UV-Absorption Spectra of Complexes Between

Some Disulfides and Iodine. I

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UV-absorption spectra of complexes between 14 disulfides, cyclic
and noncyclic, and iodine have been recorded at room temperature.
The results obtained are discussed in terms of a change in the structure
of the disulfide upon complex formation.

Spectra of donor acceptor complexes in which organic disulfides act as
electron donors were first studied by Tsubomura and Lang [1] and by Good
et al.[2] In 1962 McGlynn et al.[3] advanced the hypothesis of a change in the
structure of the disulfide when it acts as an electron donor. They based this
hypothesis on an observed redshift of the 40 kK absorption band of Am_2S_2
upon complex formation with iodine, and upon some theoretical considerations
of the change of electronic structure in the disulfide bond when acting as an
electron donor. An alternative explanation of this redshift has been proposed
by Moreau and Weiss [4] in a molecular orbital study of complexes between
tetracyanoethylene (TCNE) and disulfides with varyign dihedral angles. Their
calculations can explain not only the redshift of noncyclic disulfides but also
a blueshift of the corresponding absorption of thioctic acid which they have
observed in its complex with TCNE.[4,5] However, neither McGlynn et al. nor
Moreau and Weiss take into account the interaction between the excited
state of the disulfide and the acceptor and this interaction may well give
rise to effects even larger than those observed. Such an interaction has been
suggested by Mulliken [6] as an explanation for the blueshift of the visible
absorption of iodine upon complex formation. Moreover the assignment by
Moreau and Weiss of the peak they observe at about 310 mμ to a blue shifted
disulfide absorption band seems somewhat questionable since it would
implicate a tenfold increase in extinction coefficient upon complex formation
(as estimated from Fig. 3 of Ref. 4). The frequency difference between the
band at 310 mμ and the band at 583 mμ, assigned by Moreau and Weiss

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to CT-exitation, is about what would be expected if they were due to CT-exitation from the bonding and antibonding $3p\pi$ molecular orbitals of the disulfide bond. Both these transitions have been observed in UV absorption spectra of complexes between disulfides and iodine at 77°K in this laboratory.[7]

EXPERIMENTAL

Materials. The noncyclic disulfides were, if necessary, distilled in vacuum, then further purified by preparative GLC (Wilkens autoprep, apiezon) and dried with molecular sieves. Purities as estimated from GLC (PYE Argon Chromatograph, 5 % apiezon): Me_2S_2, Et_2S_2, Pr_2S_2, i-Pr_2S_2, t-Bu_2S_2, t-Am_2S_2: no detectable impurities; i-Bu_2S_2, s-Bu_2S_2, Me EtS_2, Me t-BuS_2, Et t-BuS_2, i-Pr t-BuS_2: traces of impurities, which in case of the mixed disulfides were the corresponding symmetric disulfides.

1,2-Dithiane was prepared and purified as in Ref. 8. It was sublimed immediately before the preparation of the stock solution. The sample contained a trace of polymer which did not dissolve in CCl_4.

1,3-Propanedithiole and 1,4-butanedithiole: pure samples were obtained from Dr. Månsson of this laboratory.

CCl_4, Fisher UV-grade was used without further purification.

Iodine, Merck *p.a.* was used without further purification.

Recording of spectra. A stock solution of the disulfide under investigation was prepared immediately before use. Since it was found that the age of the iodine solution had no influence on the resulting spectra the same iodine solution could be used as stock solution in several experiments. CCl_4 was used as solvent in all experiments reported here.

The stock solution of 1,2-dithiolane was made by titration of a solution of 1,3-propanedithiole in CCl_4 with iodine in the same solvent in presence of a small amount of water. After the titration the excess of iodine was removed by shaking with a solution of Na_2SO_3. The solution was then dried with molecular sieves and used as stock solution of disulfide. To test this method a stock solution of 1,2-dithiane was prepared in the same way from 1,4-butanedithiole. The position of the CT absorption peak did not differ from what was found when the stock solution was made from pure dithiane. The solution, however, contained a significant amount of impurities the CT-absorption of which made it impossible to obtain the frequency value at half maximum absorption on the high frequency side of the peak. It seems from the CT spectra as if much less impurities were formed in the dithiolane experiments. In these cases no difficulties were encountered in obtaining frequency values at half maximum absorption on both sides of the peak.

