

Isolation of 2-Mercaptotropone as a 2:1 Complex with  
1,1,6,6-Tetraphenylhexa-2,4-diyne-1,6-diol  
and X-Ray Crystal Structure of the Complex

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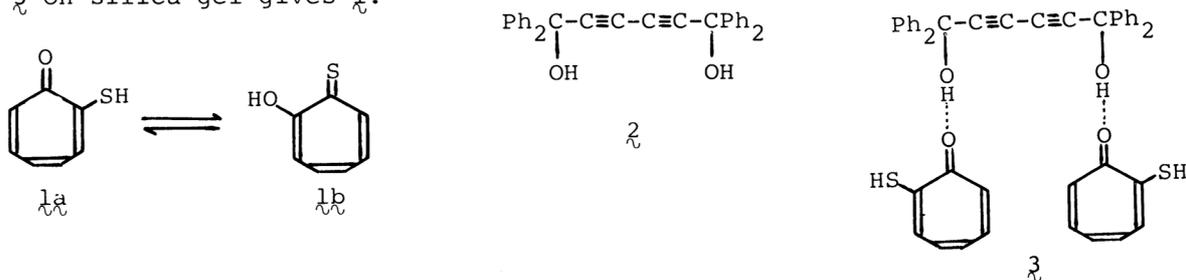
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Of two tautomers of 2-mercapto substituted tropone, 2-mercaptotropone and 2-hydroxytropothione, the former is isolated as a 2:1 complex with 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol, and infrared and electronic absorption spectra of the complex are reported. X-Ray crystal structural study shows that the 2-mercaptotropone in the complex has no bond alternation and then has a delocalized  $\pi$ -electron system.

2-Mercapto substituted tropone ( $1_a$ ) has been reported to exist as 2-hydroxytropothione ( $1_b$ ) predominantly rather than 2-mercaptotropone ( $1_a$ ) both in solution<sup>1)</sup> and in the solid state.<sup>2)</sup> We report an isolation of the former ( $1_a$ ) as a 2:1 inclusion complex with 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol ( $2$ ),<sup>3)</sup> and IR and UV-Vis spectra of the complex in the solid state. X-Ray crystal structural study of the complex disclosed that the 2-mercaptotropone has no bond alternation but has a delocalized  $\pi$ -electron system.

To a solution of  $1_a$  (0.27 g, 1.96 mmol) in petrol ether (20 cm<sup>3</sup>) was added powdered  $2$  (0.41 g, 0.99 mmol), and the mixture was kept at room temperature for 12 h to give a 2:1 complex ( $3$ ) of  $1_a$  and  $2$  (0.49 g, 72% yield) as orange prisms, mp 101-103 °C. The complex ( $3$ ) is stable and can be used for a storage of the labile  $1_a$  which is readily oxidized to form the disulfide. Column chromatography of  $3$  on silica gel gives  $1_a$ .



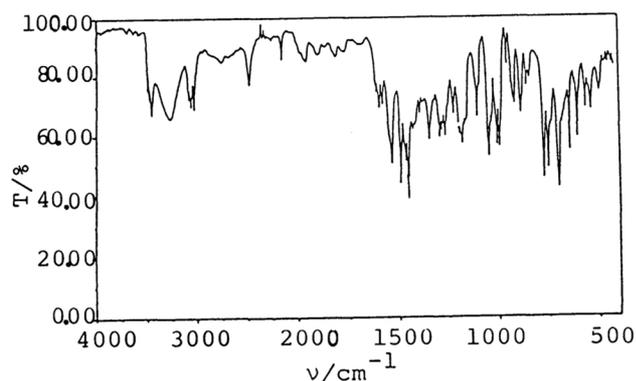


Fig. 1. IR Spectrum of  $\mathfrak{z}$  in KBr powder.

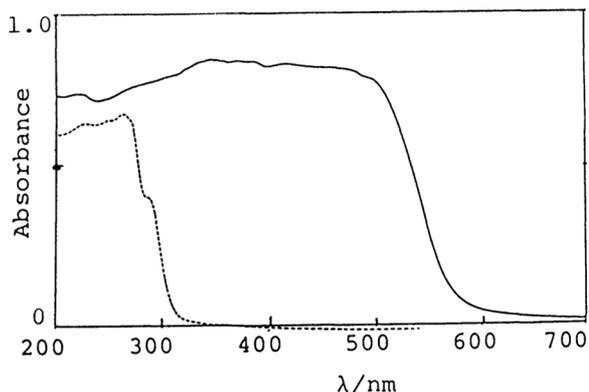


Fig. 2. UV-Vis Spectra of  $\mathfrak{z}$  (.....) and  $\mathfrak{z}$  (—) in the solid state.

