Electron Donor-Acceptor Compounds, 44[1]

Synthesis, Molecular Structure, and Electron-Donor Properties of *pseudogem*-5,8,14,17-Tetrakis(dimethylamino)[3.3]paracyclophane

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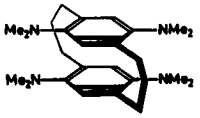
The title compound **1** consisting of two *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) units in a [3.3]paracyclophane system has been synthesized starting from **2** via **3**–**10** and **13**. The molecular structure of **1** is discussed on the basis of an X-ray structure analysis. Electron-donor properties of **1** are reported.

Elektron-Donor-Acceptor-Verbindungen, 44[1]. – Synthese, Molekülstruktur und Elektron-Donor-Eigenschaften von *pseudogem*-5,8,14,17-Tetrakis(dimethylamino)[3.3]paracyclophan

Die Titelverbindung **1**, die aus zwei *N,N,N',N'*-Tetramethyl-*p*-phenylendiamin(TMPD)-Einheiten in einem [3.3]Paracyclophan-System besteht, wurde ausgehend von **2** über **3**–**10** und **13** synthetisiert. Die Molekülstruktur von **1** wird aufgrund einer Röntgen-Strukturanalyse diskutiert. Über Elektron-Donor-Eigenschaften von **1** wird berichtet.

N,N,N',N'-Tetramethyl-*p*-phenylenediamine (TMPD), being one of the strongest electron donors of organic chemistry, found considerable interest as an efficient donor component of charge-transfer (CT) complexes. Consequently, in our programme to study orientation and distance dependences of donor-acceptor interactions we synthesized intramolecular models where TMPD units are fixed in certain geometries vis-à-vis electron acceptors like *p*-benzoquinone[2] and tetracyanoquinodimethane (TCNQ)[3] within a paracyclophane framework. In the present paper we would like to draw attention to a different problem where the preorganisation made possible by paracyclophanes may also be of interest: It is well-known that solid-state properties of CT complexes (e.g., electric conductivity) depend strongly on whether an alternating or a segregated stacking of donors and acceptors occurs. Generally, segregated stacking, like in the TCNQ complex with tetrathiafulvalene (TTF), is considered to be a requirement for metallic conductivity. In intermolecular 1:1 complexes, however, TMPD tends to crystallize with electron acceptors like chloranil[4] or TCNQ[5] in alternating stacks. It is obvious that a system where two TMPD units are linked together in a paracyclophane would no longer have the possibility to form alternating stacks of single donor and acceptor moieties but should be expected to crystallize in segregated stacks.



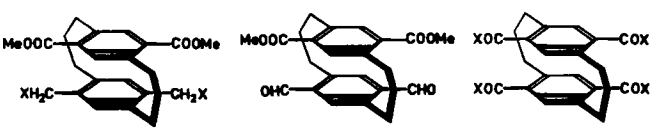
1

The most suitable candidate for such a TMPD-TMPD cyclophane would be the *pseudogem*-5,8,14,17-tetrakis(dimethylamino)[3.3]paracyclophane (**1**) of which we report here the synthesis, the determination of the molecular structure by X-ray analysis, and first experiments concerning the donor strength and the properties of a complex with TCNQ as an electron acceptor.

Synthesis of *pseudogem*-5,8,14,17-Tetrakis(dimethylamino)[3.3]paracyclophane (1)

The design of the synthesis of **1** could take advantage of the experiences with previously synthesized TMPD-paracyclophanes[2,3]. Consequently, a key intermediate should be [3.3]-paracyclophane-5,8,14,17-tetracarboxylic acid (**6**) from where via the tetrachloride (**7**) and tetraazide (**8**) by a fourfold Curtius rearrangement the four amino functions were to be introduced. Due to the crowded steric situation the permethylation of the amino groups was expected to be a crucial step, especially in view of the anticipated instability of the tetraamino compound.

As a suitable precursor for the synthesis of **6** the 14,17-bis(chloromethyl)[3.3]paracyclophane-5,8-dicarboxylic ester **2** was available[3]; the pseudogeminal structure of this compound was established by an X-ray structure determination of a direct derivative of **2**.



