

UV-Absorption Spectra of Complexes Between Some Disulfides and Iodine. II

BENGT NELANDER

Thermochemistry Laboratory, University of Lund, Chemical Center,
S-220 07 Lund 7, Sweden*

UV-spectra of complexes between 10 disulfides, cyclic and non-cyclic, and iodine have been recorded at 77°K. The results obtained are discussed in terms of a change in structure of the disulfide upon complex formation.

In the course of a series of investigations of complexes between organic disulfides and iodine, undertaken in this laboratory, it was found desirable to take up a suggestion of McGlynn *et al.*¹ to study these complexes at low temperature. Such an investigation might give more precise information on the changes in the UV-spectra of disulfides upon complex formation than that reported by McGlynn *et al.* and by Moreau and Weiss.² Besides it may demonstrate whether the disulfides undergo changes in structure upon complex formation, as was suggested by McGlynn *et al.*¹

EXPERIMENTAL

Materials. Me₂S₂ (Eastman Kodak) and *t*-Bu₂S₂ (Fluka) were distilled and then further purified by preparative GLC (Wilkins autoprep, apiezon) and dried with molecular sieves. No impurities could be detected by GLC (Pye Argon Chromatograph, 5 % apiezon).

i-Pr₂S₂ was prepared by iodine oxidation of *i*-PrSH³ (Fluka). The crude product was distilled in vacuum and then further purified by preparative GLC (Wilkins autoprep, apiezon) and dried with molecular sieves. No impurities were detected by GLC (Pye Argon Chromatograph, 5 % apiezon).

i-Pr *t*-BuS₂ was obtained by oxidation of the corresponding mercaptans (Fluka) with K₃Fe(CN)₆ as described in Ref. 4. The crude disulfide mixture was first distilled in vacuum and then further separated by preparative GLC (Wilkins autoprep, apiezon) and dried with molecular sieves. The sample used contained no impurities except for a trace of *i*-Pr₂S₂ (Pye Argon Chromatograph, 5 % apiezon).

1,2-Dithiacycloheptane was prepared from the corresponding dimercaptane (Fluka) by oxidation with FeCl₃.⁵ The disulfide was distilled in vacuum $n_D^{25}=1.5696$ (lit. $n_D^{25}=1.570^5$). Immediately before use the disulfide was distilled once more on a vacuum line. The stock solution used in the experiments reported below contained no impurities according to GLC (Pye Argon Chromatograph, 5 % apiezon).

* Sponsored by the Swedish Natural Science Research Council.

1,2-Dithiane was obtained from 1,4-butanedithiol as described in Ref. 6. The crude product was distilled in vacuum and then sublimed ($p=0.1$ torr.; no heating). Immediately before the stock solution was prepared the substance was once more sublimed under the same conditions. The sample used dissolved completely in 3-methylpentane. The stock solution used contained no impurities according to GLC (Pye Argon Chromatograph; 5 % apiezon).

2,3-Dithiatetraline was obtained by iodine oxidation of a petroleum ether solution of the corresponding dimercaptane, which in turn was prepared from α,α' -*o*-xylylene dibromide (Fluka) by the thiuronium synthesis. The disulfide was sublimed four times, the last time immediately before the stock solution was prepared. M.p. $76.2^\circ-77.2^\circ$ (lit.⁷ 80°). The sample used dissolved completely in 3-methylpentane.

1,2-Dithiolane. A 20 mM solution of 1,3-propanedithiole (Fluka, the dimercaptane contained less than 1 % impurities, Pye Argon Chromatograph, 5 % apiezon) in 3-methylpentane was oxidized with 0.05 M I_2 (in KI water solution). The excess iodine was removed by shaking a few seconds with a small amount of *ca.* 3 % Na_2SO_3 in water. The oxidized solution was then washed with water and used as a stock solution of 1,2-dithiolane. The solution obtained in this way was perfectly clear. The small water content should have no influence since a saturated solution of water in isopentane is about 3×10^{-3} M at room temperature⁸ and the solution was diluted *ca.* 25 to 100 times for the disulfide spectra and *ca.* 500 to 1000 times for the complex spectra. (In no case a Tyndall effect or any other sign of water precipitation was observed, when the solution was frozen down to $77^\circ K$.) At room temperature $\nu_{max}=30.31$ kK, $\epsilon_{max}=179$, $\nu_{min}=36.7$ kK, $\epsilon_{min}=49$ in isopentane:3-methylpentane (6:1). (Lit. $\nu_{max}=29.9$ kK, $\epsilon_{max}=147$ in aqueous ethanol⁹ and $\nu_{max}=30.3$, $\epsilon_{max}=142$ in CH_2Cl_2 .²)

2,3-Dithiaspiro(4,5)decane was obtained from Prof. Bergson, Uppsala University. The substance was distilled on a vacuum line, and since it was found by GLC (Pye Argon Chromatograph, 5 % apiezon) to contain *ca.* 10 % of an impurity, it was further purified by freezing out a small amount of the distillate on a cold finger (cooled with solid CO_2). The frozen out sample was found to contain less than 3 % impurities (GLC, Pye Argon Chromatograph, 5 % apiezon). A stock solution was prepared immediately after the freezing out was completed.

Iodine (Merck *p.a.*) was sublimed once and stored over conc. sulfuric acid until it was used.