The IR spectrum<sup>4)</sup> of  $\mathfrak{z}$  (Fig. 1) shows two  $\nu_{\text{OH}}$  (3459.7 and 3270.7  $\text{cm}^{-1}$ ) and one  $\nu_{\text{SH}}$  (2482.0  $\text{cm}^{-1}$ ). Since  $\mathfrak{z}$  shows only one  $\nu_{\text{OH}}$  absorption band at 3534.9  $\text{cm}^{-1}$  in the solid state, the two  $\nu_{\text{OH}}$  bands of  $\mathfrak{z}$  would be due to the hydrogen-bonded OH groups in the complex. Appearance of  $\nu_{\text{SH}}$  absorption, as well as strong C=O and C=C stretching absorptions characteristic of tropone structure at 1533.2 and 1463.7  $\text{cm}^{-1}$ ,<sup>2)</sup> clearly indicates the presence of  $\mathfrak{z}$  structure. Lack of strong bands due to the C-O-H group in the region of 1300-1200  $\text{cm}^{-1}$ , observed in pure  $\mathfrak{z}$ ,<sup>2)</sup> also supports the structure of  $\mathfrak{z}$  in the present complex.

On the UV-Vis spectrum<sup>4)</sup> in the solid state,  $\mathfrak{z}$  shows absorption bands at a longer wavelength region than does  $\mathfrak{z}$  in solution (Fig. 2).  $\mathfrak{z}$  shows three absorption bands in solution at 237, 268, and 420 nm.<sup>1)</sup> Furthermore,  $\mathfrak{z}$  has no absorption band at visible region as shown in Fig. 2. These results suggest that  $\mathfrak{z}$  of  $\mathfrak{z}$  is in a special circumstance which makes  $\mathfrak{z}$ , for example, planar and/or polar. In order to clarify this, X-ray crystal structural study of  $\mathfrak{z}$  was carried out.

A large orange crystal of  $\mathfrak{z}$  was cut into the size of 0.21 x 0.50 x 0.50  $\text{mm}^3$  and used for the X-ray diffraction experiments on a Rigaku AFC-5 diffractometer using Cu-K $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation. Unit cell constants were obtained by the least-squares fit using 38 reflections with  $20^\circ < 2\theta < 46^\circ$ . Crystal data are,  $(\text{C}_{30}\text{H}_{22}\text{O}_2) \cdot 2(\text{C}_7\text{H}_6\text{OS})$ , Fw = 690.9,  $F(000) = 362$ , triclinic,  $P\bar{1}$ ,  $Z = 1$ ,  $a = 11.174(2)$ ,  $b = 11.380(1)$ ,  $c = 8.479(1) \text{ \AA}$ ,  $\alpha = 110.72(1)^\circ$ ,  $\beta = 85.72(1)^\circ$ ,  $\gamma = 116.41(1)^\circ$ ,  $V = 899.3(3) \text{ \AA}^3$ ,  $D_m = 1.259 \text{ Mg m}^{-3}$  by flotation method with citric acid aqueous solution,  $D_x = 1.276 \text{ Mg m}^{-3}$ ,  $\mu = 16.43 \text{ cm}^{-1}$ . Intensity data were collected up to  $2\theta = 128^\circ$  by  $\omega$ - $2\theta$  technique, scan speed of  $\omega = 6^\circ/\text{min}$ , background counts for 4 sec for both sides. Independent 3202 reflections were obtained, in which 2471 with  $F_o > 3\sigma(F_o)$  were used for the analysis. The final R is 0.073. The structure was solved by the direct method (MULTAN78).<sup>5)</sup> The refinement was carried out by the block-diagonal least-squares method (HBL5)<sup>6)</sup> applying an unit weight for all reflections. All the hydrogen atoms were obtained on a difference map and were included in the refinement with isotropic temperature factors. All the

computations were done on a FACOM M-140F at Shimane University Computer Center and a personal computer PC-9801VM2.

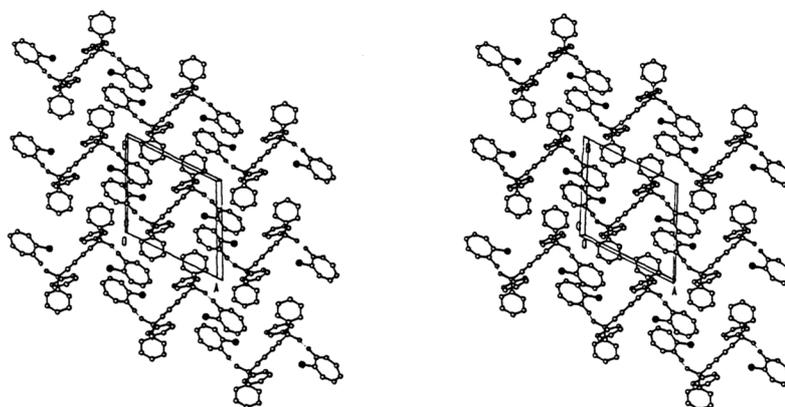


Fig. 3. Stereoscopic drawing of the crystal structure of **3** along the *c*-axis. Thin lines represent hydrogen bonds; S atoms as bold dots.

