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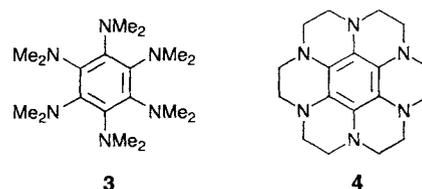
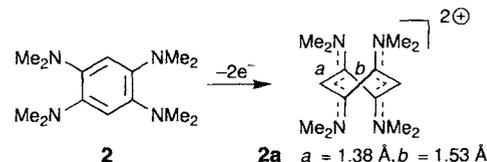
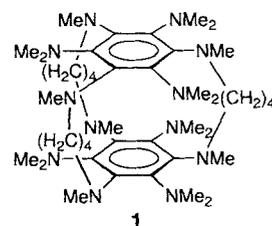
Synthesis and Structure of a Dimeric Peralkylated Hexaaminobenzene: Hexakis(dimethylamino)hexamethylhexaaza[6₃](1,3,5)cyclophane**

J. Jens Wolff,* Andreas Zietsch, Hermann Irngartinger, and Thomas Oeser

Dedicated to Professor Dr. Rolf Gleiter on the occasion of his 60th birthday

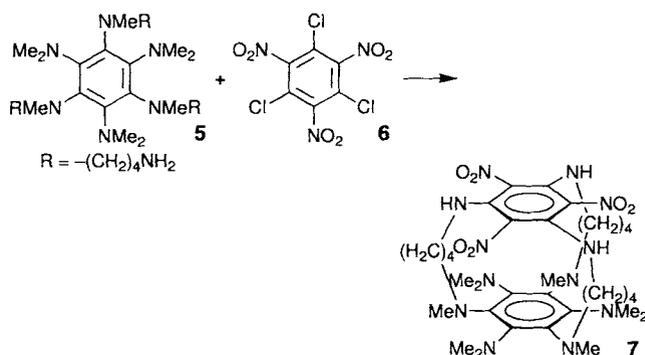
The experimental verification of theories on the kinetics of electron transfer (ET)^[1] requires the synthesis of compounds with known and well-defined structures. To this end, molecules that consist of two identical subunits symmetrically connected by a rigid spacer are especially well-suited. Both the neutral molecule and its oxidized or reduced form must be stable. Most organic compounds that fulfill these conditions,^[2] however, show such rapid ET for the intermolecular case already that its exact measurement for the intramolecular case is cumbersome and fraught with difficulties. In addition, theoretical predictions may not be equally valid for slow and fast ET processes. To reduce the rate constant, the inner reorganization energy^[3] of the ET process has to be increased; this reorganization energy is a measure of the energetic difference between the structures of the neutral molecule and its oxidized (or reduced) form. In this context, Nelsen et al. have synthesized and studied bis(hydrazines).^[4]

We reasoned that the oxidation of hexaaminobenzene derivatives should also have a high inner reorganization energy: investigations by several groups^[5] have shown that the π -system of benzenes substituted at least in 1-, 2-, 4-, and 5-positions with amino groups as in **2–4** reorganizes to a trimethinecyanine cation and a trimethinecyanine radical on loss of one electron, and to a bis(trimethinecyanine) such as **2a** on loss of two electrons. Not only is a drastic change in bond lengths associated with these oxidations, the rings also become quite nonplanar and adopt twist conformations. These effects lead to a high



kinetic barrier towards intermolecular electron transfer.^[6] To peruse this intrinsic high barrier in an intramolecular process we synthesized dimeric hexaaminobenzene derivatives that are linked together through three spacers, for example methylene chains. The distance between the two arenes should be easily adjustable. Here we report on the synthesis and the structure of **1**, a representative of this class of compounds.

