New "Proton Sponges", 13[+]

Syntheses, Structures and Basicities of 1,2,4,5-Tetrakis(dimethylamino)benzene and 2,3,6,7-Tetrakis(dimethylamino)naphthalene

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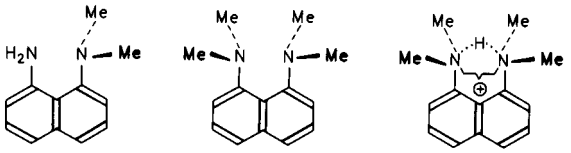
Keywords: "Proton sponge" analogues / Orientation dependence of hydrogen bonds / Cyanine structures versus aromaticity in benzene dications / Crystal structures

1,2,4,5-Tetrakis(dimethylamino)benzene (**4**) and 2,3,6,7-tetrakis(dimethylamino)naphthalene (**5**) were prepared and structurally determined. Electron-donor functions, protonation, and the geometry of intramolecular hydrogen bonds are discussed. By oxidation of **4** to its dication the benzenoid aromaticity is cancelled in favour of two independent cyanine-type units as determined by X-ray structure analysis.

Introduction

Since the late 1960s organic bases of remarkably strong basicities found special interest as so-called "proton sponges" (Alder,[1] Hibbert;[2] see ref.[3]). For these "proton sponges" two intramolecular basic centers, usually dimethylamino groups, are required, the steric orientation of which should allow the absorption of *one* proton to yield a stabilized $[N\cdots H\cdots N]^+$ hydrogen bond. By sterical shielding due to alkylation on the nitrogen atoms the stability of such hydrogen bonds is considerably increased. Usually, the effect of *N*-alkylation on the basicity of amino groups is rather small as, for example, the basicities of *N*-alkylated anilines show [pK_a (water, 25°C): aniline 4.63, *N*-methylaniline 4.85, *N*,*N*-dimethylaniline 5.15].[4] As expected, for 1,8-diaminonaphthalene the basicity is in the normal range as is the case for 1-amino-8-(dimethylamino)naphthalene (**1**) with p$K_a \approx 4.6$. If, however, each of the two amino groups of **1** are dimethylated to **2**, a dramatic increase of basicity to p$K_a = 12.1 \pm 0.1$[2] is observed, resulting from the strong hydrogen bond with short N···N distance and especially from the shielding to the outside by the four *N*-methyl substituents as shown in formula **3**.



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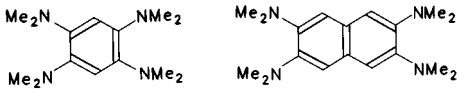
In the present paper we report on the syntheses and properties of 1,2,4,5-tetrakis(dimethylamino)benzene (**4**) and the corresponding 2,3,6,7-tetrakis(dimethylamino)-naphthalene (**5**).[5] The structures of **4** and **5** include two pairs of neighbouring dimethylamino substituents with strong electron-donating effects, and in view of their adjacent sterical positions they were originally considered to be suitable candidates for strong $[N\cdots H\cdots N]^+$ hydrogen bonds. The dimethylamino groups in **4** and in **5**, however, are not sufficiently fixed in an orientation towards each other, and due to the divergent C−N bonds of the vicinal amino groups a more angular orientation of the $[N\cdots H\cdots N]^+$ hydrogen bonds in **4** and **5** in contrast to **3** is enforced.



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Syntheses and Properties of 1,2,4,5-Tetrakis(dimethylamino)benzene (4) and 2,3,6,7-Tetrakis(dimethylamino)naphthalene (5)

1,2,4,5-Tetrakis(dimethylamino)benzene (4)

Although the precursor 1,2,4,5-tetraaminobenzene had been prepared already decades ago,[6] the tetrakis(dimethylamino) compound **4** to our knowledge had not been reported in literature. An improved synthesis of the tetraaminobenzene started from 1,3-dichlorobenzene which was nitrated preferentially in the 4,6-positions. The reaction with ammonia under pressure then yielded 1,3-diamino-4,6-dinitrobenzene which was catalytically hydrogenated to the corresponding 1,2,4,5-tetraaminobenzene, the tetrahydrochloride of which is reasonably stable.[7] The complete methylation of the amino groups was achieved by treatment of the tetrahydrochloride in acetonitrile under argon with 36.5% aqueous formaldehyde solution and sodium cyanotrihydroborate.[8] The work-up of **4** (see Experimental Section for details) yielded after repeated sublimations **4** as

[+] Part 12: H. A. Staab, C. Krieger, G. Hieber, K. Oberdorf, *Angew. Chem.* **1997**, *109*, 1946−1949; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1884−1886.

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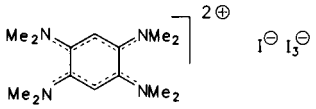
colourless crystals (m.p. 95°C) with correct elemental analysis, ^{1}H-NMR and MS data.

