-2), 116.4 (C-2a, C-8a), 124.8 (161.0, C-3, C-8), 129.7 (C-5a), 130.2 (C-8b), 153.8 (C-5, C-6). UV–vis (MeOH) λ_{max} nm (log ε): 248 (4.17), 275 (4.09), 315 (sh., 3.41), 450 (4.16), end absorption up to 560 nm. Perchlorate **6**·$HClO_4$: brown-orange crystals with mp 150–152 °C (decomp.). ^{1}H NMR (CD_3CN) δ ppm: 3.16 (12H, d, *J* 2.7 Hz, NMe_2), 7.87 (2H, d, *J* 7.7 Hz, H-3, H-8), 7.95 (2H, d, *J* 7.7 Hz, H-4, H-7), 15.98 (1H, br s, NH). ^{1}H NMR (DMSO-d_6) δ ppm: 3.17 (12H, br s, NMe_2), 7.95 (2H, d, *J* 7.5 Hz, H-3, H-8), 8.15 (2H, d, *J* 7.5 Hz, H-4, H-7), 15.52 (1H, br s, NH).

The second yellow zone gave 1-bromo-5,6-bis(dimethylamino)acenaphthylene (**5**) as dark-yellow oil, 60 mg (20%), R_f 0.37. Found: C, 60.30; H, 5.39; Br, 24.92%. Calcd for $C_{16}H_{17}BrN_2$: C, 60.58; H, 5.40; Br, 25.19%. ^{1}H NMR ($CDCl_3$) δ ppm: 2.89 (6H, s, 5-NMe_2), 2.92 (6H, s, 6-NMe_2), 6.82 (1H, d, *J* 7.7 Hz, H-4), 6.88 (1H, s, H-2), 6.92 (1H, d, *J* 7.8 Hz, H-7), 7.46 (1H, d, *J* 7.7 Hz, H-3), 7.53 (1H, d, *J* 7.8 Hz, H-8). UV–vis (MeOH) λ_{max} nm (log ε): 247 (4.16), 270 (4.12), 312 (sh., 3.46), 428 (4.09), end absorption up to 560 nm. Perchlorate **5**·$HClO_4$: brown-yellow crystals with mp 154–156 °C. ^{1}H NMR (CD_3CN) δ ppm: 3.15 (6H, d, *J* 2.5 Hz, 6-NMe_2), 3.18 (6H, d, *J* 2.9 Hz, 5-NMe_2), 7.34 (1H, s, H-2), 7.87 (2H, s, H-7, H-8), 7.87 (1H, d, *J* 7.6 Hz, H-3), 7.96 (1H, d, *J* 7.6 Hz, H-4), 16.07 (1H, br s, NH). ^{1}H NMR (DMSO-d_6) δ ppm: 3.15 (6H, s, 6-NMe_2), 3.19 (6H, d, *J* 2.0 Hz, 5-NMe_2), 7.47 (1H, s, H-2), 7.90 (1H, d, *J* 7.6 Hz, H-3), 7.95 (1H, d, *J* 7.5 Hz, H-8), 8.08 (1H, d, *J* 7.5 Hz, H-7), 8.13 (1H, d, *J* 7.6 Hz, H-4), 15.62 (1H, br s, NH).

4.3. Bromination of perchlorate 2·$HClO_4$ in acetonitrile

A solution of Br_2 (0.103 mL, 2 mmol) in MeCN (5 mL) was added dropwise with vigorous stirring for 15 min to a solution of perchlorate[3] **2**·$HClO_4$ (0.68 g, 2 mmol) in MeCN (5 mL). The reaction mixture was then stirred for 30 min at 20 °C and treated with 10% aqueous solution of sodium carbonate decahydrate (15 mL). The organic layer was separated and the aqueous phase was extracted with chloroform (3×3 mL). The organic phases were then combined and the solvents were removed to give 0.62 g (98%) of compound **5**

with the properties as has the sample prepared above. ^{1}H NMR (CD_3CN) δ ppm: 3.13 (6H, d, J 2.6 Hz, NMe_2), 3.15 (6H, d, J 2.6 Hz, NMe_2), 6.16 (2H, s, H-1, H-2), 7.85 (2H, d, J 7.8 Hz, H-3, H-8), 8.00 (2H, d, J 7.8 Hz, H-4, H-7), 16.50 (1H, br s, NH).

