Hexaaminobenzene Derivatives: Synthesis and Unusual Oxidation Behavior†,‡

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The syntheses and the electrochemical behavior of the monomeric peralkylated hexaamino(1,3)-metacyclophane **4**, the dimeric dodecaamino(1,3)cyclophane **5a**, and the dodecaamino(1,3,5)-cyclophane **6** are described. Electrochemical measurements show that the hexaaminobenzene units in **4** and **5a** undergo an unusually slow two-electron transfer attributed to the deformation of the rings into bis-cyanine cations when oxidized to the respective dication. Further oxidations to tri-, tetra-, and hexacationic units occur at more positive potentials. In the dimeric structures, no interaction between the rings can be seen in the (1,3)cyclophane, but strong interaction for the (1,3,5)cyclophane is observed.

Introduction

Electrochemistry is frequently used to probe the electron-transfer properties of organic compounds. In particular, techniques such as cyclic voltammetry give detailed information about the generation and fate of unusual oxidation states.[2,3] Often, the transfer of electrons to or from organic molecules is accompanied by structural changes, and the structures of oxidation or reduction products differ considerably from that of the starting compound. As consequences of such rearrangements, kinetic effects on the electron-transfer rate through changes in the inner reorganization energy have been discussed (see, e.g., ref 4). Moreover, in systems where at least two subsequent electron transfers are possible, the relative ordering of the redox potentials can be affected, leading to unusual behavior, including "potential inversion".[5,6] Then, the transfer of the second electron occurs thermodynamically easier than that of the first one. Still, many organic molecules show a fast electron transfer. Due to geometric rearrangements of the N−N bonds and of the substituents, hydrazines belong to the exceptions.[7−11] Some tetra- and hexaaminobenzene derivatives also behave differently from usual organic molecules. With dimethylamino functionalities at least in the 1,2,4,5-positions (**1**), two-electron oxidation leads to a bis-trimethine cyanine system with a deformed six-membered ring (Scheme 1).[12]

Similar behavior is known from hexakis(dimethylamino)benzene **2b**,[13] while both the sterically least demanding hexaaminobenzene (**2a**),[14] as well as hexaazacoronene (**3**)[15,16] with the free electron pairs forced to be in conjugation with the benzene ring, show two stepwise single-electron transfers during oxidation to the respective dications. In the case of **2b**, strong inversion of the redox potentials and slow kinetics of the overall two-electron-transfer process was suggested.[17]

Another aspect of redox-active organic molecules becomes important if more than one moiety of the molecule is capable of exchanging electrons. These centers may be independent or they may interact. Provided the redox centers are chemically identical, one would expect that their redox potentials were the same in the case of independent reactions but would attain different values if the redox state of one center affects the other one.

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† Dedicated to Prof. Dr. Günther Helmchen on the occasion of his 60th birthday.

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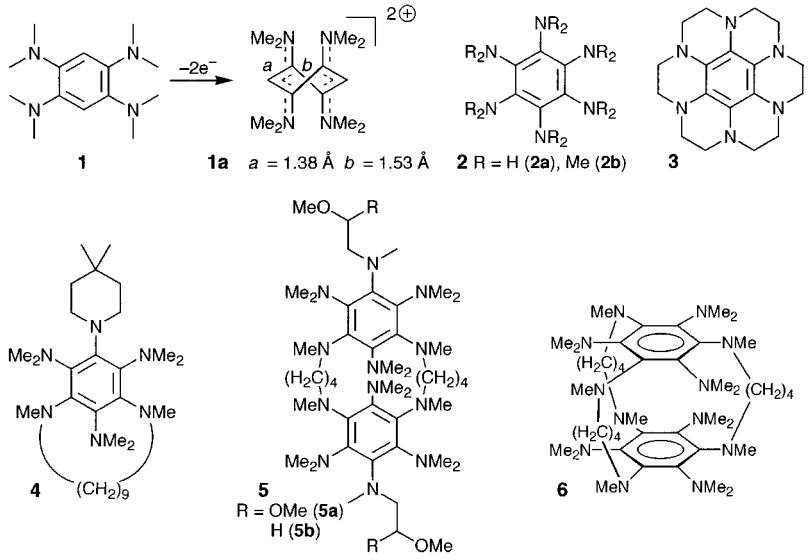
Scheme 1



The compounds investigated here are designed to explore the above aspects of the redox behavior of the hexaaminobenzene unit in various frameworks: In **4**, the structural flexibility within the central six-membered ring is constrained by incorporating the hexaaminobenzene moiety into a metacyclophane ring system. The presence of two such units in **5a**, which are flexibly linked, additionally adds the possibility of interactions between two redox-active centers. Such an interaction is expected to be even more important in sterically rigid **6**, which exhibits two almost planar and parallel hexaaminobenzene systems in a fixed distance of 5.740 Å.[18]

Along with the synthesis of **4**, **5**, and **6**, we will describe their electrochemical properties.

Results and Discussion

Synthesis. Recently, two of us reported on the S_NAr substitution of **7** with ammonia and substituted amines.[19] The rate for the second and third substitution *increases* for monoalkylamines and even more so for ammonia but *decreases* for dialkylamines. The explanation rests on the unusual steric hindrance in this hexasubstituted benzene. It causes the nitro groups to turn out of planarity and leads to a fairly slow substitution reaction. Hydrogen binding to one or more of the amino substituents, however, forces at least one of the nitro groups into conjugation with the ring. Thus, complex syntheses of cyclophanes by amino substitution of Cl substituents in **7** should be easy to perform even without the use of high-dilution conditions. It is probably also simplified by the unusual conformation of trialkylamino-substituted trinitrobenzenes:[20] the central ring deviates substantially from planarity and the aromatic π-system changes into a quinoid or a trimethine-cyanine structure. On reduction of the nitro groups, the aromatic character is restored.

Syntheses of **4**−**6** were therefore surprisingly easy. Reactions of 1,3-dichloro-5-dialkylaminobenzenes such as

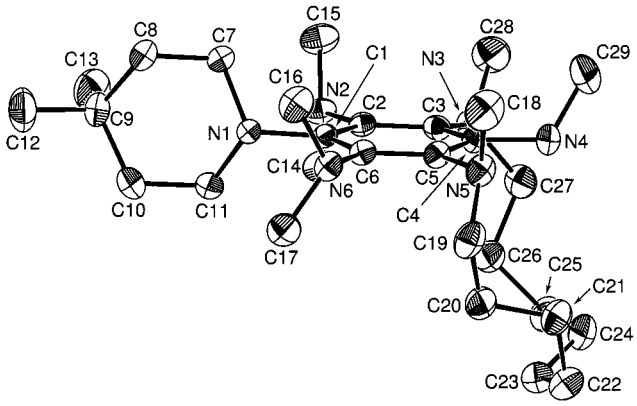


Figure 1. ORTEP drawing of the heptamethylated cyclophane **11**.

8a give the cyclophane **9** in high yields (>60%) without high dilution, and catalytic reduction with hydrogen, followed by alkylation under usual conditions, gives the heptaalkylated cyclophane **11** (Figure 1, Scheme 2, Table 3). The octaalkylated **4** can be obtained by formation of the carbamate **12**, followed by reduction with LAH (X-ray analysis of **4** was attempted, but the structure could not be resolved due to severe disorder of the cyclophane chain).

The dimer **14a** was formed when the chain length of the diamine was reduced (crystals could be obtained from DMSO; Figure 2, Scheme 3, Table 3). The reduction and complete alkylation to give **5** could be done within one step.

Finally, the (1,3,5)cyclophane **6** can be obtained from the tris(alkylamino)-substituted **22** with acceptable yields (Scheme 4).[18]

Electrochemical Analysis. Compounds **4**, **5a**, and **6** were anodically oxidized at Pt electrodes in a 1:1 mixture of CH_2Cl_2 and CH_3CN with 0.1 M NBu_4PF_6 as supporting electrolyte. The use of this mixed solvent was necessary to obtain sufficient solubility of all oxidation states. In an electrolyte based on only CH_2Cl_2 as solvent, distorted voltammograms were observed due to the precipitation of oxidation products on the electrode.

