N-Methyl-Substituted Aza[1$_n$]metacyclophane: Preparation, Structure, and Properties

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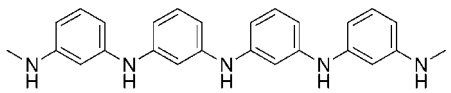
A series of aza[1$_n$]metacyclophanes (n = 3−8), which correspond to the cyclic oligomers of poly(*m*-aniline), are obtained in one step by a Pd(0)-catalyzed amination reaction of 3-bromo-*N*-methylaniline. The most stable conformations of the cyclic trimer and tetramer are determined by density functional calculations. The theoretical results show that these new macrocyclic compounds can be regarded as precursors for cyclophane-based high-spin molecules. Moreover, we describe their spectroscopic and electrochemical properties in connection with the ring size of these cyclic oligomers.

Introduction

The chemistry of high-spin organic molecules is a topical area in connection with the exploitation of organic ferromagnets.[1] The fundamental problems of creating organic ferromagnets are first that of selecting a spin-bearing molecule (or a radical center) and second that of developing strong ferromagnetic interaction between the molecules. As is well-known, chemically and thermally stable polyradicals often contain heteroatoms that serve as spin-bearing sites,[2] and they are connected to each other by *m*-phenylene units which have proven effective ferromagnetic couplers.[1] Hence, we are interested in macrocyclic oligomers of poly(*m*-aniline) **1** because of the



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fascinating possibilities that the oxidized species of these compounds show high-spin ground states.[3] Furthermore, a "closed loop" arrangement of multispin systems guarantees the robust ferromagnetically coupled spin alignment.[1f] In fact, Rajca and co-workers have demonstrated that calix[4]arene-based polyradicals are viable building blocks for high-spin polyradicals.[4]

On the other hand, a molecule composed of two building blocks, an aromatic ring and an aliphatic unit forming a bridge between two or more positions of the aromatic ring, is known as cyclophane.[5] Many kinds of cyclophanes have been synthesized for the purpose of investigation of the peculiar electronic and spectroscopic properties due to the interesting stereochemistry and, moreover, the effective binding properties as host molecules in molecular recognition chemistry.[5] In particular, calixarenes **2**, one of the [1$_n$]metacyclophanes, are ideal starting materials for preparation of various types of host molecules.[6] Although carbon is the common bridging element in useful macrocyclic compounds such as porphyrins and calixarenes, other elements such as silicon, nitrogen, phosphorus, oxygen, sulfur, and so forth can be new bridging elements to give additional chemical and physical properties. Indeed, over the past few years, a considerable number of studies have been made on the syntheses of various heteroatom-bridged [1$_n$]cyclophanes.[7]

Preparation of the aza-bridged macrocyclic oligomers, however, is definitely in need of efficient synthetic methods to form carbon−nitrogen bonds. Recently, two research groups have reported a simple catalytic method for the conversion of aryl bromides to arylamines,[8] superseding the laborious Ullmann coupling reaction.

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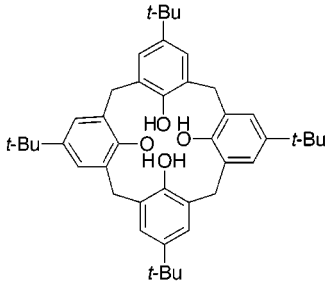

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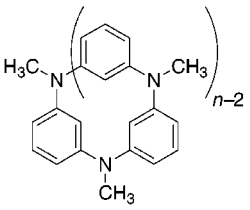


3–8 (n = 3–8)

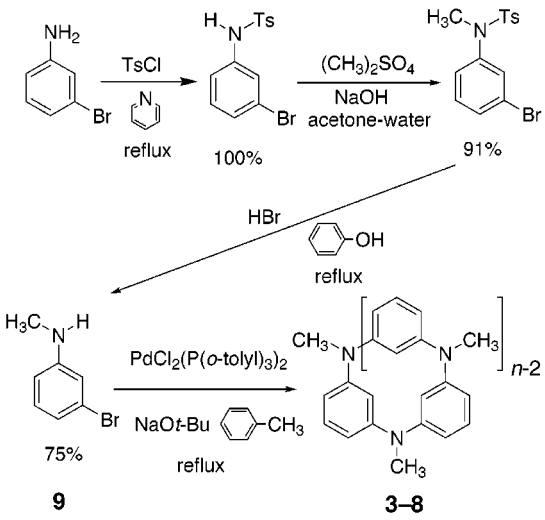
Since then, several complicated oligo- and polyarylamine compounds have been successfully prepared on the basis of this method.[9] We have applied this method to the preparation of aza-bridged [1$_n$]metacyclophanes simply using bromo-substituted *N*-methylanilines as a starting material. This attempt gave an affirmative result, and preliminarily, we have already reported on the major product **4** with its X-ray structure.[10] In the present paper, we describe a series of *N*-methyl-substituted aza[1$_n$]-metacyclophanes **3**−**8** having the prototypical macrocyclic structure of azacalix[*n*]arene. Furthermore, we performed quantum chemical calculations of the *N*-unsubstituted model compounds of **3** and **4** using density functional theory (DFT). In addition, spectroscopic and electrochemical properties of the compounds **3**−**8** are also described in connection with the ring size of the macrocycles.

