A New Mercurophilic Troponoid Tetrathiacyclophane; 2,6,8,12-Tetrathia-1(2,7),7(2,7)-ditropona-4(1,3),10(1,3)-dibenzenacyclododecaphane

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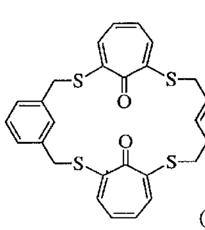
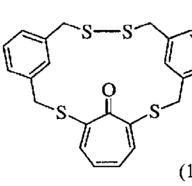
Condensation reaction of 2,7-dibromotropone with 1,3-bis(mercaptomethyl)benzene afforded 2:2- and 1:2-condensates. Their structures were determined to be new troponoid tetrathiacyclophanes by X-ray crystallographic analyses; 2:2-condensate had a 1,2-alternate conformation and was well-stacked through π–π interactions. 1:2-Condensate had approximately a cone conformation. 2:2-Condensate formed a complex with Hg(II) ion.

Calixarenes and cyclophanes have received considerable attentions in the field of supramolecular chemistry because they can form inclusion complexes with cations, anions or neutral molecules.[1] Recently, we have been interested in synthesizing the Hg(II) ion-capturing ionophores having troponoid pendant.[2] Particularly noteworthy are their reversible complexation behaviors with Hg(II) salts to enable to transport Hg(II) ions through a liquid membrane. As an approach to the practical utilization of troponoid ionophores, we report synthesis, structures, and mercurophilic properties of new troponoid tetrathiacyclophanes.

When 2,7-dibromotropone and 1,3-bis(mercaptomethyl)-benzene were reacted in the presence of potassium *t*-butoxide in *t*-butyl alcohol and *N*,*N*-dimethylformamide, a 2:2-condensate (**1**) and a 1:2-condensate (**2**) were obtained in 46 and 1% yields. Their structures were determined to be 2,6,8,12-tetrathia-1(2,7),7(2,7)-ditropona-4(1,3),10(1,3)-dibenzenacyclododecaphane and 2,6,7,11-tetrathia-1(2,7)-tropona-4(1,3),9(1,3)-dibenzenacycloundecaphane[3] by the spectral data[4,5] and the X-ray crystallographic analyses.[6,7]



1
(46%)



2
(1%)

As shown in Figure 1, condensate **1** has a 1,2-alternate conformation, in which each benzene and tropone rings directed oppositely. The dihedral angles between the least-squares plane defined by S2-S10-S17-S25 and the four aromatic rings are obtained as follows; the angle to the tropone ring defined by O1-C1-C26-C27-C28-C29-C30-C31 is 51.9 (0.3)°, that to the tropone ring defined by O2-C11-C12-C13-C14-C15-C16-C33 is 53.4 (0.3)°, that to the benzene ring defined by C19-C20-C21-C22-C23-C34 is 148.8 (0.6)°, and that to the benzene ring defined by C4-C5-C6-C7-C8-C32 is 148.9 (0.6)°, respectively.

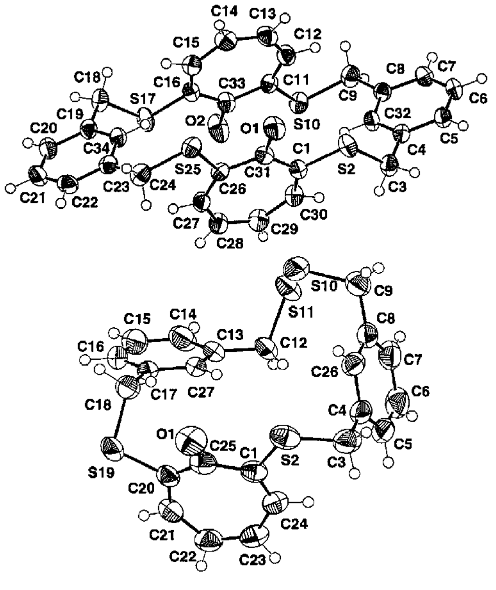


Figure 1. ORTEP drawings of **1** and **2**.