As explained in the introduction of this paper, the problem of "proton sponges" was discussed for systems where one or two pairs of dimethylamino groups, like in **3,** are in an appropriate orientation leading to especially stable hydrogen bonds. In spite of the two pairs of *ortho*-bis(dimethylamino) substituents in the 1,2- and 4,5-positions, **4** does not belong to the "proton sponge" group since the precondition of a strong "hydrogen bond" is not fulfilled for the geometrical reasons mentioned before. An additional reason obviously is that the four electron-donating groups on one benzene unit make this π-system an extremely strong electron donor, losing electrons from the lone pairs of the amino groups very easily. For example, **4** forms with 7,7,8,8-tetracyanoquinodimethane (TCNQ) in a 1:2 ratio a complex consisting of a dication of **4** and two TCNQ radical anions.

Indeed, the cyclovoltammetry of **4** (acetonitrile/0.1 M tetrabutylammonium perchlorate, "glassy carbon electrode" vs. Ag/Ag^+, ferrocene correction, $v = 220$ mVs^{-1}) indicates that the first two oxidation steps are not separable and correspond to $E_{ox} \approx -0.266$ V[5] which demonstrates the very easy formation of the dications of **4**. The dication of **4** was also obtained by treatment with iodine in acetonitrile yielding crystals of the elemental composition $C_{14}H_{26}I_4N_4$. X-ray structure analysis confirmed the presence of the 1,2,4,5-tetrakis(dimethylamino)benzene dication with iodide triiodide ($I^-\cdot I_3^-$) as dianions (**6**) (for details see Experimental Section).



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A most interesting point of the crystal structure of the dication of **4** in **6** is the remarkable difference of the C−C bond lengths within the six-membered ring which originally was the benzene basis of **4**: Two three-carbon chains $C^1-C^6-C^5$ and $C^2-C^3-C^4$ are linking the two pairs of the dimethylamino groups by a "cyanine-type" system [with bond length 138.2(5) pm] whereas the two remaining six-membered ring bonds are not part of the two cyanine

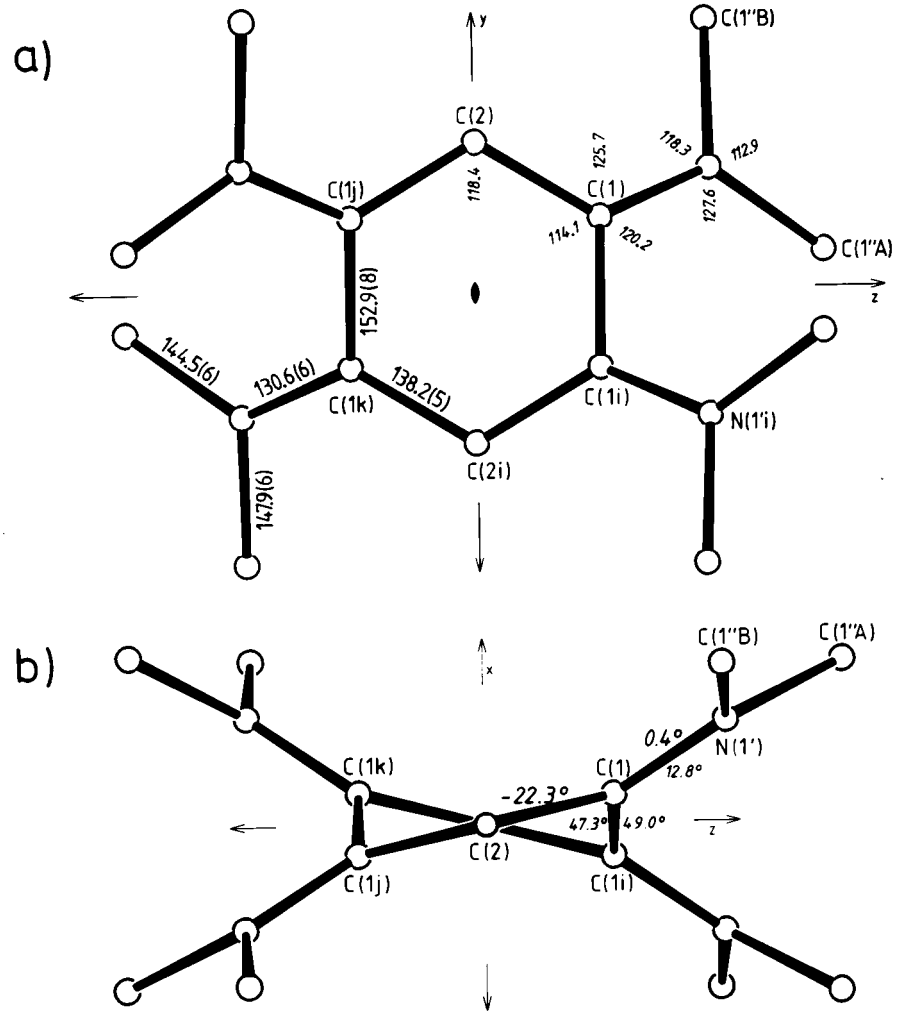

Figure 1. Structure of the dication part of **4**·$\mathbf{I^-\cdot I_3^-}$; a: upside view; b: side view along the axis C(2)···C(2i)

π-systems but keep them together in the six-membered ring; the bond lengths of 152.9(8) pm correspond to the single-bond character of these two bonds.

