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Synthesis and properties of novel thiaarenecyclynes

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Abstract—Novel thiaarenecyclynes 3 and 4 in which two thioether units and two benzene rings are alternately inserted into the single bonds of cyclooctatetrayne are synthesized. Their unique properties are described. © 2003 Elsevier Science Ltd. All rights reserved.

A novel family of cyclynes **1** having a hybrid ring structure of cyclyne, crown (or thiacrown) ether, and cyclophane are of great interest in view of the unique structure and the resulting properties. We have reported the synthesis of a small member, **2** (n=2, 1,3-diethynylbenzene units in **1**) of oxaarenecyclynes (X=O) in this family and its unprecedented Ag⁺-induced cyclization leading to the perylene skeleton formation.¹ Moreover, recently we have created supramolecular C₆₀ complexes with oxaarenecyclynes (n=4, 1,3-diethynylbenzene units and 1,4-di-ethynylbenzene units in **1**) having a large cavity.²



Judging from the characteristics (e.g. ionization potential, electron affinity, electro-negativity and standard

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* Corresponding author. Tel.: +81-6-6730-5880 (ext. 4121); fax: +86-6-6721-2721; e-mail: yamaguch@chem.kindai.ac.jp electrode potential) of the sulfur atom, which are quite different from those of the oxygen atom, hybrid thiaarenecyclynes (3 and 4) seem to be attractive. We report here the synthesis and unique properties of 3 and 4.

The synthesis of **3** and **4** is outlined in Scheme 1. Iodoaniline (**5a**: *m*-, **5b**: *p*-) was converted to triazene derivative **6**, which has a propargyl alcohol unit introduced by Sonogashira Pd coupling.³ Iodination⁴ of the triazene units of **6** gave iodo-derivative **7**. The Pd coupling between **7** and bispropargylsulfide⁵ provided compound **8**, which was converted to dibromo-derivative **9** with CBr₄/PPh₃. Finally, treatment of **9** with Na₂S/Al₂O₃⁶ provided the desired hybrid thiacyclyne **3** (53.7% overall yield) and **4** (9.1% overall yield), respectively.⁷

The structure of **3** and **4** was confirmed by spectral data (¹H, ¹³C NMR and HRMS).⁸ The ¹H and ¹³C NMR spectra of **3** and **4** are simple, indicating the high symmetry of molecules. Aromatic protons (δ 6.91) of **4** were observed up-field to those of **8b** (δ 7.36), and **9b** (δ 7.37). Since the chemical shifts of protons on the benzene ring of **3** (δ 7.27–7.57) are comparable to those of acyclic compound **8a** (δ 7.24–7.50) and **9a** (δ 7.26–7.52), the up-field shift of the aromatic proton of **4** seems to be due to shielding effects by both benzene rings which are in face-to-face relation (see Fig. 1).

The structures of **3** and **4** were determined by singlecrystal X-ray analysis (Fig. 1).⁸ As shown in Figure 1, **3** is not coplanar and has a small bond angle strain at C-C=C-C (175.3 and 177.8°, 179.6 and 177.1°) and C-S-C (100.1 and 101.4°). The size and shape of the

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Scheme 1. *Reagents and conditions*: (i) HCl aq., NaNO₂, Et₂NH, K₂CO₃, CH₃CN, H₂O; (ii) propargylalcohol, Pd(PPh₃)₂Cl₂, CuI, Et₃N; (iii) I₂, MeI; (iv) bispropargylsulfide, Pd(PPh₃)₂Cl₂, CuI, Et₃N; (v) CBr₄, PPh₃, CH₂Cl₂; (vi) Na₂S/Al₂O₃, EtOH, CH₂Cl₂.



Figure 1. ORTEP drawing of 3 and 4.

cavity of **3** are similar to those of **2**.¹ Thiaarenecyclyne **4** having 1,4-diethynylbenzene units is also not coplanar as shown in Figure 1. The bond angle strain at C–C=C–C (175.0 and 177.7°, 178.8 and 178.1°) is almost the same, but the bond angle strain at C–S–C (102.3 and 102.3°) is slightly larger than that of **3**. Both benzene rings (the average distance: 3.5 Å) are completely parallel and overlap each other.

The result is consistent with that obtained from ¹H NMR. However, the ¹H NMR spectra of **3** and **4** at different concentrations did not show any self-assembling due to π - π stacking.

