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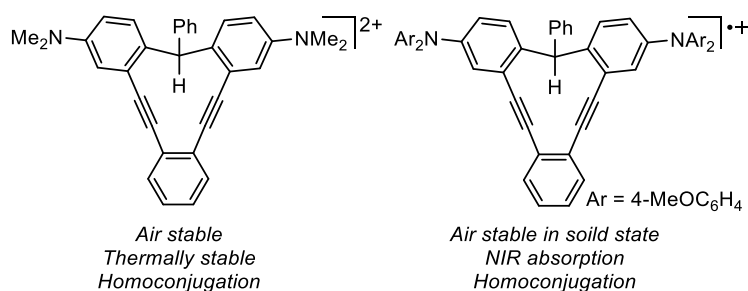
Synthesis and Properties of Cyclic π-Conjugated Molecules and Their Dication and Monoradical Cation

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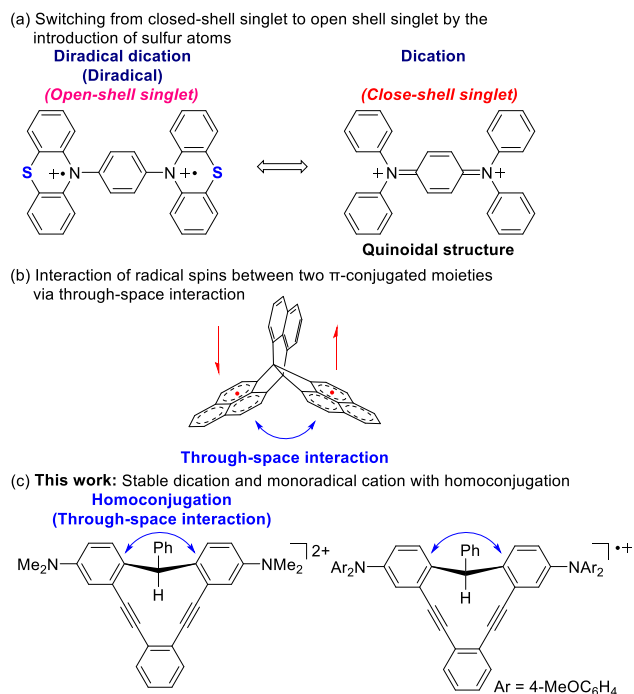
Supporting Information Placeholder

Air stable
Thermally stable
Homoconjugation

Air stable in soild state
NIR absorption
Homoconjugation

Ar = 4-MeOC$_6$H$_4$

ABSTRACT: We synthesized cyclic π-conjugated molecules by double Friedel-Crafts reaction of amino group-substituted 1,2-bis(2-phenylethynyl)benzene with Meldrum's acid derivative. The structures of the cyclic π-conjugated molecules were determined by single-crystal X-ray structure analysis. The oxidation of the dimethylamino group-substituted π-conjugated molecule with NOBF$_4$ gave a closed-shell dication that is stable at >210 °C. The monoradical cation of the di(4-methoxyphenyl)amino group-substituted π-conjugated molecule is stable in dichloromethane solution (half-life of nearly 15 days) and shows near-infrared absorption.

Resonances are known to exist between diradical cationic species (diradical species) and dication species (neutral molecules).[1] Controlling those resonances by the electronic properties of such chemical species and molecules makes it possible to create different versions. For example, Wang et al. found that the chemical species obtained by two-electron oxidation of 1,4-bis(diphenylamino)benzene forms a quinoidal structure, which is a dication with a closed-shell singlet state, whereas the related compound modified by sulfur atoms exists as a diradical dication with an open-shell structure (Figure 1a).[2] In addition, Kubo et al. recently reported a diradical species with two phenalenyl radical sites coupled antiferromagnetically via through-space interaction between the two radical sites (Figure 1b).[3] In this molecule, the two radical spins do not combine to form a closed-shell structure, but rather have an open-shell singlet state, despite the presence of through-space interaction. It would be interesting if chemical species or molecules with a similar through-space interaction (or homoconjugation) but a closed-shell singlet state, i.e., dications (or neutral molecules), could be obtained.