We will first derive the overall oxidation chemistry of **4** and characterize the individual steps by their revers-

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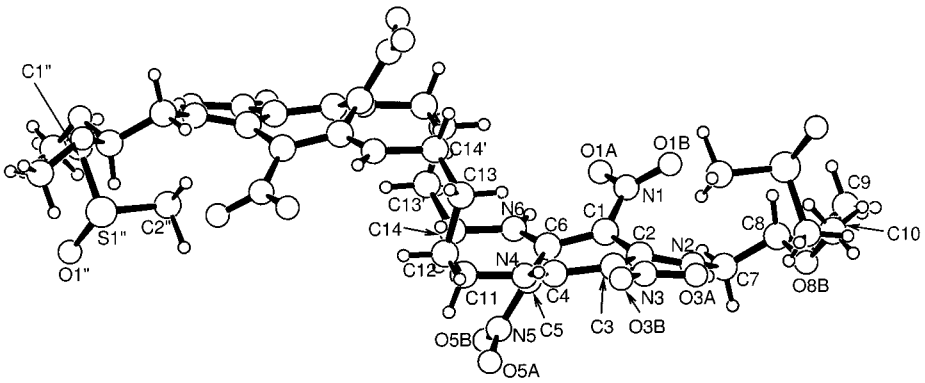
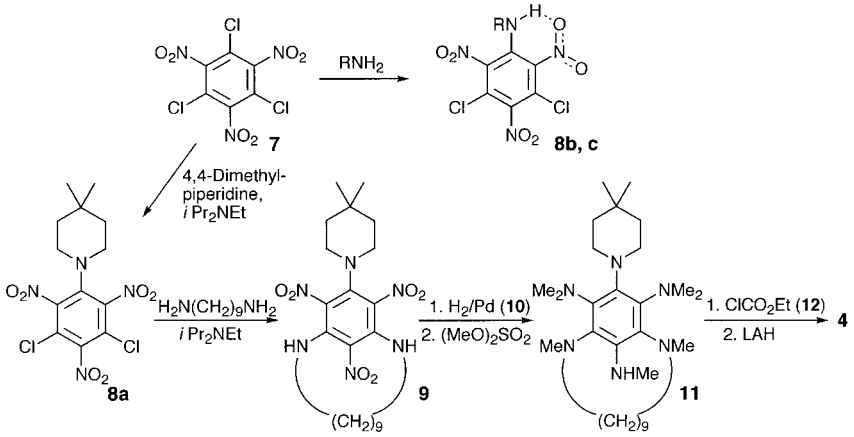
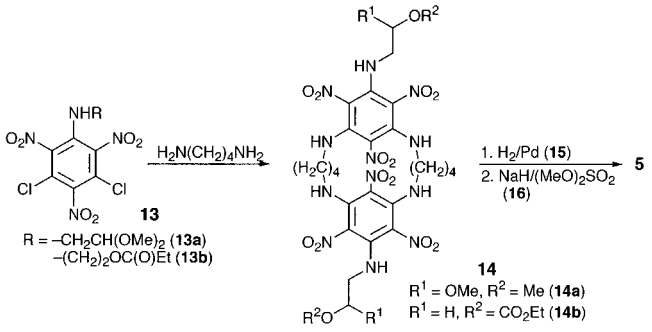


Figure 2. Stick-and-ball drawing of the dimer **14a** + DMSO.

Scheme 2



Scheme 3



ibility and formal potentials from cyclic voltammograms recorded over various potential ranges (Figure 3) up to the anodic potential limit of the electrolyte. The compound is oxidized in four separate steps (oxidation peaks 1−4). All peak currents are proportional to the concentration *c* of **4**.

The primary oxidation product generated in peak 1 is reduced in peak 10. The peak potential difference ΔE_p(1/10) is surprisingly large, indicating involvement of some chemical transformation concurrent with the electron transfer. At higher scan rates peak 1 broadens compared to peaks 2 and 3 (see below), decreases in relative height, and shifts to more positive potentials, indicating a slow rate of the electron transfer.

Further oxidation in peak 2 reveals reduction peak 8 with both peak potentials E_p^2 and E_p^8 being independent of the scan rate *v* and *c*. The corresponding peak potential separation $\Delta E_p(2/8)$ is 0.064 ± 0.007 V, and we calculate a formal potential E (2/8) = + 0.332 ± 0.004 V as the mean value of the peak potentials (Table 1). As a result of the oxidation step in peak 3, two reduction peaks 7 and 9 are observed. While the direct oxidation product is reduced in peak 7, at slower time scales ($v \leq 0.1$ V s^{-1}) a slow follow-up reaction increasingly consumes the oxidized species and the product of this reaction (not identified in this work) is reduced in peak 9. The position of peak 3 is independent of *c* (follow-up reaction of first or pseudo-first order), but in accordance with the postulated chemical step, it slightly shifts toward less positive potentials at slow scan rates.[21] At faster time scales, E_p^3 becomes independent of v[E(3/7) = +0.682 ± 0.018 V, $\Delta E_p(3/7)$ = 0.076 ± 0.013 V]. Thus, both oxidations in peaks 2 and 3 appear to be electrochemically reversible (diffusion controlled) and probably correspond to one-electron processes.

At potentials around +1.6 V, further oxidation of **4** occurs with reduction of products in signals 5 and 6. The shape of the voltammograms and their scan rate dependence is similar to that found for **2b**.[1]

It is important to determine the electron stoichiometry of the oxidation steps, to characterize the various transient intermediates formed. Unfortunately, due to the broadening of peak 1, comparison of the oxidation peak current functions is not useful in the present case. With potential step techniques (chronoampero- or -coulometry), however, even slow electron-transfer steps become diffusion-controlled and results can more easily be evaluated. The first three oxidations were examined. Peaks 4a and 4b are overlapping and close to the potential limit

