Synthesis and Redox Behavior of Wurster Blue Cyclophanes

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Two cyclophanes composed of two *p*-phenylenediamine (PPD) units connected by methylene chains of different lengths (**1c**, $n = 3$; **2c**, $n = 5$) have been synthesized. The PPD unit of cyclophane **1c** was oxidized by a two-electron transfer process to give **1c**$^{2+}$ at the first oxidation potential. In contrast, **2c** was oxidized by a one-electron transfer process to give **2c**$^{+}$ and then **2c**$^{2+}$.

Introduction

The Wurster radical, generated by the oxidation of *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD), is a well-known stable radical, and TMPD itself is a good electron donor and forms CT complexes with various acceptors.[1] Recently, several new TMPD analogs have been synthesized and their properties as electron donors have been widely studied.[2] During our investigations into CT interactions and electrochemical properties of azacyclophanes,[3] we became interested in TMPD as a cyclophane unit. CT interactions are of interest in cyclophane chemistry and remains an important subject.[4] An example of a TMPD-based cyclophane was reported by Staab et al., who incorporated a TMPD unit into a [3.3]paracyclophane skeleton and determined its electrochemical properties and its ability to form CT complexes.[5] We have synthesized another type of PPD-containing cyclophane in order to investigate the effect of distance between the two PPD units on the electrochemical properties of the cyclophanes (Figure 1). Thus, we wish to report here the synthesis and redox properties of cyclophanes **1c** and **2c**.

Results and Discussion

Synthesis of 1a−c and 2a−c

The synthesis of **2a** and **2b** has been reported previously by Stetter and Roos.[6] We improved the yields by employing a modified one-step procedure without using a high-dilution technique. *N*,*N*′-Ditosyl-*p*-phenylenediamine in DMF was allowed to react with the corresponding dibromoalkanes using sodium hydride as a base. After the usual work up, **1a** and **2a** were obtained in 25 and 56% yields, respectively (Scheme 1). Cleavage of the tosyl groups of **1a** and **2a** was readily achieved by employing 90% H_2SO_4 (100 °C, 5 min) to yield **1b** and **2b**. Compounds **1b** and **2b** were sensitive to air, particularly under moist conditions; therefore, these materials were alkylated without further purification. Methylation of **1b** and **2b** to give **1c** and **2c** could be achieved by the Eschweiler−Clarke procedure, but it is preferable to carry out this reaction under milder conditions because **1b** is more sensitive to air than **2b**. Therefore, we employed a $NaBH_4$/aq. HCHO/H_2SO_4 mixture for the methylation of **1b**.[7]

The solutions of compounds **1c** and **2c** were gradually oxidized by exposure to air, and they turned blue just like the Wurster blue radical solution. UV light irradiation also generated the blue species. Oxidation of **1c** and **2c** with an equal amount of $AgBF_4$ afforded dark-blue crystals which were less stable than the Wurster blue salt ($TMPD^{+}\cdot BF_4^{-}$) prepared similarly. The solution of **2c** oxidized by $AgBF_4$ was more stable than that of **1c**: the blue solution of the oxidized **2c** turned dark-blue in a day, but that of **1c** turned pink in half a day. These oxidation phenomena were investigated in detail by an electrochemical method as described below.

Unfortunately, the crystals of **1c**, **2c**, and their oxidized species were not suitable for crystallographic analysis and thus we cannot discuss the molecular structure of the cyclo-

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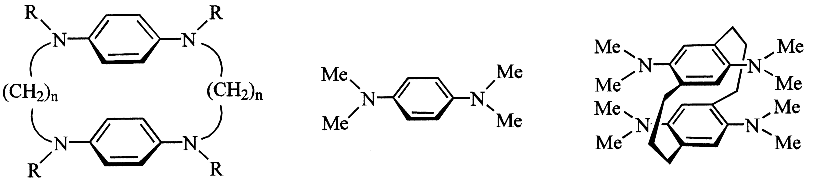
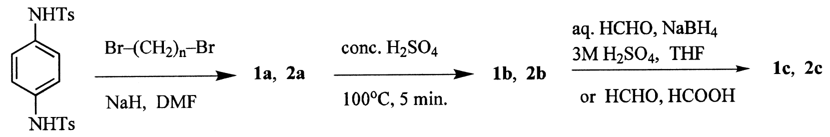