Radical species are important intermediates of various organic reactions, such as dimerization, cationic polymerization, azo formation, nucleophilic substitution, and proton transfer reactions,[4,5] and functional materials,[6] owing to

(a) Switching from closed-shell singlet to open shell singlet by the introduction of sulfur atoms
Diradical dication **Dication**
(Diradical)
(Open-shell singlet) *(Close-shell singlet)*

Quinoidal structure

(b) Interaction of radical spins between two π-conjugated moieties via through-space interaction

Through-space interaction

(c) **This work:** Stable dication and monoradical cation with homoconjugation
Homoconjugation
(Through-space interaction)

Ar = 4-MeOC$_6$H$_4$

Figure 1. Several examples of dications and (di)radical (di)cations.

their unique electronic properties.[7] However, radical species are generally unstable, their life-time is short, and they can be coupled with other radical species,[8] and thus it is necessary to stabilize them for practical use. They can be stabilized in several ways: for example, the dimerization and intermolecular π-π stacking of monoradical species,[9] the overall delocalization of electrons in aromatic systems, or the avoidance of forming quinoidal structures.[10] We report herein the synthesis of cyclic π-conjugated molecules bridged by sp^3 carbons using the double Friedel-Crafts reaction which we have recently developed.[11] By oxidizing these cyclic π-conjugated molecules, we succeeded in synthesizing a dication with closed-shell singlet states instead of open-shell singlet states and a relatively stable monoradical cation (Figure 1c). The properties of these molecules and their constituent species were investigated.

We recently reported the synthesis of five-, six-, and seven-membered cyclic π-conjugated molecules by double Friedel-Crafts reaction of electron-rich biaryl compounds with Meldrum's acid derivatives as methylenation reagents.[11,12] Using this reaction, cyclic π-conjugated molecules **3a** and **3b** were obtained in 39% and 34% yields, respectively, from amino group-substituted 1,2-bis(arylethynyl)benzene **1a** or **1b** and Meldrum's acid derivative **2** (Scheme 1). It is interesting that the cyclic structures of **3a** and **3b** were formed in spite of a long-distance between two carbon atoms of the two aromatic rings, which are the reaction sites of **1a** and **1b** (**1a**: 4.331 Å by density functional theory (DFT) calculation (B3LYP/6-31G(d))).
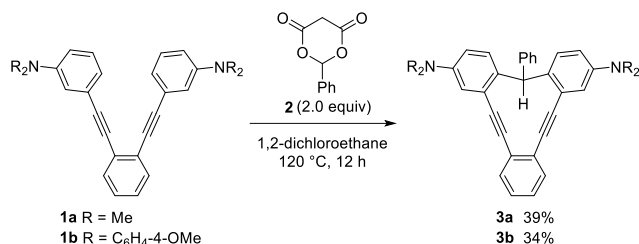

Scheme 1. Synthesis of cyclic π-conjugated molecules **3a** and **3b** by double Friedel-Crafts reaction.

The structures of **3a** and **3b** were determined by ^{1}H and ^{13}C NMR, HRMS (FAB$^+$), and single-crystal X-ray structural analysis (Figure 2). In the ^{1}H NMR spectrum of **3a**, the proton signals at the methine moiety moved down-field (6.67 ppm in $CDCl_3$) compared with that of bis(4-dimethylamino)phenylphenylmethane (5.38 ppm in $CDCl_3$).[13] This result is due to the non-shielding effect from the two alkyne moieties of **3a**. In the ^{13}C NMR spectrum of **3a**, the carbon signal at the methine moiety moved up-field (47.5 ppm in $CDCl_3$) compared with that of bis(4-dimethylamino)phenylphenylmethane (55.0 ppm in $CDCl_3$).[14] This result is due to the shielding effect from the two alkyne moieties of **3a**. The neutral π-conjugated molecules **3a** and **3b** are thermally stable and the 5% weight loss temperatures (T_{d5}) of **3a** and **3b** were 358 °C and 212 °C, respectively, as determined by thermogravimetric analysis (TGA).

