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Organometallic Synthesis, Molecular Structure, and Coloration of 2,7-Disubstituted 1,8-Bis(dimethylamino)naphthalenes. How Significant Is the Influence of “Buttressing Effect” on Their Basicity?

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On treatment of 2,7-dilithio- (**6a**) and 2,7-bis(bromomagnesio)- (**6b**) naphthalenes with a number of electrophiles, new “proton sponge” derivatives **7a**−**e**,**g**, containing iodo, methylthio, trimethylsilyl, methyl, *n*-butyl, and ethoxycarbonyl groups in *ortho*-positions to dimethylamino groups, have been synthesized. The investigation of their molecular structure, spectral characteristics, and basicity reveals that the latter is mainly determined by two groups of factors: (1) the polar effect of *ortho*-substituents and (2) the so-called “buttressing effect” representing the complex combination of various sterical interactions of *ortho*-substituents with dimethylamino groups in corresponding bases and cations. A contradictory directionality of these interactions strongly reduces the importance of the buttressing effect in the case of compounds with bulky *ortho*-substituents, which is most clearly displayed in the absence of any relationship between the size of *ortho*-substituents and the basicity. On the contrary, for proton sponges having in *ortho*-positions the electron-donating groups with lesser steric demands, both the buttressing and the polar effects act in the same direction. This is the reason for the exceptionally high basicity of 2,7-dimethoxy- (**2**) and tetrakis(dimethylamino)- (**3a**) naphthalenes. It has been found that bis(trimethylsilyl)-bis(dimethylamino)naphthalene **7d** has an *in-out* configuration of the NMe_2 groups in the solid that is the first example of its kind in the series of naphthalene proton sponges. The origin of a yellow coloring of 2,7-disubstituted proton sponges is also discussed.

Introduction

One of the most intriguing phenomena in the chemistry of naphthalene “proton sponges” is a sharp increase of their basicity at introduction of alkoxy groups in positions 2 and 7 (*ortho*).[1] Thus, whereas the pK_a value of 1,8-bis(dimethylamino)naphthalene (**1**) is equal to 12.1 (H_2O, 25 °C), for its 2,7-dimethoxy derivative **2** it is enhanced by 4 powers of 10 (pK_a 16.1).[2,3] There have been offered several explanations of this observation. According to the first one,[3−5] *ortho*-substituents, as a result of the so-called “buttressing effect”, force NMe_2 groups to be closer to each other, which increases the nitrogen lone pairs repulsion and thus destabilizes the base. As a consequence, transition to the cation provides an additional profit in free energy. Another point of view is that the main destabilizing factor in base **2** is a purely spatial hindrance arising at contact of adjacent dimethylamino and methoxy groups and removing in the protonated form.[6] Howard, on the basis of detailed quantum-chemical calculations, has concluded that the sharp fluctuations in the basicity of proton sponges are mainly connected with the differences in the strength of intramolecular hydrogen bonds (IHBs) in their cations.[7,8] A completely different opinion on this account was recently put forward in Korzhenevskaya's theoretical research.[9] It has been stated that in all proton sponges, particularly in **2**, a noticeable planarization ($sp^3 \rightarrow sp^2$ rehybridization) of the nitrogen atoms takes place, ac-

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† Rostov State University.
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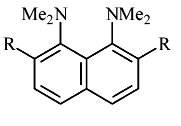
companied by a considerable twisting of the NMe_2 groups out of the ring plane. It leads to disturbance of p,π-conjugation and to an increase of p-character of the lone electron pair, both providing an essential growth in basicity.

It is noteworthy that all quoted authors assume a contribution of several factors to the basicity increase but only one factor is considered to be the most important. Attempts of a quantitative estimation of each of the named factors (excluding rehybridization) were made in refs 7 and 10.

Evidently, any of the above points means that as the volume of *ortho*-substituents is increased, the base destabilization and, hence, the basicity should be higher. Meanwhile, even a cursory inspection of 2,7-bis(dialkylamino)- (**3**),[11] 2,7-dichloro- (**4**), and 2,7-dibromo-1,8-bis(dimethylamino)- (**5**)[12] naphthalenes shows that though the buttressing effect is clearly displayed here, its value does not strongly depend on "bulkiness" of the *ortho*-substituents and most likely is determined by a combination of several factors. It is obvious that deeper insight into this problem was prevented until now by lack of a regular set of 2,7-disubstituted proton sponges in which the properties of buttressing *ortho*-functionalities would change in rather wide limits. In this connection the main goals of the present research were (1) development of a general and convenient method for preparation of *ortho*-disubstituted proton sponges and (2) investigation of their molecular structure, spectral characteristics, and basicity. We believed that realization of both of these goals would make a valuable contribution to the general understanding of the factors influencing strong basicity.



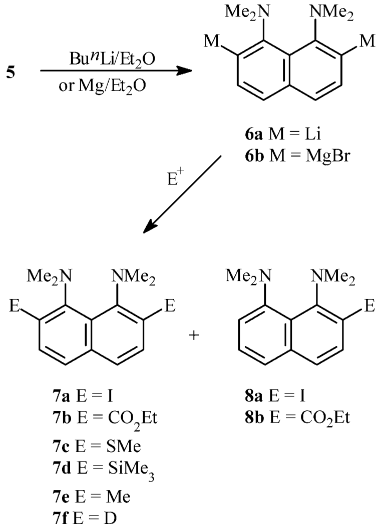
1 R = H
2 R = OMe
3 R = NMe_2 (**a**), pyrrolidino (**b**)
4 R = Cl
5 R = Br

Results and Discussion

Synthesis. In known synthetic procedures for compounds of type **2** and **3** the corresponding 2,7-dialkoxynaphthalene was used as a starting material, which was successively subjected to dinitration, reduction, and exhaustive methylation of *peri*-amino groups.[4] For the introduction of dimethylamino groups in 2- and 7-positions, 2,7-dimethoxy-1,8-dinitronaphthalene was treated with dimethylamine or pyrrolidine.[11] It is clear that only a limited number of *ortho*-disubstituted proton sponges can be obtained by such a way.

Some time ago two of us offered a method for selective *ortho*-dichlorination[13] and *ortho*-dibromination[14] of 1,8-bis(dimethylamino)naphthalene that has made dihalides **4** and **5** easily accessible. Therefore, it seemed promising to develop organometallic synthesis[15] of a wide range of 2,7-disubstituted proton sponges, first of all containing voluminous groups in *ortho*-positions (I, SMe, $SiMe_3$, etc.).

SCHEME 1



On action of 2 equiv of *n*-butyllithium on a cooled solution of dibromide **5** in dry ether, we received 2,7-dilithio derivative **6a** as a suspension. Grignard reagent **6b** was prepared by adding a solution of dibromide **5** in ether to an ethereal suspension of powdered magnesium, activated by 2−3 drops of *n*-butylbromide (Scheme 1). 2,7-Organometallic derivatives **6a** and **6b** thus obtained, owing to the increased basicity (because of a "vicinality" of four unshared lone pairs), could theoretically undergo partial protolysis by solvent to monometallic derivatives. To check this, we first quenched the reaction mixture containing compounds **6a** or **6b** with heavy water. Irrespective of the period when D_2O was added (after 0.5, 1, or 1.5 h), both compounds gave the same deuterated derivative **7f**, in which, according to NMR ^{1}H, ~90% of *ortho*-protons have been exchanged. It verified that if the protolysis really took place, its contribution is relatively small.

Dimetallic derivatives **6a,b** were treated further with 2 equiv of iodine, diethyl carbonate, dimethyl disulfide, iodomethane, or trimethylchlorosilane to produce compounds **7a−e** (Table 1, Scheme 1). Among the latter only 2,7-dimethyl derivative **7d** was earlier described as a red oil,[4] whereas in our hands it was prepared as yellow crystals with mp 51−53 °C. In two cases, namely, at action of iodine and diethyl carbonate, along with the main products **7a,b**, the monosubstituted compounds **8a,b** were also isolated in about 20% yield. On the whole, the 2,7-dilithio derivative provides better results in comparison with Grignard reagent **6b**. Besides, the generation of the latter and its interaction with electrophiles require much greater time. However, the advantages of reagent **6b** are relative cheapness of magnesium and an opportunity to work at room temperature without an inert atmosphere. As follows from Table 1, the yields of 2,7-disubstituted proton sponges are good. The only

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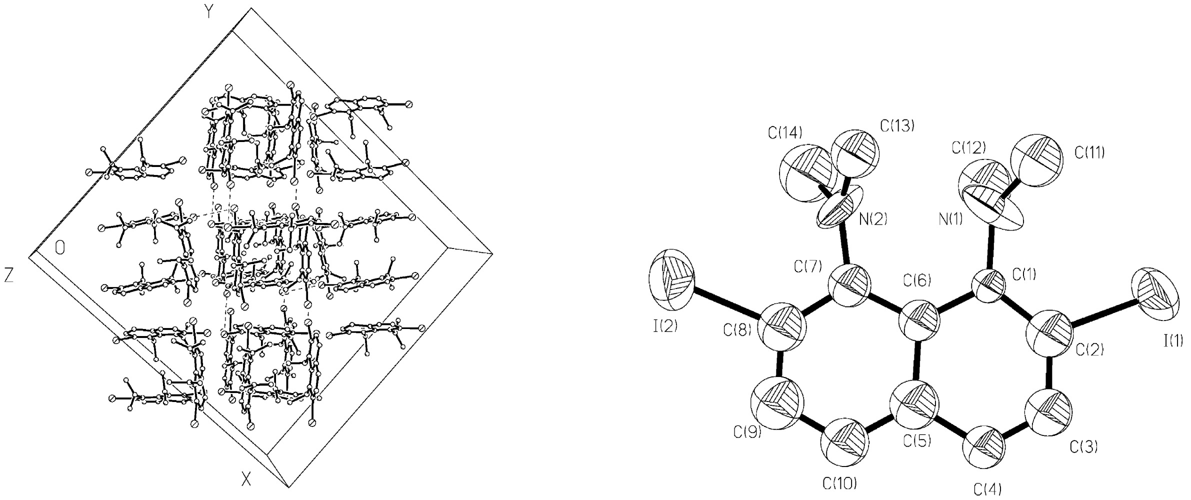


FIGURE 1. Molecular packing (left, view along *z*-axis) and side view of one of four independent molecules of diiodonaphthalene **7a** (right, thermal ellipsoids drawn at 50% probability level, hydrogen atoms are omitted for clarity).