	n	R
1a	3	Ts
1b	3	H
1c	3	Me
2a	5	Ts
2b	5	H
2c	5	Me

Figure 1. Structures of TMPD and TMPD-based cyclophanes



Scheme 1. Synthetic scheme for the preparation of cyclophanes

phanes in the solid state.[8] In the case of [*n.n*]paracyclophanes, an energy minimum is found when *n* is an odd number and the two benzene rings are in a face-to-face conformation.[9] This is true for the [7.7]paracyclophane system, as revealed by crystallographic analysis, which is reported to be almost strain-free. Therefore, the aza analog of [7.7]paracyclophane, **2c**, should have similar structural properties. Because attempts at crystallographic analyses were unsuccessful, conformational information about **1c**, **2c**, and $\mathbf{1c}^{2+}$ was obtained from Conflex calculations (see Supporting Information, for Supporting Informations see also the footnote on the first page of this article).[10] According to the results of these calculations, the two benzene rings of **2c** are in a face-to-face geometry and the distance between the two PPD units is 7.6 Å. In contrast, the two benzene rings of **1c** are slightly twisted and the distance between the two PPD units is 5.2 Å. These values agree very closely with those of the [5.5]- and [7.7]paracyclophanes; Wartini et al. determined the structures of these cyclophanes by crystallographic analysis, and they referred to the flexibility of [5.5]- and [7.7]paracyclophanes.[11]

In the case of $\mathbf{1c}^{2+}$, the four nitrogen atoms are sp^2 hybridized and conjugated with the benzene rings. The two PPD units adopted a stair-shaped geometry in order to avoid repulsion between the two positive charges, and consequently, the distance between the two benzene rings is about 3.4 Å.

Cyclic Voltammetry and Coulometry

In order to investigate the electrochemical properties, the redox potentials were measured by cyclic voltammetry (CV), and each oxidation process was analyzed by coulometry. *Figure* 2 shows the cyclic voltammograms of TMPD, **1c**, and **2c**, and the oxidation potentials thus obtained are given in Table 1. Cyclophane **2c** showed two clear peaks at −0.184 and +0.432 V (*E*/V vs Ag/AgNO$_3$), which correspond to the first and second oxidation processes, and are very similar to those of TMPD. Coulometry showed that both oxidation processes took place by a one-electron transfer process (Figure 3). In contrast, **1c** was oxidized in a different manner to that of **2c** or TMPD; two irreversible redox waves were observed in **1c**, and coulometry indicated that the first oxidation step occurred by a two-electron transfer process. This is also easily seen from the cyclic voltammetry results, in which the current of the first oxidation step is about twice that of TMPD and **2c**, as shown in Figure 2. Furthermore, the one-step-two-electron mechanism can be understood in terms of the peak separation of the first redox couple of the cyclic voltammograms. According to the equation, $\Delta E_p = 60\ (\mathrm{mV})/n$, where ΔE_p is the peak separation of a redox couple and n is the number of electrons, we found that $n = 2$ in the case of $\mathbf{1c}^{2+}$. The results of the coulometric analysis of **1c** at the second potential were not clear because an unknown oxidation process occurred and insoluble materials precipitated on the electrode. The peaks at +0.81 and +0.95 V (shown by arrows) seem to originate from the oxidation of the by-products generated by electrolysis.

