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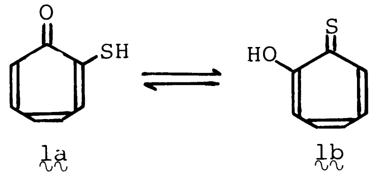
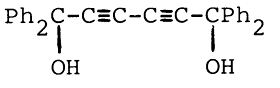
Of two tautomers of 2-mercapto substituted tropone, 2-mercaptotropone and 2-hydroxytropothione, the former is isolated as a 2:1 complex with 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol, and infrared and electronic absorption spectra of the complex are reported. X-Ray crystal structural study shows that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

2-Mercapto substituted tropone (1) has been reported to exist as 2-hydroxytropothione (1b) predominantly rather than 2-mercaptotropone (1a) both in solution1) and in the solid state.2) We report an isolation of the former (1a) as a 2:1 inclusion complex with 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol (2),3) 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 π-electron system.

To a solution of 1 (0.27 g, 1.96 mmol) in petrol ether (20 cm^3) 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 1a 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 which is readily oxidized to form the disulfide. Column chromatography of 3 on silica gel gives 1.

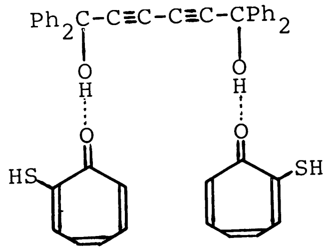


1a 1b



$Ph_2\underset{OH}{C}-C\equiv C-C\equiv C-\underset{OH}{C}Ph_2$

2



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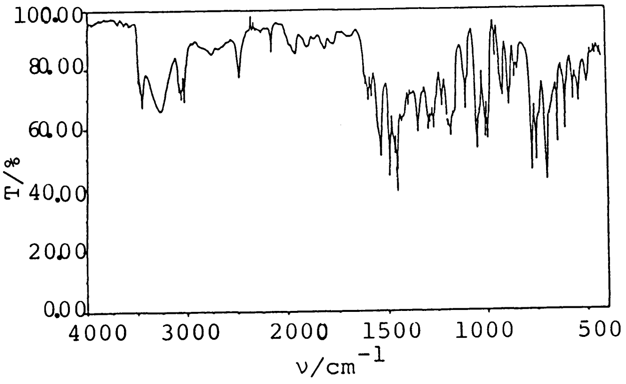

Fig. 1. IR Spectrum of **3** in KBr powder.

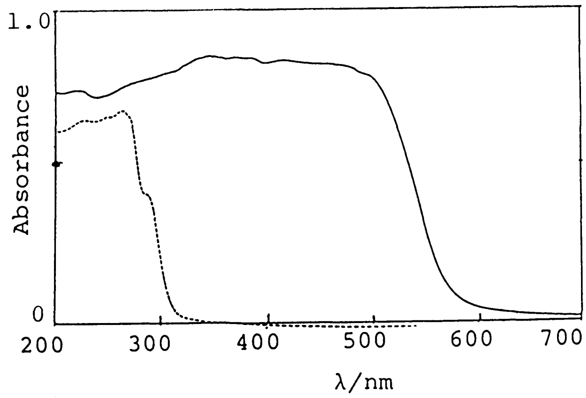

Fig. 2. UV-Vis Spectra of **2** (.........) and **3** (———) in the solid state.

The IR spectrum[4)] of **3** (Fig. 1) shows two ν_{OH} (3459.7 and 3270.7 cm^{-1}) and one ν_{SH} (2482.0 cm^{-1}). Since **2** shows only one ν_{OH} absorption band at 3534.9 cm^{-1} in the solid state, the two ν_{OH} bands of **3** would be due to the hydrogen-bonded OH groups in the complex. Appearance of ν_{SH} absorption, as well as strong C=O and C=C stretching absorptions characteristic of tropone structure at 1533.2 and 1463.7 cm^{-1},[2)] clearly indicates the presence of **1a** structure. Lack of strong bands due to the C-O-H group in the region of 1300-1200 cm^{-1}, observed in pure **1**,[2)] also supports the structure of **1a** in the present complex.

On the UV-Vis spectrum[4)] in the solid state, **3** shows absorption bands at a longer wavelength region than does **1** in solution (Fig. 2). **1** shows three absorption bands in solution at 237, 268, and 420 nm.[1)] Furthermore, **2** has no absorption band at visible region as shown in Fig. 2. These results suggest that **1a** of **3** is in a special circumstance which makes **1a**, for example, planar and/or polar. In order to clarify this, X-ray crystal structural study of **3** was carried out.

A large orange crystal of **3** was cut into the size of 0.21 x 0.50 x 0.50 mm^3 and used for the X-ray diffraction experiments on a Rigaku AFC-5 diffractometer using Cu-Kα (λ = 1.5418 Å) radiation. Unit cell constants were obtained by the least-squares fit using 38 reflections with $20° < 2\theta < 46°$. Crystal data are, $(C_{30}H_{22}O_2)\cdot 2(C_7H_6OS)$, Fw = 690.9, F(000) = 362, triclinic, $P\bar{1}$, Z = 1, a = 11.174(2), b = 11.380(1), c = 8.479(1) Å, α = 110.72(1)°, β = 85.72(1)°, γ = 116.41(1)°, V = 899.3(3) Å^3, D_m = 1.259 Mgm^{-3} by flotation method with citric acid aqueous solution, D_x = 1.276 Mgm^{-3}, μ = 16.43 cm^{-1}. Intensity data were collected up to 2θ = 128° by ω-2θ technique, scan speed of ω = 6°/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).[5)] The refinement was carried out by the block-diagonal least-squares method (HBLS)[6)] 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.