Results and Discussion

Synthesis of Aza[1$_n$]metacyclophanes 3−8. *N*-Methyl-substituted aza[1$_n$]metacyclophane was synthesized by Pd(0)-catalyzed amination reaction of 3-bromo-*N*-methylaniline (**9**) in toluene (ca. 0.2 M), by following the procedure shown in Scheme 1. As shown in our previous report,[10] this reaction afforded **4** as a white solid in moderate yield (12.9%). It is interesting to note that the main product is cyclic tetramer **4**, taking two points into consideration: (i) in the preparation of some cyclic oligoarenes including calix[*n*]arene, the tetramer tends to be selectively prepared, and (ii) according to the reaction mechanism proposed by two research groups,[8] the reaction proceeds via formation of an intermediate Pd^{II} complex coordinated with both ends of a linear oligoaniline in the last stage of the cyclization reaction. Note that the conversion of *N*-methylaniline into the *N*-methyldiarylamines cannot proceed by the Ullmann coupling reaction, probably owing to poisoning of the Cu catalyst by *N*-methylaniline.

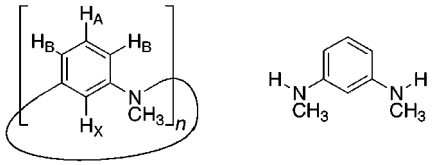
On the other hand, the GC−MS study showed that a fraction (R_f = 0.45 [*n*-hexane:CH_2Cl_2 = 1:1]) other than the fraction containing **4** (R_f = 0.65 [*n*-hexane:CH_2Cl_2 = 1:1]) contains a mixture of the azametacyclophanes **3**−**8**.

Scheme 1



9 **3–8**

Chart 1



3–8 **DMPD**

Table 1. ^{1}H NMR Chemical Shifts (δ, ppm) of Intraannular (H_X) and Extraannular (H_A and H_B) Aromatic Protons of 3−8 and DMPD in $CDCl_3$ at 298 K

	δ		
compd	H_X	H_A	H_B
3	7.10	7.12	6.67
4	6.41	7.26	6.54
5	6.61	7.15	6.58
6	6.63	7.12	6.57
7	6.61	7.11	6.55
8	6.63	7.09	6.56
DMPD	5.79	6.97	5.98

Accordingly, medium-pressure liquid chromatography (MPLC) was carried out using silica gel for isolation of the macrocycles with different sizes (eluent: EtOAc−Et_2O (4:1)). The exact molecular masses of compounds **3** and **5**−**8** were determined by high-resolution mass spectrometry, confirming their molecular formulas as $(C_7H_7N)_n$ (n = 3 and 5−8). The isolated yields of the corresponding macrocycles **3**−**8** (with the exception of **4**) were 1.6, 5.6, 2.0, 3.3, and 1.3%, respectively. It should be noted that conformation isomers are not found for the trimer **3** in contrast to the case of the methylene-bridged [1.1.1]metacyclophane.[4b]

In contrast to the *N*-methyl-substituted aza[1$_n$]metacyclophanes, we did not succeed in preparation of *N*-unsubstituted ones despite many optimization experiments (variation of related ligands and bases).

^{1}H NMR Spectroscopy. The ^{1}H NMR spectroscopic analysis supports the metacyclophane structure of compounds **3**−**8**. The aromatic AB_2X system gives rise to two triplets and a doublet of doublets. The remaining singlet is assigned to *N*-methyl protons. Table 1 lists the ^{1}H NMR chemical shifts of the intraannular (H_X) and extraannular (H_A, H_B) aromatic protons for **3**−**8**. For comparison, the data of *N*,*N*′-dimethyl-1,3-phenylenediamine (DMPD) (Chart 1) are also added. The signal of