As a characteristic property of 3 and 4 we were greatly interested in their reaction behavior toward AgOTf, because it was reported that carbocyclic cyclynes gave π complexes with Ag(I) due to Ag(I)-triple bond interaction (for instance, a sandwich-type Ag(I)- π complex from cyclotriyne⁹ and an included 1:1 Ag(I)- π complex from cyclotetrayne¹⁰), while oxaarenecyclyne 2 provided quantitatively the tetrahydrofuran ringfused pervlene 10 by Ag(I)-induced cyclization. Furthermore, reaction of unsaturated thiacrown ethers having CH=CH groups instead of CH₂CH₂ groups with AgOTf was reported to afford an inclusion complex having Ag-S bonding after 5 h.¹¹ Thus, we examined the reaction of 3 and 4 with AgOTf in benzene at ambient temperature, respectively. As a result, we observed the formation of precipitates immediately after mixing of the reaction components for both cases. In the IR spectra of both precipitates characteristic bands for thiaarenecyclyne (3 or 4) and triflate are observed although their absorption bands are shifted to somewhat shorter wavelength, suggesting that the precipitates could be the silver complexes (thiaarene-cyclyne: $Ag^+ = 1:1$ both for cases).





4

Atom	3	3–Ag complex	4	4–Ag complex
	$\overline{\delta_{\rm H}}$, mult, intgrat (J in Hz)	$\delta_{\rm H}$, mult, intgrat (J in Hz)	$\delta_{\rm H}$, mult, intgrat (<i>J</i> in Hz)	$\delta_{\rm H}$, mult, intgrat (J in Hz)
1	3.73, s, 8H	3.87, s, 8H	3.68, s, 8H	3.75, s, 8H
2	7.27, A B ₂ X, 4H	7.28, A B ₂ X, 4H	6.91, s, 8H	6.92, s, 8H
3	7.18, AB ₂ X, 2H	7.17, AB ₂ X , 2H		
4	7.57, AB ₂ X, 2H (1.5)	7.55, AB ₂ X, 2H (1.2)		

^a Spectra were recorded at 20°C. Chemical shift values are in ppm relative to 3.58 ppm in THF.



Figure 2. ORTEP drawing of 3-Ag complex (a; linear polymer, b; cyclic dimer and c; packing structure).

As shown in Table 1, ¹H NMR signals for the methylene groups to adjacent sulfur groups for both complexes appeared more downfield ($\Delta \delta = 0.14$ ppm for 3-Ag complex, and $\Delta \delta = 0.06$ ppm for 4-Ag complex) than those for aromatic protons ($\Delta \delta = 0.01-0.02$ ppm), indicating the formation of an Ag(I)-S bond.

Whether the Ag(I) ions are placed inside (inclusion) or outside the ring is of particular interest. The X-ray structure (linear polymer and cyclic dimer including the Ag–S bond) of 3–Ag complex (Fig. 2)¹² clearly indicates Ag(I) ions to be placed outside the ring, different from the unsaturated thiacrown ether–Ag(I) complex.¹¹ The marked difference in complexation rate is explained in terms of the difference in structure of both Ag(I) complexes.

We examined the thermal cyclization of 3 to 11 by refluxing in 1,3,5-trimethylbenzene for 6 h under an argon atmosphere. As a result, we observed formation of 11 as the major product (Table 2). Under the same conditions, oxaarenecyclyne 2 gave also a perylene derivative (10 in Table 2), but 4 did not provide such sort of cyclization product. The thermal cyclization leading to 10 and 11 is considered to proceed as shown in Scheme 2.

An additional characteristic property of **3** and **4** is the formation of complexes with C_{60} in CHCl₃, which is shown by a characteristic increase in 438 nm

absorption² as exemplified by Figure 3. This is very interesting because (1) the cavity size of **3** and **4** is smaller than the size of C_{60} , and (2) the oxa-analog, **2**, having almost the same cavity size as **3** does not form the C_{60} complex. The result suggests a particular interaction between the sulfur atom and C_{60} .¹³ Details of the supramolecular C_{60} complexes with **3** and **4** will be reported in due course.