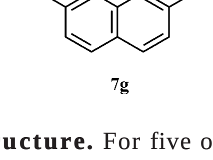
TABLE 1. Results on Interaction of Organometallics 6a and 6b with Electrophiles and Some Characteristics of Products 7 and 8

		isolated yield (%) from		
electrophile	product	**6a**	**6b**	mp[a] (°C)
D_2O	**7f**	98	94	49−50[b]
I_2	**7a**	65		86−87
I_2	**8a**	23		oil
$(EtO)_2CO$	**7b**	73	39	95−96
$(EtO)_2CO$	**8b**	20	7	oil
Me_2S_2	**7c**	90	57	112
Me_3SiCl	**7d**	11	tr	151−152[c]
MeI	**7e**	61		51.5−53[d]

[a] From MeOH. [b] From 1:1 (v/v) $MeOH/H_2O$ mixture. [c] From EtOH. [d] From *n*-octane.

exception is compound **7d**, obtained in a yield up to 11% due to, apparently, the severe steric restrictions.

In an attempt to replace diethyl ether by THF at the preparation of **6a** we have observed in a good yield the formation of earlier unknown 2,7-di-*n*-butyl-1,8-bis(dimethylamino)naphthalene (**7g**). We believe that since the C−Li bond in THF is ionized to a greater extent, the nucleophilicity of **6a** in comparison with that of **6b** increases strongly, and it quickly interacts with butylbromide forming at the lithiation of **5** (compare with ref 16).



7g

Molecular Structure. For five of the obtained compounds, **7a**−**e**, we were able to carry out X-ray experiments. Their results are shown in Figures 1 and 2 and Tables 2 and 3.

The crystal structure of diiodide **7a** is formed by four independent molecules $C_{14}H_{16}I_2N_2$ packed in mutually perpendicular stacks, parallel to diagonals [*x*,*y*] [*x*,−*y*] (Figure 1). Planes of the molecules in various stacks are practically perpendicular each other. The crystal structure of 2,7-dimethyl derivative **7e** is built of two independent molecules $C_{16}H_{22}N_2$ with a dihedral angle between their naphthalene planes of 56.5°. The crystal structures of **7b**−**d** are formed each by one independent molecule, $C_{20}H_{26}N_2O_4$, $C_{16}H_{22}N_2S_2$, or $C_{20}H_{34}N_2Si_2$ (Figure 2). Deviations of some atoms in the *ortho*-substituents from the naphthalene ring plane and the dihedral angles formed by various planes of each of the molecules are listed in Table 2.

A close examination of structures **7a**−**d** and those already described in the literature (**2**−**5**) reveals that they have a number of principal peculiarities giving a key for understanding their basicity and some other interesting properties. Among these peculiarities are (i) strong planarization of the NMe_2 groups; (ii) strong rotation of the NMe_2 groups relative to the naphthalene system; (iii) deviation of *ortho*-substituents from the ring plane; (iv) lengthening of the $C_{2(7)}$−R bonds in the compounds with electron-releasing *ortho*-substitients; (v) shortening of the N···N distance in the compounds with electron-releasing *ortho*-substitients; (vi) lengthening of the N···N distance in the compounds with heavy *d*-elements (SMe, I, $SiMe_3$) in the *ortho*-positions; (vii) absence of the significant naphthalene ring distortions in comparison with that of the parent proton sponge.

Undoubtedly, the most important of these specific features is a considerable planarization of *peri*-NMe_2 groups. Thus, the sum of valent angles at amine nitrogens in 2,7-diiodo **7a** and 2,7-bis(methylthio) **7c** derivatives reaches 356°; it is a little bit lower (353−354°) in ether **7b** and in previously investigated dihalides **4** and **5** and, especially surprising, in 2,7-bis(trimethylsilyl) derivative **7d** (the remarkable features of structure **7d** is outlined at the end of this section). It is noteworthy that even in parent molecule **1** the average sum of these angles makes 347°; this is much more than ~328° for the purely pyramidal nitrogen atom. From various properties of compound **1** (e.g., the lowered ionization potential, existence of an intensive absorption band at 340 nm, or extremely high C-nucleophilicity[1b]) one can conclude that the driving stimulus for partial planariza-

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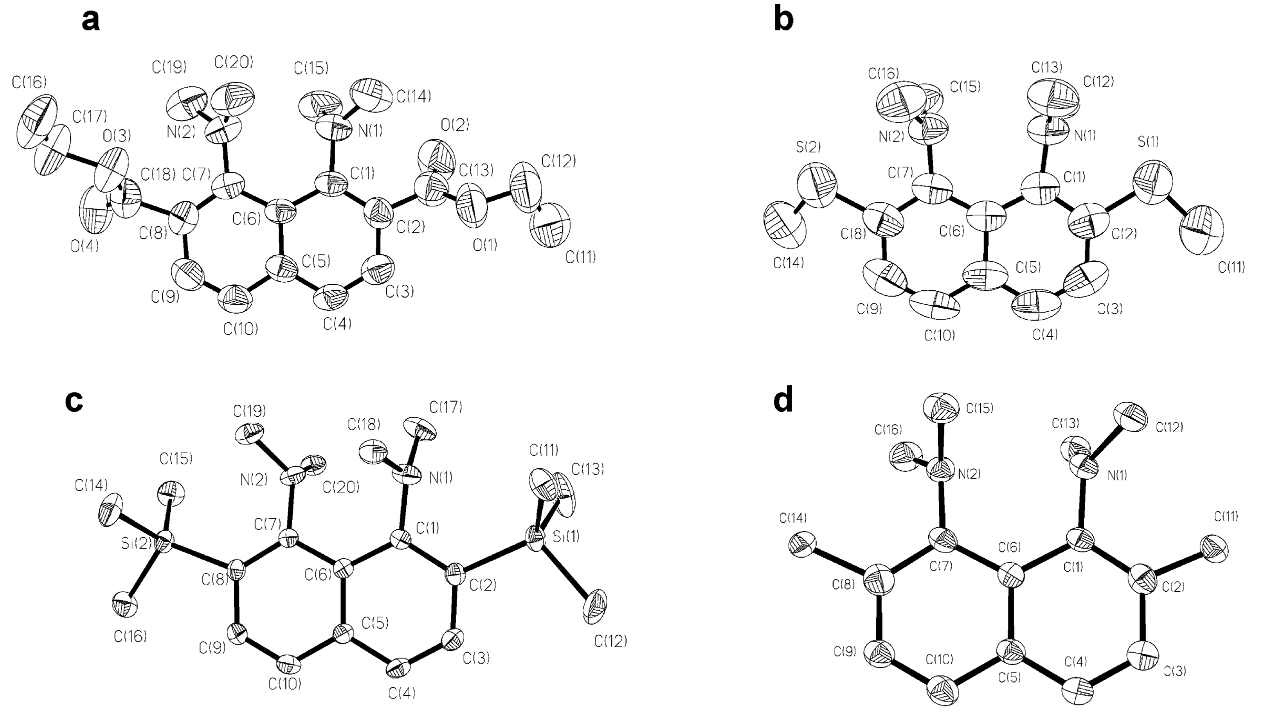

FIGURE 2. General view with atom labeling for (a) 2,7-bis(ethoxycarbonyl)- **7b**, (b) 2,7-bis(methylthio)- **7c**, (c) 2,7-bis-(trimethylsilyl)- **7d**, and (d) 2,7-dimethyl- **7e** naphthalenes (one of two independent molecules is presented). Thermal ellipsoids drawn at 50% probability level with hydrogens omitted for clarity.

TABLE 2. Deviations of Non-Naphthalene Atoms from the Naphthalene Plane (Å) and Selected Dihedral Angles (deg), Formed by Different Molecular Planes in Molecules 7a−e

compound	out-of-plane deviations (Å)		dihedral angles	deg
7a	I(1) +0.162	N(1) −0.031	C(1)···C(10) and N(1)C(11)C(12)	78.1
	I(2) −0.226	N(2) −0.186	C(1)···C(10) and N(2)C(13)C(14)	72.6
	I(3) −0.258	N(3) −0.096	C(15)···C(24) and N(3)C(25)C(26)	74.3
	I(4) +0.134	N(4) +0.086	C(15)···C(24) and N(4)C(27)C(28)	76.4
	I(5) −0.045	N(5) −0.224	C(29)···C(38) and N(5)C(39)C(40)	85.9
	I(6) +0.087	N(6) +0.016	C(29)···C(39) and N(6)C(41)C(42)	82.4
	I(7) +0.086	N(7) −0.048	C(43)···C(52) and N(7)C(53)C(54)	80.0
	I(8) −0.223	N(8) −0.167	C(43)···C(52) and N(8)C(55)C(56)	76.5
			N(1)C(11)C(12) and N(2)C(13)C(14)	42.3
			N(3)C(25)C(26) and N(4)C(27)C(28)	43.5
			N(5)C(39)C(40) and N(6)C(41)C(42)	53.5
			N(7)C(53)C(54) and N(8)C(55)C(56)	37.4
7b	C(13) −0.390	N(1) −0.158	C(1)···C(10) and N(1)C(14)C(15)	62.6
	C(18) +0.275	N(2) +0.153	C(1)···C(10) and N(2)C(19)C(20)	60.9
			N(1)C(14)C(15) and N(2)C(19)C(20)	59.4
7c	S(1) +0.025	N(1) −0.004	C(1)···C(10) and N(1)C(12)C(13)	83.8
	S(2) −0.103	N(2) +0.016	C(1)···C(10) and N(2)C(15)C(16)	83.0
			N(1)C(12)C(13) and N(2)C(15)C(16)	43.3
7d	Si(1) +0.226	N(1) +0.487	C(1)···C(10) and N(1)C(17)C(18)	105.8
	Si(2) −0.215	N(2) −0.425	C(1)···C(10) and N(2)C(19)C(20)	80.1
			N(1)C(17)C(18) and N(2)C(19)C(20)	23.8
7e	C(11) +0.11	N(1) −0.07	C(1)···C(10) and N(1)C(12)C(13)	110.2
	C(14) −0.05	N(2) −0.05	C(1)···C(10) and N(2)C(15)C(16)	109.5
	C(27) −0.10	N(3) +0.08	C(17)···C(26) and N(3)C(28)C(29)	109.4
	C(30) +0.08	N(4) −0.04	C(17)···C(26) and N(4)C(31)C(32)	107.6
			C(1)···C(6) and C(5)···C(10)	0.7
			C(17)···C(22) and C(21)···C(26)	1.1

tion of the NMe_2 groups in it is a tendency of the nitrogen lone pairs to conjugate with the aromatic π-system. The reason for further planarization of the nitrogen configuration in *ortho*-disubstituted compounds **2**−**5** and **7** is presumably steric in nature. Obviously, the buttressing effect of *ortho*-substituents will increase the repulsion of methyl groups and unshared electron pairs, which occupy in compound **1** the orbitals intermediate between sp^3 and sp^2 types. To avoid such interactions, the nitrogen atoms adopt a configuration close to trigonal, in which the lone pairs occupy the almost pure p orbitals, less stereodirected and accordingly not so strong repulsed.

