

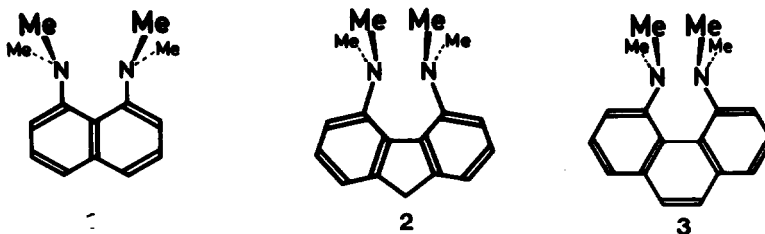
SYNTHESIS, STRUCTURE AND BASICITY OF 1,9-BIS(DIMETHYLAMINO)- DIBENZOTHIOPHENE AND 1,9-BIS(DIMETHYLAMINO)- DIBENZOSELENOPHENE ^{1,2)}

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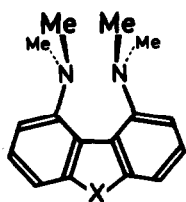
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Abstract: In the context of studies on bis(dialkylamino)arenes with neighbouring amino functions the title compounds **5** and **6** were synthesized. Their structures and those of the *monoprotonated* cations **5a** and **6a** were determined by X-ray analysis. The strong basicities of **5** and **6** ($pK_a = 11.9$ and 11.8 ± 0.1) are discussed in terms of lone pair interactions in **5** and **6** and the geometry of the $N \cdots H \cdots N$ hydrogen bonds in **5a** and **6a**.

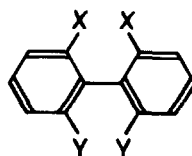
The extension of the 'proton sponge' concept from 1,8-bis(dimethylamino)naphthalene (**1**) ³⁾ to 4,5-bis(dimethylamino)fluorene (**2**) ⁴⁾ and 4,5-bis(dimethylamino)phenanthrene (**3**) ⁵⁾ offered the opportunity to study more systematically the structural factors responsible for the unusual basicities of this group of compounds ^{2a)}. The destabilizing effect of the 'lone pair' interaction between the sterically fixed amino functions of the free bases as well as the linearity and the shortness of the $N \cdots N$ distance of the $N \cdots H \cdots N$ hydrogen bond in the *monoprotonated* cations suggested a continuous increase of the basicities of **2** and **3** as compared to **1**. Experimentally, however, in the sequence **1**, **2** and **3** with pK_a values of 12.1, 12.8 and 11.5 ± 0.1 , resp., a maximum of the basicity was observed for the fluorene system **2** ^{4,5)}.



These results in the series **1** - **3** (for which possible explanations are discussed elsewhere ^{2a)}) induced us to start the syntheses of the fluorene analogues **4**, **5**, **6** and **7** where, due to the different bond lengths and bond angles of the heteroatoms in the central five-membered ring, a gradual and predictable variation of the interaction between the dimethylamino groups in the 1,9-positions was to be expected. According to force field calculations ⁶⁾ there should be a steady decrease in the $N \cdots N$ -distance in the sequence **4**, **5**, **6** and **7** with **2** to be ranked between **4** and **5**, and **3**, with the shortest $N \cdots N$ -distance, behind **7**. In this paper we would like to report on the syntheses of 1,9-bis(dimethylamino)dibenzothiophene (**5**) and 1,9-bis(dimethylamino)dibenzoselenophene (**6**), on the X-ray structure analyses of **5** and **6** and of the *monocations* **5a** and **6a**, and on the basicity determinations of **5** and **6**. Preliminary data will be given for **7** whereas the synthesis of **4** has not yet been completed.



- 4: X = O
 5: X = S
 6: X = Se
 7: X = Te

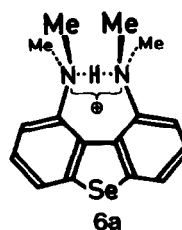
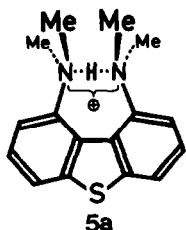


- 8: X = NMe₂, Y = Br
 9: X = NO₂, Y = Br
 10: X = NH₂, Y = Br
 11: X = NMe₂, Y = Li

For the preparation of **5** and **6** the key intermediate was 6,6'-dibromo-2,2'-bis(dimethylamino)biphenyl (**8**) which was prepared starting from 2,2'-dibromo-6,6'-dinitrobiphenyl (**9**)⁷, obtained from 1,2-dibromo-3-nitrobenzene in an Ullmann reaction (copper powder, 140-160°C; 72% yield). Reduction of **9** yielded 2,2'-diamino-6,6'-dibromobiphenyl (**10**)⁷ (iron(III) chloride, hydrazine hydrate, 93% yield). Fourfold N-methylation to **8**⁷ was achieved with sodiumhydride/dimethylsulfate in tetrahydrofuran in 68% yield.

