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Synthesis and photochromic properties of 1,2-dicyano[2.*n*]metacyclophan-1-enes

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Abstract—Novel synthesis and the photochromic properties of 1,2-dicyano[2.*n*]metacyclophan-1-enes are reported. The intramolecular cyclization of bis(cyanomethyl)arenes successfully afforded 1,2-dicyano[2.*n*]metacyclophan-1-enes in good yield. The obtained cyclophanes show photochromism and the lifetime of the colored form is dependent on the chain length (*n*). © 2001 Elsevier Science Ltd. All rights reserved.

Photochromic compounds have been extensively studied as they are potential photo-memory and photo-switching materials.[1] In photochromic compounds, dithienylethenes are of interest because of their thermally irreversible and high fatigue-resistant properties.[1a] The aromatic stabilization energy of thiophene is smaller than benzene, therefore both photoisomers have similar energy of formation and the energy barrier between them is too high to overcome thermally in this system.[1a]

On the other hand, small [*m.n*]metacyclophanes have large steric energy, which arises from steric repulsion between both aromatic rings and/or inner substituents and from electrostatic repulsion of the benzene rings.[2] Hence, the aromatic stabilization energy of the metacyclophane is getting smaller as the ring size of the metacyclophane smaller. When this system would be applied to photochromic [2.*n*]metacyclophan-1-enes, one can 'tune' the thermal stability of the photoisomers by the change of the bridge length (*n*).

Although there are some reports on the synthesis and photochromic properties of [2.*n*]metacyclophan-1-enes, it has been reported that all of the reported [2.*n*]metacyclophan-1-enes requires long steps for synthesis and no derivative except for having an alkyl.[3] The reported metacyclophan-1-enes has no absorption in visible regions, therefore they are colorless. From this point of view, we have designed [2.*n*]metacyclophan-1-enes having two cyano groups on the bridge that absorbs visible light and as thermal stability tunable photochromic compounds.

Fig. 1 shows the calculated heat of formation of dicyano[2.*n*]metacyclophanes (**3a**–**c** and **4a**–**c**) by AM1 in MOPAC 97. As the *n* number becomes smaller, the heat of formation of the open-ring form (dot line) becomes larger. This is due to the increase of the strain energy in such small cyclophanes. On the other hand, the heat of formation of the closed-ring form (solid line) decreases by decreasing *n* number. As shown in Fig. 1, when the *n* number in [2.*n*]metacyclophan-1-ene

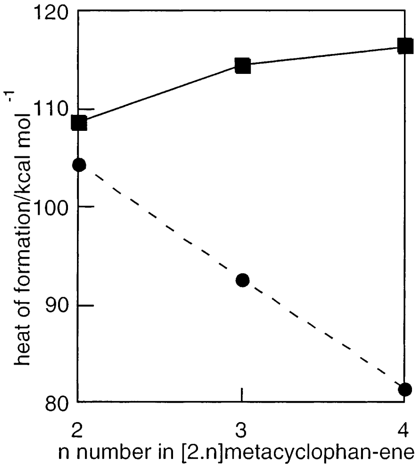

Figure 1. AM1 calculated heat of formation of 1,2-dicyano[2.*n*]metacyclolophan-1-ene (**3a**–**c** and **4a**–**c**) (solid line, closed-ring form; dot line, open-ring form).

Keywords: photochromism; cyclophane; ring-closure reaction; ring-opening reaction.

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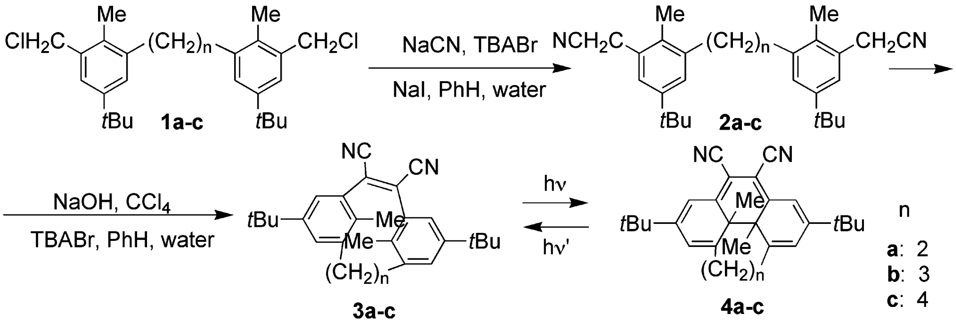

Scheme 1.

becomes smaller, the heat of formations of the open- and the closed-ring forms become closer because of their strain. Therefore, it is expected that the closed-ring form of small [2.*n*]metacyclophan-1-ene is more stable thermally than that of large metacyclophan-1-ene since the activation energy from the closed ring form of the small cyclophane would be larger than that of the large cyclophane.