2: X = Cl
3: X = OH

4

5: X = OMe
6: X = OH
7: X = Cl
8: X = N_3

2 was treated with silver nitrate in acetone/water (1 h, 70 °C; 86% yield) to yield the bis(hydroxymethyl) compound **3** (m.p. 172–173 °C) which using the pyridinium dichromate method[6] in dimethylformamide (6 h, 20 °C) was oxidized to

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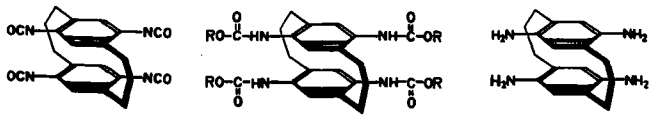
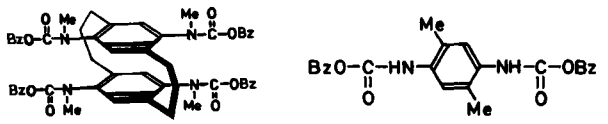
14,17-diformyl[3.3]paracyclophane-5,8-dicarboxylic ester **4** (m.p. 192–193°C; 86%). **4** with sodium cyanide/acetic acid and manganese dioxide in methanol yielded the tetramethyl ester **5** (m.p. 245–247°C, 55%)[7] which was hydrolysed (potassium hydroxide, toluene/methanol, dicyclohexano-18-crown-6) to the tetracarboxylic acid **6** (dec. > 300°C, 94%) which also was obtained by simultaneous oxidation and hydrolysis from **4** [silver(I) oxide, potassium hydroxide, methanol/water, 48 h reflux; 81%].

The tetracarboxylic acid **6** was converted with thionyl chloride/dimethylformamide (trichloromethane, 1 h reflux) into the tetrachloride **7** (dec. > 250°C; 77%). From **6** the tetraazide **8** was obtained with sodium azide (acetone/water, 1 h, 0°C; 76%); due to its instability (explosion > 105°C) it was subjected to the Curtius rearrangement (1 h, 90°C, toluene) without further purification. The resulting tetraisocyanate **9** was immediately converted into the fourfold benzyl urethane **10** (m.p. 240–241°C, 76%) and the corresponding methyl urethane **11** (m.p. 264–265°C, 90%). It was not possible to isolate the tetraamino compound **12** after basic hydrolysis of **9**. Hydrogenolysis of **10** (Pd/C, dioxane/methanol 3:1) yielded **12** as a very unstable compound extremely sensitive to oxidation. Attempts to immediately permethylate **12** to **1** with iodomethane/potassium carbonate or iodomethane/sodium hydride did not result in the eightfold methylation to **1**.



9 **10**: R = $C_6H_5CH_2$; **11**: R = Me **12**

For the synthesis of **1** it was essential to by-pass **12** and its incomplete methylation products which also are very unstable due to sensitivity to oxidation. This would be possible in case a fourfold *N*-methylation of **10** to **13** could be achieved which then would be followed by a reductive cleavage with $LiAlH_4$ directly to **1**. The methylation step was tested with 1,4-bis[(benzyloxycarbonyl)amino]-2,5-dimethylbenzene (**14**): reaction with iodomethane and sodium hydride (hexamethylphosphoric triamide, 2.5 h, 0°C) yielded 1,4-bis[(benzyloxycarbonyl)methylamino]-2,5-dimethylbenzene (m.p. 100–101°C, 83%). Under the same conditions **10** underwent fourfold *N*-methylation to **13** (m.p. 179–180°C, 59%). Reduction of **13** with $LiAlH_4$ (tetrahydrofuran, 30 min, 20°C, then 5 h reflux, under argon) led to **1** in 62% yield (colourless crystals, m.p. 245–247°C).