The UV spectra of the oxidized species were recorded with a platinum mesh electrode fitted into a quartz cell at controlled potentials which were the same as those used in the CV experiments (Figure 4). The UV spectrum of the oxidized species of cyclophane **2c** at the first peak is very similar to that of TMPD$^+$. In contrast, the spectrum of

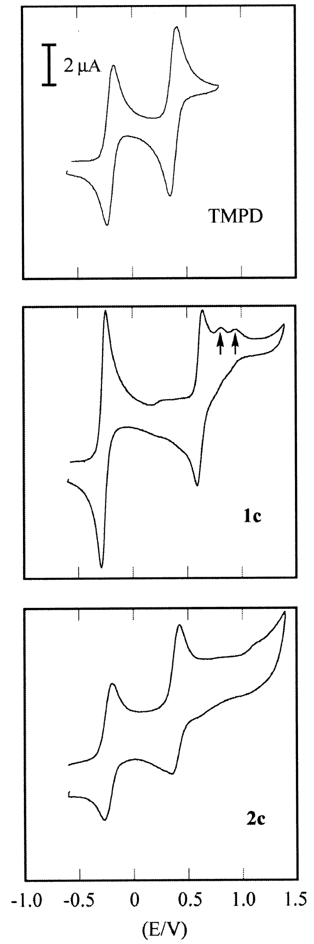


Figure 2. Cyclic voltammogram of TMPD, **1c**, and **2c** (1.0×10^{-3} mol·dm^{-3} in CH_3CN at a scan rate of 100 mV·s^{-1}). $Ag/AgNO_3$ (0.01 M) was used as the reference electrode

Table 1. Oxidation potentials of TMPD and the cyclophanes, **1c**, **2c**, and **3**

	E_{ox1} [V]	E_{ox2} [V]	E_{ox3} [V]	E_{ox4} [V]
TMPD	−0.154	+0.420	–	–
1c	$E_{ox1,2} = -0.232$		$E_{ox3\ and/or\ 4} = +0.668$	
2c	−0.184	+0.432	–	–
3	−0.242	−0.102	$E_{ox3,4} = +0.249$	

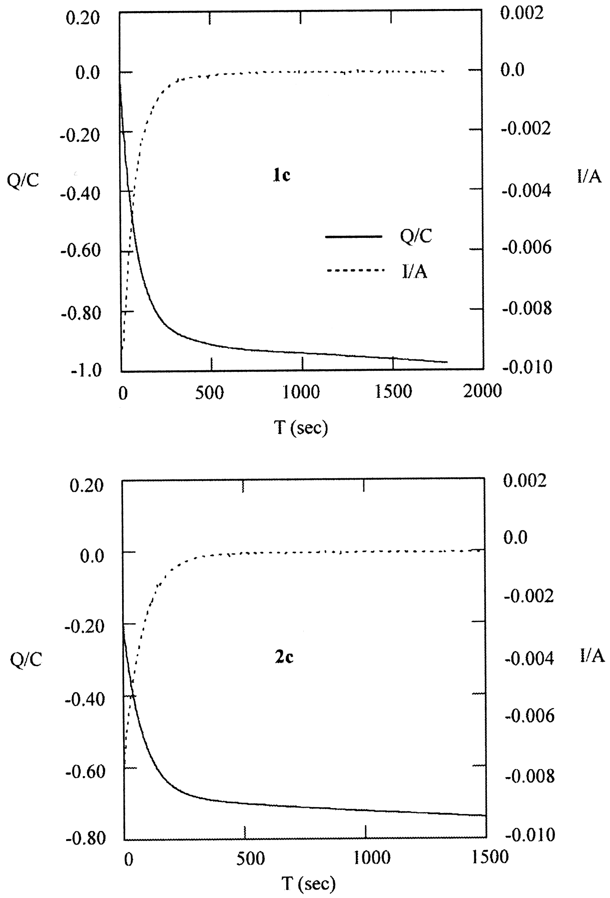


Figure 3. The results of coulometry of cyclophanes **1c** and **2c** at the first oxidation potential (5.0×10^{-4} mol·dm^{-3} in CH_3CN)

