sembled roughly the oxygen electron densities along the elongated direction. It may be noted that this is only an approximation. Least-squares refinement of the constituent atoms lowered the R to 7.1%. However, the shifts were greater than the error, and the parameters tended to oscillate. Hence the refinement based on "split atoms" was abandoned.

Intermolecular Distances

The crystal structure can be described as being composed of $TPCP^+$ and ClO_4^- in a zigzag arrangement along the b direction (Figure 3). The carbonium ions are sandwiched by the ClO_4^- groups, while the ClO_4^- (nuts) are held tightly by pairs of cations (nutcrackers). The center of the cyclopropenium ring is nearly coincident with the 2_1 axis. The molecular arrangement along one-half of the c axis is shown in two views, along the c and b axes (Figures 3 and 4, respectively). The shortest interatomic contacts in the structure are between the electronegative oxygens of the perchlorate and the formally positive carbons of the cyclopropenium ring, as illustrated in Figure 5. Some of these distances would be even shorter if the correct length for the Cl–O distance of 1.46 Å. is assumed.[26] These interactions probably explain the growth of the crystal along the b direction. All other contact distances are greater than the sum of the van der Waals radii of the respective atoms.[27]

Acknowledgments. We wish to thank Professor Ronald Breslow for kindly supplying us with the specimen; Drs. J. Stewart, J. Kraut, D. High, R. Chastain, and E. Davidson for the computer programs; and the University Research Computer Laboratory for providing large grants of computer time. This work was supported by Grant GM-10828 of the National Institutes of Health of U. S. Public Health Service.

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(26) D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).

(27) NOTE ADDED IN PROOF. It is of interest to note that West, Sadô, and Tobbey (1965, private communication) recently have found, by a normal coordinate analysis of the vibrational spectrum of trichlorocyclopropenium cation ($C_3Cl_3^+$), a value of 6.3 mdynes/Å. (considerably greater than that of benzene) for the C–C stretching force constant, indicating that the C–C bond length in the cyclopropenium derivative is in fact shorter than in benzene, and in agreement with our observation

Charge-Transfer Complexes of Disulfides with Tetracyanoethylene

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Contribution from the Photochemistry and Spectroscopy Laboratory, Northeastern University, Boston, Massachusetts 02115. *Received August 17, 1965*

Abstract: Using the Benesi–Hildebrand procedure, the association constants and extinction coefficients have been measured for a number of disulfide–TCNE complexes. In the series n-alkyl disulfides, t-butyl disulfide, and thioctic acid, K_c at 25° increases from ~0.1 to 1.2 l./mole and $-\Delta H$ increases from 0.41 to 7.2 kcal./mole in the order given. The charge-transfer transition energies decrease in the same order. It is proposed that these trends reflect the decreasing angle between the doubly occupied 3p orbitals on the adjacent sulfur atoms of the disulfides. Structures are postulated for the alkyl disulfide and cyclic disulfide complexes, which are considered quantitatively with the aid of semiempirical molecular orbital theory. With an empirically derived estimate for the exchange integral between sulfur 3p and carbon 2p orbitals situated in separate planes, the MO model provides very satisfactory agreement with the observed charge-transfer transitions and transitions assigned to the complexed components.

The donor properties of organic sulfur compounds have been the subject of numerous publications.[1,2] Alkyl sulfides and disulfides form charge-transfer complexes with iodine[3-5] which are more stable than those of the corresponding oxygen compounds.[3c,6] Of the two types of sulfur compound, the sulfides are by far the stronger donors. Inductive effects[1,3c] and a smaller overlap integral[3c,4] for the disulfide complex have been considered as explanations for this difference.

Since the interactions in the ground state of weak complexes are small, absorption bands apart from the charge-transfer transition are observed, which may be ascribed to the complexed components. These bands are generally shifted with respect to those of the uncomplexed components. A variety of interpretations have been advanced for the origin of this shift,[7] and the most reasonable ones appear to be the mutual perturbation of the donor and acceptor energy levels[8] and the removal of restrictions on symmetry-forbidden transitions.[9] McGlynn[5] has studied the ethyl disulfide–iodine complex from this point of view and found the complexed disulfide to have a smaller transition energy than the free disulfide. Using a simple molecular orbital (MO) description of the disulfide molecule, he proposes that the red shift is due to a change in the dihedral angle between the nonbonding, perpendicular 3p orbitals of the two sulfur atoms.

