

The Dication of 1,4,5,8-Tetrakis(dimethylamino)naphthalene: Properties, Crystal Structure and a Comparison with the Dication of 1,4-Bis(dimethylamino)benzene

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The dication salt $4 \cdot (I_3^-)_2$ of 1,4,5,8-tetrakis(dimethylamino)naphthalene **3** is isolated and its molecular structure established by X-ray crystallographic analysis; spectral data of **4** are compared with those of the dication **2** of 1,4-bis(dimethylamino)benzene, determined in the presence of an oxidant, *i.e.* Br_2 , Ag^+ .

Strong electron donor compounds display a fascinating array of chemical, physical and structural properties owing to their various oxidation stages. A distinct example is 1,4-bis(dimethylamino)benzene **1**: its oxidation to the radical cation $1^{\cdot+}$ of the Wurster's Blue salts has been known for more than 100 years,¹⁻³ and also the dication **2** has been isolated as $2 \cdot (ClO_4^-)_2$ salt, a colourless crystalline material, which, however, readily decomposes in solution.⁴⁻⁶ Apparently, for this reason no data concerning spectroscopic properties of **2** were found in the literature.^{5,6} Recently, we reported the

synthesis and the crystal structure of 1,4,5,8-tetrakis(dimethylamino)naphthalene **3**, in which formally two structural moieties corresponding to **1** are combined.⁷ As expected, **3** proved to be a much stronger electron donor than **1**. Whereas two separated one-electron oxidation steps at $E_{ox} = -0.30$ V and $E_{ox} = +0.29$ V ($Fe/Fe^+ = 0.00$ V, Fe = ferrocene) were found by cyclic voltammetry for **1**,⁸ in case of **3** under same conditions a reversible two-electron transition at $E_{ox} = -0.50$ V was observed, which consists of two superimposed one-electron steps and leads *via* the intermediate radical cation $3^{\cdot+}$

to the formation of the dication **4**.⁷ The radical cation of **3** was generated by oxidation with iodine and identified by EPR.⁷ Here, we report the properties of the dication **4** which are of particular interest not only in comparison with the properties of **2**, but also in the context of studies on cyanine-like dications derived from tetrakis(dimethylamino) compounds.⁸

At low temperature (-30°C) the stepwise oxidation of **3** with iodine in dichloromethane can be followed up in the VIS spectrum. In the beginning the absorption band of the radical cation $3^{\cdot+}$ at 500 nm showed up and was subsequently replaced by the band of the dication **4** at 650 nm. Oxidation of **3** with an excess of iodine (*ca.* 4 I_2) at low temperature afforded the dication salt $4 \cdot (\text{I}_3^-)_2$ which precipitated out of the dark-green solution as a black crystalline solid.[†] This compound is rather labile, particularly in solution. At room temperature $4 \cdot (\text{I}_3^-)_2$ is rapidly converted into $5\text{-H}^+ \cdot (\text{I}_3^-)_2$, which is also the product formed when **3** is oxidized by iodine at room temperature.

The structure of the dication **4** was established by X-ray diffraction. Needle-shaped black crystals of $4 \cdot (\text{I}_3^-)_2$ were obtained by addition of 4 I_2 in acetonitrile to a solution of **3** in acetonitrile at -10°C and subsequent cooling of the mixture to -30°C . Fig. 1 displays the molecular structure of the dication **4** viewed in the molecular plane (a) and from the side along the molecular twofold axis (b). The symmetry of **4** in the crystal is C_i , but comes close to C_{2h} . In support of the delocalized quinonediimmonium structure represented by **4** the dication shows clearly alternating bond lengths. The $\text{C}(1)\text{--}\text{C}(2) = 1.46(2)$, $\text{C}(3)\text{--}\text{C}(4) = 1.46(2)$, $\text{C}(4)\text{--}\text{C}(4a) = 1.41(3)$ and $\text{C}(1)\text{--}\text{C}(4a^i) = 1.44(2)$ Å distances are very close to typical $\text{C}_{\text{sp}^2}\text{--}\text{C}_{\text{sp}^2}$ single bonds (1.460 Å),⁹ whereas the $\text{C}(2)\text{--}\text{C}(3) = 1.34(2)$ Å and $\text{C}(4a)\text{--}\text{C}(4a^i) = 1.40(2)$ Å bond lengths indicate considerable double-bond character (conjugated $\text{C}_{\text{sp}^2}=\text{C}_{\text{sp}^2}$: 1.345 Å).¹⁰ Particularly the short central