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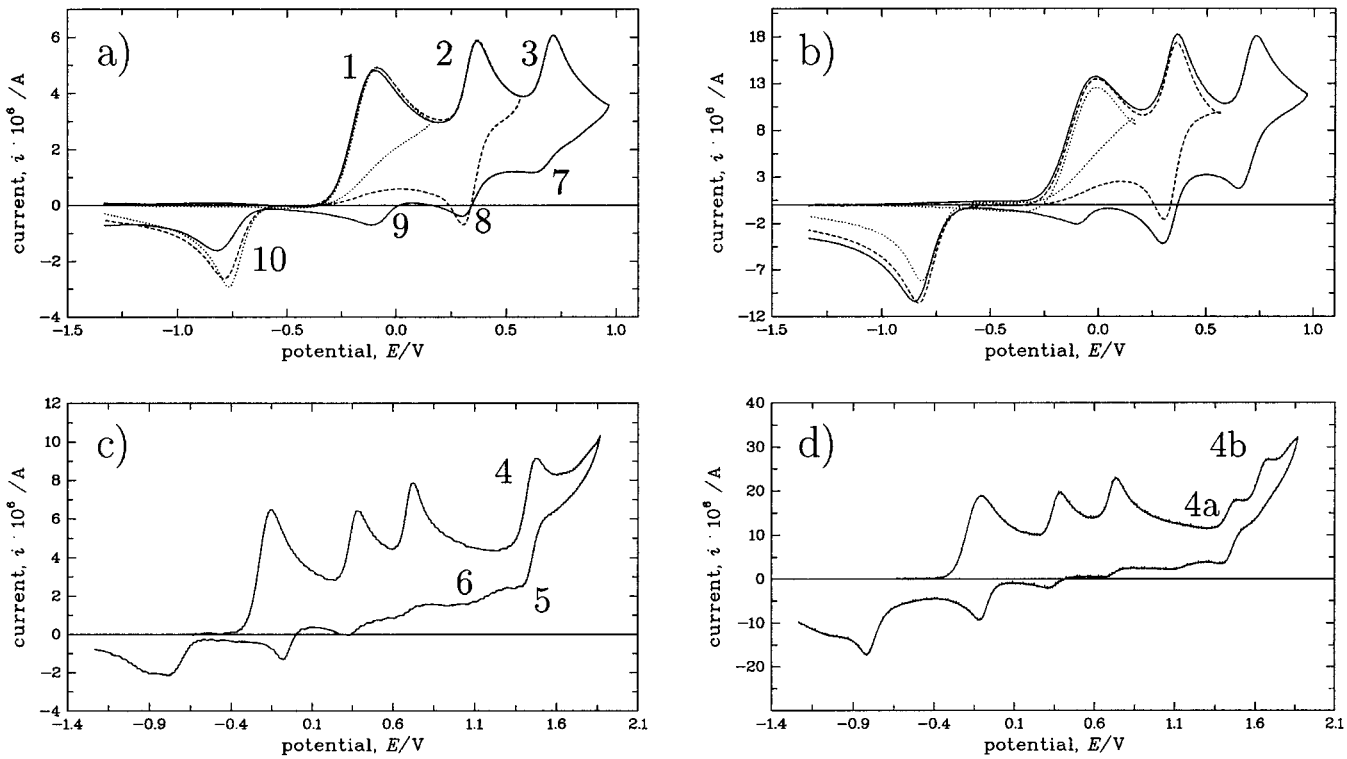
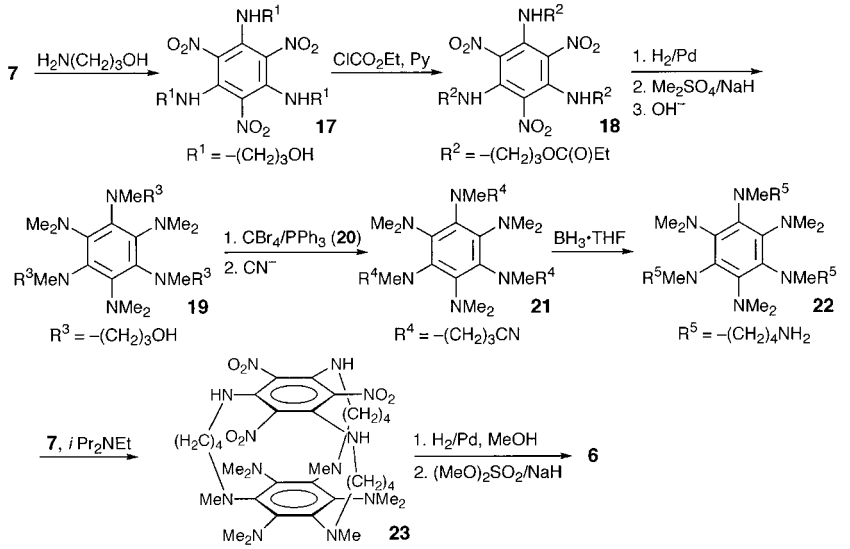


Figure 3. Cyclic voltammograms of **4** in CH_2Cl_2/CH_3CN (1:1, v/v), Pt electrode, $c = 0.21$ mM: (a, c) $v = 0.1$ V s^{-1}, (b, d) $v = 1$ V s^{-1}, (a, b) $E_\lambda = +0.166$ V (− − −), +0.566 V (···) and +0.966 V (—), (c, d) $E_\lambda = +1.866$ V.

Scheme 4



of the solvent. Hence, reactions occurring at these more positive potentials were not analyzed.

Potential step oxidation at potentials between peaks 1 and 2, between peaks 2 and 3, and at potentials positive of peak 3 was investigated under variation of the time scale of the experiments (pulse width τ). Results for the Anson plot slope,[22] $Q/\sqrt{tc}$ (chronocoulometry), and the Cottrell constant, $i\sqrt{t}/c$ (chronoamperometry), are compared (Table 2). Both experimental features are practically independent of τ but increase with the potential. If we normalize to the values at $E = +0.166$ V (after peak 1), a relative ratio of 1:1.5:2 results. These values are proportional to the numbers n of electrons transferred, which must be integers. Therefore, the electron stoichiometry for the oxidation of **4** in peaks 1, 2, and 3, respectively, must be 2:3:4, confirming one-electron steps at the higher potentials and indicating a two-electron process at low potential. The ratio $Q(2\tau)/Q(\tau)$ (chronocoulometry; Table 2) is expected to approach 0.414 for a simple electron transfer.[23] In accordance with the slow follow-up reaction seen after peak 3 in the cyclic voltammograms, its value slightly increases with increasing E and τ.

In exhaustive electrolysis experiments, **4** was oxidized at potentials between peaks 1 and 2. The charge trans-

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Table 1. Formal Redox Potentials (in V) for Polyaminobenzenes 2b,[17] 4, and 5a

	$E_1^{0\,a}$	$E_2^{0\,b}$	$E_3^{0\,b}$
2b	−0.365 ± 0.005	+0.330 ± 0.005	+0.580 ± 0.010
4	−0.433 ± 0.019	+0.332 ± 0.004	+0.682 ± 0.018
5a	−0.343 ± 0.029	+0.324 ± 0.009	+0.698 ± 0.013
	$E_1^{0\,c}$		$E_2^{0\,c}$
6	−0.247 ± 0.002		−0.119 ± 0.001

[a] Redox potentials for two-electron oxidation of hexaaminobenzene units. [b] Redox potentials for one-electron oxidation steps. [c] Two separate one-electron steps for oxidation to dication, ΔE_p = 0.05 ± 0.01 V and 0.043 ± 0.004 V, respectively.

Table 2. Chronocoulometric and Chronoamperometric Results[a] for 4

		E/V		
	τ/s	+0.166	+0.566	+0.966
$Q/\sqrt{tc}$ [a,b]	0.1	48.5	76.7	95.7
	1.0	45.5	66.9	84.9
	10.0	49.2	74.6	89.3
$(Q/\sqrt{tc})/(Q/\sqrt{tc})_{E=+0.166V}$	0.1	1.00	1.58	1.97
	1.0	1.00	1.47	1.87
	10.0	1.00	1.52	1.82
$Q(2\tau)/Q(\tau)$ [a]	0.1	0.47 ± 0.03	0.53 ± 0.05	0.48 ± 0.007
	1.0	0.44 ± 0.02	0.45 ± 0.005	0.49 ± 0.004
	10.0	0.51 ± 0.02	0.51 ± 0.02	0.64 ± 0.005
$i\sqrt{t}/c$ [a,c]		21.6	33.5	45.9
$(i\sqrt{t}/c)/(i\sqrt{t}/c)_{E=+0.166V}$		1.00	1.55	2.12

[a] Mean values from experiments at c = 0.07, 0.14, and 0.21 mM. [b] Chronocoulometry, in C cm^3 s$^{-1/2}$ mol^{-1}. [c] Chronoamperometry, in A cm^3 s$^{1/2}$ mol^{-1}, mean values from all τ.

ferred corresponds to two electrons per molecule, in accordance with the potential step results.

Based on these data, we assume formation of a di-, tri-, and tetracation from **4** with increasing potential. Since the reverse peak 7 is observed already at v = 0.2 V s^{-1} in the case of **4** rather than v = 1.0 V s^{-1} for **2b**,[17] the kinetic stability of **4**$^{4+}$ is somehow higher than that of **2b**$^{4+}$. Further oxidation to a hexacation is seen at +1.6 V in analogy to **2b**.[1]

The large value of ΔE_p(1/10) and its scan rate dependence are explained by slow kinetics of this process and occurrence of potential inversion, as in the case of **2b**.[17] For analogous systems the overall two-electron redox potential was determined by potentiometric titration.[4,17] For **2b**, E was equal to the mean value of the peak potentials within experimental error.[17] Since the amount of **4** available was too small to perform the extensive experiments necessary for potentiometric determination, we thus estimated E^0 (**4**/**4**$^{2+}$) from E_p^1 and E_p^{10} to be −0.433 ± 0.019 V.

The cyclic voltammetric pattern of **5a** (Figure 4) is similar to that of **4**. The formal potentials for the three redox processes initiated by oxidation in peaks 1, 2, and 3 were calculated as for **4** and are listed in Table 1. Again, potentials are independent of c. As compared to **4**, the second and third oxidation step exhibit slightly increased ΔE_p.

