Cyclic Oligo(thio-2,5-thienylenes) (Sulfur-bridged Calixarenes)

Juzo Nakayama,* Naoki Katano, Yoshiaki Sugihara, and Akihiko Ishii
Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338

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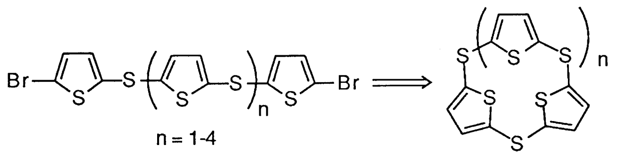
Thiacalix[4]-, thiacalix[5]-, and thiacalix[6]arenes were synthesized by condensation of dibromo derivatives of the corresponding linear oligomers with Na_2S. An X-ray diffraction analysis was performed on the last compound.

We have recently reported the preparation of a series of oligo(thio-2,5-thienylenes) and their dibromo derivatives (**1**).[1,2] As a natural consequence, our next target was focused on the conversion of these oligomers into the corresponding cyclic oligomers (thiacalix[n]arenes) (**2**). These compounds would be of much interest as cyclic oligo(thio-2,5-thienylenes), macrocyclic thioethers, and heterocalixarenes. Very recently König et al. have communicated the preparation of the thiacalix[4]arene **2b** (n =2 for **2**) which is composed of four thiophene and sulfide moieties.[3,4] They obtained **2b** only in very small amounts (1% yield) by reaction of 2,5-dilithiothiophene with SCl_2. This prompted us to communicate our results in this field preliminarily.[5]



