

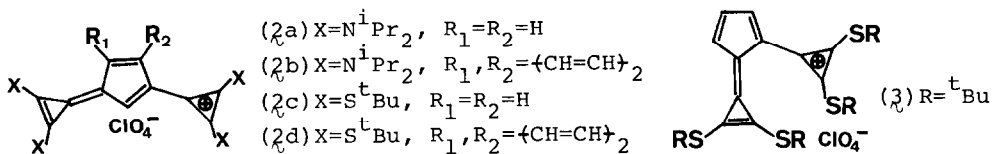
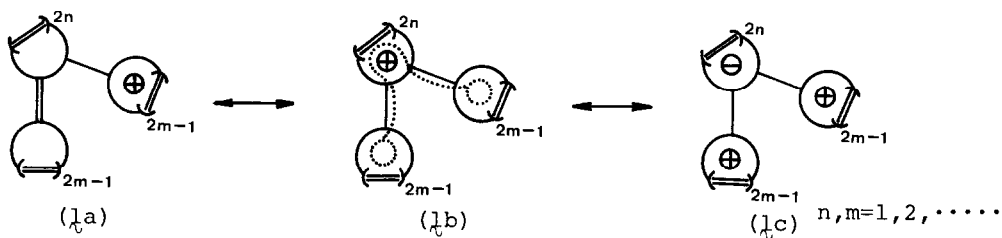
NOVEL DOUBLY CROSS-CONJUGATED CATIONS: 1,2- and 1,3-BIS(DITHIO-  
 CYCLOPROPENYLIO)CYCLOPENTADIENIDES

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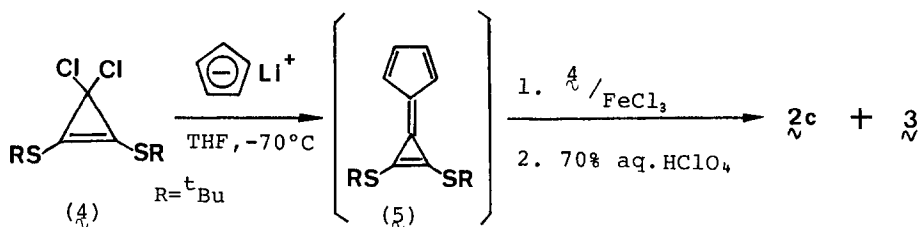
*Summary:* The titled cationic systems with a doubly cross-conjugated 3-5-3  
 membered ring have been successfully synthesized. The change of electronic  
 structure due to difference of substituent and substitution mode is discussed  
 on the basis of their spectral data.

Doubly cross-conjugated cationic system which has  $C_{2v}$  molecular symmetry  
 is generally shown as the formula  $1_{\sim}$ . Such a system is of considerable  
 interest from the following view points: (1) Which resonance structure ( $1a$ ,  
 $1b$  or  $1c$ ) mainly contributes to the ground state of  $1_{\sim}$ ?, and (2) how the  
 electronic structure changes by the different substitution mode of the three  
 rings? As a first example of this system, we reported the synthesis of  
 1,3-bis(diaminocyclopropenylio)cyclopentadienide ( $2a$ ) and its benzo-analogue  
 ( $2b$ ), and the large contribution of the tripolar structure (type  $1c$ ) to its  
 ground state.<sup>1</sup> Here we wish to communicate novel doubly cross-conjugated  
 cations, alkylthio-substituted bis(cyclopropenylio)-cyclopentadienides and  
 indenide ( $2c$ ,  $2d$  and  $3$ ) which have two different substitution modes.