The synthesis of 1,2-dicyano[2.*n*]metacyclphan-1-enes (**3a**–**c**)[4] is shown in Scheme 1. Compounds **3a**–**c** have been synthesized via five steps from commercially available *t*-butyltoluene. The preparation of bis(chloromethyl) derivatives **1a**–**c** was carried out as in the literature.[5] The bis(cyanomethyl) derivatives **2a**–**c** were obtained by the treatment of **1a**–**c** with NaCN in the presence of a phase transfer catalyst. Although a similar intermolecular coupling reaction of the cyanomethylarene to form dicynoethene linkage has been described in the literature,[6] the ring closure reaction to form cyclophane (**2** to **3**) is found to be applicable to the synthesis of small cyclophane systems by intramolecular dicyanoethene formation. Surprisingly, the yield for the formation of the smallest [2.2] system, which is supposed to be the most distorted, turned out to be the best compared with the others. With an even number of incorporated methylene groups in the cyclophane bridge, the yields of the ring closure reaction were fairly good ($n=2$, 32%; $n=4$, 21%), and a poor yield was found when there was an odd number of methylene groups in the cyclophane bridge ($n=3$, 4.9%). This is probably due to the conformation of the intermediates. The intermediates for [2.2] and [2.4]metacyclophane-1-enes are more stable than that for [2.3]cyclophan-1-ene. The ^{1}H NMR spectral signal of the inner methyl groups of [2.4], [2.3] and [2.2] metacyclophan-1-enes were observed at 1.02, 0.86 and 0.73 ppm (recorded at 270 MHz at 298 K in $CDCl_3$), respectively. These methyl protons were shifted to the higher magnetic field by the shielding effect of the opposite benzene rings.[7] Therefore, in this condition, the synthesized metacyclophan-1-enes are assigned *anti*-conformation, and are suitable for photocyclization reaction.[3b,8]

The photochromic reactions of [2.2] **3a** and [2.3] **3b** are shown in Figs. 2 and 3. The thermal ring-opening reaction (back reaction) was too fast to measure the absorption spectral change of compound **3c** to **4c** ($n=4$). Upon irradiation of 366 nm light, a pale yellow solution of **3a** or **3b** in hexane–CH_2Cl_2 (9:1) turned to violet and the absorption maxima appeared at 555 nm (**4a**, $\varepsilon_{555}=3540$)[9] or 555 nm (**4b**), which are attributed to the closed-ring form (**4a** or **4b**). The spectra returned to the initial one by visible light irradiation (>500 nm). The conversion of **3a** to **4a** was 68% upon irradiation with 366 nm light. The closed-ring form **4a** ($n=2$) was isolated by HPLC (silica gel, eluent: hexane/AcOEt (6:1)) since the thermal decolorlation of **4a** to give **3a** was very slow.

The closed ring forms (**4a**, **4b**) gradually isomerized to give the initial metacyclophan-1-ene at room temperature even in the dark. Thus, the photoreactions of **3a**

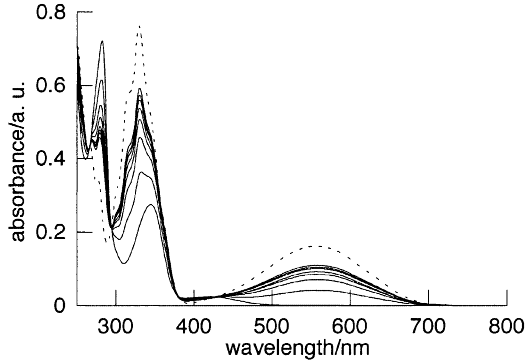

Figure 2. Absorption spectral change of **3a** in hexane–CH_2Cl_2 (9:1) upon irradiation with 366 nm light. Dot line is the spectrum of the closed-ring form **4a**.