4.4. Bromination of 5,6-bis(dimethylamino)acenaphthylene (2) in DMF

Method A: a solution of NBS (0.53 g, 3 mmol) in DMF (25 mL) was added dropwise with vigorous stirring for 15 min and at −15 °C to a solution of **2** (0.72 g, 3 mmol) in DMF (25 mL). The resulting mixture was diluted with equal volume of water and the reaction products were taken up into hexanes (3×15 mL). The extract was evaporated to dryness at room temperature and the residue was chromatographed on silica gel with $CHCl_3$ elution. This gave 0.11 g (9%) of dibromide **6** and 0.10 g (10%) of monobromide **5** with the properties identical to those of authentic samples.

Method B: a solution of NBS (1.78 g, 20 mmol) in DMF (5 mL) was added with vigorous stirring for 30 min and at −15 °C to a solution of diamine **2** (0.96 g, 4 mmol) in DMF (10 mL). Then the cooling was ceased, the mixture was diluted with water (10 mL), containing several drops of aqueous ammonia, and then extracted with hexanes (4×10 mL). The solvent was removed and the residue was chromatographed (silica gel, CCl_4). The first bright-red fraction with R_f 0.78 gave 0.23 g (10%) of 1,2,4,7-tetrabromo-5-dimethylamino-6-methylamino-acenaphthylene (**10**) as red crystals with mp 152–154 °C (from EtOH/H_2O 1:1, v/v). Found: C, 33.39; H, 2.23; Br, 59.00%. Calcd for $C_{15}H_{12}Br_4N_2$: C, 33.37; H, 2.24; Br, 59.20%. ^{1}H NMR ($CDCl_3$) δ ppm: 3.02 (6H, s, 5-NMe_2), 3.30 (3H, s, 6-NMe), 7.63 (1H, s, H-8), 7.69 (1H, s, H-3), 9.92 (1H, br s, NH). IR ($CHCl_3$) ν cm^{-1}: 3185 (N–H), 3045, 2977, 2965, 2875, 2855 (C–H), 1640, 1602, 1590 (C=C+ring). The second orange fraction with R_f 0.60 gave 0.18 g (10%) of 1,2,4-tribromo-6-dimethylamino-5-methylamino-acenaphthylene (**9**), the properties of which are the same as those of the material prepared earlier.[14]

4.5. 1,2,4-Tribromo- (8) and 1,2,4,7-tetrabromo-5,6-bis(dimethylamino)acenaphthylenes (11)

A solution consisting of tribromide **9** (0.046 g, 0.1 mmol) and MeI (5 mL) was refluxed for 150 h. Then iodomethane was deleted on the water bath, the residue was washed with Et_2O and dissolved in MeCN (5 mL). The resulting solution was treated with 10% aqueous Na_2CO_3 (10 mL) and the product **8** thus formed was extracted with hexanes (3×5 mL). This gave 0.044 g (93%) of red crystalline compound with mp 155–156 °C (from EtOH/H_2O 1:1, v/v). Found: C, 40.03; H, 3.20; Br, 50.61%. Calcd for $C_{16}H_{15}Br_3N_2$: C, 40.43; H, 3.16; Br, 50.53%. ^{1}H NMR ($CDCl_3$) δ ppm: 2.88 (6H, s, 6-NMe_2), 3.06 (6H, s, 5-NMe_2), 6.90 (1H, d, J 7.9 Hz, H-7), 7.44 (1H, d, J 7.9 Hz, H-8), 7.73 (1H, s, H-3). Perchlorate **8**·$HClO_4$: yellow crystals with mp 300–302 °C (decomp. from EtOH). Found: C, 33.45; H, 2.83; Cl+Br, 47.77%. Calcd for $C_{16}H_{16}Br_3ClN_2O_4$: C, 33.40; H, 2.80; Cl+Br, 47.81%. ^{1}H NMR (CD_3CN) δ ppm: 2.26 (6H, d, J 1.1 Hz, 5-NMe_2), 3.34 (6H, d, J 4.2 Hz, 6-NMe_2), 7.91 (1H, d, J 7.7 Hz, H-7), 8.00 (1H, s, H-3), 8.02 (1H, d, J 7.7 Hz, H-8), 16.59 (1H, br s, NH).