The donor properties of **4** are different from the majority of organic electron donors which normally donate just one electron; if according to the potentials more than one electron is transferred, it usually occurs step by step according to different potentials. In the case of **4**, however, the simultaneous transfer of two electrons is favoured by the conversion of the benzenoid system into two "cyanine" systems as the bond lengths clearly demonstrate (Figure 1a).[5]

As explained in the introduction of this paper, the problem of "proton sponges" was discussed for systems where one or two pairs of dimethylamino groups like those in **3** are in an appropriate orientation for stable hydrogen bonds. This is not the case for **4** where the preconditions are sterically less favourable for intramolecular $[N\cdots H\cdots N]^+$ hydrogen bonds because in the two pairs of *ortho*-positioned C−N bonds the neighbouring dimethylamino groups point into divergent directions. To check this concept, an excess of aqueous hydrogen bromide solution (48%) was added slowly to a solution of **4** in diethyl ether leading to a white gum-like sediment which was washed with diethyl ether; the residue was crystallized from methanol as colourless prisms. From the elemental analysis and the physical data it was clear that a dibromide of **4** including two molecules of water was formed in about 93% yield, with a melting point of 226−227°C (dec.). This structure was supported by ^{1}H NMR (360 MHz, [D$_6$]DMSO, 303 K), showing a slightly broadened singlet at δ = 2.84 (24 H) for the eight methyl groups and a broadened singlet at δ = 7.15 of the two benzene protons. For the "ammonium protons" no ^{1}H-NMR signal was visible, obviously due to the fast exchange with the hydrate protons. The X-ray structure analysis of **4·2HBr·2H$_2$O** was solved with the expected result that no short and symmetrical hydrogen bonds between neighbouring dimethylamino groups are observed for the dication of **4** (see Figure 2) (for details see Experimental Section).

In analogy to the formation of the dibromide dihydrate of **4** (Figure 2) the bis(tetrafluoroborate) of **4** was obtained by adding aqueous tetrafluoroboric acid (36%) to a solution of **4** in diethyl ether. By crystallization of the precipitate from methanol white needles of m.p. 290−291°C were obtained in 70% yield. Elemental analysis, ^{1}H-NMR and further analytical data are in agreement with the bis(tetrafluoroborate) of **4**. Although an X-ray structure analysis is not yet available, most probably the structure of **4** in **4·2HBF$_4$** is analogous to that shown in Figure 2 for the corresponding dibromide dihydrate.

2,3,6,7-Tetrakis(dimethylamino)naphthalene (5)

The synthesis of **5**, in which benzene as aromatic spacer is replaced by naphthalene, started from 2,7-dihydroxynaphthalene; with a Bucherer reaction (SO_2-saturated concentrated ammonia solution, autoclave, 17 h, 150°C) the 2,7-diaminonaphthalene (95% yield, m.p. 158−159°C) was obtained, which after recrystallization from water in the presence of activated charcoal forms needles for which elemen-

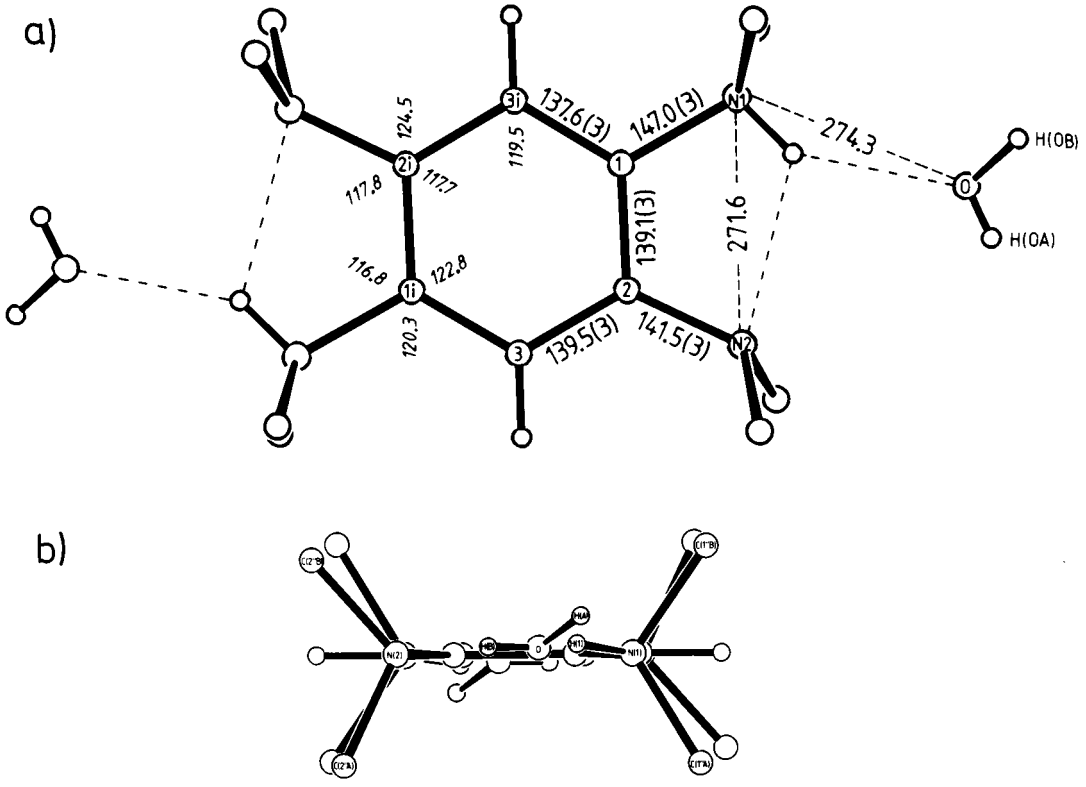

Figure 2. Structure of the dication part of **4·2HBr·2H$_2$O** in a top-view (a) and in a side-view (b)

