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Concept of Superbasicity of 1,8-Bis(dialkylamino)naphthalenes (“Proton Sponges”)

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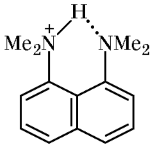
Abstract—Superbasic properties of naphthalene “protone sponges” are determined by the *p* character of the unshared electron pair on the nitrogen atom of the dialkylamino group and by distortion of the n,π^* conjugation.

The superbasic properties of 1,8-bis(dimethylamino)naphthalene were reported for the first time in 1968 by Alder and co-workers [1]. Its basicity constant turned out to be anomalously high (pK_{BH^+} 12.34) as compared. e.g., with *N*,*N*-dimethylaniline (pK_{BH^+} 5.15 [2]) or 1-dimethylaminonaphthalene (pK_{BH^+} 4.83 [2]). These findings aroused a great interest, as follows from numerous publications on this topic (see [3–6] and references therein) which is now considered to be an important field of modern organic chemistry [7].

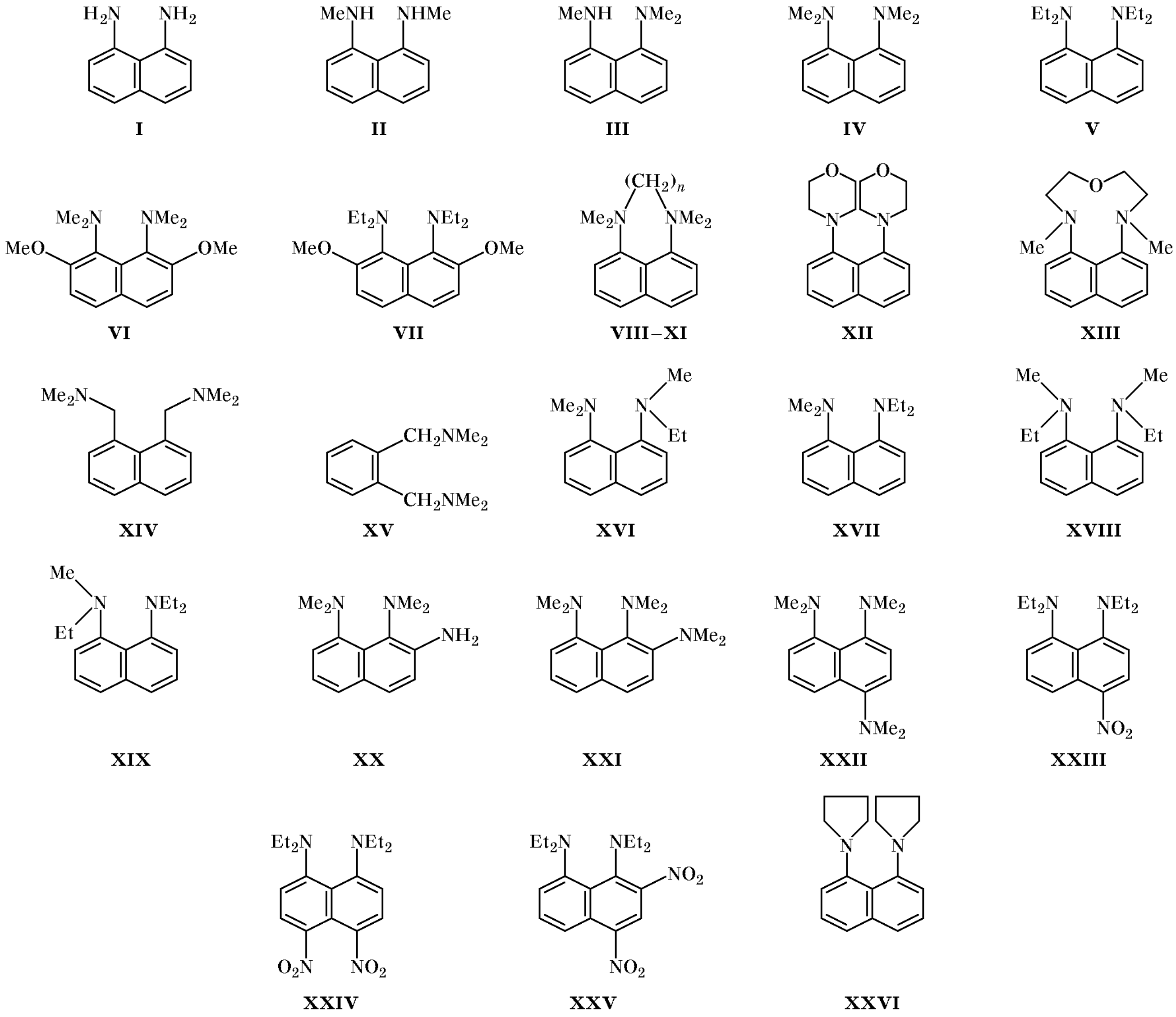
New compounds structurally related to 1,8-bis(dimethylamino)naphthalene have been synthesized (some structures are shown in Scheme 1), and the data on their reactivity and physical properties have been thoroughly reviewed [3–6]. The most attention was given to superbasic properties of such compounds. It was shown that they are characterized by high basicity and low rate of deprotonation of conjugate ammonium cations ($\ll 10^{10}$ $l\,mol^{-1}\,s^{-1}$; see table). The low rate of deprotonation was explained by formation of a strong hydrogen bond between the proton attached to one nitrogen atom and the other nitrogen. The formation of such bond is favored by spatially close arrangement of the dimethylamino groups, and its strength originates from the appearance of a six-membered H-chelate ring (see structure **A** below). The existence of monoprotonated proton sponges as structures like **A** is now considered to be the main factor responsible for their superbasic properties. The protonation and H-bonding ($\overset{+}{N}-H\cdots N$) reduces steric deformation intrinsic to the neutral diamine molecule due to repulsion of lone electron pairs of nitrogen atoms of the two nearby dimethylamino groups.


