New "Proton Sponges", 14[+]

Isomeric Tetrakis(dimethylamino)naphthalenes: Syntheses, Structure-Dependence of Basicities, Crystal Structures, and Physical Properties

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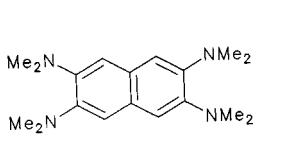
For comparison to the recently described 2,3,6,7-tetrakis(dimethylamino)naphthalene (**1**) the three isomers **2**, **3**, and **4** were synthesized. The basicities of this group of isomers are strongly dependent upon the different mutual orientations of the pairs of dimethylamino substituents: only the isomers **3** and, partially, **4**, both with dimethylamino groups in adjacent *peri*-positions of the naphthalene, are strong "proton sponges". For the isomers **1** and **2** with the same number and kind of twofold dimethylamino substituents in neighbouring *ortho*-positions, however, no significant basicity increase is observed. To explain this difference between the two groups of isomers it is suggested that in the *ortho*-pairs of **1** and **2** the C–N bonds diverge considerably, leading to an increased N···N distance and consequently to less stable $[N\cdots H\cdots N]^+$ hydrogen bonds in contrast to the parallel C–N bonds in the *peri*-substituted isomers **3** and **4**. X-ray crystal structure analyses of the bases and of some of the salts derived therefrom were solved and are discussed. Cyclic voltammetry indicates that **1** to **4** are strong electron donors, reacting easily to radical cations or dications which with suitable acids have been obtained as salts.

Introduction

In continuation of our preceding work on "proton sponges"[1–3] we investigated the interaction between basic groups in well-defined distances and orientations. Interesting examples of this concept are the tetrakis(dimethylamino)naphthalenes **1**,[1] **2**, **3**, and **4** of which all four isomers contain two pairs each of two adjacent dimethylamino groups. For **1**, **2**, and **3** these pairs of dimethylamino substituents are in *ortho*-positions to each other, whereas the isomer **4**, the 1,4,5,8-tetrakis(dimethylamino)naphthalene, has two pairs of these substituents in the four *peri*-positions of naphthalene. As will be shown by the basicity data, there is a very strong difference of the isomers **1**,[1] **2**, and **3** each with two pairs of dimethylamino groups in *ortho*-positions, compared to the isomer **4** with twofold pairs of dimethylamino substituents in the four *peri*-positions.

In the present paper we are reporting the syntheses of the isomers **2**, **3**, and **4**, and especially the differences of structures and physical properties for **1**[1] to **4**. Results of X-ray structure analyses of most of these "proton sponges" and of derivatives of them will be discussed as well as spectroscopic properties of these isomers which differ only in the positions of the four sets of two neighbouring dimethylamino groups each.



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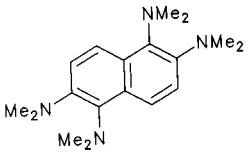

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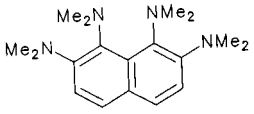

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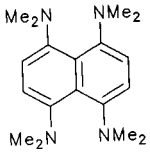

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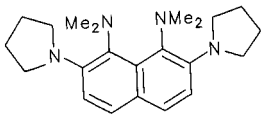

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As further variation of the amino substituents on naphthalene the 2,7-bis(1-pyrrolidinyl)-1,8-bis(dimethylamino) analogue **5** was prepared; with regard to basicity **5** resembles **3** rather closely. For the detailed structure of **5** an X-ray structure analysis was also solved (see below).

Syntheses

1,2,5,6-Tetrakis(dimethylamino)naphthalene (2)

For the synthesis of **2**, 2,6-dimethoxy-1,5-dinitronaphthalene[4] was treated with an excess of dimethylamine

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(DMF, 90 °C, autoclave) to replace the methoxy groups by dimethylamino substituents (45% yield). Catalytic hydrogenation of the nitro groups (Pd/charcoal, THF) yielded the corresponding amino groups which immediately were methylated to **2** which was isolated as tetrafluoroborate **2** · **$(HBF_4)_2$** (ca. 12% for the two steps). For further synthetic details and the characterization of the product see Experimental Section.

1,2,7,8-Tetrakis(dimethylamino)naphthalene (3)

The synthesis of **3** started from 2,7-dimethoxy-1,8-dinitronaphthalene[5] which was treated with an excess of dimethylamine to yield 2,7-bis(dimethylamino)-1,8-dinitronaphthalene (yield 84%). Catalytic hydrogenation of the nitro groups (Pd/charcoal, THF) and subsequent methylation yielded **3** isolated as tetrafluoroborate which by fractional crystallization and treatment with aqueous sodium hydroxide yielded **3** (see Experimental Section). For both of the products **3** and **5** as tetrafluoroborates the crystal structure has been solved (see below).