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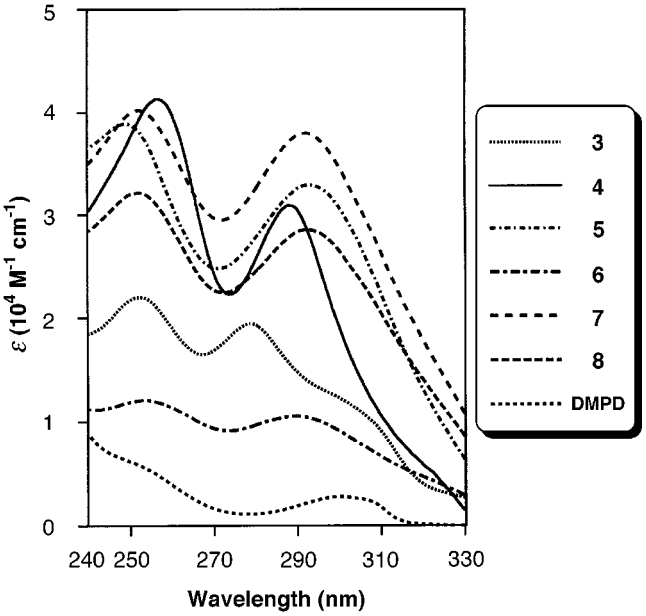

Figure 1. UV−vis spectra of **3**−**8** and DMPD in cyclohexane at 298 K.

Table 2. UV−Vis Spectral Data[a] of 3−8

compd	λ_{max} (nm)	log ϵ (M^{-1} cm^{-1})
3	279, 252	4.29, 4.34
4	288, 257	4.49, 4.62
5	293, 249	4.52, 4.59
6	290, 254	4.02, 4.08
7	292, 252	4.58, 4.60
8	293, 252	4.46, 4.51

[a] Recorded in cyclohexane at 298 K.

H_X for cyclic trimer **3** shows the strongest low-field shift of those of **3**−**8**. The deshielding effect of **3** is probably attributed to the influence of the diamagnetic ring current of the two adjacent benzene rings due to the highly intraannular strain. Macrocycles with ring sizes other than three or four show a similar chemical shift. On the other hand, the intraannular proton signal of **4** is shifted to a weak higher field as compared to those of **5**−**8**. These results suggest that there is no intraannular strain in the larger cyclic oligomers **5**−**8**. In the ^{13}C NMR spectra of **3**−**8**, no noticeable difference is found. As a whole, the simple ^1H and ^{13}C NMR spectra of **3**−**8** indicate conformational mobility at room temperature in solution.

UV−Vis Spectroscopy. As shown in Figure 1, the UV−vis spectra of the macrocycles **3**−**8** in cyclohexane at 298 K have essentially the same features, showing two bands at around 250 and 290 nm. For comparison, the spectrum of DMPD is also added. The observed absorption wavelengths (λ_{max}) and molar absorption coefficients (ϵ) are summarized in Table 2. In the present macrocyclic oligomers, it is seen that the longest absorption wavelength increases with increasing ring size of oligomers up to the pentamer **5**, and there is no more shift in going from **6** to **8**. This means that a certain limitation on extensive conjugation occurs at around the pentamer **5**.

Electrochemical Properties. The first oxidation potentials (E_1^{ox}) of **3**−**8** were determined by cyclic voltammetry in CH_2Cl_2 with *n*-Bu_4NClO_4 as the electrolyte. These are shown in Table 3. All the compounds exhibited an irreversible oxidation which typically results from an unstable radical cation undergoing a chemical reaction before it is oxidized into the polycationic states. As will be described in the next section, this may be rationalized in terms of an immediate benzidine formation reaction. Moreover, the E_1^{ox} value decreases with increasing ring size of oligomers up to the pentamer **5**, and finally, the value levels off in **6** (ca. 0.62 V vs SCE). This result is similar to the behavior of UV−vis spectra for **3**−**8**, indicating that effective conjugation length reaches the upper limit around the hexamer **6**.

Table 3. Cyclic Voltammetric First Oxidative Peak Potentials[a] for 3−8

compd	E_1^{ox} (V vs SCE[b])	compd	E_1^{ox} (V vs SCE[b])
3	+0.81	**6**	+0.62
4	+0.79	**7**	+0.62
5	+0.72	**8**	+0.63

[a] Conditions: 0.1 M *n*-Bu_4NClO_4 in CH_2Cl_2, potential vs Fc/Fc^+, Pt electrode, 298 K, scan rate 100 mV s^{-1}. [b] Potentials were converted to SCE using the following equation: $E_{SCE} = E_{obsd}(Fc/Fc^+) + 0.48$.