A

However, the decisive role of the $\overset{+}{N}-H\cdots N$ hydrogen bonding in superbasic properties of proton sponges does not follow unambiguously from detailed analysis of their basicity constants and hydrogen bond parameters, as well as from comparison with basicities of some amino- and methylamino-substituted naphthalene derivatives. The data given in table for compounds **I**–**IV** suggest that successive replacement of hydrogen in the *peri*-amino groups by methyl groups in going from **I** to **III** leads to gradual rise in their basicity, in keeping with the generally accepted views on the electron-donor effect of methyl group. When all hydrogens in the amino groups are replaced by methyl groups (compound **IV**), the basicity increases very sharply, by more than 7 log units.

Naturally, a question arises: if the formation of hydrogen bond is indeed crucial for the high basicity of compound **IV**, why its effect is observed only on exhaustive replacement of hydrogen by methyl groups in both amino groups? There is no doubt that hydrogen bond is also formed in protonated molecules **I**–**III** which exhibit normal acid–base properties like the other arylamines.

Scheme 1.



VIII, $n = 2$; **IX**, $n = 3$; **X**, $n = 4$; **XI**, $n = 5$.

The hydrogen bond in 1,8-diaminonaphthalenes can be characterized on a quantitative level by the distance between the nitrogen atoms. Depending on that distance, the H bond may be linear or may deviate from linearity (∠NHN 140–178°; see [3, 5] and references therein); correspondingly, such H bonds should differ in strength. No correlation was found [5] between pK_{BH^+} values and N···N distances in neutral and protonated forms of 1,8-bis(dimethylamino)naphthalene and its analogs. The lack of a relation between these parameters for protonated forms of proton sponges was also noted in [21].

Another quantitative parameter of a hydrogen bond may be deprotonation rate constant in the series of monoprotonated forms. Unfortunately, the available data do not allow us to select a series of compounds for which the basicity constants and deprotonation rates were measured under similar conditions. The values of *k* for 1,8-bis(dimethylamino)naphthalene (**IV**), measured in different solvents (see table), are of the same order of magnitude; therefore, they are comparable at least on a qualitative level.

