Cyclophanes

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Preparation and Characterization of *N*-Anisyl-Substituted Hexaaza[1$_6$]paracyclophane**

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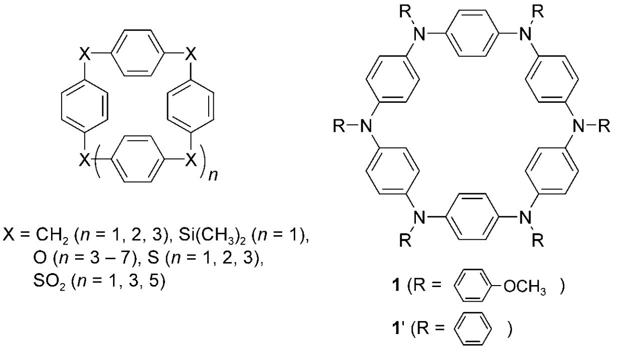
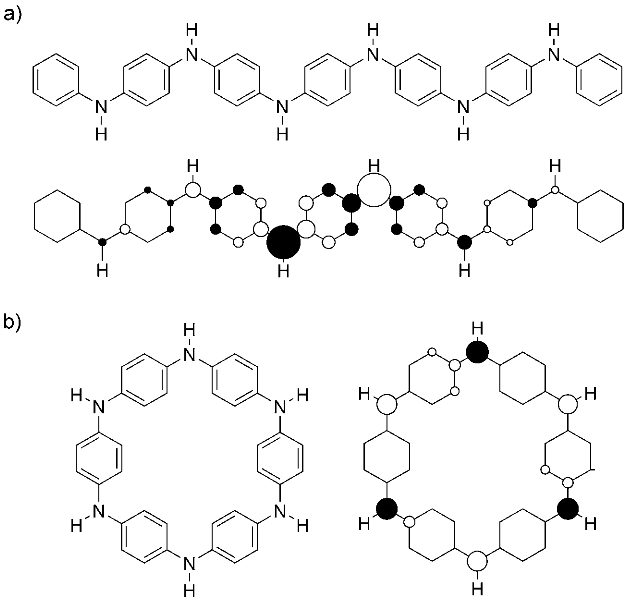
As opposed to the thoroughly studied carbon-bridged calixarenes,[1] heteroatom-bridged [1$_n$]metacyclophanes and their derivatives have recently attracted much attention mainly because of novel structure-property relationships originating from the replacement of methylene bridges with heteroatom bridges.[2] On the other hand, only a few reports are known for [1$_n$]paracyclophanes, probably as a result of the difficulty in synthesizing them (Scheme 1).[3,4]



Scheme 1. Reported heteroatom-bridged [1$_n$]paracyclophanes and hexaaza[1$_6$]paracyclophane **1** and **1′**.



Scheme 2. Schematic views of HOMOs of a) linear and b) cyclic hexamers of polyaniline.

Aza[1$_n$]paracyclophanes can be viewed as macrocyclic oligomers of polyaniline, which is one of the well-known organic conducting polymers.[5] As is apparent from the simple Hückel MO calculations, the HOMOs for linear and cyclic oligoanilines assume different aspects, as exemplified in Scheme 2. As for the linear hexamer, the large MO coefficients are concentrated on the central *para*-phenylenediamine (PD) moiety. Owing to the localized HOMO character, the ESR studies on the radical cations of linear oligoanilines showed that the spin was confined to the central PD moiety, and therefore, spin delocalization took place only to a small extent.[6] In contrast, the HOMO coefficients of the cyclic hexamer is mainly distributed equally on six nitrogen nuclei. In fact, according to the DFT calculations, the HOMO coefficients of all-*N*-phenyl-substituted hexaaza[1$_6$]paracyclophane (**1′**) is delocalized over the macrocyclic molecular backbone, and therefore, the DFT-predicted spin density distribution in the corresponding radical cation discerns the delocalized character (Figure 1). In this respect, it is interesting to examine the spin distribution of the radical cation of cyclic oligoanilines in conjunction with the question: to what extent is an unpaired electron delocalized within the polyaniline backbone?

However, the preparation of aza[1$_n$]paracyclophanes are hitherto unknown, and the elucidation of their electronic properties is in demand from the viewpoint of materials chemistry. This communication reports the synthesis and characterization of electronic structures of all-*N*-anisyl-substituted hexaaza[1$_6$]paracyclophane (**1**) and its oxidized species.