tal analysis, ^{1}H-NMR and MS data are in accordance with the expected structure. Bromination of 2,7-diaminonaphthalene to 2,7-diamino-3,6-dibromonaphthalene was obtained with *N*-bromosuccinimide in 1,4-dioxane. DC control proved the predominant bromination expected for the 3,6-positions; however, additional bromination in the *peri*-positions of naphthalene always occurred to some extent. Due to the higher reactivity of bromo substituents in the *peri*-positions these bromo substituents can be removed by reductive debromination with tin in acetic acid to yield the wanted product 2,7-diamino-3,6-dibromonaphthalene after crystallization from toluene (76% yield, m.p. 229−230°C). For ^{1}H-NMR, MS data and further details of the synthesis of **5** see the Experimental Section.

The next step of the synthesis of **5** was the reductive methylation of the two amino groups according to the earlier mentioned method of Borch and Hassid:[8] To the above-mentioned 2,7-diamino-3,6-dibromonaphthalene in acetonitrile 36.5% aqueous formaldehyde solution was added under argon, followed by sodium cyanotrihydroborate, and after a few minutes glacial acetic acid was added. After 3 h of stirring at 20°C, the solvents were distilled off and the product was chromatographed on alumina with *n*-hexane/ethyl acetate (50:1). Of the fraction with $R_f \approx 0.3$ the solvent mixture was distilled off, leaving a light-yellow oil which at about −20°C solidified and was crystallized from *n*-hexane (93%, m.p. 51−52°C of a wax-like solid), yielding correct elemental analysis, ^{1}H-NMR and MS data.

The last two steps of the synthetic route to **5** were the substitution on the amino groups which, in principle, according to the method mentioned for the preparation of **4**, were methylated to yield 2,3,6,7-tetrakis(dimethylamino)-naphthalene (**5**) (see Experimental Section); **5** forms colourless crystals of m.p. 170−171°C (from *n*-hexane). An X-ray structure analysis of **5** is shown in Figure 3 in a vertical view onto the naphthalene plane for which the bond lengths and bond angles are in the normal range and the naphthalene skeleton is planar. The nitrogen atoms of the dimethylamino groups are nearly within the naphthalene plane.

Of **5**, the iodide triiodide was obtained analytically pure as well as **5·2HBr·2H$_2$O**, the tetrafluoroborate **5·2HBF$_4$**,

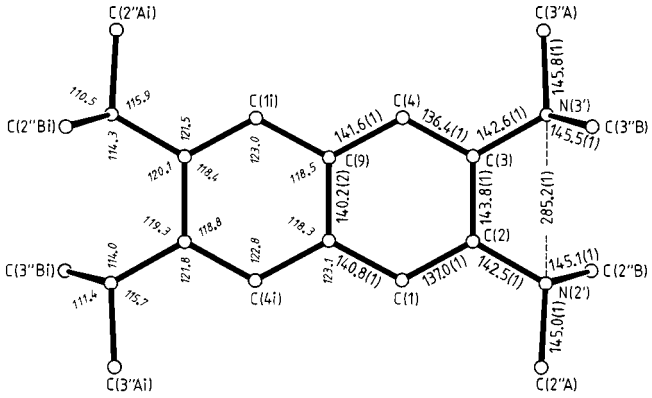

Figure 3. Structure of **5** (vertical view)

and the complex of **5** with TCNQ. For **5** itself and its iodide triiodide, the dihydrobromide dihydrate as well as for the complex **5·2HBr·4H$_2$O** X-ray structure analyses were solved[9] (for details see Experimental Section).

Of the dihydrobromide of **5** which was obtained as tetrahydrate, the dication has fairly normal bond lengths in the naphthalene part (Figure 4). Thus, the "cyanine-type" structure of the benzene dication is obviously not transferable to the more extended aromatic system of naphthalene. The protonation of the dication of **5** occurs on opposite dimethylamino groups on N(3′) linked to C(3) and to N(6′) of the 6-dimethylamino group. For the two bis(dimethylamino) groups on either side of the naphthalene **5** the N···N distances are determined to 285.2 pm which explains the fact that a stable hydrogen bond with the hydrogen atom in the centre is not favoured.

One further interesting aspect of 2,3,6,7-tetrakis(dimethylamino)naphthalene (**5**) is that it is a structural isomer of 1,4,5,8-tetrakis(dimethylamino)naphthalene which is one of the most interesting bifunctional "proton sponges". In the following papers of this series the syntheses and properties of this and other tetrakis(dimethylamino)naphthalenes will be dealt with.