Stereoscopic view<sup>7)</sup> of the crystal structure of **3** is shown in Fig. 3. One host molecule works as two hydrogen bond donors and connects two guests with host to guest ratio of 1:2. The OH...O hydrogen bond of 2.824 Å plays an important role to the host-guest interaction. There is stacking between two guest molecules related by a center of symmetry (C3...C7 = 3.499 Å), but no stacking among host molecules. Other spaces are fully occupied by van der Waals contacts among the constituents of the crystal. The stacking of  $\lambda_a$  in **3** is comparable to that in graphite (ca. 3.5 Å). This might be a reason for that  $\lambda_a$  in **3** shows absorption bands at longer wavelength region than does  $\lambda$  in solution (Fig. 2). Fig. 3 also shows that two guest molecules are packed in the anti-directions each other. Due to the pucking in anti-directions, dimerization of  $\lambda_a$  to disulfide is probably prevented.

Bond lengths and angles of  $\lambda_a$  in **3** with numbering of the atoms are shown in Fig. 4. Bond alternation is little observed in  $\lambda_a$ . The bond lengths of C-C except C<sub>1</sub>-C<sub>2</sub> and C<sub>3</sub>-C<sub>4</sub> are in good agreement with the standard aromatic value of 1.394 Å.<sup>8)</sup> The C<sub>1</sub>-C<sub>2</sub> bond length of 1.465 Å is slightly shorter than the value of the C<sub>sp</sub><sup>2</sup>-C<sub>sp</sub><sup>2</sup> single bond (1.48 Å),<sup>9)</sup> so that this bond is included in the  $\pi$ -electron delocalization only to a small extent. Consequently,  $\lambda_a$  has a delocalized structure as B in Fig. 4. This delocalization has probably a relation to the UV-Vis spectrum of  $\lambda_a$  in **3** (Fig. 2). However, it is not clear why the C<sub>3</sub>-C<sub>4</sub> bond length (1.349 Å) is extremely shorter than others.

Delocalized structure has never been reported for 2-mercapto substituted tropone and tropolone. As an exception, ferric tropolonate (**4**) has been reported to have a delocalized structure as is shown in Fig. 5.<sup>10)</sup> Bond lengths of **4** are comparable to those of  $\lambda_a$ . However, this is a case of a strongly coordinated metal complex. Therefore, it is interesting that  $\lambda_a$  in **3** has a very similar electronic structure to that of tropolone in **4**.

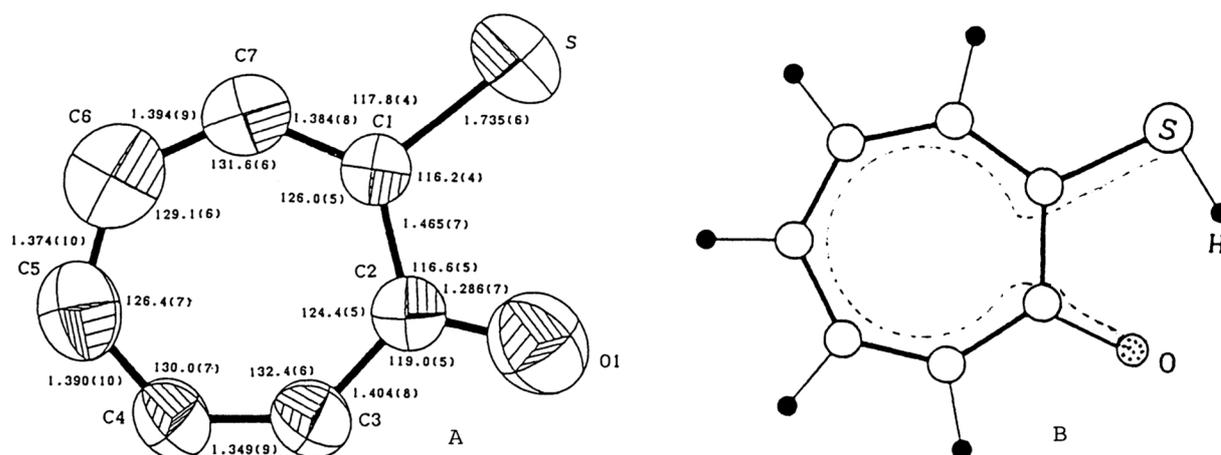


Fig. 4. Bond lengths and angles with numbering of the atoms (A) and a delocalized structure (B) of  $la$  in  $3$ .

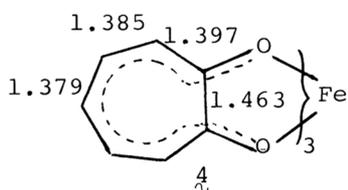


Fig. 5. Bond lengths of ferric tropolonate  $(4).10$

F. Toda, K. Tanaka, N. Tanaka, K. Hamada, and T. Fujiwara wish to thank for the Ministry of Education, Science and Culture for Grant-in-Aid for co-operative Research(A), No. 60303027, and F. Toda, K. Tanaka, and T. Asao also thank for co-operative Research(A), No. 60303005.

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(Received December 26, 1987)