cyclophane **1c**$^{2+}$ is quite different. From the results of CV, coulometry, and UV spectroscopy, **1c**$^{2+}$ can be assigned to either a singlet dication **1c**$^{2+}$ (A) or a quinonediimine-PPD structure **1c**$^{2+}$ (B), as shown in Scheme 2, rather than to a triplet bis-monoradical form.[12] This was further supported by ESR measurements, in which **1c**$^{2+}$ showed no ESR signal. In the case of **2c**$^{+}$, broad temperature-dependent sinusoidal signals were observed in the ESR spectra. Figure 5 shows the ESR spectra of **2c**$^{+}$ along with that of TMPD^{+}. The UV/Vis spectra of **1c**, **1c**$^{2+}$ (A), and **1c**$^{2+}$ (B) were predicted by ZINDO calculations based on their Conflex-optimized structures (Supporting Information). Although the calculated spectrum of **1c** coincided very well with the observed one, the spectra of **1c**$^{2+}$ (A) and **1c**$^{2+}$ (B) did not accurately coincide with the experimental spectrum; each had structure in common with the experimental spectrum. Therefore, the dication species could not be specified as either **1c**$^{2+}$ (A) or **1c**$^{2+}$ (B).

Because the two PPD units of cyclophane **1c** are close to each other (5.2 Å), effective CT interactions can be expected and an electron can easily transfer from one PPD unit to another by a through-space interaction. Thus, a dication is generated at the first oxidation potential. In contrast, each PPD unit of **2c** is sufficiently separated (7.6 Å) so that electron transfer from the neutral PPD unit to the PPD^{+} unit rarely occurs. Therefore, one-electron transfer occurred and the oxidation potentials are similar to those of TMPD.

Interestingly, these redox processes and oxidation potentials are quite different from those of Staab's cyclophane **3**, although the experimental conditions were the same as those used by Staab and co-workers.[5] Namely, the first and second oxidation peaks were observed independently, but the third and fourth oxidation peaks could not be distinguished. These phenomena can be related to the structures of the cyclophanes. Cyclophane **3** is a [3.3]paracyclophane system in which the PPD unit is rigidly fixed in a face-to-face conformation. The two units are almost paral-

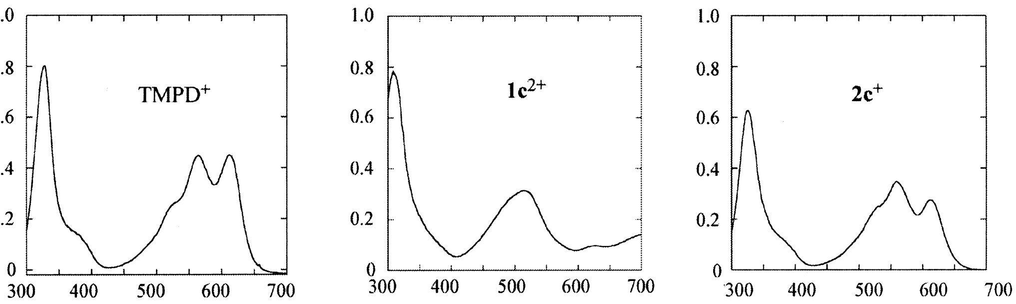
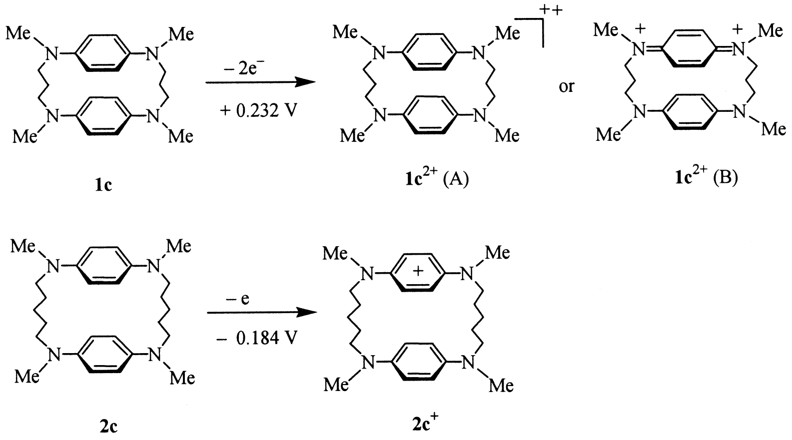