The additional mechanism to remove the steric strain in the *ortho*-disubstituted proton sponges is a significant

TABLE 3. Selected Structural Characteristics of *ortho*-Disubstituted Proton Sponges and van der Waals Radii of *ortho*-Substituents

compd	*ortho*-substituent	van der Waals (Å)[a]	*r*(N···N) (Å)	∠ NMe$_2$-ring (deg)[b]	sum of CNC angles at N (deg)	*T* (K)	ref
1	H	1.10	2.792	40	347.2; 346.9	RT	17
1	H	1.10	2.804	39	347.2; 346.5	100	18
2	OMe	1.40	2.756	74	346.4; 345.9	190	19
3a	NMe$_2$	1.50	2.770	58	356.8; 355.6	RT	11
4	Cl	1.80	2.768	71	353.0; 352.8	RT	20
5	Br	1.95	2.775[c]	69	354.3; 353.5[c]	100	21
7a	I	2.15	2.82(2)[c]	80	357.0; 356.4[c]	110	*d*
7b	CO$_2$Et		2.760(3)	56	353.3; 353.0	110	*d*
7c	SMe	1.85	2.830(3)	84	359.7; 352.4	110	*d*
7d	SiMe$_3$	3.90	2.925(3)	78	355.3; 350.4	110	*d*
7e	Me	2.00	2.749(4)[e]	70	352.6; 352.5[e]	120	*d*

[a] See ref 23. [b] Average values for two NMe$_2$ groups. [c] Average value for four independent molecules in one unit cell. [d] This work. [e] Average value for two independent molecules.

rotation of dimethylamino groups around the N−C$_{ar}$ bonds. Whereas the angle between the average ring plane and the CNC plane of the NMe$_2$ groups in **1** is only 40°, it reaches 82° in iodide **7a** and sulfide **7c** and 78° in bis(trimethylsilyl) derivative **7d** (Table 3). At such magnitudes of torsion angle, the conjugation of dimethylamino groups with the ring π-system in **7a** and **7c** should not exceed 3% from the maximum value for a completely plane model of these proton sponges (for proton sponge **1** this parameter really makes ∼60%; see the section on basicity below).[22] Noticing that in dichloride **4** the similar angle is 71°, one can conclude that there exists an approximate dependence between the volume[23] of *ortho*-substituents in proton sponges, on one hand, and the degree of planarization of the NMe$_2$ groups as well as the angle of their rotation about the N−C$_{ar}$ bonds on the another hand.

The situation is more complicated in the case of ethoxycarbonyl derivative **7b**. In this molecule the angle of NMe$_2$-twisting is only 56°, resembling in this respect compound **3a**. Accordingly, the extent of planarization of the NMe$_2$ groups in **7b** is a little bit less. It is worth noticing that **7b** is the only compound among those discussed here in which the direct conjugation between dimethylamino groups and *ortho*-substituents is possible. From this it follows that its geometry most likely reflects the compromise between steric and conjugation effects.

The planarization and rotation of the dimethylamino groups in *ortho*-disubstituted proton sponges lead to one more remarkable geometrical consequence. As is known, in molecule **1** the spatial divergence of the NMe$_2$ groups is mainly due to the plane distortion of the naphthalene ring.[17] In particular, it concerns *peri*-carbon atoms connecting with the amine nitrogens. In molecule **1** the atoms N-1 and N-8 are deviated from the average ring plane in the opposite directions by ∼0.4 Å.[17] As it seen from Table 2, in compounds **7a,c** this deviation is much smaller and, for example, for **7c** does not exceed 0.02 Å. In fact, the geometry of **7c** resembles the structure of cation **1H**$^+$ rather than that of free base **1**. In general, there is a reversed proportional dependence between the distortion of the ring plane and planarization of the NMe$_2$ groups. The data for ester **7b**, occupying in this respect an intermediate position between proton sponge **1** and compounds **7a,c**, are the best example.

Along with changes in configuration of dimethylamino groups, there are two additional mechanisms to reduce the repulsive interaction between four neighboring substituents in *ortho*-disubstituted proton sponges. The first one is a rather distinctive deviation of the 2- and 7-substituents out of the mean ring plane. Interestingly, both of the substituents are deviated in the opposite direction and the values of such deviations are quite different from each other (Table 2). The second mechanism is realized only in the proton sponges with electron-donating groups in the *ortho*-positions. It consists of considerable elongation of the bonds between ring carbon atoms and *ortho*-substituents. For instance, in the case of 2,7-dimethyl derivative **7e** the average length of these bonds is equal to 1.57 Å compared to 1.50 Å for the standard C$_{sp2}$−C$_{sp3}$ bond.

Let us turn now to the structure of **7d**. Obviously, its peculiarities are caused by the special bulkiness of trimethylsilyl groups. Along with abnormally strong and quite understandable deviations of all substituents from the ring plane and strong increase of the N···N distance in **7d** (see Tables 2 and 3), the most outstanding feature of this molecule is the unusual conformation of the dimethylamino groups. Whereas the electronic pair of one of them is oriented inside the space between nitrogens (*in*-configuration) as occurs in other proton sponges (Figure 3a), the electron pair of the other group is pointed toward the *ortho*-substituent (*out*-configuration) (Figure

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(19) Woolf, A. A. as cited in *Adv. Phys. Org. Chem.* **1986**, *22*, 166 (CCDC reference code JAHWEU).

(20) Glowiak, T.; Majerz, I.; Malarskii, Z.; Sobczyk, L.; Pozharskii, A. F.; Ozeryanskii, V. A.; Grech, E. *J. Phys. Org. Chem.* **1999**, *12*, 895−900.

(21) Bienko, A. J.; Latajka, Z.; Sawka-Dobrowolska, W.; Sobczyk, L.; Ozeryanskii, V. A.; Pozharskii, A. F.; Grech, E.; Nowicka-Scheibe, J. *J. Chem. Phys.* **2003**, *119*, 4313−4319.

(22) These estimations of extent of conjugation are based on application of the well-known ratio $M = M_0 \cos^2 \varphi$, where M and M_0 stand for mesomeric effects in sterically disturbed and plane forms of the molecule, correspondingly, and φ is a torsion angle between conjugated fragments under consideration: *Uspekhi Stereokhimii*; Klyain, V., de la Mare, P. B. D., Eds.; GNTI Khimicheskoi Literatury: Moscow, 1961, p 547. English edition: Wepster, B. M. In *Progress in Stereochemistry*; Klyne, W., de la Mare, P. B. D., Eds.; Butterworths: London, 1954−1958; Vols. 1 and 2.

(23) We have chosen here as a crude measure of volume (“bulkiness”) of *ortho*-substituents their van der Waals radii: Charton, M. *Prog. Phys. Org. Chem.* **1976**, *8*, 235. Since nonspherical *ortho*-substituents in the solid proton sponges adopt conformation with the methyl groups to be *trans* to the *peri*-NMe$_2$ groups, their van der Waals values are given for the central element only.

TABLE 4. Ultraviolet Spectra of 2,7-Disubstituted 1,8-Bis(dimethylamino)naphthalenes

compd	R	solvent	λ_{max} (nm, log ϵ)	color
1	H	$CHCl_3$	341 (4.09)	colorless
5	Br	EtOH	234 (4.63), 316 (3.56)	dark-yellow
7a	I	EtOH	229 (sh., 4.46), 255 (4.61), 333 (sh., 3.47)	dark-yellow
7b	CO_2Et	MeCN	231 (4.67), 288 (3.72), end absorption up to 350 nm	bright-yellow
7c	SMe	MeCN	278 (4.57), 343 (3.51), 358 (3.58)	yellow
7d	$SiMe_3$	*n*-octane	258 (4.60), 337 (3.73)	greenish-yellow
7e	Me	*n*-octane	303 (3.72)	yellow

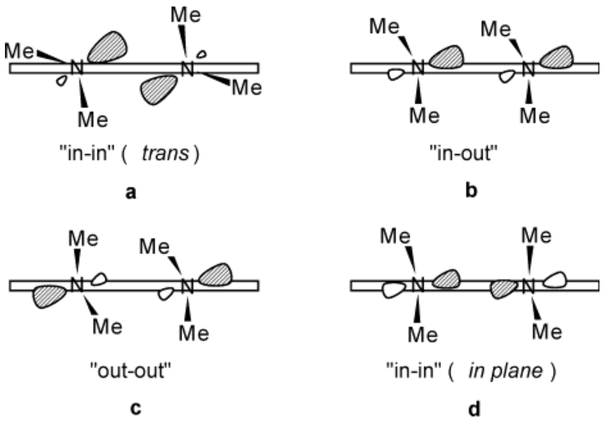

FIGURE 3. Possible types of nitrogen configuration in naphthalene proton sponges (white rectangles stand for side view of the naphthalene ring).