From the stock solutions of iodine and the disulfide under investigation three solutions were prepared for each spectrum, with total concentrations of iodine (C_I) and disulfide (C_S), resp. I: $(C_I, 0)$, II: $(0, C_S)$ and III: (C_I, C_S). In the reference beam of the spectrophotometer (Unicam SP 700) were placed two cells, one with solution I and one with solution II, and in the sample beam two cells, one with solution III and one with pure solvent.

Since the concentrations of free iodine and disulfide in solution III are less than in I and II, respectively, because of the complex formation, the spectrophotometer will overcompensate for the absorption of these species. However, since the concentration changes are small in the concentration intervals used (0.5 mM$\leq C_I \leq 15$ mM; 0.5 mM$\leq C_S \leq 10$ mM) and since the free components absorb little around the CT maximum the overcompensation does not influence the measurement of the absorption maximum to a significant extent. This is shown by a simple calculation:

The optical density of the reference beam is

$$D_{ref} = C_S\varepsilon_S + C_I\varepsilon_I$$

and in the sample beam

$$D_S = X\varepsilon_X + (C_S - X)\varepsilon_S + (C_I - X)\varepsilon_I$$
$$[R_2S_2 \cdot I_2] = X$$

We can here put $X = K \cdot C_S C_I$ (K, stability constant of the complex) which is sufficiently accurate for our purpose. The difference in optical density is thus given by

$$D_s - D_{ref} = K C_S C_I (\varepsilon_X - \varepsilon_I - \varepsilon_S)$$

in the interval around the CT maximum we can put

$$\varepsilon_S - \varepsilon_S{}^o = k_s (\nu - \nu^o); \quad \varepsilon_I - \varepsilon_I{}^o = k_I (\nu - \nu^o)$$

$$\varepsilon_X - \varepsilon_X{}^o = -1/2 \, L_X (\nu - \nu^o)^2$$

where $\varepsilon_s{}^o$, $\varepsilon_1{}^o$ and $\varepsilon_X{}^o$ are the values at ν^o, the position of the true CT absorption maximum. The difference between the maximum measured ν_m, and the true maximum ν^o is then given by:

$$\nu_m - \nu^o = - \frac{k_s + k_I}{L_X}$$

From measurements made in connection with the detemination of the position of the CT absorption of $Et_2S_2 \cdot I_2$ (Beckmann DU spectrophotometer) reported below was obtained: for iodine $\varepsilon_{33.3} = 33$, $\varepsilon_{31.3} = 17$, and for Et_2S_2 $\varepsilon_{33.3} = 65$, $\varepsilon_{31.3} = 10$ and thus $k_I = 8$ and $k_s = 28$ (ν in kK).

If we assume that the CT absorption peak can be approximated by

$$\varepsilon_X = \varepsilon_X{}^o \cdot \exp[-a(\nu - \nu^o)^2]$$

we obtain $L_X = 2a\varepsilon_X{}^o$, using the values given in Table 1 for the band width at half maximum absorption of $Et_2S_2 \cdot I_2$ we can calculate $a = 0.051$. In the measurement mentioned above we got $\varepsilon_X{}^o = 15000$. Thus we get $L_X = 1530$ and $\nu_m - \nu^o = -0.02$ kK.

In order to test the method the position of the CT absorption maximum of $Et_2S_2 \cdot I_2$ was determined by taking up the spectrum of a solution containing known amounts of disulfide and iodine. The absorption of the free components was subtracted by means of spectra of solutions of the pure components and the stability constant of the complex obtained in this laboratory.[9] These measurements were made on a Beckman DU spectrophotometer fitted with a thermostated cell compartment which could be kept at $25.0 \pm 0.1°C$. The result obtained agreed within the uncertainty limits in Table 1 with what was obtained from the Unicam experiments.

A further check on the method was obtained by recording eight spectra of Et t-BuS$_2 \cdot I_2$ with varying total concentrations of iodine and disulfide as described above. In six experiments where $0.808 \geq C_S \geq 5.79$ mM and $15.5 \geq C_I \geq 1.55$ mM the results all fell within the limits in Table 1. When the iodine concentration was further increased the maximum moved ca. 0.5 kK towards lower frequencies, probably because the spectrophotometer could no longer compensate for the iodine absorption.

In connection with the measurements both the Unicam spectrophotometer and the Beckman DU spectrophotometer were calibrated against the known frequencies of a Zn-lamp.

RESULTS

The results obtained are given in Table 1.