[†] *Characterization of the new compounds:* *N,N,N',N'*-tetramethyl-*[5,8-bis(dimethylamino)-1,4-dihydronaphthalene-1,4-diylidene]diumonium bis(triiodide)*, $4 \cdot (\text{I}_3^-)_2$: A solution of iodine (51 mg, 0.2 mmol) in dry dichloromethane (4 cm^3) was added to a solution of **3** (15.5 mg, 0.05 mmol) in dry dichloromethane (1 cm^3) at -10°C . After cooling to -30°C the separated black crystals were collected, 56 mg (89%), *decomp.* $\geq 130^\circ\text{C}$. VIS (acetonitrile, -30°C): $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$ mol dm^{-3} cm^{-1}) 643 (4.02). IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 3070w, 2920w, 1580m, 1550s, 1510m, 1430m, 1410m, 1360s, 1190m, 1160m, 1060w, 995w, 810m. ^1H NMR (500 MHz, CD_3CN , -33°C): δ 7.71 (4 H, s, 2-,3-,6-,7-H), 3.65 (12 H, s, CH_3), 2.38 (12 H, s, CH_3). FAB-MS [*N*-bromoacetamide(NBA)/trifluoroacetic acid (TFA) (1%) matrix]: molecular mass calculated for **4** ($\text{C}_{18}\text{H}_{28}\text{N}_4$) $M^+ = 300.2$, $[M + 1]^+ = 301.2$; $m/z = 150.6$ [$(M + 1)^{2+}$, 15], 150.1 (M^{2+} , 100), 149.6 [$(M - 1)^{2+}$, 5], 149.0 (50).

6,7-Bis(dimethylamino)2,3-dihydro-1,1,3-trimethyl-1H-perimidinium- $\text{H}^+(\text{I}_3^-)_2$ [$5 \cdot \text{H}^+(\text{I}_3^-)_2$]: ^1H NMR (500 MHz, CD_3CN): δ 18.19 (1 H, br s, $\text{N} \cdots \text{H--N}$), 8.00 (1 H, d, 3J 9 Hz, 5-H), 7.99 (1 H, d, 3J 9 Hz, 8-H), 7.94 (1 H, d, 9-H), 7.19 (1 H, d, 4-H), 4.80 (2 H, s, 2-, 2-H), 3.49 (6 H, s, 1-, 1- NCH_3), 3.34 (3 H, s, 3- NCH_3), 3.16 (6 H, d, 3J 3 Hz, 6-,6- NCH_3), 3.01 (6 H, d, 3J 2 Hz, 7-,7- NCH_3); all assignments are based on NOE (nuclear Overhauser effect) experiments. FAB-MS [*NBA/TFA* (1%) matrix]: molecular mass calculated for **5** ($\text{C}_{18}\text{H}_{27}\text{N}_4$) = 299.2; $m/z = 299.2$ (M^+ , 100%).

N,N,N',N'-Tetramethyl-(2,5-cyclohexadiene-1,4-diylidene)diammonium diperchlorate **2** (ClO_4^-)₂:⁴ UV-VIS (0.03 mol dm^{-2} silver tetrafluoroborate in acetic acid): $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$ mol dm^{-3} cm^{-1}) 316 (4.01). ^1H NMR (500 MHz, CD_3CN , bromine): δ 7.83 (4 H, s, 2-,3-,5-,6-H), 3.88 (12 H, s, CH_3); (360 MHz, 0.03 mol dm^{-3} silver tetrafluoroborate in $\text{CD}_3\text{CO}_2\text{D}$): δ 7.99 (4 H, s, 2-,3-,5-,6-H), 3.45 (12 H, s, CH_3).