The point of departure for this study was McGlynn's suggestion[5] that the shift of the –S–S– absorption should

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(1) R. J. Niedzielski, R. S. Drago, and R. L. Middaugh, *J. Am. Chem. Soc.*, **86**, 1694 (1964); this paper cites much of the earlier literature.

(2) R. S. Drago, B. Wayland, and R. L. Carlson, *ibid.*, **85**, 3125 (1963).

(3) (a) N. W. Tideswell and J. D. McCullough, *ibid.*, **79**, 1031 (1957); (b) J. D. McCullough and D. Mulvey, *ibid.*, **81**, 1291 (1959); (c) H. Tsubomura and R. P. Lang, *ibid.*, **83**, 2085 (1961); (d) R. P. Lang, *ibid.*, **84**, 4438 (1962).

(4) M. Good, A. Major, J. Nag-Chaudhuri, and S. P. McGlynn, *ibid.*, **83**, 4329 (1961).

(5) S. P. McGlynn, J. Nag-Chaudhuri, and M. Good, *ibid.*, **84**, 9 (1962).

(6) M. Tamres and M. Brandon, *ibid.*, **82**, 2134 (1960).

(7) G. Briegleb, "Elektronen-Donator-Acceptor Komplexe," Springer Verlag, Berlin, 1961, Chapter 5.

(8) S. Nagakura, *J. Am. Chem. Soc.*, **80**, 520 (1958).

(9) J. Czekalla, *Z. Elektrochem.*, **63**, 1157 (1959).

be enhanced with stronger acceptors such as tetracyanoethylene (TCNE). The specific aims of this work were to ascertain the effect of changes in the structure of the disulfide on the charge-transfer and complexed component transitions. It was of particular interest to examine five-membered ring disulfides in which complexation is not likely to bring about marked changes in geometry. The disulfide–TCNE complexes have been briefly described in a preliminary communication.[10] In this paper we report their thermodynamic and spectral properties in detail and present a semiempirical MO model to account for the spectral features.

Experimental Section

Materials. The chemicals employed in this work were in most cases of the highest commercially available quality, which were rigorously further purified. For liquids, the purity was checked by gas chromatography (g.c.) with an F & M Model 720 temperature-programmed dual column instrument. Columns packed with 10% Triton X-305 on Chromosorb P (8 ft. × 0.25 in.) and with 20% silicone gum rubber on Chromosorb P (4 ft. × 0.25 in.) provided satisfactory analyses in all cases. The melting and boiling points given here are uncorrected.

The solvent, dichloromethane (Matheson Coleman and Bell), was washed repeatedly with 5% sodium carbonate solution and finally with water. It was distilled from phosphorus pentoxide under nitrogen with a 100-cm. long Podbielniak Heligrid-packed column using an 18:1 reflux ratio. The material had b.p. 40.0–40.2° (760 mm.) and a minimum purity of 99.9% (g.c.). Dichloromethane has been used in previous spectrophotometric studies with TCNE; complex formation involving this solvent appears to be negligible.[11]

The most critical impurities in the disulfides are the corresponding thiols. These react with TCNE,[4,12] and this probably accounts for the unsuccessful previous attempt to generate a stable disulfide–TCNE complex.[6] Methyl, ethyl, *n*-butyl, and *t*-butyl disulfides (Eastman Kodak Co.) were purified by washing with sodium hydroxide solution (Vogel's method[13]) followed by fractional distillation. The liquids had b.p. 109–110° at 760 mm. (methyl), 151–152° at 760 mm. (ethyl), 90° at 3 mm. (*n*-butyl), and 66° at 4 mm. (*t*-butyl), and had purities of better than 99.9% (g.c.). Samples of butyl disulfide of similar purity were also obtained by the iodine oxidation of 1-butanethiol.[13] Phenyl disulfide was prepared by the ferric chloride oxidation of thiophenol.[14] The recrystallized, vacuum-dried material had m.p. 60–60.5° (lit.[14] 59–60°) and an ultraviolet spectrum in pentane which duplicates the published data.[15] Benzyl disulfide (Eastman Kodak Co.) was recrystallized several times from spectral grade 2-propanol and had m.p. 71–72° (lit.[16] 71°).