Isopentane and 3-methylpentane (Phillips Petroleum Comp. techn. grade) were purified as described in Ref. 10. For the experiments with $i-Pr_2S_2$ the hydrocarbons were used within an hour after the last step of the purification was finished. In the other experiments the hydrocarbons were further purified by distillation through newly regenerated molecular sieves into a vacuum line with grease free valves.¹¹ Here they were degassed by repeated freezing down to $77^\circ K$, pumping down to a pressure of less than 10^{-4} torr and thawing. This procedure was repeated till no significant rise in the pressure was observed when the valve between the cooled down hydrocarbon and the rest of the vacuum system was opened. Treated in this manner the hydrocarbons could be stored on the vacuum line for several weeks.

Recording of spectra. The spectra were recorded on a Unicam SP 700 double beam recording spectrophotometer fitted with a liq. N_2 cooled cell compartment as described by Rosengren *et al.*¹² The spectrophotometer was calibrated using Phillips spectral lamp type 93106 E (Zn). All spectra were recorded in percent transmission, having two similar quartz cells in the two beams of the spectrophotometer, one with pure solvent and one with the solution under investigation. The difference in absorption in the two beams of the spectrophotometer due to different absorption of the two cells themselves, and to different absorption in the two light paths of the cell compartment, were determined in separate experiments and corrected for afterwards.

The solvent in all experiments reported here was a mixture of isopentane and 3-methylpentane (6:1). This mixture forms a glass at $77^\circ K$, which loses its rigidity at $83^\circ K$.¹³

Great care was exercised in preventing the atmosphere from getting into contact with the solvent, since it has been shown that O_2 in hydrocarbons decreases their transmission at wave numbers above *ca.* 45 kK¹⁰ and changes completely the absorption spectrum of dissolved iodine at $77^\circ K$.¹⁴

Stock solutions of iodine and of the disulfide under investigation were prepared in 3-methylpentane, purified according to the method of Ref. 10, but not degassed. The

stock solutions of iodine used were *ca.* 15 mM and the disulfide stock solutions used ranged from 20 mM to 100 mM. Prior to an experiment, they were diluted between 100 and 1000 times with solvent, purified and degassed as described above. No precautions were taken to protect the stock solution from the atmosphere, since the small amount of oxygen added to the solution to be investigated from the stock solutions should easily be removed in the degassing of the cell described above.

In the $i\text{-Pr}_2\text{S}_2$ experiments, the hydrocarbons from the "quick distillation" were distilled in vacuum ($p=12$ torr) into a mixing vessel (vol. 50 ml). Between 25 μl and 600 μl of stock solutions were added to the solvent from Hamilton micro syringes through a glass tube (inner diameter *ca.* 2.5 mm). A stream of dry N_2 through the glass tube kept the atmosphere away from the solvent. The solution was mixed with a magnetic stirrer. Part of the solution was forced into the cell, through a glass tube, using a small overpressure of N_2 . (The cell was flushed with dry N_2 immediately before it was filled.) The filled cell was transferred to a vacuum line, where it was degassed by repeated freezing with liq. N_2 , pumping to a pressure of less than 10^{-4} torr and thawing (3 to 4 times), before it was sealed off at 77°K.

In the remaining experiments the cell itself was used as mixing vessel. The cell was attached to a vacuum line with grease-free valves¹¹ with a special vacuum tight Viton O-ring seal. It was evacuated to less than 10^{-4} torr. The solvents were distilled into the cell from storage bottles on the vacuum line by cooling the cell with solid CO_2 and ethanol. The solvent volume was measured at this low temperature using the figures of Rosen-gren¹³ to correct for the changes in volume with temperature. A valve between the cell and the vacuum line was closed and the cell brought to room temperature. Measured quantities of the stock solutions were added to the cell from calibrated capillaries, while a stream of dry N_2 kept the atmosphere away from the solvent. The degassing of the cell was performed as above.

Using the values of the stability constant and heat of formation of the $i\text{-Pr}_2\text{S}_2$ iodine complex at room temperature, 4.5 l/mole and -4.7 kcal/mole resp. (in CCl_4 ¹⁵), the stability constant at 83°K (the softening temperature of the solvent) is estimated to be *ca.* 4×10^9 l/mole. From this estimate it seems to be a straightforward matter to obtain spectra of disulfide iodine complexes at 77°K. All one has to do is to prepare a solution with $[\text{I}_2]$ *ca.* 10^{-5} M and with a slightly higher disulfide concentration (ϵ_{max} of the most intense absorption band of $i\text{-Pr}_2\text{S}_2 \cdot \text{I}_2$ is *ca.* 17000 at room temperature) record its spectrum at 77°K and correct for the absorption of the free disulfide assuming that all iodine is consumed in forming a 1:1 complex. The estimate of $K_{83^\circ\text{K}}$ is very uncertain since ΔH may vary considerably with temperature, but a more serious complication is the low solubility of iodine at low temperatures, the effect of which is hard to evaluate theoretically. Therefore, in order to investigate the possibilities for studying the disulfide iodine complexes at 77°K, spectra were recorded of a number of solutions having the

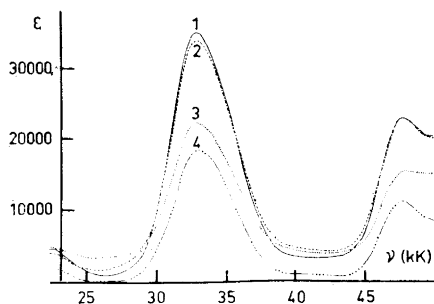


Fig. 1. Spectra of solutions having the same concentration of iodine and varying concentrations of $i\text{-Pr}_2\text{S}_2$, 77°K. $[\text{i-Pr}_2\text{S}_2]/[\text{I}_2]=4.7$, (curve 1); 3.5, (curve 2); 2.4, (curve 3); 1.2, (curve 4).