The pK_{BH^+} and *k* values for compounds **IV**–**XI** change in the opposite directions. On the other hand, the same parameters for compounds **IV** and **XII**, as well as for **X** and **XI**, change in parallel, i.e., lower deprotonation rate constants correspond to lower basicity constants. In going from **XI** to **XIII**, the

Basicity constants pK_{BH^+} and deprotonation rate constants k of monoprotonated forms of proton sponges

Comp. no.	pK_{BH^+} (solvent)	k, l mol^{-1} s^{-1} (solvent)
I	4.61 (water) [1], 10.99 (MeCN) [8]	
II	5.61 (water) [1], 11.95 (MeCN) [8]	
III	6.43 (water) [1], 12.91 (MeCN) [8]	
IV	12.34 (water) [1], 12.10 (water) [9], 12.03 (water) [10], 12.00 (water) [11], 18.18 (MeCN) [12], 17.28 (MeCN) [13], 11.5 (20% dioxane) [9], 7.47 (DMSO) [11]	1.9×10^5 (water) [14], 2.9×10^5 (20% DMSO) [15], 6.1×10^5 (30% DMSO) [15], 4.5×10^5 (35% DMSO) [14], 4.6×10^5 (35% dioxane) [14]
V	12.7 (20% dioxane) [9], 18.95 (MeCN) [12]	1.6×10^4 (30% DMSO)
VI	16.3 (water) [16]	4.4×10^2 (60% DMSO) [16]
VII	16.6 (water) [16]	3.3 (60% DMSO) [16]
VIII	4.62 (water) [17]	5×10^7 (water) [17]
IX	10.27 (water) [17]	
X	13.6 (30% DMSO) [17]	4.7×10^5 (30% DMSO) [17]
XI	13.0 (30% DMSO) [17]	5.2×10^4 (30% DMSO) [17]
XII	7.49 (water) [18]	1.21×10^3 (water) [18]
XIII	12.9 (30% DMSO) [18]	6.2×10^3 (30% DMSO) [18]
XIV	18.26 (MeCN) [13]	
XV	18.75 (MeCN) [13]	
XVI	18.5 (MeCN) [19]	
XVII	18.7 (MeCN) [19]	
XVIII	18.7 (MeCN) [19]	
XIX	18.9 (MeCN) [19]	
XX	10.3 (DMSO) [20]	
XXI	9.0 (DMSO) [20]	
XXII	8.0 (DMSO) [20]	
XXIII	15.33 (MeCN) [12]	
XXIV	11.78 (MeCN) [12]	
XXV	15.50 (MeCN) [12]	
XXVI	10.00 (water) [17]	

deprotonation rate constant decreases by an order of magnitude, whereas pK_{BH^+} changes insignificantly. Thus, there are no clear trends in the variation of kinetic and thermodynamic parameters of proton sponges.

The basicity constants pK_{BH^+} of compounds **IV**, **XIV**, and **XV** were found [13] to vary in the opposite direction to the strength of hydrogen bond formed on their protonation (which was estimated by IR spectroscopy). Compound **XV** is the most basic, while the hydrogen bond therein is the weakest. On the other hand, the electron-donor effect of the dimethylamino group in **XV** on pK_{BH^+} and the electron-acceptor effect of the $Me_2\overset{+}{N}H$ group on the diprotonation constant (p$K_{BH^{2+}}$ 11.46) are stronger than analogous effects in compound **XIV**. Therefore, pK_{BH^+} of **XV** should be greater, and p$K_{BH^{2+}}$ should be smaller than the corresponding parameters of **XIV**. However, the diprotonation constant of **XIV** (p$K_{BH^{2+}}$ 11.43) is reduced, for monoprotonation gives rise to a stronger hydrogen bond. As a result, the diprotonation constants of **XIV** and **XV** are almost similar. Thus the basic properties of compounds **XIV** and **XV** are determined mainly by the electronic effects of substituents rather than by the strength of the $\overset{+}{N}-H\cdots N$ bond. It should also be noted that both mono- and diprotonation constants of diamines **XIV** and **XV** can readily be determined. The difference in their values (ΔpK_{BH^+} ~7 log units) is comparable with that typical of common amines (ΔpK_{BH^+} 3–5 log units). Due to formation of a strong hydrogen bond on monoprotonation, addition of the second proton to proton sponges is considerably hindered, the p$K_{BH^{2+}}$ value is very low (–9.0 [11]), and the difference between the first and the second protonation constants approaches ~20 log units. If the strength of hydrogen bond is estimated by the difference pK_{BH^+} – p$K_{BH^{2+}}$, the H bond in monoprotonated compound **IV** turns out to be much stronger than in **XIV** and **XV**, but the latter compounds are stronger bases.

Thus the above analysis casts doubt on the existing concept of the determining role of the $\overset{+}{N}-H\cdots N$ hydrogen bond in superbasic properties of 1,8-bis(dimethylamino)naphthalene and its analogs. In the present article we propose a different explanation for the high basicity of proton sponges.