Of the cyclic disulfides, *dl*-thioctic acid (Aldrich Chemical Co. or British Drug Houses, Ltd.) was used without further purification. It had m.p. 60–61° (lit.[16] 61–61.5°), and comparison with material which had been recrystallized three times from petroleum ether showed both samples to give quantitatively identical charge-transfer spectra. 1,2-Dithiolane (trimethylene disulfide) was prepared by the iodine or ferric chloride oxidation of 1,3-propanedithiol.[17] The sample employed had m.p. 72.5–74° (lit.[17] 73–74°), and its spectrum in dichloromethane ($\lambda_{\max}$ 330 mμ (ϵ 142)) compared favorably with the reported spectrum[18] in ethanol ($\lambda_{\max}$ 334 mμ (ϵ 150)). The method of Barltrop, Hayes, and Calvin[18] was employed to prepare 1,2-dithiane (tetramethylene disulfide), which had the reported physical properties. This disulfide slowly polymerizes at room temperature but could be stored at −80° in dichloromethane solution. Tetrahydrothiophene (Eastman Kodak Co.) was distilled through a Podbielniak spinning-band column, and had b.p. 124.0° (760 mm.) (lit.[16] 121.2° (699 mm.)). High-purity samples of this compound as well as of methyl disulfide and ethyl disulfide were also obtained from the U. S. Bureau of Mines.

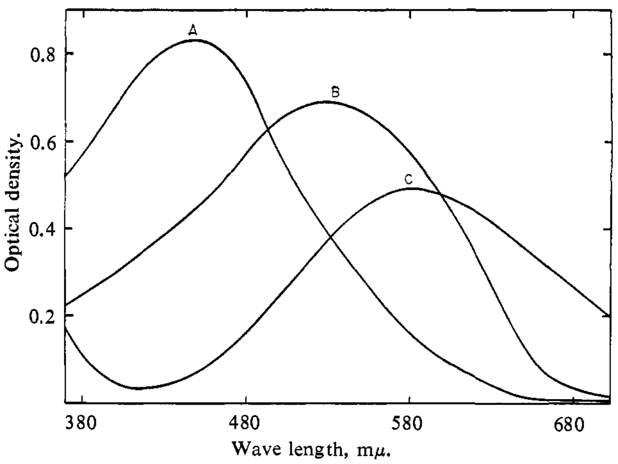

Figure 1. Charge-transfer bands of disulfide–TCNE complexes in dichloromethane (d = 1.00 cm.): A, 0.040 M ethyl disulfide, 0.050 M TCNE; B, 0.00845 M *t*-butyl disulfide, 0.050 M TCNE; C, 0.0279 M thioctic acid, 0.0473 M TCNE.

Tetracyanoethylene (Eastman Kodak Co.) was twice recrystallized from chlorobenzene and twice sublimed at 100° (1 mm.). The melting point (197–198°, sealed tube) and ultraviolet and infrared spectra agreed with published data.[19] The moisture-sensitive material was stored under vacuum over solid sodium hydroxide. Iodine (analytical reagent) and tetracyanoquinodimethane[20] were used without purification, and chloranil (Eastman Kodak Co.) was recrystallized from ethanol.

Measurement Procedures. All the spectra were measured with a Beckman Model DK-1 recording spectrophotometer. The matched 1-cm. or 10-cm. path length stoppered quartz cells were accommodated in a specially constructed aluminum block which fits into the sample compartment, and through which water from a precision constant temperature bath is rapidly circulated. The temperature control was better than ±0.1°. The volumetric ware was calibrated according to accepted procedures, and the solutions were made up to volume after equilibration in the constant-temperature bath. Only freshly distilled solvent was used. For the stability-constant measurements an excess of donor was used with concentrations in the range 0.1–1 M (donor) and 10^{-4}–10^{-3} M (acceptor). It was necessary to employ the 10-cm. spectrophotometer cells with the very weak donors in order to bring the optical density readings into the 0.2–1.5 range. The pure solvent served as the reference in all cases.

