

to many previous studies of dissociation. Our time-resolved results predict a homogeneous line broadening of the transitions to 83 and 95  $\text{cm}^{-1}$  that is much larger than the one to 198  $\text{cm}^{-1}$ , consistent with the observed broadening in the excitation spectra.<sup>4b</sup> It is important, however, to note that while these large line widths predict fast decay of the initially excited state, the rate with which the predissociated stilbene is produced is much lower ( $\tau = 34\text{--}45$  ps) and is limited by the VP rate from the intermediate state to which energy has been redistributed. Thus, the line width (if homogeneous) reflects the initial decay process (e.g., IVR) which may not be the rate-determining step of the reaction. This is consistent with the proposal of ref 4b for the description of the line broadening of the stilbene-helium excitation spectra. Line-width measurements have been used previously for deducing predissociation rates<sup>9a</sup> and their dependence on the mode excited<sup>9b</sup> in the ground electronic state of relatively smaller molecules. The separation of IVR from VP made here for large molecules could also be important in describing the dissociation dynamics of these systems, as discussed recently.<sup>10</sup>

Real-time studies of IVR,<sup>11</sup> VP,<sup>12,2</sup> and reaction rates<sup>1,13</sup> will certainly improve our understanding of dynamics and hopefully find general conditions for nonstatistical reactions such as those reported here.

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## Hexakis(1,3-dithiol-2-ylidene)cyclohexane with Two Different Conformations of the Six-Membered Ring

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Since Reppe discovered the synthesis of cyclooctatetraene by the tetramerization of acetylene using nickel catalyst,<sup>1</sup> active investigation has been continuing toward cyclooligomerization of many olefins, acetylenes, and cumulenes catalyzed by nickel and

the other transition-metal complexes.<sup>2</sup> However, it was quite unknown whether cyclooligomerization of cumulenes bearing sulfur substituents occurs by a transition-metal complex catalyst. Recently we succeeded in the synthesis of tetrakis(1,3-dithiol-2-ylidene)cyclobutane, a promising electron donor for organic metals, by Ni(0)-catalyzed reductive cyclodimerization of 2,2'-(1,2-dibromoethanediyldene)bis(1,3-dithiole).<sup>3</sup> By using DMF as a medium of the reaction in place of THF, cyclotrimerization was found to proceed preferentially to provide a new type of [6]radialene, hexakis(1,3-dithiol-2-ylidene)cyclohexane (**1**). Very interestingly, the central six-membered ring of **1** was found to be in a twisted-boat conformation, which was converted to a thermodynamically more stable chair one by heating in solution or by electrochemical two-electron oxidation at room temperature. In this paper we wish to report the synthesis, structural feature, and characteristic properties of dodecacarbomethoxy- and hexabenzosubstituted derivatives of **1**, **1a** and **1b**, respectively.

Under argon atmosphere the reaction of 2,2'-(1,2-dibromoethanediyldene)bis(4,5-dicarbomethoxy-1,3-dithiole) (**2a**)<sup>4</sup> with 5 equiv of Zn-Cu<sup>5</sup> in the presence of 0.3 equiv of Ni(PPh<sub>3</sub>)<sub>4</sub> in dry DMF (room temperature, 0.5 h) gave **1a** (orange crystals, mp > 300 °C)<sup>6</sup> in 35% yield together with the corresponding [4]radialene (yield 5%). In a similar manner **1b** was obtained as yellow crystals (mp > 300 °C) from 2,2'-(1,2-dibromoethanediyldene)bis(1,3-benzodithiole) (**2b**)<sup>4</sup> in 72% yield<sup>7</sup> (Scheme 1). Of the two [6]radialenes, **1b** was successfully obtained as single crystals by recrystallization from CS<sub>2</sub>/chlorobenzene/ether,<sup>8</sup> and the molecular structure was determined by the X-ray crystallographic analysis (see Figure 1).<sup>9</sup> The remarkable structural feature of **1b** is the twisted-boat conformation of the central

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(4) The dibromo derivatives were synthesized in almost quantitative yields by the reaction of the corresponding 2,2'-(ethanediyldene)bis(1,3-dithiole) with 2 equiv of NBS in CH<sub>2</sub>Cl<sub>2</sub> at room temperature.