Ionization potentials. According to Mulliken's theory of charge transfer complexes [10,11] the frequency of the CT absorption maximum should increase with increasing ionization potential of the donor for complexes between a series of donors with a common acceptor. This rule seems to be obeyed surprisingly well even by widely different donors.[10] Unfortunately, the ionization potentials of the compounds studied here have been measured only for Me_2S_2 [12-15] and Et_2S_2.[12,13,15] It is seen from Table 1 that the CT absorption band of $Me_2S_2 \cdot I_2$ lies at a lower frequency than that of $Et_2S_2 \cdot I_2$ contrary to what could be expected from the ionization potentials. In order to investigate this phenomenon further the ionization potentials of the disulfides studied have to be estimated.

Table 1.

Donor	r_{m}	$\Delta r_{1/2}$	Asymmetry parameter
$Me_2S_2(5)$	32.06 ± 0.06	8.10	1.23
$MeEtS_2(4)$	32.17 ± 0.08	7.65	1.15
$Et_2S_2(4)$	32.30 ± 0.09	7.34	1.08
$Pr_2S_2(1)$	31.95	7.23	1.11
$i\text{-}Bu_2S_2(2)$	31.57 ± 0.03	7.50	1.11
Me $t\text{-}BuS_2(1)$	32.37	6.29	1.04
$i\text{-}Pr_2S_2(2)$	31.94 ± 0.02	7.03	1.09
$s\text{-}Bu_2S_2(1)$	31.77	6.94	1.06
Et $t\text{-}BuS_2(6)$	32.00 ± 0.05	6.52	1.05
$i\text{-}Pr$ $t\text{-}BuS_2(2)$	31.87 ± 0.02	6.90	1.05
$t\text{-}Bu_2S_2(1)^a$	29.73	6.42	1.19
$t\text{-}Am_2S_2(1)$	29.37	6.57	1.17
1,2-Dithiane$(1)^a$	28.65	4.55	1.02
1,2-Dithiane$(3)^b$	28.64 ± 0.04	—	—
1,2-Dithiolane(3) ^{a,b}	26.86 ± 0.04	6.07	1.05

$\Delta r_{1/2}$ peak width at half maximum absorption. Asymmetry parameter, defined by Briegleb,[10] $\Delta r_{1/2}/2(r_{\mathrm{m}} - r_{\mathrm{L}})$ where r_{L} is the frequency at half maximum absorption on the low frequency side of the band.

The numbers given in parenthesis behind the names of the disulfides are the numbers of experiments performed in each case, except for Et $t\text{-}BuS_2$ as described above. The uncertainty limits give the maximum deviation from the mean value in case more than one experiment was made.

^{a} These values may be compared to those reported in Ref. 4. $t\text{-}Bu_2S_2 \cdot I_2$: 29.85 kK, 1,2-dithiane: 28.74 kK, and 1,2-dithiolane: 27.40 kK.

^{b} Titration experiments as described in the text.

When doing this it is necessary to take into account the influence of the dihedral angle, $\angle C_1S_1S_2/S_1S_2C_2$, on the ionization potential. This has been done with a simple MO-method described by Bergson.[16] He gives the orbital energies of the bonding and antibonding $3p\pi$ MO's of the disulfide bond as

$$\varepsilon_{3p\pi} = \varepsilon_{90} - \frac{\gamma |\cos \theta|}{1 + 0.129 |\cos \theta|}$$

$$\varepsilon_{3p\pi^*} = \varepsilon_{90} + \frac{\gamma |\cos \theta|}{1 - 0.129 |\cos \theta|}$$

respectively. (θ, dihedral angle)

γ is a combination of molecular integrals which is taken to be an empirical parameter. The value of γ is obtained from UV absorption spectra of disulfides with known dihedral angles assuming that their most low frequent UV-absorption band is due to excitation from the $3p\pi^*$ orbital to an orbital whose energy does not depend to an appreciable extent on the dihedral angle.