Theoretical Consideration. The molecular structures for the *N*-unsubstituted model compounds of **3** and **4** were optimized using the density functional theory (DFT).[11] Becke's 1988 gradient-corrected exchange functional[12] together with Perdew and Wang's 1991 gradient-corrected correlation functional[13] was employed in the gradient-corrected DFT calculations. All the calculations were performed by using the 6-31G* split-valence plus polarization basis set.[14] The optimized structures are shown in Figure 2. The model compound of **3** (Figure 2a) takes a partial cone (two benzene rings are oriented in one direction and the remainder in another direction) conformation with C_s symmetry. As shown in Figure 3a, the optimized cone conformer (all the benzene rings are oriented in the same direction) with C_{3v} symmetry lies 10.2 kcal/mol above the partial cone conformer. Furthermore, a planar conformer with D_{3h} symmetry lies 57.9 kcal/mol above the partial cone conformer. It is interesting to note that the distance between the intraannular protons pointing the same direction (1.78 Å) is within the sum of van der Waals radii for the hydrogen atom (2.40 Å).[15] This suggests that the most favorable conformation of **3** is determined to minimize the intraannular proton−proton repulsive interaction.[16] On the other hand, the model compound of **4** adopts a 1,3-alternate conformation (adjacent benzene rings are oriented in the opposite directions) with S_4 symmetry (Figure 2b), and the optimized geometry is in quite good agreement with a reported X-ray structure[10] of **4**, except for the small values of the calculated dihedral angles between adjacent benzene rings. This is probably ascribed to removal of *N*-methyl groups in the model calculations. As shown in

(11) All the calculations were performed with the Gaussian 94 suite of programs: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, P. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision E.2; Gaussian, Inc.: Pittsburgh, PA, 1995.

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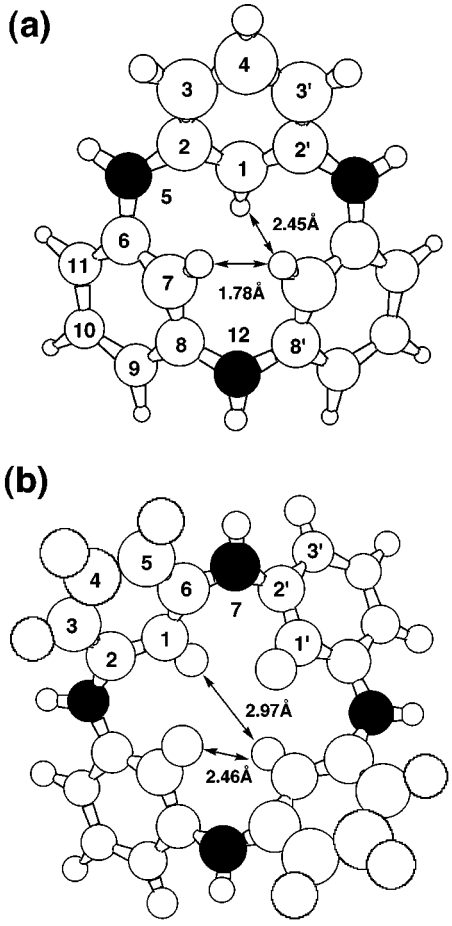


Figure 2. BPW91/6-31G* optimized structures of the model compounds (a) **3** and (b) **4**. The plane defined by the nitrogen atoms (shown in black) is parallel to the plane of the page. Selected dihedral angles (deg): (a) C1−C2−N5−C6 22.5, C2−N5−C6−C7 32.4, C7−C8−N12−C8′ 58.1; (b) C1−C6−N7−C2′ −10.8, C6−N7−C2′−C1′ −43.3.

Figure 3b, the optimized 1,2-alternate conformer with C_s symmetry and cone conformer with C_{4v} symmetry lie 7.3 and 31.0 kcal/mol above the 1,3-alternate conformer, respectively.

Since **3** is expected to be the most strained one of cyclic oligomers **3**−**8**, we estimated the strain using the isodesmic reactions for the model compounds of **3** and **4**, as shown in Scheme 2.[17] From this analysis, we obtained the stabilization energies by macrocyclization of 1.7 and 8.0 kcal/mol per aniline unit for the model compounds **3** and **4**, respectively. A decrease of this value in **3** clearly shows an increase of the strain energy on going from **4** to **3**. Hence, **3** can be considered as highly strained.