According to Edwards and Pearson [22], basic properties of organic compounds are determined mainly by structural features of the corresponding neutral molecules. From this viewpoint, replacement of all hydrogen atoms in amino groups by methyl radicals should lead to drastic changes in the structure of these groups and of the molecule as a whole, which are responsible for the anomalously high basicity of proton sponges. Study of the equilibrium $BH^+ + OH^- \rightleftharpoons B + H_2O$ [where B is 1,8-bis(dimethylamino)naphthalene] showed [23] that the rate of deprotonation of conjugate acid BH^+ is lower than the rate of deprotonation of common anilines, while the rate of proton addition is comparable with the corresponding values for less basic compounds (by 5 log units); i.e., no specific features were observed in the protonation. These data suggest that basic properties of 1,8-bis(dimethylamino)naphthalene are determined by the same factors (inductive, conjugation, and steric effects) as for the other *N*,*N*-dialkylarylamines.

In keeping with the data of [24–28], the effect of *N*-alkyl groups on the basicity constants of aliphatic and aromatic amines is determined mainly by steric factor. Sterically (rather than electronically) induced $sp^3 \rightarrow sp^2$-rehybridization of atomic orbitals of the nitrogen atom leads to increase in the *p*-character of the lone electron pair and anomalous change of basic properties. For example, the ~sp^3-hybridized nitrogen atom in aniline [29–32] becomes sp^2-like in *N*,*N*-dimethylaniline [32–34], which favors considerable increase of the π-character of its lone electron pair [35]. Such structural variations enhance conjugation between the dimethylamino group and π-system of the benzene ring [36, 37]. Nevertheless, the basicity of *N*,*N*-dimethylaniline is greater than the basicity of aniline, for the rehybridization effect prevails over delocalization [35]. Here, as with other aliphatic and aromatic amines having alkyl groups on the nitrogen, almost no electron-donor (+*I*) effect of the methyl groups is observed [26–28].

In view of the above stated it was important to elucidate the role of the state of the nitrogen lone electron pair (LEP) in 1,8-bis(dimethylamino)naphthalene as compared to anilines. Platts *et al.* [38] estimated the state of LEP through the charge density thereon. As follows from the values given for ammonia (0.5803), methylamine (0.5931), dimethylamine (0.6021), trimethylamine (0.6083), and 1,8-bis(dimethylamino)naphthalene (0.5996), the latter occupies an intermediate place between methylamine and dimethylamine. Had the basicity constant of 1,8-bis(dimethylamino)naphthalene depended only on the charge density, it would be intermediate between pK_{BH^+} for methylamine (10.62 [2]) and dimethylamine (10.76 [2]), i.e., ~10.7 log units. This value is sufficiently high, though it is slightly lower than the experimental one (ΔpK_{BH^+} 1.64). The nitrogen LEP of trimethylamine is characterized by the largest charge density, as compared to methylamine and dimethylamine; therefore, triethylamine should be the strongest base. However, the experimental data show the opposite pattern: trimethylamine is the least basic among methylamines (pK_{BH^+} 9.77 [2]). Furthermore, the nitrogen LEP of *N*,*N*-dimethylaniline has a charge density of 0.6125 (i.e., the largest among those given above) [38], but its basicity constant is as low as 5.15 [2]. Therefore, no correlation exists between pK_{BH^+} and charge density on the nitrogen LEP.

According to [28], a relation between the basicity constants and charges on the nitrogen atom is possible only for amines in which hybridization of the nitrogen atom does not change. Otherwise, i.e., for amine series where rehybridization of the nitrogen AOs occurs under the influence of various factors, we can speak about only on parallelism in the variation of the above quantities. When hybridization of the nitrogen atom is not fixed, the basicity constants of amines correlate better with the *p*-character of the nitrogen LEP [25, 27].