In the single-crystal X-ray structures, cyclic π-conjugated molecules **3a** and **3b** have twisted structures to avoid the steric repulsion from the phenyl group (Figure 2). In addition, two C≡C triple bonds are bent and the angles of the C≡C–C bonds at the *ortho*-phenylene sides are approximately 168° (**3a**) and 167° (**3b**), due to the long distance between the two aniline moieties and the flexibility of the C≡C triple bonds. The distances between two carbon atoms at the ipso-positions of the two aromatic rings in **3a** and **3b** are 2.543 Å and 2.686 Å, respectively, which indicates a C–C single bond between the two ipso-carbon atoms is not formed by the formation of a quinoidal structure.
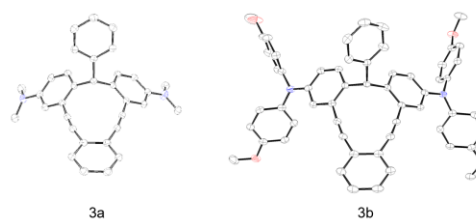
Figure 2. Single crystal X-ray structures of cyclic π-conjugated molecules **3a** and **3b**. ORTEP plot of **3a** and **3b** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

The DFT calculations of **3a** and **3b** showed that the HOMO and LUMO energies of **3a** were -4.94 and -1.22 eV, respectively (an energy gap of 3.72 eV), and the HOMO and LUMO energies of **3b** were -4.60 and -1.32 eV, respectively (an energy gap of 3.28 eV). The HOMO and LUMO of **3a** and **3b** are delocalized at the two aminophenyl moieties and 1,2-bis(phenylethynyl)benzene moieties, respectively. Interestingly, homoconjugation is observed between two aromatic rings with an amino group in the HOMO-1 orbitals of **3a** and **3b** (**3a**: -5.15 eV; **3b**: -4.71 eV) (Figure 3).
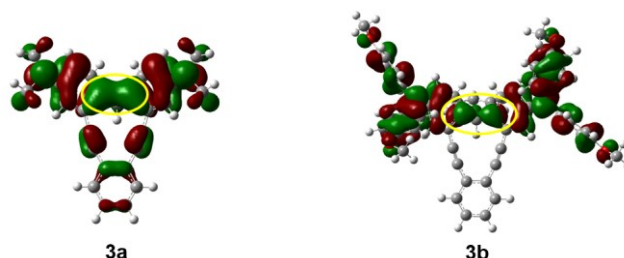
Figure 3. Homoconjugation (yellow circle) at the HOMO-1 of cyclic π-conjugated molecules **3a** and **3b** (B3LYP/6-31G(d)).

In the cyclic voltammogram of **3a** in dichloromethane at room temperature in the presence of $^nBu_4NPF_6$ as a supporting electrolyte, two overlapping irreversible oxidation waves were observed at a scan rate of 0.10 V/s whereas almost reversible two-electron oxidation occurred at the scan rate of 0.50 V/s (see Figure S15 in the Supporting Information). These results indicate that the diradical dication of **3a** is not stable, and a dication species is formed (judging from electron spin resonance (ESR) and superconducting quantum interference device (SQUID), see below) (Figure 4a). In contrast, reversible one-electron oxidation of **3b** is observed at 0.58 V (vs Fc/Fc$^+$)[16] at a scan rate of 0.50 V/s, suggesting that **3b** can be oxidized to its monoradical cation (Figure 4b).

The oxidation of **3a** with $NOBF_4$, which has a higher oxidation potential (0.87 V vs Fc/Fc$^+$ in CH_3CN) than **3a** (0.70 V vs Fc/Fc$^+$ in CH_3CN),[15] gave cyclic dication species **4a** (Scheme 2a). In contrast, monoradical cation **4b** was obtained by one-electron oxidation of **3b** (0.58 V vs Fc/Fc$^+$ in dichloromethane) with magic blue (0.70 V vs Fc/Fc$^+$ in dichloromethane) (Scheme 2b).
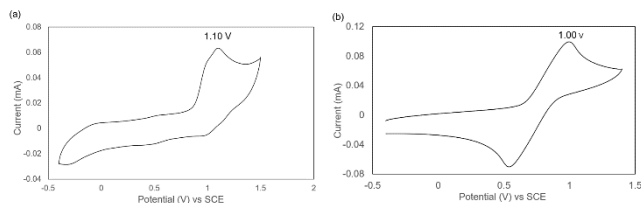
Figure 4. Cyclic voltammetry of cyclic π-conjugated molecules in 0.10 M ^{n}Bu$_4$NPF$_6$ in CH$_3$CN or dichloromethane, 2.0 mM analyte; glassy carbon (diameter: 3 mm, geometry: circle), Pt wire, and Ag wire as working, counter, and reference electrodes, respectively; IUPAC plotting convention: (a) **3a** (0.10 V/s, CH$_3$CN, Pt electrode) and (b) **3b** (0.50 V/s, dichloromethane, Pt electrode, the first oxidation peak).