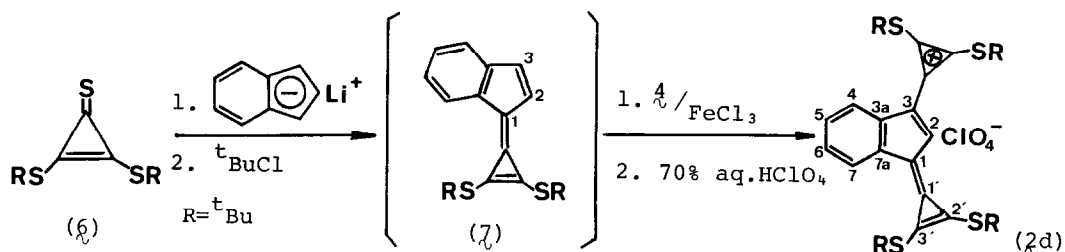
Three alkylthio-substituted doubly cross-conjugated cations can be syn-  
 thesized as follows. By the reaction of bis (*t*-butylthio)dichlorocyclopro-



pene ( $\overset{\sim}{4}$ )<sup>2</sup> with lithium cyclopentadienide in THF was *in situ* prepared 5,6-bis-(*t*-butylthio)calicene ( $\overset{\sim}{5}$ )<sup>3</sup>, which was further reacted with  $\overset{\sim}{4}$  in the presence of anhydrous ferric chloride at  $-70^\circ\text{C}$ . Treatment of the reaction mixture with aq.  $\text{HClO}_4$  and subsequent recrystallization from  $\text{CH}_2\text{Cl}_2$  - ether afforded yellow crystals of  $\overset{\sim}{3}$  (perchlorate salt, mp.  $147\text{--}148^\circ$  (dec.)) in 51% yield. The recrystallization filtrate contained a small amount of  $\overset{\sim}{2c}$  together with a tarry materials. Purification of  $\overset{\sim}{2c}$  by the repeated preparative thin layer chromatography on silica gel using ethyl acetate as an eluent gave yellow semisolid in 5% yield.<sup>4</sup>



The same type of reaction using indenide in place of cyclopentadienide didn't afford the benzo-analogue of  $\overset{\sim}{2c}$ . This might be due to no formation of 5,6-dithiobenzo[*b*]calicene ( $\overset{\sim}{7}$ ) because of the difficulty of  $\text{HCl}$ -elimination in chloroindenylidithiocyclopropene. However, as shown below reactions of bis(*t*-butylthio)cyclopropenethione ( $\overset{\sim}{6}$ )<sup>5</sup> with indenide, then with *t*-butylchloride and further with  $\overset{\sim}{4}$  in the presence of anhydrous ferric chloride, and successive treatment of the reaction mixture with 70% aq.  $\text{HClO}_4$  and



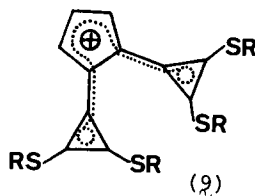
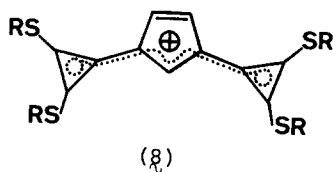
recrystallization from  $\text{CH}_2\text{Cl}_2$  - ether afforded 1,3-bis(dithiocyclopropenylo)indenide ( $\overset{\sim}{2d}$ ) (perchlorate salt, mp.  $151\text{--}154^\circ$  (dec.)) as yellow needles in overall yield of 14%. In this method only 1,3-substituted product was obtained. The preference of 1,3-substitution to 1,2-substitution might be due to predominant formation of the more stable 3-position attacked adduct than the 2-position attacked adduct possessing an unfavorable *o*-quinoid structure.

The spectral data of  $\overset{\sim}{2c}$ ,  $\overset{\sim}{2d}$  and  $\overset{\sim}{3}$  are summarized in Table I. As for nmr spectral data of  $\overset{\sim}{2c}$  and  $\overset{\sim}{2d}$  which have 1,3-substitution mode, all  $^1\text{H}$ - and  $^{13}\text{C}$ -signals of cyclopentadienide moieties appear considerably at lower magnetic field than those of  $\overset{\sim}{2a}$  and  $\overset{\sim}{2b}$ .<sup>6</sup> This suggests that for 1,3-substitution

Table I. The spectral data of  $\tilde{2}c$ ,  $\tilde{2}d$  and  $\tilde{3}$ .