Potential step experiments supply relative n values of 1:1.5:2. However, in contrast to **4**, electrolysis between peaks 1 and 2 results in a charge corresponding to the transfer of four electrons. The electron stoichiometry for the oxidation of **5a** must thus be described as 4:6:8 in the first three steps. Apparently in peak 1, both hexaaminobenzene units are oxidized at almost identical potentials to their respective dicationic states, producing a tetracation. If this electrolysis is performed in pure CH_2Cl_2 electrolyte, a microcrystalline product precipitates. It was, however, not possible to obtain crystals of sufficient quality for X-ray crystallographic analysis. The n values show that by further oxidation of **5a**$^{4+}$, hexa- and then octacations are produced. In analogy to the results for **2b** and **4**, further oxidation in the peaks at higher potentials may finally lead to a dodecacation.

Table 3. Structure Determination Summary[a] of 11 and 14a

	11	**14a**
emp formula	$C_{29}H_{54}N_6$	$C_{28}H_{40}N_{12}O_{16}$·4DMSO
cryst size (mm)	0.4 × 0.7 × 0.8	0.5 × 0.5 × 0.35
habit	colorless prisms	yellow prisms
solvent	Et_2O	DMSO
cryst syst	triclinic	triclinic
space grp	$P\bar{1}$	$P\bar{1}$
unit cell (Å) a	10.444(2)	11.268(3)
b	10.674(2)	12.423(2)
c	15.044(6)	10.440(2)
(deg) α	109.26(2)	105.12(1)
β	94.05(3)	111.60(2)
γ	106.07(2)	80.00(2)
volume (Å^3)	1496.9	1306.8
Z	2	1
formula wt (g mol^{-1})	487	1113
calcd density (g cm^{-3})	1.08	1.42
absorpt correction	empirical	empirical (Ψ scans)
corr factor (max/min)	−	−1.0/0.97
absorpt coeff (mm^{-1})	0.06	0.27
F(000)	540	588
range of Θ (deg)	2−29	2−28
collected reflns	7964	6556
independent reflns	7964	6238
observed reflns	5096	5173
H atoms refined[b]	none	all N−H
resid elec density (e Å^{-3})	0.35/−0.3	0.55/−0.56
params refined	317	360
R/R_w	0.070/0.109	0.069/0.180

[a] Four-circle diffractometers, rt, Mo Kα radiation. Programs for structure solution: **11**, SHELXTL plus; **14a**, SIR88. $I \geq 2.5\Delta \geq I$). [b] Those hydrogen atom positions that were located on the electron density difference map and refined isotropically.

A comparison of the reverse peaks in the cyclic voltammograms of **5a** shows that the stabilities of the oxidized forms are comparable to the corresponding ones for **4**. By further comparing the chronoamperometric and chronocoulometric currents for **4** and **5a** to the respective results for **2b**, we estimate the diffusion coefficients D(**4**) = 7 × 10^{-6} cm^2 s^{-1} and D(**5a**) = 6.7 × 10^{-6} cm^2 s^{-1}. They are only slightly smaller than D(**2b**) = 8.2 × 10^{-6} cm^2 s^{-1}.[17]

While **4** and **5a** show rather similar cyclic voltammograms, the current−potential curves for **6** are considerably different (Figure 5). The low solubility of **6** even in the solvent mixture used here makes background subtraction extremely important. Four oxidation peaks are observed, with peaks 1 and 2 as well as peaks 3 and 4 closely spaced together. Reduction signals 6 and 5 are related to the oxidations in peaks 1 and 2, respectively (formal potentials in Table 1). On the other hand, for peaks 3 and 4 unequivocal reduction peaks are not observed. Peak 5 increases with increasing v, indicating a slow follow-up reaction of the product formed in the second oxidation step. Electrolysis at potentials after the first and second oxidation peak indicates the stepwise formation of a one- and a two-electron oxidation product,

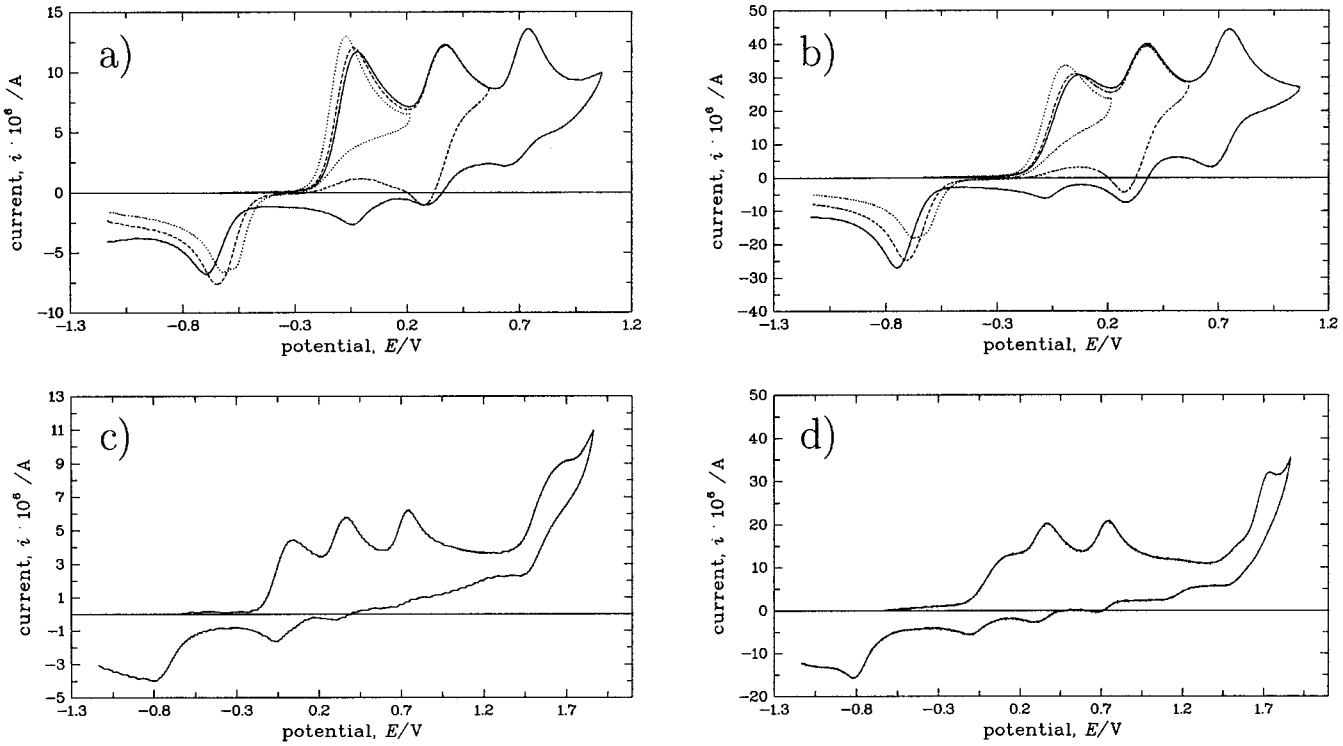

Figure 4. Cyclic voltammograms of **5a** in CH_2Cl_2/CH_3CN (1:1, v/v), Pt electrode: (a, c) $v = 0.1$ V s^{-1}, (b, d) $v = 1$ V s^{-1}, (a, b) $c = 0.21$ mM, $E_\lambda = +0.216$ V (– – –), +0.566 V (···) and +1.066 V (—), (c, d) $c = 0.17$ mM, $E_\lambda = +1.866$ V.