1,4,5,8-Tetrakis(dimethylamino)naphthalene (4)

The synthesis of **4** started from 1,3-dimethylperimidinone[6] which was nitrated in the 6- and 7-positions on the naphthalene part to 1,3-dimethyl-6,7-dinitroperimidin-2-one. The carbonyl group was hydrolytically split off (potassium hydroxide in hot methanol, 4 h, under argon), yielding 1,8-bis(methylamino)-4,5-nitronaphthalene (recrystallized from DMF; m.p. 235° C, dec.; 66% yield). Hydrogenation of the nitro groups (H_2/Pd) and *N*-methylation (dimethyl sulfate/NaH) yielded **4** (recrystallized from pentane, m.p. 193° C; yield 31%). The high molecular symmetry of **4** is reflected by its ^{1}H-NMR spectrum (in DMSO) showing only two singlets at δ = 2.65 (24 H) and 6.75 (4 H). Compound **4** is a "twofold proton sponge" with two dimethylamino pairs in the *peri*-positions, thus leading easily to a double protonation. X-ray crystal analyses of salts of **4** with hydrogen bromide or tetrafluoroboric acid prove the structures **4** · **2 HBr** and **4** · **$(HBF_4)_2$** with a twofold protonation of **4**.

1,8-Bis(dimethylamino)-2,7-bis(1-pyrrolidinyl)naphthalene (5)

Starting from 2,7-dimethoxy-1,8-dinitronaphthalene the reaction with pyrrolidine in DMF replaced the two methoxy groups. Hydrogenation (H_2, Pd/C, THF) of the nitro groups yielded 1,8-diamino-2,7-bis(1-pyrrolidinyl)naphthalene which was *N*-methylated by dimethyl sulfate to the product **5** wanted (for details see Experimental Section). X-ray analysis proved that the molecular structure and conformation of **5** are similar to the structure of **3**.

Basicities of Tetrakis(dimethylamino)naphthalenes

One of the most interesting and specific properties of "proton sponges" are their basicities which are usually quoted in pK_a-values in aqueous solutions. Due to the poor solubility of the bases **1** to **5** in water, all measurements of these new bases, however, had to be made in [D_6]dimethyl sulfoxide (DMSO). The pK_a-values for **1** to **5** were obtained by referring to the pK_a scale (DMSO, 30 °C) with 2,7-dimethoxy-1,8-bis(dimethylamino)naphthalene (pK_a = 16.1 ± 0.1)[3b] and 6,7-bis(dimethylamino)-2,3-dihydro-1,3-dimethyl-1*H*-perimidine[6] (pK_a = 15.0 ± 0.4)[7] in DMSO as solvent. In this DMSO scale for **4** a first protonation with pK_a = 14.4 and a second protonation with pK_a = 9.5 were observed. For **3**, a pK_a = 15.8, and for **5** a similar basicity of pK_a = 15.5 were determined as was to be expected due to the similarity of the two structures involved. These data, however, are limited and should be considered to be still of tentative value. Usually the optimal conformation for high basicities, particularly due to the neighbouring *ortho*- and *peri*-substitutions, cannot yet precisely be taken into account in contrast to rigid molecular structures. Especially the conformations of substituents in DMSO solutions are difficult to estimate. In any case, however, the remarkably high basicities of the compounds with *peri*-substitution of suitably orientated basic groups are of interest, especially since the protonation of neighbouring basic groups increases the basicity due to the formation of stabilizing hydrogen bonds.

Cyclic Voltammetry

The oxidation potentials of **3**, **4**, and **5** were measured using a glassy carbon electrode vs. Ag/AgCl in acetonitrile/0.1 M tetrabutylammonium perchlorate. The cyclovoltammogram of **4** shows a reversible two-electron transition at $E^0_{1,2} \approx -0.50$ V produced by two superimposed one-electron steps. Further oxidation reveals four joint reversible oxidation steps representing overlapping pairs of tri- and tetracations. Apparently, oxidation of **4** leads primarily to the formation of two dications which may be further oxidized. In fact, the crystal structure determination reveals a stable dication of **4**. For **2** and **3**, as well as for **5**, the first two oxidation steps could not be separated, and due to the diversity of the results of cyclic voltammetry of the substituted 1,8-bis(dimethylamino)naphthalenes reliable complete results are not yet available. In any case, however, it can be suggested that the tetrakis(dimethylamino)naphthalenes **3** and **4** are stronger electron donors than the isomers **1** and **2**. Of **3** and **4**, radical cations can be generated by oxidation with iodine or other electron acceptors leading to dication salts. For example, by oxidation of **4** with an excess of iodine at low temperature the dication salt with two I_3^- anions is formed as black crystals showing in solution a strong absorption band with a maximum at λ_{max} = 643 nm (log ε = 4.02; in acetonitrile, 243 K). The crystal structure was solved by X-ray structure analysis, proving an extensive charge delocalization similar to a delocalized quinone diimmonium structure.