2-Br_{7.5}: Bromine was added dropwise to a solution of **1** (10 mg, 0.06 mmol) in dry acetonitrile (2 cm^3) at 0°C until the colour of the reaction mixture changed from violet to brown-red. On cooling to -30°C lustrous bronze-coloured crystals separated, which were collected, 35 mg (76%), *m.p.* (*decomp.*) 80°C . IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 3090m, 1610s, 1580s, 1510w, 1450m, 1400s, 1230w, 1130w, 1050w, 830s. ^1H NMR (500 MHz, CD_3CN , -33°C): δ 7.80 (4 H, s, 2-,3-,5-,6-H), 3.88 (12 H, s, CH_3).

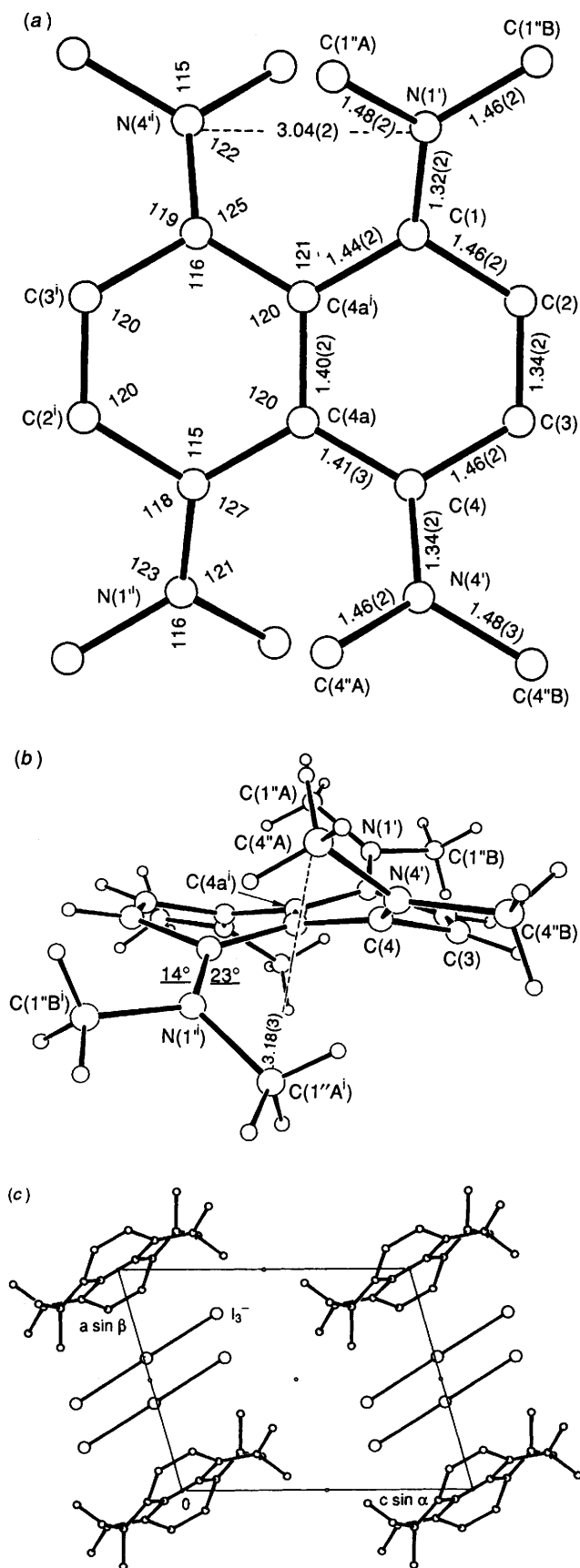
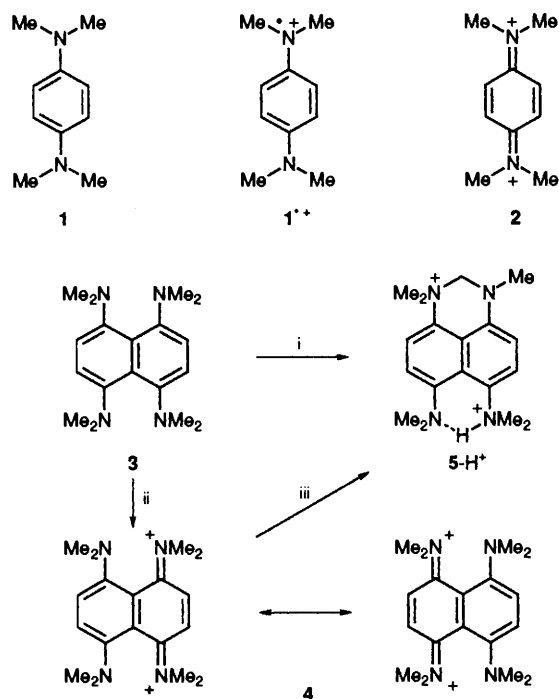