In the following it is assumed that the dihedral angle of all 1,2-dithiolane derivatives is $27.5°$ (the value obtained by Foss et al. for 1,2-dithiolane-4-carboxylic acid [17]) and that of all 1,2-dithiane derivatives is $60°$ (the value obtained by Foss et al. for the 3,6-dicarboxylic acid of dithiane [18]). Lacking data, the

dihedral angles of all noncyclic disulfides except t-Bu$_2$S$_2$ and t-Am$_2$S$_2$ were assumed to be 84.7°, the value obtained for Me$_2$S$_2$ by Sutter et $al.$[19] The dihedral angle of t-Bu$_2$S$_2$ was calculated to be 96.4° from the dipole moment data of Rogers and Campbell [20] assuming that the dihedral angle of Bu$_2$S$_2$ is 84.7°. The dihedral angle of t-Am$_2$S$_2$ was assumed to be equal to that of t-Bu$_2$S$_2$. To obtain a value of γ we plot values of ν_{max} for a number of disulfides against $|\cos\theta|/(1-0.129|\cos\theta|)$ (θ the dihedral angle CSS/SSC). The result is shown in Fig. 1. From the figure it is seen that the value of γ depends on the type of carbon atoms next to the disulfide bond. In the following three different values of γ are used; for disulfides having two tertiary carbon atoms next to the disulfide bond 17.83 kK, for other disulfides having at least one tertiary or secondary carbon atom next to the disulfide bond 13.68 kK, and for all other disulfides 10.29 kK.
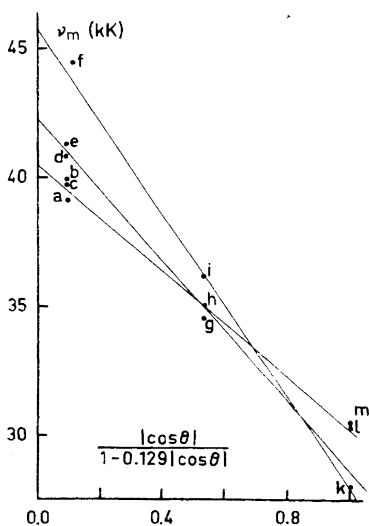

Fig. 1. ν_{max} of free disulfide *versus* $|\cos\theta|/[1-0.129|\cos\theta|]$ (see text). Me$_2$S$_2$ (a); Et$_2$S$_2$ (b); Bu$_2$S$_2$ (c); i-Pr$_2$S$_2$ (d); t-Bu i-PrS$_2$ (e); t-Bu$_2$S$_2$ (f); 1,2-dithiane (g); 3,6-dimethyl-1,2-dithiane (h); 3,3,6,6-tetramethyl-1,2-dithiane (i); 3,3,5,5-tetramethyl-1,2-dithiolane (k); 1,2-dithiolane (l); and 2,3-dithia(4,5)spirodecane (m). (a) (b) (c) (d) from Ref. 21; (e) $\nu_m(77°K)=41.26$, Ref. 7; (f) $\nu_m(77°K)=44.48$, Ref. 7; (g) $\nu_m(298°K)=34.47$ (this work); (h) from Ref. 22; (i) (k) from Ref. 23.
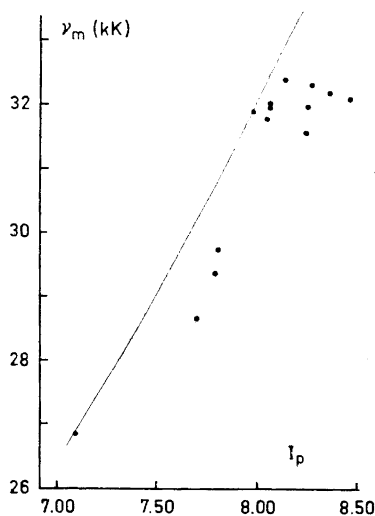
Fig. 2. ν_{max} of disulfide, iodine complex *versus* I$_p$ (eV) of the free disulfide. The curve is obtained from the equation of Hastings et $al.$ (see text).

In order to obtain ionization potentials we have to calculate the ε_{90}-values and assume Koopmans' theorem to be valid. The ε_{90}-values have been calculated with the method of Franklin,[24] using his parameter values for the hydrocarbon residues. The parameters for the disulfide bond were obtained

from the ε_{90}-values of Me_2S_2 and Et_2S_2, calculated from the photoionization values of the ionization potentials with the formulas given above. Me_2S_2 was treated as a united atom in the sense of Franklin. The ε_{90}-values of 1,2-dithiane and 1,2-dithiolane were assumed to be equal to that of Pr_2S_2. The ionization potentials obtained in this way are given in Table 2. They are probably slightly better than those given in Ref. 25.