Here we calculated the ^{1}H NMR chemical shifts within the gauge-independent atomic orbital (GIAO) approach[18]

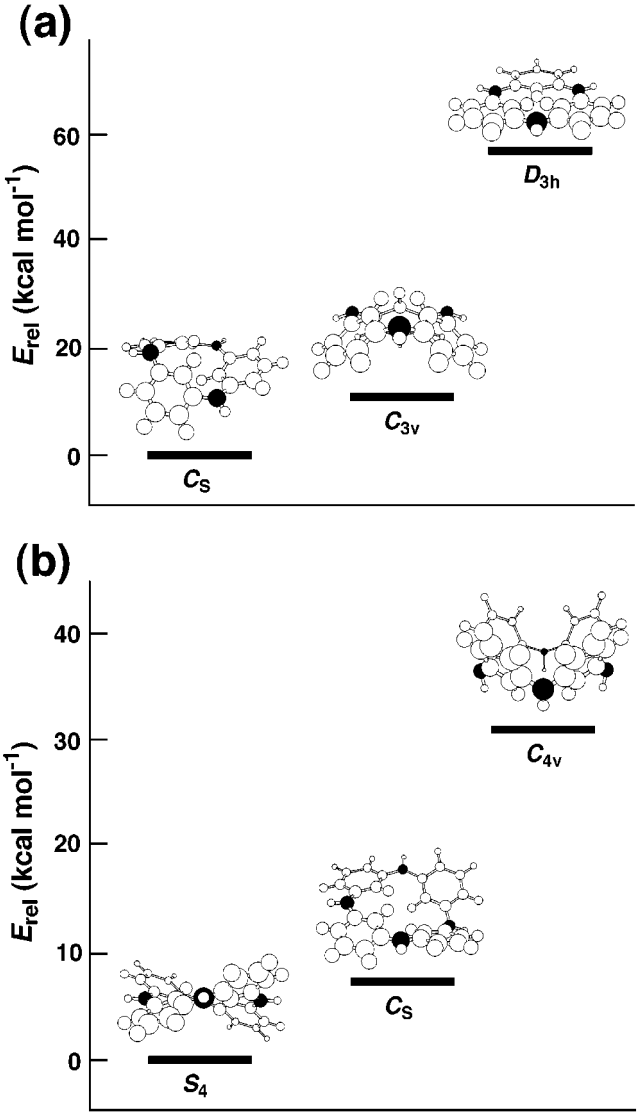
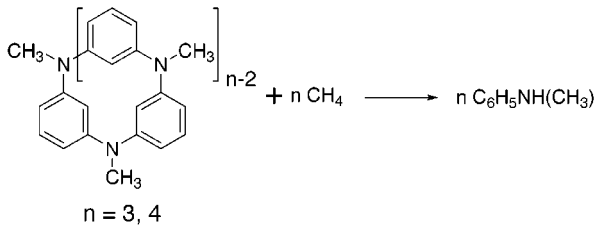


Figure 3. Schematic diagrams of relative energies among some conformers of (a) **3** and (b) **4**.

Scheme 2



using the B3LYP/6-31G* optimized structures. As can be seen in Table 4, the calculated chemical shifts for the extraannular protons are in good agreement with the experimental values. However, the shift for the intraannular proton does not change on going from **3** to **4**. This is partly because the calculated dihedral angles between adjacent benzene rings are slightly small compared with those of the X-ray structure. Moreover, it seems probable that **4** adopts the more distorted conformation in solution than in the solid state to avoid the short proton−proton contact. The calculated chemical shift of 9.2 for intraan-

(16) Unfortunately, only disordered crystals of **3** have been grown, and to date, we have failed to refine the molecular structure completely even by a low-temperature measurement. Benzene rings are orientationally disordered upward and downward to the plane defined by three nitrogen atoms. Hence, the conformation of **3** is hardly determined. Only two [1.1.1]metacyclophanes have been determined to adopt the partial cone conformation by X-ray analysis: (a) Sergeev, V. A.; Ovchinnikov, Yu. É.; Nedel'kin, V. I.; Astankov, A. V.; Andrianova, O. B.; Shklover, V. E.; Zamaev, I. A.; Struchkov, Yu. T. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1998**, *37*, 1440. (b) Yoshida, M.; Goto, M.; Nakanishi, F. *Organometallics* **1999**, *18*, 1465.

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Table 4. Calculated ^{1}H NMR Chemical Shifts (δ, ppm)[b] of Intraannular (H_X) and Extraannular (H_A and H_B) Aromatic Protons of Model Compounds 3 and 4

		δ		
	method	H_X	H_A	H_B
3 (C_s)[a]				
	GIAO/HF/6-311G**	7.31[c]	7.40[c]	6.57[c]
	GIAO/HF/6-311+G**	7.55[c]	7.48[c]	6.59[c]
3 (D_{3h})[a]				
	GIAO/HF/6-311G**	9.19	7.59	6.59
	GIAO/HF/6-311+G**	9.27	7.59	6.58
4 (S_4)[a]				
	GIAO/HF/6-311G**	7.45	7.55	6.32[c]
	GIAO/HF/6-311+G**	7.65	7.62	6.39[c]

[a] Optimized at the BPW91/6-31G* level. [b] The magnetic shielding of tetramethylsilane (TMS) as a standard was computed at the same level of theory to calibrate the isotropic chemical shifts (δ). [c] The protons corresponding to each chemical shift are classified into chemically different groups owing to the molecular symmetry utilized in the calculation. However, the classified protons should have the same time-averaged chemical environment and therefore the same chemical shifts in the actual NMR spectrum. Hence, the calculated chemical shifts are averaged for comparison with the experimental values.

nular proton in the planar conformer (D_{3h}) of **3** suggests that the closer the adjacent intraannular protons are, the more downfield the signal for their protons shifts.