Fig. 1 Molecular structure of $4 \cdot (\text{I}_3^-)_2$: (a) Top-view of **4**, showing the atom-labelling scheme, bond distances (Å) and angles ($^\circ$, standard deviation about 1°). (b) Side-view along the molecular twofold axis, showing the intramolecular distance between the *endo* *N*-methyl groups and torsion angles about the exocyclic C–N bond. (c) Packing diagram projected down the *b*-axis, showing the positions of I_3^- .



Scheme 1 Reagents and conditions: i, 4 I₂, acetonitrile, 25 °C, 10 min, ca. 90%; ii, 4 I₂, dichloromethane, -10 °C, ca. 90%; iii, acetonitrile, 25 °C, 10 min, ca. 90%

C(4a)–C(4aⁱ) bond [1.40 (2) Å] is incompatible with cyanine-like substructures requiring a central single bond. Owing to the extensive charge delocalization the nitrogens in **4** become almost sp²-hybridized [deviation from the C(1), C(1^aA), C(1^bB) plane 0.07 Å, from the C(4), C(4^aA), C(4^bB) plane 0.08 Å], and the dimethylamino groups tend to adopt a coplanar arrangement with respect to the naphthalene skeleton. Opposed to that is the steric interaction between the two pairs of *peri* dimethylamino groups. The very short distance between the *endo* *N*-methyl groups of 3.18(3) Å [Fig. 1(b)], significantly shorter than the sum of their van der Waals radii (≈4 Å), indicates strong steric interaction, which obviously is the major factor determining the molecular structure of **4**. This steric interaction effects not only a marked distortion of the dimethylamino groups about the N–C_{naph} bond [mean torsion angles: C(1^aA)–N(1ⁱ)–C(1)–C(4aⁱ) 23°, C(1^bB)–N(1ⁱ)–C(1)–C(2) 14°], but also forces the naphthalene skeleton to adopt a twofold boat conformation [Fig. 1(b)], in which C(1) and C(4) are displaced downwards, and C(1ⁱ) and C(4ⁱ) upwards by 0.27 Å out of the C(2), C(3), C(4a), C(2ⁱ), C(3ⁱ), C(4aⁱ) plane (deviations from the plane ≤0.01 Å), yielding an interplanar angle of 22° between the C(2), C(1), C(4aⁱ) and C(2), C(3), C(4a), C(4aⁱ) planes. The positions of the I₃⁻ counterions, which are arranged in channels between the dication arrays in the *b* direction, are shown in Fig. 1(c).

The crystal structure of 4·(I₃⁻)₂, proving an extensive charge delocalization, implies a restricted rotation of the dimethylamino groups about the N–C_{naph} bond in solution. Indeed, **4** in the ¹H NMR spectrum shows only one singlet for the ring hydrogens (δ = 7.71) indicating that all four dimethylamino groups are equivalent. Therefore, the two singlets of the NCH₃ hydrogens (δ = 3.65, 2.38) must be assigned to the *endo* and *exo* methyl groups. Owing to the positive charge of **4** the ¹H NMR signals are shifted to lower field as compared with **3**, [²H₆]DMSO: δ = 6.75 (ring hydrogens), 2.65 (NCH₃).⁷