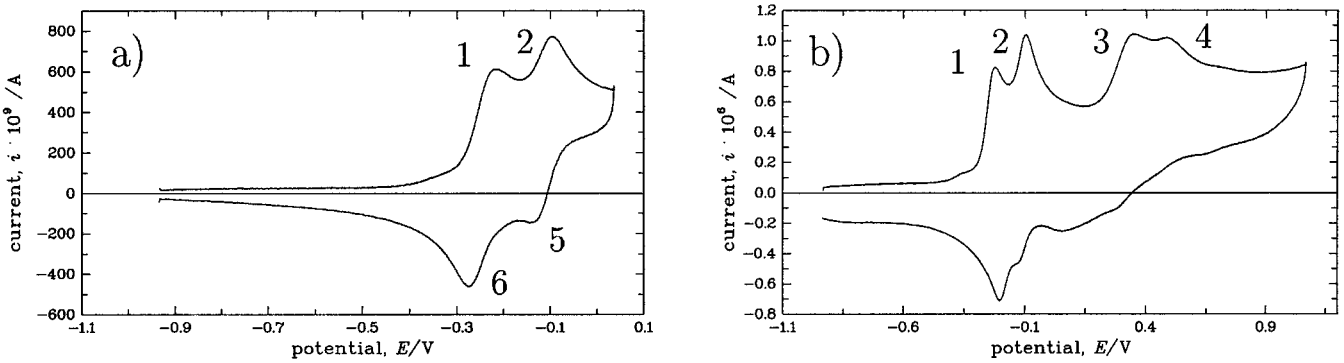

Figure 5. Cyclic voltammograms of **6** in CH_2Cl_2/CH_3CN (1:1, v/v), Pt electrode, $v = 0.2$ V s^{-1}, $c = 0.033$ mM: (a) $E_\lambda = +0.036$ V, (b) $E_\lambda = +1.066$ V.

which we assign as a monocation and a dication. At least the dication must be described as a transient species at the voltammetric time scales used.

Conclusion

All investigated hexaaminobenzene derivatives are easily oxidized. Chemically almost reversible reactions lead up to a dication for **6**, to a tetracation for the monomer **4**, and to an octacation for the dimeric structure **5a**. Further oxidation is chemically irreversible, and the higher oxidation states are not stable on the time scales of our experiments.

The primary electron-transfer processes for **4** and **5a** are *two*-electron transfer reactions and show an unusual separation of the oxidation and reduction potentials. They are quasireversible most probably due to the strong geometrical changes to twisted cyanine structures on oxidation (see also **2b**[17]). In the (1,3,5)cyclophane **6**, however, two reversible *one*-electron steps are closely spaced. Interactions between hexaaminobenzene moieties in the dimeric structures can thus be detected only for **6**, where the potentials of the first two one-electron processes are separated, but not for **5a** which shows a four-electron-transfer oxidation.

The results indicate considerable differences between the electrochemical behavior of **2b**, **4**, and **5a** on one and **6** on the other side. We attribute this difference to the particular steric situation brought about by the three alkyl bridges in **6**. The twist structures accessible for **2b**, **4**, and **5a** in the respective oxidation states can probably not be formed in **6**. As a result, the two- or four-electron oxidation product is not stabilized and potential inversion is not observed. Linking the two hexaaminobenzene units in close distance enhances their interaction, which leads to a further splitting of the oxidation into one-electron processes.

It is also instructive to compare the redox potentials for the oxidation steps of **2b**, **4**, and **5a** (Table 1; values

for **6** correspond to different oxidation steps, see above, and are not comparable to those for **2b**, **4**, and **5a**). Several structural features may be responsible for the variations in the E^0. Among these are the geometry of the aromatic core (planarity of the six-membered ring, conformation of the dimethylamino groups) and the electron density of the ring.

Primary oxidation of compounds **2b** and **5a** occurs at almost the same potential, while **4** undergoes electron transfer at a less positive potential. Incorporation of the hexaaminobenzene unit into the metacyclophane forces the dimethylamino substituents into an almost perpendicular conformation with respect to the aromatic core (see Figure 1 for **11** which we use as a model for **4**). The nitrogen lone pair interaction with the aromatic π-system becomes worse, and consequently, the free energy of **4** is increased. If we assume that the dication biscyanine structure in all cases causes strong conjugation of the dimethylamino groups with the corresponding C_3 fragment, the free energy difference between **4** and $\mathbf{4}^{2+}$ decreases. Hence, oxidation occurs at more negative potentials.

The second redox process takes place at nearly the same potential in all three compounds, indicating that the free energy difference between di- and trication is similar in the three compounds.

The third redox process appears about 0.1 V easier for **2b** as compared to the other compounds, so the additional features in the structure of **4** and **5a** must render this step more difficult energetically. Valence-bond structures of the tetracation show that four positively charged nitrogen atoms are arranged adjacently at the ring and that the nitrogens in the cyclophane ring are affected in *each* resonance structure. Since the cationic nitrogen atoms probably attain coplanarity with the benzene core (sp^2), additional strain is expected in the cyclophane ring. This increases the free energy of $\mathbf{4}^{4+}$ and $\mathbf{5a}^{8+}$ but cannot have an influence on **2b**.

Synthesis of a doubly dodecahydrogenated bis-hexaazatriphenylene should further increase the difference between oxidation potentials of a mono- and a dication because steric stiffness should be increased. Work to synthesize such a compound is currently in progress.

Experimental Section

Melting points: hotstage microscope and Büchi B-540 uncorrected. NMR spectra: 300.133 MHz for ^{1}H, 75.469 MHz for ^{13}C, and $CDCl_3$ as the solvent, unless noted otherwise. **CAUTION**: *polynitro compounds may be explosive! We have not encountered any violent decomposition with the compounds reported here but advise the use of special care.*

Chemicals were obtained from commercial sources with the exception of 1,3,5-trichloro-2,4,6-trinitrobenzene[24,25] (**7**), 4,4-dimethylpiperidine[26,27] (via 4,4-dimethylglutarimide, colorless needles, mp 146−146.5 °C, first fm. 50% EtOH, then water), 1-(4,4-dimethylpiperidino)-3,5-dichloro- (**8a**), 1-(2-ethoxycarbonyloxyethyl)-3,5-dichloro- (**13a**) and 1-(2,2-dimethoxyethyl)-3,5-dichloro-2,4,6-trinitrobenzene (**13b**).[19]

1,11-Diaza-13,15,17-triamino-14-(4,4-dimethylpiperidino)[11]metacyclophane (**10**). A suspension of **9**·1.5 CH_2Cl_2 (550 mg, 0.98 mmol, prepared in analogy to the piperidine derivative[28]) in EtOAc (15 mL) and a small amount of water (0.1 mL) was hydrogenated at 65 °C/atmospheric pressure with 10% Pd/C (100 mg). The air-sensitive solution could be used directly for 7-fold methylation to give **11**. Satisfactory NMR spectra can only be obtained under careful exclusion of oxygen. Two conformers are present; some signals are not resolved: ^{1}H NMR δ 0.56 (centered m, 2 H), 0.96 (s, 6 H), 1.00−1.20 (m, 8 H), 1.27−1.38 (m, 4 H), 1.45 (q, J = 5.8 Hz, 4 H), 2.89 (dt, J = 13.3, 6.8 Hz, 2 H), 3.00 (dt, J = 11.3, 5.6 Hz, 4 H), 3.22 (ddd, J = 12.9, 7.6, 5.2 Hz, 2 H), 3.85 (br s, 8 H); ^{13}C NMR δ 24.79, 24.99, 26.30, 27.37, 27.45, 28.12, 28.19, 40.35, 40.44, 44.31, 46.07, 46.11, 112.02, 112.11, 117.15, 117.17, 136.83, 138.70, 138.73.