Figure 4. UV spectra of oxidized species at the first oxidation potentials



Scheme 2. Proposed scheme for the oxidation of cyclophanes **1c** and **2c**

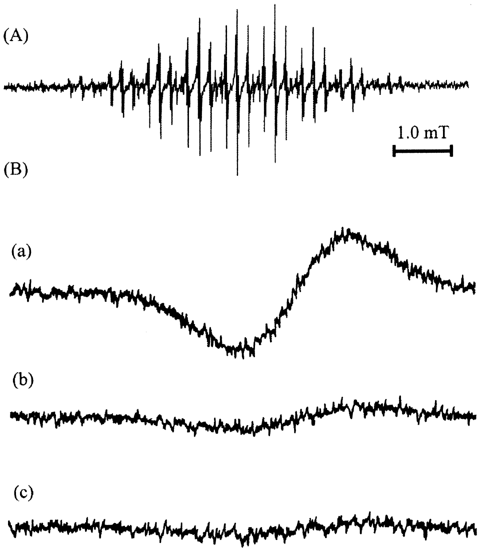


Figure 5. ESR spectra of (A) $\mathrm{TMPD^+}$ and (B) $\mathbf{2c}^+$ at (a) 293 K, (b) 253 K, and (c) 223 K

lel and the PPD units are much closer (3.49 Å) together than in **1c**.[5] From the crystallographic analysis of **3** the distortion of the two benzene rings was considered to result from the steric repulsion between the facing four dimethylamino groups. Thus, the distortion and the distance between the PPD units affect the oxidation potentials of the cyclophane. In contrast, **1c** and **2c** are almost strain-free, as described above. Only the distance between the two PPD units affects the redox potentials.

Further evidence for this property of unimolecular or bimolecular behavior of the PPD units of cyclophanes **1c** and **2c** is inferred from CT complex formation as follows. Cyclophane **2c** formed a deep-blue CT complex with 1,3,5-trinitrobenzene (TNB), and the ratio of the components of the complex **2c**/TNB was 1:2, as determined by elemental analysis. In contrast, cyclophane **1c** formed a 1:1 CT complex with TNB (Figure 6), even though a large excess of TNB was added. The UV spectra of these complexes ($\mathrm{CH_3CN}$) were similar to that of $\mathrm{TMPD^+}$ obtained by electrolysis. The specific bands at $\lambda > 300$ nm are as follows: **1c**·TNB; $\lambda = 326, 535, 575, 625$ nm, $\mathrm{TMPD^+}$; $\lambda = 326, 528, 562, 612$ nm. Thus, the structures of the CT complexes can be regarded as being of $\mathrm{D^{\cdot+}{\cdot}A^{\cdot-}}$ type. In the case of **1c**, the spectrum in the range of 300−700 nm did not change even in the presence of an excess of TNB; so the complex **1c**·2TNB seems to be a very weak complex. Therefore, **1c** acts as a single donor to electron acceptor. However, the intensities of the absorption bands of **1c**·TNB and **2c**·2TNB complexes in the range of 300−700 nm were quite weak compared with those of $\mathrm{TMPD^+}$ and $\mathbf{2c}^+$, which suggests that the complexes dissociate easily in dilute solution. The differences in the ratios of the components of the complexes were attributed to the donor properties of the cyclophanes. The distance between the two PPD units of **1c** is short enough for interactions to occur, thus, intramolecular interactions cause **1c** to be a single donor. In contrast, each PPD unit of **2c** independently acts as a donor because the units are sufficiently separated. This explanation coincides with those based on the electrochemical properties.

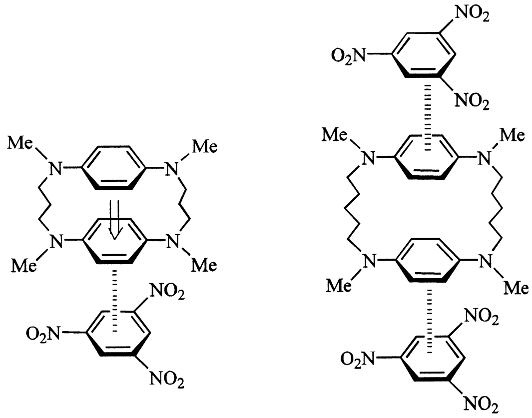


Figure 6. CT complexes of the cyclophanes **1c** and **2c** with 1,3,5-trinitrobenzene

Conclusions

By altering the distances between the two PPD units in the cyclophane skeleton, significant differences in the redox properties and CT complex formation were observed. Cyclophane **1c**, in which two PPD units are connected by shorter methylene chains, acts as a single donor. In contrast, the PPD units in cyclophane **2c** behave independently. This simple molecular design has shown that the interactions and changes in the properties of the redox unit depend upon the distance separating the two PPD units.