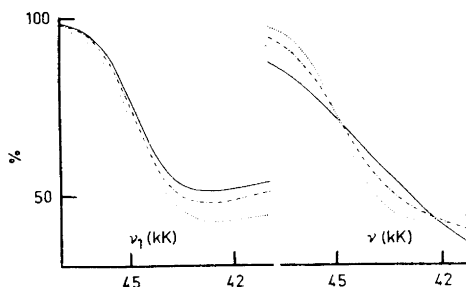


Fig. 2. Spectra of $i\text{-Pr}_2\text{S}_2 \cdot \text{I}_2$ during thawing (% transmission, no corrections applied). Left part: — 85°K; - - - 110°K; 140°K Right part: 140°K; ——— 160°K; ——— 175°K

same iodine concentration but with varying excesses of disulfide. The spectra were corrected for excess disulfide, assuming that all iodine was used up in forming a 1:1 complex. These corrections are rather small for the solutions studied here, less than 1 % of the total absorption below 35 kK even for the largest excess of disulfide. The spectra are given in Fig. 1 as $\epsilon(R_2S_2I_2)$ obtained under the assumption above. From the figure it is seen that the spectra obtained are qualitatively similar having absorption bands at the same positions. The absorption at the two strong absorption bands increases with increasing disulfide concentration but is roughly equal for the two solutions having largest excess of disulfide. Between the strong absorption bands the behavior is irregular. These observations suggest that the spectra are due to a combination of complex, precipitated iodine and to a minor extent free disulfide. The close similarity of the two solutions having the largest disulfide excess indicates that the complex is formed almost quantitatively in these cases. The "absorption spectrum" of precipitated iodine varies considerably with the cooling conditions,^{10,14} this is probably the cause of the irregular behavior of the spectra between the strong absorption bands.

In order to investigate the complex formation further, spectra of $i\text{-Pr}_2S_2 \cdot I_2$ were recorded during the warming up from 77°K to room temperature. Approximate temperatures of the cell were obtained from a five junction thermocouple having one series of junctions fastened to the outside of the cell and the other series at room temperature. Between 77°K and *ca.* 130°K small irregular changes occur, possibly due to changes in crystal size distribution of the precipitated iodine. Between 130°K and 190°K the strong absorption bands at 33 kK and 47 kK disappear and the weak absorption band at 22.6 kK moves to 19.2 kK (iodine absorption). All spectra in this temperature region go through three isosbestic points at 45.0 kK, 42.1 kK, and 20.3 kK. Above 190°K the spectra are simple superpositions of disulfide and iodine spectra. The observation of the three isosbestic points strongly supports the assumption of only one complex.

In order to investigate further the influence of iodine precipitation on the spectra obtained, the same cell was frozen down at high, intermediate, and low cooling rate and spectra recorded each time. The conditions were so chosen that more iodine should precipitate than in a normal experiment, the iodine concentration was higher than in the other experiments and the excess of disulfide less.

Fig. 3 shows the spectra obtained around the 22.6 kK band which is most sensitive to iodine precipitation. From the figure it is seen that the position of the absorption maximum is hardly affected by the cooling conditions, but ϵ_{\max} varies significantly.

It should be possible to ensure complete complexing of the iodine at 77°K using a large excess of disulfide, but the spectrophotometric accuracy seriously limits the possible excess of disulfide, especially if one wants to have reliable complex spectra above *ca.* 40 kK. Therefore a rather small excess of disulfide was used in the experiments reported below (*ca.* 3 to 5 times), the effect of iodine precipitation was investigated by recording

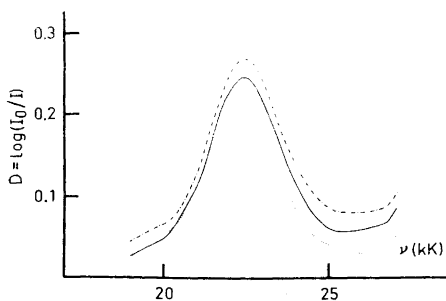


Fig. 3. Spectra of $i\text{-Pr}_2S_2 \cdot I_2$ at 77°K High (—), intermediate (---) and low (···) cooling rate (the same cell was used).

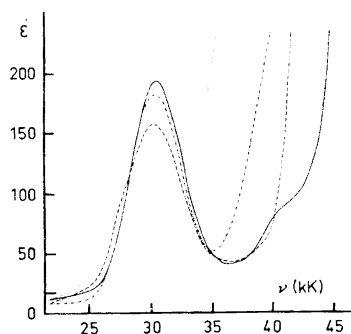


Fig. 4. Spectra of solutions of 1,2-dithiolane. ··· 1.1 mM, 77°K; — 0.76 mM, 77°K; — 0.46 mM, 77°K; --- 0.35 mM, 298°K.

at least three spectra for each complex studied using different excess of disulfide. The complex spectra reported below were obtained by correcting the recorded spectra for the absorption of the free disulfide as described above, using disulfide spectra obtained in connection with the complex spectra. The ϵ values given were obtained assuming complete complex formation.

