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# THEORETICAL STUDY OF PROTON TRANSFER FOR 1,8-BIS(N,N-DIMETHYLAMINO)NAPHTHALENE (DMAN) BY HYPERCHEM PROGRAM

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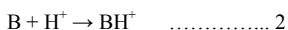
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**ABSTRACT:** Proton Sponge, 1,8-bis(N,N-dimethylamino)naphthalene, was optimized and studied as a strong base to find the ability for N-to-N proton transfer and the effect of adding substituents groups to Proton Sponge considering it as a original compound. All calculations, Total Energy, Energy of Transition State, Proton Affinity, Microwave Frequency and Intensity have been carried out by using HyperChem8.0 package. The most effect on increase Proton Affinity appeared by adding methyl group at para while the most effect on decrease it by adding fluoride at meta. In same time adding (O-(C=O)-O-Phenyl) group at para have the most effect on increase Energy of Transition State while adding chloride at para have the most effect on decrease it.

## 1. INTRODUCTION

1,8-Bis(dimethylamino) naphthalene is a chemical compound that was first prepared in 1968 by Roger Alder FRS at the University of Bristol [1]. It is often referred by the trade name Proton Sponge (PS for short), Sigma-Aldrich [2]. This compound is a diamine in which the two dimethyl amino groups are attached on the same side or peri position of a naphthalene system. Spectroscopic properties and very high basicity are interesting properties of Proton sponge [3]. With a pKa of 12.1, for its conjugate acid in aqueous solution, 1,8-bis(dimethylamino) naphthalene is one of the strongest amine bases known, although it only absorbs protons slowly—hence the trade name. The high basicity is attributed to the relief of strain upon protonation and/or the strong interaction between the nitrogen ion pairs [4].

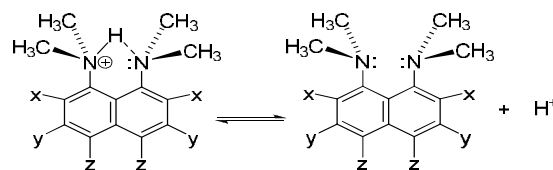
However, the molecule is sterically hindered, making it a weak nucleophile. Because of this combination of properties, it has been used in organic synthesis as a strong base and a highly selective non-nucleophilic base [5]. The spectroscopic properties of Proton-sponge are very interesting for researchers of molecular chemistry and have been researched for a long time. Proton-sponge emits a double fluorescence in various solutions due to the mixture of two ground-state species [6]. The proton affinity of an anion or of a neutral atom or molecule is a measure of its gas-phase basicity. The energy released in the following reactions [7]:



Moving the proton from one N to the other is a chemical reaction, although a subtle one. This type of proton transfer may be similar to how protons are transferred in enzyme active sites [8]. In this work the Compute, Transition State function in HyperChem has been used to automatically locate the highest energy point along the proton transfer path, by comparing Transition State of PS with Transition State of PS<sup>+</sup> after adding organic groups to find the effect of this groups on Proton Affinity for PS.

## 2. COMPUTATIONAL DETAILS

The MO calculations were carried out by the Austin Model 1 (AM1) semiempirical method [9], implemented in the HyperChem8.0 package [10]. Adding substituted and conjugate acids following the order in scheme 1 and table 1.



Scheme 1 : Substituted groups positions and formation of conjugate acids

Transition state by making reaction has been found with set Lambda value to 0.51 and estimate of the transition state as kind of an average of the reactant and product ion structures. After that setting of the R. M. S. gradient done to about 0.001 and the max number of cycles to 500 or more. After that Energy of Transition State ( $E_{TS}$ ) and compute vibrations has been getting by calculating of single point in HyperChem8.0 package.

Compounds	X	Y	Z
Original compound	H	H	H
C 1	F	H	H
C 2	H	F	H
C 3	H	H	F
C 4	CH <sub>3</sub>	H	H
C 5	H	CH <sub>3</sub>	H
C 6	H	H	CH <sub>3</sub>
C 7	Cl	H	H
C 8	H	Cl	H
C 9	H	H	Cl
C 10	H	H	O-O-Phenyl
C 11	H	H	O-CH <sub>3</sub> -O- Phenyl
C 12	H	H	O-(C=O)-O- Phenyl

Table 1 : Substituted groups positions with PS

### 3. RESULT

The strong basicity of PS is due (in part at least) to the way of N atoms to stabilize  $H^+$  of the acid form by forming a strong hydrogen bond. This hydrogen bond decreases the acidity of the acid form, leading to the high pKa [11]. Perhaps it is also true that the basic form is destabilized by repulsion between the N non-bonding electrons. This happens because the two dimethyl amino groups are oriented "face-to-face" in order to minimize the steric interference of the attached methyl groups [12].

In table 2, Total Energy ( $E_{Total}$ ) for PS and for all compound that suggested with different groups and Proton Affinity for all compound has been calculated. From table 2, Adding fluoride (F) to PS will decrease PA (Proton Affinity) following the order  $m < p < o$ , chloride (Cl) will decrease PA following the order  $m < o < p$ , methyl ( $CH_3$ ) will increase PA following the order  $o < m < p$ , adding groups as (O-O-Phenyl) will increase PS basicity, (O- $CH_3$ -O-Phenyl) will decrease PS basicity and adding groups as (O-(C=O)-O-Phenyl) will decrease PA but less than (O-O-Phenyl) do. Comparing with all fluoride at meta was the lost basicity and methyl at para was the biggest basicity.

