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1,2,5,6- and 1,2,7,8-Tetrakis(dimethylamino)naphthalenes and Their Dications: Syntheses and Properties

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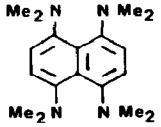
Abstract: The new electron donor compounds **3** and **4** were synthesized and their properties were studied. Oxidation with iodine produced the corresponding dications. An X-ray crystal study of the dication **13** gives evidence of a cyanine-like structure.

The fascinating properties of the strong electron donor and "double proton sponge" 1,4,5,8-tetrakis(dimethylamino)naphthalene (**1**)[1,2] encouraged us to extend our studies to 1,2,5,6- and 1,2,7,8-tetrakis(dimethylamino)naphthalenes (**3** and **4**, respectively), which, as structural isomers, are also related to 2,3,6,7-tetrakis(dimethylamino)naphthalene (**2**).[3,4] Whereas **1** can be considered to consist of two 1,4-bis(dimethylamino)benzene moieties, the structural isomers **2**, **3** and **4** enclose two differently coupled 1,2-bis(dimethylamino)benzene elements.



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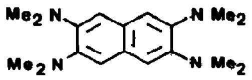

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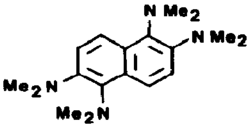

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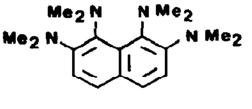

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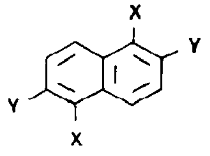
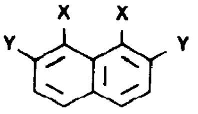
For the synthesis of **3**, 2,6-dimethoxy-1,5-dinitronaphthalene (**5**)[5] was treated with excess of dimethylamine in dimethylformamide (autoclave, 24 h, 90°C) to give the 2,6-bis(dimethylamino) compound **6**[6] (red needles, m. p. 178-179°C, 45% yield). Catalytic hydrogenation of **6** (5% Pd on charcoal, tetrahydrofuran) afforded the rather unstable 1,5-diamino-2,6-bis(dimethylamino)naphthalene (**7**) which was directly converted by a fourfold N-methylation (sodium hydride, dimethyl sulfate, tetrahydrofuran)[7] into **3**, isolated as **3**·$(HBF_4)_2$ salt[6] [m. p. 270°C (decomp.), *ca.* 12% yield referred to **6**]. Subsequent treatment with aqueous sodium hydroxide afforded the neat base **3**[6] (colourless needles, m. p. 135-136°C, 91%). In accordance with the structure, the ^1H-NMR spectrum of **3** (360 MHz, $[D_6]$acetone, 303 K, assignments based on NOE) shows singlet signals for the 2,6- (δ = 2.72, 12H) and 1,5-dimethylamino hydrogens (δ = 2.97, 12H) and doublets for the ring hydrogens at the 3,7- (δ = 7.30, ^3J = 9.1 Hz) and 4,8-positions (δ = 7.92).

A similar synthetic approach led to the isomer **4**. The 2,7-bis(dimethylamino) compound **9**[6] (orange needles, m. p. 146°C, 85% yield), obtained by reaction of 2,7-dimethoxy-1,8-dinitronaphthalene (**8**)[8] with excess of dimethylamine in dimethylformamide (pressure flask, 70 h, room temperature), was hydrogenated

(5% Pd on charcoal, tetrahydrofuran) and the formed unstable **10** directly converted by N-methylation[7] into **4**, isolated as **4**·$(HBF_4)_2$ salt[6] [m.p. 232-234°C (decomp.), *ca.* 9% yield referred to **9**). Repeated recrystallization afforded **4**·HBF_4 [m.p. 254-256°C (decomp.)][6] and treatment of the salts with base provided neat **4**[6] [yellow needles, m. p. 78-80°C (decomp.); ^1H-NMR (500 MHz, [D_6]dimethyl sulfoxide, 303 K, assignment based on NOE): δ = 2.60 (s, 12H, 2,7-NMe_2), 2.91 (s, 12H, 1,8-NMe_2), 7.20 (d, ^3J = 8.7 Hz, 3,6-H), 7.42 (d, 4,5-H)].