13 Bz = $C_6H_5CH_2$ **14**

Elemental analysis and all spectroscopic data are in accordance with structure **1**. In the mass spectrum the molecular ion (m/z = 408) gives rise to the base peak, and there are no fragment ions at all with relative intensities > 3% indicating the readiness of the electronic system of **1** to accommodate a positive charge. In ^1H NMR (360 MHz, [D_6]benzene), in addition to the multiplets of the bridge methylene protons, only two singlets at δ = 2.47 (24H) and 6.41 (4H) are observed for the eight *N*-methyl groups and the four aromatic protons. The UV spectrum, too, corresponds to structure **1**: λ_{max} (lg ε) = 306 nm (3.67), 260 (4.19), in methanol; 310 (3.74), 261 (4.27), in acetonitrile [TMPD, for comparison: λ_{max} (lg ε) = 317 nm (3.2), 262 (4.2), in ethanol].

Molecular Structure of 1

Single crystals of **1** were obtained by crystallisation from ether: space group $P\bar{1}$ with a = 838.5(1), b = 892.0(1), c = 1021.7(1) pm, α = 65.34(1), β = 62.19(1), γ = 65.58(1)°; Z = 1; D_x = 1.148 g cm^{-3}. Intensity measurements (Enraf-Nonius CAD 4, Mo-K_α radiation, graphite monochromator) resulted in 3592 symmetry-independent reflections (up to sin Θ/λ = 7.2 nm^{-1}) of which 2661 were rated as observed [$I \geqq 1.96\ \sigma(I)$]. The structure was solved by direct method (MULTAN) and was refined by full-matrix least-squares technique using anisotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for hydrogen atoms; R = 0.051[8].

The molecular structure of **1** is shown in Fig. 1 in the projection onto the planes of the aromatic rings. The two rings are parallel-shifted perpendicular to the C(4)···C(7) axis by 50 pm. As is seen in this view the cyclophane bridges form a 'quasi-chair' conformation in which the central carbon atoms of the two bridges point away from the dimethylamino substituents. The side-view (Fig. 2) shows the 'twisted-boat' deformation of the aromatic rings. This deformation with angles of 10.8 and 10.9° is significantly stronger than in any other known [3.3]paracyclophane structure[9]. A consequence of this ring deformation is the long transanular distance between the central parts of the aromatic rings (349 pm). Of the four dimethylamino substituents one *N*-methyl unit each is nearly coplanar with the

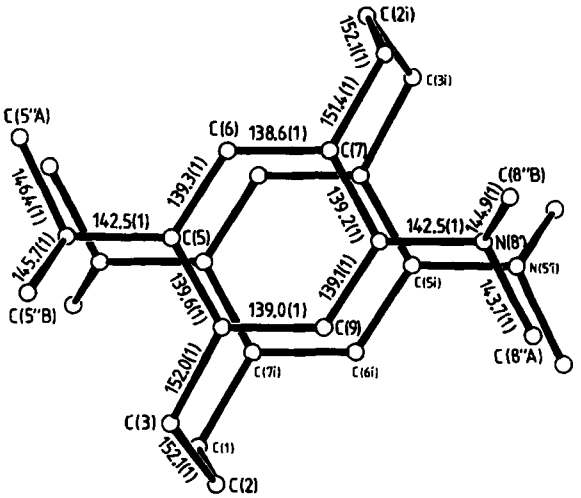


Fig. 1. Molecular structure of **1** in a top-view perpendicular to the aromatic rings with bond lengths (in pm; standard deviation in brackets)

ring whereas in other TMPD-[3.3]paracyclophanes the dimethylamino groups under the steric influence of the neighbouring cyclophane bridges show a stronger rotation out of the aromatic ring planes.