The title compound (**1**) was not obtained by the simple single-step coupling reaction from *para*-halogenated secondary arylamines. In addition, convergent fragment coupling synthesis[1] from the combinations of simple secondary arylamines and aryl halides was also unsatisfactory to us. For example, an equimolar coupling reaction of *N*,*N′*-bis(4-

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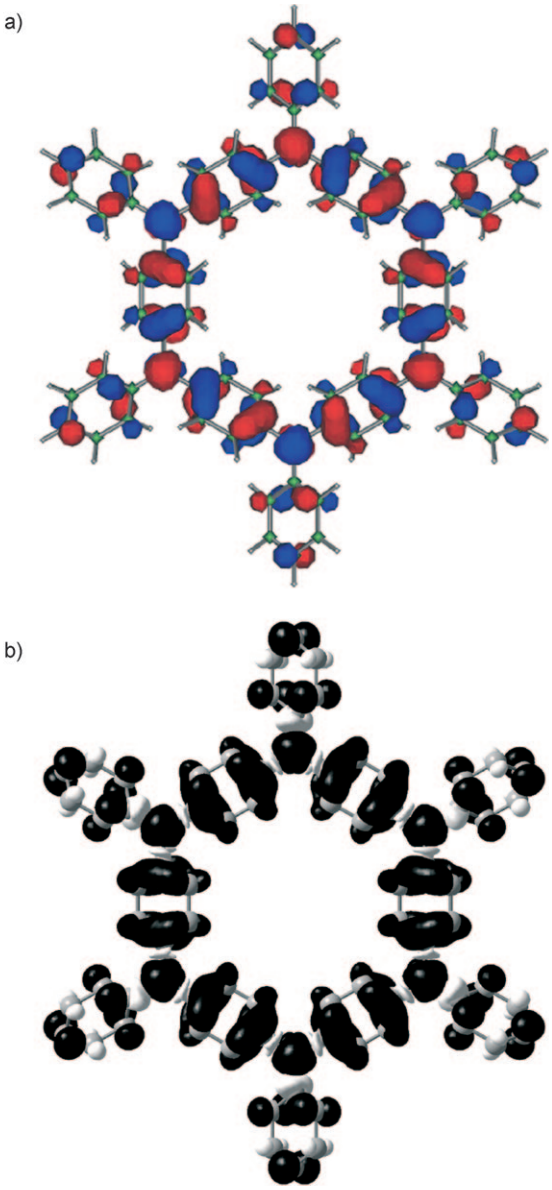
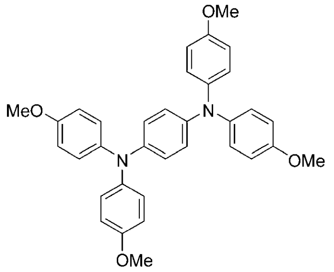


Figure 1. a) HOMO (B3LYP/6-31G*[7]) of **1′** calculated by DFT and b) the spin density distribution (black: positive spin, white: negative spin; spin isosurface value = 0.0003 electron/au^3; UB3LYP/EPR-III//ROB3LYP/6-31G*[7]) of $\mathbf{1'}^{\bullet+}$.

anisyl)-1,4-phenylenediamine and *N*-anisyl-4,4′-dibromodiphenylamine in the presence of the phosphine-ligated palladium catalyst (Buchwald–Hartwig aryl amination reaction[8]) did not afford the cyclic product, even after 5 days reaction. During our synthetic attempts, however, we noticed that the hexaaza[1$_6$]paracyclophane structure (**2**) can be directly prepared at room temperature from *N*,*N*′-di(4-anisyl)-1,4-benzenediamine and Boc-protected *N*,*N*-bis(4-bromophenyl)amine in the presence of [Pd(dba)$_2$] and P(*t*Bu)$_3$ as catalyst (Scheme 3).[9] After removal of the Boc groups with TFA, the palladium-catalyzed coupling of the macrocycle (**2**) and *p*-bromoanisole afforded **1** as a pale yellow solid. The observed simple ^{1}H NMR spectrum of **1** is diagnostically consistent with the macrocyclic structure: singlet signal for six phenylene rings, AA′XX′ signals for six N-substituted anisyl groups, and a singlet signal for six methoxy groups.