(5) Ni(PPh<sub>3</sub>)<sub>4</sub> was generated in situ by the reaction of Ni(PPh<sub>3</sub>)<sub>2</sub>Br<sub>2</sub> with 20 equiv of Zn-Cu couple in the presence of 2 equiv of PPh<sub>3</sub> and immediately used for the reductive cyclotrimerization of **2**. By use of the other Ni(0) complexes, e.g., Ni(1,5-cyclooctadiene)<sub>2</sub> and Ni(PPh<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>, in place of Ni(PPh<sub>3</sub>)<sub>4</sub>, **1** was also obtained and showed the same <sup>13</sup>C NMR and electronic spectra. Attempts to isolate 2,2'-(ethenediyldene)bis(1,3-dithiole)s (cumulenes substituted with 1,3-dithioles) under several conditions were unsuccessful.

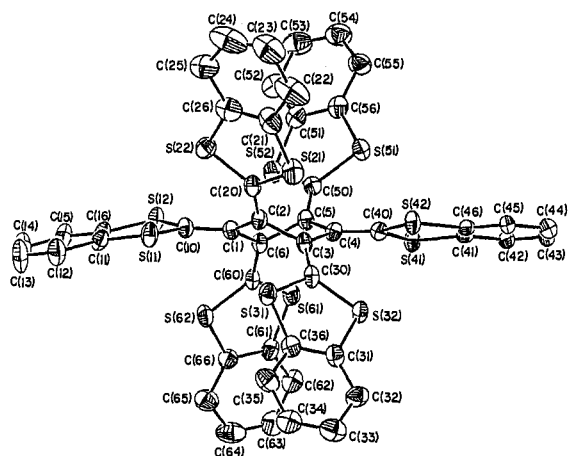
(6) Decarbomethoxylation of **1a** was carried out by heating with LiBr-H<sub>2</sub>O in HMPA at 95–155 °C. However, the targeted parent system was not obtained.

(7) The corresponding [4]radialene was also obtained in 5% yield. All the [4]- and [6]radialenes showed satisfactory elemental analyses and mass spectra.

(8) When **1a** was recrystallized from CS<sub>2</sub>/benzene/hexane, apparently single crystals were formed in the solution. However, isolation of the crystals from the solution was unsuccessful, because the crystals became powdered as a result of ready evaporation of the solvents.

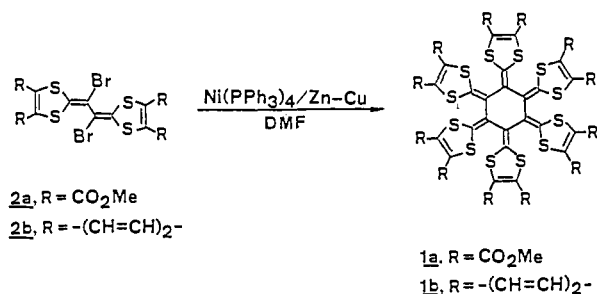
(9) Crystal data of **1b**: C<sub>48</sub>H<sub>24</sub>S<sub>12</sub>, FW = 985.5, monoclinic, space group P2<sub>1</sub>/n, *a* = 20.978 (5) Å, *b* = 12.318 (2) Å, *c* = 21.887 (4) Å, β = 117.58 (1)°, *U* = 5013 (2) Å<sup>3</sup>, *D<sub>x</sub>* = 1.305 g cm<sup>-3</sup>, *Z* = 4. X-ray diffraction data were measured on a Rigaku four-circle diffractometer using nickel-filtered Cu Kα radiation. A total of 8066 reflections were collected up to 2θ = 120° by the θ-2θ scan technique. The crystal structure was solved by the direct method (MULTAN-78) (Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. "MULTAN-78: A System Computer Program for the Automatic Solution of Crystal Structures from X-ray Diffraction Data"; University of York, England, and Louvain, Belgium, 1978) and refined by the full-matrix least-squares (XRAY-76) (Stewart, J. M. "XRAY-76"; Report TR-446, University of Maryland, 1976) by using the 6182 observed reflections [*I*<sub>o</sub> > 3σ(*F*<sub>o</sub>)] to the *R* index of 0.134 including non-hydrogen atoms with anisotropic temperature factors and hydrogen atoms with isotropic ones. The limited accuracy of the refinement resulted from the difficulty of the assignment for some diffused electron densities which may be from the disordered packing of the crystal solvent, CS<sub>2</sub>, chlorobenzene, or ether. The second crystal obtained from the mixed solution of CS<sub>2</sub>, chlorobenzene, and hexane is isomorphous with the present crystal (*a* = 20.985 (5) Å, *b* = 12.341 (2) Å, *c* = 21.896 (4) Å, β = 117.47 (1)°). The full set of data on the second crystal were collected by the use of graphite monochromatized Mo Kα radiation up to 2θ = 50°. The structure analysis gave the same difficulty as the present one. The detailed molecular structure of **1b** should await the X-ray analysis on the other form of the crystal.