8 was converted into **11** by lithiation (n-butyllithium, tetrahydrofuran, -78°C), and reaction of **11** with bis(phenylsulfonyl)sulfid yielded **5**⁷ (16% yield; colourless crystals, mp 130 - 132°C). The corresponding selenophene **6**⁷ was obtained from **11** in tetrahydrofuran after addition of selenium (7% yield; colourless crystals, mp 136 - 137°C). Analogously, by use of tellurium, **7** was isolated. Due to the poor yield, however, **7** was characterized only by ¹H-NMR and MS as well as by its isolation as *mono*(tetrafluoroborate) for which ¹H-NMR data including the strongly downfield-shifted signal for the N···H···N proton support the structure [$\delta = 3.08$ (d, $J = 2.3$ Hz, 12H), 7.55 ('t', $J = 7.6$ Hz, 2H), 7.83 (d, $J = 8.0$ Hz, 2H), 8.34 (d, $J = 8.0$ Hz, 2H), 18.86 (br. s, 1H); [D₆]DMSO, 360 MHz].

In accordance with the typical behaviour of 'proton sponges', **5** and **6** form, even with excess of tetrafluoroboric acid, the *monoprotonated* species **5a** · BF₄[⊖]⁷ and **6a** · BF₄[⊖]⁷ [$\delta(\text{N} \cdots \text{H} \cdots \text{N}) = 19.06$ (**5a**) and 19.28 (**6a**); [D₆]DMSO, 500 MHz]. The basicities of **5** and **6** were derived from transprotonation experiments determining the equilibria between **1** and its *monoprotonated* form on the one side and **5a** and **5** and **6a** and **6**, resp., on the other side using the ¹H-NMR signal intensities [[D₆]DMSO, 500 MHz]. In this way $\text{p}K_{\text{a}} = 11.9 \pm 0.1$ was obtained for **5** and $\text{p}K_{\text{a}} = 11.8 \pm 0.1$ for **6**. Thus, both compounds are strong 'proton sponges' with basicities ranked between **2** and **3**.



Of **5** and **6** as well as of the **5a**- and **6a**-*mono*(tetrafluoroborates) X-ray structure analyses were solved⁸. The fact that for both compounds the structures of the free bases can be compared with those of the *monoprotonated* species is of special value to understand the strong basicities of **5** and **6** in terms of sterical factors. Figure 1A shows the strong sterical strain in **5** as a result of the repulsive interaction between the dimethylamino groups which leads to a very remarkable deviation from planarity: The torsion around the C(4B)-C(5B) bond of the dibenzothiophene system amounts to 21.3° and results in deviations of

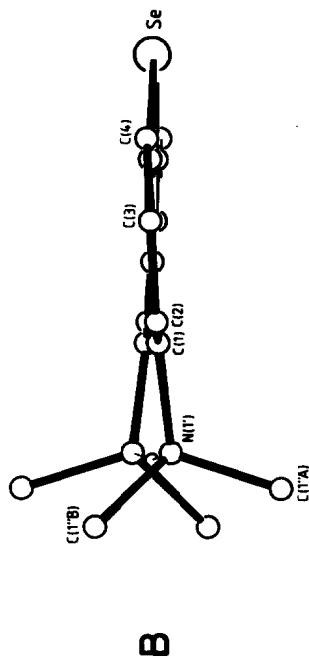
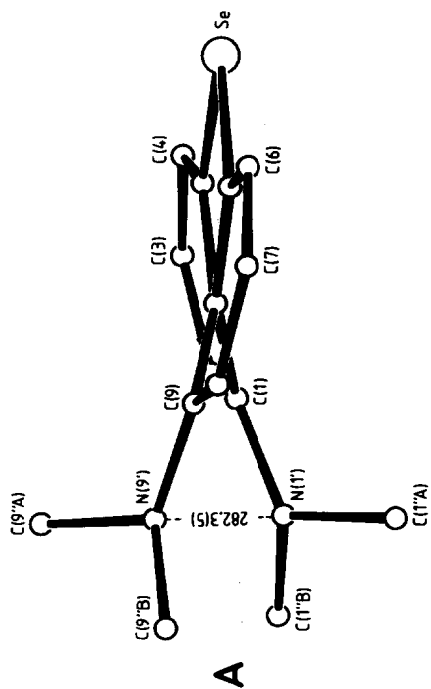


Figure 1. Structures of **5** (A) and of the 5a-Part of 6a-Tetrafluoroborate (B) in Side-Views ⁸⁾