Molecular Structures by X-ray Crystallography

The crystal structure of **4** and its diprotonated dication **4** · **2 HBr** · **5 H_2O** were already discussed based on prelimin-

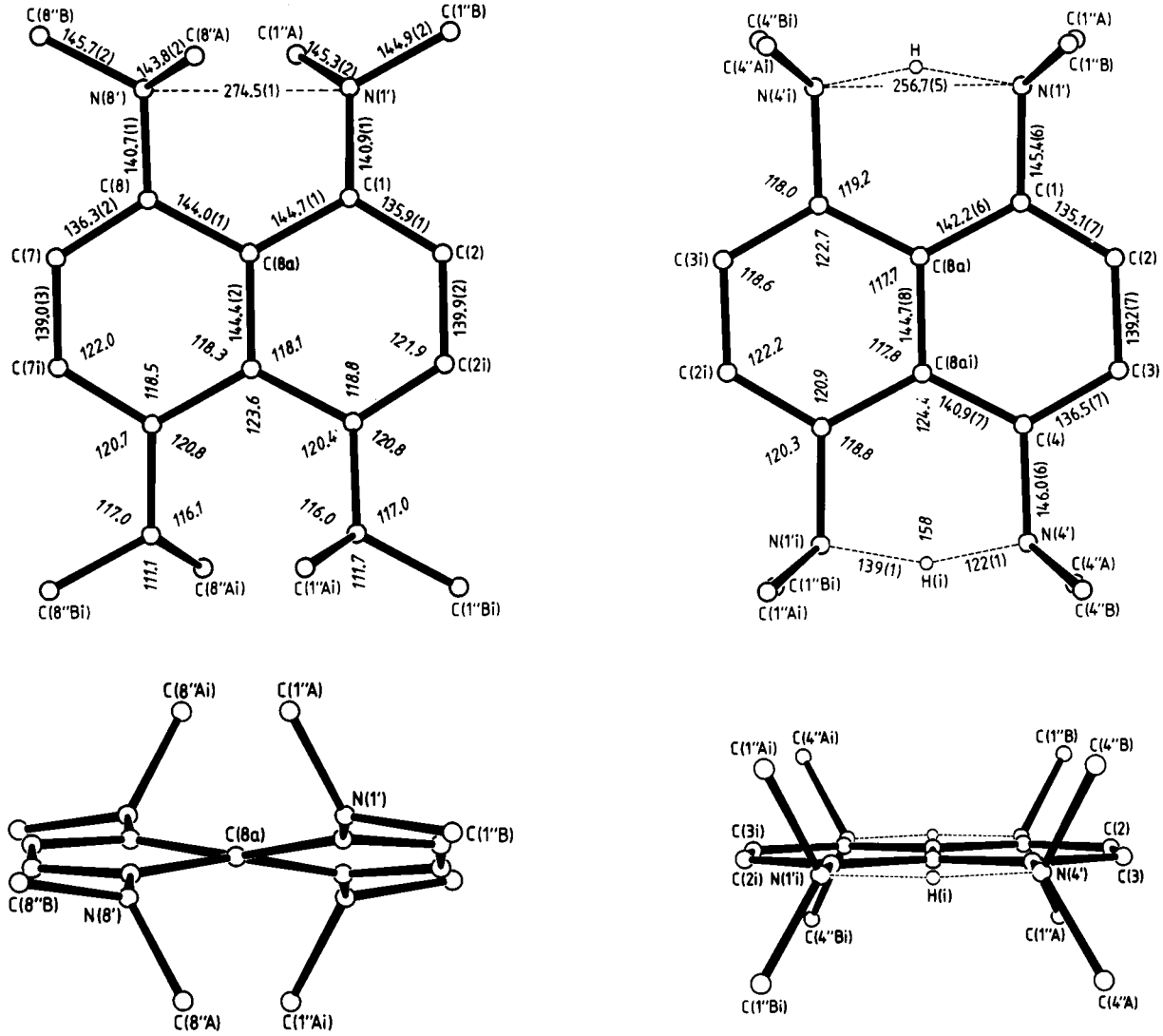

Figure 1. Molecular structure of 1,4,5,8-tetrakis(dimethylamino)naphthalene (**4**); a: vertical and along central axis; b: corresponding views at the diprotonated dication of **4** · **2 HBr** · **5** H_2O

ary data in a short communication.[8] One of the interesting results of the crystal structure analysis of **4** was that the two six-membered rings of naphthalene are twisted along the central C(8a)–C(8ai) axis, obviously due to the four dimethylamino groups in the four *peri*-positions (Figure 1a). By diprotonation with hydrogen bromide and crystallization from water, the **4**–dibromide–pentahydrate (m.p. 247 °C) was obtained of which the molecular structure was determined by X-ray analysis (Figure 1b). In the dication of **4** the naphthalenes including the four C–N bonds to the *peri*-substituents are completely planar, and the N···N distance between neighbouring *peri*-Me_2N substituents is significantly shorter than for the unprotonated **4**.