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**Figure 1.** Molecular structure of **1b** by an ORTEP drawing with thermal ellipsoid at 30% probability level for non-hydrogen atoms. The hydrogen atoms were omitted for clarity.

### Scheme I



six-membered ring. This is the first example of crystallographic determination of a six-membered ring in a twisted-boat conformation, although there are reports of infrared spectroscopic detection of the twisted-boat conformation of cyclohexane itself<sup>10</sup> and of isolation of sterically crowded cyclohexanes preferentially adopting a twisted-boat conformation.<sup>11</sup> The torsional angles around C—C bonds in the ring are 63.2° for the C(2)—C(3) bond, 62.9° for the C(5)—C(6) bond, and about 30° for the other bonds. The present structure is strikingly different from the crystal structure of hexakis(ethylidene)cyclohexane,<sup>12</sup> which has the [6]radialene skeleton in a chair conformation slightly flattened compared with that of cyclohexane itself. The mean values of endocyclic C—C bond and exocyclic C=C bond distances are 1.49 and 1.34 Å, respectively. The 1,3-dithiole-2-ylidene rings are puckered with the puckered angles from 0.6 to 16.6°.

By heating in appropriate solvents both the [6]radialenes were found to be converted to new compounds, **1a'** (yellow crystals, mp > 300 °C) and **1b'** (pale yellow crystals, mp > 300 °C), respectively,<sup>13</sup> which also have hexakis(1,3-dithiole-2-ylidene)-cyclohexane structures from the elemental analyses and mass and <sup>13</sup>C NMR spectra.<sup>14</sup> In the electronic spectra, **1a',b'** showed visible absorption bands at the shorter wavelength region compared

with those of **1a,b** ( $\lambda_{\max}^{\text{CHCl}_3}$  (log  $\epsilon$ ) 331 (4.79), 386 nm (4.50) for **1a** and 286 (4.56), 354 nm (4.65) for **1a'**;  $\lambda_{\max}^{\text{benzene}}$  (log  $\epsilon$ ) 338 (4.55), 393 nm (4.23) for **1b** and 354 nm (4.67) for **1b'**), suggesting less effective  $\pi$  conjugation between 1,3-dithiole rings for **1a',b'**. Also, the different electrochemical behavior between **1** and **1'** corresponds to the above result. Thus, the cyclic voltammograms, which were measured in the voltage range of 0 to +2.0 V vs. Ag/AgCl at room temperature,<sup>15</sup> showed three oxidation waves at each potential of +0.73, +0.89, and +1.13 V for **1a** and of +0.43, +0.65, and +0.81 V for **1b**,<sup>16</sup> while for the converted products only one oxidation wave appeared at considerably higher positive potential (+1.14 V for **1a'** and +0.82 V for **1b'**).<sup>16</sup> The interesting phenomena were observed in the cyclic voltammetric measurements of **1a,b**. At the first scanning, three oxidation waves appeared as described above. However, as the scanning number increases, these waves gradually disappeared and instead one new wave corresponding to that of **1a',b'** began to appear. On the basis of the measurement in the limited voltage range, it is indicated that such a change occurs at the second wave, which is due to oxidation from the radical cation to dication states of **1a,b**. From these results, particularly the electronic spectra,<sup>17-20</sup> it is apparent that the six-membered ring in **1a',b'** has a chair conformation, where two neighboring 1,3-dithiole rings interact less effectively.

