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The basicity of 1,8-bis(dimethylamino)naphthalene and the hybrid state of the nitrogen atoms of its dimethylamino groups

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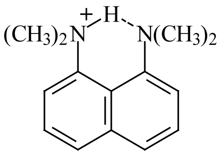
Abstract—The superbasic properties of 1,8-bis(dimethylamino)naphthalene and its analogues are the result of mainly two factors: violation of conjugation of the dimethylamino group with the π-system of the naphthalene rings and high p-character of the nitrogen lone electron pair. © 2002 Elsevier Science Ltd. All rights reserved.

A number of aromatic amines are known to have unusually high basic properties, for example 1,8-bis-(dimethylamino)naphthalene. The value of its basicity constant[1] ($pK_a = 12.34$) is ~ 7 orders higher than those for aniline[2] ($pK_a = 4.60$), *N*,*N*-dimethylaniline[2] ($pK_a = 5.15$) and 1-dimethylaminonaphthalene[2] ($pK_a = 4.83$).

Most researchers[3–5] correlate the manifestation of the uniquely high basic properties of these compounds to formation on monoprotonation of a strong hydrogen bond N^+–H...N (Scheme 1). The protonated molecule becomes more stabilized due to a decrease in steric deformation caused by repulsion of the lone pairs of the nitrogen atoms in the two closely arranged dimethylamino groups.

On the other hand, there are data in literature, which make doubtful the role of H-bonding in the superbasic properties manifested by 'proton sponges'. Thus, it has been shown[4] that the expected correlation between basicity constants and the distances between the nitrogen atoms of the dialkylamino groups is not realised.



Scheme 1.

There is another example of this phenomenon. Successive substitution of the hydrogen atoms of the amino groups of 1,8-diaminonaphthalene with methyl groups causes a step-by-step increase of the basicity[1] constants (4.61; 5.61; 6.43), but a very sharp rise is noticed when all the hydrogen atoms are substituted. If such a strong increase of pK_a in the latter case is linked to N^+–H...N hydrogen bond formation, why is such a considerable effect only manifested after total substitution of the hydrogen atoms of the amino groups and not observed at partial substitution?

In this paper we present our understanding of the reasons for the superbasic properties of 1,8-bis-(dimethylamino)naphthalene and its analogues.

While studying the equilibrium $BH^+ + OH^- \Leftrightarrow B + H_2O$ for 1,8-bis(dimethylamino)naphthalene[6] it has been established that the rate of deprotonation of a conjugated acid BH^+ compared to the rate of more normal anilines is slowed down and at the same time the proton addition proceeds at rates similar to bases with pK_a's weaker by 5 units, i.e. there is no peculiarity in the protonation reaction.

This fact allowed us to conclude that the basic properties of 1,8-bis(dimethylamino)naphthalene are determined by the same factors (i.e. inductive, conjugative and steric effects) as for other *N*,*N*-dialkylaryls, and additionally the superbasicity, is related to major changes in the structure of the molecule which are taking place only after substitution of all the amino group hydrogen atoms with methyl groups.

Keywords: amines; proton sponges; basicity; hybridization.

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It is generally accepted that the basic properties of nitrogen compounds are due to the electron lone pair on the nitrogen atom. It has been shown[7–10] that the basicity constant values of alkyl- and arylamines are determined by the p-character (p) of the lone pair. It has been established that the electron-donor inductive effect (+I) of alkyl groups located near the nitrogen atom is not manifested in the basicity constants of amines, however, their steric effect is dominating. As a result $sp^3 \rightarrow sp^2$-rehybridisation of the nitrogen atom orbitals takes place and the p-character of the electron lone pair is increased. Thus, under the effect of methyl groups, the sp^3-hybridised nitrogen atom in aniline,[11] becomes closer to an sp^2-hybrid in *N*,*N*-dimethylaniline.[11] The latter facilitates a considerable increase in the p-character,[11] resulting in a considerable increase in the conjugation of the dimethylamino group with the π-system of the benzene ring.[11,12] The basicity of *N*,*N*-dimethylaniline compared to aniline is nevertheless increased but at the expense of the prevailing rehybridisation effect upon the delocalisation effect.[12]

Under the effects of an isopropyl group the nitrogen atom hybridisation in *N*,*N*-diisopropylaniline becomes closer to sp^2 and the p-character of the lone pair is more pronounced. At the same time, a diisopropylamino group is brought out[9] of the plane of the benzene ring, hence the degree of electron lone pair delocalisation upon the ring is decreased. According to data[9,13] conjugation of this group with the π-electron system of the benzene ring ($\sigma^0_{\mathrm{R}} = -0.52$) is higher than in the case of an amino group ($\sigma^0_{\mathrm{R}} = -0.47$), but lower than a dimethylamino group ($\sigma^0_{\mathrm{R}} = -0.54$). In this case, the basicity of *N*,*N*-diisopropylaniline is 3.6 pK_a units higher than aniline.

Hence, if an electron lone pair of a nitrogen atom of a dialkylamino group has a high p-character and its conjugation with a ring π-system is decreased, the basicity of such an arylamine can be considerably increased.

