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1,9-Dithia[2.2]paracyclophane: Synthesis, Molecular Structure, and Properties

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Introduction

Since the isolation of [2.2]paracyclophane from a polymer mixture and its identification by X-ray analysis,[1−3] many cyclophanes have been synthesized and their chemical and physical properties have been extensively studied.[4,5] In the polymer field, it has long been recognized that strained [2.2]paracyclophanes are useful precursors of thin poly(arylene−ethylene) films which are inert and transparent and have excellent barrier properties to nitrogen, oxygen, carbon dioxide, and hydrogen gases and to moisture vapor. Strained [2.2]paracyclophanes undergo vapor-phase pyrolysis under reduced pressure at high temperature (600 °C) to give very reactive *p*-quinodimethanes quantitatively which condense on a cold surface below 30 °C and polymerize spontaneously to give colorless transparent films free from contamination and cross-linking.[6,7] To date, [2.2]paracyclophane,[6] 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane,[7] 1,1,9,9-tetrafluoro[2.2]paracyclophane,[8] 1,9-dichloro[2.2]paracyclophane,[9] [2.2](2,5)thiophenophane,[10] [2.2](2,5)pyridinophane,[11] [2.2](2,5)pyrazinophane,[11] and *N,N′*-dimethyl[2.2](2,5)pyrrolophane[11] have been studied as precursors of *p*-quinodimethane-type monomers because they carry ethylene groups as bridges. In contrast to the large number of ethylene-bridged [2.2]paracyclophanes, there are few heteroatom-bridged [2.2]paracyclophanes except for 1,1,2,2,9,9,10,10-octamethyl-1,2,9,-10-tetragerma[2.2]paracyclophane[12] and 1,1,2,2,9,9,10,10-octamethyl-1,2,9,10-tetrasila[2.2]paracyclophane.[13] Although heteroatom-bridged [2.2]metacyclophanes such as 1,10-dithia[2.2]metacyclophane, 1-oxa-10-thia[2.2]-metacyclophane, and 1-thia-10-aza[2.2]metacyclophane have been successfully prepared by Vögtle *et al.*,[14−16] heteroatom-bridged [2.2]paracyclophanes such as 1,9-dithia[2.2]paracyclophane (**1**), 1,9-dioxa[2.2]paracyclophane, and 1,9-diaza[2.2]paracyclophane have not yet been synthesized. It is expected that the vapor-phase pyrolysis of these heteroatom-bridged [2.2]paracyclophanes would form very reactive *p*-quinonoid compounds such as *p*-thioquinone methide, *p*-quinone methide, and *p*-quinone methide imine in a pure state, which would be polymerizable after the fashion of *p*-quinodimethane.

This paper describes the first successful synthesis of a 1,9-dithia[2.2]paracyclophane (**1**), its properties, and its molecular structure as determined by X-ray crystallography. The synthesis is accomplished by the application of both a cesium effect[17,18] and a high dilution effect.[19]

Results and Discussion

Cyclophane **1** was prepared successfully according to Scheme 1.

Bis(*p*-carboxyphenyl) disulfide (**3**) was prepared in 91% yield from *p*-aminobenzoic acid (**2**) in accordance with the preparation of dithiosalicylic acid[20] from anthranilic acid. The diacid **3** was converted to bis(*p*-(methoxycarbonyl)-phenyl) disulfide (**4**) in 93% yield by reaction with thionyl chloride, followed by esterification with methanol. The reduction of **4** with LiAlH$_4$ in ether at room temperature for 1 h gave a 71% yield of *p*-mercaptobenzyl alcohol (**5**), which was subsequently treated with HBr at room temperature to afford *p*-mercaptobenzyl bromide (**6**). However, upon evaporation of the solvent, decomposition of **6** took place to yield oligomeric materials. Owing to the difficulty in isolating **6** in a pure state, **6** was used in the subsequent reaction without isolation. A self-coupling reaction of **6** in refluxing acetonitrile containing cesium hydroxide under high dilution conditions afforded cyclophane **1** in 3.0% yield and a cyclic trimer (**7**) in 12% yield, together with a large amount of oligomer and polymer. The cyclophane **1** could be sublimed at about 135 °C at a pressure of 0.1 mmHg.