Tetrabromide **11** was synthesized analogously and 0.044 g of compound **10** gave 0.037 g (82%) of the product as red crystalline substance with mp 141–142 °C (from EtOH/H_2O 2:1, v/v). Found: C, 34.70; H, 2.56; Br, 57.65%. Calcd for $C_{16}H_{14}Br_4N_2$: C, 34.69; H, 2.55; Br, 57.70%. ^{1}H NMR ($CDCl_3$) δ ppm: 3.02 (12H, s, NMe_2), 7.67 (2H, s, H-3, H-8). Perchlorate **11**·$HClO_4$: yellow crystals, darkened above 260 °C, melting with decomposition at 290–292 °C (from EtOH). Found: C, 29.45; H, 2.30; Cl+Br, 54.25%. Calcd for $C_{16}H_{15}Br_4ClN_2O_4$: C, 29.37; H, 2.31; Cl+Br, 54.26%. ^{1}H NMR (CD_3CN) δ ppm: 3.43 (12H, d, J 2.6 Hz, NMe_2), 8.04 (2H, s, H-3, H-8), 18.84 (1H, br s, NH).

4.6. Bromination of 5,6-bis(dimethylamino)acenaphthene (12) in DMF

A solution of NBS (0.36 g, 2 mmol) in DMF (25 mL) was added dropwise with vigorous stirring for 30 min and at −15 °C to a solution of **12**[3] (0.24 g, 1 mmol) in DMF (10 mL). The resulting mixture was diluted with equal volume of water containing several drops of ammonia and the reaction products were taken up into hexanes (3×10 mL). The solvent was removed and the residue was analyzed by ^{1}H NMR spectroscopy showing the presence of dibromide **6** (22%), monobromide **5** (14%) and the unreacted starting substrate **12** (up to 64%).

4.7. Hydrogenation of 1,2-dibromo-5,6-bis(dimethylamino)acenaphthylene (6)

A suspension consisting of compound **6** (0.39 g, 0.1 mmol), 5% Pd/C (0.02 g), Na_2CO_3·$10H_2O$ (0.50 g) and MeOH (30 mL) was hydrogenated at room temperature and atmospheric pressure for 10 min. Then the catalyst was filtered off, the solution was diluted with the same amount of water and the acenaphthene **12** was extracted with hexanes (3×15 mL). The solvent was removed to give 0.23 g (97%) of compound **12** with the properties as has the sample described previously.[3]

4.8. 4-Chloro-5,6-bis(dimethylamino)acenaphthylene (15)

A solution of NCS (0.53 g, 0.4 mmol) in $CHCl_3$ (50 mL) was added dropwise with intense stirring at −15 °C for 15 min to a solution of acenaphthylene **2** (0.96 g, 4 mmol) in $CHCl_3$ (50 mL). The reaction mass was then washed with water (100 mL), the organic phase was evaporated to dryness and the residue was chromatographed (Al_2O_3 III, *n*-hexane). The main red fraction with R_f 0.89 gave 0.88 g (80%) of compound **15** as red oil. Found: C, 60.98; H, 6.20; Cl, 13.12%. Calcd for $C_{16}H_{17}ClN_2$: C, 70.46; H, 6.24; Cl, 13.03%. ^{1}H NMR ($CDCl_3$) δ ppm: 2.89 (6H, s, 6-NMe_2), 3.06 (6H, s, 5-NMe_2), 6.79 (1H, d, J 5.0 Hz, H-1), 6.92 (2H, m, H-2, H-7), 7.43 (1H, d, J 7.3 Hz, H-8), 7.59 (1H, s, H-3). UV–vis (EtOH) λ_{max} nm (log ε): 245 (4.21), 264 (4.14), 310 (3.45), 402 (3.89), end absorption up to 550 nm. IR (liquid film) ν cm^{-1}: 3100, 3070, 2970, 2915, 2850, 2810, 2780 (C–H), 1600, 1580, 1500, 1450 (C=C+ring). Perchlorate **15**·$HClO_4$: yellow crystals with

mp 265–267 °C (from EtOH). Found: C, 51.45; H, 4.80; Cl, 19.13%. Calcd for $C_{16}H_{18}Cl_2N_2O_4$: C, 51.47; H, 4.83; Cl, 9.03%. ^{1}H NMR (DMSO-d_6) δ ppm: 3.12 (6H, s, 5-NMe_2), 3.36 (6H, d, J 4.3 Hz, 6-NMe_2), 7.16 (1H, d, J 5.4 Hz, H-2), 7.23 (1H, d, J 5.4 Hz, H-1), 7.93 (2H, m, H-3, H-8), 8.16 (1H, d, J 7.7 Hz, H-7), 15.77 (1H, br s, NH).