According to X-ray analysis data[14] the coplanarity of dimethylamino groups is violated compared to naphthalene rings in 1,8-bis(dimethylamino)naphthalene. The values of the nitrogen atom valency angles [measured $C_{Ar}NC_1$ and $C_{Ar}NC_2$ (C_1 and C_2-carbon atoms of methyl groups) at 117.5° and 118.5° and calculated ab initio values (117.5° and 119.1°)][15] show that nitrogen atom hybridisation is close to sp^2 and that the p-character of the electron lone pair should be rather high. Calculation[8] (the value of 111.5° was used for the C_1NC_2 angle) gives a value of 0.907 p-character. Having compared this value with the values of p in ammonia (0.690), methyl- (0.770), dimethyl- (0.786), and trimethylamines (0.728) it can be seen that it is the highest, therefore the basicity constant should be the highest too. The correlation equation, connecting basicity constants with the p-character of an electron lone pair of a nitrogen atom for the series ammonia; methyl-; dimethyl-; trimethylamine and 1,8-bis(dimethylamino)-naphthalene, is as follows:

$$pK_a = (-0.69\pm0.64)+(14.40\pm0.83)\ p;\ \text{for } n=5;\ S_0 = 0.14;\ r = 0.994$$

Some structural peculiarities of neutral and monoprotonated structures of molecules of 1,8-bis(dimethylamino)naphthalene become more understandable from this point of view.

Thus, a considerable planarity of the structure with dimethylamino groups too close to each other enhances a repulsive interaction between them. Coulombic interaction enhances steric repulsion because of the high charge density. As a result, to use the molecule of this ‘proton sponges’ is structurally destabilised.

On protonation of 1,8-bis(dimethylamino)naphthalene $sp^2 \rightarrow sp^3$-rehybridisation of the atomic orbitals of nitrogen of the protonated dimethylamino group takes place (in protonated amines the nitrogen atom is always sp^3-hybridised[16]). Only one of the dimethylamino groups now has a planar structure which considerably decreases the repulsion between the neutral and protonated dimethylamino groups, and as a result,[3,4] the distance between them is decreased from 279 pm (neutral molecule) to 260–255 pm. Moreover, up until now, there was no precise data[5] on whether a N^+–H...N hydrogen bridge is symmetrical or asymmetrical in ‘proton sponges’. Concluding that as a result of the $sp^2 \rightarrow sp^3$-rehybridisation of nitrogen atomic orbitals on protonation, the N^+–H bond acquires a higher s-character and becomes stronger and shorter, so it is evident that a proton will be closer to the protonated nitrogen atom, i.e. the N^+–H...N bridge is asymmetrical.

Thus, the superbasic properties of 1,8-bis(dimethylamino)naphthalene and its analogues are the result of two factors: violation of conjugation of a dimethylamino group with the π-system of the naphthalene rings and the high value of the p-character of the nitrogen electron lone pair.

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References

1. Alder, R. W.; Bowman, P. S.; Steele, W. R. S.; Winterman, D. R. *J. Chem. Soc.*, *Chem.Commun*. **1968**, 723–724.
2. Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution*; Butterworths: London, 1964; pp. 13–95.
3. Staab, H. A.; Saupe, T. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 865–1008.
4. Llamas-Saiz, L; Foces-Foces, C.; Elguero, J. *J. Mol. Struct*. **1988**, *328*, 297–323.
5. Pozharskii, A. F. *Uspechi Khimii*. **1998**, *67*, 3–27 [*Russ. Chem. Rev*. **1998**, *67*, Engl. Trans.].

6. Hibbert, F. *J. Chem. Soc., Chem. Commun.* **1973**, 463–464.
7. Korzhenevskaya, N. G.; Mestechkin, M. M.; Matveev, A. A. *Zh. Obshch. Khim.* **1992**, *62*, 626–628 [*Russ. J. Gen. Chem.* **1992**, *62*, Engl. Trans.].
8. Korzhenevskaya, N. G. *Ukr. Khim. Zh.* **1994**, *60*, 193–198 [*Ukr. Chem. J.* **1994**, *60*, Engl. Trans.].
9. Korzhenevskaya, N. G. *Reakts. Sposobn. Org. Soed.* **1988**, *25*, 159–164 [*Org.React.* **1988**, *25*, 170-175, Engl. Trans].
10. Korzhenevska, N. G. *Dokl. Akad. Nauk UkSSR.* **1993**, *9*, 123–126.
11. Aroney, M. J.; Le Fevre, R. J. W. *J. Chem. Soc.* **1956**, 2775–2778.
12. Korzhenevskaya, N. G.; Mestechkin, M. M.; Chotii, K. Ju.; Abdusalamov, A. B.; Ulanenko, K. B.; Rybachenko, V. I. *Zh. Obshch. Khim.* **1992**, *62*, 1148–1150 [*Russ. J. Gen. Chem.* **1992**, *62*, Engl. Trans.].
13. Korzhenevskaya, N. G.; Titov, E. V.; Chotii, K. Ju.; Chekhuta, V. G. *Zh. Org.Khim.* **1987**, *23*, 1228–1230 [*J. Org. Chem. USSR* **1987**, *23*, Engl. Trans.].
14. Einspahr, H.; Robert, J. B.; Marsh, R. E.; Roberts, J. D. *Acta Crystallogr.* **1973**, *B29*, 1611–1615.
15. Platts, J. A.; Howard, S. T.; Wozniak, K. *J. Org. Chem.* **1994**, *59*, 4647–4651.
16. Freuer, W. *Z. Chem.* **1981**, *44*, 58.