With the thioctic acid–TCNE complex spectral measurements in the disulfide absorption region could be made with 1-cm. cells. The weak ethyl disulfide complex, however, required a very short path length. For this purpose a cell was constructed from round, quartz plates which are separated by an annular Teflon shim (0.04–0.15 mm. thick).[21] This assembly is firmly compressed between bolted metal rings. A small off-center hole through one of the quartz plates, which can be closed with a Teflon plug, allows the solution to be introduced with a capillary dropper. With this cell the reference beam passed through air, and it was necessary to make separate measurements with the solution and the solvent.

Results

In contrast with iodine–disulfide complexes in which the charge-transfer band appears between the disulfide and blue-shifted iodine bands, the TCNE complexes show well-separated absorption in the 400–600-mμ region. Some typical curves are shown in Figure 1.

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[10] W. M. Moreau and K. Weiss, *Nature*, in press.

[11] R. Merrifield and W. Phillips, *J. Am. Chem. Soc.*, 80, 2778 (1958).

[12] W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *ibid.*, 80, 2783 (1958).

[13] A. Vogel, "A Textbook of Practical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 498.

[14] C. Wang and S. G. Cohen, *J. Am. Chem. Soc.*, 79, 1924 (1957).

[15] R. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, spectrum no. 152.

[16] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. 3, Chemical Publishing Co., Inc., New York, N. Y., 1960, pp. 395–400.

[17] T. J. Wallace, *J. Am. Chem. Soc.*, 86, 2018 (1964).

[18] J. A. Barltrop, P. M. Hayes, and M. Calvin, *ibid.*, 76, 4348 (1954).

[19] C. E. Looney and J. R. Downing, *ibid.*, 80, 2840 (1958).

[20] Kindly supplied by Dr. S. Chatterjee, Air Force Cambridge Research Laboratories.

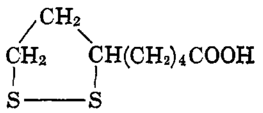
[21] This versatile design was suggested by Dr. R. N. Wiener.

Table I. Spectral and Thermodynamic Properties of the Disulfide–TCNE Complexes in Dichloromethane Solution

Disulfide	λ_{max},[b] mμ	Temp., °C.	$K_c\epsilon$	$\delta K_{c\epsilon}$[a]	K_c, l./mole	δK_c	ϵ	$\delta\epsilon$	$-\Delta H$,[d] kcal./mole
Methyl	425	25.0	342	±11	0.16	±0.09	2150	±1200	0.41
c		6.0	359	14					
Ethyl	450	25.0	411	4	0.14	0.03	3000	700	
n-Butyl	460	25.0	460	6	0.09	0.01	5200	500	
t-Butyl	530	25.0	1640	9	0.36	0.13	4600	1000	1.5
		14.0	1780	63	0.41	0.06	4300	500	
		5.0	1960	96	0.57	0.18	3450	1100	
Phenyl	510	25.0	448	58	1.5	0.5	290	80	
Benzyl	405	25.0	805	9	2.6	0.2	310	25	
Thioctic acid	583	25.0	7950	290	1.2	0.3	6500	1300	7.2
		5.0	18900	1330	3.1	0.6	6200	1200	
Tetrahydrothiophene	510	25.0	1140	60	0.60	0.08	1900	250	

[a] The uncertainties, δ, are the standard deviations. [b] Charge-transfer band. The position does not change with temperature. [c] The conditions were such that only $K_c\epsilon$ could be obtained. [d] Computed from the temperature variation of $K_c\epsilon$. The uncertainty in ΔH is estimated as ±0.1 kcal./mole.

The bands are seen to be broad, the half-intensity widths[22] being 7900 cm.$^{-1}$ for the ethyl disulfide complex and 5300 cm.$^{-1}$ for the thioctic acid (I) complex.