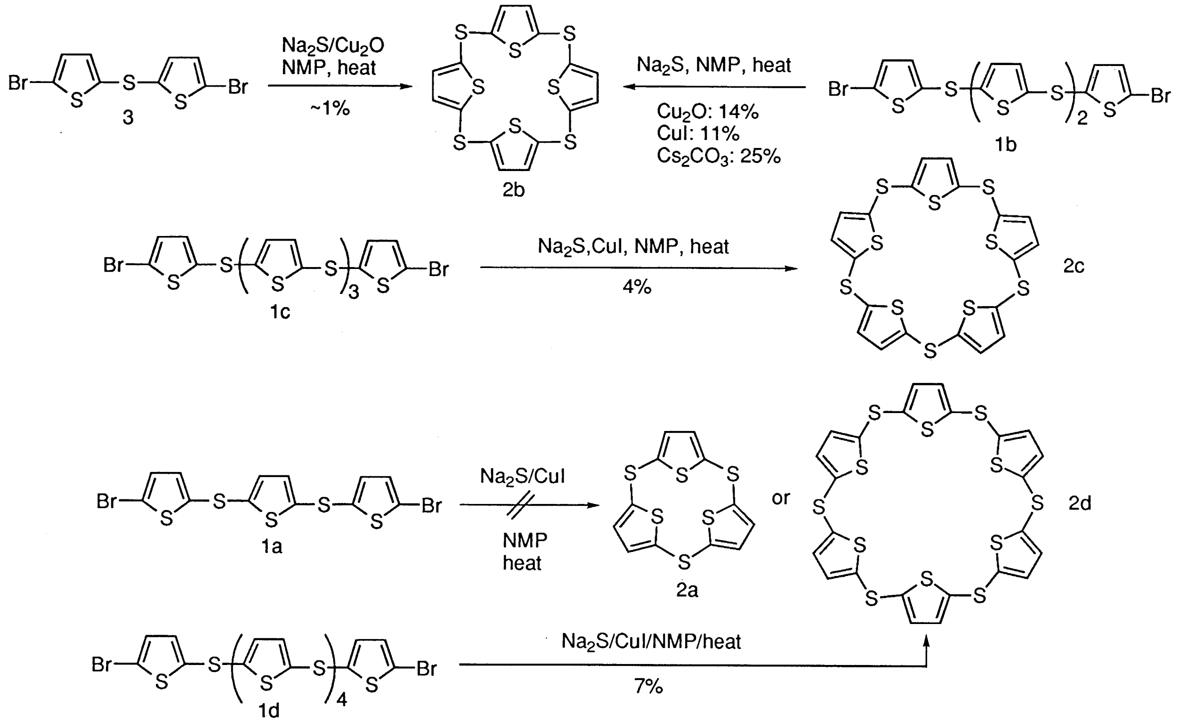
n = 1-4

1 **2**

Our first attempt to prepare the thiacalix[4]arene **2b** by heating the dibromide **3**[1] with anhydrous Na_2S[6] in NMP (1-methyl-2-pyrrolidinone) at 180-190 °C in the presence of Cu_2O[7] gave the desired product in very low yield with difficulty of its separation from other products.[8] We then tried the preparation of **2b** by heating the dibromide **1b**[1] with Na_2S in NMP at 180-190 °C in the presence of Cu_2O or CuI. These reactions gave **2b** in 14 and 11% yields. The reaction was faster in the presence of CuI than in the presence of Cu_2O (76 h for Cu_2O; 21 h for CuI). Finally we found that a more improved yield of **2b** (25%) was produced, when **1b** was heated with Na_2S in the presence of Cs_2CO_3 at 140-150 °C for 23 h. NMR data[9] of our calixarene **2b** agreed with those reported by König et al.[3,8] Thus, the ^1H NMR spectrum showed only one singlet at δ 6.98 and the ^{13}C NMR spectrum only two peaks at δ 132.2 and 140.4, which are indicative of the chemical equivalency of the four thiophene rings. In these syntheses, formation of higher calixarenes containing eight or more thiophene rings was not observed.

Similarly, the thiacalix[5]arene (**2c**)[9] was prepared in 4% yield by heating the dibromide **1c**[1] with Na_2S in NMP at 180-190 °C for 20 h in the presence of CuI.[10] The ^1H NMR spectrum of **2c** showed only one singlet at δ 7.05 and the ^{13}C NMR spectrum only two peaks at δ 133.4 and 138.5.

Finally, preparation of the thiacalix[3]arene (**2a**) and thiacalix[6]arene (**2d**) was examined. The reaction of the dibromide **1a**[1] with Na_2S was first examined under a variety of conditions by changing concentration of substrates, reaction



temperatures, and amount of CuI. However neither thiacalix[3]arene **2a** nor **2d** formed; the reaction always gave complex mixtures consisting of polymeric compounds having a linear structure. Thus, preparation of **2d** was examined by heating the dibromide **1d**[1] with Na_2S in NMP at 180-190 °C for 20 h, which produced the expected calix[6]arene **2d** in 7% yield.[10] Also for this compound, the ^1H NMR showed only one singlet at δ 7.02 and the ^{13}C NMR only two peaks at δ 132.9 and 138.0.

Figure 1 shows UV/Vis spectra of **2b-d** determined in $CHCl_3$. In linear oligomers **1**, molar absorption coefficients (ε) and the longest absorption maxima (λ_{max}) increase progressively with an increasing number of thiophene ring.[1] However, in cyclic series, although ε values increase with an increasing number of thiophene ring, λ_{max} values do not; 298 nm for **2b**, 288 for **2c**, and 294 for **2d**. These suggest that the conformation of **2b**, whose λ_{max} is the largest, is the most flexible, and thus conjugation between thiophene units through sulfide bonding takes place most effectively for this compound.

Single crystals suitable for X-ray diffraction analysis were obtained only for **2d** after much effort. Molecular structure of **2d**, in which six thiophene rings are arranged in a geometrically regular way, is given in Figure 2.[11] All of the thiophene rings and sulfide bonds are normal in bond lengths and bond angles. The followings are informative on the molecular geometry and the size of the cavity of **2d**. The sulfur atoms S(3) and S(9), and S(5) and S(11) of the diagonal thiophene rings exist in a face-to-face way with interatomic distances of 6.71 and 8.97 Å, respectively, while the sulfur atoms S(1) and S(7) of the remaining one pair of the diagonal thiophene rings are placed in an opposite direction with interatomic distance of 9.61 Å. The six sulfur atoms of the sulfide bond constitute a distorted chair-like structure with interatomic distances of S(2)-S(8), 11.23; S(4)-S(10), 8.89; S(6)-S(12), 11.86 Å.