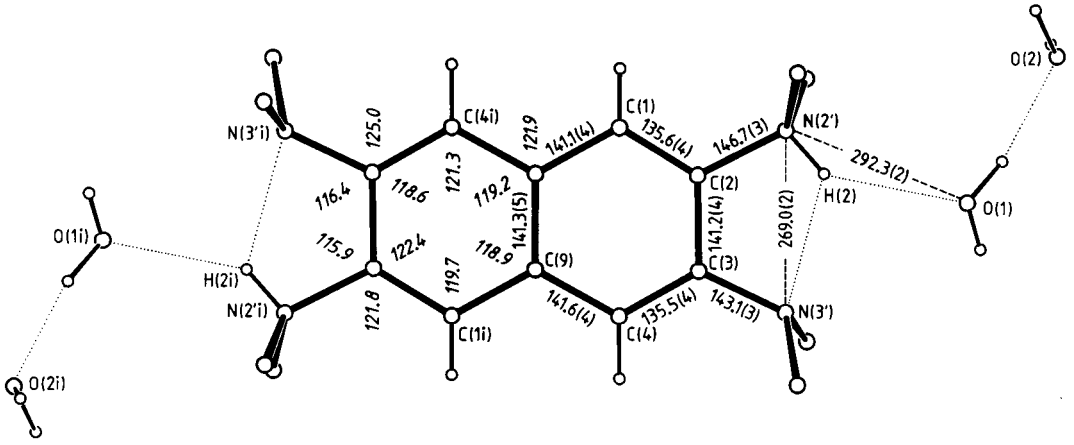

Figure 4. Structure of the 2,3,6,7-tetrakis(dimethylamino)naphthalene dication part of **5·2HBr·4H$_2$O**

Experimental Section

General Remarks: Melting points: Büchi SMP-20; Bock Monoscop for m.p. > 220°C (uncorrected values). − Elemental analyses: Elemental Analyzer 1106, Carlo Erba. − IR: Spectrometer Beckman IR-4240 (KBr pellets). − UV/Vis: Cary 2300, Varian. − ^{1}H-NMR: Bruker WP-80, HX-360, AM-500; intern. standard TMS. − MS: Dupont CEC 21-492; Finnigan MAT 212; IE: 70 eV, temperature mentioned for individual spectra. − Analytical DC: Polygram Alox N/UV$_{254}$, Macherey-Nagel; HPLC: Spectro 8800 Dupont; CC aluminium oxide N, activ. II−III (0.063−0.2 mm, Merck); flash chromatography: Merck 60 (0.04−0.063 mm, 5 cm/min). − Cyclovoltammetry: Universal Modular Polarograph E 310 Bruker; Scanning Potentiostat 362, EG&G Princeton Applied Research.

1,2,4,5-Tetrakis(dimethylamino)benzene (4): To a suspension of 568 mg (2.00 mmol) of 1,2,4,5-tetraaminobenzene tetrahydrochloride in 30 mL of acetonitrile under argon 3.00 mL (40.0 mmol) of a 36.5% aqueous formaldehyde solution and 700 mg (11.1 mmol) of sodium cyanotrihydroborate were added. The reaction was rather vigorous, and the mixture warmed up to about 40°C whilst the colour of the solution changed from violet via red, orange and yellow to brown. The deposit formed was dissolved by addition of a small amount of glacial acetic acid. After 3 h of stirring, the solvent was distilled off, to the residue 40 mL of 2 N potassium hydroxide solution was added, and this solution was extracted three times with 40 mL of diethyl ether each. The combined organic phases were washed with 40 mL of 0.5 N potassium hydroxide solution and then three times with 20 mL of 1 N hydrochloric acid each. To the acid phase solid potassium hydroxide was added until the solution opacified and reacted strongly basic. This solution was extracted four times with 40 mL each of diethyl ether, the combined extracts were dried with potassium carbonate, and the solvent was distilled off. The residue crystallized in brown needles which were sublimed twice (3−4 Torr, 100°C oil-bath temperature) to yield 135 mg (27%) of colourless crystals of m.p. 95°C. − ^{1}H NMR (360 MHz, $CDCl_3$, 303 K): δ = 2.76 (s, 24 H, NCH_3), 6.56 (s, 2 H, ar-H). − MS; *m/z* (%): 250 (100) [M^+], 220 (12), 125 (3) [M^{++}]. − $C_{14}H_{26}N_4$ (250.39): calcd. C 67.16, H 10.47, N 22.38; found C 67.19, H 10.52, N 22.14.

1,2,4,5-Tetrakis(dimethylamino)benzene (4) − 7,7,8,8-Tetracyanoquinodimethane (TCNQ) Complex: To 25.0 mg (0.10 mmol) of **4**, dissolved in 5 mL of acetonitrile, a hot solution of 41.0 mg (0.20 mmol) of 7,7,8,8-tetracyanoquinodimethane in 10 mL of acetonitrile was added dropwise. After standing for several hours, from the blue-green solution in acetonitrile deep violet metallic shining needles were separated and recrystallized from acetonitrile. **4** reacts as a donor in a 1:2 ratio with the acceptor TCNQ yielding 29.1 mg (44%) of the **4·(TCNQ)$_2$** complex; m.p. 213°C (dec.). − Electron spectrum (acetonitrile, $c = 7.1\cdot10^{-6}$ mol/L): λ_{max} (log ε) = 277 nm (4.10), 392 (5.29), 676 (3.90), 740 (4.39) 836 (4.61). − $C_{14}H_{26}N_4\cdot(C_{12}H_4N_4)_2$ (658.77): calcd. C 69.28, H 5.20, N 25.51; found C 70.12, H 5.06, N 25.96.