The crystal structure analysis of 1,2,7,8-tetrakis(dimethylamino)naphthalene (**3**) had very similar results as those found for **4**: The methyl groups of the bis(dimethylamino) substituents in 2- and 7-positions are slightly turned away from the *peri*-substituents at the 1- and 8-positions of the naphthalene in **3**. Compared to the structural arrangement in **4** the introduction of a possible "buttressing" effect of the methyl groups in the 2,7-*ortho*-positions leaves the N1′···N8′ distance with 277.0 pm almost unaffected (**3**: N1′···N8′ distance: 274.5 pm). The twisting along the central C8a–C4a bond of the naphthalene skeleton within the range of about 4° to 12° is not significantly affected by the accumulation of substituents in the 1,2,7,8-positions of the naphthalene in **3** (see Figure 2).

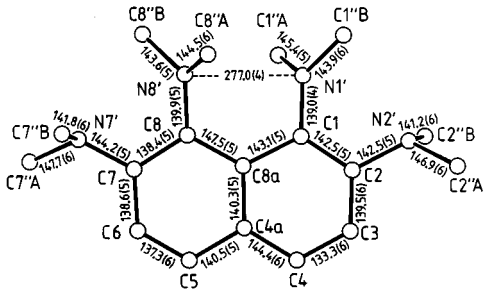

Figure 2. Molecular structure of 1,2,7,8-tetrakis(dimethylamino)-naphthalene (**3**), an isomer to **4** (see Figure 1)

Table 1. Crystallographic data and refinement parameters[9]

	3	**4**	**4 · 2 HBr · 5 H_2O**	**5**
Formula	$C_{18}H_{28}N_4$	$C_{18}H_{28}N_4$	$C_{18}H_{40}Br_2N_4O_5$	$C_{22}H_{32}N_4$
Molecular mass	300.5	300.5	552.4	352.5
Crystallized from	hexane	pentane	water	pentane
Crystal size [mm]	0.4 × 0.3 × 0.2	0.2 × 0.2 × 0.1	0.3 × 0.1 × 0.1	0.3 × 0.2 × 0.2
Crystal system	monoclinic	orthorhombic	tetragonal	tetragonal
Space group	$P2_1/c$	*Pbcn*	*P4/n*	$P4_22_12$
a [pm]	1113.8(6)	1007.1(1)	1814.2(2)	1540.5(4)
b [pm]	1056.8(6)	1746.3(2)		
c [pm]	1563.4(8)	1018.5(1)	793.2(1)	832.6(1)
β [°]	104.59(4)			
Z	4	4	4	4
Symmetry of molecule in crystal		C_2	C_i	C_2
F_{000} [e]	656	656	1144	768
$D_{calcd.}$ [gcm^{-3}]	1.120	1.114	1.406	1.186
μ [mm^{-1}] (Mo-K_α)	0.069	0.068	3.11[a]	0.071
Unique reflections	3129	2158	3329	1165
measured[b]	6.0	6.8	6.7	6.2
up to (sinθ/λ) [nm^{-1}]				
Observed reflections [I 2.0σ(I)]	2045	1300	1579	674
Refinement R	0.078	0.042	0.046	0.040
$(\Delta/\sigma)_{max}$	0.01	0.01	0.01	0.01

[a] An empirical absorption correction was performed (refined from ψ-scans, τ_{max} = 0.998, τ_{min} = 0.692). – [b] Enraf–Nonius CAD4 diffractometer, Mo-K_α radiation (λ = 71.073 pm, θ/2θ scans).

Compared to the *all-peri*-dimethylamino substitutions in **4**, the 2- and 7-dimethylamino groups in **3** favour the protonation in the hydrogen bond between the 1- and 8-dimethylamino groups of naphthalene. In fact, the crystal structure reveals a nearly complete planarization of the naphthalene skeleton of **3H$^+$**, and for the [N···H···N]$^+$ hydrogen bond the N···N distance with 256 pm is similarly as short as that of the protonated dication of **4** (see Figure 1b). In contrast to the protonated two-fold *peri*-substituted **4b**, however, the hydrogen bonding in **3H$^+$** is clearly unsymmetrical with regard to the nitrogens in 1- and 8- positions. In Table 1 the crystallographic data of the tetrakis(dimethylamino)naphthalenes **3**, **4**, and **5** as well as those of the protonated complex are listed.