I

The latter value is close to that reported for some weak complexes of iodine with aromatic hydrocarbons.[23]

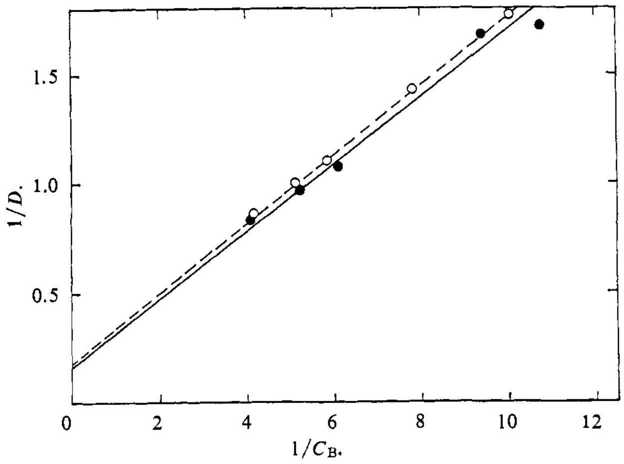


Figure 2. Plots of eq. 1 for the thioctic acid–TCNE complex in dichloromethane at 25.0°, with d = 1.00 cm.: -O-, C_A = 8.29 × 10^{-4} *M*; -●-, C_A = 7.90 × 10^{-4} *M*.

The preliminary indications were that the TCNE complexes are quite weak, with association constants (K_c) ~ 1 or less. Indeed, logarithmic plots of the optical density (D) at the charge-transfer maximum against the donor concentration (C_D) for a series of solutions in which the TCNE concentration (C_A) was kept constant had uniform slopes in the range 0.96–1.01 for methyl, ethyl, *n*-butyl, *t*-butyl, and phenyl disulfides. The latter compounds also showed maxima at a mole fraction of 0.5 in continuous variation plots.[24] While neither of these results can be considered to unequivocally establish the stoichiometry of the complexes,[25] a 1:1 association is assumed with reasonable confidence.

Values of K_c and the molar extinction coefficient of the complex (ϵ) were obtained by the analysis of spectral data using the Benesi–Hildebrand procedure.[26] At the charge-transfer maxima, no corrections for donor and acceptor absorption were necessary. In many of the experiments the acceptor concentration was kept constant, thereby allowing use of the modified form of the Benesi–Hildebrand relation (eq. 1, d = path length

$$\frac{d}{D} = \left[\frac{1}{K_c\epsilon C_A}\right]\frac{1}{C_D} + \frac{1}{\epsilon C_A} \qquad (1)$$

in cm.) which offers some advantages for weak complexes.[27] Plots of $1/D$ against $1/C_D$ for the thioctic acid complex is shown in Figure 2. The scatter of points is typical of that obtained in all the experiments. By suitable choice of path length and C_A, it was always possible to meet Person's criterion for the significant evaluation of K_c and ϵ, *i.e.*, $(C_D)_{max} > 0.1(1/K_c)$.[28] Slopes and intercepts were obtained by least-squares analysis, and the standard deviations were computed in the usual manner.

Table I presents the results for seven disulfides and one sulfide. The uncertainties, which appear to be realistic, decrease with increasing stability of the complex as predicted.[26,27] The values of K_c and ϵ are probably somewhat more reliable than those reported for some other weak complexes since measurements could be made without spectral interference by the donor or acceptor.[29,30] The differences in K_c for the

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[22] Estimated from plots of molar extinction coefficient against the frequency in cm.$^{-1}$.

[23] J. Peters and W. B. Person, *J. Am. Chem. Soc.*, **86**, 10 (1964).

(24) P. Job, *Ann. chim. phys.*, [10] **9**, 113 (1928).

(25) *Cf.* ref. 7, Chapter 12. Perusal of the recent literature indicates that only in a few cases is *any* attempt made to establish the stoichiometry of charge-transfer complexes.

(26) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

(27) P. R. Hammond, *J. Chem. Soc.*, 479 (1964).

(28) W. B. Person, *J. Am. Chem. Soc.*, **87**, 167 (1965).

(29) N. B. Jurinski and P. A. D. de Maine, *ibid.*, **86**, 3217 (1964).

(30) For some additional examples, see K. Conrow, G. D. Johnson, and R. E. Bowen, *ibid.*, **86**, 1025 (1964).

