Synthesis and Properties of Cyclic [5]*meta*-Phenyleneacetylene and Its Corresponding Cyclophane Polyone, $[2_5]$(1,3)Cyclophanedecaone

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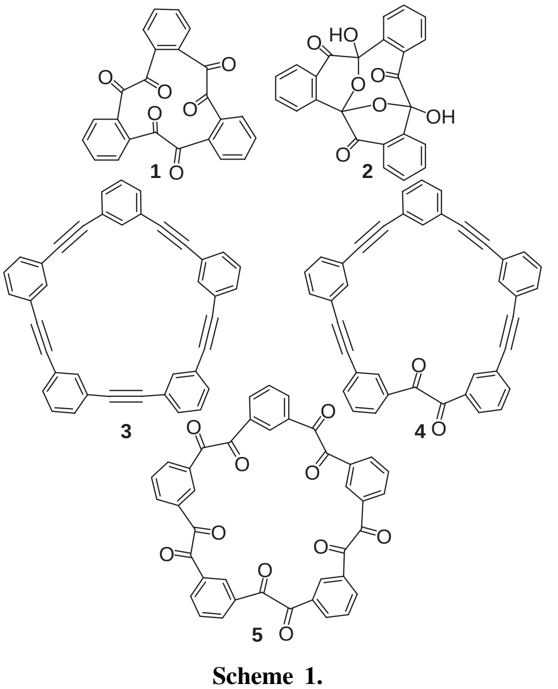
The cyclic [5]*meta*-phenyleneacetylene (**3**) ([5]CMPA) and its corresponding cyclophane polyones **4** and **5** are synthesized. **3**, a "missing link" between [4]CMPA and [6]CMPA, shows a fairly pronounced emission, indicating a rigid structure, whereas **5** is colorless in contrast to conventional diarylethane-1,2-diones owing to its conformational mobility and all-s-cis and twisted dione structure.

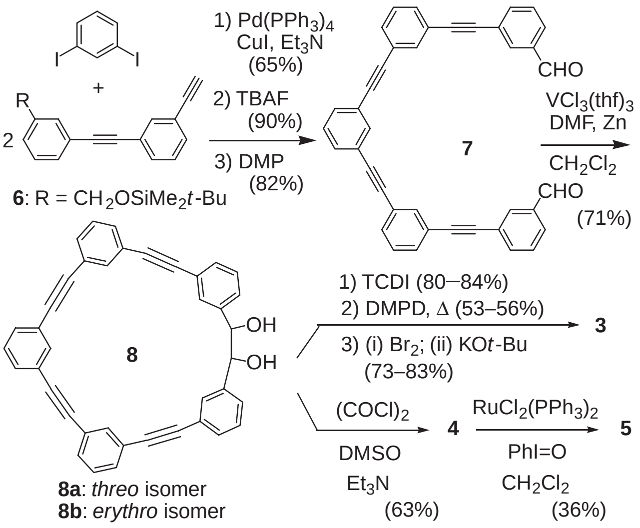
There has been considerable interest in phenylene–acetylene–macrocycles (PAM) and cyclic polyketones from experimental and theoretical viewpoints.[1,2] Although diarylethane-1,2-diones such as benzil and its derivatives are well known, only a limited number of cyclic polyketones composed of diaryl-1,2-dione units have been reported to date.[3] We have recently reported the synthesis of the macrocyclic hexaketone monohydrate **2** formed via the intramolecular cyclization of the tribenzo[12]annulenehexaone (**1**).[3b] **2** has a very stable hemi-acetal structure, and its thermal dehydration under reduced pressure results in its decomposition presumably owing to the instability of **1**. To examine novel properties of cyclic polyketones, we prepared $[2_5]$(1,3)cyclophanedecaone (**5**) together with [5]CMPA (**3**)[4] and the dione **4**.