Although we could not obtain single crystals suitable for the X-ray structural analysis of **1**, the B3LYP/6-31G* optimized structure of **1′** showed that the six nitrogen atoms are predicted to be coplanar, whereas each triphenylamine moiety adopts a propeller-like conformation, in which the torsion angles of the phenyl rings range from 39.6° to 43.1° (Figure 1 and Figure S3 in the Supporting Information).

Cyclic voltammetry and differential pulse voltammetry (DPV) of **1** in dichloromethane (0.1 M $n\mathrm{Bu_4N^+BF_4^-}$, 100 mV s^{-1}) at 298 K showed five oxidation processes as shown in Figure S1 in the Supporting Information. The first four oxidation processes were chemically reversible after repeated potential cycling in dichloromethane. The oxidation potentials [E_{ox} vs. $\mathrm{Fc}^{0/+}$ (ne)] of **1** were determined to be −0.28 (1e), −0.17 (1e), +0.20 (1e), +0.45 (1e), and +0.72 V (peak potential, 2e), and therefore, **1** was oxidizable up to a hexacation species according to six redox-active triarylamine centers. Notably, the first and second oxidation potentials of the macrocyclic oligmer **1** are much lower than the first oxidation potentials of the related linear oligomers [−0.13 V for the dimer **4** and −0.11 V for the trimer **5**],[10] which were measured under the same conditions. Furthermore, the increase of electron-donating ability by macrocyclization of oligo-*p*-arylamines is remarkable as compared with that by macrocyclization of oligo-*m*-arylamines.[11]



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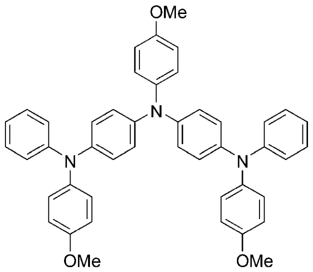

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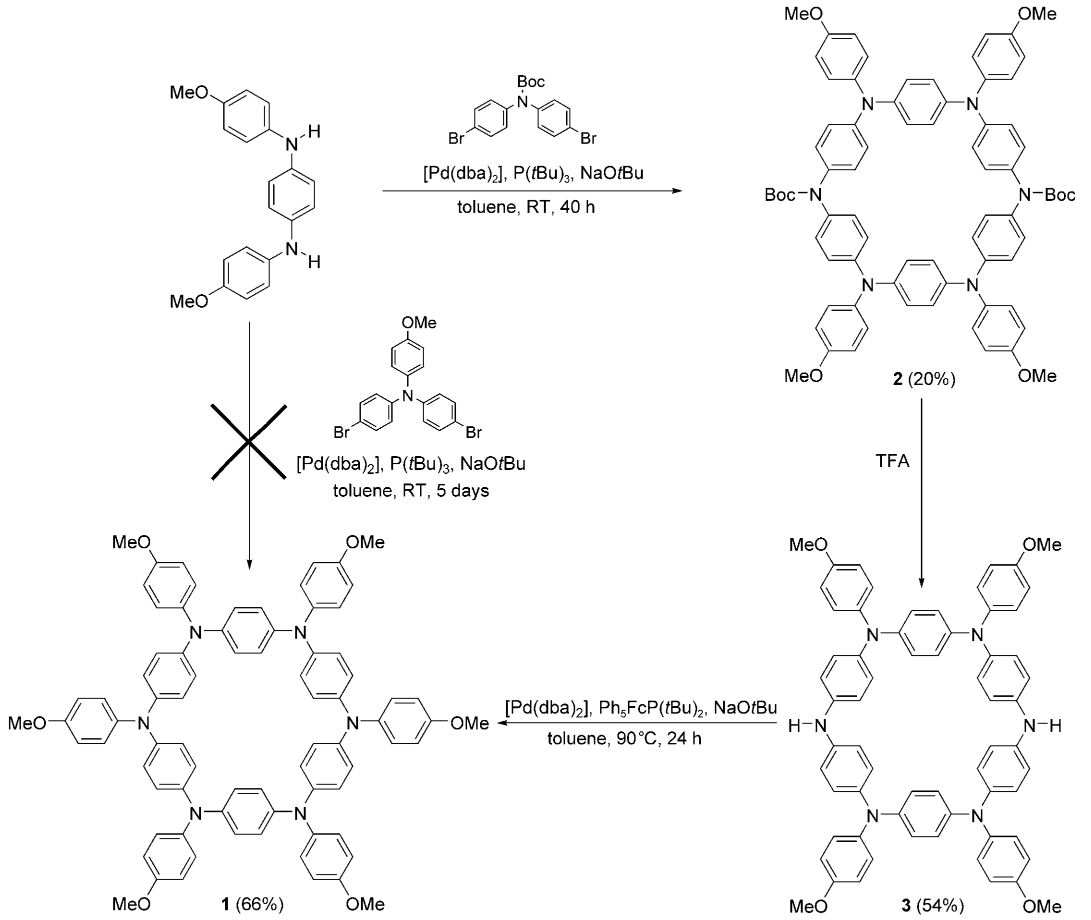
The ESR spectrum of $\mathbf{1}^{\bullet+}$ generated by chemical oxidation of **1** by one equivalent of tris(4-bromophenyl)aminium hexachroloantimonate in dichloromethane at 195 K showed a multiplet hyperfine structure, and the observed *g* value is 2.0028 (Figure 2a). The splitting pattern can be explained by the presence of six equivalent nitrogen nuclei and 24 hydrogen nuclei, although the broadness of the signals suggests additional small hyperfine coupling constant (Figure 2b). The optimum simulation of the observed spectrum gave the following values: $a_{\mathrm{N}} = 0.205$ mT (6N) and $a_{\mathrm{H}(ortho)} = 0.021$ mT (24H), and the contributions from the negligible hydrogen nuclei were incorporated in the line width of the spectral simulation (0.10 mT). Moreover, the hyperfine structure did not change in the temperature range from −60 to 20 °C (Figure S2 in the Supporting Information), and hence, this result clearly demonstrates that the generated spin is delocalized over the macrocyclic molecular backbone.