In the ^{1}H NMR spectrum of cyclophane **1**, the aromatic protons appear at 6.98 and 6.73 ppm as two split signals in an AB pattern, shifted upfield by 0.18−0.35 ppm relative to *p*-(methylthio)toluene (7.16 and 7.08 ppm). This is ascribed to the anisotropic effect of one benzene ring on the aromatic protons of the other ring and to the rehybridization of the benzene carbon atoms due to ring deformation. The molecular structure of cyclophane **1**, determined by X-ray crystallographic analysis, is shown in Figure 1 and the intramolecular bond lengths and angles are summarized in Table 1. The benzene rings are bent into a boat shape, and the carbon−sulfur bond lengths (S(1)−C(2) 1.774 Å and C(8)−S(1) 1.860 Å) deviate slightly from the normal values (1.75 Å for sp^2 carbon−sulfur and 1.81 Å for sp^3 carbon−sulfur).[21] The bridging bond lengths, interplanar space distances, and geometrical parameters (α_1, α_2, β_1, β_2, γ_1, and γ_2) of cyclophane **1** are summarized in Table 2 together with the corresponding values of [2.2]paracyclophane. The C(2) and C(6) atoms of the benzene rings are displaced

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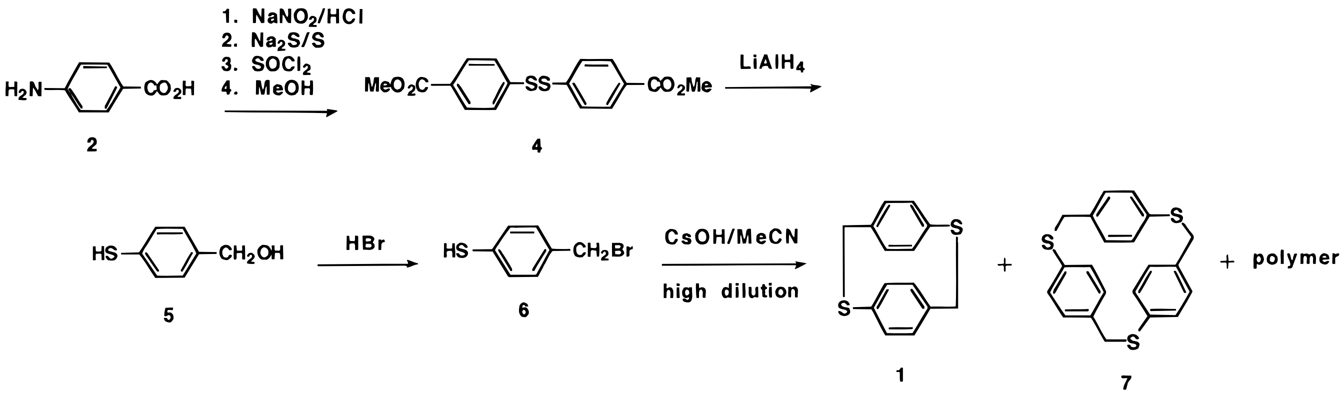
Scheme 1



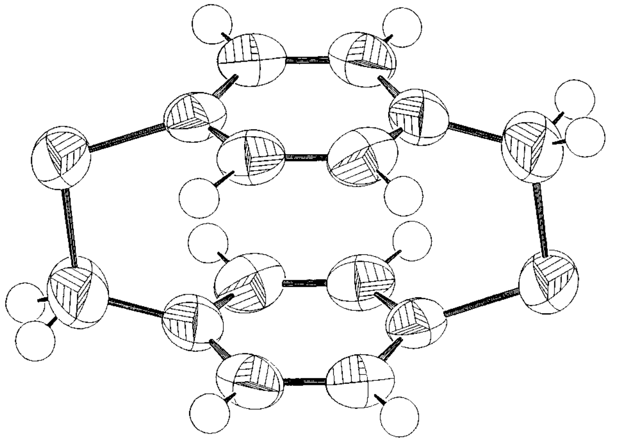
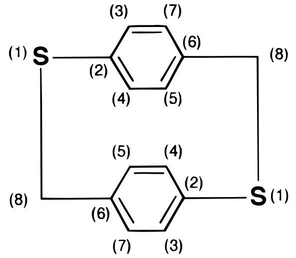


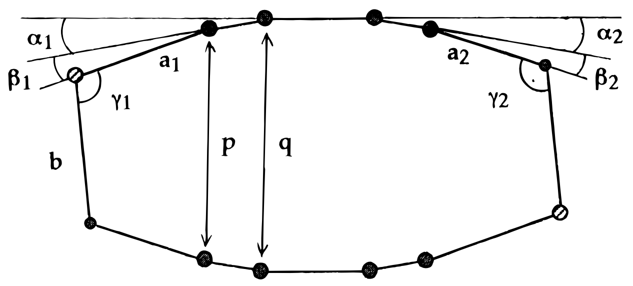
Figure 1. ORTEP drawing of the crystal structure of cyclophane **1**. The thermal ellipsoids are plotted at the 6.2% probability level.