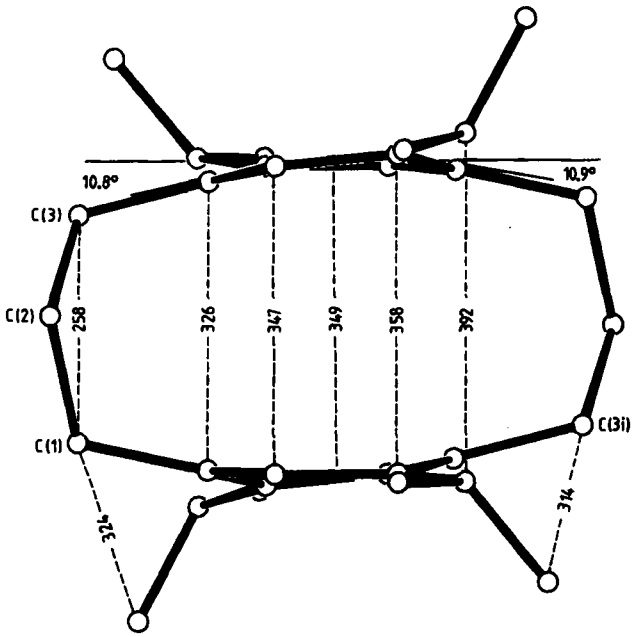


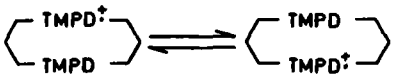
Fig. 2. Molecular structure of 1 in a side-view showing the 'twist-boat' deformation of the aromatic rings and the transanular distances (in pm)

In the crystal lattice 1 forms stacks of molecules along the *b*-axis. Due to the bulky *N*-methyl groups pointing upwards and downwards the interplanar distance between the aromatic rings of two neighbouring molecules within the stack is too long (493 nm), however, to allow stronger intermolecular $\pi\cdots\pi$-interactions.

Electron-Donor Properties of 1

As a double TMPD-system 1 is expected to show four oxidation steps. By cyclic voltammetry the first and second oxidation potentials were determined to be $E_1^{ox} = -242$ V and $E_2^{ox} = -0.102$ V as clearly reversible one-electron stages; the third and fourth oxidation steps could not be separated ($E_{3,4}^{ox} \cong +0.249$ V). Under the same conditions (0.1 M tetrabutylammonium perchlorate, acetonitrile, platin-disk electrode, potentials measured against Ag/Ag^+, $V = 0.1$ V s^{-1}) TMPD itself shows the following oxidation potentials: $E_1^{ox} = -0.206$ V and $E_2^{ox} = +0.378$ V. This means that the first oxidation of 1 occurs at a more negative potential in spite of the steric hindrance of the mesomeric effect of the electron-donating dimethylamino substituents which is clearly demonstrated by the potentials of 2,5-dimethyl-TMPD ($E_1^{ox} = +0.081$ and $E_2^{ox} = +0.242$ V)[10]. Obviously, in 1 the neighbouring electron-rich donor ring compensates for the hindrance of the substituent effect, thus making 1 an even stronger electron donor than TMPD itself.

The first oxidation step of 1, which corresponds to the formation of Wursters Blue radical cation from TMPD, is also easily reached by oxidation with bromine in methanol. Its formation can be recorded in the UV/VIS spectra by the development of two strong new absorption bands at $\lambda_{max} =$ 580 and 385 nm. For this radical cation of the Wursters Blue type, due to the specific structure of 1, an electron exchange of the following type was to be expected for which the hyperfine structure of the ESR signal is in accordance with a fast exchange rate for the radical electron[11]:



With tetracyanoquinodimethane (TCNQ) 1 forms a complex which from toluene is obtained in metallic black crystals. According to elemental analysis this complex has the 1/TCNQ stoichiometry of 1:2. First conductivity measurements on single crystals show room-temperature conductivity $\sigma = 1.5\ (\Omega\ cm)^{-1}$ along the longer crystal axis which is about six powers of ten higher than observed for the 1:1 complex of TCNQ and TMPD. Further details concerning the solid state properties of the complex 1 · $(TCNQ)_2$ and attempts to correlate these to the crystal structure will be published separately[12].

Experimental

Dimethyl pseudogem-14,17-Bis(hydroxymethyl)[3.3]paracyclophane-5,8-dicarboxylate (3): 900 mg (2.0 mmol) of dimethyl *pseudogem*-14,17-bis(chloromethyl)[3.3]paracyclophane-5,8-dicarboxylate (2)[3] in 1 l of acetone/water (1:1) was heated with 1.76 g (10 mmol) of silver nitrate for 1 h at 70°C. The precipitate was filtered off, and the filtrate was concentrated in vacuo and extracted with dichloromethane. The organic solutions were dried, the solvents were distilled off in vacuo, and the residue was dissolved in acetone/water (1:1). On distilling off the solvents 710 mg (86%) of 3 crystallized: colourless crystals, m.p. 172–173°C (from toluene). – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 1.6 (br. s, 2H), 1.9–3.7 (m, 12H), 3.93 (s, 6H), 4.53 ('s', 4H), 6.90 (s, 2H), 7.39 (s, 2H). – MS: *m/z* (%) = 412 (55, M^+), 394 (10), 376 (100), a.o.