1,11-Diaza-1,11-dimethyl-13,15-bis(dimethylamino)-17-methylamino-14-(4,4-dimethylpiperidino)[11]-metacyclophane (**11**)**.** KOH (1.00 g, 17.8 mmol) followed by degassed dimethyl sulfate (2.00 g, 15.8 mmol) were added to a solution of the crude amine **10** (from the reduction of 2.97 mmol of **9**). After 1 h, more sulfate (2.00 g) was added and the mixture heated to 45−50 °C for 1 h. The mixture was cooled and filtered, and the residue was washed with CH_2Cl_2. The solvents were evaporated, and the residue was filtered over alumina (basic, act. III; CH_2Cl_2) to give crude **11** (1.67 g) which was extracted with Et_2O. The residue was dissolved in CH_2Cl_2 and a byproduct removed by vapor diffusion of petroleum ether (bp 30−40 °C). The mother liquor and the ethereal extracts were combined and chromatographed (neutral alumina, act. II, light petroleum/EtOAc = 50/1) to give colorless **11**, which was crystallized from Et_2O to give colorless prisms (620 mg, 43% over two steps): mp 153−155 °C; ^{1}H NMR δ 0.73−0.92 (m, 2 H), 1.01 (s, 6 H), 0.92−1.26 (m, 8 H), 1.26−1.41 (m, 4 H), 1.45 (pseudo-t, J = 5.5 Hz, 4 H), 2.64 (s, 3 H), 2.75 (br s, 6 H), 2.80 (br s, 6 H), 2.84 (s, 6 H), 2.95−3.19 (m, 8 H), 5.11 (br s, 1 H); ^{13}C NMR δ 26.01, 26.15, 26.77, 27.19, 28.53, 28.72, 37.44, 39.73, 39.98, 43.88, 45.35, 45.83, 47.58, 47.90, 53.29, 137.89, 145.81, 148.27, 150.14. Anal. Calcd for $C_{29}H_{54}N_6$ (486.79): C, 71.55; H, 11.18; N, 17.26. Found: C, 71.55; H, 11.19; N, 17.28.

1,11-Diaza-1,11-dimethyl-13,15-bis(dimethylamino)-17-methoxycarbonylmethylamino-14(4,4-dimethylpiperidino)[11] metacyclophane (**12**)**.** NaH (1.2 g) and methylchloroformate (2 mL) were added under argon to a solution of **11** (700 mg, 1.44 mmol) in anhydrous, degassed THF (50 mL). The mixture was heated to reflux for 16 h, and excess hydride was destroyed by careful addition of water. Extraction with Et_2O (3×), chromatography (neutral alumina, act. III; cyclohexane/EtOAc = 4/1) gave colorless prisms (395 mg, 0.73 mmol, 51%), mp 187.5−189 °C (EtOH). **12** exists as a mixture of conformers in solution. Only regions for ^{1}H absorptions are therefore given: ^{1}H NMR δ 0.69−1.36 (20 H, 7 CH_2 in cyclophane chain and 2 CH_3 of piperidine substituent), 1.38−1.47 (4 H, CH_2 of C3 and C5 of piperidine substituent), 2.48−2.80 (21 H, 7 N−CH_3), 2.90−3.70 (11 H, 4 N−CH_2, 1 O−CH_3); ^{13}C NMR signals partially overlap δ 24.94, 24.98, 25.81, 25.91, 26.40, 26.67, 26.72, 27.32, 27.83, 28.36, 28.62, 37.63, 39.57, 43.29, 43.68, 44.28, 44.81, 45.38, 47.37, 47.50, 47.57, 52.00, 52.21, 52.48, 54.47, 55.13, 55.19, 135.07, 140.00, 140.87, 144.91, 146.03, 146.61, 150.59, 150.65, 150.73, 152.58, 152.67, 152.82, 157.11, 157.30, 157.72. Anal. Calcd for $C_{31}H_{56}N_6O_2$ (544.83): C, 68.34; H, 10.36; N, 15.43. Found: C, 68.34; H, 10.61; N, 15.44.

1,11-Diaza-1,11-dimethyl-14-(4,4-dimethylpiperidino)-13,15,17-tris(dimethylamino)[11]metacyclophane (**4**)**.** In anhydrous, degassed Et_2O (100 mL) was heated **12** (480 mg, 0.881 mmol) under argon with LAH (500 mg) to reflux for 2−3 days. The excess LAH was destroyed with EtOAc, and then 0.5 mL of water, 0.5 mL of saturated KOH, and finally 0.5 mL of water were added. The filtered precipitate was extracted for 4 h in a Soxhlet apparatus with Et_2O. Chromatography (neutral alumina, act. III; cyclohexane/EtOAc = 50/1) and

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crystallization from heptane (104 mg, 0.208 mmol, 24%) gave **12** as colorless prisms: mp 150−151 °C; ^{1}H NMR δ 0.71−1.32 (m, 14 H), 0.98 (s, 6 H), 1.42 (t, J = 5.6 Hz, 4 H), 2.75 (br s, shoulder at 2.72, 18 H), 2.79 (s, 6 H), 2.85−3.12 (m, 8 H); ^{13}C NMR δ 24.45, 26.34, 27.53, 27.98, 28.46 (br), 28.71, 39.71, 45.36 (br), 45.66, 45.73 (br), 47.52, 55.73, 149.17, 151.09, 152.02, 152.07. Anal. Calcd for $C_{30}H_{56}N_6$ (500.82): C, 71.95; H, 11.27; N, 16.78. Found: C, 72.11; H, 11.37; N, 16.84. The crystal structure could not be resolved properly.

1,6,13,18-Tetraaza-9,21-bis(2,2-dimethoxyethylamino)-8,10,12,20,22,24-hexanitro[6$_2$](1,3)cyclophane (14a). Under argon, solutions in 100 mL of dichloromethane each of **13a** (3.50 g; 9.09 mmol)[19] and 1,4-diaminobutane (875 mg; 9.93 mmol) together with *N*-ethyldiisopropylamine (Hünig's base; 2.39 g, 18.5 mmol) were added simultaneously to degassed, anhydrous CH_2Cl_2 (200 mL) over the course of 45 min with stirring. Stirring was continued for 12 h, and then the mixture was filtered over a sintered glass frit (P3). It was concentrated to 50 mL, and the crude product was precipitated by adding light petroleum. It was washed with light petroleum and dried. Dissolution in CH_2Cl_2 and chromatography (neutral alumina, act. III; acetone/CH_2Cl_2/EtOAc = 1/1/1) gave a yellow powder (910 mg, 1.14 mmol, 25%) of **14a**: mp >200 °C dec; ^{1}H NMR (DMSO-d_6) δ 1.60−1.98 (br, m, 8 H), 2.8−3.9 (vbr, 12 H), 3.35 (s, 12 H), 4.65 (t, J = 4.6 Hz, 2 H), 9.92 (br s, 2 H), 10.99 (br s, 2 H), 11.29 (br s, 2 H); ^{13}C NMR (DMSO-d_6) δ 25.20 (br), 48.55 (br), 49.82, 54.95, 101.21, 106.21, 113.4 (vbr), 117.2 (vbr), 150.4 (vbr), 153.3 (vbr), 153.87; HR-MS (FAB$^+$) calcd for M + H$^+$ 801.2764, found 801.2832; calcd for M + Na$^+$ 823.2583, found 823.2617.

1,6,13,18-Tetraaza-9,21-bis(2-ethoxycarbonyloxyethylamino)-8,10,12,20,22,24-hexanitro[6$_2$](1,3)cyclophane (14b). In analogy from **13b**[19] (10.0 g, 24.2 mmol), 1,4-diaminobutane (2.21 g, 25.0 mmol), and Hünig's base (6.20 g, 48.0 mmol). Chromatography (250 g neutral alumina, act. III; acetone/CH_2Cl_2/EtOAc = 1/1/1) yielded **14b** as a yellow powder (2.70 g, 3.15 mmol, 26%): mp >210 °C dec; ^{1}H NMR δ 1.17 (t, J = 7.2 Hz, 6 H), 1.75 (vbr, 8 H), 2.95−3.90 (vbr m, 12 H), 4.08 (q, J = 7.1 Hz, 4 H), 4.33 (br m, 4 H), 9.96 (br s, 2 H), 10.91 (br s, 2 H), 11.26 (br s, 2 H); ^{13}C NMR δ 14.12, 25.22 (br), 64.10, 64.87 (br), 106.07, 112.5 (vbr), 117.5 (vbr), 150.0 (vbr), 152.4 (vbr), 154.31, 154.52; HR-MS (FAB$^+$) calcd for M + H$^+$, 857.2662, found 857.2716; calcd for M + Na$^+$ 879.2481, found 879.2535.