Experimental Section

General Procedure: All melting points were measured in Ar-sealed tubes and are uncorrected. ^1H NMR spectra were recorded with a JEOL GSX-270 spectrometer (270 MHz). The electrochemical measurements were performed with a polarograph (Fuso, Model 312) connected to a function generator (NF Circuit Design Block Co., Model FG-121B). The working electrode was a platinum wire, while the counter electrode was a platinum plate, the reference electrode being Ag/0.01 M $AgNO_3$. The scan rate was 100 $mV \cdot s^{-1}$. The solvent used was CH_3CN, and dissolved oxygen was removed by passing CH_3CN-saturated nitrogen gas through the liquid prior to measurement. Tetrabutylammonium perchlorate was used as a supporting electrolyte (0.1 $mol \cdot dm^{-3}$ in CH_3CN). All measurements were carried out at 25 ± 0.5 °C. Coulometry was performed under constant-potential conditions with a high current potentiostat. A copper anode and a platinum mesh cathode were used. During the electrolysis, the anode compartment was stirred continuously with a magnetic stirrer. ESR spectra were recorded with an X-band ESR spectrometer (Echo Electronics) combined with an electromagnet (JEOL, JM-360) with 100 kHz modulation; care was taken to avoid power saturation and the modulation amplitudes were at most 0.01 mT. The time constant of the spectrometer was 0.5 s and the sweep rate was as slow as 2 h per spectrum. The magnetic fields were measured with a proton NMR gaussmeter (JEOL, JMF-3). Variable temperature measurements (±1°C) were made by using a temperature control apparatus (JEOL, UTC-2AX/JES-VT-3AT). Radical solutions of **1c** and **2c** were prepared by electrolysis with gold electrodes in CH_3CN in the presence of tetrabutylammonium perchlorate as a supporting electrolyte. The preparations were carried out after deaeration by several freeze-pump-thaw cycles. In the optical measurements, the radical solutions of **1c** and **2c** were sealed in quartz cells of 2 mm path length. The Conflex calculations were carried out on CAche system and ZINDO calculations were calculated based on the Conflex-optimized structures.

***N,N′,N′′,N′′′*-Tetratosyl-1,5,12,16-tetraaza[5.5]paracyclophane (1a):** *N,N′*-Ditosyl-*p*-phenylenediamine (20 g, 48 mmol) and sodium hydride (60% in mineral oil, 4.2 g) were dispersed in DMF (1 L) and stirred at 50 °C. After an hour, the temperature was raised to 120 °C and a solution of 1,3-dibromopropane (9.70 g, 48 mmol) in DMF (200 mL) was added dropwise over a period of 4 h; the resultant solution was stirred for another 2 h. The solution was then poured into hot brine, and the precipitates were collected by suction filtration. Recrystallization of the tan powder thus obtained from dichloromethane yielded **1a** as a colorless powder (11.1 g, 25%). Further recrystallization from a benzene/dichloromethane mixture gave the analytically pure benzene adduct. M.p. 323.3−324.2 °C. ^1H NMR ($CDCl_3$): $\delta = 7.42, 7.28$ [ABq, $^3J(H,H) = 8$ Hz, 16 H, Ts-Ar-H], 6.70 (s, 8 H, Ar-H), 3.52 [t, $^3J(H,H) = 7$ Hz, 8 H, N-CH_2-], 2.45 (s, 12 H, Ts-CH_3), 1.27 [quint, $^3J(H,H) = 7$ Hz, 4 H, N-CH_2-CH_2-] ppm. $C_{46}H_{48}N_4O_8S_4 \cdot C_6H_6$: calcd. C 63.01, H 5.49, N 5.65; found C 62.79, H 5.41, N 5.55. FAB-MS: $m/z = 912.3$ [M^+].