RESULTS

The ϵ_{\max} values at 77°K of the lowest UV-band of the free disulfides studied here are given in Table 1. In the course of this investigation it was found that the spectra of 1,2-dithiolane and 2,3-dithia(4,5)spirodecane did not follow Lambert-Beer's law at 77°K although they did so at room temperature. Between *ca.* 35 kK and 45 kK the absorption increased faster than the square of the concentration. At lower wave numbers the deviations were smaller, for 1,2-dithiolane, $\epsilon(=D/[\text{disulfide}])$ increased somewhat with the concentration, for 2,3-dithia(4,5)spirodecane it decreased. These spectral effects were not affected by the last step in the purification of 2,3-dithia(4,5)spirodecane described above. One solution of 2,3-dithia(4,5)spirodecane was frozen down to 77°K, the spectrum recorded, the cell brought to room temperature and then frozen down again and the spectrum was recorded a second time. The two

Table 1.

Donor	Free disulfide		"23 band"			"47 band"		
	ν_m	ν_m	ϵ_m	$\Delta\nu_{1/2}$	ν_m	ϵ_m	$\Delta\nu_{1/2}$	
i-Pr ₂ S ₂	40.60	22.52	2880	2.62	47.60	23400	4.24	
Me ₂ S ₂	39.18	22.60	3620	3.96	49.3	13900	5.94	
(CH ₂) ₅ S ₂	38.71	23.0 ^a	— ^a	— ^a	46.68	— ^a	— ^a	
i-Pr <i>t</i> -BuS ₂	41.26	22.56	2860	2.57	47.03	21200	3.41 ^f	
<i>t</i> -Bu ₂ S ₂	44.48	22.69	2980	2.52	46.18	25200	3.78 ^g	
C ₆ H ₄ (CH ₂ S) ₂	35.10	23.4 ^b	7650 ^b	— ^b	— ^c	— ^c	— ^c	
(CH ₂) ₄ S ₂	34.47	22.93 ^c	3030 ^c	2.79 ^c	47.10	13900	4.44 ^f	
(CH ₂) ₃ S ₂	30.47	— ^d	— ^d	— ^d	— ^e	— ^e	— ^e	
C ₆ H ₁₀ (CH ₂ S) ₂	30.67	— ^d	— ^d	— ^d	— ^e	— ^e	— ^e	

^a Strong iodine precipitation in all experiments.

^b Large overlap with CTI.

^c Small overlap with CTI.

^d Completely disappeared under CTI.

^e No band was observed, see text.

^f $2(\nu_m - \nu_L)$, ν_L , wave number at half maximum absorption on the low wave number side. The absorption started to rise on the high wave number side before the half maximum peak height was attained.

^g Asymmetry, $\Delta\nu_{1/2}/2(\nu_m - \nu_L) = 1.14$.

spectra obtained were identical. For both five ring disulfides, the iodine complex spectra were corrected for the absorption of the free disulfide using the UV-spectrum of the least concentrated disulfide solution. This is not entirely correct since concentration of free disulfide in the complex solutions was much smaller than that of the least concentrated disulfide solution. It seems,

however, from plots of ϵ versus concentration for the disulfide solutions, as if ϵ should not change significantly when the concentration is decreased below the lowest concentration studied here. Besides, below *ca.* 46 kK the corrections for disulfide absorption are small compared to the absorption of the complex.

The data obtained from the complex spectra at 77°K are given in Table 1. All complex spectra except those of the five ring disulfides showed a weak band at *ca.* 22.5 kK (ϵ_{\max} *ca.* 2500). The data on this band given here are somewhat uncertain, especially the ϵ_{\max} and $\Delta\nu_{1/2}$ values, since they are quite sensitive to even small amounts of precipitated iodine. Attempts to increase the total concentration of the complex in order to increase the ratio of complex to precipitated iodine failed both for $\text{Me}_2\text{S}_2 \cdot \text{I}_2$ and 1,2-dithiane $\cdot \text{I}_2$. The spectra obtained showed a strong general absorption from *ca.* 20 kK to 51 kK, the absorption bands observed at lower total concentrations appeared as peaks and shoulders superimposed upon the general absorption.

All complexes studied showed a strong band ($\epsilon_{\max} > 14000$) between 24.6 kK (1,2-dithiolane $\cdot \text{I}_2$) and 32.7 kK (i-Pr₂S₂ $\cdot \text{I}_2$), the data obtained for this band are given under CT I in Table 2. Most complexes showed another strong band ($\epsilon_{\max} > 13000$) around 47 kK. The data for this band, "47-band", in Table 1 are somewhat uncertain since the corrections for the absorption of the free disulfide are large in this spectral region. The "47-band" was not

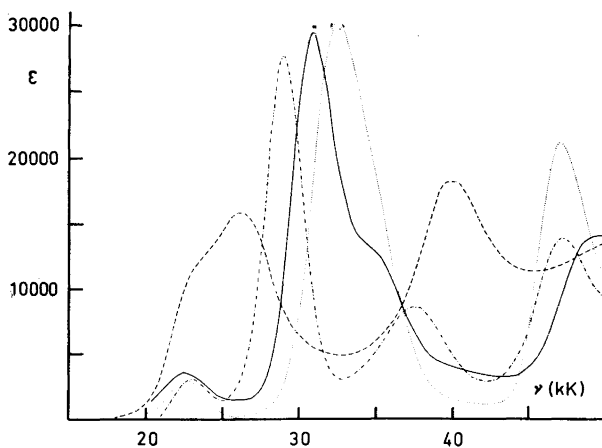


Fig. 5. Spectra of different disulfide-iodine complexes at 77°K. — $\text{Me}_2\text{S}_2 \cdot \text{I}_2$; - - - 1,2-dithiane $\cdot \text{I}_2$; ... i-Pr *t*-BuS₂ $\cdot \text{I}_2$; — · — 2,3-dithia[4,5]spirodecane.

observed for 2,3-dithiatetraline $\cdot \text{I}_2$ and for the two five ring disulfide complexes. For 2,3-dithiatetraline the strong absorption of the free disulfide made it impossible to record the complex spectrum above 43 kK. For the two five ring disulfide complexes $\epsilon_{47\text{kK}}$ was greater than 10000 but no maximum appeared.