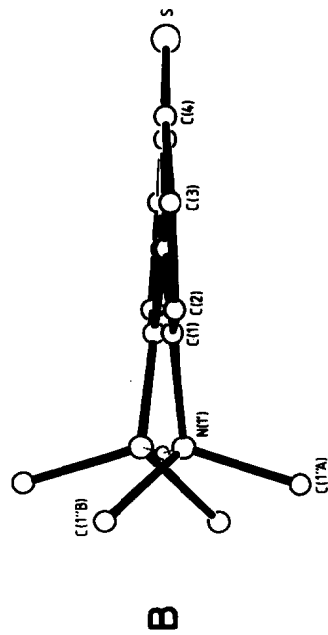
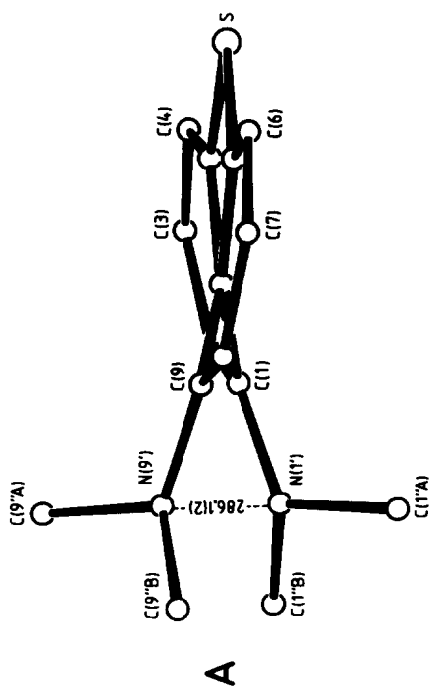


Figure 2. Structures of **6** (A) and of the 6a-Part of 6a-Tetrafluoroborate (B) in Side-Views ⁸⁾

C(1) and C(9) from the mean plane through the atom of the five-membered ring by central 3.31 and 30.3 pm, respectively. Correspondingly N(1') and N(9') deviate by 74.8 and 65.6 pm from this mean plane resulting in an N...N distance of 286.1 pm. The comparison of the structure of **5** with that of **5a** (Figure 1B) shows immediately the strong release of sterical strain due to the introduction of a very strong N...H...N hydrogen bond on protonation of **5**: In **5a** the torsion around the central bond C(4B)-C(4B') is reduced from 21.3° to only 7.7°; C(1) and N(1') deviate from the mean plane through the five-membered ring by only 9.9 and 24.9 pm. Correspondingly the N...N distance is reduced by 27.4 pm to 258.7 pm in the N...H...N hydrogen bond which has an arrangement very close to linearity (angle 175°).

The structures of **6** and **6a** (Figures 2A and B) are very similar to **5** and **5a**. The most remarkable feature in the comparison between **6** and **6a** is again the very strong release in sterical strain by the formation of the N...H...N hydrogen bond on protonation which leads to a remarkable approach to planarity in **6a**. The N...N-distance is shortened by protonation from 282.3 to 257.3 pm; the very short N...H...N hydrogen bond in this case, too, is nearly linear (angle 175°).

These results support very strongly the idea that the unusually high basicity of the 'proton sponge' family is due to strong destabilizing steric interactions between the neighbouring dialkylamino groups (including lone-pair repulsion) in the neutral diamines and to the reduction of this steric strain by the protonation leading to strong N...H...N hydrogen bonds for which the geometrical conditions (linearity, short N...N-distance) are especially favorable.

References and Notes

- 1) Dedicated to Professor *Emanuel Vogel*, University of Köln, at the occasion of his 60th birthday, remembering with pleasure the long time we enjoyed as fellow-travelers through the fascinating world of organic chemistry (H. A. St.).
- 2) New 'Proton Sponges'. 6. - a) Part 5: H. A. Staab, T. Saupe, *Angew. Chem. Int. Ed. Engl.* (in press); b) Part 4: M. A. Zirnstein, H. A. Staab, *Angew. Chem.* **99** (1987) 460; *Angew. Chem. Int. Ed. Engl.* **26** (1987) 460.
- 3) R. W. Alder, P. S. Bowman, W. R. S. Steele, D. R. Winterman, *J. Chem. Soc., Chem. Commun.* **1968**, 723; R. W. Alder, M. R. Bryce, N. C. Goode, N. Miller, J. Owen, *J. Chem. Soc., Perkin Trans. I* **1981**, 2840, and literature cited therein.
- 4) H. A. Staab, T. Saupe, C. Krieger, *Angew. Chem.* **95** (1983) 748; *Angew. Chem. Int. Ed. Engl.* **22** (1983) 731.
- 5) T. Saupe, C. Krieger, H. A. Staab, *Angew. Chem.* **98** (1986) 460; *Angew. Chem. Int. Ed. Engl.* **25** (1986) 451.
- 6) M. Höne, Ph.D. Thesis, University of Heidelberg 1987; for these calculations programs MM2 (82)/MMP2, Molecular Design Ltd., Hayward, Cal. were used.
- 7) For these compounds correct elemental analyses were obtained; the spectroscopic data are in agreement with the structures suggested.
- 8) Atomic coordinates for these structures have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K..