5: X = NO_2, Y = OMe
6: X = NO_2, Y = NMe_2
7: X = NH_2, Y = NMe_2





8: X = NO_2, Y = OMe
9: X = NO_2, Y = NMe_2
10: X = NH_2, Y = NMe_2
11: X = NMe_2, Y = H
12: X = NMe_2, Y = OMe

The ^1H-NMR spectrum of **4**·HBF_4 [500 MHz, [D_6]dimethyl sulfoxide, 303 K]: δ = 2.70 (s, 12H, 2,7-NMe_2), 3.30 (d, ^3J = 2.2 Hz, 12H, 1,8-NMe_2), 7.85 (d, ^3J = 8.8 Hz, 3,6-H, assigned by NOE), 8.12 (d, 4,5-H), 19.81 (m, 1H, NH)], shows the expected downfield shift for the signal of the $[N{-}H\cdots N]^{\oplus}$ proton. The basicity of **4** was determined by ^1H-NMR studies of protonation-deprotonation equilibria in [D_6]dimethyl sulfoxide[9] yielding pK_a = 11.2 [referred to 1,8-bis(dimethylamino)naphthalene (**11**): pK_a = 7.5,[10] and 1,8-bis(dimethylamino)-2,7-dimethoxynaphthalene (**12**): pK_a = 11.5] on the dimethyl sulfoxide pK_a scale.[10] **4** is slightly less basic than the "super sponge" **12**.

In case of **2** the cyclic voltammogram shows two separated one-electron oxidation steps at E_{ox} = –0.01V and +0.07 V (data referred to Fc/Fc^+ = 0.00 V, Fc = ferrocene).[3] For the strong electron donor **1**, on the other hand, a reversible two-electron transition, composed of two superimposed one-electron steps, is found cyclvoltammetrically at E_{ox} = –0.50 V.[1] Similarly, under analogous conditions of measurement,[11] also for **3** (E_{ox} = –0.13 V) and **4** (E_{ox} = –0.33 V) non separable two-electron transitions are observed. Despite strong steric interactions of the adjacent dimethylamino groups, **4** proves to be a stronger electron donor than **3**.

The superposition of the two one-electron steps points out that considerable conformational changes take place on oxidation , as it has been demonstrated for **1** and its dication.[1,2] Oxidation of **3** and **4** with four mole equivalents of iodine at low temperature (–30°C, dichloromethane) led to the formation of the corresponding dication salts,[6] **13**·$(I_3^-)_2\cdot I_2$ [black prisms, m.p. 259-260°C (decomp.), 97%; ^1H NMR (500 MHz, [D_3]acetonitrile, 303 K, assignments based on NOE and ^{13}C,^1H-correlated spectra): δ = 3.31 (s, 12H, 1,5-NMe_2), 3.41 (s, 12H, 2,6-NMe_2), 6.81 (d, ^3J = 9.7 Hz, 3,7-H), 7.50 (d, 4,8-H); Vis-spectrum (acetonitrile, 240 K): λ_{max} (lgε) = 685 (3.88) nm] and **14**·$(I_{\sim 8})^{2-}$ [black-brown powder, m.p. 83-84°C (decomp.), 73%; ^1H NMR (500 MHz, [D_3]acetonitrile, 303 K, assignments based on NOE): δ = 3.20 (br. s, 12H, 1,8-NMe_2), 3.24 (s, 12H, 2,7-NMe_2), 6.70 (d, ^3J = 8.8 Hz, 3,6-H), 7.28 (d, 4,5-H); Vis-spectrum (acetonitrile, 240 K): λ_{max} (lgε) = 723 (4.31), 426 (4.29) nm].

The molecular structure of the dication **13** (Figure 1) was established by X-ray diffraction. In the crystalline state **13** shows C_i symmetry. The dications are arranged in an alternating stack along the *b*-axis (∡ 30°) with each dication being separated by two I_3^- counterions. The additional I_2 molecules are placed parallel to this array in channels along the *b*-axis. Owing to extensive charge delocalization the dimethylamino groups tend to adopt a coplanar arrangement with respect to the naphthalene skeleton [torsion angles: C(4a^i)-C(1)-N(1')-C(1"A) 169.8(5)°, C(4a^i)-C(1)-N(1')-C(1"B) 4(1)°, C(3)-C(2)-N(2')-C(2"A) 159.4(6)°, C(3)-C(2)-N(2')-C(2"B) –3(1)°]. The nitrogens become almost sp^2-hybridized, as indicated by the mean trigonal angle of 119°, although the dimethylamino groups are substantially deformed owing to steric compression, particularly the C(1"A)-N(1')-C(1"B) [112.5(5)°] and C(2"A)-N(2')-C(2"B) [114.6 (6)°] angles. The steric interactions also force the naphthalene skeleton to adopt a twofold "envelope" conformation (Figure 1), in which C(1) and C(1^i), corresponding to C_i symmetry, are displaced by 24 pm out of the naphtalene mean plane in opposite direction.