The spectra of all complexes except those of $i\text{-Pr}_2\text{S}_2$ and $i\text{-Pr } t\text{-BuS}_2$ showed an absorption band (CT II in Table 2) somewhere between 32.6 kK and 39.9 kK. For $(\text{CH}_2)_5\text{S}_2 \cdot \text{I}_2$ and $\text{Me}_2\text{S}_2 \cdot \text{I}_2$ this band was visible only as a shoulder on the band called CT I above.

DISCUSSION

The reason for the deviations from Lambert-Beer's law in the five ring disulfide spectra at 77°K is not clear. It does not seem, however, as if they are due to an impurity in the disulfides since it would then be difficult to understand why the spectral changes of 2,3-dithia(4,5)spirodecane were unaffected by the last step in the purification of this compound in spite of the fact that gas chromatography showed an improvement in the purity from *ca.* 90 % to better than 97 %. Besides, the two five ring disulfides were prepared from entirely different starting materials and in entirely different ways but the spectral changes look much the same for both compounds. Another possible explanation is that the solubility of the disulfides decreases so rapidly with decreasing temperature that the disulfides precipitate in part when the solutions are frozen down. The spectral changes would then be due to microcrystals. This explanation seems a bit doubtful considering that identical spectra were obtained from two different freezings of the same cell. The remaining possibility seems to be a reversible formation of some kind of dipole aggregates containing varying numbers of disulfide molecules. The reason why this behaviour is limited to the five ring disulfides and was not observed for the other disulfides studied here might be the larger dipole moment of the five ring compounds [$\mu(2,3\text{-dithia}(4,5)\text{spirodecane})=2.84 \text{ D}^{16}$] as compared to the other disulfides [$\mu(1,2\text{-dithiane})=2.57 \text{ D}^{17}$ and for most non cyclic disulfides $\mu \text{ ca. } 2 \text{ D}^{18-22}$]. Besides, the steric requirements for association are favorable for the five ring compounds where the alkyl groups are kept away from the disulfide bond, thus facilitating the close approach of two disulfide molecules.

Spectra of disulfide-iodine complexes in solution have been studied by a number of authors^{1,2,23-26} and the two wave number bands observed in this work have been assigned to a shifted iodine band (the band at *ca.* 22.5 kK) and charge transfer absorption. The band observed in this work at *ca.* 47 kK has not been reported before. Its position is rather insensitive to the disulfide of the complex, which should then indicate that it is due to a shifted iodine absorption. The fact that it was not observed for the five ring disulfide complexes is probably due to a strong (triple) overlap between the "47-band", the band at *ca.* 40 kK and another strong band, probably the strong band observed for the free five ring disulfides in this region. The band observed here between *ca.* 32 kK and 40 kK has only been reported for 1,2-dithiane·I₂, by Moreau and Weiss,² and they assigned it to a shifted disulfide band. From Table 2 it is seen that its position varies with the disulfide in the complex roughly in the same way as the previously assigned charge-transfer band, but in the reverse direction. The large variations in position should rule out the possibility that the band is due to a shifted iodine absorption. Since the direction of the variations in position of the band for different disulfides are

Table 2.

Donor	CT I				CT II			
	ν_m	ϵ_m	$\Delta\nu_{1/2}$	asym.	ν_m	ϵ_m	$\Delta\nu_{1/2}$	asym.
i-Pr ₂ S ₂	32.73	35 000	5.31	1.29	— ^d	— ^d	— ^d	— ^d
Me ₂ S ₂	30.90	29 400	— ^b	— ^b	34.5 ^e	13 300 ^e	— ^e	— ^e
(CH ₂) ₅ S ₂	29.86	— ^a	— ^a	— ^a	32.8 ^e	— ^a	— ^a	— ^a
i-Pr t-BuS ₂	32.52	29 800	5.00	1.33	— ^d	— ^d	— ^d	— ^d
t-Bu ₂ S ₂	30.35	27 300	3.51	1.04	36.60	8 200	— ^c	— ^c
C ₆ H ₄ (CH ₂ S) ₂	27.81	17 100	— ^c	— ^c	35.04	10 500	— ^c	— ^c
(CH ₂) ₄ S ₂	29.01	27 600	2.87	1.05	37.41	8 600	6.06	0.957
(CH ₂) ₃ S ₂	24.60	15 400	— ^c	— ^c	39.76	16 100	— ^c	— ^c
C ₆ H ₁₀ (CH ₂ S) ₂	26.26	15 500	— ^c	— ^c	39.94	18 100	— ^c	— ^c

$$\text{Asym.} = \Delta\nu_{1/2}/2(\nu_m - \nu_L)$$

^a Strong iodine precipitation in all experiments.

^b Overlap with CT II made it impossible to obtain these values.

^c Overlap with neighbor bands made it impossible to obtain these values.

^d No band was observed.