1,5,12,16-Tetraaza[5.5]paracyclophane (1b): Compound **1a** (5 g, 5.48 mmol) was mixed with 90% sulfuric acid (10 mL), and the mixture was maintained at 100 °C for 5 min. The solution was poured into water (100 mL) and made alkaline with potassium carbonate. The resultant mixture was extracted with dichloromethane (5 × 25 mL), and the aqueous layer was saturated with sodium chloride and extracted with dichloromethane (4 × 25 mL). The organic layers were combined and dried with potassium carbonate. Evaporation of the solvent gave almost pure reddish-brown prisms (1.11 g, 68%). This material was used for the synthesis of **1c** without further purification. M.p. 239.2−240.6 °C. ^1H NMR ($CDCl_3$): $\delta = 6.37$ (s, 8 H, Ar-H), 3.40 (s, 4 H, NH), 3.17 [t, $^3J(H,H) = 7$ Hz, 8 H, N-CH_2-CH_2-], 1.61 [quint, $^3J(H,H) = 7$ Hz, 4 H, N-CH_2-CH_2-] ppm. HRMS (FAB): calcd. for $C_{18}H_{24}N_4$: 296.2001; found: 296.1988.

***N,N′,N′′,N′′′*-Tetramethyl-1,5,12,16-tetraaza[5.5]paracyclophane (1c):** Sodium borohydride (408 mg, 10.8 mmol) and **1b** (223 mg, 0.752 mmol) were suspended in THF (10 mL), and the mixture was added to a cold solution of 3 $mol \cdot dm^{-3}$ H_2SO_4 (1.22 mL) and 37% formalin (0.75 mL). The THF layer was separated and the aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined extracts were dried with potassium carbonate. After evaporation of the solvent, the residual material was passed through an alumina column with dichloromethane as the eluent to yield **1c** (105 mg, 40%) as a pale yellow powder. M.p. 148−150 °C. ^1H NMR ($CDCl_3$): $\delta = 6.53$ (s, 8 H, Ar-H), 3.22 [t, $^3J(H,H) = 7$ Hz, 8 H, N-CH_2-], 2.81 (s, 12 H, N-CH_3), 1.49 [quint, $^3J(H,H) = 7$ Hz, 4 H, N-CH_2-CH_2-] ppm. EI-MS: $m/z = 352$ [M^+]. $C_{22}H_{32}N_4$: calcd. C 74.96, H 9.15, N 15.89; found C 74.74, H 9.00, N 15.58.

***N,N′,N",N′′′*-Tetratosyl-1,7,14,20-tetraaza[7.7]paracyclophane (2a):** Compound **2a** was prepared similarly to compound **1a**. Recrystallization of the crude material from a dichloromethane/benzene mixture afforded fine pale brown crystals (56%). M.p. 312.3−313.6 °C (ref.[6], 311 °C, corrected). ^1H NMR ($CDCl_3$): $\delta =$

7.28, 7.44 [ABq, ^3J(H,H) = 8 Hz, 16 H, Ts-Ar-H], 6.84 (s, 8 H, Ar-H), 3.41 [t, ^3J(H,H) = 7 Hz, 8 H, N-CH$_2$-], 2.45 (s, 12 H, Ts-CH$_3$), 1.25 (m, 8 H, N-CH$_2$-C*H*$_2$-CH$_2$-), 1.01 (m, 4 H, N-CH$_2$-CH$_2$-C*H*$_2$-) ppm. FAB-MS: m/z = 968.3 [M$^+$].