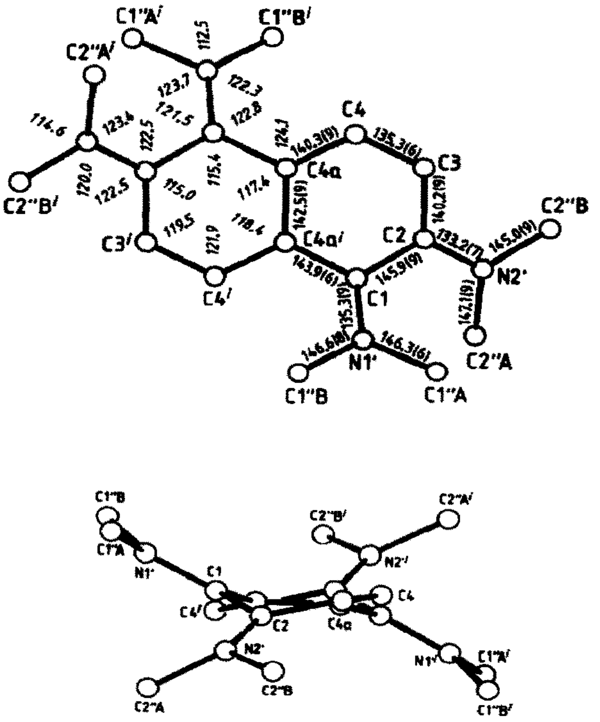
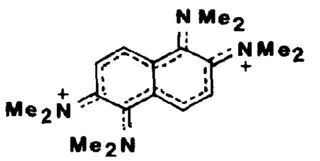
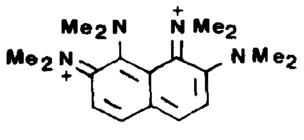


Figure 1. Molecular structure of **13**. Above: top view of the naphthalene skeleton with bond lengths [pm] and angles [°]; below: side view.[12]

In support of a highly delocalized π–sytem with "cyanine-like" features the dication **13** shows no clearly alternating bond lengths. Particularly the C(1)-C(2) [145.9(9) pm] and the central C(4a)-C(4a^i) bond [142.5(9) pm], which are very close to typical $C_{sp}2$–$C_{sp}2$ single bonds (146.0 pm)[14] indicate the presence of "pentacyanine-like" substructures, represented by the N(1'), C(1), C(4a^i),C(4^i), C(3^i), C(2^i), N(2'^{i}) and N(2'), C(2), C(3), C(4), C(4a), C(1^i), N(1'^{i}) chains. All connecting bonds show considerable double-bond character (conjugated $C_{sp}2$=$C_{sp}2$: 135.5 pm).[14] HMO-calculations of a corresponding model system predict for **13** also a cyanine-like structure.[15]

13





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In agreement with this structure the ring hydrogen resonances of **13** (δ = 7.17, 7.80, [D_6] acetone) are only slightly shifted to higher field as compared to the corresponding signals of **3** (δ = 7.30, 7.92), whereas in case of quinonediimmonium structures significant shifts to lower field are observed.[2] Hence, the ^{1}H-NMR data of **14** (δ = 7.02, 7.49, [D_6] acetone) as compared to those of **4** (δ = 7.22, 7.43) support rather a cyanine-like than a quinone-diimmonium structure.

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12. N,N,N',N'-Tetramethyl[2,6-bis(dimethylamino)-1,5-dihydronaphthalen-1,5-diylidene]diammonium-bis(triiodide) [$\mathbf{13}\cdot(I_3^-)_2\cdot I_2$]: Black crystals from acetonitrile; cell constants: a = 774.6(2), b = 1041.3(3), c = 1179.0(3) pm, α = 108.66(2), β = 108.19(2), γ = 99.83(2)°, $V = 810(1)\cdot 10^6$ pm^3, Z = 1, $D_{calc.} = 2.699$ g·cm^{-3}, $\mu(\text{Mo-K}_\alpha) = 75.99$ cm^{-1}, F(000) = 588 e; crystal system: triclinic, space group: $P\bar{1}$ (No. 2); 3229 reflections ($\sin\theta/\lambda \le 6.6$ nm^{-1}) measured, 2264 reflections [$I \ge 3.0\ \sigma(I)$] observed, empirical absorption correction (Ψ-scans) $\tau_{min} = 58.09$, $\tau_{max} = 99.75$. Structure solved by heavy-atom method (PATTERSON); refinement $R/R_w = 0.036/0.044$.[13]
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