^e Shoulder, data refer to inflection point.

opposed to the variations in position of the absorption band of the free disulfides in this region, it seems highly improbable that it can be assigned to a shifted disulfide absorption. Of the remaining possibilities charge-transfer from the disulfide to the iodine seems most probable. A reasonable assumption seems to be that the band under consideration is due to excitation of an electron from the $3p\pi$ orbital of the disulfide²⁷ to an empty orbital on the iodine molecule. The previously assigned charge-transfer band is then due to excitation from the $3p\pi^*$ orbital of the disulfide to the same orbital on the iodine molecule. If this assignment is correct we should expect the wave number difference between the two bands to vary as the difference in orbital energy of the $3p\pi$ and $3p\pi^*$ orbitals. This difference can be obtained from Bergson's formulae²⁷ as

$$\frac{2\gamma |\cos \theta|}{1 - (0.129 |\cos \theta|)^2}$$

where θ is the dihedral angle of the disulfide (CSS/SSC) and γ an empirical parameter.

In Ref. 26 values of γ were obtained for different types of disulfides; disulfides having two tertiary carbon atoms next to the disulfide bond, $\gamma=17.8$ kK; disulfides having one tertiary or two secondary carbon atoms next to the disulfide bond, $\gamma=13.7$ kK; and disulfides having primary carbon atoms or methyl groups next to the disulfide bond, $\gamma=10.3$ kK. In Ref. 1 and 26 it was made probable that the dihedral angles (CSS/SSC) of the disulfides change upon complex formation with iodine. In order to test the assignment above, we disregard this possibility to begin with and assume that the dihedral angles of the complexed disulfides to be the same as those of the free disulfides,

which are taken to be: 1,2-dithiolane ^a and 2,3-dithia(4,5)spirodecane ^b 27.5°, 1,2-dithiane ^a 60°, 2,3-dithiatetraline ^c 60.5°, 1,2-dithiacycloheptane ^c 80°, *t*-Bu₂S₂ 96.4°, and for the remaining noncyclic disulfides ^a 84.7.

Since the two bands CT I and CT II overlap strongly for most complexes, it was necessary to correct for the overlap in order to get reliable values for the wave number difference. This correction was done by approximating each of the two bands with a Gaussian peak, the width, height and position of which were adjusted to get maximum agreement with the measured spectrum. The use of Gaussian peaks may be questioned (see Ref. 29), however, for the complexes of 1,2-dithiane and *t*-Bu₂S₂, where the two bands were approximately separated, they were well represented with Gaussian peaks. No attempt was made to correct the wave number differences of 2,3-dithiatetraline·I₂ and 2,3-dithia(4,5)spirodecane·I₂, since the overlap seemed rather small in these cases. CT I of 1,2-dithiolane·I₂ was corrected for its overlap with the shifted iodine absorption using the same method. In all cases the overlapping bands were represented with Gaussian peaks well within the experimental uncertainties. The results of this resolution are given in Table 3. From Fig. 6 it is

Table 3. Results of resolution in Gaussian peaks.

Donor	ν_m	CT I $\Delta\nu_{1/2}$	f^a	ν_m	CT II $\Delta\nu_{1/2}$	f^a	δ^b
<i>i</i> -Pr ₂ S ₂	32.45	3.95	0.58	35.40	4.08	0.27	2.95
Me ₂ S ₂	30.75	3.19	0.39	34.63	5.53	0.33	3.88
(CH ₃) ₃ S ₂	29.53	3.90	— ^c	34.00	6.65	— ^c	4.47
<i>i</i> -Pr <i>t</i> -BuS ₂	32.25	3.55	0.44	35.05	3.75	0.22	2.80
<i>t</i> -Bu ₂ S ₂	30.37	3.42	0.42	36.60	5.81	0.19	6.23
(CH ₃) ₄ S ₂	29.07	2.86	0.36	37.42	5.37	0.22	8.35
(CH ₃) ₃ S ₃	25.57	7.05	0.45				

^a See Ref. 23, 24.

^b $\nu_m(\text{CT II}) - \nu_m(\text{CT I})$.

^c Strong iodine precipitation in all experiments.

seen that the wave number difference between the two bands, CT I and CT II, varies approximately in the expected manner but the deviations are probably significant. There are at least two effects which might contribute to these deviations. The first is the change in dihedral angle upon complex formation mentioned above. The second effect is the difference in resonance energy of the two different excited states of the complex, resulting from the two different ways of excitation. A brief calculation will illustrate this. We use Mulliken's picture of a charge-transfer complex as stabilized by resonance between a no bond structure $\psi_0 = \mathcal{A}(\psi_D\psi_A)$ and a dative structure ^{28,29,30} $\psi_1 = \mathcal{A}(\psi_D^+\psi_A^-)$.

^a See Ref. 26 and references therein.

^b Assumed to be the same as that of 1,2-dithiolane.

^c Obtained from the UV-spectrum using Bergson's formulae ²⁷ and the parameter values of Ref. 26.

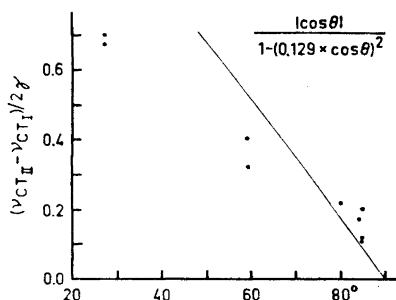


Fig. 6. $\nu_{\text{CTII}} - \nu_{\text{CTI}} / 2\gamma$ versus the dihedral angle of the free disulfide (see text).

The line is $|\cos\theta|/[1 - (0.129 \cos\theta)^2]$.