Table 2. ¹H NMR (300 MHz, δ (CDCl₃)) spectral data of perylene derivatives (10 and 11)

Atom	10 (X=O)	11 (X=S)	
	$\delta_{\rm H}$, mult, intgrat (J in Hz)	$\delta_{\rm H}$, mult, intgrat (<i>J</i> in Hz)	
1	5.56, s, 4H	4.71, <i>s</i> , 4H	
2	5.28, s, 4H	4.38, s, 4H	
3	7.66, s, 2H	7.73, s, 2H	
4 (or 6)	7.37, d, 2H (7.8)	7.76, d, 2H (7.5)	
5	7.59, t, 2H (7.8)	7.58, t, 2H (7.5)	
6 (or 4)	7.77, d, 2H (7.8)	7.88, d, 2H (7.5)	



Scheme 2. Pathway of thermal reaction of heteroarenecyclynes (2 and 3).



Figure 3. Absorption spectra of C_{60} (3.25×10⁻⁵ mol dm⁻³) in the presence of thiaarenecyclyne 3 in CHCl₃. Concentration of 3: 0.00, 3.25, 7.50, 14.0 (×10⁻⁵ mol dm⁻³) from bottom.

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- 8. Spectral data for 3: ¹H NMR (300 MHz, CDCl₃), δ 3.70 (s, 8H), 7.17 (AB₂X, 2H), 7.32 (AB₂X, 4H), 7.61 (AB₂X, 2H); ¹³C NMR (75.4 MHz, CDCl₃), δ 21.1, 83.1, 85.7, 123.3, 128.2, 130.9, 135.8; IR (KBr, cm⁻¹) 2933, 2910, 2223, 1592, 1567, 1477, 1104, 1247, 1220, 900, 892, 798, 682, 673, 493, 460; HRMS (FAB, positive ion mode) calcd 368.0693 for C₂₄H₁₇S₂, found 369.0754.

Spectral data for 4: ¹H NMR (300 MHz, CDCl₃), δ 3.65 (s, 8H), 6.95 (s, 8H); ¹³C NMR (75.4 MHz, CDCl₃), δ 23.2, 83.4, 87.5, 122.6, 130.9; IR (KBr, cm⁻¹) 2939, 2904, 2206, 1913, 1508, 1402, 1274, 1245, 1220, 1203, 894, 836, 719, 707, 673, 541, 493; HRMS (EI, positive ion mode) calcd 368.0693 for C₂₄H₁₇S₂, found 368.0674.

Crystal data for **3**: $C_{24}H_{16}S_2$, M=368.51, triclinic, $P\overline{1}$, a=8.605(1), b=10.9919(11), c=11.307(2) Å, $\beta=88.17(1)^\circ$, V=923.8(3) Å³, Z=2, $D_{calcd}=1.325$ g/cm³, R=0.041, $R_w=0.103$, Rigaku Mercury, 10476 measured reflections, Mo-K α , 4139 unique ($R_{int}=0.029$), 251 variables [$I>-10.00\sigma(I)$]. Crystal data for 4: $C_{24}H_{16}S_2$, M=368.51, monoclinic, $P2_1/c$, a=8.635(2), b=12.727(3), c=8.809(1) Å, $\beta=108.878(4)^\circ$, V=916.0(4) Å³, Z=2, $D_{calcd}=1.336$ g/cm³, R=0.040, $R_w=0.096$, Quantum CCD area detector coupled with a Rigaku AFC8 Diffractometer, 7343 measured reflections, Mo-K α , 2014 unique ($R_{int}=0.053$), 142 variables [$I>2\sigma(I)$].

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- 12. Crystal data for **3–Ag** complex: $[Ag_2(C_{24}H_{16}S_2)_2]$ -(CF₃SO₃)₂(C₆H₆) (for linear polymer) $[Ag_2(C_{24}H_{16}S_2)_2]$ -(CF₃SO₃)₂ (for cyclic dimer), M=2579.93, triclinic, $P\bar{1}$, a=12.2131(13), b=15.051(1), c=15.830(2) Å, $\beta=$ 67.519(5)°, V=2502.2(4) Å³, Z=1, $D_{calcd}=1.712$ g/cm³, R=0.029, $R_w=0.092$, Rigaku Mercury, 19893 measured reflections, Mo-K α , 10931 unique ($R_{int}=0.018$), 10931 variables [$I>-0.00\sigma(I)$].
- 13. From Yoshida's concept,² which regards C_{60} as a transition metal-like superatom, this interaction is considered to be coordination of the sulfur atom to C_{60} . This is understandable from **3** (or **4**)-Ag⁺ complex formation.