The structure of the **3**-related 2,7-bis(1-pyrrolidinyl)-1,8-bis(dimethylamino)naphthalene (**5**) (Figure 3) turned out to be similar to that of **3**.

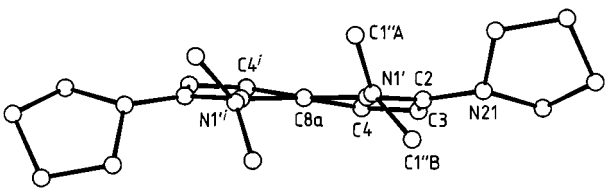

Figure 3. Molecular structures of **5**

Experimental Section

General: M.p.: Büchi SMP-20; for m.p. > 250 °C: Bock monoscope (m.p. uncorrected). – IR: Perkin–Elmer FT-IR 1760X. – UV/Vis: Cary 2300 Varian. – MS: Jeol JMS SX 102 A; DuPont CEC 21–492; Finnigan MAT 212 (only most prominent peaks are listed, usually I_{rel} > 10%); FAB spectra (LSIMS, positive; 3-nitrobenzyl alcohol/1% TFA); VG Analytical ZAB 2E/70 SE (I_{rel} > 15%). – ^{1}H NMR: Bruker Physik HX 360 and AM 500 (internal reference: tetramethylsilane, solvent signals C*H*DCl_2, δ = 5.32; C*H*Cl_3, δ = 7.26; [D_5H]MSO, δ = 2.50). – Microanalyses: Elemental Analyzer 1106, Carlo Erba. – Analytical TLC: DC Micro Cards Polygram SIL G/UV_{254} and ALOX N/UV_{254}, Macherey–Nagel. – Cyclovoltammetry: Potentiostat PAR 362 (EGG Princeton Applied Research), glassy carbon electrode, reference electrode Ag/AgCl, platinum counterelectrode; 0.1 M tetrabutylammonium perchlorate/degassed acetonitrile, measurements at 295 K; oxidation potential referred to ferrocene (+0.352 V).

1,8-Bis(methylamino)-4,5-dinitronaphthalene: A suspension of 5.0 g (16.5 mmol) of 1,3-dimethyl-6,7-dinitro-1*H*-perimidin-2-one[6] in a solution of 75 g of potassium hydroxide in 500 mL of methanol under argon was heated under stirring for 4 h under reflux until complete conversion of starting material. After cooling, the reaction mixture was neutralized with 5 N HCl; the precipitated product was washed with water followed by methanol, and the dried product was crystallized from DMF: 3.0 g (66%), dark-red coloured needles, m.p. 235 °C (dec.); R_f = 0.3 (SIL, ethyl acetate). – ^{1}H NMR (360 MHz, [D_6]DMSO): δ = 2.91 (s, 6 H, N-CH_3), 6.63 (d, 2 H, ^3J = 9.0 Hz, 2,7-H), 7.60 (s, 2 H, NH), 8.18 (d, 2 H, 3,6-H). – $C_{12}H_{12}N_4O_4$: calcd. C 52.17, H 4.38, N 20.28; found C 52.35, H 4.56, N 20.25.

1,8-Bis(dimethylamino)-4,5-dinitronaphthalene: For further *N*-methylation, of the preceding compound 1.0 g (3.6 mmol), 5.0 mL of methyl iodide (11.4 g, 80 mmol), and 29.0 g (0.21 mol) of powdered potassium carbonate in 200 mL of DMF under argon were stirred at ambient temperature for 1 d. Then 10 mL of 2 N of methanolic potassium methoxide was added, and the reaction mixture was stirred for further 4 h. Addition of water to the mixture precipitated the product which was centrifugated, washed with water and methanol; crystallization from DMF yielded 350 mg (32%) of the product wanted: dark-red needles, m.p. 280 °C (dec.). – ^{1}H-NMR (360 MHz, [D_6]DMSO): δ = 2.97 (br. s, 12 H, NMe_2), 6.88 (d, 2 H, ^3J = 9.0 Hz, 2,7-H), 8.14 (d, 2 H, ^3J = 9.0 Hz, 3,6-H). – $C_{14}H_{16}N_4O_4$: calcd. C 55.26, H 5.30, N 18.41; found C 55.46, H 5.43, N 18.47.