The title compounds **3**–**5** were synthesized as shown in Scheme 1.[5] The Sonogashira coupling of **6** with 1,3-diiodobenzene, followed by desilylation and oxidation with the Dess–Martin periodinate (DMP) yielded the tetrayne-dialdehyde **7**. The vanadium-mediated pinacol coupling[6] of **7** gave a mixture of the *threo*-diol **8a** and *erythro*-diol **8b** (threo/erythro = 3/2). The reaction of **8a** with 1,1′-thiocarbonyldiimidazole (TCDI) in refluxing toluene, followed by treatment with 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine[7] (DMPD) in refluxing benzene produced (*Z*)-olefin in 45% overall yield. The reaction of **8b** also yielded (*E*)-olefin in 45% overall yield. (*Z*)- and (*E*)-olefins were allowed to react successively with Br_2 and KO*t*-Bu to produce **3** in 73 and 83% yields, respectively. To synthesize **4** and **5**, a mixture of **8** was converted into the diketone **4** using the Swern oxidation. Further oxidation of **4** with $RuCl_2(PPh_3)_2$ (10 mol %)–PhI=O (excess) and $RuO_2{\cdot}2H_2O$ (10 mol %)–PhI=O (excess) produced **5** in 36 and 18% yields, respectively (Scheme 2).[3b]



Scheme 1.

[5]CMPA (**3**) without substituents is fairly fluorescent in solution ($\Phi_F = 0.20$ in THF) because of its rigid planar structure.[8] However, a film cast on a glass plate showed no fluorescence owing to the π–π stacking interaction in solid state, although the ^{1}H NMR and UV spectra of **3** showed no concentration or temperature dependence in $CDCl_3$ or C_6D_6, reflecting no self-aggregation in $CDCl_3$ or C_6D_6. Note that [5]CMPA represents a missing link between the well-known [4]CMPA (4PAM)[9] and [6]CMPA (6PAM).[10]



Scheme 2. Synthesis of [5]CMPA (**3**) and its corresponding ketones **4** and **5**.

Previously, we reported that tribenzo[12]annulene-1,2-di-

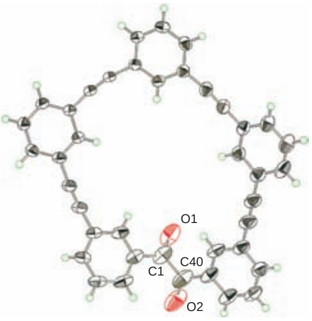


Figure 1. ORTEP view of **4**. Selected bond lengths and angles: C1–O1 = 1.226(3) Å, C40–O2 = 1.229 Å, C1–C40 = 1.524 Å, O1–C1–C40 = 116.9(3)°, and O2–C40–C1 = 119.5°.

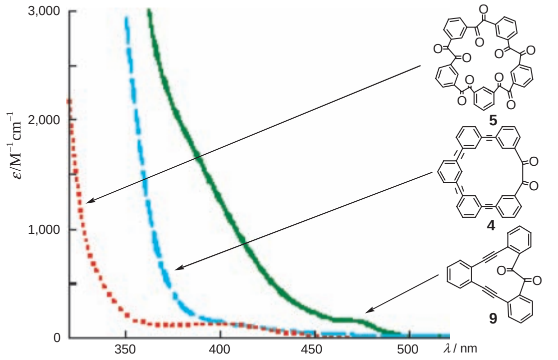


Figure 2. UV–vis spectra of the cyclic polyketones **4**, **5**, and **9** in CH_2Cl_2 at room temperature.

one (**9**) forms two different conformers in crystals, i.e., yellow and colorless plates.[6a] Thus, the UV–vis spectrum and color of diarylethane-1,2-diones reflect the dihedral angle of vicinal carbonyl groups.[11] [5]CMPA-dione **4** produced yellow plates from CH_2Cl_2–(i-Pr)$_2$O–hexane, and its structure was determined by X-ray analysis.[12] As shown in Figure 1, the two carbonyl groups of **4** are twisted with a dihedral angle of 115.3° and the benzil chromophore can produce a yellow color.