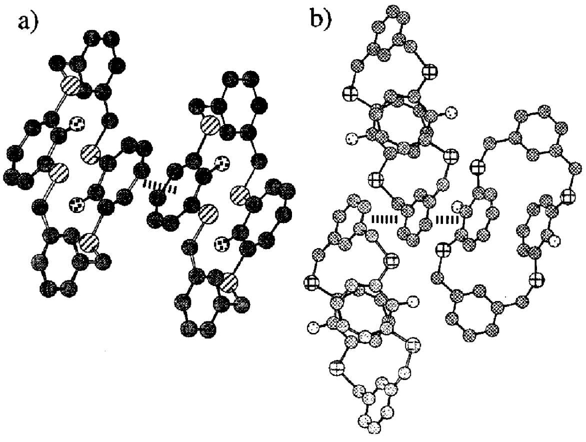


Figure 2. Two segments of π–π interactions showing a) tropone-tropone and b) benzene-benzene-tropone stacking arrangements.

It is reported that deviations of the carbonyl carbon and oxygen atoms of 3-azidotropone[7] from the least-squares plane by C2-C3-C4-C5-C6-C7 are given in 0.03 and 0.06 Å. In the case of condensate **1**, the angle between the least-squares plane defined by C1-C2-C7 and the least-squares plane defined by C2-C3-C6-C7 is 3.3 (2)°. Deviations of O1, O2, C31, and C33 from the least squares planes by C1-C30-C29-C28-C27-C26 and C-11-C12-C13-C14-C15-C16 were 0.092, 0.094, 0.039, and 0.043 Å, respectively. Thus, the planarity of the tropone rings of **1** was comparable to those of approximately planar tropone[9] and 3-azidotropone.[8] As shown in Figure 2, the shortest intermolecular distance between two neighboring tropone rings, whose carbonyl groups directed oppositely, is 3.42 Å, that between two neighboring benzene rings is 3.65 Å, and that between tropone and benzene rings is 3.63 Å, respectively. They are within π–π interaction distances (3.3–3.8 Å).[10]

When condensate **1** was mixed with various metal salts (3 eq.) such as alkali metal salts (LiCl, NaCl, KCl), alkaline earth metal salts ($MgCl_2$, $CaCl_2$, $BaCl_2$), and transition metal salts ($NiCl_2$, $CuCl_2$, $ZnCl_2$, $AgNO_3$), no ^{1}H NMR spectral changes were observed in $CDCl_3$. Upon addition of $HgCl_2$ (3 eq.), only the chemical shift of the carbonyl carbon was changed ($\Delta\delta$ = -1.9) in the ^{13}C NMR spectrum. This means that Hg(II) ion is coordinated with the tropone carbonyl oxygen atom to form a side-on complex. The Hg(II) complex liberated Hg(II) ion upon acidification with 5 M hydrochloric acid as detected in the ^{1}H and ^{13}C NMR spectroscopy, suggesting that condensate **1** could be used as a Hg(II) ion carrier.

Figure 3 shows the representative results of the transport of Hg(II) ion by **1** using a U-type cell.[11] It is clear that condensate **1** transported Hg(II) ion through a liquid membrane although the transport rate of **1** was slower than those[2] of tropunoid dithiocrown ethers. The release of Hg(II) ions to the receiving phase was due to the repulsive interaction between Hg(II) ion and the tropylium ion induced by protonation of the tropone carbonyl group.[2]

On the other hand, condensate **2** has approximately a cone conformation: the dihedral angles between the least-squares plane defined by S2-S10-S11-S19 and the three aromatic rings are 90.8 (0.5)° for the tropone ring, 93.0 (0.9)° for the benzene ring defined by C4-C5-C6-C7-C8-C26, and 147.7 (0.8)° for the benzene ring defined by C13-C14-C15-C16-C17-C27, respectively. The angle between the least-squares plane defined by C1-C20-C25 and the plane defined by C1-C20-C21-C24 is 19.5 (3)°. The corresponding angle for **1** is smaller than that for **2.**

