

**SYNTHESIS OF MERCUROPHILIC DICYANOHEPTAFULVENES
BY REMOTE SUBSTITUTION OF 5,8,11,14,17-PENTAOXA-2,20-
DITHIABICYCLO[19.4.1]HEXACOSA-21,23,25-TRIEN-26-ONE
AND ITS HOMOLOGUES WITH MALONONITRILE**

Kanji Kubo, Akira Mori, and Hitoshi Takeshita*

*Institute of Advanced Material Study, 86, Kyushu University, Kasuga-koen,
Kasuga, Fukuoka, 816, Japan*

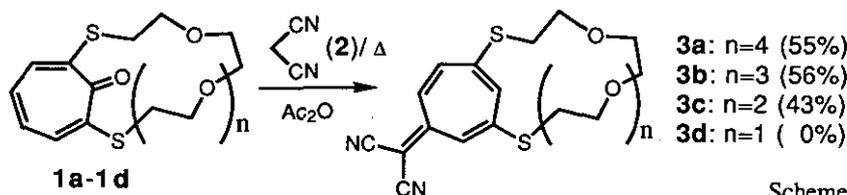
Abstract—5,8,11,14,17-Pentaoxa-2,20-dithiabicyclo[19.4.1]hexacosa-21,23,25-trien-26-one and its homologs gave, *via* remote substitution, dithio-crown-etherated 8,8-dicyanoheptafulvene derivatives upon heating in acetic anhydride. The dithio-crown-etherated dicyanoheptafulvenes efficiently extract and reversibly transport Hg^{++} ion.

Previously, we have synthesized a remarkably efficient mercuriphilic dithio-crown derivative, 5,8,11,14-tetraoxa-2,17-dithiabicyclo[16.4.1]tricoso-18,20,22-trien-23-one (**1b**) and its homologues,¹ and these compounds showed a reversible complexation, which has been explained in terms of the Coulomb cation-cation repulsive interaction between mercuric ion and a hydroxytropylium ion formed upon acid treatment. Meanwhile, we have found a remote substitution of sterically hindered tropones to 8,8-dicyanoheptafulvene derivatives upon treatment with malononitrile (**2**) in acetic anhydride.²

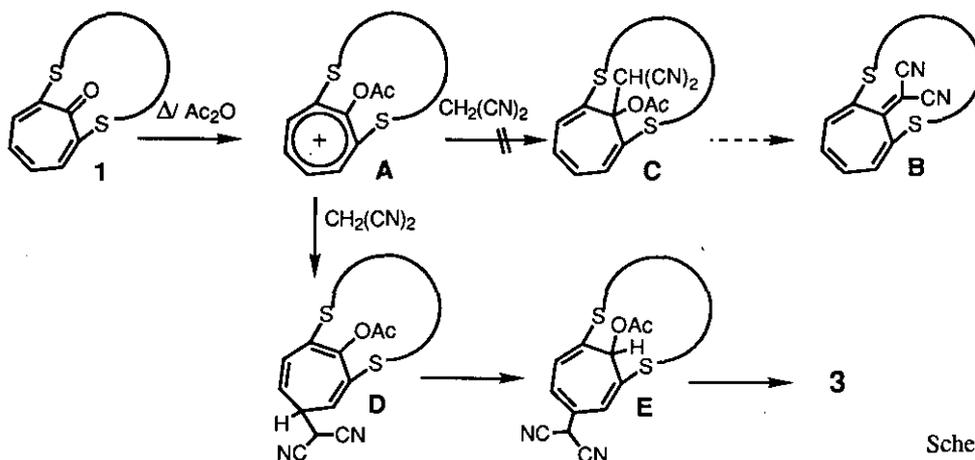
Therefore, it is desirable to extend the complexation study to heptafulvene derivatives, which also form a cycloheptatrienylium system upon acidification. Herein, we describe the results, synthesis and mercuriphilic properties of such heptafulvene derivatives prepared from appropriate tropones and **2**.

A mixture of 5,8,11,14,17-pentaoxa-2,20-dithiabicyclo[19.4.1]hexacosa-21,23,25-trien-26-one (**1a**) and **2** was heated in acetic anhydride for 1 h to give, *via* column chromatography, red-crystalline heptafulvene (**3a**), mp 70-

71 °C, in a 55% yield, which was identified to be a remote-condensation product,² 23-dicyanomethylene-5,8,11,14,17-pentaoxa-2,20-dithiabicyclo[19.4.1]hexacos-1(26),21,24-triene.

