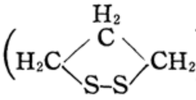
On the Near Ultraviolet Absorption Bands of Disulfides

By Akira Kuboyama

(Received May 15, 1957)

The alkyl disulfides whose two sulfur atoms adjoin each other, such as diethyl disulfide¹⁾ ($C_2H_5—S—S—C_2H_5$) and cystine¹⁾ show the longest wave length absorption maximum around 250 mμ (log $\varepsilon \sim 2.5$) in alcohol or water. But trimethylene disulfide²⁾ (TMD)  $\left(H_2C\langle^{\,C H_2}_{\,S-S}\rangle CH_2\right)$ and its derivative, 6,8-thioctic acid²⁾ (α-lipoic acid) have an absorption maximum about 330mμ (log $\varepsilon \sim 2.2$) in 95% ethanol. This red-shift observed with cyclic disulfides is remarkable as compared with open chain disulfides (OCD) and will be treated in this communication. R. S. Mulliken³⁾ regarded the bands under consideration as due to

---

1) H. Ley and B. Arend, *Z. Phys. Chem.*, *B* **17**, 177 (1932).

2) R. B. Whitney and M. Calvin, *J. Chem. Phys.*, **23**. 1750 (1955).

3) R. S. Mulliken, *J. Chem. Phys.*, **3**, 506 (1953).

the electronic transitions, $3p_S$(nonbonding)→$4s_S$[*1]. Here, probably 3p non-bonding orbitals are somewhat admixed with $3s_S$, but, now, as the first approximation this hybridisation is ignored. Briefly expressed by the molecular orbital method, $3p_S$ and $4s_S$ orbitals of disulfides split into $(3p_{S_1}\pm 3p_{S_2})$ and $(4s_{S_1}\pm 4s_{S_2})$, respectively, by the exchange intraction, and so the transition corresponding to the longest wavelength absorption is $(3p_{S_1}-3p_{S_2})\rightarrow(4s_{S_1}+4s_{S_2})$. According to this Mulliken's assignment, the above problem can be reasonably explained as follows. The S–S bond distances for TMD and OCD are assumed to be nearly equal. The energy of the upper molecular orbital $(4s_{S_1}+4s_{S_2})$ may be considered nearly equal to each other for TMD and OCD, since the overlapping between $4s_{S_1}$ and $4s_{S_2}$ is almost invariant with the rotation around the S–S axis. So, this red-shift which corresponds to the transition energy diminution ($\varDelta E_1$), 1.20 eV., may be explained on the basis of the lower orbital $(3p_{S_1}-3p_{S_2})$ energy. It may be thought that the mutual twist angle (θ) of the two C–S bonds around the S–S bond is nearly 90° for OCD, as for N,N-diglycyl-L-cystine dihydrate[4]. The situation is the same for dichlor disulfide[5], and hydrogen peroxide[6]. This is mainly due to the repulsive interaction between $3p_{S_1}$ and $3p_{S_2}$. On the other hand, the two C–S bonds of TMD are forced to take nearly cis-direction to each other around the S–S bond. By a molecular model, the maximum value of θ for TMD is ca. 40°. If θ for OCD and TMD are assumed to be 90° and 40°, respectively, the calculated overlap integral values (S) of $3p_{S_1}$ and $3p_{S_2}$ are zero and $(0.136\times\cos 40°=)0.103$. This means that in TMD the splitting between two orbital $(3p_{S_1}\pm 3p_{S_2})$ levels by the exchange interaction is much greater than that in OCD. Thus, the transition energy diminution can be qualitatively explained.

The fact that the OCD's 250 mμ bands are long-drawn-out absorptions is thought to be due to the change of θ-value caused by the thermal twisting vibration of the two C–S bonds around the S–S bond. In this connection, further comment will be made on the observed absorption specrum of hydrogen peroxide vapor[7]. This band with the continuously increasing intensity from 375 mμ to at least 215 mμ, may also be due to the transition, $(2p_{O_1}-2p_{O_2})\rightarrow(3s_{O_1}+3s_{O_2})$[3].

The rotational barrier height ($\varDelta E_r$) of the two C–S bonds around the S–S bond in disulfides can be roughly estimated from the above data. As is easily known from the above discussion, the energy (E_1) corresponding to the transition $(3p_{S_1}-3p_{S_2})\rightarrow(4s_{S_1}+4s_{S_2})$ and the total energy (E_2) of the four electrons of the two non-bonding orbitals $(3p_{S_1}\pm 3p_{S_2})$ are changeable with the angle θ. If we take OCD as the standard, the changes in these two quantities with θ can be represented by the following two formulae[8]:

$$\varDelta E_1=-(\beta-E_S S)/(1-S),$$

$$\varDelta E_2=2\{(\beta-E_S S)/(1+S)-(\beta-E_S S)/(1-S)\}$$

where, β, E_S and S denote the resonance integrals, the energy of 3ps orbital and the overlap integrals, respectively. For the derivation of the above formulae, it is assumed that θ is 90° for OCD. From these two formulae the following simple relation can be derived:

$$\varDelta E_2=\varDelta E_1\times 4S/(1+S)$$

Under the assumption that the change in the total energy of non-bonding electrons (E_2) is the most important factor in determining $\varDelta E_r$ and others such as the repulsive interaction between two alkyl groups and electrostatic interaction between C–S bonds can be neglected, $\varDelta E_2$ for $\theta=0°$ roughly equals to $\varDelta E_r$. If further reasonable assumption that $\varDelta E_1$ is proportional to S which is proportional to $\cos\theta$ is used, $\varDelta E_r$ equals $(1.20/\cos\theta_{\text{TMD}})\times 0.544/1.136$ e.v.. Here, θ_{TMD} denotes θ in TMD. If θ_{TMD} is 40°, $\varDelta E_r$ is 0.76 eV. This value is in good agreement with the one (0.74 eV.) obtained for dichlor disulfide by K. Hirota and T. Oka[5] from the wave number of the twisting vibration (106 cm.$^{-1}$).

The author wishes to express his sincere thanks to Dr. S. Nagakura of the Institute of Science and Technology, Tokyo University, for his kind guidance.

Faculty of Agriculture,
Miyazaki University.
Miyazaki

---

*1) In the following, subscription X denotes X atom

*2) Subscription S_1, S_2 denote the two sulfur atoms of disulfides.

4) H.L. Yakel and E. W. Hughes, *Acta Cryst.*, **7**, 291 (1954).

5) K. Hirota and T Oka, Presented at the Symposium on Structural Chemistry, Nagoya (1956).

6) J. T. Massey and D. R. Bianco, *J. Chem. Phys.*, **22**, 442 (1954).

*3) The overlap intehral values were obtained by Mulliken et al's table, *J. Chem. Phys.*, **17**, 1248 (1949), assuming the atomic distance to be 2.04A; D.P. Stevenson and J. Y. Beach, *J. Am. Chem. Soc.*, **60**, 2872 (1938).

*4) S for $\theta=0°$ is 0.136.

7) H. C. Urey, L. H. Dawsey and F. O. Rice, *J. Am. Chem. Soc.*, **51**, 1371 (1929).

8) C. A. Coulson, "Valence". Oxford (1952) p. 78.