To better understand the irreversible redox properties of **3**−**8**, the monocationic state of the model compound **4** was computed at the BPW91/6-31G*//BPW91/6-31G* level. The optimized structure retains the 1,3-alternate conformation with S_4 symmetry, similar to the most favorable one in the neutral state. The calculated Mulliken spin density distributions indicate that the highest spin density (+0.13) resides on the extraannular ortho carbon atoms to the amino groups. This finding strongly suggests that the benzidine formation reaction takes place at the ortho position in the oxidation of the macrocycles such as **3**−**8**. In fact, it is known that introduction of protecting substituent groups onto the 4- and 6-positions of the *m*-phenylene moiety brings a reversible redox behavior to *N*,*N*,*N*′,*N*′-tetraphenyl-*m*-phenylenediamine in contrast with an irreversible behavior of the unsubstituted one.[19] Therefore, it can be rationalized that the macrocycles **3**−**8** show the irreversible oxidation potential.

Cyclic oligo(*m*-aniline)s such as **3**−**8** are classified as coextensive non-Kekulé molecules if they have a planar structure. The coextensive non-Kekulé molecules have quasi-degenerate nonbonding molecular orbitals (NBMOs) which are mutually orthogonal but overlap in their spatial distributions. Hence, when these MOs are singly occupied by electron spins, strong exchange interaction is expected and the energies of the high-spin states of these molecules lie well below those of the corresponding low-spin states. The mechanism of spin alignment is essentially the same as that of Hund's rule in atomic systems.[20] In **3**−**8**, the molecular structures are highly deviated from the planar structure, and therefore, the MOs can be altered by their distortion. However, the situation remains unchanged at least for the optimized structures of model compounds **3** and **4**, indicating that

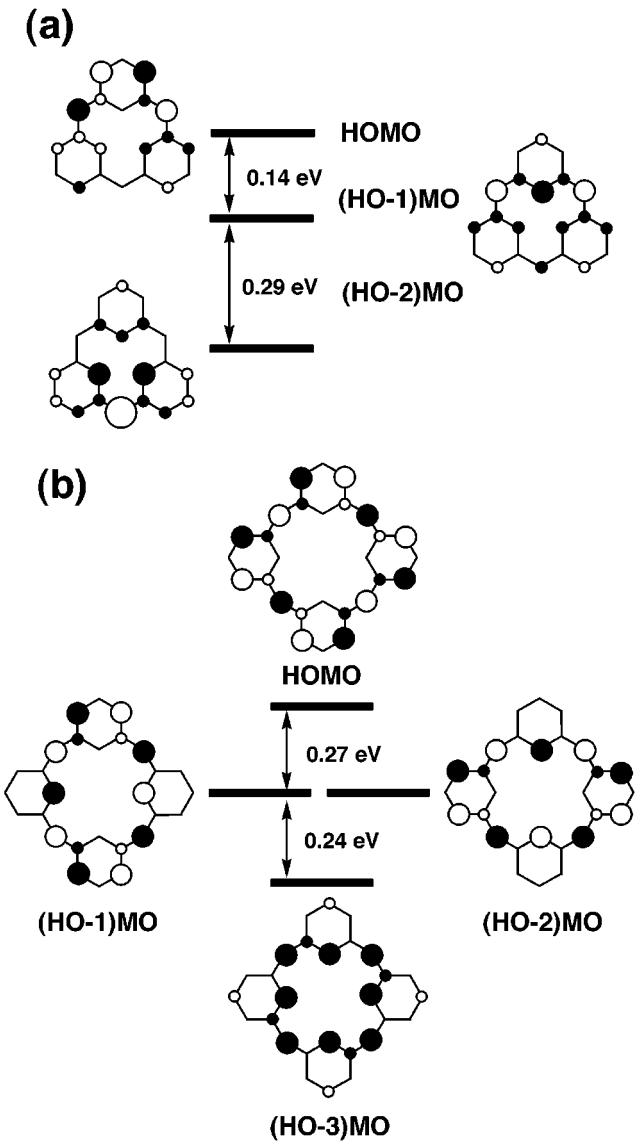

Figure 4. Relative energy levels of the frontier Kohn−Sham (KS) orbitals for the model compounds **3** and **4** on the basis of BPW91/6-31G* calculations. The schematic KS orbitals are depicted after the expansion of the nonplanar structure onto the plane of the page.

they still have coextensive non-Kekulé electronic structures, as shown in Figure 4. As a result, the tetracationic state of **4** (tricationic state for **3**) has the possibility of being a high-spin molecule with a quintet (quartet for **3**) ground state.