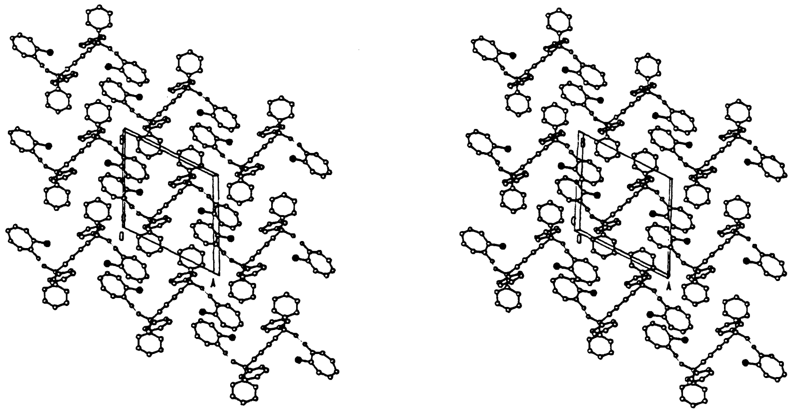

Fig. 3. Stereoscopic drawing of the crystal structure of **3** along the c-axis. Thin lines represent hydrogen bonds; S atoms as bold dots.

Stereoscopic view[7)] 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 constitutors of the crystal. The stacking of **1a** in **3** is comparable to that in graphite (ca. 3.5 Å). This might be a reason for that **1a** in **3** shows absorption bands at longer wavelength region than does **1** 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 **1a** to disulfide is probably prevented.

Bond lengths and angles of **1a** in **3** with numbering of the atoms are shown in Fig. 4. Bond alternation is little observed in **1a**. The bond lengths of C-C except C_1-C_2 and C_3-C_4 are in good agreement with the standard aromatic value of 1.394 Å.[8)] The C_1-C_2 bond length of 1.465 Å is slightly shorter than the value of the $C_{sp}2$-$C_{sp}2$ single bond (1.48 Å),[9)] so that this bond is included in the π-electron delocalization only to a small extent. Consequently, **1a** has a delocalized structure as B in Fig. 4. This delocalization has probably a relation to the UV-Vis spectrum of **1a** in **3** (Fig. 2). However, it is not clear why the C_3-C_4 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.[10)] Bond lengths of **4** are comparable to those of **1a**. However, this is a case of a strongly coordinated metal complex. Therefore, it is interesting that **1a** in **3** has a very similar electronic structure to that of tropolone in **4**.

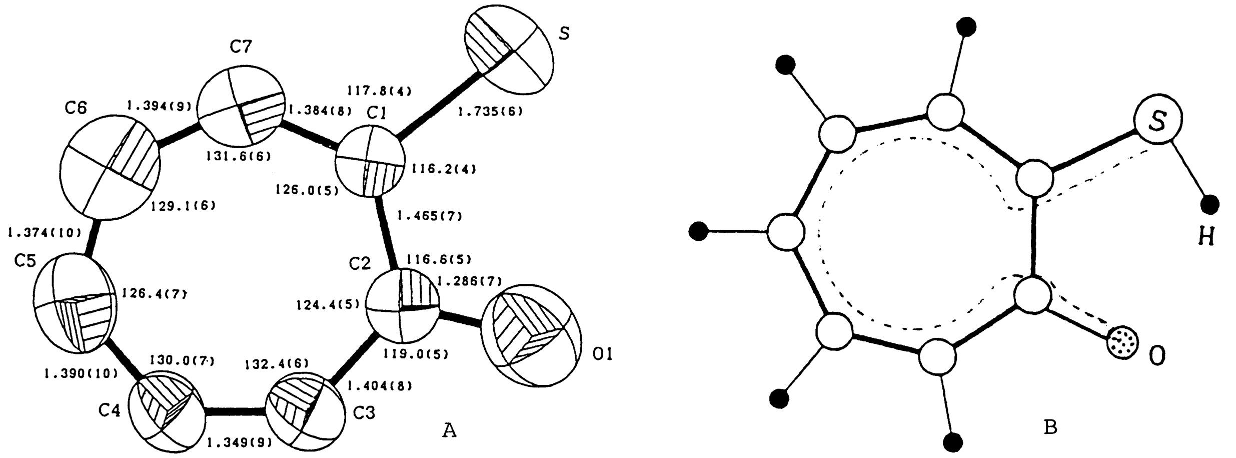

Fig. 4. Bond lengths and angles with numbering of the atoms (A) and a delocalized structure (B) of **1a** in **3**.

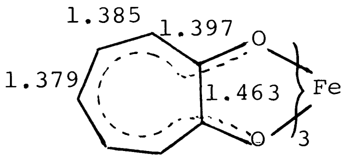

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Fig. 5. Bond lengths of ferric tropolonate (**4**).[10)]

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