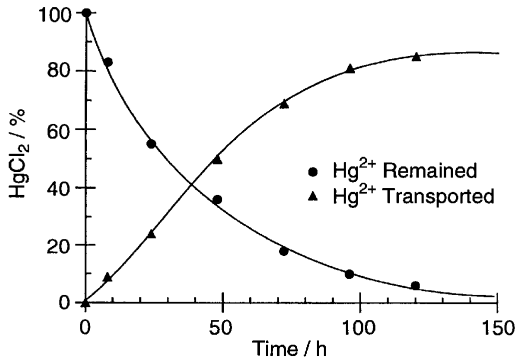


Figure 3. Transport experiment of $HgCl_2$ with **1** in a U-type cell.

In conclusion, a new carrier **1** for Hg(II) ion was developed. The X-ray crystallographic analysis disclosed that **1** had a 1,2-alternate conformation and was well-stacked through π–π interactions while condensate **2** had approximately a cone conformation.

References and Notes

†† Deceased on October 1, 1998.

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3 New nomenclature of phanes. See W. H. Powell, *Pure Appl. Chem.*, **70**, 1513 (1998).

4 **1**: yellow crystals, mp 194–195 °C ($CHCl_3$), ^{1}H NMR ($CDCl_3$) δ 4.08 (8H, s), 6.86–6.90 (4H, m), 7.07–7.10 (4H, m), 7.19–7.24 (6H, m), and 7.40 (2H, s); ^{13}C NMR δ 36.1, 128.0, 128.5, 128.7, 129.1, 129.3, 136.3, 149.0, and 177.1; HR-MS (FAB) Found: 545.0717, Calcd for $C_{30}H_{24}O_2S_4$+H: 545.0737.

5 **2**: yellow crystals, mp 214.5–215.5 °C ($CHCl_3$), ^{1}H NMR ($CDCl_3$) δ 3.57 (4H, s), 4.25 (4H, s), 6.62–6.66 (2H, m), 6.99 (2H, s), 7.10–7.11 (2H, m), and 7.17–7.21 (2H, m); ^{13}C NMR δ 35.1, 43.2, 128.1, 128.2, 128.6, 129.0, 129.7, 133.7, 136.6, 137.7, 148.0, and 180.0; EI-MS $[M]^+$ 440 (37); Found: C, 62.52; H, 4.60%, Calcd for $C_{23}H_{20}OS_4$: C, 62.69; H, 4.57%.

6 Crystal data of **1**: $C_{30}H_{24}O_2S_4$, monoclinic, $P2_1/n$, a = 12.297 (2) Å, b = 18.927 (5) Å, c = 11.6270 (10) Å, β = 112.493 (12) °, V = 2500.3 (8) Å^3, Z = 4, Mr = 544.73, Dx = 1.447 Mgm^{-3}, refinement on F^2 (SHELXL97),[12] $wR(F^2)$ = 0.1098, $R[F^2{>}2\sigma(F^2)]$ = 0.035.

7 Crystal data of **2**: $C_{23}H_{20}OS_4$, monoclinic, $P2_1/n$, a = 17.322 (4) Å, b = 8.779 (2) Å, c = 14.286 (3) Å, β = 103.28 (2)°, V = 2114.4 (8) Å^3, Z = 4, Mr = 440.63, Dx = 1.384 Mgm^{-3}, refinement on F^2 (SHELXL97),[12] $wR(F^2)$ = 0.1539, $R[F^2{>}2\sigma(F^2)]$ = 0.0507.

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11 The transport experiment was carried out using a U-type cell (aqueous layer I (10 cm^3): metal salts (5 mmol), organic phase: $CHCl_3$ (20 cm^3): **1** (5 mmol), aqueous layer II (10 cm^3): 2 M HCl).

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