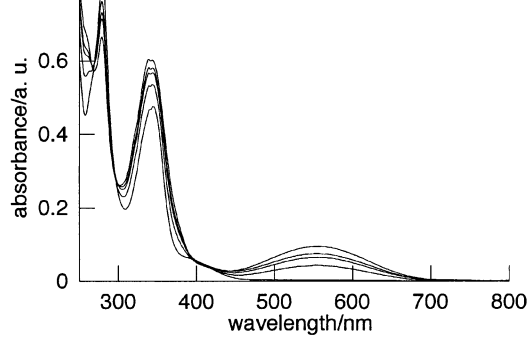

Figure 3. Absorption spectral change of **3b** in hexane–CH_2Cl_2 (9:1) upon irradiation with 366 nm light.

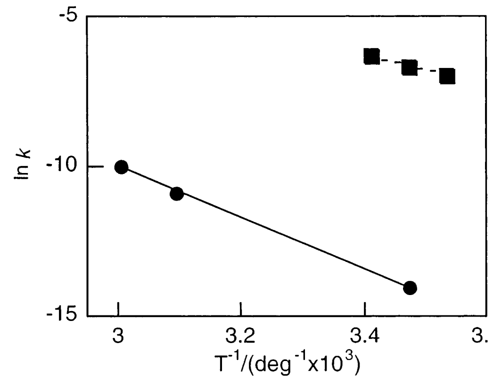

Figure 4. Arrhenius plots for thermal ring-opening reaction of **4a** (solid line) and **4b** (dot line).

and **3b** to give **4a** and **4b** are thermally reversible. The thermal isomerizations of **4a** and **4b** were studied and are from Arrhenius plots (Fig. 4). The activation energies for thermal reactions from **4a** to **3a** and from **4b** to **3b** are determined as 17.0 and 10.5 kcal mol^{-1}, respectively. The pre-exponential factors are 6.6×10^{6} s^{-1} for **4a** and 1.2×10^{4} s^{-1} for **4b**. For example, the half-life time of [2.2] **4a** at 273 K is calculated as 53 days, while that of [2.3] **4b** is 25 minutes. The difference of the activation energies of **4a** and **4b** is due to the difference of the formation of energies of the open ring form **3a** and **3b** and that of the closed ring form **4a** and **4b**.

Although the formation of the closed ring form **3b** is thermally reversible, the thermal reaction is so slow that the quantum yields for the cyclization reaction and the ring opening reaction could be estimated.[10] The quantum yield for the cyclization reaction of **3a** was 0.39 by 313 nm light and that of the back reaction of **3b** was 0.27 by 517 nm light. The quantum yield for cyclization reaction of **3a** is a little larger than 1,2-bis(benzo-1-thien-3-yl)-1,2-dicyanoethene ($\Phi_{O\rightarrow C}=0.35$),[11] since *cis–trans* isomerization was prevented and the photo-inactive *syn* conformation did not exist in the [2.2]metacyclophan-1-ene system.[3b]

Acknowledgements

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4. **3a**: mp 222.0–224.0°C; ^{1}H NMR (270 MHz, CDCl$_3$, 25°C, TMS): $\delta=0.73$ (s, 6H), 1.30 (s, 18H), 2.50 (d, $J=8$ Hz, 2H), 2.98 (d, $J=8$ Hz, 2H), 7.19 (s, 4H); MS (70 eV): m/z (%): 396 (10) [M^+], 325 (100); **3b**: mp 269.5 –271.0°C; ^{1}H NMR (270 MHz, CDCl$_3$, 25°C, TMS): $\delta=0.86$ (s, 6H), 1.31 (s, 18H), 1.98 (quintet, $J=7$ Hz, 2H), 2.42–2.52 (m, 2H), 2.62–2.72 (m, 2H), 7.16 (d, $J=2$ Hz, 2H), 7.20 (d, $J=2$ Hz, 2H); MS (70 eV): m/z (%): 410 (23) [M^+], 339 (100); **3c**: mp 264.0–265.0°C; ^{1}H NMR (270 MHz, CDCl$_3$, 25°C, TMS): $\delta=0.90$–1.11(m, 2H), 1.02 (s, 6H), 1.32 (s, 18H), 1.33–1.50 (m, 2H), 2.21–2.31 (m, 2H), 2.72–2.77 (m, 2H), 7.03 (d, $J=2$ Hz, 2H), 7.32 (d, $J=2$ Hz, 2H); MS (70 eV): m/z (%): 424 (92) [M^+], 409 (100).
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9. ^{1}H NMR spectrum of **4a** (270 MHz, CDCl$_3$, 25°C, TMS): $\delta=1.10$ (s, 18H), 2.20 (d, $J=9$ Hz, 2H), 2.61 (d, $J=9$ Hz, 2H), 5.76 (s, 2H), 6.08 (s, 2H).
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