4.9. 4,7-Dichloro-5,6-bis(dimethylamino)acenaphthylene (16)

Compound **16** was synthesized by analogy using 0.96 g (4 mmol) of **2** and 1.07 g (8 mmol) of NCS. The bright-red fraction with R_f 0.95 gave 1.04 g (85%) of dichloride **16** as red crystals with mp 106–108 °C (from MeOH). Found: C, 62.51; H, 4.80; Cl, 23.19%. Calcd for $C_{16}H_{16}Cl_2N_2$: C, 62.54; H, 5.21; Cl, 23.13%. ^{1}H NMR ($CDCl_3$) δ ppm: 3.01 (12H, s, NMe_2), 6.85 (2H, s, H-1, H-2), 7.50 (2H, s, H-3, H-8). ^{13}C NMR ($CDCl_3$, ^1J/Hz) δ ppm: 43.7 (134.9, NMe), 128.0 (165.8, C-3, C-8), 129.0 (C-2a, C-8a), 129.2 (C-5a), 129.3 (170.9, C-1, C-2), 135.1 (C-8b), 137.6 (C-4, C-7), 147.9 (C-5, C-6). UV–vis (EtOH) λ_{max} nm (log ε): 252 (4.34), 319 (3.55), 334 (3.58), 389 (3.75), 479 (sh., 3.21), end absorption up to 575 nm. Perchlorate **16**·$HClO_4$: yellow crystals, darkened above 234 °C, do not melt up to 300 °C (from EtOH). Found: C, 47.05; H, 4.13; Cl, 26.01%. Calcd for $C_{16}H_{17}Cl_3N_2O_4$: C, 47.12; H, 4.17; Cl, 26.13%. ^{1}H NMR (DMSO-d_6, 70 °C) δ ppm: 3.41 (12H, d, J 2.9 Hz, NMe_2), 7.26 (2H, s, H-1, H-2), 8.01 (2H, s, H-3, H-8), 18.14 (1H, br s, NH).

4.10. 1,2-Dibromo-4,7-dichloro-5,6-bis(dimethylamino)acenaphthylene (20)

A solution of NCS (0.053 g, 0.4 mmol) in $CHCl_3$ (5 mL) was added with stirring at −15 °C for 30 min to a solution of dibromide **6** (0.078 g, 0.2 mmol) in $CHCl_3$ (5 mL). Then the cooling was ceased and the reaction mass was further stirred for 2 h at room temperature. The resulting mixture was washed with the same amount of water, the solvent was removed and the residue was chromatographed (silica gel, chloroform) to give pure halogenide **20** (0.082 g, 89%) as red crystals with mp 132–133 °C (from EtOH). ^{1}H NMR ($CDCl_3$) δ ppm: 3.01 (12H, s, NMe_2), 7.48 (2H, s, H-3, H-8). Perchlorate **20**·$HClO_4$: yellow crystals with mp 305–306 °C (decomp. from EtOH). Found: C, 34.12; H, 2.60; Cl+Br, 47.15%. Calcd for $C_{16}H_{15}Br_2Cl_3N_2O_4$: C, 33.99; H, 2.67; Cl+Br, 47.07%. ^{1}H NMR (DMSO-d_6) δ ppm: 3.34 (12H, br s, NMe_2), 8.04 (2H, s, H-3, H-8), 18.22 (1H, br s, NH).

Hydrogenation of polyhalide **20** was performed by analogy with compound **6**. This gave compound **21** in near quantitative yield.

4.11. 4,7-Dichloro-5,6-bis(dimethylamino)acenaphthene (21)

A suspension consisting of compound **16** (0.31 g, 1 mmol), 5% Pd/C (0.15 g) and EtOH (20 mL) was hydrogenated at room temperature and atmospheric pressure for 30 min. After the catalyst was filtered off, the resulting solution was evaporated to dryness. Yield of acenaphthene **21** was 0.30 g (99%). Pink-beige crystals with mp 135–136 °C (from MeOH). Found: C, 62.15; H, 5.03; Cl, 22.91%. Calcd for $C_{16}H_{18}Cl_2N_2$: C, 62.14; H, 5.82; Cl, 22.98%. ^{1}H NMR ($CDCl_3$) δ ppm: 2.95 (12H, s, NMe_2), 3.26 (4H, s, H-1, H-2), 7.17 (2H, s, H-3, H-8). Perchlorate **21**·$HClO_4$: colourless crystals with mp 230–231 °C (decomp. from EtOH/H_2O 1:1, v/v). Found: C, 46.73; H, 4.22; Cl, 26.08%. Calcd for $C_{16}H_{19}Cl_3N_2O_4$: C, 47.14; H, 4.20; Cl, 26.09%. ^{1}H NMR (DMSO-d_6, 70 °C) δ ppm: 3.37 (12H, d, J 2.6 Hz, NMe_2), 3.44 (4H, s, H-1, H-2), 7.61 (2H, s, H-3, H-8), 18.14 (1H, br s, NH).