We tried to synthesize the monoradical cation of **3a** by the reaction of 1.0 equivalent of NOBF$_4$ with **3a**. However, **4a** was still obtained and some amount of **3a** was recovered. The dicationic species of **3b** was also not formed (instead **4b** was obtained) using Magic Green, which has the highest oxidation potential among our possessing oxidants, probable because the oxidation potential of Magic Green (1.54 V vs SCE) is lower than the second oxidation potential of **3b** (1.62 V vs SCE).
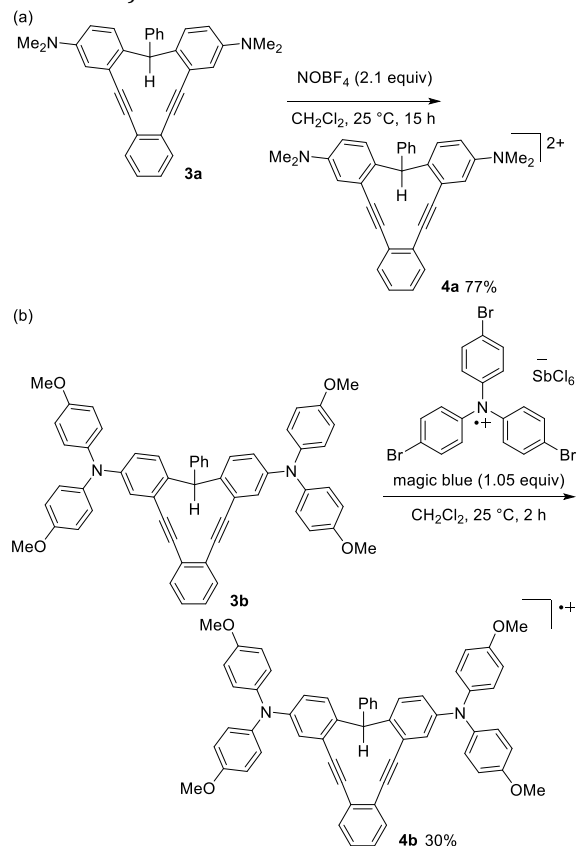

Scheme 2. Synthesis of dication **4a** and monoradical cation **4b** by the oxidation of **3a** with NOBF$_4$ and **3b** with magic blue, respectively.

The structures of **4a** and **4b** were determined by ^{1}H and ^{13}C NMR, HRMS (FAB$^+$), and single-crystal X-ray structural analysis. It is noteworthy that **4a** and **4b** were relatively stable: dication **4a** did not decompose for more than one month in air, and the 5% weight loss temperature (T$_{d5}$) of **4a** was 212 °C as determined by TGA. Monoradical cation **4b** could be handled in air. Although dimerization of the

radical species occurs in some cases,[8a] the dimerization of **4b** was not observed. One reason for this stability is steric hindrance of the phenylmethine moieties. Although we attempted to generate the diradical dication species by the oxidation of acyclic compounds **1a** and **1b**, oligomerization (and/or polymerization) proceeded, and the desired monomer diradical dication species were not obtained. These results indicate that the bridging phenylmethylene moiety is important for the stabilization of **4a** and **4b**. The half-life of **4b** in dichloromethane (dark) was 14.8 days (for the details, see Supporting Information). Only one weak singlet signal was observed at g = 2.0031 in the solid state at 25 °C in the ESR spectrum of **4a**[16] and the SQUID shows no ferromagnetic signal. These results indicate the existence of **4a** as a dication (closed-shell singlet state). In contrast, the ESR spectrum of **4b** shows a strong singlet signal at g = 2.0030 in the solid state at 25 °C, indicating the formation of a monoradical cation (Figure S19). The SQUID spectrum of **4b** shows χ$_{mol}$T = 0.375, which indicates a monoradical cation (Figure S14).