None of the standard cyclophane syntheses^[7] are suitable for the construction of the sterically encumbered **1**. We reasoned, however, that the cyclization of a hexaaminobenzene derivative of type **5** with trinitrotrichlorobenzene (**6**) in a nucleophilic aromatic substitution reaction should be possible. First, we found that **6** and the model compound hexakis(dimethylamino)benzene (**3**) form a weak charge transfer (CT) complex.^[8] Preor-



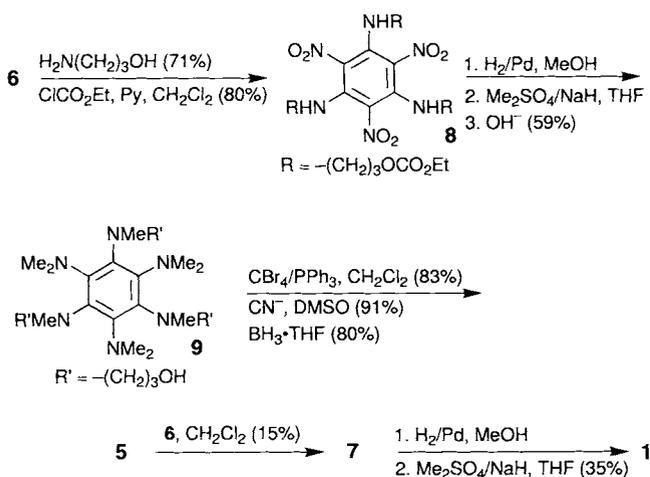
ganization of reactants **5** and **6** is therefore possible. Moreover, the ring in amino-substituted trinitrobenzenes deviates strongly from planarity,^[9] and cyclization is thus facilitated. Furthermore, we had found that the second and especially the third substitution of the chloro groups in **6** with monoalkylamines by the S_NAr mechanism are favored with respect to the first substitution even though the electron density formally increases with each substitution: the repulsive interactions of the chlorine atoms force the nitro groups to rotate strongly out of the plane of the ring. In contrast, after substitution of **6** with monoalkylamines the nitro groups form intramolecular hydrogen

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bonds with the NH groups and are nearly coplanar with the ring. The formation of a Meisenheimer complex is favored through increased conjugation.^[10]

We synthesized the substituted hexaaminobenzene **5** by the following sequence. Compound **6** was transformed into the tris-carbonate **8** by threefold nucleophilic aromatic substitution with aminopropanol and protection of the triol under standard conditions. Reduction of the nitro groups and peralkylation, followed by removal of the carbonate protecting groups gave triol **9**. After **9** had been transformed into the corresponding tribromide, the amino alcohol chains were lengthened by a Kolbe sequence; subsequent reduction with diborane then gave **5**. The reaction of **5** with **6**—not under special high-dilution conditions—led to the isolation of pure **7** in 15% yield. Compound **7** was then transformed into **1** in two steps.



We have performed a structural analysis of **1** (Figure 1), because the precise knowledge of geometrical parameters is a prerequisite for investigations on electron transfer. In addition, to the best of our knowledge, no structural analysis of a [6₃]metacyclophane has been published.^[11] The two six-mem-

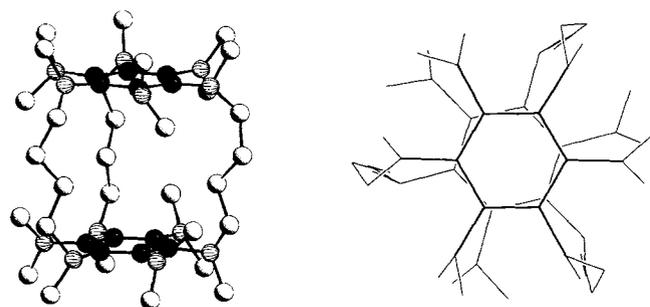


Figure 1. Side view (left) and top view (right) of **1** in the crystal.

bered rings are nearly planar; their least-squares planes are nearly parallel and form an angle of 0.18(4)° at a distance of 5.740(4) Å. This geometry is a consequence of the steric requirements of the three chains in 1-, 3-, and 5-positions, which adopt a close to extended conformation.^[12] A reduction in the distance between the rings and hence a diminution of the sizeable intramolecular cavity is energetically favorable only if the two six-membered rings are rotated with respect to each other.^[13] Accordingly, the six-membered rings are only slightly displaced

but rotated by 12°, quite in contrast to the structures of [6.6]paracyclophanes of comparable ring size.^[11b,c] in which the rings lie parallel but are displaced with respect to each other. The distance between the rings is therefore markedly smaller in those paracyclophanes.