As compared with tetrakis(1,3-benzodithiole-2-ylidene)cyclobutane,<sup>21</sup> **1b** has rather the lower first oxidation potential. This might bring much expectation that **1b** can also be used as a donor for organic metals. Unfortunately, **1b** could not form charge-transfer complexes even with familiar strong acceptors such as tetrafluorotetracyanoquinodimethane and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone.

**Supplementary Material Available:** Tables of fractional atomic coordinates and interatomic bond distances in **1b** and physical properties and spectral data of all new compounds, **1a,a'** and **1b,b'** (4 pages). Ordering information is given on any current masthead page.

(15) The cyclic voltammograms were measured in CH<sub>2</sub>Cl<sub>2</sub> (**1a,a'**) or benzonitrile (**1b,b'**) containing 0.1 M *n*-Bu<sub>4</sub>NClO<sub>4</sub> as supporting electrolyte by use of platinum working and counter electrodes and a standard Ag/AgCl reference electrode (scan rate: 50 mV/s).

(16) For **1a,b** the first wave appearing at the lowest potential region is electrochemically reversible, but the second and third waves are irreversible. From change of peak currents with respect to sample concentrations, it is determined that the first and second waves involve one-electron transfer, respectively, and in the third wave two electrons migrate. On the other hand, for **1a',b'** the observed one wave, involving migration of two electrons, is electrochemically irreversible.

(17) In order to determine the distinct molecular structure of **1'**, the X-ray crystallographic analysis is necessary. However, many attempts to get the single crystals available for this analysis by recrystallization from the solvent systems of (CH<sub>2</sub>Cl<sub>2</sub>, benzene, or chlorobenzene)/hexane for **1a'** and of CS<sub>2</sub>/(benzene, chlorobenzene, toluene, benzonitrile, or anisole)/hexane or cyclohexane for **1b'** were unsuccessful. The chair conformation of **1'** can be determined from the close relationship of the electronic absorption band in the longest wavelength region,  $\lambda_{\max}$ , vs. the dihedral angle between two neighboring  $\pi$  systems (a measure for the  $\pi$ -conjugation degree),  $\theta$ . Thus, in a series of permethylated [n]radialenes, their  $\lambda_{\max}$ 's tend to shift to the shorter wavelength region with increasing number of central *n*-membered ring (i.e., with decreasing  $\theta$ ): 309.5 (hexane), 307 (sh) (cyclohexane), 284 (sh) (cyclohexane), and 248 nm (cyclohexane) for the [3]-,<sup>18</sup> [4]-,<sup>19</sup> [5]-,<sup>20</sup> and [6]-radialenes.<sup>19</sup> Such a relation could be applicable to **1** and **1'** with the same 1,3-dithiole [6]radialene structures. From  $\lambda_{\max}(\mathbf{1}) > \lambda_{\max}(\mathbf{1}')$  (see electronic spectral data in the text) and the minimal  $\theta$  value of 38° for **1** (from the X-ray data), **1'** should have a larger  $\theta$  value than 38°, indicating that the conformation is undoubtedly chair.

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(13) For instance, when **1a** and **1b** were heated to 79 °C in xylene, the conversion rates obeyed the first-order kinetics and the half-lives ( $t_{1/2}$ ) were 38.5 and 25.2 min for **1a** and **1b**, respectively.

(14) The converted products, **1a',b'**, showed satisfactory elemental analyses and mass spectra. The <sup>13</sup>C NMR spectral data measured in CDCl<sub>3</sub> are as follows: **1a**,  $\delta$  53.3, 121.8, 128.2, 132.6, 159.8; **1a'**,  $\delta$  53.4, 120.7, 130.1, 132.2, 159.7; **1b**,  $\delta$  121.5, 123.9, 125.1, 137.4 (the cyclohexane ring carbon signals did not appear); **1b'**,  $\delta$  121.5, 122.8, 125.3, 132.0, 137.3.