DFT calculations (B3LYP/6-31G(d)) of **4a** showed that the HOMO and LUMO energies of **4a** are -11.25 and -10.26 eV, respectively (an energy gap of 0.99 eV). The spin densities of **4b** are mainly localized at two nitrogen atoms and their surrounding aromatic rings (see Figure S22 in the supporting information). Interestingly, homoconjugation exists at the HOMO-1 orbital (-11.31 eV, Figure 5). The reason for the formation of the dication, not diradical dication, is probably spin-spin interactions through homoconjugation.
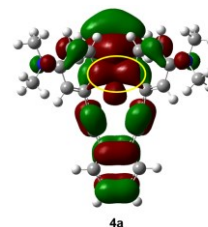
Figure 5. Homoconjugation (yellow circle) at the HOMO-1 of cyclic π-conjugated molecules **4a** (B3LYP/6-31G(d)).

Interestingly, UV absorption and strong near-infrared absorption were observed at 368 and 768 nm, respectively, in the UV-vis-NIR spectrum of **4b** (Figure 6).[17] The absorption at 368 nm is indicated as a intramolecular charge transfer and the absorption at 768 nm is mainly contributed by the transition from HOMO-4 to SOMO by TDDFT calculation (UB3LYP/6-311++G(d,p), CH$_2$Cl$_2$)(for the detail, see the Supporting Information).
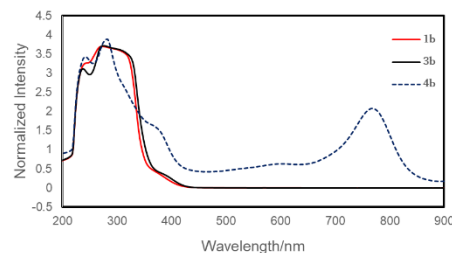
Figure 6. UV-Vis-NIR spectra of **1b**, **3b** and **4b**.

In summary, we synthesized cyclic π-conjugated molecules by double Friedel-Crafts reaction of amino group-substituted 1,2-bis(arylethynyl)benzene with Meldrum's acid

derivative. The structures of the cyclic π-conjugated molecules were determined by ^{1}H and ^{13}C NMR, mass spectrometry, and single-crystal X-ray structure analysis. DFT calculations revealed homoconjugation between the two aromatic rings in the cyclic neutral molecules and the dication. In cyclic voltammograms of the cyclic π-conjugated molecule with two dimethylamino groups, irreversible two-electron oxidation occurred. In contrast, a reversible one-electron oxidation peak was observed in the case of the cyclic π-conjugated molecule with two bis(4-methoxyphenyl)amino groups. Although the oxidation of the cyclic π-conjugated molecule having two dimethylamino groups gave a dication, a monoradical cation was obtained by the oxidation of the cyclic π-conjugated molecule bearing two bis(4-methoxyphenyl)amino groups. The dication was synthesized to avoid the formation of a quinoidal structure. The dication is stable in air and when heated. Interestingly, monoradical cations are stable and can be stored in a dichloromethane solutions in the dark with a half-life of approximately 15 days. This stability is probably due to the steric hindrance of the phenylmethine moieties. In the ESR spectrum and SQUID measurement of the monoradical cation, a singlet signal with $\chi_{mol}T = 0.375$ was observed, indicating a monoradical cation. DFT calculations of the two cyclic π-conjugated molecules and dications showed the existence of homoconjugation between two aromatic rings with an amino group. The reason for the formation of dications, not diradical dications, is probably spin-spin interactions through homoconjugation. In the UV-vis-NIR spectrum of the monoradical cation, a π-π* transition peak and near-infrared absorption were observed.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its online Supporting Information.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details and characterization and spectral data of the compounds (PDF)

Accession Codes

CCDC 2350885(**3a**), 2350886(**4a**) and 2350887(**3b**).

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Notes

The authors declare no competing financial interest.

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