$C_{24}H_{28}O_6$ (412.5) Calcd. C 69.89 H 6.84
Found C 69.64 H 7.04

Dimethyl pseudogem-14,17-Diformyl[3.3]paracyclophane-5,8-dicarboxylate (4): To a solution of 6.0 g (16 mmol) of pyridinium dichromate[9] in dry dimethylformamide under stirring a solution of 656 mg (1.6 mmol) of 3 in 6 ml of dimethylformamide was added, and the mixture was stirred for 6 d at 20°C. After addition of 300 ml of water and extraction with dichloromethane the organic extracts were washed extensively with water, dried over sodium sulfate, and evaporated in vacuo. The remaining yellow crystals were chromatographed on silica from dichloromethane/ether (50:1) to yield 562 mg (86%) of 4 of m.p. 192–193°C. – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 2.0–2.9 (m, 8H), 3.5–3.9 (m, 4H), 3.89 (s, 6H), 7.35 (s, 2H), 7.41 (s, 2H), 10.12 (s, 2H). – MS: *m/z* (%) = 408 (95, M^+), 376 (100), a.o.

$C_{24}H_{24}O_6$ (408.5) Calcd. C 70.57 H 5.92
Found C 70.43 H 6.02

Tetramethyl pseudogem-[3.3]Paracyclophane-5,8,14,17-tetracarboxylate (5): 300 mg (0.73 mmol) of 4, 3.58 g (73 mmol) of sodium cyanide, 6.36 g (73 mmol) of manganese dioxide (precipitated, active), 1.24 ml of acetic acid, and 50 ml of methanol were heated in a sealed tube for 24 h to 65–70°C. From the reaction mixture the

solvents were distilled off, and the residue was extracted in a Soxhlet extractor with dichloromethane for 16 h. From the extract the solvent was distilled off, the residue was chromatographed on silica from dichloromethane/ether (50:1) to yield after evaporation of the solvents 187 mg (55%) of **5**, m.p. 245–247°C (from acetone). – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 2.0–2.8 (m, 8H), 3.5–3.9 (m, 4H), 3.88 (s, 12H), 7.46 (s, 4H). – MS: *m/z* (%) = 468 (35, M^+), 437 (45), 436 (100), 404 (66), 372 (64) a.o.

$C_{26}H_{28}O_8$ (468.5) Calcd. C 66.66 H 6.02
Found C 66.68 H 6.16

pseudogem-[3.3]Paracyclophane-5,8,14,17-tetracarboxylic Acid (**6**)

a) 200 mg (0.43 mmol) of **5** in 20 ml of toluene was heated in the presence of 1.0 g (17.8 mmol) of potassium hydroxide, 32 mg of dicyclohexano-18-crown-6, and 0.2 ml of methanol for 24 h under reflux. The reaction mixture was extracted with 25 ml of water, the water solution was extracted with ether and acidified: The voluminous precipitate after cooling was filtered off, washed with water, and dried at 65°C: 166 mg (94%) of raw **6**. The material which was difficult to obtain in analytical purity was used for the preparation of **7** without further purification. – ^{1}H NMR (80 MHz, [D_6]dimethyl sulfoxide): δ = 1.6–3.9 (m, 12H), 7.39 (s, 4H), 12.3 (br. s, 4H).

b) To a solution of 5.0 g (89 mmol) of potassium hydroxide in 20 ml of methanol/water (9:1) the concentrated aqueous solution of 2.0 g (11.4 mmol) of silver nitrate and then 100 mg (0.245 mol) of **4** was added, and the reaction mixture was heated under stirring for 48 h under reflux. After addition of 30 ml of water, filtration of the insoluble, and extraction of the aqueous solution with ether the solution was acidified, and the precipitate was washed and dried according to procedure a): 81 mg (81%) of raw **6** which again was used for the next step without further purification.