1,2,4,5-Tetrakis(dimethylamino)benzene Iodide Triiodide (4·I·I$_3$): To 25 mg (0.10 mmol) of **4** in 3 mL of acetonitrile 50.8 mg (0.20 mmol) of iodine in 10 mL of acetonitrile was added. On standing for several hours at room temperature, from the dark-green solution black-violet crystals separated and were recrystallized from acetonitrile: 29.2 mg (39% yield), m.p. 272°C (dec. from 190°C on). − ^{1}H NMR (360 MHz, [D$_6$]DMSO, 303 K): δ = 3.34 (s, 24 H, NCH_3), 5.85 (s, 2 H). − Electron spectrum (CH_3CN): λ_{max} (log ε) = 290 nm (4.74), 368 (4.46), 392 sh (4.43), 573 (3.38). − C14H26N4·I4 (758.01): calcd. C 22.18, H 3.46, I 66.97, N 7.39; found C 22.39, H 3.37, I 66.88, N 7.17.

1,2,4,5-Tetrakis(dimethylamino)benzene Dihydrobromide Dihydrate [4·(2HBr·2H$_2$O)]: To 100 mg (0.40 mmol) of **4** in 10 mL of diethyl ether 1 mL (5.93 mmol) of 48% hydrobromic acid was added dropwise, and immediately a white gum-like sediment was formed. After 30 min, the solvent was decanted, and the residue was washed with 10 mL of diethyl ether; the sediment then was crystallized from methanol. The crystals were obtained after removing the solvent as colourless prisms suitable for an X-ray structure analysis (see below): 167 mg (93% yield), m.p. 226−227°C (methanol). − ^{1}H NMR (360 MHz, [D$_6$]DMSO, 323 K): δ = 2.84 (s, 24 H, NCH_3), 4.0 (br. s, NH and H_2O), 7.15 (br. s, 2 H, ar-H); (360 MHz, [D$_6$]DMSO/D_2O 1:1, 303 K): δ = 2.95 (s, 24 H, NCH_3), 8.02 (s, 2 H, ar-H). − $C_{14}H_{26}N_4\cdot2HBr\cdot2H_2O$ (448.24): calcd. C 37.51, H 7.20, Br 35.65, N 12.50; found C 37.63, H 7.25, Br 35.83, N 12.25.

1,2,4,5-Tetrakis(dimethylamino)benzene Bis(hydrotetrafluoroborate) [4·(HBF$_4$)$_2$]: To a solution of 25 mg (0.10 mmol) of **4** in 4 mL of diethyl ether 0.2 mL (0.86 mmol) of 36−38% fluoroboric acid was added dropwise. The sediment formed immediately was filtered off and crystallized from methanol to yield 30 mg (70%) of m.p. 290−291°C. − ^{1}H NMR (360 MHz, [D$_6$]DMSO, 303 K): δ = 2.86 (s, 24 H, NCH_3), 7.36 (br. s, 2 H, ar-H), 10.38 (br. s, NH). − $C_{14}H_{26}N_4\cdot2HBF_4$ (426.01): calcd. C 39.47, H 6.63, B 5.08, N 13.15; found C 39.48, H 6.89, B 4.88, N 13.07.

2,7-Diaminonaphthalene: 150 mL of concentrated aqueous ammonia solution (*d* = 0.91 g/mL) under ice-cooling was saturated with sulfur dioxide. In this solution 6.00 g (37.5 mmol) of 2,7-dihydroxynaphthalene was suspended. This mixture was heated in an autoclave under stirring to 150°C for 17 h. The precipitate formed after cooling was filtered off, the filtrate was extracted twice with 50 mL of ethyl acetate each, and the filtration residue was taken up in ethyl acetate. The combined organic phases were extracted three times with 80 mL of 1 N hydrochloric acid. The aqueous phase was alkalized with solid potassium hydroxide up to strongly alkaline reaction which then was extracted four times with 50 mL each of ethyl acetate. After drying the organic extract with potassium carbonate, the solvent was distilled off leaving a beige powder which was crystallized from water on addition of activated charcoal: 5.63 g (95%) of 2,7-diaminonaphthalene, m.p. 158°C. − ^{1}H NMR (360 MHz, [D$_6$]DMSO, 303 K): δ = 5.0 (br. s, 4 H, 2,7-NH_2), 6.47 (d, J_m = 2.1 Hz, 2 H, 1,8-H), 6.52 (dd, J_m = 2.1 Hz, J_o = 8.6 Hz, 2 H, 3,6-H), 7.29 (d, J_o = 8.6 Hz, 2 H, 4,5-H). − MS; *m/z* (%): 158 (100) [M^+], 130 (15), 79 (8) [M^{++}]. − $C_{10}H_{10}N_2$ (158.20): calcd. C 75.92, H 6.37, N 17.71; found C 75.87, H 6.36, N 17.42.