- \mathcal{A} is an appropriate antisymmetrizer.
 ψ_{D} is the wave function of the free donor, modified by the electrostatic interaction with the acceptor.
 ψ_{A} is the wave function for the free acceptor, modified by the electrostatic interaction with the donor.
 ψ_{D^+} is a wave function for the donor ion obtained by removing one electron from the $3p\pi^*$ orbital, modified by electrostatic interaction with the acceptor ion.
 ψ_{A^-} is a wave function for the acceptor ion, modified by electrostatic interaction with the donor ion.

We supplement this picture with a third structure

$$\psi_2 = \mathcal{A}(\psi_{\text{D}^+}, \psi_{\text{A}^-})$$

ψ_{D^+} is a wave function for the excited donor ion obtained by removing one electron from the $3p\pi$ orbital of the disulfide, modified by electrostatic interaction with the acceptor ion. We put $\langle 0|H|0\rangle = H_{00}$, $\langle 1|H|1\rangle = H_{11}$, $\langle 1|H|0\rangle = \beta$, $\langle 0|0\rangle = \langle 1|1\rangle = \langle 2|2\rangle = 1$, $\langle 1|0\rangle = S$ (H is the complete Hamiltonian of the system). In addition, we assume $\langle 2|H|1\rangle = \langle 2|H|0\rangle = \langle 2|1\rangle = \langle 2|0\rangle = 0$. The reason for the last assumptions is that the approximate symmetry at the disulfide bond is probably C_2 and ψ_2 on one hand and ψ_0 and ψ_1 on the other should belong to different representations of this group. This symmetry difference should be no hindrance to charge transfer absorption as discussed by Murell.³¹ Under the given assumptions we obtain

$$E_{\text{N}} = H_{00} - \frac{(\beta - H_{00}S)^2}{H_{11} - H_{00}} \quad \text{Energy of the ground state.}$$

$$E_{\text{E}} = H_{11} + \frac{(\beta - H_{11}S)^2}{H_{11} - H_{00}} \quad \text{Energy of the first excited state.}$$

$$E_2 = H_{22} \quad \text{Energy of the second excited state.}$$

$$H_{11} - H_{00} = I_{\text{D}} - E_{\text{A}} - G_1 + G_0$$

I_{D} is the vertical ionization potential of the donor.

E_{A} is the vertical electron affinity of the acceptor.

G_0 is the sum of several terms including the electrostatic interaction between the donor and acceptor molecules at the equilibrium distance of the complex.

G_1 is the sum of several terms, the dominating term being the electrostatic attraction between the donor and acceptor ions at the equilibrium distance of the complex; see Refs. 30 and 31.

$$H_{22} - H_{00} = I_D - E_A - G_1' - G_0 + \delta\epsilon_S$$

G_1' corresponds to G_1 for the excited donor ion and the acceptor ion.

$\delta\epsilon_S$ is the excitation energy of the donor ion, which in the following is approximated by the orbital energy difference between the $3p\pi^*$ and $3p\pi$ orbitals of the disulfide.

We now assume $G_1' = G_1$, this is probably not too dangerous since the overlap between the two $3p$ orbitals of the two sulfur atoms is rather small. Under these assumptions we get:

$$(\hbar\nu)_{\text{CT I}} = I_D - C + (\beta_0^2 + \beta_1^2)/(I - C) \quad (1)$$

$$(\hbar\nu)_{\text{CT II}} = I_D - C + \beta_0^2/(I - C) + \delta\epsilon_S$$

$$(\hbar\nu)_{\text{CT II}} - (\hbar\nu)_{\text{CT I}} = \delta\epsilon_S - \beta_1^2/(I - C) \quad (2)$$

$$(C = E_A + G_1 - G_0; \beta_0 = \beta - H_{00}S; \beta_1 = \beta - H_{11}S.)$$

From (2) we see that we have to correct the orbital energy difference from Bergson's formulae with the resonance energy of the first excited state of the complex to obtain the difference in excitation energy of the two different charge transfer states. If we make the usual assumptions that C , β and S are constant through the series of disulfide complexes and if we neglect the variations in β_0 and β_1 due to variations in H_{00} and H_{11} only three parameters are needed to correlate the positions of the two bands with the ionization potential of the disulfide for the whole series of complexes studied. In order to make this correlation we use the estimated orbital energies of the disulfides at 90° dihedral angle of Ref. 26 together with Bergson's formulae for the change in orbital energy of the $3p\pi^*$ orbital with dihedral angle.^{26,27} We assume $S=0.1$ (see Ref. 30). The two remaining constants can now be obtained from the positions of the two charge transfer bands of one single complex if we make an assumption about the dihedral angle of the complexed disulfide. In the following we assume that the dihedral angle of 2,3-dithia(4,5)-spirodecane does not change upon complex formation. This is a natural assumption in view of the slow variation of the orbital energy of $3p\pi$ and $3p\pi^*$ with dihedral angle for dihedral angles below *ca.* 30° . Using the positions of the charge transfer bands of the 2,3-dithia(4,5)spirodecane complex we obtain:

$$\beta_0 = -7.56 \text{ kK}; \beta_1 = -9.39 \text{ kK}; C = 38.9 \text{ kK}$$

Using these parameters together with the values of the orbital energies at 90° dihedral angle and Bergson's formulae for the changes in orbital energies with dihedral angle, we can calculate the dihedral angle of the complexed disulfide necessary to explain the position of CT I (method I) or to explain the wave number difference between CT II and CT I (method II). The dihedral angles resulting from these two estimates are given in Table 4 together with the corresponding estimates of Ref. 26 (at room temperature). The values in Table 4 are obtained under the assumption that the dihedral angle preferably

Table 4. Estimated dihedral angles of complexed disulfides.