Comp.	ir (KBr) [cm <sup>-1</sup> ]	uv $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ [nm]	$\epsilon$	<sup>1</sup> H-nmr (CDCl <sub>3</sub> ) $\delta$ [ppm]	<sup>13</sup> C-nmr (CDCl <sub>3</sub> ) $\delta$ [ppm]
$\tilde{2}c$	1760, 1445	275 (4.29), (4.79)	406	7.57 (t, 1H, H <sub>2</sub> , J=2.0 Hz), 6.83 (d, 2H, H <sub>4,5</sub> , J=2.0Hz), 1.78 (s, 36H, <sup>t</sup> Bu)	31.6, 52.0 ( <sup>t</sup> Bu), 109.3 (C <sub>1,3</sub> ), 121.2 (C <sub>4,5</sub> ), 130.7 (C <sub>2</sub> ), 141.6 (C <sub>1</sub> ), 146.2 (C <sub>2',3'</sub> )
$\tilde{2}d$	1750, 1428	241 (4.53), (sh, 4.32), 278 (4.23), 304 (sh, 4.12), 340 (sh, 3.70), 436 (sh, 4.47), 463 (4.96)	260	8.30 (s, 1H, H <sub>2</sub> ), 7.87 (m, 2H, H <sub>4,7</sub> ), 7.35 (m, 2H, H <sub>5,6</sub> ), 1.78 (s, 36H, <sup>t</sup> Bu)	31.6, 52.0 ( <sup>t</sup> Bu), 104.4 ( C <sub>1,3</sub> ), 118.4 (C <sub>5,6</sub> ), 123.8 (C <sub>4,7</sub> ), 135.2 (C <sub>3a</sub> , 7a), 135.6 (C <sub>2</sub> ), 139.8 ( C <sub>1</sub> ), 145.5 (C <sub>2',3'</sub> )
$\tilde{3}$	1760, 1460	273 (4.22), (3.85), 436 (4.01)	350	7.40 (d, 2H, H <sub>3,5</sub> , J= 3.8Hz), 6.65 (t, 1H, H <sub>4</sub> , J=3.8Hz), 1.74 ( s, 36H, <sup>t</sup> Bu)	31.9, 52.6 ( <sup>t</sup> Bu), 106.7 (C <sub>1,2</sub> ), 122.8 (C <sub>4</sub> ), 132.3 (C <sub>3,5</sub> ), 141.8 (C <sub>1</sub> ), 147.8 (C <sub>2',3'</sub> )

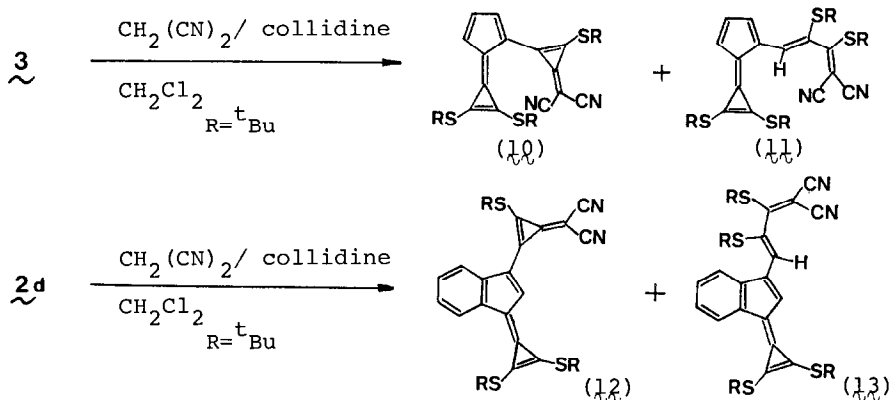
system having thio-group ( $\tilde{2}c$  and  $\tilde{2}d$ ) the resonance structure of type  $\tilde{1}a$  dominantly contributes to its ground state and the contribution of a tripolar structure (type  $\tilde{1}c$ ) is small in contrast with the case of  $\tilde{2}a$  and  $\tilde{2}b$ , because of a less conjugation effect of thio-group on the cyclopropenium ring than that of amino-group. As for the structure of type  $\tilde{1}b$ , the appearance of the <sup>13</sup>C-signals of C<sub>2</sub> at fairly low magnetic field ( $\tilde{2}c$ , 130.7;  $\tilde{2}d$ , 135.6ppm) relative to other carbon signals of cyclopentadienyl ring indicates that the positive charge of cyclopropenium moieties is somewhat poured into C<sub>2</sub> of  $\tilde{2}c$  and  $\tilde{2}d$ , as shown in the formula  $\tilde{8}$ . The <sup>13</sup>C-average chemical shift of cyclopentadienyl ring of  $\tilde{3}$  ( $\delta_{\text{av}}=120.2\text{ppm}$ ) which has 1,2-substitution mode appears somewhat at lower magnetic field than that of  $\tilde{2}c$  ( $\delta_{\text{av}}=118.3$ ), and