In analogy to the formation of **4**, oxidation of **1** with an excess of bromine afforded 2·(Br₃₋₄⁻)₂ as lustrous bronze-coloured crystals. In accord with its structure the ¹H NMR spectrum shows only two singlets [δ = 7.80 (4 H) and 3.88 (12

H)]. Likewise to **4**, these resonances are observed at lower field than those of the uncharged educt 1 ([²H₆]DMSO: δ = 6.69 and 2.75, respectively). In contrast to 2·(ClO₄⁻)₂,^{4,5} which in solution and in KBr partially decomposes (indicated, e.g. by the immediate appearance of the violet 1^{+•}), the salts 2·(Br₃₋₄⁻)₂ and 4·(I₃⁻)₂ showed no visible decomposition in KBr. Their IR spectra are characterized by a remarkably small number of sharp absorption bands,† a result, which is obviously related to the high symmetry of the dications. As indicated by 2·(Br₃₋₄⁻)₂, reduction of **2** in solution can be suppressed in the presence of an oxidative agent. Following this line, it was possible to measure ¹H NMR and UV–VIS spectra of 2·(ClO₄⁻)₂ dissolved in anhydrous acetic acid containing 0.03 mol dm⁻³ dry AgBF₄. The first absorption band of **2** is found at 316 nm which agrees well with theoretical predictions: 289 nm (PP results) and 307 nm (MM results).¹⁰ This is a remarkable blue shift compared to the first absorption band of 1^{+•} (≈ 610 nm). The first absorption bands of **4** (650 nm) and 3^{+•} (500 nm), on the other hand, are considerably less separated and their order is reversed. The dye character of 1^{+•}, 3^{+•} and **4** can be associated with a favourable charge delocalization, in which all dimethylamino groups equally participate.

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- (a) UV-VIS spectrum: A. C. Albrecht and W. T. Simpson, *J. Am. Chem. Soc.*, 1955, **77**, 4454. 1^{+•}·ClO₄⁻ (H₂O): λ_{max}/nm (log ε mol dm⁻³ cm⁻¹) 260 (3.6), 325 (4.3), 380s (3.6), 530s (3.8) 565 (4.09), 610 (4.10). (b) Crystal structure: 1^{+•}·ClO₄⁻: J. L. de Boer and A. Vos, *Acta Crystallogr. Sect. B.*, 1972, **28**, 835, 839. 1^{+•}·I₃⁻: J. L. de Boer, A. Vos and K. Huml, *Acta Crystallogr. Sect. B.*, 1968, **24**, 542.
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† Crystal data for C₁₈H₂₈N₄·2I₃: needle-shaped black crystal obtained by oxidation of **3** with iodine (4 I₂) in dry acetonitrile at -10 °C and subsequent cooling to -30 °C. Dimensions 0.02 × 0.02 × 0.08 mm, *M* = 1061.9, space group *P* $\bar{1}$ (No. 2), symmetry of the molecule in crystal: *C*_i; *a* = 8.628(2), *b* = 9.715(3), *c* = 9.975(3) Å, α = 101.72(2), β = 98.65(2), γ = 112.92(2)°, *U* = 729.2 (7) Å³, *Z* = 1, *D*_c = 2.42 g cm⁻³, μ(Mo–Kα) = 63.40 cm⁻¹, *F*(000) = 482 e. The intensity data were collected using an Enraf-Nonius CAD-4 circle diffractometer with graphite-monochromated Mo–Kα radiation (λ = 0.71069 Å, θ/2θ scanning technique) and were corrected for absorption using Ψ-scan (τ_{max} = 99.73, τ_{min} = 82.84) data. Total number of unique reflections 2859 (sinθ/λ ≤ 0.62 Å⁻¹), of which 1514 [*I* ≥ 3.0σ(*I*)] were classified to be observed. The structure was solved by the heavy-atom method (Patterson). In the refinement anisotropic thermal parameters were applied for all non-hydrogens and isotropic thermal parameters for the ring hydrogens. Methyl hydrogens were placed geometrically and included in the structural factors calculation, but not refined. The final cycle of refinement converged with *R* = 0.058 and *R*_w = 0.071; max(Δ/σ) = 0.08, Δρ_{max} = 1.5 e Å⁻³. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.