3b).[24] To the best of our knowledge, such *in-out* configuration of the NMe_2 group in the naphthalene proton sponge series is observed here for the first time.[25,26] In our opinion, it can be caused by attractive interaction of the nitrogen lone pair with vacant d-orbitals of the silicon atom,[27] acting together with unprecedentally strong spatial repulsion of the methyl groups. A reality of such an interaction, besides the very fact of inversion of the nitrogen pyramid, is supported by the deviation of the nitrogen and silicon atoms in the same way from the average ring plane (Table 2), as well as by the N···Si distance (3.03 Å), which is much less than the sum of N and Si van der Waals radii (3.65 Å). Interestingly, the N···Si distance for the second (noninverted) NMe_2 group is 3.36 Å, and apparently, it is also able to participate in a weaker p,d-interaction with another silicon atom. Quite clearly the inversion of the second amino group in **7d** is prevented because in the thus arising *out-out* configuration (Figure 3c) the spatial repulsion of four methyl groups becomes too big.

One can assume that both the p,d-interaction and the inversion of one dimethylamino group are responsible for the strong increase (instead of the expected reduction) in the N···N distance from 2.80 Å in compound **1** to 2.93 Å in **7d**. Obviously, asymmetrical structure of formally symmetric molecule **7d**, measured at 110 K, represents the “frozen” *in-out* conformer that may be partly the result of crystal packing forces. At room temperature and in a solution this structure equilibrates with the mirror *out-in* conformer; the mechanism of this interconversion most likely includes inversion of one nitrogen atom to produce the *in-in* conformer, which then inverts the other nitrogen (obviously, the interconvertion via *out-out* conformer is sterically impossible). With this in mind, the average sum of CNC angles at the N atoms in compound **7d** becomes formally equal to 358°, which exceeds the sums given in Table 3.[28]

We consider that the p,d-interaction of the nitrogens and *ortho*-substituents is also displayed in molecules **7a,c** since they both have reduced distances N···I (average 3.28 Å versus the sum of van der Waals, 3.53 Å) and N···S (2.88 versus 3.35 Å). It cannot be excluded that a tendency to such interactions is the additional stimulus for the flattening of nitrogen configuration in **7a** and **7c** (the spatial arrangement of the NMe_2 groups in **7c** is very close to that depicted in Figure 3d).

Coloring and Electronic Absorption Spectra. A remarkable feature of all 2,7-disubstituted 1,8-bis(dimethylamino)naphthalenes is a yellow coloring sharply distinguishing them from colorless **1** (Table 4). At first sight it looks rather surprising, since an introduction in *ortho*-positions of such groups as SMe, Hal, $SiMe_3$ does not extend the chain of conjugation. The only exception is compound **7b** in which the conjugation between the NMe_2 and CO_2Et groups is formally possible. However, in view of large distortions in the geometry of this molecule (see above), it is unlikely that such a conjugation will be large enough to shift the long-waved π,π^*-transition band into a visible region.

We believe that the literature data[4] for bridgehead diamines **9** and **10** may serve as a basis for the understanding of coloring of 2,7-disubstituted proton sponges.

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[24] For the sake of convenience, the terms *in* and *out* are used here with reference to orientation of the unshared electron pairs, instead of to the position of substituents at nitrogens as is accepted in the nomenclature for so-called *in-out* isomerism: Alder, R. W.; East, S. P. *Chem. Rev.* **1996**, *96*, 2097−2111. It should be stressed that because of the flat geometry of amino groups the nitrogen lone pairs occupy almost pure p-orbital and the degree of “in-ness” and “out-ness” here is rather small, i.e., the question is of preferential orientation.

[25] “*in-out*” Conformation of the NMe_2 groups in the proton sponge as theoretically possible was mentioned for the first time in the pioneering X-ray study of Einspahr and co-workers (see ref 18). Recent investigation of the proton sponge by fluorescence spectroscopy revealed that in the gas phase the molecule adopts two different conformations (DMAN-1 and DMAN-2), the first of which is similar to that existing in the solid (see ref 26). On the basis of ab initio calculations, the second and less stable conformer DMAN-2 was referred to the structure with one NMe_2 group being in flattened and orthogonal to the naphthalene ring configuration and with conformation of another NMe_2 group similar to that in DMAN-1. Evidently, the structure of DMAN-2 is quite close to that of **7d**, though full similarity between both of these fragments is still absent.

[26] Szemik-Hojniak, A.; Zwier, J. M.; Buma, W. J.; Bursi, R.; van der Waals, J. H. *J. Am. Chem. Soc.* **1998**, *120*, 4840−4844.

[27] The X-ray data specify that a similar p,d-interaction between dimethylamino and *ortho*-trialkylsilyl groups is also clearly distinctive in the benzene series: Wetzel, T. G.; Dehnen, S.; Roesky, P. W. *Organometallics* **1999**, *18*, 3835−3842.

[28] A record flattening of the amine nitrogen among all naphthalene proton sponges, including bridgehead amines **9** and **10**, belongs to the 2,5-diformyl derivative of **1**. In this compound the NMe_2 group *ortho* to the CHO group is completely flat (360°): Pozharskii, A. F.; Aleksandrov, G. G.; Vistorobskii, N. V. *Zh. Org. Khim.* **1991**, *27*, 1536−1543 (English edition, *Russ. J. Org. Chem.*).

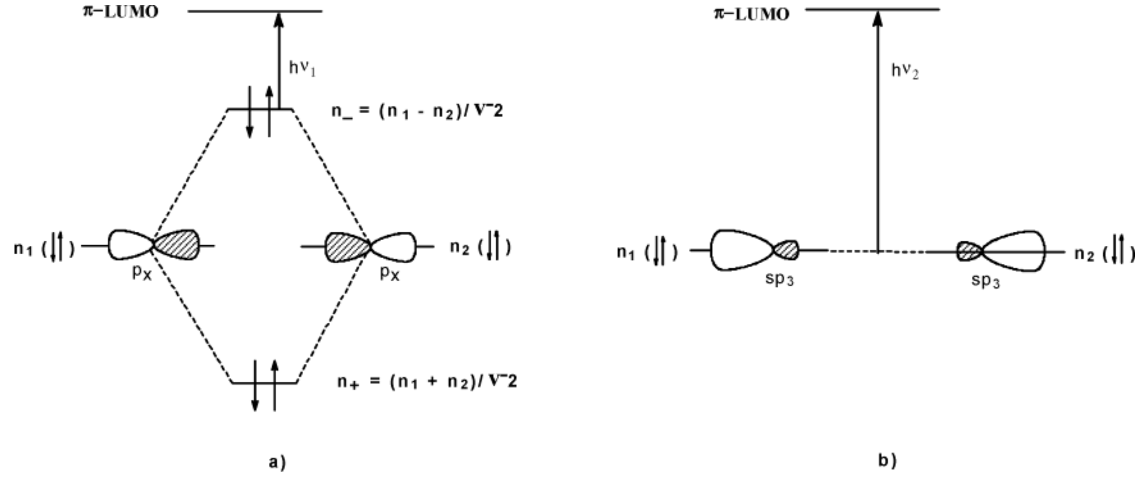
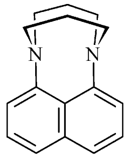
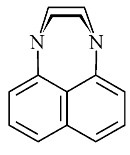


FIGURE 4. Scheme of possible energy levels and electron transitions for nitrogen lone pairs in compounds **9** (a) and **10** (b).

The former diamine was described as yellow needles with λ_{max} 276 (lgϵ 3.76), 286 (3.80) and 379 (2.37); the latter one is colorless crystals with λ_{max} 277 (3.83) and 280 (3.85) (both in *iso*-octane).



9



10

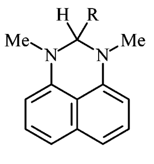
In compound **9** the trimethylene bridges fix the nitrogens in an almost flat configuration (as in Figure 3d; average sum of CNC angles 355.8°).[29] Correspondingly, the nitrogen lone pairs, which occupy the p-orbitals (98% p-character) orthogonal to the p-orbitals of the naphthalene moiety, cannot conjugate with the latter. At such the structure the ultraviolet spectrum of diamine **9** should resemble that of naphthalene [λ_{max} 220 (log ϵ 5.0), 275 (4.0), 297−310 (2.8)],[30] as it occurs at transition from base **1** to its chelated monocation.[1b] However, the UV spectrum of **9** contains an absorption band with λ_{max} 379 nm, which is absent in the naphthalene spectrum. In our opinion the only reasonable explanation of its appearance can be as follows. As a result of spatial proximity and orientation of the lone electron pairs in **9**, they interact with splitting of the energetic levels as shown in Figure 4a. As a consequence, the gap of energy between the highest occupied molecular n orbital and the lowest unoccupied π-orbital becomes quite small and results in bathochromic shift of the long-wave band that tails into the visible region. Since the orbitals involved in the n → π* transition are orthogonal to each other, this absorption band is formally forbidden and has low intensive ill-defined structure.

Unlike compound **9**, the CH_2-CH_2 bridges in diamine **10** fix the nitrogen atoms in a pyramidal *out-out* configuration, and their lone pairs occupy now sp^3-orbitals, focused *outside* and therefore removed from each other (approximately as shown in Figure 3c). This reduces the splitting of energetic levels (see Figure 4b), and the energy of the first electron transition for diamine **10**, $h\nu_2$, turns out to be much more than the $h\nu_1$ value for compound **9**. There is no wonder that diamine **10** is a colorless substance with a naphthalene-like UV spectrum.

It is evident that the coloration of 2,7-disubstituted proton sponges has the same roots as in the case of compound **9**, with the only difference that the planarized orthogonal configuration of the nitrogens is induced here by *ortho*-substituents. In agreement with this picture is the fact that according to the X-ray data the angle between the axes of the nitrogen lone electron pairs in the compounds of type **5** and **7** does not exceed 5−7°.

It is necessary to emphasize that the maximum of the long-wave absorption band for almost all of the substances received by us, as well as for diamine **9**, does not reach the visible region, i.e., their coloring is caused by a low intensive end absorption.[31]

NMR ^{1}H Spectra. The proton spectra of the *ortho*-disubstituted proton sponges due to their symmetry are quite simple, and chemical shift changes of each particular compound are generally in accord with its structure, namely, nitrogen planarization and lack of conjugation between NMe_2 groups and the ring π-system (Table 5). Analysis of the NMR ^{1}H spectrum of 1,3-dimethyl-2,3-dihydroperimidine (**11a**), in which the conditions for effective conjugation between the nitrogen atoms and the naphthalene system are realized in the best way,[34,35] shadows an importance of these factors.