1,4,5,8-Tetrakis(dimethylamino)naphthalene (4): In the first step the nitro groups of the preceding compound were hydrogenated (1.0 g,

3.3 mmol) in 150 mL of ethyl acetate in the presence of 0.4 g of palladium/charcoal by hydrogen in a shaking apparatus (12 h, at normal pressure) until the hydrogenation came to a stop. The solution was filtered from the catalyst under argon, and the ethyl acetate was evaporated in vacuo. The residue, 1,8-diamino-4,5-bis(dimethylamino)naphthalene, was dissolved in dry tetrahydrofuran with 2.44 g (19.4 mmol) of dimethyl sulfate and 0.51 g (21.2 mmol) of sodium hydride. The solution was heated under reflux for 5 h and then stirred at room temperature for further 12 h. Excess of sodium hydride was decomposed by methanol, sodium hydroxide solution (10 g of NaOH in 110 mL of water) was added, and after addition of ligroin (b.p. 40 °C) the organic phase was separated and three times extracted with ether. The united organic phases were dried with magnesium sulfate, filtered, and the solvent was distilled off. The raw **4** was further purified by chromatography on aluminium oxide with dichloromethane/ethyl acetate (from 1:1 to 10:1). Crystallization from pentane yielded 310 mg (31%) of **4**, m.p. 193.5 °C. – ^{1}H NMR (500 MHz, [D$_6$]DMSO, 30 °C): δ = 2.65 (s, 24 H, NMe_2), 6.75 (s, 4 H, 2,3,6,7-H). – MS: *m*/*z* (%) = 300 (100) [M^+]; high resolution: found 300.2314 ± 0.0001. – $C_{18}H_{28}N_4$: calcd. C 71.96, H 9.39, N 18.65; found C 72.02, H 9.51, N 18.53.

4–(Hydrogen tetrafluoroborate)$_2$ [4(HBF$_4$)$_2$]: To a solution of **4** in diethyl ether an excess of tetrafluoroboric acid in diethyl ether was added, and the precipitate formed was separated and washed with a small amount of methanol. The tetrafluoroborate of **4** was crystallized from ethanol/water (dec. ca. 280 °C). – ^{1}H NMR (500 MHz, [D$_6$]DMSO, 30 °C): δ = 3.14 (s, 24 H, NMe_2), 8.39 (s, 4 H, 2,3,6,7-H), 18.80 (br. s, 2 H, N···H···N). – $C_{18}H_{30}B_2F_8N_4$: calcd. C 45.41, H 6.35, N 11.77; found C 45.18, H 6.61, N 11.58.

2,7-Bis(dimethylamino)-1,8-dinitronaphthalene: To a solution of 9.45 g (34 mmol) 2,7-dimethoxy-1,8-dinitronaphthalene in 50 mL of DMF were added 30.0 g (0.67 mol) of dimethylamine, condensed in 5 mL of DMF at –10 °C. After sealing the flask, the mixture was stirred at room temperature for 3 d. Then by addition of water the product precipitated and was filtered off and recrystallized from methanol to yield 8.72 g (84%) as orange needles of m.p. 146 °C. – ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.91 [s, 12 H, $N(CH_3)_2$], 7.45 (d, 2 H, ^3J = 9.0 Hz, 3,6-H), 7.96 (d, 2 H, 4,5-H); on irradiation at δ = 2.91 [$N(CH_3)_2$] an NOE response to 3,6-H (δ = 7.45) was observed. – ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ = 43.3 [q, $N(CH_3)_2$], 118.4 and 132.7 (2 d, 3,6-C, 4,5-C), 120.3, 123.1, 131.7 (3 s, 2,7-C, 4a-C, 8a-C), 148.6 (s, 1,8-C). – $C_{14}H_{16}N_4O_4$: calcd. C 55.26, H 5.30, N 18.41; found C 55.07, H 5.15, N 18.27.

1,8-Dinitro-2,7-bis(1-pyrrolidinyl)naphthalene: A mixture of 19.0 g (68.3 mmol) of 2,7-dimethoxy-1,8-dinitronaphthalene,[4] 113 mL (1.37 mol) of pyrrolidine and 290 mL of DMF in a sealed tube was stirred at room temperature for 4 d. Afterwards by addition of water to the mixture the precipitate was filtered off, washed with water and diethyl ether, and crystallized from acetone: 21.8 g (90%) orange needles, m.p. 207–208 °C. – ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 1.91 (m, 8 H, 3′- and 4′-H), 3.31 (m, 8 H, 2′- and 5′-H), 7.16 (d, 2 H, ^3J = 9.2 Hz, 3,6-H), 7.80 (d, 2 H, 4,5-H). – ^{13}C NMR (91 Hz, [D$_6$]DMSO): δ = 25.0 (t, 3′,4′-C), 49.7 (t, 2′,5′-C), 114.5 and 132.1 (2d, 3,6-C, 4,5-C), 118.7, 120.5, 126.4 (3 s, 2,7-C, 4a-C, 8a-C), 144.4 (s, 1,8-C). – $C_{18}H_{20}N_4O_4$: calcd. C 60.67, H 5.66, N 15.72; found C 60.94, H 5.72, N 15.57.