Table 1. Bond Lengths and Angles of Cyclophane 1



	Bond Lengths (Å)		
S(1)−C(2)	1.774(4)	S(1)−C(8)	1.860(8)
C(2)−C(3)	1.387(6)	C(2)−C(4)	1.387(6)
C(3)−C(7)	1.385(6)	C(4)−C(5)	1.374(7)
C(5)−C(6)	1.389(6)	C(6)−C(7)	1.381(7)
C(6)−C(8)	1.497(8)		
	Bond Angles (deg)		
C(2)−S(1)−C(8)	103.4(3)	S(1)−C(2)−C(3)	120.8(3)
S(1)−C(2)−C(4)	120.0(3)	C(3)−C(2)−C(4)	118.4(4)
C(2)−C(3)−C(7)	119.8(4)	C(2)−C(4)−C(5)	120.4(4)
C(4)−C(5)−C(6)	120.7(4)	C(5)−C(6)−C(7)	117.7(4)
C(5)−C(6)−C(8)	120.2(5)	C(7)−C(6)−C(8)	121.6(5)
C(3)−C(7)−C(6)	120.9(4)	S(1)−C(8)−C(6)	113.2(4)

Table 2. Bridging Bond Lengths, Interplanar Distances, and Strain Angles of Cyclophane 1 and [2.2]Paracyclophane



cyclophane **1**		[2.2]paracyclophane[4]	
a_1 (Å)	1.774	$a_1 = a_2$ (Å)	1.551
a_2 (Å)	1.497		
b (Å)	1.860		1.593
p (Å)	2.883		2.778
q (Å)	3.134		3.093
α_1 (deg)	10.0	$\alpha_1 = \alpha_2$ (deg)	12.6
α_2 (deg)	10.2		
β_1 (deg)	9.8	$\beta_1 = \beta_2$ (deg)	11.2
β_2 (deg)	7.6		
γ_1 (deg)	103.4	$\gamma_1 = \gamma_2$ (deg)	113.7
γ_2 (deg)	113.2		

out of the plane of the other four atoms (C(3), C(4), C(5), and C(7)) toward the cyclophane cavity by 10.0° (α_1) and 10.2° (α_2), respectively, which is less than in the case of [2.2]paracyclophane (12.6°). Also, the exocyclic bonds of C−S and C−CH$_2$ at the bridgehead carbon atoms of the benzene rings are bent less ($\beta_1 = 9.8°$ and $\beta_2 = 7.6°$) than those in [2.2]paracyclophane (11.2°), indicating a smaller degree of distortion of the benzene ring. The distance between the two benzene rings (3.134 Å) is a little larger than that of [2.2]paracyclophane (3.093 Å), but much less than van der Waals contact distance (3.4 Å). The increase in the distance is apparently a consequence of the longer bond length between carbon and sulfur (1.860 Å) compared to that of a carbon−carbon bond (1.593 Å). The electronic absorption spectra of cyclophane **1** and *p*-(methylthio)toluene in THF are shown in Figure 2, wherein cyclophane **1** shows a large amount of broadening compared to *p*-(methylthio)toluene, suggesting the loss of ring planarity and a marked π-electron interaction of both benzene rings as seen in the paracyclophane series.[22] The mass spectrum of cyclophane **1** shows peaks at 244 (50%) assignable to the molecular ion peak of cyclophane **1**, 122 (100%), and 78 (12%). The peak at 122 is equal exactly to half the molecular weight of cyclophane **1**. Therefore, it is suggested that, when cyclophane **1** is pyrolyzed in the vapor-phase, a reactive intermediate *p*-thioquinonemethide is formed. Studies of polymerizations of cyclophane **1** by vapor-phase pyrolysis are now in progress.

Experimental Section

Melting points are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded at 270 and 67.8 MHz in CDCl$_3$ or DMSO-d_6 with TMS as an internal standard. EI mass spectra were recorded at 70 eV.