11 R = H (**a**), Ph (**b**)

A noticeable feature in the NMR ^{1}H spectra of *ortho*-disubstituted proton sponges is the increased spin−spin coupling constants $J_{3,4}$ reaching 8.6−9.0 Hz. The nature of this phenomenon remains locked for a while as we have not found any correlation between the $J_{3,4}$ values

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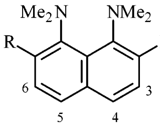
[29] Alder, R. W.; Goode, N. C.; King, T. J.; Mellor, J. M.; Miller, B. W. *J. Chem. Soc., Chem. Commun.* **1976**, 173−174.

[30] Balasubramaniyan, V. *Chem. Rev.* **1966**, *66*, 567−641.

TABLE 5. ^{1}H NMR Spectra of *ortho*-Disubstituted 1,8-Bis(dimethylamino)naphthalenes and Reference Compound 11a (in CDCl$_3$)



compd	R	δ, ppm					$J_{3,4}$ (Hz)	$d_{3,4}$[a] (Å)	ref
		NMe	Δδ	H-3(6)	H-4(5)	R			
1	H	2.81	0.00	7.31	7.37	6.94	7.9	1.334	*b*
2	OMe	2.89	0.08	7.06	7.48	3.89	9.0	1.365	4, 19
3a	NMe$_2$	2.97	0.16	7.19	7.40	2.65	8.6	1.353	*b*
4	Cl	2.96	0.15	7.31	7.43		8.8	1.349	13, 20
5	Br	2.96	0.15	7.35	7.51		8.7	1.354	14, 21
7a	I	2.97	0.16	7.20	7.81		8.6	1.31	*b*
7b	CO$_2$Et	2.92	0.11	7.36	7.42	1.40; 4.39	8.4	1.350	*b*
7c	SMe	2.96	0.15	7.21	7.55	2.46	8.7	1.344	*b*
7d	SiMe$_3$	2.86	0.05	7.43	7.50	0.37	8.3	1.353	*b*
7e	Me	2.94	0.13	7.11	7.41	2.38	8.1		*b*
7f	D	2.77	−0.04	7.27	7.33		8.0		*b*
7g	*n*-Bu	2.94	0.13	7.17	7.46	0.97; 1.46; 1.65; 2.70	8.3		*b*
11a		3.03	0.22	7.35	7.23	6.55	8.4	1.341[c]	33

[a] Data for unsubstituted naphthalene (see ref 32): $J_{3,4}$ 8.3 Hz, $d_{3,4}$ 1.381 Å. [b] This work. [c] For compound **11b**.

TABLE 6. ^{1}H NMR Data for Proton Complexes of *ortho*-Disubstituted 1,8-Bis(dimethylamino)naphthalenes

compd	R	solvent	δ, ppm				$J_{NMe,NH}$ (Hz)	ref
			NMe$_2$, d	H-3(6), d	H-4(5), d	N···H···N, m		
1·HClO$_4$	H	CD$_3$CN	3.11	7.71	8.05	18.69	2.64	1b
3a·HBF$_4$	NMe$_2$	DMSO-d_6	3.30	7.85	8.12	19.81	2.20	11
4·HClO$_4$	Cl	DMSO-d_6	3.37	7.83	8.20	19.91	2.45	14, 36
5·HClO$_4$	Br	CD$_3$CN	3.41	7.89	7.96	20.33	2.64	14
		DMSO-d_6	3.40	7.98	8.09	20.09	2.41	14
7a·HClO$_4$	I	CD$_3$CN	3.43	7.73	8.19	20.46	2.48	*a*
		DMSO-d_6	3.43	7.83	8.20	20.21	2.24	
7c·HBF$_4$	SMe	CD$_3$CN	3.38	7.70	7.97	20.40	2.65	*a*
		DMSO-d_6	3.39	7.75	8.07	20.17	2.35	
7d·HClO$_4$	SiMe$_3$	CD$_3$CN	3.26	7.97	8.00	20.69	2.58	*a*
		DMSO-d_6	3.26	7.94	8.06	20.44	2.34	
7e·HBF$_4$	Me	DMSO-d_6	3.26	7.45	7.93	20.10	2.53	*a*
7g·HClO$_4$	*n*-Bu	DMSO-d_6	3.27	7.52	7.95	20.18	2.41	*a*

[a] This work.

and the lengths of the corresponding C(3)−C(4) bonds ($d_{3,4}$), which are also given in Table 5.

In the NMR ^{1}H spectra of cations of studied compounds (Table 6) the position of the chelated *NH*-proton is particularly interesting. While in parent cation **1H**$^+$ δ_{NH} is about 18.7 ppm, in the *ortho*-disubstituted cations it frequently exceeds 20 ppm, and in addition a clear dependence exists between the δ_{NH} value and the volume of *ortho*-substituents (the influence of a solvent on δ_{NH} is discussed in ref 14). The greatest δ_{NH} value (20.7 ppm) is observed for cation **7d-H**$^+$ with trimethylsilyl groups, and the smallest one (20.1 ppm) is for its 2,7-dimethyl counterpart **7e-H**$^+$. One could assume (see, for instance, ref 14) that in the *ortho*-disubstituted cations the *NH*-proton is "squeezed out" from the plane of the naphthalene ring into the zone of a stronger diamagnetic field, which causes this downfield shift. However, the recent X-ray data of **4** and **5** as hydrobromides have shown that the bridge proton in these structures lies strictly in the naphthalene plane.[20,21]

In our opinion, the only reasonable explanation of the *NH*-proton downfield shift in the NMR ^{1}H spectra of *ortho*-disubtituted proton sponge cations consists of essential strengthening of the IHB that leads to an additional deshielding of the chelated proton. Unfortunately, at the present time we have not yet resolved X-ray structures of proton complexes of compounds synthesized in this work. Nevertheless, already available crystal-

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(31) One of the referees suggested that the yellow color of *ortho*-disubstituted naphthalene proton sponges could be due to the presence of trace amounts of the corresponding radical-cations arising at contact of the samples with air oxygen. These amounts of microimpurities are small enough to be detected by ordinary physical methods (e.g., GC/MS) but can contribute to the color. From the authors' point of view, this suggestion is disputable and deserves a separate study.

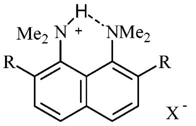
(32) (a) Ehrlich, H. W. W. *Acta Crystallogr.* **1957**, *10*, 699−705. (b) Cruickshank, D. W. J. *Acta Crystallogr.* **1957**, *10*, 504−508. (c) Cruickshank, D. W. J. *Tetrahedron* **1962**, *17*, 155−162.

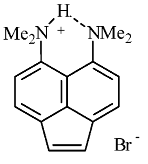
(33) Ozeryanskii, V. A.; Filatova, E. A.; Sorokin, V. I.; Pozharskii, A. F.; *Russ. Chem. Bull.* **2001**, *50*, 846−853.

(34) Espenbetov, A. A.; Pozharskii, A. F.; Struchkov, Yu. T.; Suslov, A. N. *Khim. Geterotsikl. Soed.* **1985**, 977−985. An X-ray analysis of 2-phenyl-2,3-dihydroperimidine **11b** has shown that, despite the effective conjugation in this system, the nitrogen atoms are yet not completely planar and the average sum of valent angles at them is ~354°.

(35) Pozharskii, A. F.; Suslov, A. N.; Starshikov, N. M.; Popova, L. L.; Kluev, N. A.; Adanin, V. A. *Zh. Org. Khim.* **1980**, *16*, 2216−2228 (English edition, *Russ. J. Org. Chem.*).

TABLE 7. Selected X-ray Parameters of IHB for Proton Complexes of Some Proton Sponges





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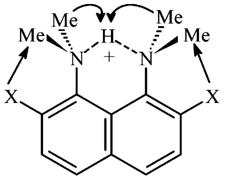
compd/R	X^-	r(N···N) (Å)	∠NHN (deg)	av sum of CNC angles at N (deg)	T (K)	ref
1/H	$CuCl_4^-$	2.584	157.5	336.5	rt	37
1/H[a]		2.595	155.0	336.4		
4/Cl	Br^-	2.561	165.0	342.7	rt	20
5/Br	Br^-	2.547	162.1	342.9	100	21
13	Br^-	2.671	156.2	336.9	200	38

[a] Average values for a series of 38 structures with $\mathbf{1H}^+$ cations extracted from CCDC.

lographic data for salts **4**·HBr and **5**·HBr leaves no doubts in correctness of the above assumption. In both these cations an appreciable linearization (by 5−7°) of the IHB and small but distinctive reduction of the N···N distance are observed (Table 7). The reason for these structural changes is undoubtedly connected with "pressure" that is rendered by the *ortho*-substituents on the *N*-methyl groups directed to their side. Consequently, the *N*-methyls are raised above the *ortho*-substituents and inturn press the *NH*-proton into the space between nitrogens (**12**).



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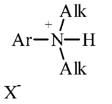
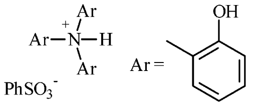
The clear-cut evidence of this process is an essential planarization of the nitrogen atoms (about 6°) in cations $\mathbf{4H}^+$ and $\mathbf{5H}^+$ in comparison with cation $\mathbf{1H}^+$ and its acenaphthylene analogue $\mathbf{13H}^+$ (see Table 7). Inspection of CCDC data has disclosed that this planarization is record one for nonbridged ammonium salts with one *NH*-bond. The average sum of CNC angles in the cations of type **A** (the data embrace 16 structures) is equal to 335.3°, and only in triarylammonium salt **B** it is as high as 340.5°.



A



B

Basicity. The pK_a values determined by us for the *ortho*-disubstituted proton sponges together with some earlier available data are presented in Table 8. The measurements were carried out in dimethyl sulfoxide with the help of NMR ^{1}H by competitive transprotonation between a base and a cation of two compounds comparable in their pK_a values.[11,40] Table 8 also contains the data on electronic and steric effects of the corresponding groups (accepted from ref 41), namely, inductive (σ_I), resonance (σ_R), and usual (σ_p) Hammett constants, and also steric Taft parameter E_s for *ortho*-substituents (a positive E_s value means that the *ortho*-substituent influences on the reaction center is lesser than a methyl group).