pseudogem-[3.3]Paracyclophane-5,8,14,17-tetracarbonyl Chloride (**7**): 50 mg (0.12 mmol) of **6** in 4 ml of trichloromethane after addition of 2 ml of thionyl chloride and 2 drops of dimethylformamide was heated 1 h to reflux. The solvent and excess thionyl chloride were distilled off in vacuo, and the residue was crystallized from trichloromethane: 46 mg (77%), dec. > 250°C. – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 2.1–3.0 (m, 8H), 3.4–3.8 (m, 4H), 7.75 (s, 4H). – MS: *m/z* (%) = 484 (6, M^+, 4 Cl), 449 (100, 3 Cl), a.o.

$C_{22}H_{16}Cl_4O_4$ (486.2) Calcd. C 54.35 H 3.32 Cl 29.17
Found C 54.06 H 3.04 Cl 29.28

pseudogem-5,8,14,17-Tetrakis[(benzyloxycarbonyl)amino][3.3]-paracyclophane (**10**): To a solution of 177 mg (0.36 mmol) of **7** in 300 ml of acetone at 0°C a solution of 0.75 g (11.5 mmol) of sodium azide in 10 ml of water, also cooled to 0°C, was added. The reaction mixture was stirred 1 h at 0°C and then evaporated in vacuo at 0°C to a volume of 50 ml. Addition of 2 l of ice/water precipitated the tetraazide **8** which was separated, washed with water, and dried: 142 mg of **8** which decomposes (explosion!) above 105°C. Without further characterisation **8** was dissolved in 40 ml of toluene and heated for 1 h to 90°C for the conversion into the tetraisocyanate **9**. After addition of 0.5 ml (4.7 mmol) of benzyl alcohol and heating under reflux for 24 h the solvents were distilled off and the residue was crystallized from toluene: 142 mg (76%) of **10**, m.p. 240–241°C. – ^{1}H NMR (360 MHz, [D_6]dimethyl sulfoxide): δ = 1.60–1.75 (m, 2H), 2.05–2.20 (m, 2H), 2.25–2.40 (m, 4H), 2.65–2.80 (m, 4H), 5.05 and 5.11 (AB, *J* = 12.5 Hz, 8H), 6.58 (s, 4H), 7.25–7.45 (m, 20H), 8.78 (br. s, 4H).

$C_{50}H_{48}N_4O_8$ (833.0) Calcd. C 72.10 H 5.81 N 6.73
Found C 71.82 H 5.83 N 6.64

pseudogem-5,8,14,17-Tetrakis[(methoxycarbonyl)amino][3.3]-paracyclophane (**11**): 120 mg (0.23 mmol) of **8** prepared as for the preparation of **10** (see above) was heated for 1.5 h in 30 ml of toluene to reflux. After addition of 30 ml of methanol the mixture was kept boiling for further 24 h. Evaporation of the solvents in vacuo to a volume of 15 ml led to the crystallization of 110 mg (90%) of **11**, m.p. 264–265°C. – ^{1}H NMR (360 MHz, [D_6]dimethyl sulfoxide): δ = 1.6–1.8 (m, 2H), 2.0–2.2 (m, 2H), 2.3–2.4 (m, 4H), 2.65–2.8 (m, 4H), 3.62 (s, 12H), 6.58 (s, 4H), 8.60 (br. s, 4H).

$C_{26}H_{32}N_4O_8$ (528.6) Calcd. C 59.08 H 6.10 N 10.60
Found C 58.85 H 6.07 N 10.37

1,4-Bis[(benzyloxycarbonyl)methylamino]-2,5-dimethylbenzene: 220 mg (0.50 mmol) of 1,4-bis[(benzyloxycarbonyl)amino]-2,5-dimethylbenzene[13] in 10 ml of hexamethylphosphoric triamide was treated at 0°C with 1.27 ml (20 mmol) of iodomethane and 240 mg (10 mmol) of sodium hydride and stirred for 2.5 h. After dilution with 10 ml of ether the reaction mixture was hydrolysed by careful addition of 70 ml of water under ice-cooling. The water layer was separated and extracted with ether. The organic phase was washed with water, dried (sodium sulfate), and the solvent was evaporated. The residue was chromatographed on silica from toluene/acetone (85:15). Crystallization of the residue of the eluate from ether yielded 180 mg (83%), m.p. 100–101°C. – ^{1}H NMR (80 MHz, [D_2]dichloromethane): δ = 2.11 (s, 6H), 3.19 (s, 6H), 5.13 (s, 4H), 7.04 (s, 2H), 7.28 (br. s, 10H).