4.12. Chlorination of 5,6-bis(dimethylamino)acenaphthene (12) with NCS in chloroform

A solution of NCS (0.134 g, 1 mmol) in $CHCl_3$ (10 mL) was added with stirring at −15 °C for 15 min to a solution of compound **12**[3] (0.120 g, 0.5 mmol) in $CHCl_3$ (10 mL). Then the reaction mixture was washed with water (50 mL), containing several drops of aqueous ammonia, the organic phase was evaporated and the residue was chromatographed (Al_2O_3 III, n-hexane). The first bright-red zone with R_f 0.95 gave red crystals of dichloride **16** (9 mg, 6%) and the second orange zone with R_f 0.89 gave chloride **15** as red oil (4 mg, 3%). The spectral properties of these compounds are identical with those revealed by authentic samples.

4.13. 1,4,7-Trichloro-5,6-bis(dimethylamino)acenaphthylene (19)

A solution of chlorine (0.086 g, 2.4 mmol) in AcOH (5 mL) was added with stirring for 15 min to a solution of **2** (0.288 g, 1.2 mmol) in AcOH (5 mL). The resulting mixture was stirred for an additional hour, diluted with water (10 mL) and neutralized with concd NH_4OH. The reaction products were extracted with CCl_4 (3×5 mL), the solvent was removed and the residue was subjected to TLC (Al_2O_3, n-octane). The red zone with R_f 0.85 gave 0.066 g (16%) of trichloroacenaphthylene **19** as red crystals with mp 54–56 °C (from MeOH). Found: C, 56.20; H, 4.45; Cl, 31.02%. Calcd for $C_{16}H_{15}Cl_3N_2$: C, 56.25; H, 4.45; Cl, 31.13%. ^{1}H NMR ($CDCl_3$) δ ppm: 3.02 (6H, s, NMe_2), 3.04 (6H, s, NMe_2), 6.75 (1H, s, H-2), 7.43 (1H, s, H-3), 7.59 (1H, s, H-8).

4.14. Iodination of 5,6-bis(dimethylamino)acenaphthylene (2) in acetic acid

A solution of I_2 (0.51 mg, 2 mmol) in AcOH (15 mL) was added with stirring for 15 min to a solution of **2** (0.48 g, 2 mmol) in AcOH (15 mL). After that the solution was stirred for 30 min more and the major part of AcOH was distilled off. The residue was diluted with water (20 mL) and concd NH_4OH (10 mL). The products were extracted with CCl_4 (3×20 mL), the extract was evaporated to a minimal volume and chromatographed (silica gel, $CHCl_3$). The first yellow-orange zone with R_f 0.60 gave orange crystals of 5,6-bis(dimethylamino)-1,2-diiodoacenaphthylene (**23**), 0.035 g (36%), mp 95–97 °C (from MeOH). Found: C, 39.20; H, 3.20; I, 51.75%. Calcd for $C_{16}H_{16}I_2N_2$: C, 39.21; H, 3.29; I, 51.78%. ^{1}H NMR ($CDCl_3$) δ ppm: 2.92 (12H, s, NMe_2), 6.85 (2H, d, J 7.7 Hz, H-4,7), 7.39 (2H, d, J 7.7 Hz, H-3, H-8). The second yellow zone with R_f 0.32

allowed to collect 0.011 g (15%) of 5,6-bis(dimethylamino)-1-iodoacenaphthylene (**24**) as orange oil. Found: C, 52.76; H, 4.70; I, 34.76%. Calcd for $C_{16}H_{17}IN_2$: C, 52.76; H, 4.71; I, 34.84%. ^{1}H NMR ($CDCl_3$) δ ppm: 2.90 (6H, s, 6-NMe_2), 2.92 (6H, s, 5-NMe_2), 6.82 (1H, d, *J* 7.7 Hz, H-4), 6.93 (1H, d, *J* 7.3 Hz, H-7), 7.13 (1H, s, H-2), 7.38 (1H, d, *J* 7.7 Hz, H-3), 7.48 (1H, d, *J* 7.3 Hz, H-8).

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