The $C_{Ar}NC^1$ and $C_{Ar}NC^2$ bond angles (C^1 and C^2 are the methyl carbon atoms) in 1,8-bis(dimethylamino)naphthalene are 117.1 and 118.5° [38] (the corresponding values calculated *ab initio* are 117.5 and 119.1°), indicating that the hybridization of the nitrogen atoms approaches sp^2. This means that the *p*-character (*p*) of their lone electron pairs is fairly high. The calculation according to the procedure reported in [25], assuming that the C^1NC^2 angle is 111.5° [28], gives $p = 0.907$. This value is the largest among those found [25] for ammonia (0.690), methylamine (0.770), dimethylamine (0.786), and trimethylamine (0.728); therefore, the basicity constant of proton sponge should also be the largest. The following correlation was found for the basicity constants and *p*-characters of the nitrogen LEP for the series ammonia, methylamine, dimethylamine, trimethylamine, and 1,8-bis(dimethylamino)naphthalene:

$$pK_{BH^+} = -(0.64 \pm 0.64) + (14.40 \pm 0.83)p;$$
$$n = 5,\ s = 0.14,\ r = 994.$$

In terms of the above, some structural features of the neutral molecule and monoprotonated form of 1,8-bis(dimethylamino)naphthalene [3–6] can be understood more clearly. Considerable flattening of the nearby dimethylamino groups enhances their mutual repulsion. The steric repulsion is supplemented by the Coulomb repulsion due to high charge density on the nitrogen atoms, so that the neutral molecule of proton sponge is structurally destabilized. According to the X-ray diffraction data [39], the dimethylamino groups in **IV** deviate from coplanarity with the naphthalene system. The degree of conjugation between the dimethylamino groups and the aromatic π-system can be estimated from ε_{max} values corresponding to the n,π^*-electron transition (λ_{max} 336 nm in hexane). Better conjugation with dimethylamino group than with amino is characterized by greater ε_{max} value: 8600 $l\,mol^{-1}\,cm^{-1}$ for aniline [37] and 15800 $l\,mol^{-1} \times cm^{-1}$ for *N*,*N*-dimethylaniline [37]. Some distortion of conjugation with diisopropylamino group is accompanied by decrease of ε_{max} to 9600 $l\,mol^{-1}\,cm^{-1}$ [37]. In going from 1,8-diaminonaphthalene (ε_{max} = 9450) to 1,8-bis(dimethylamino)naphthalene (ε_{max} = 8300 $l\,mol^{-1} \times cm^{-1}$) the parameter ε_{max} does not increase, as might be expected by analogy with *N*,*N*-dialkylanilines [37], but decreases. This fact indicates essential loss of conjugation between the dimethylamino groups and naphthalene π-system. As a result, the basicity of 1,8-bis(dimethylamino)-naphthalene becomes comparable to that of alkylamines. For example, steric repulsion of branched isopropyl groups considerably increases bond angles at the nitrogen atom in triisopropylamine (up to 115.7° [27]); this value is close to the bond angles in proton sponges. Correspondingly, the *p*-character of the nitrogen LEP increases, and the basicity constant of triisopropylamine (pK_{BH^+} 11.86 [25]) approaches the values typical of proton sponges. Methylamine and dimethylamine in acetonitrile (pK_{BH^+} 18.37 and 18.73, respectively [40]) are even more basic than proton sponges.

Protonation of proton sponges leads to $sp^2 \rightarrow sp^3$-rehybridization of the nitrogen AO (the nitrogen atom in protonated amines is always sp^3-hybridized [41]). In the protonated form only one dimethylamino group can be planar. Therefore, the repulsion between the neutral and protonated dimethylamino groups becomes considerably weaker, and the N–N distance shortens from 2.79 Å in the neutral molecule to 2.60–2.55 Å [3]. An attractive interaction thus appears, which is favored by formation of the $\overset{+}{N}-H\cdots N$ hydrogen bond due to high *p*-character of LEP of the nonprotonated nitrogen atom [42]. It remains unclear (see [6] and references therein) whether the $\overset{+}{N}-H\cdots N$ hydrogen bridge in proton sponges is symmetrical or not. Assuming that $sp^2 \rightarrow sp^3$-rehybridization of the nitrogen AO, occurring on protonation, increases the *s*-character of the $\overset{+}{N}-H$ bond (i.e., it becomes shorter and stronger), the hydrogen atom should be located closer to one nitrogen atom, i.e., the H bond should be unsymmetrical.

The lone electron pair on the nitrogen atom in *N*,*N*-dimethylaniline is characterized by not only the largest (compared to methylamines) charge density (0.6080 [38]) but also the highest *p*-character (0.920 [35]). At the same time, *N*,*N*-dimethylaniline is the weakest base in this series. The reason is delocalization of the nitrogen LEP over the benzene ring due to its high *p*-character and especially due to coplanar arrangement of the dimethylamino group with respect to the benzene ring (see [43] and references therein).