1,7,14,20-Tetraaza[7.7]paracyclophane (2b): Compound **2b** was prepared similarly to compound **1b** as brown crystals in 47% yield. This material was used in the subsequent methylation reaction without further purification. M.p. 174.6−176.3 °C (ref.[6], 178.5 °C, corrected). ^{1}H NMR (CDCl$_3$): δ = 6.44 (s, 8 H, Ar-H), 3.06 [t, ^3J(H,H) = 7 Hz, 8 H, N-CH$_2$-], 1.57 [quint, ^3J(H,H) = 7 Hz, 8 H, N-CH$_2$-C*H*$_2$-CH$_2$-], 1.45 (m, 4 H, N-CH$_2$-CH$_2$-C*H*$_2$-) ppm. HRMS (FAB): calcd. for $C_{22}H_{32}N_4$: 352.2627; found 352.2627.

***N,N′,N′′,N′′′*-Tetramethyl-1,7,14,20-tetraaza[7.7]paracyclophane (2c):** A solution of **2b** (760 mg, 2.16 mmol), HCOOH (90%, 3 mL, 70.4 mmol), and aq. HCHO (37%, 3 mL, 39.9 mmol) was heated at 100 °C with stirring for 2 h. After adding concd. HCl (0.5 mL), the solution was concentrated to dryness by heating. To the resultant mixture was added an excess of aq. K_2CO_3 and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined extracts were dried with K_2CO_3 and the solvent evaporated. Recrystallization of the resultant material from a methanol/dichloromethane mixture gave **2c** as a white powder (419 mg, 48%). M.p. 136−138 °C. ^{1}H NMR (CDCl$_3$): δ = 6.72 (s, 8 H, Ar-H), 3.17 [t, ^3J(H,H) = 7 Hz, 8 H, N-CH$_2$-], 2.80 (s, 12 H, N-CH$_3$), 1.62 [quint, ^3J(H,H) = 7 Hz, 8 H, N-CH$_2$-C*H*$_2$-CH$_2$-], 1.46 [quint, ^3J(H,H) = 7 Hz, 4 H, N-CH$_2$-CH$_2$-C*H*$_2$-] ppm. EI-MS: m/z = 408 [M$^+$]. $C_{26}H_{40}N_4$: calcd. C 76.42, H 9.87, N 13.71; found C, 76.43, H 9.83, N 13.58.

CT Complexes with 1,3,5-Trinitrobenzene: An excess of a solution of 1,3,5-trinitrobenzene in benzene was added to a solution of the cyclophane in benzene. Heptane was added to the resultant deep-blue solution which was then concentrated. The dark blue crystals were collected and recrystallized from benzene/heptane.

1c·TNB: M.p. 119−120 °C (dec). ^{1}H NMR (CDCl$_3$): δ = 9.39 (s, 3 H, Ar-H), 6.53 (s, 8 H, Ar-H), 3.23 [t, ^3J(H,H) = 7 Hz, 8 H, N-CH$_2$-], 2.81 (s, 12 H, N-CH$_3$), 1.50 (m, 4 H, N-CH$_2$-C*H*$_2$-CH$_2$-) ppm. $C_{28}H_{35}N_7O_6$: calcd. C 59.46, H 6.24, N 17.33; found C 59.43, H 6.22, N 17.32.

2c·2TNB: M.p. 166−166.1 °C (dec). ^{1}H NMR (CDCl$_3$): δ = 9.38 (s, 6 H, Ar-H), 6.71 (s, 8 H, Ar-H), 3.17 [t, ^3J(H,H) = 7 Hz, 8 H, N-CH$_2$-], 2.80 (s, 12 H, N-CH$_3$), 1.62 [quint, ^3J(H,H) = 7 Hz, 8 H, N-CH$_2$-C*H*$_2$-], 1.46 [quint, ^3J(H,H) = 7 Hz, 4 H, N-CH$_2$-CH$_2$-C*H*$_2$-] ppm. $C_{38}H_{46}N_{10}O_{12}$: calcd. C 54.67, H 5.55, N 16.78; found C 54.88, H 5.54, N 16.70.

Supporting Information: *x,y,z* files of the Conflex-optimized structures of **1c**, **1c**$^{2+}$ (diradical form), and **2c**. Predicted UV/Vis spectra of **1c** and **1c**$^{2+}$ by ZINDO along with the experimental UV/Vis spectra of **1c** and **1c**$^{2+}$ in CH$_3$CN (see also the footnote on the first page of this article).

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