The average endocyclic C–C and exocyclic C–N bond lengths in **1** are comparable to those in **3**;^[5b] however, the C–N bond lengths in **1** are a little shorter (C–C: 1.404(4), 1.406(4) Å vs. 1.402(2) Å; C–N: 1.422(3), 1.431(3) Å vs. 1.440(2) Å).

Preliminary cyclovoltammetric measurements indicate that **1** undergoes chemically reversible oxidation up to the tetracation with separate peaks for the oxidation of the two rings.^[14] Despite the large interring distance in the neutral molecule, pronounced interaction of the π-systems is evident at least in the oxidized form.

Experimental Section

All new compounds gave correct data for C, H, N, Br in combustion analyses.

7: A solution of **5** (1.23 g, 2.42 mmol) and ethyldiisopropylamine (970 mg, 7.50 mmol) in 100 mL of anhydrous CH₂Cl₂ and a solution of **6** [15] (791 mg, 2.50 mmol) in 100 mL of anhydrous CH₂Cl₂ were added simultaneously under argon within 2 h to 700 mL of stirred CH₂Cl₂. The reaction mixture was stirred for 16 h at room temperature then filtered. The filtrate was concentrated to a volume of ca. 25 mL and filtered over 100 g neutral aluminum oxide, (activity III; CH₂Cl₂/ethyl acetate 2/1). Subsequent chromatography (100 g neutral aluminum oxide, activity III) gave **7** as a yellow microcrystalline powder (decomp >220°C) which was used in the next step. For microanalysis, **7** was recrystallized from mesitylene. ¹H NMR (300 MHz, CDCl₃; all signals broadened): δ = 0.97, 1.66, 1.73 (together 12H), 2.44 (s, 3H), 2.60 (s, 18H), 2.70 (s, 6H), 2.98 (s, 6H), 3.81 (s, 6H), 9.42 (s, 1H), 11.25 (s, 2H). Due to poor solubility and excessive broadening ¹³C NMR data could not be obtained. Elemental analysis for C₃₃H₅₄N₁₂O₆ (714.9): calcd. C 55.45, H 7.61, N 23.51; found C 55.75, H 7.76, N 23.30. Further dilution in the cyclization reaction had no significant influence on the yields.

1: Catalytic reduction (10% Pd/C, MeOH) of **7** at ambient pressure and 50°C for ca. 24 h and subsequent methylation (dimethylsulfate, NaH, THF in analogy to ref. [16]) under argon provided **1**. The product was isolated by continuous extraction with diethyl ether and crystallized from toluene in 35% overall yield (decomp >240°C). ¹H NMR (300 MHz, [D₂]tetrachloroethane, 343 K): δ = 1.32 (br, 12H), 2.69 (br, 36H), 2.78 (br, 18H), 3.06 (br, 12H). ¹³C NMR (75.5 MHz, [D₂]tetrachloroethane, 343 K): δ = 27.76, 43.79, 44.31, 56.49; signals for aromatic carbon atoms were not detectable due to poor solubility. Elemental analysis for C₄₂H₇₈N₁₂ (751.2): calcd. C 67.16, H 10.47, N 22.38; found C 67.26, H 10.31, N 22.44.

Structural analysis of **1**: Colorless six-sided plates (cut piece 0.50 × 0.50 × 0.25 mm) from toluene under argon. C₄₂H₇₈N₁₂ (751.2); triclinic, P1̄, a = 10.433(1), b = 10.441(1), c = 23.631(5) Å; α = 84.06(2), β = 78.43(1), γ = 60.13(1)°, Z = 2; V = 2186.9(6) Å³; ρ_{calcd} = 1.14 g cm⁻³; μ = 0.07 mm⁻¹, F(000) = 828; Enraf-Nonius CAD4 diffractometer. MoK_α radiation, graphite monochromator, ω–2θ scans. 2.3° ≤ θ ≤ 28.0°; 10771 reflections, 10519 independent and 6213 observed reflections [I > 2σ(I)]. Solution by direct methods (SHELXS-86 [17]), full-matrix least-squares refinement versus F² (SHELXL-93 [18]); heavy atoms anisotropic, H atoms at calculated positions. 701 parameters refined. R = 0.097 (R_w = 0.295), S = 1.07, largest and smallest residual electron density peaks: 0.52 and –0.40 e Å⁻³, respectively. The methyl and methylene groups are disordered. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depositary number CSD-406008.