<center>DISCUSSION</center>

Fig. 2 shows the ν_{max} values of the CT-band as a function of the estimated ionization potentials. The over all variation of the ν_{max} values with the ionization potentials is what could be expected from theory, but among the noncyclic disulfides some seemingly irregular variations occur. These can be understood, however, in terms of a change in dihedral angle suggested by McGlynn et al.[3] In order to get an idea of the magnitude of the changes necessary to explain the variations, we could try to estimate the ionization potentials leading to the observed CT absorption maxima and then calculate the change in dihedral angle from the difference between the two estimates of the ionization potential by means of Bergson's formula. To get ionization potentials from the observed CT absorption maxima we have used the formula given by Hastings et al.[26] for the dependency of the CT-excitation energy on the ionization potential of the donor.

$$h\nu_{CT} = I_p - C_1 + \frac{C_2}{I_p - C_1}$$

where ν_{CT}, frequency at charge transfer absorption maximum, I_p ionization potential of the donor, C_1 and C_2, see Refs. 10 and 11. $C_1 = 38.0$ kK, $C_2 = 147$ $(kK)^2$.

The parameters in the formula were evaluated from the CT-excitation energies and ionization potentials of 1,2-dithiolane and i-Pr t-BuS_2, assuming that these two compounds do not change their dihedral angles upon complex formation. The choice of 1,2-dithiolane should not be too dangerous since the ionization potential of this compound should be quite insensitive to changes in dihedral angle. The choice of i-Pr t-BuS_2 is more questionable, however, but since the ionization potential of a disulfide decreases when the dihedral angle changes from 90° the estimates of ionization potentials from the CT-excitation energies should be lower than those obtained by the first method. This would not be the case if we choose any other noncyclic disulfide as unchanged upon complex formation. Further support for the assumption that the dihedral angle of i-Pr t-BuS_2 does not change much upon complex formation is obtained from a study of disulfide iodine complexes at 77°K.[7] It was found that the charge transfer absorption band splits in two when the dihedral angle of the disulfide deviates from 90°, ε_{max} of the low frequency peak is approximately twice that of the high frequency peak. The difference in excitation energy is roughly equal to the orbital energy difference between the $3p\pi$ and $3p\pi^*$ MO's obtained from Bergson's formulas. The relatively low asymmetry of the CT-absorption band of i-Pr t-$BuS_2 \cdot I_2$ at room temperature indicates that the dihedral angle of the complexed disulfide does not deviate too much from 90°.

Table 2.

Donor	$-\varepsilon_{90}$	I_p Calc. as descr. in the text	I_p from $h\nu_{CT}$	$\angle$ CSS/SSC	Δ
Me_2S_2	8.59	8.46	8.00	64	21°
Me EtS$_2$	8.49	8.36	8.01	70	15
Et_2S_2	8.40	8.27	8.04	74	11
Pr_2S_2	8.38	8.25	7.97	73	12
i-Bu$_2$S$_2$	8.36	8.23	7.92	71	14
Me t-BuS$_2$	8.31	8.15	8.05	81.5	3.5
i-Pr$_2$S$_2$	8.22	8.06	7.98	82	3
s-Bu$_2$S$_2$	8.21	8.05	7.95	82	3
Et t-BuS$_2$	8.22	8.06	7.99	82.5	2.5
i-Pr t-BuS$_2$	8.14	7.98	7.97	*85*	—
t-Bu$_2$S$_2$	8.06	7.81	7.62	101	4.5
t-Am$_2$S$_2$	8.05	7.80	7.55	102.5	6
1,2-Dithiane	8.38	7.70	7.43	47.5	12.5
1,2-Dithiolane	8.38	7.10	7.10	*27.5*	—

The parameters of Franklin's method[24] used to calculate ε_{90} are: e $= 13.31$ eV;[24] b $= 1.55$ eV;[24] f $= 8.59$ eV, this work; c $= 0.683$ eV, this work.

Under the assumptions given above we have calculated the dihedral angles of the complexed disulfides given in Table 2. In order to show what confidence can be put in these values the underlying assumptions are summarized below together with some arguments in their favour.

1. The experimental errors in the CT-excitation energies are sufficiently small.

The experimental errors are probably not much larger than the uncertainty limits given in Table 1, at least not for the noncyclic compounds which are easily purified by preparative GLC. These uncertainties do not seriously effect the estimated changes in dihedral angle.*

2. The CT-excitation energy varies almost linearly with the vertical ionization potential of the donor in the complex.

This assumption should be quite good since the complex formation takes place at the disulfide bond. The alkyl substituents just act as small perturbations on the SS-bond. Thus the parameters of Hastings' formula can be expected to be constant at least through the series of noncyclic disulfides.