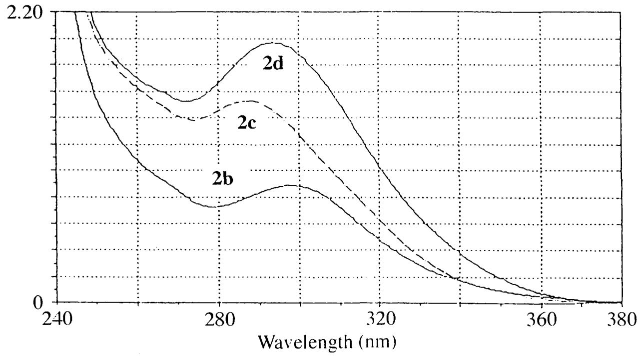


Figure 1. UV/vis spectra of **2b-d** in $CHCl_3$.

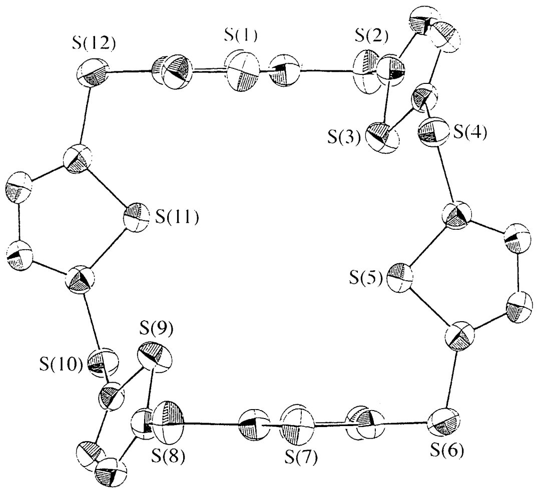


Figure 2. Molecular structure of **2d**.

References and Notes

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5 This work was presented at the 27th Congress of Heterocyclic Chemistry, October, 1996, Morioka, Japan, Book of Abstracts, p. 358.
6 Anhydrous Na_2S was purchased from Aldrich.
7 E. Jones and I. M. Moodie, *Org. Synth.*, Coll. Vol. VI, 558 (1988).
8 The use of bis(5-lithio-2-thienyl) sulfide, instead of 2,5-dilithiothiophene, failed to give **2b**.[3]
9 In every synthesis of **2**, **1** and Na_2S were used in the molar ratio of 1:1. Thiacalix[4]arene (**2b**): mp 242.0-243.5 °C (lit.,[3] mp 200 °C, dec); colorless granules (from $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ = 6.98 (s); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ = 132.2 (d), 140.4 (s); UV/vis ($CHCl_3$) λ_{max} (ε) 298 (17700); MS *m/z* 456 (M^+). Thiacalix[5]arene (**2c**): mp 196-197 °C; colorless flocks (from cyclohexane); ^1H NMR (200 MHz, $CDCl_3$) δ = 7.05 (s); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 133.4 (d), 138.5 (s); UV/vis ($CHCl_3$) λ_{max} (ε) 288 (30600); MS *m/z* 570 (M^+). Thiacalix[6]arene (**2d**): mp 234-235 °C; colorless needles (from chlorobenzene); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.02 (s); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 132.9 (d), 138.0 (s); UV/vis ($CHCl_3$) λ_{max} (ε) 294 (39400); MS *m/z* 684 (M^+).
10 Preparation of **2c** and **2d** in the presence of Cs_2CO_3 is under way.
11 Cystal data for **2d**: $C_{24}H_{12}S_{12}$, M_r = 685.15, triclinic, $P1$, a = 5.670(1) Å, b = 9.169(3) Å, c = 13.598(3) Å, α = 98.44(1) °, β = 90.59(1) °, γ = 104.38(1) °, V = 676.6(3) Å^3, Z = 1, D_x = 1.681 Mgm^{-3}, Mo K_α radiation, λ = 0.71073 Å, T = 298 K, crystal size; 0.32x0.04x0.03 mm, 1506 observed reflections, $I > 3.00\sigma$ (I), R = 0.046, R_w = 0.053.