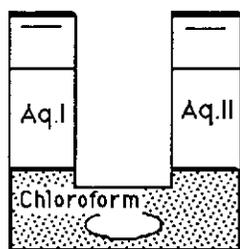


Similar treatment of 5,8,11,14-tetraoxa-2,17-dithiabicyclo[16.4.1]tricos-18,20,22-trien-23-one (**1b**) and 5,8,11-trioxa-2,14-dithiabicyclo[13.4.1]cosa-15,17,19-trien-20-one (**1c**) with **2** also gave red crystals, 20-(dicyanomethylene)-5,8,11,14-tetraoxa-2,17-dithiabicyclo[16.4.1]tricos-1(23),18,21-triene (**3b**), mp 133-134 °C, and 17-dicyanomethylene-5,8,11-trioxa-2,14-dithiabicyclo[13.4.1]cosa-1(20),15,18-triene (**3c**), mp 175-177 °C, in 56 and 43% yields, respectively, but 5,8-dioxa-2,11-dithiabicyclo[10.4.1]heptadeca-12,14,16-trien-17-one (**1d**)³ was unreactive under those conditions. Therefore, the reaction of 5-oxa-2,8-dithiabicyclo[7.4.1]tetradeca-9,11,13-trien-14-one (**1e**) with **2** was not even attempted. For the reaction mechanism, provided is Scheme 2, where the first step of the reaction is a formation of an acetoxytropylium ion (A), and the absence of *ipso*-product (B) might be attributable to the steric hindrance in the intermediate (C). On the other hand, an intermediate (D) leading to the remote-condensate is eligible for a thermally-allowed 1,5-hydrogen shift to an intermediate (E).⁴



As like as the troponoid analogues,⁵ these heptafulvenes formed crystalline complexes with Hg⁺⁺ ion. Extraction of Hg⁺⁺ ion into chloroform-*d* containing (**3a-c**) was checked by ¹H nmr spectroscopy; **3a** and **3b** revealed clear

^1H nmr change due to the complexation, but the change of **3c** by complexation was not conclusive. However, according to the experiments using a *U*-type cell (Figure 1),⁶ all these **3a-c** transported Hg^{++} ion selectively, and, in parallel to that with **1**, the Cu^{++} ion did not interfere the transportation of Hg^{++} . The extraction into an organic layer containing the crown ethers and the reverse-extraction into an aqueous layer (2M HCl) occurred quite smoothly. Indeed, the most satisfactory results obtained with **3a** is far better than any previous ones ever studied. The results are summarized in Figure 2. It is also worthy to note that the efficiency of the transportation sharply dropped when **3b** or **3c** was used; under the same conditions, the transportation rate for **3b** or **3c** was less than 30% to that for **3a**.

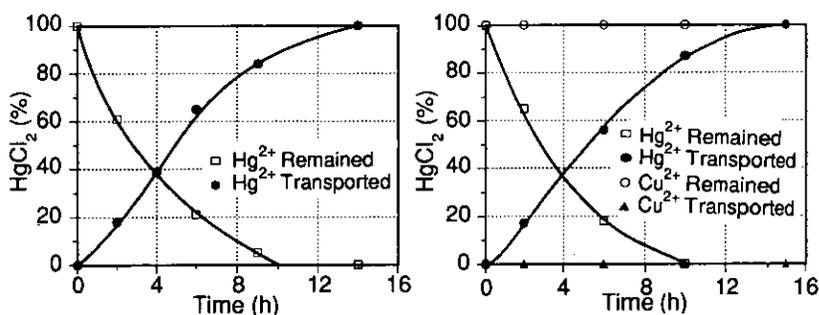


Aq. I (10 cm³) : HgCl_2 (\approx 5 mg)

Aq. II(10 cm³) : 2M HCl

CHCl_3 (20 cm³) : **3**(\approx 20 mg)

Figure 1. The *U*-type cell.



i) Hg^{++} ion without Cu^{++} ion

ii) Hg^{++} ion with Cu^{++}

Figure 2. Transportation of Hg^{++} ion with **3a**.

In the case of troponoid analogues, **1b** is better than **1a**. The difference in the fitted ring sizes between **1** and **3** must be due to a difference in their substitution patterns; *i.e.*, in **3**, the electronegative dicyanomethylene, a terminal of conjugated π -system, is distant from the sulfur atoms, other site of coordination. In this respect, the ^{13}C nmr of **3a** induced a significant complexation shifts ($\Delta\delta$) in the chemical shifts for aromatic carbon signals, but not with the cyano groups, to suggest a role of its π -system for the complexation.³ However, informations deduced from the nmr data should be carefully taken into account, and the structure of **3a**- Hg^{++} complex should be discussed after the X-ray analysis.⁷

The markedly selective and reversible complex formation with Hg^{++} observed in **1** is now extended to **3**. The results clearly show that the protonation is responsible to a ready liberation of Hg^{++} ion by acidification to generate 6π -cationic system for the seven-membered ring and to cause the Coulomb repulsion with complexed Hg^{++} ion. This may be attributed to the difference with the benzenoid counterpart.