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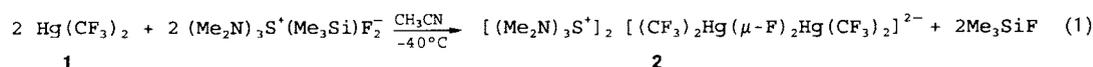
$[(\text{CF}_3)_2\text{Hg}(\mu\text{-F})_2\text{Hg}(\text{CF}_3)_2]^{2-}$: Synthesis, Structure, and Reactivity**

Detlef Viets, Enno Lork, Paul G. Watson, and
Rüdiger Mews*

Dedicated to Professor Oskar Glemser
on the occasion of his 85th birthday

In the past few years mercuria-heterocycles have been successfully used as host molecules for halide ions X^- ($\text{X} = \text{Cl}, \text{Br}, \text{I}$).^[1,2] Previously, the 2:1 adduct of 1,2-phenylenedimercury dichloride and tetraphenylphosphonium chloride, the first anionic organomercury derivative, was structurally characterized.^[3] Mononuclear organomercury compounds, R^1HgR^2 also show acceptor properties, which are particularly pronounced for perfluoroalkyl derivatives; Emelús and Lagowski used conductivity measurements to show that bis(trifluoromethyl)mercury, the first perfluorinated organometallic compound,^[4] undergoes addition of halide ions ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) in aqueous solution to form $[(\text{CF}_3)_2\text{HgX}]^-$ and $[(\text{CF}_3)_2\text{HgX}_2]^{2-}$.^[5] Korpár-Čolig et al. were able to isolate the crystalline salts $\text{Ph}_4\text{A}^+[(\text{CF}_3)_2\text{HgX}]^-$ ($\text{A} = \text{P}, \text{As}; \text{X} = \text{Cl}, \text{Br}, \text{I}$) under similar conditions by using larger organic cations. The X-ray crystal structures indicated halide-bridged dimers in the solid-state, for example, $[(\text{CF}_3)_2\text{Hg}(\mu\text{-Cl})_2\text{Hg}(\text{CF}_3)_2]^{2-}$.^[6] All attempts to synthesize the corresponding fluoro complexes have been unsuccessful to date.

By reacting $(\text{CF}_3)_2\text{Hg}$ with TAS fluoride $(\text{Me}_2\text{N})_3\text{S}^+\text{Me}_3\text{SiF}_2^-$ [$\text{TAS} = (\text{Me}_2\text{N})_3\text{S}^+$],^[7] we have been able to synthesize the first anionic fluoromercury complex [Eq. (1)].



Compound **2** was isolated as a colorless solid at -40°C by precipitation from an acetonitrile solution with diethyl ether. The ^{19}F NMR spectrum showed the expected two resonances at $\delta = -35.3$ (s, CF_3) and -83.6 (s, br, HgF); Hg-F coupling ($^2J = 1324 \text{ Hz}$) appeared only for the CF_3 . However, from the available data it is not possible to conclude whether the complex is monomeric or dimeric in solution.

The X-ray crystal structure analysis^[8] (Figure 1) indicates dimeric units in the solid state.^[9] The anion of **2** is isostructural with that of the analogous chloro derivative.^[6] The central four-membered Hg_2F_2 ring (Hg-F 239.5(7) and 241.8(7) pm, F-Hg-F 82.4(2)°) is formed by interaction of the lone pairs of electrons of the bridging fluoride ions with the empty p orbitals of the Hg centers. The original, linear C-Hg-C bond of the starting material $\text{Hg}(\text{CF}_3)_2$ ^[10,11] is significantly deformed in the anion, although with a bond angle of 162.1(5)°, sp character still dominates.

The distance between Hg and the fluoride bridges is similar to the Hg-F distance in the predominately ionic HgF_2 (Hg-F 240 pm, CN 8).^[12] The Hg-C distances of 208.6(14) in the solid state and 210.5(13) pm in the gas phase do not differ considerably from those of the starting material **1** (210.9(16))^[10] and

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