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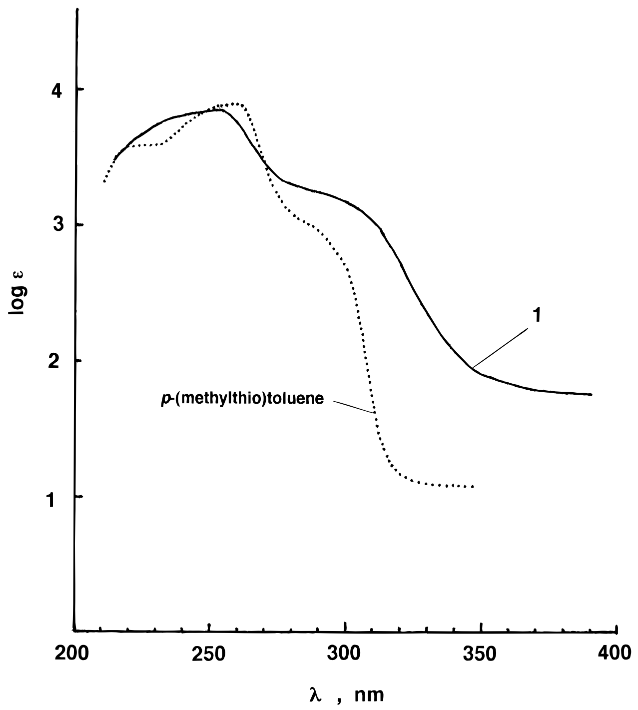

Figure 2. Electronic absorption spectra of **1** (—) and *p*-(methylthio)toluene (- - -) in THF.

Bis(*p*-carboxyphenyl) Disulfide (3). Diacid **3** was prepared from *p*-aminobenzoic acid (**2**) and was recrystallized from acetonitrile to give a pale yellow solid: yield 91%; mp 300 °C dec; IR (KBr) 3200, 1653, 1560, 1397, 1271 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.65 (d, J = 8.4 Hz, 4H), 7.98 (d, J = 8.4 Hz, 4H), 12.98−13.01 (br s, 2H). Anal. Calcd for $C_{14}H_{10}O_4S_2$: C, 54.88; H, 3.30; O, 20.89; S, 20.93. Found: C, 55.24; H, 3.40, S, 20.86.

Bis(*p*-(methoxycarbonyl)phenyl) Disulfide (4). Diacid **3** (20.1 g, 65.4 mmol) was dissolved in 100 mL of thionyl chloride and refluxed for 2 h. Excess thionyl chloride was distilled off to give a yellow viscous oil, which was dissolved in 50 mL of ether, and then the resulting solution was filtered to remove insoluble material. The ether solution was added to a mixture of 100 mL of Et_3N and 200 mL of MeOH at reflux over 30 min and then refluxed for 2 h. The reaction mixture was evaporated under reduced pressure to give a brown solid, which was dissolved in 100 mL of $CHCl_3$. The resulting solution was washed three times with 100 mL of H_2O, dried over anhydrous $MgSO_4$, concentrated to a 10-mL volume, and then passed through a silica gel column using $CHCl_3$ as eluent. The second elution band portion was collected and dried under reduced pressure to afford a brown solid, which was recrystallized from a solution of benzene and hexane to give 20.3 g (93%) of **4** as pale brown needles: mp 103−105 °C; IR (KBr) 1680, 1561, 1408, 1264 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.97(d, J = 7.4 Hz, 4H), 7.53 (d, J = 7.4 Hz, 4H), 3.94 (s, 6H); MS *m/z* (%) 334 (M$^+$, 66), 302 (100), 271 (100), 184 (80), 167 (15), 139 (26), 136 (28), 120 (32), 108 (17), 69 (30). Anal. Calcd for $C_{16}H_{14}O_4S_2$: C, 57.46; H, 4.23; O, 19.14; S, 19.17. Found: C, 57.51; H, 4.29; S, 19.23.

***p*-Mercaptobenzyl Alcohol (5).** To the suspension of 5.0 g (132 mmol) of $LiAlH_4$ in 300 mL of ether was added dropwise a solution of 12.2 g (36.5 mmol) of **4** in 200 mL of THF at rt, and then the solution was stirred for an additional 1 h. To the reaction mixture was added slowly 100 mL of H_2O, and then the resulting solution was acidified by concentrated HCl. The ether layer was washed with H_2O and dried over anhydrous $MgSO_4$. The filtrate was evaporated under reduced pressure to give a yellow oil, which was dissolved in $CHCl_3$, and the resulting solution was passed through a silica gel column using $CHCl_3$ as eluent. The yellow band portion was collected and dried under reduced pressure to afford a pale yellow solid, which was recrystallized from hexane to give 8.07 g (71%) of **5** as white plates: mp 51−52 °C; IR (KBr) 3306, 2528, 1567, 1467, 1023 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.27 (d, J = 6.8 Hz, 2H), 7.22 (d, J = 6.8 Hz, 2H), 4.64 (s, 2H), 3.45 (s, 1H), 1.70 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 129.6, 129.5, 127.8, 138.3, 64.8; MS *m/z* (%) 140 (M$^+$, 100), 139 (25), 123 (22), 111 (39), 109 (18), 107 (51), 77 (67), 69 (15), 65 (15), 51 (15). Anal. Calcd for C_7H_8OS: C, 59.06; H, 5.76; S, 22.87; O, 11.41. Found: C, 59.12; H, 5.69; S, 22.90.