The UV/Vis/NIR spectroscopic change upon electrochemical oxidation from **1** through $\mathbf{1}^{\bullet+}$ to $\mathbf{1}^{2+}$ was recorded



Scheme 3. Synthetic route for **1**. Boc = *tert*-butoxycarbonyl, dba = *trans,trans*-dibenzylideneacetone, TFA = trifluoroacetic acid.

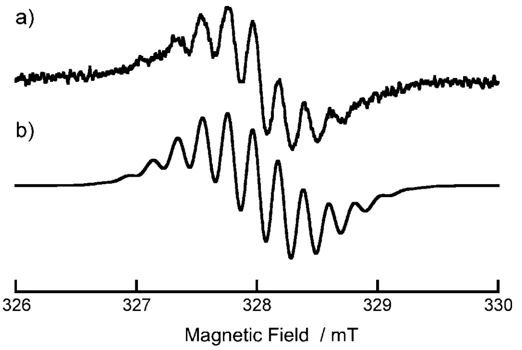


Figure 2. ESR spectra of $1^{\cdot +}$: a) in CH_2Cl_2 at 233 K; b) simulated.

by using an optically transparent thin-layer electrochemical cell (Figure 3). Upon oxidation of **1**, two absorption bands appeared at 0.76 and ≈ 2.7 eV and the initial absorption band (3.56 eV) decreased, which can be ascribed to formation of radical cation $\mathbf{1}^{\cdot +}$. Judging from the ESR analysis of $\mathbf{1}^{\cdot +}$, the lowest energy band is attributable to the charge resonance (CR) band originating from spin delocalization over the entire molecule. Further oxidation to dication $\mathbf{1}^{2+}$, the lowest energy band showed a hypsochromic shift to 0.83 eV, as was often observed in the related macrocyclic oligoarylamines.[10b,12]

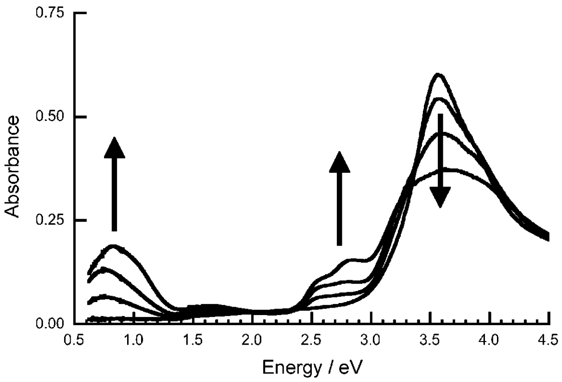


Figure 3. UV/Vis/NIR spectra of the stepwise electrochemical oxidation of **1** to $\mathbf{1}^{2+}$ in CH_2Cl_2/0.1 M $nBu_4N^+BF_4^-$ at room temperature.