The significance of the latter factor for basic properties of *N*,*N*-dialkylanilines can be illustrated with *N*,*N*-diisopropylaniline as an example. The presence of bulky isopropyl radicals makes the amino group considerably more flattened than those in amines with unbranched alkyl groups. The hybridization of the nitrogen atom becomes closer to sp^2 [35–37], and the *p*-character of its LEP increases. On the other hand, the diisopropylamino group insignificantly deviates from the benzene ring plane [37, 43] for steric reasons, and the degree of delocalization of the nitrogen LEP over the aromatic ring is somewhat reduced. According to [36], the conjugation between the π-system of the benzene ring and diisopropylamino group (σ_R^0 = –0.52) is stronger than for amino group (σ_R^0 = –0.47) but weaker than for dimethylamino group (σ_R^0 = –0.54). The basicity constant of *N*,*N*-diisopropylaniline (pK_{BH^+} 8.20 [37]) is considerably greater than the basicity of aniline (by 3.6 log units).

A conclusion can be drawn that high *p*-character of the nitrogen LEP in combination with even insignificant reduction of the degree of its delocalization over the benzene ring considerably increases the basicity of such arylamine. Therefore, superbasic properties of 1,8-bis(dimethylamino)naphthalene originate from the high *p*-character of the lone electron pair on the nitrogen atom, on the one hand, and distortion of coplanarity between the protonated dimethylamino group and naphthalene core, on the other. This statement is supported by the high basicity of compounds **XIV** and **XV** in which the dimethylamino groups and the aromatic system are separated by methylene units which hamper effective conjugation. As a result, the hybridization of the nitrogen AOs and its LEP should be similar to that typical of aliphatic amines. Therefore, the basicities of these compounds should also be similar, as is the real case (cf. pK_{BH^+} values for compounds **XIV** and **XV** and methylamines).

The effect of the above two factors on the basicity of proton sponges is also obvious from comparison of pK_{BH^+} values of compounds **VIII**–**XI**. The nitrogen atoms in molecule **VIII** are separated by two CH_2 units whose position with respect to the naphthalene ring plane is rigidly fixed. The conjugation between the amino groups and the naphthalene π-system is not broken, and the basicity constant of compound **VIII** is relatively low and is comparable with the basicity constant of 1-dimethylaminonaphthalene (pK_{BH^+} 4.83 [2]) in which the conjugation with the dimethylamino group is also retained. As the number of methylene units in the $N(CH_2)_nN$ bridge rises (compounds **IX**–**XI**), rotation of the methylamino group due to steric repulsion becomes possible. As a result, the conjugation with the naphthalene π-system weakens, and the basicity increases.

As shown in [28, 35, 37], ethyl groups on the nitrogen make the amino group more flattened (as compared to methyl groups) and provide greater increase in the *p*-character of the nitrogen LEP; naturally, this is reflected in the basicity constants (cf. pK_{BH^+} of aniline, 4.60 [2], *N*,*N*-dimethylaniline, 5.15 [2], and *N*,*N*-diethylaniline, 6.57 [2]). Therefore, in going from 1,8-bis(dimethylamino)naphthalene (**IV**) to 1,8-bis(diethylamino)naphthalene (**V**), as well as on successive replacement of methyl groups in **IV** by ethyl (compounds **XVI**–**XIX**) increase of pK_{BH^+} must be expected.

Comparison of the basicity constants of compounds **IV**–**VII** and also of **XX** and **XXI** shows that +*M*-substituents (such as MeO, NH_2, and NMe_2) in the *ortho*-position considerably increase basic properties of proton sponges. This was explained [20] by the “boosting effect” which has an electrostatic rather than steric origin. We believe that the influence of *ortho*-substituents can be rationalized in a different way without resorting to “new effects.”

It has long been known [44] that in some reaction series there is no polar conjugation with +*M*-substituents located in the *ortho*-position with respect to the reaction center, but logarithms of the equilibrium and rate constants are linearly related to the inductive constants of those substituents. This is the result of steric hindrance to conjugation owing to distortion of coplanarity of *ortho*-substituted phenyl group with the reaction center [44]. In this respect, naphthalene proton sponges are unique models: the conjugation between the dimethylamino groups and the naphthalene system is broken even in unsubstituted molecule. Therefore, these compounds are more sensitive to *ortho*-substitution which leads to further disruption of coplanarity. According to the data of [44], even such *ortho*-substituents as halogens are capable of notably hindering conjugation.