1,6,13,18-Tetraaza-9,21-bis(2,2-dimethoxyethylamino)-8,10,12,20,22,24-hexaamino[6$_2$](1,3)cyclophane (15a). A suspension of the cyclophane **14a** (910 mg, 1.14 mmol) in 25 mL of methanol was hydrogenated under normal pressure with 200 mg of 10% Pd/C as catalyst at 50 °C until the solution was no longer colored. The catalyst was removed through filtration in a Schlenk frit (P3) and the solvent removed under argon. Drying in an oil pump vacuum at 50 °C for 30 min gave the polyamine **15a** as a colorless, glassy solid (511 mg, 0.823 mmol, 72%). The air-sensitive compound was used directly in the methylation step.

1,6,13,18-Tetraaza-9,21-bis(2-ethoxycarbonyloxyethylamino)-8,10,12,20,22,24-hexaamino[6$_2$](1,3)cyclophane (15b) was obtained in analogy from **14b** (5.00 g, 5.84 mmol) with 1.00 g of catalyst in 80 mL of methanol. **15b** was obtained as a colorless, air-sensitive glassy solid (3.50 g, 5.17 mmol, 89%) which was used directly in the next step.

1,6,13,18-Tetraaza-9,21-bis(2,2-dimethoxyethyl-*N*-methylamino)-8,10,12,20,22,24-hexakis(dimethylamino)-1,6,13,18-tetramethyl[6$_2$](1,3)cyclophane (5a). Oil-free NaH (74 mmol from washing of 2.2 g of an 80% suspension with dry pentane) was added under argon to a solution of crude amine **15a** (511 mg, 0.823 mmol) in 25 mL of dry THF. After addition of dimethyl sulfate (1 mL), the mixture was heated to reflux. In the course of 3 h, further sulfate (1.5 mL total) was added in portions. Reflux was continued for 3 h and the mixture then stirred overnight at room temperature. The excess NaH was carefully destroyed by addition of water, and the mixture was extracted with Et_2O. The ethereal layers were washed with saturated brine and dried. The solvent was removed and the residue chromatographed on neutral alumina (act. III, 90 g; cyclohexane/EtOAc = 20/1). Colorless leaflets from EtOAc (293 mg, 0.335 mmol, 41%): mp 218−222 °C dec; ^{1}H NMR δ 1.05−1.25 (br, 8 H), 2.41 (br, s, 18 H), 2.64, 2.67 (two br s, tot. 36 H), 3.02 (br, m, 8 H), 3.15 (d, J = 4.8 Hz, 2 H), 3.17 (d, J = 4.4 Hz, 2 H), 3.36 (s, 6 H), 3.41 (s, 6 H), 4.67 (t, J = 4.6 Hz, 1 H), 4.72 (t, J = 4.6 Hz, 1 H); ^{13}C NMR δ 26.37, 42.72, 42.78, 43.83, 44.56, 45.11 (br), 45.33 (br), 45.53 (br), 45.87 (br), 53.34, 53.47, 56.31 (br), 56.47 (br), 59.66, 105.87, 106.14, 151.10 (br), 151.51 (br), 153.89 (br), 154.03 (br). Conformers are present; two sets of signals are apparent for O-CH_3, and the acetal resonance $CH(OMe)_2$, 8 N-CH_3, and 3 N-CH_2 signals are resolved. Anal. Calcd for $C_{46}H_{88}N_{12}O_4$ (873.29): C, 63.27; H, 10.16; N, 19.25. Found: C, 63.21; H, 10.09; N, 19.07.

1,6,13,18-Tetraaza-9,21-bis(2-hydroxyethyl-*N*-methylamino)-8,10,12,20,22,24-hexakis(dimethylamino)-1,6,13,18-tetramethyl[6$_2$](1,3)cyclophane (16). From oil-free NaH (4.80 g, 200 mmol), crude **15b** (3.50 g, 5.17 mmol) in anhydrous THF (70 mL), and a solution of dimethyl sulfate (23.5 g, 186 mmol) in 30 mL of THF as described above. After 12 h reflux, the mixture was cooled to 0 °C, 50 mL of EtOAc was added, and the excess NaH was destroyed by the careful addition of 5 mL of glacial acetic acid and then water (50 mL). The aqueous layer was extracted twice with Et_2O, and the combined organic layers were filtered over neutral alumina (100 g, act. III; cyclohexane/EtOAc = 5/1). The solvent was removed, the remaining brown oil taken up in EtOH (300 mL) and heated to reflux, and 20% KOH was added. The mixture was heated for another 5 min and was then stirred at room temperature overnight. It was concentrated to one-third of its volume, 1 N HCl (70 mL) was added, and the mixture was extracted with diethyl ether. Then the aqueous phase was made alkaline with KOH, and the product was extracted with diethyl ether and chromatographed (neutral alumina, act. III; cyclohexane/EtOAc = 3/1) to give **16** as a colorless powder (1.81 g, 2.31 mmol, 45% from **14b**): mp >210 °C (begins to darken); ^{1}H NMR δ 1.18 (br, m, 8 H), 2.43 (s, 18 H), 2.63, 2.66, 2.68, 2.70 (4 s, 36 H totally), 3.09 (br, m, 8 H), 3.17 (t, J = 5.7 Hz, 2 H), 3.23 (t, J = 6.3 Hz, 2 H), 3.75 (t, J = 5.5 Hz, 2 H), 3.82 (t, J = 5.8 Hz, 2 H); ^{13}C NMR could not be obtained due to solubility problems; HR-MS (FAB$^+$) M + H$^+$, calcd 784.6606, found 785.6593.

1,6,13,18-Tetraaza-9,21-bis(2-methoxyethyl-*N*-methylamino)-8,10,12,20,22,24-hexakis(dimethylamino)-1,6,13,18-tetramethyl[6$_2$](1,3)cyclophane (5b). From NaH (1.20 g, 50.0 mmol) and a solution of **16** (1.20 g, 1.53 mmol) in THF (50 mL) and then dimethyl sulfate (1.26 g, 10 mmol) as described above. Chromatography (neutral alumina, act. III; cyclohexane/EtOAc = 20/1) gave **5b** as a colorless powder (820 mg, 1.01 mmol, 66%): mp 203−205 °C(EtOH); ^{1}H NMR δ 1.17 (br m, 8 H), 2.42 (br s, 18 H), 2.63, 2.65, 2.66 (3 s, total 36 H), 3.02−3.25 (br m, 12 H), 3.35, 3.39 (2 s, total 6 H), 3.58−3.69 (br m, 4 H); ^{13}C NMR δ 26.40, 42.71, 43.07, 43.61, 45.14, 45.53, 45.80, 56.34, 56.46, 58.80, 58.88, 72.43, 151.09 (br), 151.50, 151.81, 153.32 (br), 153.67 (br). Conformers are present as in the case of the acetal **5a**. C_{Ar}-Signals are resolved. Anal. Calcd for $C_{44}H_{84}N_{12}O_2$ (813.24): C, 64.99; H, 10.41; N, 20.67. Found: C, 65.03; H, 10.35; N, 20.44.

1,3,5-Trinitro-2,4,6-tris(3-hydroxypropylamino)benzene (17). A mixture of 3-amino-1-propanol (15.00 g, 199.7 mmol) and MeOH (15 mL) was added within 1 h to a vigorously stirred solution of **7**[24,25] in MeOH (250 mL). After additional stirring for 1 h, AcOH (2 mL) was added, and the mixture was concentrated to a volume of 25 mL. Chromatography of the deep yellow oil (silica gel, EtOAc/MeOH = 4/1) and concentration gave **17** as yellow prisms: mp 199−200 °C dec; ^{1}H NMR (DMSO-d_6) δ1.88 (br p, J = 5.7 Hz, 6 H), 3.63 (m, 6 H), 3.64 (m, 6 H), 4.99 (br s, 3 H), 10.4 (br s, 1 H), 11.5 (br s, 2 H); ^{13}C NMR (DMSO-d_6) δ 30.98, 48.18, 59.44, 111.1 (vbr), 152.53 (br). Anal. Calcd for $C_{15}H_{24}N_6O_9$ (432.40): C, 41.67; H, 5.59; N, 19.44. Found: C, 41.63; H, 5.63; N, 19.33.