Prompted by the finding of good electron-donating ability of **1**, we have checked the possibility of formation of charge-transfer (CT) complexes with acceptor molecules. For example, combining solutions of **1** and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) as a typical acceptor molecule in dichloromethane showed a superposition of the absorptions of $\mathbf{1}^{\cdot +}$ (0.78 eV) and $TCNQ^{\cdot -}$ (≈ 1.5 eV[13]), as shown in Figure 4. Furthermore, the IR spectrum of the isolated powder sample displayed a characteristic decrease in the

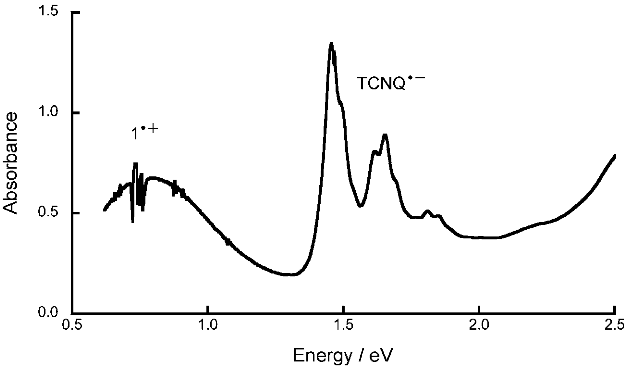


Figure 4. Vis/NIR absorption spectrum of the combined solution of **1** and TCNQ in CH_2Cl_2 at room temperature.

wavenumber (ν_{CN}) corresponding to the CN bond stretching vibration of TCNQ [observed $\nu_{CN} = 2180\ cm^{-1}$; $2223\ cm^{-1}$ for neutral TCNQ and $2183\ cm^{-1}$ for TCNQ$^{\bullet-}$], as is often utilized as a measure of charge transfer in the CT complex with TCNQ.[14] Thus, this observation indicates a complete charge transfer has occur from **1** to TCNQ.

In summary, we succeeded in synthesizing an aza[1_n]paracyclophane **1**. The ESR analysis resulted in the delocalized spin distribution for the radical cation of the cyclic oligoaniline, in contrast to the spin confinement for the radical cation of linear oligoanilines. Furthermore, the electrochemical studies revealed that **1** can be regarded as a good electron donor, so that the CT complex can be easily obtained with electron acceptors such as TCNQ. In addition, electronic structures for the higher oxidation states including $\mathbf{1}^{2+}$, should be intriguing from the viewpoints of aromaticity in macrocyclic conjugated system, molecular magnetism in toroidal molecular spin system, and so forth.[15] Studies on these topics are currently underway.

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[9] In this palladium-catalyzed macrocyclization reaction, we isolated the Boc-protected aza[1_9]paracyclophane in 8.7% yield. In addition, we detected the formation of small quantity of the Boc-protected aza[1_{12}]paracyclophane from the FABMS study, but we could not isolate it. The remainder was mainly polymeric material.

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[15] As pointed out by one of the reviewers, there exists the possibility that the aromaticity in $\mathbf{1}^{2+}$ is observed through the NMR studies. In fact, upon oxidation of **1**, the semiquinoidal structural changes in macrocyclic skeleton were expected from the B3LYP/6-31G* calculations for the higher oxidation states of $\mathbf{1}'$ (Figure S3b in the Supporting Information), and furthermore, the nucleus-independent chemical shift (NICS) value for $\mathbf{1}'^{2+}$ calculated at the center of the plane defined by the six nitrogen atoms was comparable to that of benzene at the same level of calculations (GIAO/B3LYP/6-311G*//B3LYP/6-31G*; Figure S4 in the Supporting Information). Our preliminary experiments to record the NMR spectrum of $\mathbf{1}^{2+}$ were unsuccessful owing to unavoidable paramagnetic impurities.