particularly <sup>13</sup>C-signals of C<sub>3,5</sub> of  $\tilde{3}$  is observed at much lower magnetic field as compared with other carbon signals. These results suggest that the contribution of tripolar structure is also small in case of  $\tilde{3}$  and the positive charge of cyclopropenium moieties is delocalized on C<sub>3</sub> and C<sub>5</sub> of  $\tilde{3}$  in a some extent as shown in the formula  $\tilde{9}$ . This is supported from the bathochromic shift (30nm) of the uv absorption maximum of  $\tilde{3}$  compared with

that of  $\tilde{2}c$  which corresponds to the difference of conjugation in  $\tilde{8}$  and  $\tilde{9}$ .

Reaction features of alkylthio-substituted bis(cyclopropenylio)cyclopentadienides and indenide are as follows. When these salts were treated with trifluoroacetic acid- $d_1$  in  $CDCl_3$ , the H-D exchanged products on their cyclopentadienyl and indenyl parts were obtained. This presents a striking contrast to the previous observation on the exclusive formation of protonated adducts in case of amino-analogue ( $\tilde{2}a$  and  $\tilde{2}b$ ). Furthermore, the thio-analogue was susceptible to the reaction with nucleophile. For example, the reaction of  $\tilde{3}$  with malononitrile in the presence of collidine gave 1-(dicyanotriafulvenyl)calicene ( $\tilde{10}$ ) in 25% yield along with a cyclopropenium ring-opened product ( $\tilde{11}$ ) in 17% yield. From the reaction of  $\tilde{2}d$  under the same reaction condition as above the corresponding benzo-derivatives ( $\tilde{12}$ ) and ( $\tilde{13}$ ) were obtained in respective yields of 42 and 10%. In contrast, such a reaction could not be seen for the amino-analogue at all.



#### References and Notes

1. Z. Yoshida, S. Araki and H. Ogoshi, *Tetrahedron Lett.*, 19 (1975).
2. This compound was prepared by the reaction of  $\tilde{6}$  and thionyl chloride.
3. Z. Yoshida, *Pure Appl. Chem.*, **54**, 1059 (1982).
4. The reason why the 1,2-substitution mode was preferred in thio-analogue ( $\tilde{5}$ ) in spite of the preference of 1,3-substitution in its amino-analogue is that the reactivity of calicene toward electrophile is essentially the highest at  $C_1$ -position but 5,6-bis(di-*iso*-propylamino)calicene is highly hindered from the attack of electrophile at  $C_1$ -position by the bulky di-*iso*-propylamino group.
5. Reaction of tris(*t*-butylthio)cyclopropenium salt with anhydrous sodium bicarbonate in refluxing ethyl acetate gave this compound in 90% yield.
6.  $\tilde{2}a$ ,  $^1H$ -nmr ( $CDCl_3$ )  $\delta$  6.67(d, 2H,  $H_{4,5}$ ,  $J=2.2Hz$ ) and 7.18(t, 1H,  $H_2$ ,  $J=2.2Hz$ ),  $^{13}C$ -nmr ( $CDCl_3$ ) 104.8( $C_{1,3}$ ), 116.3( $C_{4,5}$ ) and 118.4( $C_2$ );  $\tilde{2}b$ ,  $^1H$ -nmr ( $d_6$ -DMSO) 7.50-7.38(m, 2H), 7.43(s, 1H,  $H_2$ ), 7.00-6.86(m, 2H).

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