TABLE 8. Basicity Constants (pK_a) of Some *ortho*-Disubstituted 1,8-Bis(dimethylamino)naphthalenes (DMSO-d_6, 22 °C) and Electronic and Steric Constants of the Substituents (See Text)

compd	R	pK_a (±0.05)	σ_p	σ_I	σ_R	E_s
2	OMe	11.5[a]	−0.27	0.26	−0.500	0.97
3a	NMe_2	11.2[b]	−0.87			
7e	Me	9.8[c]	−0.17	−0.05	−0.141	0.000
7c	SMe	8.1[c]	0.00	0.19	−0.186	
1	H	7.5[d]	0	0	0	
7d	$SiMe_3$	7.0[c,e]	−0.07	−0.11	−0.044	
4	Cl	6.8[c,f]	0.227	0.47	−0.161	0.18
7a	I	6.7[c]	0.18	0.40	−0.197	−0.20
5	Br	6.5[c,f]	0.232	0.45	−0.176	0.01

[a] According to refs 2 and 11. [b] From ref 11. [c] This work. [d] From ref 39. [e] Extrapolated from acetonitrile scale. It was not possible to find the exact pK_a value for **7d** because of its low solubility at room temperature in acetonitrile and especially in DMSO. However, a transprotonation experiment at 42 °C has shown that in CD_3CN the equilibrium $\mathbf{1{\cdot}H}^+ + \mathbf{7d} \rightleftarrows \mathbf{1} + \mathbf{7d{\cdot}H}^+$ is shifted to the left, thus giving a value of 18.03 against 18.50 for **1** (see ref 12). [f] See also ref 12.

From the analysis of molecular structure and trends in pK_a changes for studied compounds it is possible to conclude that their basicity is determined by an interplay of several factors among which are (i) polar effect of *ortho*-substituents, (ii) electrostatic repulsion between lone electron pairs of the NMe_2 groups, (iii) reduction of conjugation between *peri*-dimethylamino groups and the naphthalene system, (iv) increase of p-character of the nitrogen lone pairs, (v) increase of the IHB strength in the cation, (vi) increase of steric strain in the cation, (vii) p,d-interaction of the dimethylamino groups with d-elements of such *ortho*-substituents as SMe, $SiMe_3$, Br, and I, (viii) changes in solvation caused by introduction of *ortho*-substituents.

It is rather difficult to estimate a contribution of each of these factors with sufficient accuracy taking in mind that they can strongly vary at passing from one compound to another. Nevertheless, from some analogies and physical characteristics alongside with intuitive speculations we have tried to weigh each factor in semiquantitative manner using a "plus-minus" system (Table 9). The increase in basicity with each 0.5 pK_a relative to parent compound **1** corresponds to one "+"-sign, while the same

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TABLE 9. Estimated Influence of Different Factors on Basicity of *ortho*-Disubstituted Proton Sponges Relative to Parent Compound 1[a]

	compound								
	2	**3a**	**7e**	**7c**	**1**	**7d**	**4**	**7a**	**5**
R	OMe	NMe_2	Me	SMe	H	$SiMe_3$	Cl	I	Br
pK_a (DMSO)[b]	11.5	11.2	9.8	8.1	7.5	7.0	6.8	6.7	6.5
$\Delta pK_a = pK_a(R) - pK_a(H)$	4.0	3.7	2.3	0.6	0	−0.5	−0.7	−0.8	−1.0
polar effect of R	++++	+++	+++	0	0	+	− − −	− −	− − −
repulsion between lone pairs of *peri*-NMe_2 groups in free base	++	0	−	− −	0	− − −	−	− −	−
lack of conjugation between *peri*-NMe_2 and naphthalene ring in free base	1.5+	0.5+	1.5+	1.5+	0	1.5+	1.5+	1.5+	1.5+
increase of lone pairs p-character in free base	−	+++	++	+++	0	+++	++	+++	++
IHB	+	+	+	+	0	+	+	+	+
steric strain in protonated form	0	−	− −	−	0	− −	− −	− −	− −
p,d-interaction in free base	0	0	0	−	0	−	0	−	−
solvation of base/cation pair	+	+	−	0	0	− −	0	0	0
total sum of "+" and "−"	+8.5	+7.5	+3.5	+1.5	0	−1.5	−1.5	−1.5	−2.5

[a] "+" represents an increase in basicity of ca. 0.5 pK_a; "−" represents a decrease in basicity of ca. 0.5 pK_a; "0" represents no influence. [b] Taken from Table 8.

reduction in basicity is marked by one "−". A sum of pluses and minuses shown at the bottom of Table 9 after its multiplication by 0.5 gives estimated basicity change for each compound and approximately corresponds to the experimental value.

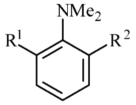
As it follows from Table 9, all 2,7-disubstituted proton sponges are clearly divided into two groups, each consisting of four compounds: those with basicities larger than the basicity of parent sponge **1** and those having lower pK_a values. Notably, all compounds from the first list have in *ortho*-positions electron-donating groups, whereas less basic sponges carry electron-withdrawing *ortho*-functionalities (**7c** and **7d** are two minor exceptions possibly reflecting certain influence of steric factors). This tendency gave an idea that the role of polar effect of *ortho*-susbstituents on proton sponge basicities is especially important. Let us consider now plus-minus marks in details.

Polar Effect of *ortho*-Substituents. Only four from eight investigated compounds possess basicity larger than that of diamine **1**. These are 2,7-dimethoxy **2**, 2,7-bis(dimethylamino) **3a**, and 2,7-dimethyl **7e** derivatives and sulfide **7c**. The first three have especially great basicities that corresponds to the electron-donating nature of the OMe, NMe_2, and Me groups; in the case of the CH_3S group the inductive and the resonance effects counterbalance each other ($\sigma_p = 0$).

At first sight, tetraamine **3a**, which from the standpoint of relative electron-releasing ability of the NMe_2 and CH_3O groups should be more basic than **2**, falls out of this row. The origin of this inconsistency is obvious: *ortho*-dimethylamino groups in **3a** are twisted off the ring system by 64° and their nitrogens are pyramidalized, with resulting weakening of the $+M$-effect.[11] From the correlation $M = M_0 \cos^2 \varphi$ (see ref 22) it is easy to estimate that the effective σ_p-constant of the NMe_2 groups in **3a** hardly exceeds −0.15 to −0.18.

The data in Table 10 demonstrate that the influence of *ortho*-substituents on basicity of *N*,*N*-dimethylanilines and proton sponges is similar in principle. As far as one *o*-OMe or *o*-Me group raises the basicity of dimethylanilines by ~1 and ~0.75 pK_a, respectively, (for mixtures of water/ethanol, 1:1), one can deduce that two such groups in compounds **2** and **7e** should enlarge pK_a by 2 and 1.5 units, respectively. Since this increase originates mainly from the electron-donating effect of the substituents, four "pluses" in the "polar effect" line (Table 9) are put for compound **2** and three for **3a** and **7e**.

TABLE 10. Basicity Constants of *ortho*-Substituted *N,N*-Dimethylanilines[a]



R^1	R^2	solvent	pK_a
H	H	H_2O	5.12
H	H	H_2O/EtOH (1:1, v/v)	4.39
H	Me	H_2O	6.11
H	Me	H_2O/EtOH (1:1, v/v)	5.15
Me	Me	H_2O	5.86, 6.10
H	OMe	H_2O/EtOH (1:1, v/v)	5.42
H	NMe_2	H_2O	6.64[b]
H	Br	H_2O	4.31

[a] According to ref 42. [b] Accepted from ref 43. Extrapolation of 5.42 value for 2-methoxydimethylaniline gives pK_a 6.38 in H_2O.

All three *ortho*-dihalides **4**, **5** and **7a** are less basic than the parent compound **1**, which also agrees with known electron-withdrawing nature of the halogeno groups. From the relative basicity of 2-bromo-*N*,*N*-dimethylaniline (Table 10), we have rated the contribution of electron effect of two chlorine, bromine, and iodine atoms in **4**, **5** and **7a** as three, three, and two "−", correspondingly. A weak electron-donating effect of the $SiMe_3$ groups is marked as one "+".

Repulsion between Lone Pairs of Dimethylamino Groups. This factor is considered by most investigators[6,7,10] as one of the leading in increasing the basicity of proton sponge **1** (its importance was, however, argued in a theoretical study based on semiempirical calculations[44]). Judging by X-ray data for 2,7-dimethoxy derivative **2**, the hybridization of its nitrogen atoms is almost unchanged in comparison with compound **1**, while the N···N distance is little shortened. All of this along with strong twisting of the NMe_2 groups and neighborhood of the OMe groups means that the repulsion between

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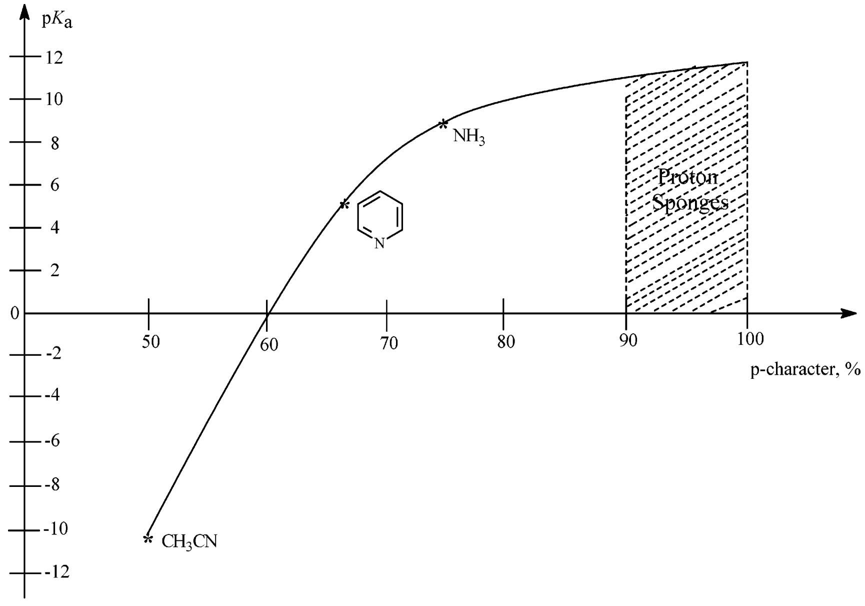

FIGURE 5. Approximate dependence of nitrogen basicity on p-character of unshared electron pair (H_2O scale).

unshared electron pairs in **2** can only increase. So we have valued a contribution of this factor for molecule **2** as being "++". The repulsion of the lone pairs in tetrakis(dimethylamino) derivative **3a** seems to be weaker because *peri*-dimethylamino groups are twisted here to a lesser extent and undergo greater flattening than in **2**. Therefore *peri*-nitrogen lone pairs in **3a** occupy almost pure and less stereodirected p-orbitals. All this gives a ground to evaluate this factor for **3a** as negligibly small (mark "0"). We suppose that flattening and orthogonality of the NMe_2 groups for all other *ortho*-disubstituted proton sponges having bulky *ortho*-functionalities (especially for trimethylsilyl derivative **7d**) should lead to some basicity decrease in comparison with reference compound **1**.