As shown above with *N*,*N*-diisopropylaniline as an example, the basicity considerably increases due to insignificant loss of conjugatuion with the diisopropylaminogroup in which the lone electron pair on the nitrogen has a high *p*-character. Insofar as the *p*-character of the nitrogen LEP in proton sponges is also high, a stronger disruption of conjugation with the dimethylamino groups, caused by *ortho*-substituents, should increase the basicity to a greater extent. Assuming that the effect of *ortho*-substituents in proton sponges has an inductive origin, the higher basicity of *ortho*-amino derivative **XX**, as compared to *ortho*-dimethylamino-substituted proton sponge **XXI** can readily be explained: the inductive electron-acceptor effect of the amino group (σ_I^0 = 0.09 [44]) is weaker than that of the dimethylamino group (σ_I^0 = 0.19 [44]).

According to [44], the same +*M*-substituents in the *para*-position give rise to a strong polar conjugation with the reaction center. The difference in pK_{BH^+} between compound **IV** and *para*-substituted analog **XXII** is as small as 0.5 log unit, i.e., it is much smaller than could be expected. A possible reason is that the interaction between two dimethylamino groups in the *para*- and *peri*-positions is weakened due to loss of coplanarity between the dimethylamino group and the naphthalene system in compound **XXII**. Obviously, the same factor is responsible for the weak effect of the *para*-nitro group in 1,8-bis(diethylamino)-4-nitronaphthalene (**XXIII**), ΔpK_{BH^+} = 3.62. The effect of the second *para*-nitro group (compound **XXIV**) is almost the same, ΔpK_{BH^+} = 3.55 log units. For comparison, in going from *N*,*N*-diethylaniline (pK_{BH^+} 6.57 [2]) to its *para*-nitro analog (pK_{BH^+} 1.75 [2]), the basicity decreases by 4.82 log units.

The effect of a nitro group in the *ortho*-position (compound **XXV**) seems to be even more surprising; the basicity constant of **XXV** is slightly greater than that of *p*-nitro analog **XXIII** (see table). Presumably, in this case factors responsible for anomalous basic properties of proton sponges (such as flattening of the diethylamino group, increased *p*-character of the nitrogen LEP due to steric effect of alkyl radicals and electron-acceptor effect of the nitro group, and stronger distortion of conjugation with the diethylamino group due to steric effect of the *ortho*-nitro group) are more powerful than the effect of the second nitro group.

In going from *N*-phenylmorpholine (pK_{BH^+} 3.20 [2]) to 1,8-dimorpholinonaphthalene (**XII**) the basicity increases to a lesser extent (ΔpK_{BH^+} 4.3). Unlike the proton sponges considered above, the nitrogen atoms in *N*-phenylmorpholine and compound **XII** have sp^3 configuration [45] which is fixed by their cyclic structure. Taking into account the lack of delocalization of the lone electron pairs over the naphthalene ring, the basicity of 1,8-dimorpholinonaphthalene should be comparable with the basicity of *N*-alkylmorpholines. In fact, the pK_{BH^+} values of *N*-methyl- and *N*-ethylmorpholines are 7.38 and 7.67 [2], respectively.

The same is also true of the other naphthalene proton sponges in which the nitrogen atoms of the *peri*-substituents are incorporated in a cyclic fragment. For instance, the basicity constant of 1,8-bis(1-pyrrolidinyl)naphthalene (**XXVI**) is close to that found for *N*-methylpyrrolidine (pK_{BH^+} 10.36 [2]).

Unlike 1,8-dimorpholinonaphthalene, the state of the nitrogen atom in compound **XIII** is not fixed by a cyclic structure. As in the other proton sponges, the nitrogen hybridization in **XIII** approaches sp^2; therefore, the *p*-character of the nitrogen LEP is sufficiently high, and the basicity of **XIII** is also high.

Thus, the anomalously high basicity of 1,8-bis(dimethylamino)naphthalene and its analogs is determined by two main factors: (1) sp^2-like hybridization of the nitrogen atoms of the dimethylamino groups and hence high *p*-character of the lone electron pairs and (2) rupture of conjugation between the dimethylamino group and the naphthalene π-system. We believe that the role of intramolecular hydrogen bond is secondary.

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