

3. Die relative Luftfeuchtigkeit, berechnet nach der Formel (3), weicht z. T. ganz erheblich von den drei anderen Grössen ab, besonders wenn der Gesamtdruck sich dem Teildruck des Wasserdampfes nähert (für reinen Wasserdampf hat sie natürlich keinen Sinn). Von der Benützung dieser Grösse in Sorptionsmessungen wird daher abgeraten.

4. Der relative Wasserdampfdruck, die Aktivität des Wassers und die relative Partialdichte des Wasserdampfes können in Sorptionsmessungen abwechslungsweise benutzt werden, wenn ein Fehler der obengenannten Grössenordnung ausser acht gelassen werden kann. Sonst wird die ausschliessliche Benutzung des relativen Wasserdampfdruckes empfohlen.

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168. The N1s ESCA Spectrum of Protonated 1,8-Bis-(Dimethylamino) Naphthalene (“proton sponge”)¹

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Summary. The ESCA spectrum of protonated 1,8-bis-(dimethylamino)naphthalene (“proton sponge”) (I) has been recorded in the region of N1s binding energies. The results indicate that IH^+ possesses an *unsymmetrical* $\text{N}-\text{H}\cdots\text{N}$ hydrogen bridge.

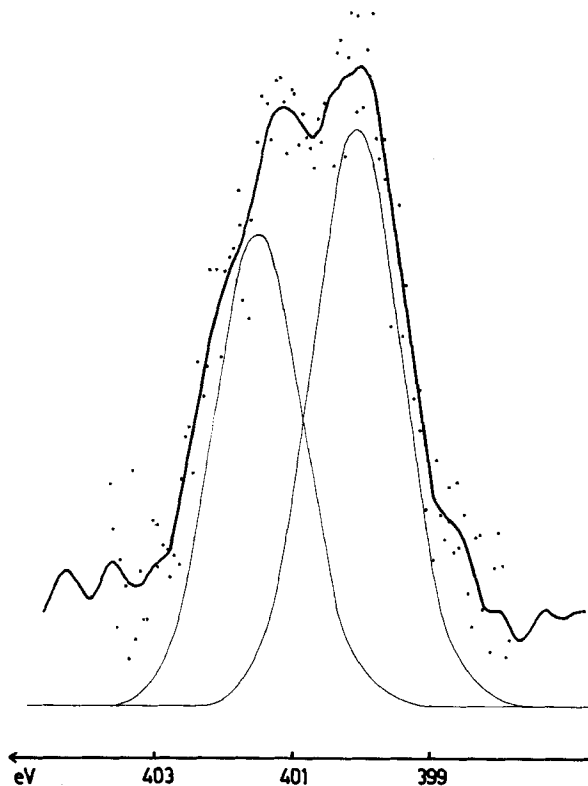
The remarkable basicity of 1,8-bis-(dimethylamino)naphthalene (I) has been attributed to relief of steric strain upon protonation [1]. Evidence for a reduction of the severe hindrance of the N-methyl groups in (I) by rotating the $-\text{N}(\text{CH}_3)_2$ groups out of their optimal conjugating position has been obtained by NMR-studies [1] of I as well as by ESR-studies [2] of its radical anion. However, this distortion alone would lead to an unfavorable N-lone pair interaction, which can be rationalized on the basis of Pauli's principle [3]. Reduction of this destabilizing effect could be achieved by increasing the $\text{N}\cdots\text{N}$ distance. An X-ray crystallographic analysis of I [4] has indicated that the nitrogen atoms of the rotated $-\text{N}(\text{CH}_3)_2$ groups are situated $\sim 0.42 \text{ \AA}$ above and below the naphthalene ring plane, which results in an $\text{N}\cdots\text{N}$ distance of $\sim 2.6 \text{ \AA}$ or $\sim 0.15 \text{ \AA}$ larger than that expected for a structure with parallel $\text{C}_{\text{ar}}-\text{N}$ bonds. Clearly, protonation of I will favorably decrease the lone pair interaction,

¹) Trade mark of Aldrich Chemicals Co., Milwaukee, Wisconsin (USA).

the size of an N-H group and particularly of an N⁺-H group being smaller than that of an N-lone pair.

The N...N distance in I makes IH⁺ a likely candidate for observing a symmetrical N...H...N hydrogen bridge²⁾. NMR. studies of I in TFAA [1] as well as an X-ray diffraction analysis of IH⁺ X⁻ [6], where X⁻ involves a liganded metal atom, could not unambiguously distinguish between equivalent or non-equivalent N-atoms. It has been stated that for problems of this kind the time scale of the diffraction and particularly of the NMR. experiment is inappropriate [5]. A "faster" technique is provided by the ESCA-experiment [7], where the ionization process of a core electron takes place within $\sim 10^{-16}$ sec. Hence non-equivalent atoms should be distinguishable even in a rapid equilibrium.

Fig. 1 displays the ESCA spectrum of IH⁺ BF₄⁻ in the region of the N1s binding energies (E_b). The smoothed out curve shows two distinct maxima of approximately the same height indicating that the two N-atoms in IH⁺ are non-equivalent. This can be rationalized on the basis of an *unsymmetrical* N-H...N hydrogen bridge. Deconvolution into two bands (variable line width) yields the core ionization potentials (E_b) of the two N-atoms at 400.1 eV and 401.5 eV (reference E_b(C1s) = 285 eV



ESCA spectrum of IH⁺ BF₄⁻ in the region of N1s binding energies

²⁾ For a discussion of O-H...O vs. O...H...O hydrogen bonds as a function of O...O distance see ref. [5].

[8]). The first value, which will correspond to the N-atom carrying no formal charge is higher by ~ 1 eV than that observed in neutral I (399.2 eV). Furthermore the splitting between the above values ($\Delta E_b = 1.4$ eV) is much smaller than that between e.g. piperidine (397.8 eV) [9] and its hydrochloride (400.4 eV) [9]. This might indicate that the hydrogen bridge in IH^+ is not far from being symmetric. A rather flat double potential would also explain the large standard deviation of 0.15 Å found for the proton position in IH^+ from the X-ray crystallographic work [6].

Experimental evidence indicates that certain carboxylic acid salts have symmetrical hydrogen bonds in the crystalline state [5]. However, by changing over to the liquid state, these hydrogen bonds are not even approximately symmetrical. This might suggest, although it would be difficult to prove, that IH^+ has also an unsymmetrical hydrogen bond in solution, being already unsymmetrical in the crystal.

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169. Zur Reaktionsweise von Enaminen mit Cyclopropenen IV¹⁾ ²⁾ Einsatz von Ketenacetalen

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Summary. A new interpretation – based on a reevaluation of the spectroscopic properties of products **16** to **27** – is proposed for the reaction of diphenyl-cyclopropenone **14** and -thione **15**

¹⁾ Aus den Dissertationen von H. W. Krapf (1970) und M. A. Steinfels (1972).

²⁾ Auszüge dieser Resultate wurden von M. A. Steinfels an der Herbsttagung der Schweizerischen Naturforschenden Gesellschaft, Sektion Organische Chemie, am 9. Oktober 1971 in Fribourg vorgetragen.

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