Lack of Conjugation between Dimethylamino Groups and Aromatic π-System. A comparison of the pK_a for *N*,*N*-diethylaniline (6.56) and benzoquinuclidine (7.79) testifies that transition from a conjugated arylamine to that with completely disturbed conjugation leads to the basicity increase of 1.2 pK_a. Together with the data of Table 3 it means that this factor can increase the basicity of parent sponge **1** approximately by 0.5 pK_a. At introducing the majority of *ortho*-substituents, *peri*-dimethylamino groups become almost perpendicular to the naphthalene ring (Table 3, Figure 3d), and their residual conjugation with the naphthalene π-system falls down to 2−22% of that in molecule **1** (Table 11). This may enhance the basicity of these proton sponges by ~0.7 pK_a. The only exception is tetraamine **3a**, in which the turning of *peri*-NMe_2 groups relative to the naphthalene ring plane is smaller (Table 3); hence it is not reasonable in this case to neglect fully this residual conjugation.

TABLE 11. Lone Pairs p-Character of *peri*-Dimethylamino Groups and Degree of Their Conjugation with the Aromatic π-System (*M*) Relative to Parent Compound 1 (M_0)

compd	R	p-character[a] (%)	*M* (%)
1	H	91	59[b]
2	OMe	90	14
3a	NMe_2	97	47
4	Cl	95	19
5	Br	96	22
7a	I	98	5
7b	CO_2Et	95	53
7c	SMe	97	2
7d	$SiMe_3$	98	7
7e	Me	95	20

[a] Calculated according to ref 45. [b] Relative to an idealized flat model.

Increase of p-Character of Nitrogen Lone Pairs in Free Base. It is well-known that increasing of p-character of the lone pair enhances the basicity of nitrogen atom. Thus, in the sequence acetonitrile (sp-hybridization)−pyridine (sp^2)−ammonia (sp^3) the pK_a changes from −11 to 5.2 and then to 9.2. The remarkable peculiarity of the compounds studied in this work consists of a strong planarization of *peri*-dimethylamino groups, whose lone electron pairs occupy essentially nonhybridized p-orbitals (Table 11). Therefore one could expect that this factor would lead to a strong jump of their basicity. However, not too great pK_a values for derivatives with especially flat NMe_2 groups (**7a**,**c**,**d**) bring some doubts on this account. Actually, it is easily seen that transition from a sp- to sp^2-hybridized nitrogen atom is accompanied nearly by 1 pK_a unit increase per each percent of p-increase. At the same time, in the interval between sp^2 and sp^3 states, the lone pairs p-character must increase by 2% for the same positive change. Further graphical extrapolation of these data shows that at transition from a sp^3 to fully planarized nitrogen atom, in order to increase the basicity by 1 pK_a unit, it is necessary to raise the p-character of a lone electron pair by about 4% (see Figure 5). Since the nitrogen electron pairs in reference compound **1** already have 91% of the p-character, one can conclude that the increase of pK_a owing to this factor for *ortho*-disubstituted proton sponges cannot exceed 1−1.5 pK_a units (cf. data in Tables 9 and11).

p,d-Interaction in Free Base with Heavy *ortho*-Substituents. Above, from some geometrical peculiarities of diamines **7a**,**c**,**d**, we have made a suggestion about existence in these molecules of p,d-interaction between the amine nitrogens and the *ortho*-substituents. Since the pK_a values of compounds **7a**,**c**,**d** are quite close to the pK_a of proton sponge **1**, it would be reasonable to assume that this factor, if indeed it operates, may reduce their basicity not more than by 0.5 pK_a unit (one "−" in Table 9).

Strengthening of Intramolecular Hydrogen Bonding in the Cations. Discussing the NMR ^{1}H spectra, we have already pointed out the strengthening of IHB in the cations of *ortho*-disubstituted proton sponges. This strengthening is approximately equal for all compounds of this series and has not such a dramatic character as it appears at transition from cations of partially alkylated 1,8-diaminonaphthalenes to protonated 1,8-bis(dimethylamino)naphthalene **1H**$^+$ (the contribution of IHB in the basicity increase of **1** is estimated to be at least 3 pK_a units[1b]). Therefore, it is unlikely that this factor can provide basicity growing of the studied compounds of more than 0.5 pK_a above **1**. This point is outlined in Table 9 with one "+" for all *ortho*-disubstituted proton sponges.

Steric Strain in Protonated *ortho*-Disubstituted Proton Sponges. It is well established that the steric strain in base **1** is almost completely relieved on protonation, and this is an additional reason for the high basicity of proton sponges.[1] In the case of *ortho*-disubstituted compounds, perhaps with the exclusion of **2**, the role of this factor is obviously reversed. The specificity of their cations, as was mentioned above, is the increase of steric repulsion between the NMe$_2$ groups and *ortho*-substituents that cannot be ignored. Certainly, this will bring to the reduction of basicity, even essential for more voluminous *ortho*-substituents.

Solvation Factors. It is hardly possible to estimate precisely enough the role of solvation on the basis of available data. In general, we may suppose that an introduction of hydrophobic groups, e.g., methyl or trimethylsilyl, will inhibit solvation of the cation and thus exert some reducing in basicity. Contrary to that, such substituents as *o*-OMe or *o*-NMe$_2$ might favor solvation and bring to some increase in pK_a.

From the preceding discussion it follows that all basicity changes for 2,7-disubstituted proton sponges are mainly determined by two groups of factors: (1) the polar effect of *ortho*-substituents and (2) the buttressing effect. The latter, unlike its earlier simplified interpretation, actually represents a complex conglomerate of various steric in nature interactions between the *ortho*-substituents and *peri*-NMe$_2$ groups, which are displayed both in the free bases and in corresponding cations. Some of these interactions lead to basicity increase, whereas others promote its decrease. A balance of these contradictory tendencies strongly differs for compounds with bulky *ortho*-substituents (SMe, I, Br, SiMe$_3$, etc.) and with *ortho*-substituents with lesser steric demands (OMe, NMe$_2$). For the former, the components of buttressing effect almost cancel each other, which in a paradoxical way minimizes its influence on the pK_a values. In result, the basicity of such compounds is dependent mostly on the polar effect of *ortho*-groups rather than on their bulkiness and varies in the narrow interval relative to the parent proton sponge. For the second type of compounds, such as **2** and **3a**, the polar and the "buttressing" effects generally act in the same direction, leading to exceptionally high basicities. 2,7-Dimethyl derivative **7e** in this respect occupies an intermediate position. Interestingly, despite a complex interplay of many contradictory factors, a general mode of the basicity changes for all 2,7-disubstituted proton sponges, with minor exceptions, is in agreement with the polar effect of *ortho*-substituents.

Conclusions

In summary, we have developed a new general method for the preparation of 2,7-disubstitited naphthalene proton sponges and studied their structure, basicity, and some other properties. It was shown that all basicity changes in this class of compounds are determined mainly by the polar effect of *ortho*-substituents and the buttressing effect. The latter results in significant geometry changes both in the free bases and the cations. Some of these changes promote an increase in basicity, whereas others lead to its decrease. The striking consequence of the overlap of these contradictory trends is a negligible dependence between the basicity of 2,7-disubstituted proton sponges, on one hand, and the volume of *ortho*-substituents, on the other hand. Actually, all principle changes in the basicity are mainly determined by the polar effect of *ortho*-substituents. In this respect, the only difference between the proton sponges and *N*,*N*-dimethylanilines consists of the scale of influence of *ortho*-substituents on the basicity, which in the former series is considerably higher. We have also shown that 2,7-bis(trimethylsilyl)-1,8-bis(dimethylamino)naphthalene is the first proton sponge derivative with *in-out* configuration of the NMe$_2$ groups in the solid.

Experimental Section

X-ray Measurements. Measurements on compounds **7a**−**d** were conducted at 110 K (120 K for **7e**) with a Bruker AXS SMART 1000 diffractometer , equipped with a CCD detector (Mo $K\alpha$ line, graphite monochromator, ω-scanning, scan pitch 0.3°, frame measuring time 30 s).[46] The structures were solved by direct methods and subsequent Fourier syntheses using the SHELXS-97 program.[47] Structures **7b**−**e** were refined by the full-matrix least-squares technique against F^2 in anisotropic approximation for all non-hydrogen atoms with the SHELXL-97 program.[48] Iodines and nitrogenes in **7a** were refined in anisotropic full-matrix approximation, and carbons in an isotropic approximation. The absorption correlation for **7a,d** was carried out semiempirically.[49] The H atoms for **7b**−**e** were calculated and refined in an isotropic approximation. An absorption correction was applied using the SADABS program.[49] The main crystallographic data and some experimental details are given in Table 12. All inquiries about atomic coordinates for **7a**−**e**, bond lengths, and angles can be obtained on request from CCDC (ref nos. 222998−223002).