1,3,5-Trinitro-2,4,6-tris(3-ethoxycarbonyloxypropylamino)benzene (18). Chloroformic acid ethyl ester (22.79 g, 210.0 mmol) was added to the suspension of the trihydroxy compound **17** (15.00 g, 34.69 mmol) in CH_2Cl_2 (200 mL). Within

1 h, pyridine (18.19 g, 230.0 mmol) was added, the alcohol dissolved, and the mixture became hot. After 1 h further, the volume was reduced to 25 mL, and the hydrochloride formed was separated by filtration. Chromatography (silica gel, EtOAc/cyclohexane = 2/1) gave **18** (18.03 g, 27.80 mmol, 80%). From toluene, prisms were slowly obtained: mp 105−108 °C; ^{1}H NMR δ 1.21 (t, J = 7.1 Hz, 9 H), 2.06 (br p, J = 6.2 Hz, 6 H), 3.48 (br p, J = 5.8 Hz, 6 H), 4.09 (q, J = 7.1 Hz, 6 H), 4.17 (t, J = 5.7 Hz, 6 H), 10.8 (vbr, 3 H); ^{13}C NMR δ 14.04, 20.52, 46.90, 64.11, 64.80 111.8 (br), 152.5 (br), 154.72. Anal. Calcd for $C_{24}H_{36}N_6O_{15}$ (648.59): C, 44.45; H, 5.60; N, 12.96. Found: C, 44.43; H, 5.53; N, 12.93.

1,3,5-Tris(3-hydroxypropyl)methylamino-2,4,6-dimethylaminobenzene (19). The trinitro compound **18** (10.00 g, 15.42 mmol) was hydrogenated (Pd/C, 1.0 g, as a catalyst) in MeOH (120 mL) for 18 h until the mixture was colorless. The mixture was filtered, the solvent evaporated, and the residue dried at 60 °C/0.2 Torr to give a colorless oily residue (7.75 g, 13.9 mmol, 90%). It was dissolved under Ar in dry THF, oxide- and oil-free NaH (11.20 g, 466.7 mmol) was added, then one-half of a solution of dimethyl sulfate (45.0 mL, 59.6 g, 473 mmol) in THF (50 mL) was added dropwise at room temperature. The second half was added within 2 h at reflux. The mixture was cooled after 12 h in an ice bath, and EtOAc (50 mL), AcOH (15 mL), then water (100 mL), finally saturated bicarbonate (100 mL) were added cautiously. The mixture was extracted with EtOAc (3 × 100 mL), and the organic phase was washed with saturated brine and filtered over neutral alumina (150 g, act. III, cyclohexane/EtOAc = 2/1). The carbonate protecting groups were cleaved by warming the solution in EtOH (500 mL), adding 20% KOH (80 mL), and heating to reflux for 5 min. About two-thirds of the solvent was evaporated and the residue acidified with 1 N HCl and extracted with diethyl ether. The aqueous phase was basified with KOH and extracted with Et_2O (3×). The etheral phase was dried, the solvent evaporated, and the residue crystallized from toluene to give **19** as a colorless powder (4.27 g, 9.11 mmol, 66%): mp 164.5−165.5 °C; ^{1}H NMR (DMSO-d_6) δ 1.74 (br m, 6 H), 2.62 (br s, 9 H), 2.66 (br s, 18 H), 2.94 (br m, 6 H), 3.41 (br q, J = 5.9 Hz, 6 H), 4.35 (br t, 5.1 Hz, 3 H); ^{13}C NMR (DMSO-d_6) δ 32.12, 40.31, 41.71, 53.73, 59.47, 150.91, 153.05. Anal. Calcd for $C_{24}H_{48}N_6O_3$ (468.69): C, 61.51; H, 10.32; N, 17.93. Found: C, 61.57; H, 10.01; N, 17.79.

1,3,5-Tris(3-bromopropyl-*N*-methylamino)-2,4,6-dimethylaminobenzene (20). At 0 °C, Ph_3P (5.67 g, 21.6 mmol) in THF (10 mL) was added within 5 min to a solution of **19** (2.25 g, 4.80 mmol) and CBr_4 (5.97 g, 18.0 mmol) in dry, O_2-free THF (70 mL). Stirring was continued for 5 min at 0 °C and then at rt overnight. The mixture was filtered, the solvent evaporated, the residue dissolved in 1 N HCl (50 mL) and extracted with Et_2O, and the aqueous phase made alkaline again with KOH and extracted 3× with Et_2O. The resulting yellowish oil was chromatographed (neutral alumina, act. III, EtOAc/cyclohexane = 1/25) to give slowly crystallizing, colorless **20** (2.61 g, 3.97 mmol, 83%): mp 99−101 °C (hexane); ^{1}H NMR δ 2.20 (br p, J = 7.3 Hz, 6 H), 2.64 (s, 9 H), 2.68 (s, 18 H), 3.07 (br t, J = 7.9 Hz, 6 H), 3.42 (br t, J = 6.6 Hz, 6 H); ^{13}C NMR δ 32.18 (shoulder at ca. 32.21), 42.22 (br), 44.96, 55.92, 151.35, 153.25. Anal. Calcd for $C_{24}H_{45}Br_3N_6$ (657.40): C, 43.85; H, 6.90; N, 12.78; Br, 36.47. Found: C, 44.10; H, 6.98; N, 12.78; Br, 36.26.

1,3,5-Tris(3-cyanopropyl-*N*-methylamino)-2,4,6-dimethylaminobenzene (21). *Caution! Cyanide dissolved in DMSO passes through the skin! Use two pairs of gloves!* Dry, powdered NaCN (3.35 g; 68.4 mmol) was added to a solution of **20** (3.00 g, 4.56 mmol) in dry DMSO (50 mL), and the mixture was stirred for 3 h. Dilution with water (100 mL), extraction with EtOAc (3) and chromatography (neutral alumina, act. III, EtOAc/cyclohexane = 1/4) gave **21** as a slowly crystallizing oil (2.07 g, 4.18 mmol, 91%): mp 111−112 °C (fine, colorless needles fm. heptane); ^{1}H NMR δ 1.97 (br p, J = 7.6 Hz, 6 H), 2.33 (t, J = 7.2 Hz, 6 H), 2.64 (br s, 9 H), 2.68 (br s, 18 H), 3.06 (br t, J = 8.0 Hz, 6 H); ^{13}C NMR δ 15.39, 24.63, 42.17 (br), 44.90, 55.97, 119.59, 151.30, 153.06. Anal. Calcd for $C_{27}H_{45}N_9$ (495.72): C, 65.42; H, 9.15; N, 25.43. Found: C, 65.52; H, 9.21; N, 25.15.

1,3,5-Tris(4-aminobutyl-*N*-methylamino)-2,4,6-dimethylaminobenzene (22). Borane−THF complex (75 mL of a 1 M solution) was added to **21** (1.50 g, 3.03 mmol) in degassed, anhydrous THF (75 mL), and the mixture was heated to reflux for 3 h. After the mixture was cooled to 0 °C, 2 N HCl (75 mL) was cautiously added, and after 20 min at room temperature, the mixture was made alkaline with KOH and then extracted with Et_2O (3×). After drying and evaporation of the solvent, a colorless, glassy compound was obtained (1.23 g, 2.42 mmol, 80%) which could be used without further purification.

Electrochemical Investigations. Electrochemical experiments were performed with a BAS 100 B/W electrochemical workstation.

Details of the electrochemical cells as well as preparation and purification of the electrolyte components were described previously.[17] Dichloromethane (Burdick and Jackson, stabilized with cyclohexene) was distilled through a packed column, and then dried over activated Al_2O_3 (basic, activated at 400 °C and 10^{-4} mbar for 4 h).

All potentials are reported versus an external fc/fc$^+$ (fc = ferrocene) standard in the solvent used. The voltammograms are background and iR-drop corrected.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-158460 (**11**) and CCDC-158459 (**14a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

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