Interestingly, **5** is colorless in solution and in solid state. As shown in Figure 2, the longest absorption maximum of **5** at 395 nm ($\varepsilon = 125$) is slightly shorter than that of **4** at 402 nm ($\varepsilon = 140$), and its absorption intensity is very weak in spite of **5** having ten carbonyl groups. Generally, the n–π^* absorption of *s-cis*-diones occurs at shorter wavelength than that of *s-trans*-diones,[3a] and a twisted conformation with a dihedral angle of 90° between two carbonyl groups leads to the smallest conjugation and shortest absorption maximum with the weakest absorption coefficient. By considering our observations of **9**,[3b,13] all-s-cis and/or twisted conformation in **5** can be expected.

The molecular structure of **5** was estimated by PM3 calculations.[14] The calculated preferred conformation has a C_1 symmetry with ten s-cis- and/or twisted carbonyl groups that show insufficient conjugation between the diketones and aromatic rings. As reported previously, the conformational change of pentabenzo[20]annulene with an essential C_5 symmetry is very rapid in solution.[15] Similarly, the conformational change of **5** is very rapid in solution owing to the several minimum energy conformations of **5**, and the ^{1}H NMR spectra of **5** in CD_2Cl_2 at 25 and −80° are almost the same.

In summary, we synthesized **3** (5PAM) which represents the "missing link" of a series of [n]CMPAs (nPAMs) and characterized it by comparing its absorption and emission spectra with those of [4]CPMA and [6]CPMA.[8] Furthermore, we also synthesized the unique [2_5](1,3)cyclophanedecaone (**5**) using our oxidation procedure. The decaone **5** is a colorless, stable compound that shows a very rapid conformational change in solution. We believe that macrocyclic polycarbonyl compounds will open up a new perspective on functional and biologically active materials.

This work was supported in part by a Grant-in-Aid for Scientific Research from JSPS. We are grateful to Dr. Yoshihiro Miyake (the University of Tokyo) for the measurements of high-resolution mass spectra and to Dr. Hideo Enozawa and Prof. Haruo Matsuyama for helpful discussions.

References and Notes

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4 Parent cyclic [5]*meta*-phenyleneacetylene (**3**) (5PAM) is abbreviated to [5]CMPA.[1c]

5 For the synthesis of **3**–**8**, see Supporting Information which is available electronically on the CSJ-Journal Web site; http://www.csj.jp/journals/chem-lett/.

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8 For the absorption and emission data of **3** and related compounds, see Supporting Information.

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11 The n–π^* transitions of benzil and related α-diketones vary in position with a change in the dihedral angle between the carbonyl groups, and a twisted conformation with a dihedral angle of 90° between two carbonyl groups results in the shortest absorption maximum. In contrast, *s-trans*-α-diketones have a pronounced conjugation, indicating a bathochromic shift: N. J. Leonard, A. J. Kresge, M. Oki, *J. Am. Chem. Soc.* **1955**, *77*, 5078, and references cited therein.

12 Crystal data for **4**: formula $C_{40}H_{20}O_2$; fw 532.59; crystal system, monoclinic; space group, $P2_1/n$ (#14); $a = 12.866(2)$; $b = 12.488(3)$; $c = 18.245(3)$ Å; $\beta = 106.76(1)°$; $V = 2797.9(5)$ Å^3; $Z = 4$; $D_C = 1.264$ g cm^{-3}; number of observation ($I > 3.00\sigma(I)$, $2\theta < 54.99°$) = 3150; $R_1 = 0.045$, $_wR_2 = 0.1697$. Crystallographic data for **4** and **9**[13] have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no CCDC 299150 and CCDC 688483, respectively.

13 For the structure and spectal data of **9**, see Supporting Information.

14 For the MO calculations of **5**, see Supporting Information.

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Published on the web (Advance View) June 21, 2008; doi:10.1246/cl.2008.784