***p*-Mercaptobenzyl Bromide (6).** Alcohol **5** (2.2 g, 15.7 mmol) was dissolved in 150 mL of ether. To the resulting solution was added 50 mL of HBr, and the solution was stirred for 20 h at rt. The organic layer was dried over anhydrous $MgSO_4$. The filtrate was evaporated under reduced pressure to give a white solid, which was measured by gel permeation chromatography (GPC) (standard polystyrenes, THF eluent) to show many peaks, corresponding to the number average of molecular weights of 200−2000. It was difficult to isolate bromide **6** in a pure state because of its instability.

1,9-Dithia[2.2]paracyclophane (1). Alcohol **5** (3.0 g, 21.7 mmol) was dissolved in 300 mL of ether. To the resulting solution was added 90 mL of HBr, and the solution was stirred for 20 h at rt. The water layer was extracted three times with 50 mL of ether, and the extracts were combined with the organic layer and then dried over anhydrous $MgSO_4$. The filtrate was added dropwise to a refluxing mixture of 1700 mL of acetonitrile and 4.41 g (21.7 mmol) of cesium hydroxide monohydrate over a period of 20 h, and heating at reflux was continued for 33 h. After cooling, the mixture was filtered to remove insoluble materials, the solvent was evaporated *in vacuo*, and the residue was dissolved in 300 mL of ethyl acetate. The resulting solution was washed with H_2O three times, dried over anhydrous $MgSO_4$, and concentrated to 20 mL under reduced pressure. The residue was passed through a silica gel column using $CHCl_3$ as eluent. The first elution band portion was collected and concentrated to give a residue, which was dissolved in a solution of benzene and hexane (1:1 by volume). The resulting solution was passed through a silica gel column using a solution of benzene and hexane (1:1 by volume) as eluent, and the first and second elution band portions were collected to give cyclophane **1** and cyclic trimer **7** as white solids, respectively, which were recrystallized from hexane to give colorless needles.

Cyclophane 1: 80 mg (3.0%); mp 164−166 °C; ^{1}H NMR ($CDCl_3$) δ 6.98 (d, J = 7.0 Hz, 4H), 6.73 (d, J = 7.0 Hz, 4H), 4.34 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 131.1, 133.0, 140.6, 137.8, 42.4; MS m/z (%) 244 (M$^+$, 50), 122 (100), 78 (12). Anal. Calcd for $C_{14}H_{12}S_2$: C, 68.80 H, 4.96; S, 26.24. Found: C, 68.68; H, 4.95; S, 26.37.

Cyclic trimer 7: 300 mg (11.5%); mp 152−153 °C; ^{1}H NMR ($CDCl_3$) δ 6.94 (q, J = 4.4 Hz, 12H), 4.00 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 127.0, 129.1, 130.9, 134.7, 37.3; MS m/z (%) 366 (M$^+$, 100), 244 (55), 122 (82), 78 (14). Anal. Calcd for $C_{21}H_{18}S_3$: C, 68.80; H, 4.96; S, 26.24. Found: C, 68.72; H, 4.98; S, 26.30.

X-ray Structure of 1.[23] The crystal dimensions were 0.20 × 0.30 × 0.40 mm. Data collection was done at rt with graphite-monochromatized copper Kα radiation (λ = 1.541 78 Å). Twenty reflections were used for the unit cell determination, corresponding to a monoclinic cell in the space group *C*2/*c* (No. 15) with the following lattice parameters: a = 12.560(2) Å, b = 7.885(1) Å, c = 11.891(5) Å, α = 90.00(0)°, β = 99.70(1)°, γ = 90.00(0)°, V = 1160.9(3) Å. For Z = 4 and formula weight 244.40, the calculated density was 1.40 g/cm^3. A total of 1446 reflections were measured in the range $3.0° < 2\Theta < 130.0°$ by the $2\Theta-\omega$ scan method with a scan rate of 12°/min; 968 reflections were considered as observed. The structure was solved by the direct methods and refined by full matrix least-squares refinement for non-hydrogen atoms anisotropically. All hydrogen atoms were located by the difference Fourier map and are included in the refinement with isotropic temperature factors. The final R factors were 0.0612 and R_w = 0.0631.

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[23] The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.