2,7-Diamino-3,6-dibromonaphthalene: In 170 mL of 1,4-dioxane, through which argon had been passed for 10 min, 3.00 g (18.96 mmol) of 2,7-diaminonaphthalene was dissolved. After addition of 10.1 g (56.7 mmol) of *N*-bromosuccinimide, the reaction mixture was stirred for 3 h at room temperature under argon.After heating to reflux, 20 mL of glacial acetic acid and then 4.50 g (37.9 mmol) of tin in four portions were added. The reaction mixture was heated under reflux for 18 h. After cooling, solid potassium hydroxide was added until reaching strongly alkaline condition. Five-fold extraction with 100 mL of ethyl acetate each yielded an organic phase which was washed with saturated sodium chloride solution and dried with magnesium sulfate. The solvents were distilled off, and the residue was crystallized from toluene after treating with activated charcoal: 4.57 g (76% yield), m.p. 229−230°C (from toluene). − ^{1}H NMR (360 MHz, [D$_6$]DMSO, 303 K): δ = 5.32 (br. s, 4 H, 2,7-NH_2), 6.74 (s, 2 H, 1,8-H), 7.78 (s, 2 H, 4,5-H). − MS; *m/z* (%): 314 (100) [M^+], 236 (12), 208 (27), 157 (10) [M^{++}]. − $C_{10}H_8Br_2N_2$ (316.0): calcd. C 38.01, H 2.55, Br 50.57, N 8.87; found C 38.05, H 2.44, Br 50.44, N 8.62.

3,6-Dibromo-2,7-bis(dimethylamino)naphthalene: 1.30 g (4.11 mmol) of 2,7-diamino-3,6-dibromonaphthalene was suspended in 150 mL of acetonitrile which under argon had repeatedly been distilled. 8 mL (103 mmol) of a 36.5% formaldehyde solution and then 1.93 g (30.8 mmol) of sodium cyanotrihydroborate were added. After 10 min, 1.5 mL of glacial acetic acid was added dropwise. Then the reaction mixture was kept stirring for 3 h at room temperature. Afterwards, the solvent was distilled off, the residue was dissolved in 100 mL of diethyl ether and three times washed with 50 mL each of 2 N sodium hydroxide solution. After drying the organic phase with magnesium sulfate, the solvent was evaporated. The oily residue was chromatographed on aluminium oxide with *n*-hexane/ethyl acetate (50:1). With $R_f \approx 0.3$ a yellow oil was obtained which solidified at −20°C; crystallization from *n*-hexane yielded 1.42 g (93%) of a yellowish wax-like product (m.p. 51−52°C). − ^{1}H NMR (360 MHz, $CDCl_3$, 303 K): δ = 2.87 (s, 12 H, NCH_3), 7.26 (s, 2 H, 1,8-H), 7.88 (s, 2 H, 4,5-H). − MS; *m/z* (%): 370 (100) [M^+, 2 Br], 369 (19), 291 (20), 185 (20) [M^+] a. o. − $C_{14}H_{16}Br_2N_2$ (372.10): calcd. C 45.19, H 4.33, Br 42.95, N 7.53; found C 45.46, H 4.33, Br 42.97, N 7.32.

2,3,6,7-Tetrakis(dimethylamino)naphthalene (5): A solution of 1.00 g (2.69 mmol) of the preceding 3,6-dibromo-2,7-bis(dimethylamino)naphthalene in 10 mL of dry tetrahydrofuran was cooled to −78°C and dropwise added to 3.40 mL (5.44 mmol) of a 1.6 M solution of butyllithium in *n*-hexane. After 20 min, this suspension was warmed up to −8°C, stirred for further 20 min, and then was transferred to a solution of 1.35 g (4.91 mmol) of diphenylphosphoryl azide (DPPA) in 50 mL of water-free tetrahydrofuran at −78°C under argon. After 2 h of stirring at this temperature and 1 h of further stirring at −20°C, the solution was cooled again to −78°C, and dropwise 6.20 mL (21.6 mmol) of a 3.5 M solution of sodium bis(2-methoxyethoxy)aluminium hydride ("SMEAH") in toluene were added. The reaction mixture then was warmed up to 0°C under foaming, and a white sediment was formed. The suspension under argon was filtered through an inverse frit, and the residue on the filter was washed with 20 mL of ethyl acetate and then with 10 mL of saturated sodium chloride solution. The organic phase of the filtrate was 2,7-diamino-3,6-bis(dimethylamino)naphthalene which was immediately methylated on the two free amino groups. For that reason under argon 2.20 mL (26.3 mmol) of a 36.5% aqueous formaldehyde solution and then 600 mg (9.55 mmol) of sodium cyanotrihydroborate were added as was, after 10 min of stirring at room temperature, 0.8 mL of glacial acetic acid. After 16 h of further stirring, the solvents were distilled off in vacuo, and the remaining residue was dissolved in 50 mL of 2 N sodium hydroxide solution. This solution was extracted three times with 30 mL each of diethyl ether. The combined organic phases then were extracted three times with 40 mL each of 1 N hydrochloric acid. The remaining aqueous phase was made strongly alkaline by solid potassium carbonate and then again extracted three times with 30 mL each of diethyl ether. After drying the organic phase with potasssium carbonate, the solvent was evaporated in vacuo. The residue was chromatographed on aluminium oxide with *n*-hexane/ethyl acetate (50:1; $R_f \approx 0.25$). The product fraction after removal of the solvents in vacuo was crystallized from *n*-hexane to yield colourless prisms of **5**: 98.2 mg (13%), m.p. 170−171°C (*n*-hexane). − ^{1}H NMR (360 MHz, CD_2Cl_2, 303 K): δ = 2.83 (s, 24 H, NCH_3), 7.02 (s, 4 H, ar-H). − MS; *m/z* (%): 300 (100) [M^+], 270 (24), 239 (10), 126 (10), 97 (8), 96 (14), 95 (20), 94 (18), a. o. − $C_{18}H_{28}N_4$ (300.45): calcd. C 71.96, H 9.39, N 18.65; found C 72.07, H 9.44, N 18.42.