$C_{26}H_{28}N_2O_4$ (432.5) Calcd. C 72.20 H 6.52 N 6.48
Found C 72.41 H 6.64 N 6.62

pseudogem-5,8,14,17-Tetrakis[(benzyloxycarbonyl)methylamino][3.3]paracyclophane (**13**): To 100 mg (0.12 mmol) of **10** in 10 ml of hexamethylphosphoric triamide at 0°C 152 ml (24 mmol) of iodomethane and 288 mg (12 mmol) of sodium hydride was added, and the reaction mixture was kept with stirring for 2.5 h at 0°C. After addition of 10 ml of ether hydrolysis was achieved by adding carefully 70 ml of water under ice-cooling. The aqueous solution was separated and extracted with ether. The combined organic solutions were washed with water, dried (sodium sulfate), and evaporated in vacuo. The residue was chromatographed on silica from toluene/acetone (9:1) and crystallized from ether: 63 mg (59%) of **13**, m.p. 179–180°C. – ^{1}H NMR (80 MHz, [D_2]dichloromethane): δ = 1.8–2.7 (m, 12H), 3.36 (s, 12H), 5.00 ('s', 8H), 6.79 (s, 4H), 7.1–7.3 (m, 20H).

$C_{54}H_{56}N_4O_8$ (889.1) Calcd. C 72.95 H 6.35 N 6.30
Found C 72.95 H 6.55 N 6.32

pseudogem-5,8,14,17-Tetrakis(dimethylamino)[3.3]paracyclophane(=N,N,N′,N′,N″,N″,N‴,N‴-Octamethyl-pseudogem-[3.3]-paracyclophane-5,8,14,17-tetramine, **1**): To 47 mg (0.053 mmol) of **13** in 10 ml of tetrahydrofuran under argon 80 mg (2.12 mmol) of $LiAlH_4$ was added at room temperature. After 30 min at room temperature the reaction mixture was heated to reflux for 5 h. Under ice-cooling water was added dropwise for hydrolysis, and 20 ml of 25% aqueous potassium hydroxide solution was added. After extraction with ether the combined organic phases were dried (sodium sulfate) and evaporated: 13.4 mg (62%) of **1**, m.p. 245–247°C (from ether). – ^{1}H NMR (360 MHz, [D_6]benzene): δ = 1.9–2.05 (m, 2H), 2.15–2.25 (m, 2H), 2.47 (s, 24H), 2.45–2.60 (m, 4H), 3.15–3.25 (m, 4H), 6.41 (s, 4H). – MS: *m/z* (%) = 408 (100, M^+).

$C_{26}H_{40}N_4$ (408.6) Calcd. C 76.42 H 9.87 N 13.71
Found C 76.48 H 9.75 N 13.76

CAS Registry Numbers

1: 105562-32-1 / **2**: 87386-98-9 / **3**: 105562-33-2 / **4**: 105562-34-3 / **5**: 105562-35-4 / **6**: 105562-36-5 / **7**: 105562-37-6 / **8**: 105562-38-7 / **9**: 105562-39-8 / **10**: 105562-40-1 / **11**: 105562-41-2 / **12**: 105562-42-3 / **13**: 105562-43-4 / **14**: 105562-44-5 / **14** (*N,N'*-dimethyl): 105562-45-6 / $PhCH_2OH$: 100-51-6 / MeI: 74-88-4

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[8] Further information concerning the X-ray structure analysis of **1** including the lists of atomic coordinates, thermal parameters, bond lengths, and bond angles may be requested from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, with indication of the registry number CSD 52113, the authors' names, and the reference to this publication.

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