1,8-Bis(dimethylamino)-2,7-dilithionaphthalene (6a). A solution of Bu^{n}Li (1.07 mL, 1.6 mmol) in *n*-hexane was added

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TABLE 12. Experimental Parameters and Main Crystallographic Data for Compounds 7a−e

	compound				
	7a	**7b**	**7c**	**7d**	**7e**
empirical formula	$C_{14}H_{16}I_2N_2$	$C_{20}H_{26}N_2O_4$	$C_{16}H_{22}N_2S_2$	$C_{20}H_{34}N_2Si_2$	$C_{16}H_{22}N_2$
formula weight	466.09	358.43	306.48	358.67	242.36
crystal system	monoclinic	rhombic	monoclinic	monoclinic	monoclinic
space group	Cc	$P2_12_12_1$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a (Å)	29.528(7)	8.450(3)	8.452(3)	12.951(4)	8.327(5)
b (Å)	25.968(4)	10.353(4)	18.545(5)	13.422(4)	9.363(6)
c (Å)	16.720(4)	22.915(9)	11.165(3)	12.233(3)	35.90(2)
α (deg)	90	90	90	90	90
β (deg)	103.066(8)	90	110.302(9)	91.413(6)	96.51(1)
γ (deg)	90	90	90	90	90
U (Å^3)	12489(5)	2004.6(1)	1641.3(8)	2125.8(10)	2781(3)
Z	16	4	4	4	8
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.7103
D_c (g cm^{-3})	1.992	1.188	1.240	1.121	1.158
μ (cm^{-1})	2.008	0.083	0.317	0.171	0.068
reflections collected	9243	4450	5339	6535	11694
reflections unique	5251	2983	2978	4209	4564
with $[F_0 > 4\sigma(F_0)]$	2038	1664	932	2804	2690
no. of parameters ref	369	235	181	353	325
R (int)	0.077	0.051	0.054	0.061	0.075
$(2\theta)_{max}$, (deg)	54	60	54	60.06	55.56
ranges: h	$-37 \leq h \leq 31$	$-11 \leq h \leq 5$	$-10 \leq h \leq 7$	$-16 \leq h \leq 17$	$-10 \leq h \leq 10$
k	$-32 \leq k \leq 29$	$-12 \leq k \leq 14$	$-23 \leq k \leq 20$	$-18 \leq k \leq 8$	$-12 \leq k \leq 10$
l	$-7 \leq l \leq 21$	$-32 \leq l \leq 14$	$-10 \leq l \leq 14$	$-12 \leq l \leq 16$	$-46 \leq l \leq 32$

with stirring to a solution of bromide **5**[14] (300 mg, 0.81 mmol) in Et_2O (2 mL) under Ar at −20 °C. The resulting beige suspension of compound **6** was kept at −20 °C for 10 min and was used in subsequent reactions.

1,8-Bis(dimethylamino)-2,7-bis(bromomagnesio)naphthalene (6b). Magnesium powder (250 mg, 10.4 mmol; activated with iodine or 0.03 mL of dry *n*-butyl bromide) and Et_2O (3 mL) were placed into a flask equipped with a stirrer, a reflux condenser, and a dropping funnel with protection from atmospheric moisture. Then a solution of dibromide **5** (100 mg, 0.27 mmol) in Et_2O (3 mL) was added with vigorous stirring, and the reaction mixture was stirred and refluxed for 2−2.5 h until **5** was completely consumed (TLC control). The resulting greenish-yellow solution of Grignard reagent **6b** was used in subsequent conversions.

1,8-Bis(dimethylamino)-2,7-diiodonaphthalene (7a). A solution of I_2 in Et_2O was added portionwise to a suspension of compound **6a** (prepared from 100 mg of **5** as described above) at −20 °C until the brown color of iodine persisted. The reaction mixture was kept at −20 °C for 20 min, allowed to warm to room temperature and washed with 5% aqueous $Na_2S_2O_3$. The organic layer was separated, dried over Na_2SO_4, and concentrated to dryness. Recrystallization of the residue from methanol gave 83 mg (65%) of diiodonaphthalene **7a** as bright-yellow crystals. Perchlorate **7a**·$HClO_4$: colorless plates, mp 248 °C (dec, from MeCN). Anal. Calcd for $C_{14}H_{17}ClI_2N_2O_4$: C, 29.68; H, 3.02; N, 4.94; I+Cl, 51.06. Found: C, 29.82; H, 3.06; N, 4.96; I+Cl, 51.15.

The NMR ^1H of the crude reaction mixture also shows, in a quantity of 1/3 of that found for **7a**, the presence of **1,8-bis(dimethylamino)-2-iodonaphthalene** (**8a**), which was not isolated. NMR ^1H ($CDCl_3$, δ, ppm, J/Hz): 2.71 (s, 6H), 2.98 (s, 6H), 7.14 (m, 2H), 7.31 (t, 1H, $J = 7.66$), 7.40 (dd, 1H, $^3J = 7.98$, $^4J = 1.14$), 7.78 (d, 1H, $J = 8.58$).

1,8-Bis(dimethylamino)naphthalene-2,7-dicarbonic Acid Diethyl Ester (7b). Diethyl carbonate (0.6 mL, 4.95 mmol) was added in small portions to a suspension of lithium derivative **6a** (prepared from 600 mg of **5** as described above) at −20 °C. The reaction mixture was kept at −20 °C for 10 min, allowed to warm to room temperature, and poured into water. The ethereal layer was separated, and the aqueous layer was extracted with $CHCl_3$ (3 × 2 mL). The solvents were removed, and the residue was chromatographed. The first yellow fraction (R_f 0.75) was ester **7b**: yellow crystals, 430 mg (73%). IR (ν/cm^{-1}): 1700 (C═O); 1600, 1540, 1500 (ring).

Further elution afforded **1,8-bis(dimethylamino)-2-ethoxycarbonylnaphthalene** (**8b**): light-yellow transparent oil, 92 mg (20%). ^1H NMR ($CDCl_3$, δ, ppm, J/Hz): 1.40 (t, 3H, $^3J = 7.12$), 2.77 (s, 6H), 2.91 (s, 6H), 4.39 (quart, 2H, $^3J = 7.12$), 6.97 (br t, 1H, $J = 4.50$), 7.31 (m, 2H), 7.36 (d, 1H), 7.42 (d, 1H, $J = 8.3$).

1,8-Bis(dimethylamino)-2,7-bis(methylthio)naphthalene (7c). (Method A) To a stirred suspension of compound **6a** (prepared from 100 mg of **5** as described above) was added dimethyl disulfide (1.5 mL, 0.27 mmol) in one portion and at −20 °C. The resulting pure yellow solution was kept at −20 °C for 10 min, allowed to warm to room temperature, and poured into water (15 mL). The ethereal layer was separated, and the aqueous layer was extracted with $CHCl_3$ (3 × 3 mL). The solvents were removed, and the residue was ground with methanol (2 × 2 mL) yielding sulfide **7c** (74 mg, 90%) as yellow crystals. Tetrafluoroborate **7c**·HBF_4: colorless plates, mp 228−229 °C (dec, from H_2O). Anal. Calcd for $C_{16}H_{23}BF_4N_2S_2$: C, 48.78; H, 5.88; N, 7.11. Found: C, 48.97; H, 5.76; N, 7.02. The compound is oxidized on attempt to prepare the salt with chloric acid!

(Method B) A solution of Me_2S_2 (2 mL) in Et_2O (4 mL) was added dropwise with intense stirring to a solution of Grignard reagent **6b** (prepared as described above) at +5 °C. The suspension so formed was stirred at room temperature for 1 h and hydrolyzed with saturated aqueous NH_4Cl. After standard workup the residue was chromatographed and yielded 47 mg (57%) of compound **7c**, which was identical in properties to the pattern synthesized according to method A.

1,8-Bis(dimethylamino)-2,7-bis(trimethylsilyl)naphthalene (7d). Trimethylchlorosilane (3.6 mL, 28.3 mmol) was added at once to a suspension of compound **6a** (prepared from 600 mg of **5** as described above) at −20 °C. The reaction mixture was kept at −20 °C for 2 h and then at room temperature for 3 h and poured into water. The ethereal layer was separated, and the aqueous layer was made basic with ammonia and extracted with $CHCl_3$ (3 × 2 mL). The solvents were removed, and the residue was ground with MeOH (3 mL), filtered off, and recrystallized from EtOH to yield 63 mg (11%) of compound **7d** as greenish-yellow crystals. Perchlorate **7d**·$HClO_4$: colorless plates, mp 190 °C (dec, from EtOH). Anal.

Calcd for $C_{20}H_{35}ClN_2O_4Si_2$: C, 52.32; H, 7.68; Cl, 7.72; N, 6.10. Found: C, 52.40; H, 7.73; Cl, 7.89; N, 6.14.

1,8-Bis(dimethylamino)-2,7-dimethylnaphthalene (7e). Methyl iodide (0.5 mL, 8.3 mmol) was added in one portion to a suspension of compound **6a** (prepared from 306 mg, 0.82 mmol of **5** as described above) at −20 °C. The reaction mixture was vigorously stirred at room temperature for 10 min and then poured into water (15 mL). After standard workup and chromatography the yield of methylnaphthalene **7e** collected as yellow crystals was 122 mg (61%): Mp of tetrafluoroborate **7e**·HBF_4 (228−229 °C from H_2O) is in accordance with ref 4.

2,7-Dideiterio-1,8-bis(dimethylamino)naphthalene (7f). To a stirred suspension of compound **6a** (prepared from 288 mg, 0.77 mmol of **5** as described above) was added D_2O (99.8%, 0.4 mL, 21 mmol) in one portion at 0 °C. The reaction mixture was stirred intensely for 15 min at room temperature and poured into water (10 mL). After standard workup 164 mg (98%) of compound **7f** was obtained as light-cream crystals.

2,7-Di-*n*-butyl-1,8-bis(dimethylamino)naphthalene (7g). A solution of Bu^nLi (0.67 mL, 1.08 mmol) was added to a solution of dibromide **5** (200 mg, 0.54 mmol) in THF (2 mL) at −20 °C. The reaction mixture was kept at −20 °C for 20 min and then at room temperature for 1 h and poured into water (15 mL). Standard workup of the organic layer followed by chromatography afforded 97 mg (60%) of compound **7g** as transparent yellowish-brown oil. Anal. Calcd for $C_{22}H_{34}N_2$: C, 80.92; H, 10.50; N, 8.58. Found: C, 81.05; H, 10.43; N, 8.62. Perchlorate **7g**·$HClO_4$: colorless needles, mp 173−175 °C (dec, from H_2O). Anal. Calcd for $C_{22}H_{35}ClN_2O_4$: C, 61.89; H, 8.26; N, 6.56; Cl, 8.30. Found: C, 61.74; H, 8.36; N, 6.53; Cl, 8.44.

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Supporting Information Available: General experimental information, and crystallographic information files in cif format for structures **7a**−**e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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