2,3,6,7-Tetrakis(dimethylamino)naphthalene 7,7,8,8-Tetracyanoquinodimethane (TCNQ) Complex: To a solution of 5.4 mg (18 μmol) of **5** in 2 mL of acetonitrile under warming a solution of 3.7 mg (18 μmol) of TCNQ in 2 mL of dichloromethane was added. After a few days, black prisms were precipitated from the green-blue solution, which were separated and dried in vacuo: 3.8 mg (73% yield), m.p. 207°C (dec.). − $C_{18}H_{42}N_{18}{\cdot}35C_{12}H_4N_4$ (1015.12): calcd. C 70.99, H 4.17, N 24.84; found C 70.96, H 4.12, N 25.18.

2,3,6,7-Tetrakis(dimethylamino)naphthalene 2,6-Dihydrobromide Tetrahydrate (5·2HBr·4H$_2$O): To 15.0 mg of **5** in 3 mL of diethyl ether, 0.1 mL (0.59 mmol) of a 48% aqueous hydrogen bromide solution was added leading to a flaky white precipitate which was decanted and washed with 5 mL of diethyl ether. Crystallization from methanol yielded colourless to white crystals which were separated and dried on air. The colourless plates [17.4 mg (65%), m.p. 223−224°C (from methanol)] were used for an X-ray analysis

Table 1. Crystallographic data and refinement parameters of **4·I$^-$I$_3^-$**, **4·2HBr·2H$_2$O**, **5**, and **5·2HBr·4H$_2$O**

	4·I$^-$·I$^-_3$	**4·2HBr·2H$_2$O**	**5**	**5·2HBr·4H$_2$O**
Empirical formula	$C_{14}H_{26}I_4N_4$	$C_{14}H_{32}Br_2N_4O_2$	$C_{18}H_{28}N_4$	$C_{18}H_{38}Br_2N_4O_4$
Molecular mass	758.01	448.24	300.45	534.35
Crystallized from	acetonitrile	methanol	n-hexane	methanol
Crystal size [mm]	0.2 × 0.1 × 0.1	0.2 × 0.2 × 0.1	0.2 × 0.1 × 0.1	0.3 × 0.2 × 0.15
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	*Ibam*	$P2_1/c$	$P2_1/n$	$P2_1/n$
a [pm]	875.5(4)	620.8(1)	1110.2(2)	704.1(2)
b [pm]	1109.8(2)	795.4(2)	738.4(2)	2276.4(4)
c [pm]	2311.2(7)	2058.4(3)	1207.1(2)	796.5(2)
β [°]	90	98.38(1)	116.28(1)	102.71(1)
Z	4	2	2	2
Symmetry of molecule in crystal	D_2	C_i	C_i	C_i
F_{000} [e]	1400	460	328	552
$D_{calcd.}$ [g·cm^{-3}]	2.242	1.480	1.135	1.425
μ [mm^{-1}] (Mo-K_α)	5.50	4.02	0.064	3.25
Unique reflections {measured up to (sinθ/λ) [nm^{-1}]}	1456 {6.90}	2543 {6.80}	2219 {6.72}	2964 {6.83}
Observed reflections [$I \geq 2.0\ \sigma(I)$]	1040	1660	2040	2102
Refinement *R*	0.039	0.035	0.043	0.041
$(\Delta/\sigma)_{max}$	0.01	0.01	0.01	0.01

which confirmed the structure. – ^{1}H NMR (360 MHz, [D$_6$]DMSO, 303 K): δ = 2.94 (br. s, 24 H, NCH_3), 7.29 (br. s, 2 H, ar-H), 8.08 (br. s, 2 H, ar-H), 9.4 (br. s, NH); – (360 MHz, [D$_6$]DMSO/D_2O 1:1, 303 K): δ = 3.04 (s, 24 H, NCH_3), 8.31 (s, 4 H, ar-H). – $C18H28N4{\cdot}2HBr{\cdot}4H_2O$ (534.33): calcd. C 40.46, H 7.17, Br 29.91, N 10.49; found C 40.62, H 7.03, Br 29.73, N 10.22.

X-ray Structure Analyses: The X-ray structure analyses were obtained by using an Enraf-Nonius CAD 4 diffractometer (Mo-K_α radiation; λ = 71.073 pm, θ/2θ scans); empirical absorption correction performed (ψ scans). – Table 1 lists the crystallographic data and refinement parameters.

Acknowledgments

We thank the Volkswagen-Stiftung, Hannover, for the generous support of these investigations.

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Received August 31, 1999
[O99505]