3. The ionization potentials of the free disulfides vary upon alkyl substitution similarly to those of other homologous series of compounds.

The use of Franklin's method is a quantitative expression for this assumption. This assumption is not too daring. At least qualitatively the changes in ionization potential upon alkyl substitution follow similar trends in several homologous series of compounds.

4. Bergson's formula gives a correct description of the variation in ionization potential with dihedral angle.

This assumption is impossible to verify strictly because the necessary data are lacking. The formula reproduces well the changes in UV-absorption

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* See, however, the discussion below of the possibility of resolving the CT-band in two peaks.

spectrum of free disulfides upon changes in dihedral angle, but it is by no means certain that it does so for the changes in ionization potential.

The estimated changes in dihedral angle upon complex formation fall in four groups, the first and second consist of Me_2S_2 and $Me\ EtS_2$, in the third group are all disulfides with $-CH_2-$ groups next to the SS-bond, while the last group is composed by all noncyclic disulfides having secondary or tertiary carbon atoms next to the SS-bond. This behaviour is easily understood if it is assumed that the dihedral angle preferably decreases upon complex formation, since then the steric repulsion between the alkyl groups would increase in the required order. From Bergson's model of the SS-bond one will expect that the potential energy of the complexed disulfide instead of having a minimum when the dihedral angle is 90° will have shallow minima symmetrically around this value. The interaction between the alkyl groups will destroy this symmetry, however. The distance between them is so long that the interaction between them should still be attractive at least for those having only primary carbon next to the SS-bond.

Thus one should expect a preferable decrease in dihedral angle upon complex formation. This expectation gets some support from the fact that the dihedral angle of free Me_2S_2 is 84.7°, significantly less than 90°, the value expected from simple MO-theory. (The dihedral angle of H_2S_2 is 90.6°.[27])

The asymmetry parameters, defined in Table 1, group themselves in the same four groups as do the changes in dihedral angle, a larger change in dihedral angle being connected with a more asymmetric CT-absorption band. This is probably due to the splitting of the CT-absorption band when the dihedral angle deviates from 90° referred to above. Indeed, it is possible to resolve the CT-absorption band of $Me_2S_2 \cdot I_2$ obtained in this work into two Gaussian peaks (see Fig. 3) with a frequency separation of 4100 cm^{-1}. If we

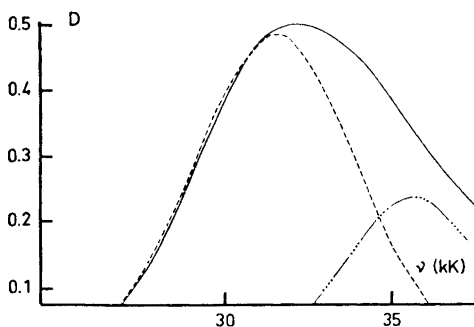*Fig. 3.* Resolution of ν_{CT} ($Me_2S_2 \cdot I_2$) in two Gaussian peaks.

assume that the two peaks of the resolution correspond to excitation from the symmetric and antisymmetric $3p\pi$ molecular orbitals of the SS bond and use the formulas of Ref. 7 to obtain the dihedral angle corresponding to this frequency difference, we find that the dihedral angle of the complexed disulfide is 69°. The agreement between this value and the one given above is, however, fortuitous since in the calculation above the wave number of experimentally obtained maximum was used to calculate the change in ionization potential.

If instead the wave number of the maximum of the low wave number peak of the resolution in Fig. 2 is used the dihedral angle of the complexed disulfide is estimated to be 60°. The latter way of estimating the dihedral angle of the complexed disulfide is of course in principle more correct than to use the experimental position of the maximum of the CT-band. However, the resolution in Fig. 2 is very uncertain since it was not possible to use more than part of the CT-band due to the strong absorption of the free disulfide and iodine which made it impossible to obtain the high wave number part of the CT-band.

In their work on the complexes between tetracyanoethylene and disulfides Moreau and Weiss did not observe any effects similar to those reported in this work. Indeed the CT-absorption maxima they report fall nicely on a smoothe curve when plotted against the ionization potentials reported above. However, this is what one should expect from Bergson's model, since the complexes between disulfides and tetracyanoethylene are much weaker than the corresponding iodine complexes. Thus the contribution to the ground state from the "dative bond structure" should be less which will lead to a smaller change in dihedral angle upon complex formation.

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