Conclusion

In the present study, we accomplished the preparation of the aza-bridged [1$_n$]metacyclophanes **3**−**8** with use of a Pd(0)-catalyzed amination reaction under pseudo-high-dilution conditions in moderate yields and found that their spectral and electrochemical properties change with increasing ring size (or decreasing intraannular strain) up to around cyclic pentamer **5**. In particular, it seems that the cyclic trimer **3** has the most strained structure in the reported [1$_3$]cyclophanes to the best of our knowledge. From the DFT calculations, the present macrocycles can be considered as a coextensive non-Kekulé molecular system, which leads to realization of high-spin

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molecules, despite having nonplanar molecular structures. Although **3**−**8** showed irreversible oxidation behaviors, it is anticipated that the introduction of suitable substitutents onto the extraannular ortho positions to the amino groups enables us to generate polycationic high-spin states of these macrocycles.[21] Preparation of derivatives of this type is the subject of our future investigation.

Experimental Section

General Procedures. Commercial grade reagents were used without further purification. Toluene and CH_2Cl_2 were refluxed over and then distilled from calcium hydride under argon before use. Elemental analyses were performed by the Microanalytical Center, Kyoto University.

***N*-Methyl-3-bromoaniline (9)** was prepared by the modified method of Willstätter and Pfannenstiel[22] from 3-bromoaniline via tosyl amide and methylation with dimethyl sulfate, followed by hydrolysis of the resulting *N*-methyl tosyl amide by the method of Snyder and Heckert.[23] A mixture of 3-bromoaniline (25.0 g, 0.145 mol) and tosyl chloride (27.7 g, 0.145 mol) in pyridine (70 mL) was heated with stirring under reflux for 20 min. After cooling, the reaction mixture was added to 120 mL of ice-cold water. The white precipitate was filtered and washed thoroughly with water; the crude tosylated product was quantitatively obtained and used without further purification. Next, to a solution of the tosyl amide (15.5 g, 0.048 mol) and NaOH (3.3 g, 0.083 mol) in acetone−water (2:1) was added dimethyl sulfate (9.9 g, 0.078 mol) dropwise with stirring. After 2 h of stirring, the brown organic layer was separated, washed with water, and dried over $MgSO_4$. After evaporation of the solvent, the crude *N*-methylated product was obtained quantitatively as a pale yellow solid. Finally, a mixture of *N*-methyl tosyl amide (14.2 g, 0.042 mol) and phenol (14 g, mol) in 48% HBr (70 mL) was heated under reflux with stirring for 1 h. After cooling, the reaction mixture was washed with Et_2O. To the aqueous layer was added NaOH aqueous solution to alkaline. Liberated amine was taken up with Et_2O. The organic layer was dried over $MgSO_4$. Evaporation of the solvent afforded **9** (7.1 g, 91%) as a pale brown liquid: ^{1}H NMR ($CDCl_3$, 270 MHz) δ (ppm) 2.77 (s, 3H), 3.78 (br s, 1H) 6.46−6.50 (m, 1H), 6.70 (t, J = 2.2 Hz, 1H), 6.77−6.81 (m, 1H), 7.00 (t, J = 8.1 Hz, 1H). Anal. Calcd for C_7H_8NBr: C, 45.19; H, 4.33; N, 7.53; Br, 42.95. Found: C, 45.13; H, 4.26; N, 7.53; Br, 43.04.

Condensation Reaction of *N*-Methyl-3-bromoaniline. A mixture of 3-bromo-*N*-methylaniline (2.0 g, 11 mmol), $NaOBu^t$ (1.4 g, 15 mmol), and [$PdCl_2$(P(*o*-tolyl)$_3$)$_2$] (0.17 g, 0.22 mmol) in toluene (90 mL) was heated under Ar atmosphere at 100 °C for 19 h, following the reported procedure.[24] After the usual workup, the crude product was chromatographed on SiO_2 (*n*-hexane:CH_2Cl_2 = 1:1 as eluent). A fraction (R_f = 0.65) afforded **4** as a white solid. Another fraction (R_f = 0.45) was purified by MPLC on SiO_2 (*n*-hexane:ether = 4:1 as eluent). **3** (R_f = 0.50), **5** (0.40), **6** (0.35), **7** (0.30), and **8** (0.20) were isolated as white solids.