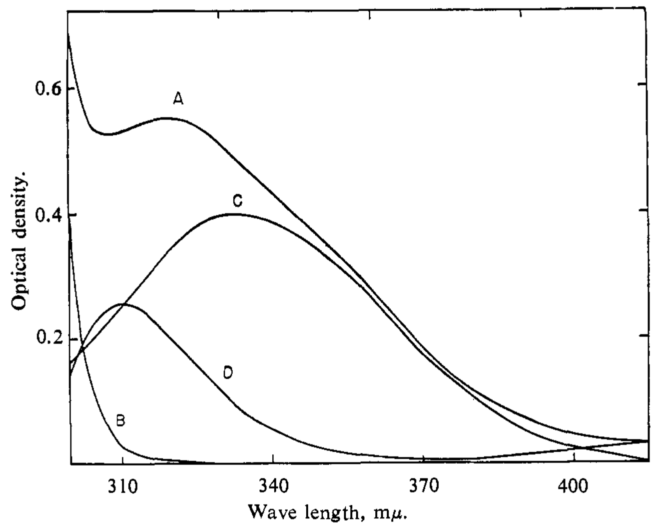

Figure 3. Resolution of the spectrum of a dichloromethane solution 0.0473 M in TCNE and 0.0279 M in thioctic acid (d = 1.00 cm.): A, solution spectrum; B, free TCNE; C, free -S-S- absorption; D, complexed -S-S- absorption.

three straight-chain alkyl disulfides are obviously not significant, although the increasing trend of $K_c\epsilon$ is clear.

The charge-transfer maxima of some additional disulfide- and sulfide-TCNE complexes are given in the earlier paper,[10] where significant trends are noted. The spectra exhibit a marked solvent dependence. Thus in ethyl acetate the *n*-butyl disulfide complex has a maximum at 410 mμ, compared with 460 mμ in dichloromethane. The spectral characteristics of complexes with some other acceptors are given in Table II.

Table II. Spectral Characteristics of Some Other Disulfide Complexes

Disulfide	λ_{max}, mμ[a] Iodine[b]	Chloranil	TCNQ
Methyl	~300		
Ethyl	302[c]		
n-Amyl	303[c]		
t-Butyl	335	465[d]	510[d]
Tetramethylene	348	465[d]	510[d]
Trimethylene	365		
Thioctic acid	365	550	625

[a] In dichloromethane unless otherwise noted. [b] Iodine in dichloromethane has λ_{max} 500 mμ. Shifted bands, not corrected for uncomplexed iodine, appeared in the region 470–495 mμ. [c] In carbon tetrachloride; *cf.* ref. 4 and 5. [d] These bands appear as barely resolved maxima in the tail of the acceptor absorption.

We note that the maxima for the iodine complexes of the simple alkyl disulfides are very close and are probably identical within experimental error. Thioctic acid is the only compound which shows well-separated charge-transfer absorption with chloranil and tetracyanoquinodimethane (TCNQ).

Figure 3 shows the absorption of a thioctic acid–TCNE solution and its resolution into the component bands due to uncomplexed TCNE and disulfide and complexed disulfide. This was accomplished using K_c and ϵ from Table I in conjunction with the optical density at the charge-transfer maximum. The shift of the -S-S- band is apparent even in the unresolved curve. The resolved shift of 23 mμ is probably reliable to ±3 mμ. With the ethyl disulfide–TCNE complex, the resolution is much less reliable owing to the small magnitudes of K_c and ϵ. Further, with this system the component absorptions overlap considerably, and hence bands due to complexed disulfide and complexed TCNE cannot be unequivocally resolved. Figures 4 and 5 show the curves for two solutions in which the donor:acceptor ratios are 133 and 7, respectively. The complexed component curves (D) are quite similar even though the optical densities of the free TCNE and the free disulfide are inverted in the two cases. The general shape and position of this absorption thus appear to be real, and not due to experimental artifacts. The greater resolution in Figure 4 is not significant and is probably due to the density differences approaching the photometric resolution limit of the instrument. If the two maxima in curve D represent separate species, the implication is that the complexed -S-S- absorption is shifted relative to the free -S-S- absorption either 0–2 mμ to shorter wave lengths or ~6 mμ to longer wave lengths, with complementary conclusions (~9- or ~15-mμ blue shifts) for the TCNE absorption. The significance of