Donor	Method I	Method II	From Ref. 26
i-Pr ₂ S ₂	89°	76°	82°
Me ₂ S ₂	60°	69°	64°
(CH ₂) ₃ S ₂	61°	67°	—
i-Pr <i>t</i> -BuS ₂	90°	76°	85 ^{ca}
<i>t</i> -Bu ₂ S ₂	96°	107°	101°
(CH ₂) ₄ S ₂	58°	53°	48°
C ₆ H ₄ (CH ₂ S) ₂	47°	58°	—
(CH ₂) ₃ S ₂	12°	24°	28 ^{ca}
C ₆ H ₁₀ (CH ₂ S) ₂	28 ^{ca}	28 ^{ca}	—

^a Assumed value.

decreases upon complex formation. From the formulae given above it is impossible to tell whether the dihedral angle is below or above 90° but, as was argued in Ref. 26, the long distance between the two alkyl groups on different sides of the disulfide bond makes it probable that their interaction is attractive. The differences between the three estimates in Table 3 are hardly significant in view of the underlying assumptions. The estimates from $(h\nu)_{CTI}$ depend strongly upon the rather crude ionization potential estimates of Ref. 27 and upon the assumption that it is possible to correlate both ionization potential change and red shift of the UV-absorption band with changing dihedral angle using the same parameter. The estimate from the wave number difference depends strongly upon the assumption that it is possible to calculate the excitation energy of the disulfide ion from an orbital energy difference of the neutral disulfide.

Acknowledgement. The gift of a sample of 2,3-dithia(4,5)-spirodecane from Professor G. Bergson, Uppsala, is gratefully acknowledged.

REFERENCES

- McGlynn, S. P., Nag-Chaudhuri, J. and Good, M. J. *Am. Chem. Soc.* **84** (1962) 9.
- Moreau, W. M. and Weiss, K. *J. Am. Chem. Soc.* **88** (1966) 204.
- Vogel, A. I. *A Textbook of Practical Organic Chemistry Including Qualitative Analyses*, Longmans, Green and Co., London, New York, Toronto 1948.
- Allan, D. T., Cullam, T. V., Dean, R. A. and Fidler, F. A. *J. Am. Chem. Soc.* **73** (1951) 3627.
- Schöberl, A. and Gräfe, H. *Ann.* **614** (1958) 66.
- Claesson, G., Androes, G. and Calvin, M. J. *Am. Chem. Soc.* **83** (1961) 4357.
- Lüttringhaus, A. and Hägele, K. *Angew. Chem.* **67** (1955) 304.
- Hildebrand, J. H. and Scott, R. L. *The Solubility of Non Electrolytes*, ACS Monograph Series, (3.Ed.), Reinhold, New York.
- Barltrop, J. A., Hayes, P. M. and Calvin, M. J. *Am. Chem. Soc.* **76** (1954) 4348.
- Nilsson, O. *Acta Chem. Scand.* **21** (1967) 1501.
- Private communication from Dr. Rosengren, Thermochem. Lab., Lund.
- Rosengren, Kj., Sunner, S. and Timm, D. *Acta Chem. Scand.* **16** (1962) 467.
- Rosengren, Kj. *Acta Chem. Scand.* **16** (1962) 1421.

14. Timm, D. *Acta Chem. Scand.* **20** (1966) 2219.
15. Nelander, B. and Norén, I. *Acta Chem. Scand.* To be published.
16. Krackov, M. H., Bergson, G., Biezais, A. and Mautner, H. G. *J. Am. Chem. Soc.* **88** (1966) 1759.
17. Kalff, H. T. and Havinga, E. *Rec. Trav. Chim.* **81** (1962) 282.
18. Westlake, Jr., H. E., Laequer, H. L. and Smyth, C. P. *J. Am. Chem. Soc.* **72** (1950) 436.
19. Kushner, L. M., Gorin, G. and Smyth, C. P. *J. Am. Chem. Soc.* **72** (1950) 477.
20. Woodrow, C. C., Cormac, M. and Miller, J. G. *J. Chem. Phys.* **19** (1959) 951.
21. Rogers, M. and Campbell, T. *J. Am. Chem. Soc.* **74** (1952) 4742.
22. Vasil'eva, V. N. and Gur'yanova, E. N. *Zh. Fiz. Khim.* **33** (1959) 1976.
23. Tsubomura, H. and Lang, R. *J. Am. Chem. Soc.* **83** (1961) 2085.
24. Good, W., Major, A., Nag-Chaudhuri, J. and McGlynn, S. P. *J. Am. Chem. Soc.* **83** (1961) 4329.
25. Moreau, W. M. and Weiss, K. *Nature* **208** (1965) 1203.
26. Nelander, B. *Acta Chem. Scand.* **23** (1969) 2127.
27. Bergson, G. *Arkiv Kemi* **12** (1958) 233.
28. Briegleb, G. *Elektronen-Donator-Acceptor-Komplexe*, Springer, Berlin, Göttingen, Heidelberg 1961.
29. Mulliken, R. S. *J. Am. Chem. Soc.* **56** (1952) 801.
30. Mulliken, R. S. and Person, W. B. *Ann. Rev. Phys. Chem.* **13** (1962) 107.
31. Murell, J. N. *Quart. Rev. (London)* **15** (1961) 191.

Received November 27, 1968.