Data for Triaza[1$_3$]metacyclophane (3): mp 130−131 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ (ppm) 3.30 (s, 9H), 6.67 (dd, J = 8.1, 2.2 Hz, 6H), 7.10 (t, J = 2.2 Hz, 3H), 7.12 (t, J = 8.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ (ppm) 37.0, 112.0, 117.6, 129.1, 150.6; IR (KBr, cm^{-1}) 685, 778, 868 (1,3-disubstituted benzene); UV−vis (cyclohexane) λ_{max} (log ϵ) 252 (4.34), 279 (4.29); EI HRMS m/z (M^+) calcd for $C_{21}H_{21}N_3$ 315.1735, found 315.1731.

Data for Tetraaza[1$_4$]metacyclophane (4): mp 280 °C dec; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 3.20 (s, 12H), 6.42 (t, J = 2.4 Hz, 4H), 6.55 (dd, J = 8.3, 2.4 Hz, 8H), 7.27 (t, J = 8.3 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100.5 MHz) δ (ppm) 40.2, 112.4, 113.8, 130.7, 149.4; IR (KBr, cm^{-1}) 701, 775, 846 (1,3-disubstituted benzene); UV−vis (cyclohexane) λ_{max} (log ϵ) 257 (4.62), 288 (4.49); FAB HRMS m/z (M^+) calcd for $C_{28}H_{28}N_4$ 420.2314, found 420.2313.

Data for Pentaaza[1$_5$]metacyclophane (5): mp 65−66 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 3.19 (s, 15H), 6.58 (dd, J = 7.8, 2.0 Hz, 10H), 6.61 (t, J = 2.0 Hz, 5H), 7.15 (t, J = 7.8 Hz, 5H); ^{13}C NMR ($CDCl_3$, 100.5 MHz) δ (ppm) 40.0, 113.2, 113.4, 129.7, 149.7; IR (KBr, cm^{-1}) 705, 783, 879 (1,3-disubstituted benzene); UV−vis (cyclohexane) λ_{max} (log ϵ) 249 (4.59), 293 (4.52); EI HRMS m/z (M^+) calcd for $C_{35}H_{35}N_5$ 525.2892, found 525.2885.

Data for Hexaaza[1$_6$]metacyclophane (6): mp 280 °C dec; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 3.21 (s, 18H), 6.57 (dd, J = 8.1, 2.2 Hz, 12H), 6.63 (t, J = 2.2 Hz, 6H), 7.12 (t, J = 8.1 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100.5 MHz) δ (ppm) 40.2, 112.9, 113.0, 129.7, 149.5; IR (KBr, cm^{-1}) 700, 762, 867 (1,3-disubstituted benzene); UV−vis (cyclohexane) λ_{max} (log ϵ) 254 (4.08), 290 (4.02); EI HRMS m/z (M^+) calcd for $C_{42}H_{42}N_6$ 630.3471, found 630.3495.

Data for Heptaaza[1$_7$]metacyclophane (7): mp 104−105 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ (ppm) 3.17 (s, 21H), 6.55 (dd, J = 7.8, 2.4 Hz, 14H), 6.61 (t, J = 2.4 Hz, 7H), 7.11 (t, J = 7.8 Hz, 7H); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ (ppm) 40.2, 112.9, 113.4, 129.7, 149.7; IR (KBr, cm^{-1}) 702, 776, 885 (1,3-disubstituted benzene); UV−vis (cyclohexane) λ_{max} (log ϵ) 252 (4.60), 292 (4.58); EI HRMS m/z (M^+) calcd for $C_{49}H_{49}N_7$ 735.4049, found 735.4075.

Data for Octaaza[1$_8$]metacyclophane (8): mp 221−222 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ (ppm) 3.18 (s, 24H), 6.56 (dd, J = 7.8, 2.0 Hz, 16H), 6.63 (t, J = 2.0 Hz, 8H), 7.09 (t, J = 7.8 Hz, 8H); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ (ppm) 40.2, 112.8, 113.4, 129.6, 149.7; IR (KBr, cm^{-1}) 702, 778, 884 (1,3-disubstituted benzene); UV−vis (cyclohexane) λ_{max} (log ϵ) 252 (4.51), 293 (4.46); EI HRMS m/z (M^+) calcd for $C_{56}H_{56}N_8$ 840.4628, found 840.4628.

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Supporting Information Available: Supporting Information Available: Optimized BPW91/6-31G* geometries of the model compounds **3** and **4**, and the Mulliken spin densities of the model compound **4**$^+$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) A reviewer has remarked that replacement of the *N*-methyl group by the other one without hydrogens improves the irreversible redox behavior of the present system. This may be another way to realize the high-spin azacyclophanes.

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