2,6-Bis(dimethylamino)-1,5-dinitronaphthalene: To a suspension of 10.75 g (38.6 mmol) of 2,6-dimethoxy-1,5-dinitronaphthalene[5] in 120 mL of DMF in an autoclave 47.6 g (1.06 mol) of dimethylamine in 20 mL of DMF, cooled down to –10 °C, was added. The sealed mixture was stirred at 90 °C for 1 d. Addition of water to the cooled mixture precipitated the product which was filtered off, washed with water, and dried. Crystallization from acetone yielded 5.26 g (45%) of the wanted product: dark-red needles, m.p. 178–179 °C, R_f = 0.4 (ALOX, cyclohexane/ethyl acetate, 5:1). – ^{1}H NMR (360 MHz, [D$_6$]acetone): δ = 2.95 (s, 12 H, NMe_2), 7.61 (d, 2 H, ^3J = 9.5 Hz, 3,7- or 4,8-H), 7.67 (d, 2 H, 4,8- or 3,7-H). – MS; *m*/*z* (%): 305 (11), 304 (100) [M^+], 211 (14), 198 (17), 197 (64) a. o. – $C_{14}H_{16}N_4O_4$: calcd. C 55.26, H 5.30, N 18.41, found C 55.38, H 5.35, N 18.12.

1,2,7,8-Tetrakis(dimethylamino)naphthalene (3). – a) Isolation as HBF$_4$ Salts: A solution of 5.0 g (16.4 mmol) of 2,7-bis(dimethylamino)-1,8-dinitronaphthalene (see above) in 100 mL of THF was hydrogenated (1.0 g, 5% Pd on charcoal, 3 bar, 12 h) to 1,8-diamino-2,7-bis(dimethylamino)naphthalene obtained as dark-red oil which was dissolved in 100 mL of anhydrous tetrahydrofuran under argon. To this solution a suspension of 4.2 g (175 mmol) of sodium hydride in 50 mL of tetrahydrofuran was added. To this mixture, stirred and heated under reflux, 15.5 mL (20.7 g, 164 mmol) of dimethyl sulfate was added dropwise within 15 h. After heating under reflux for 17 h and cooling the reaction mixture to room temperature, the excess of sodium hydride was decomposed by adding 1.5 mL of methanol, then 50 mL of 12.5% aqueous ammonium hydroxide solution and 75 mL of *n*-pentane. The organic layer was separated, the mixture was extracted with 3 × 300 mL of diethyl ether. The combined organic phases were concentrated under reduced pressure; the residue, dissolved in diethyl ether, was filtered through a short column of deactivated alumina. To the eluate under stirring 1 mL of methanol and then 5 mL of 54% tetrafluoroboric acid/diethyl ether were added; after 2 d at –18 °C, the precipitate was filtered off and crystallized from methanol yielding two products: Fraction A: 480 mg (6%) of an $(HBF_4)_2$ salt as colourless powder of m.p. 232–234 °C (dec.): $C_{18}H_{30}B_2F_8N_4$: calcd. C 45.41, H 6.35, N 11.77; found C 46.85, H 6.66, N 12.22; fraction B: 35 mg (0.5%) of an HBF_4 salt of **3** as colourless platelets, m.p. 254–256 °C (dec.). – ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.70 (s, 12 H, 2,7-NMe_2), 3.30 (d, 12 H, ^3J = 2.2 Hz, 1,8-NMe_2), 7.85 (d, 2 H, ^3J = 8.8 Hz, 3,6-H), 8.12 (d, 2 H, 4,5-H), 19.81 (m, 1 H, N···H···N). – MS (LSIMS); *m*/*z* (%): 691 (10) [$M_2HBF_4H^+$ + 2 H], 690 (28) [$M_2HBF_4H^+$ + H], 689 (10) [$M_2HBF_4H^+$], 303 (17) [MH^+ + 2 H], 302 (95) [MH^+ + H], 301 (100) [MH^+]. – $C_{18}H_{28}N_4$: calcd. 300.2314; found 300.2323. – $C_{18}H_{28}N_4HBF_4$: calcd. C 55.68, H 7.53, N 14.43; found C 55.52, H 7.50, N 14.20.

b) A suspension of 680 mg (1.4 mmol) of tetrafluoroborate **3** · **HBF$_4$** in 100 mL of 2 N sodium hydroxide solution and 110 mL of *n*-pentane under argon was stirred until the salt had been dissolved. The organic layer was separated, and the aqueous phase was extracted three times with 50 mL of *n*-pentane each. The combined organic solutions were concentrated in vacuo leaving a residue which was treated with warm pentane to filter off the insoluble inorganic impurities. Concentration of the filtrate and crystallization of the residue from hexane yielded 295 mg (ca. 55%) of **3** as yellow needles [m.p. 78–80 °C, R_f = 0.9 (ALOX, diethyl ether)]. – ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.60 (s, 12 H, 2,7-NMe_2), 2.91 (s, 12 H, 1,8-NMe_2), 7.20 (d, 2 H, ^3J = 8.7 Hz, 3,6-H), 7.42 (d, 2 H, 4,5-H), assignment by NOE. – MS; *m*/*z* (%): 300 (100) [M^+], 256 (12), 254 (10), 242 (25), 241 (47), 240 (42), 227 (47), 226 (29), 225 (12), 211 (11), 197 (10), 112 (12). – $C_{18}H_{28}N_4$: calcd. C 71.96, H 9.39, N 18.65; found C 71.97, H 9.57, N 18.40.