Compounds	$E_{Total}$ Compound Kcal / mol	$E_{Total}$ Conjugated Acid Kcal / mol	PA Kcal / mol
P S	56559.2	56737.9	178.7
C1	78298.3	78474.5	176.2
C2	78301.9	78472.7	170.8
C3	78297.3	78471.3	174.0
C4	63741.1	63920.2	179.1
C5	63748.2	69328.2	180.0
C6	63738.3	63919.7	181.4
C7	73162.4	73336.8	174.4
C8	73168.2	73341.2	173.0
C9	63157.8	73333.0	175.2
C10	12389.5	12407.4	179.0
C11	13122.0	13139.3	173.0
C12	14471.8	14489.5	177.0

Table 2 :  $E_{Total}$  and PA for PS and Substituted groups with PS

Moving the proton from one N to the other is a chemical reaction, although a subtle one. This type of proton transfer may be similar to how protons are transferred in enzyme active sites [13], i.e. along a pre-formed hydrogen bond between two ideally oriented bases. For these symmetric amines the barrier height for the forward and reverse reactions are identical. It's not obvious if the proton transfer should be very easy (low barrier) or more difficult (high barrier) for these kinds of compounds compared to "normal" acid-base reactions [14].

From table 3, Adding fluoride (F) to PS will increase  $E_{TS}$  following the order  $p < m < o$ , chloride (Cl) will increase  $E_{TS}$  following the order  $p < o < m$ , methyl ( $CH_3$ ) will increase  $E_{TS}$  following the order  $p < o < m$ , adding groups as (O-O-Phenyl) will increase  $E_{TS}$  in large amount, (O- $CH_3$ -O-Phenyl) will increase  $E_{TS}$  but it less than (O-O-Phenyl) increase it and adding groups as (O-(C=O)-O-Phenyl) will increase  $E_{TS}$  more than any other groups. Because  $E_{TS}$  represents a threshold, so that increasing  $E_{TS}$  by the interaction increase the difficulty of transporting of the proton and direction of the reaction, that will increase the difficulty of transporting the proton from N to another N.

Compounds	$E_{TS}$ Kcal / mol	Microwave Frequency	Intensity
Original Compound	3398.96	1664.55	1899.84
C1	3417.78	1331.33	1707.65
C2	3415.09	1366.75	1693.92
C3	3410.81	1654.09	1866.62
C4	39956.22	1585.19	1921.72
C5	3985.62	1532.85	1984.94
C6	3932.95	1604.71	1788.22
C7	3355.71	1567.61	1829.01
C8	3358.03	1664.46	1887.19
C9	3350.88	1616.42	1845.18
C10	6037.87	1656.54	1853.82
C11	5922.13	1582.89	1779.07
C12	6707.15	1649.39	1881.55

Table 3 :  $E_{TS}$ , Microwave Frequency and Intensity for PS and Substituted groups with PS

That is caused by many reasons but the important one coming from conjugated resonance that it happening between interaction group and ring in original compound as it was electron withdrawing or electron donating. Groups effects appear on PA, as electron withdrawing groups decrease it while electron donating increase it. Hence that mean electron withdrawing decrease basicity increase acidity and electron donating groups increase basicity decrease acidity, as it in literature.

Distances between N-H and N-N has been calculated for 1,8-Bis(dimethylamino) naphthalene and for all suggested compounds. In table 4 , the smallest distance (hydrogen bond) between N-H it come when N-N is in the heights amount accrue at C5 , when the substituted is CH<sub>3</sub> at meta position. Also the heights distance (hydrogen bond) between N-H it come when N-N is in the smallest amount accrue at C7 , when the substituted is Cl at ortho position .

Compounds	N-H Distance A <sup>o</sup>	N-N Distance A <sup>o</sup>
Original Compound	1.06959	2.72036
C1	1.07440	2.69888
C2	1.06975	2.71883
C3	1.07037	2.71079
C4	1.07660	2.69251
C5	1.06946	2.72197
C6	1.07118	2.69507
C7	1.07866	2.69017
C8	1.06955	2.72134
C9	1.07190	2.69028
C10	1.07005	2.71074
C11	1.07033	2.70298
C12	1.07048	2.70682

Table 4 : Distance between N-H & N-N for PS and Substituted groups with PS

#### 4. CONCLUSION

In summary, the ability for N-to-N proton transfer and the effect of adding Substitutes to PS considering it as original compound has been study. The most effect on increase Proton Affinity appeared by adding methyl group at para while the most effect on decrease it by adding fluoride at

meta. Adding groups as (O-O-Phenyl) will increase  $E_{TS}$  in large amount , (O-CH<sub>3</sub>-O-Phenyl) will increase  $E_{TS}$  but it less than the amount of (O-O-Phenyl) will increase it. In same time adding (O-(C=O)-O-Phenyl) group at para have the most effect on increase  $E_{TS}$  while adding chloride at para have the most effect on decrease it. The smallest distance (Hydrogen bond) between N-H it come when N-N is in the heights amount accrue at C5 , when the substituted is CH<sub>3</sub> at meta position. While the heights distance (hydrogen bond) between N-H it come when N-N is in the smallest amount accrue at C7 , when the substituted is Cl at ortho position.

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