REFERENCES

1. K. Kubo, A. Mori, and H. Takeshita, *Chem. Express*, 1992, 7, 945.
2. A. Mori, B. Z. Yin, A. Endo, and H. Takeshita, *Chem. Lett.*, 1992, 855.
3. The nmr spectral data (270 MHz for ^1H and 67.5 MHz for ^{13}C spectra in CDCl_3), as well as electronic spectra, of new heptafulvenes are listed below:

3a: $\delta(\text{H})=3.15(2\text{H}, \text{t}, J=6.6 \text{ Hz}), 3.21(2\text{H}, \text{t}, J=5.5 \text{ Hz}), 3.67(16\text{H}, \text{s}), 3.77(2\text{H}, \text{t}, J=6.6 \text{ Hz}), 3.84(2\text{H}, \text{t}, J=5.5 \text{ Hz}), 6.65(1\text{H}, \text{dd}, J=12.5, 2.2 \text{ Hz}), 6.76(1\text{H}, \text{br s}), 6.90(1\text{H}, \text{dd}, J=2.2, 1.8 \text{ Hz}),$ and $7.07(1\text{H}, \text{dd}, J=12.5, 2.2 \text{ Hz})$. $\delta(\text{C})=32.5, 32.9, 66.3, 68.3, 69.5, 70.7(3\text{C}), 71.0(4\text{C}), 71.2, 115.5, 115.6, 121.6, 127.3, 132.3, 137.5, 149.1, 154.5,$ and 158.5 . $\lambda_{\text{max}}^{\text{CHCl}_3}=313 \text{ nm}$ ($\epsilon=23300$), 332 (17600), and 439 (23300).

3a-Hg $^{++}$: $\delta(\text{H})=3.15(2\text{H}, \text{t}, J=7.0 \text{ Hz}), 3.28(2\text{H}, \text{t}, J=5.5 \text{ Hz}), 3.66-3.84(20\text{H}, \text{m}), 6.63(1\text{H}, \text{dd}, J=12.8, 2.2 \text{ Hz}), 6.65(1\text{H}, \text{dd}, \text{br s}), 6.85(1\text{H}, \text{br s}),$ and $7.09(1\text{H}, \text{dd}, J=12.8, 2.2 \text{ Hz})$. $\delta(\text{C})=31.4, 33.3, 67.1, 67.7, 68.1, 70.0(4\text{C}), 70.2(2\text{C}), 70.5, 70.6, 115.3, 115.5, 122.1, 126.7, 132.6, 137.5, 148.8, 152.4,$ and 158.6 .

3b: $\delta(\text{H})=3.14(2\text{H}, \text{t}, J=5.9 \text{ Hz}), 3.21(2\text{H}, \text{t}, J=5.5 \text{ Hz}), 3.62-3.71(12\text{H}, \text{m}), 3.76(2\text{H}, \text{t}, J=5.9 \text{ Hz}), 3.84(2\text{H}, \text{t}, J=5.5 \text{ Hz}), 6.64(1\text{H}, \text{dd}, J=12.5, 1.8 \text{ Hz}), 6.88(2\text{H}, \text{br s}),$ and $7.10(1\text{H}, \text{dd}, J=12.5, 2.2 \text{ Hz})$. $\delta(\text{C})=32.7, 33.9, 66.2, 67.8, 70.2, 70.3, 70.6, 70.8, 71.0, 71.1, 71.2, 115.6, 115.7, 121.3, 128.0, 132.1, 137.5, 148.8, 154.8,$ and 158.6 . $\lambda_{\text{max}}^{\text{CHCl}_3}=312 \text{ nm}$ ($\epsilon=16900$), 332 (16800), and 438 (23300).

3c: $\delta(\text{H})=3.21(2\text{H}, \text{t}, J=5.5 \text{ Hz}), 3.23(2\text{H}, \text{t}, J=5.5 \text{ Hz}), 3.56-3.68(8\text{H}, \text{m}), 3.77(2\text{H}, \text{t}, J=5.5 \text{ Hz}), 3.83(2\text{H}, \text{t}, J=5.5 \text{ Hz}), 6.71(1\text{H}, \text{dd}, J=12.1, 2.2 \text{ Hz}), 7.02(1\text{H}, \text{br s}), 7.09(1\text{H}, \text{dd}, J=12.1, 2.2 \text{ Hz}),$ and $7.13(1\text{H}, \text{dd}, J=2.2, 1.5 \text{ Hz})$. $\delta(\text{C})=33.3, 33.9, 65.8, 68.9, 70.4, 70.5, 70.9, 71.2, 71.5, 115.6, 115.7, 124.9, 128.6, 132.6, 137.7, 150.0, 153.3,$ and 158.6 . $\lambda_{\text{max}}^{\text{CHCl}_3}=314 \text{ nm}$ ($\epsilon=9400$), 337 (9400), 446 (14000).
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5. H. Takeshita, A. Mori, and S. Hirayama, *J. Chem. Soc., Chem. Commun.*, 1989, 564; A. Mori, B. Z. Yin, and H. Takeshita, *Chem. Express*, 1992, 7, 313.
6. The U-type cell used was the same as the previous apparatus, described in ref. 1.
7. According to the X-ray crystallographic study with **1c**-Hg $^{++}$ complex, which will be reported in future, nearly perpendicular geometry of the tropone ring to the dithio-crown ring was observed, and the Hg $^{++}$ is on the one side of carbonyl oxygen and the sulfur atoms. However, in the ^1H nmr spectrum, its α -methylene protons of thioether groups appeared as magnetically-equivalent 2H triplets, and Hg $^{++}$ is in the equilibrium conditions. Also, this should be the case for **3a** as could be judged from the nmr data.

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