1,2,7,8-Tetrakis(dimethylamino)naphthalene Hydrobromide (3HBr): Through a column of 10 g of Sephadex DEAE A-25, which was treated with aqueous sodium bromide solution, a solution of 19 mg (0.05 mmol) of **3** · **HBF$_4$** in water was filtered, and the filtrate was

concentrated in vacuo; recrystallization of the residue from ethanol yielded **3 · HBr** as colourless needles which made it possible to carry out an X-ray crystal structure determination as shown in Table 1 and Figure 3.

1,2,5,6-Tetrakis(dimethylamino)naphthalene (2). – a) $\mathbf{2 \cdot (HBF_4)_2}$ was prepared in analogy to $\mathbf{3 \cdot (HBF_4)_2}$ starting from 2,6-dimethylamino-1,5-dinitronaphthalene[5] of which a solution of 1.0 g (3.3 mmol) in 50 mL of THF was hydrogenated at 3 bar in the presence of 200 mg of 5% palladium/charcoal to yield 1,5-diamino-2,6-bis(dimethylamino)naphthalene (colourless powder, m.p. 136–137 °C; R_f = 0.6, ALOX, cyclohexane/ethyl acetate, 1:1, with 1% triethylamine). This compound was *N*-methylated by 1.20 g (50 mmol) of sodium hydride in 10 mL of anhydrous THF under argon and 3.10 mL (4.2 g, 33 mmol) of dimethyl sulfate. The mixture was heated for 2.5 h and stirred at room temperature for 19 h; then 18 mL of 10% aqueous ammonium hydroxide and 6 mL of methanol were added, and the crude product was filtered through deactivated alumina by using diethyl ether with 1% triethylamine as eluent. Addition of 1 mL of tetrafluoroboric acid (54% in diethyl ether) precipitated the 2-bis(tetrafluoroborate) which was recrystallized from methanol to yield 190 mg (12%) of $\mathbf{2 \cdot (HBF_4)_2}$, colourless powder of m.p. 270 °C (dec.). – ^{1}H NMR (360 MHz, [D$_3$]acetonitrile): δ = 3.08 (s, 12 H, 1,5-NMe$_2$), 3.23 (s, 12 H, 2,6-NMe$_2$), 7.92 (d, 2 H, ^3J = 9.3 Hz, 3,7-H), 8.35 (d, 2 H, 4,8-H), 10.69 (br. s, 2 H, N-H). – MS; *m*/*z* (%): 301 (22), 300 (100) [M$^+$], 285 (11), 270 (45), 269 (24), 241 (25), 240 (26), 239 (22) a. o. – $C_{18}H_{30}B_2F_8N_4$: calcd. C 45.41, H 6.35, N 11.77; found C 45.24, H 6.42, N 11.55.

b) The target molecule **2** was prepared from the tetrafluoroborate as described above for **3**: 400 mg (0.84 mmol) of $\mathbf{2 \cdot (HBF_4)_2}$, using 400 mL of diethyl ether and 100 mL of 2 N sodium hydroxide solution, yielded a product which was recrystallized from *n*-hexane yielding 230 mg (91%) of **2** as colourless needles, m.p. 135–136 °C, R_f = 0.6 (ALOX, cyclohexane/ethyl acetate, 30:1). – ^{1}H NMR (360 MHz, [D$_3$]acetonitrile): δ = 2.72 (s, 12 H, 2,6-NMe$_2$), 2.96 (s, 12 H, 1,5-NMe$_2$), 7.31 (d, 2 H, ^3J = 9.1 Hz, 3,7-H), 7.88 (d, 2 H, 4,8-H). – MS; *m*/*z* (%): 301 (14), 300 (100) [M$^+$], 270 (22), 269 (11), 241 (12), 240 (10) a. o. – $C_{18}H_{28}N_4$: calcd. C 71.96, H 9.39, N 18.65; found C 71.83, H 9.56, N 18.51.

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[9] Crystallographic data (excluding structure factors) for the structures **4** and **5** reported in this paper have been deposited at the Cambridge Crystallographic Data Center as supplementary publication No. CCDC-102268–102270. Copies of the data can be obtained free of charge on application to: CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk

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