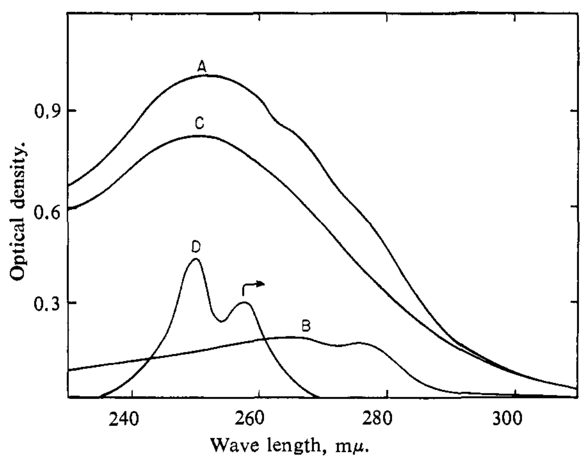

Figure 4. Resolution of the spectrum of a dichloromethane solution 0.232 M in ethyl disulfide and 1.74 × 10^{-3} M in TCNE (d = 0.075 mm.): A, solution spectrum; B, free TCNE; C, free -S-S- absorption; D, complexed -S-S- and TCNE absorption.

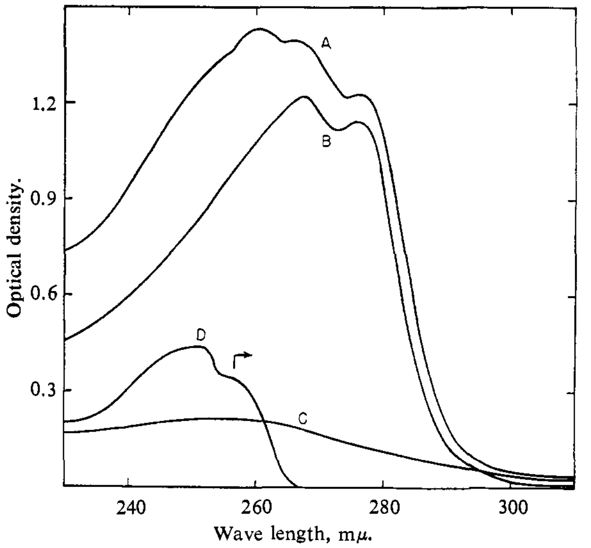

Figure 5. Resolution of the spectrum of a dichloromethane solution 0.0113 M in TCNE and 0.0794 M in ethyl disulfide (d = 0.075 mm.). The labels are the same as in Figure 4.

such assignments is further obscured by the effect errors in K_c and ϵ (a *minimum* of ±20%) have on the resolution of the spectra.

Discussion

Since all the TCNE complexes are weak, the possible contribution of contact charge transfer must be considered.[31] From the most stringent point of view,[27] only six of the K_c values quoted in Table I are significant. Criteria for contact charge transfer are generally the temperature variation of ϵ and decreasing values of ϵ for increasing values of K_c in a series of related complexes. Table I shows that ϵ is temperature independent within experimental error for the two quoted cases. For the series methyl, ethyl, *n*-butyl, *t*-butyl disulfides, and thioctic acid, the ϵ values with one exception (*n*-butyl) increase with K_c. The same trend is shown by the oscillator strengths,[21] which increase from 0.08 for ethyl disulfide to 0.15 for thioctic acid. The enthalpy of formation values for the complexes, obtained from the temperature dependence of $K_c\epsilon$, are clearly in the order methyl disulfide < *t*-butyl disulfide < thioctic acid, and support the trend of K_c. The phenyl and benzyl disulfide complexes have anomalously low extinction coefficients in relation to their stability constants. With these disulfides the aromatic rings may modify the nature of the charge-transfer interaction, perhaps by acting as donor sites or by overlap with the sulfur orbitals (in phenyl disulfide).[32] In limiting further discussion, therefore, to the alkyl disulfide and thioctic acid complexes, we feel justified in assuming that the charge-transfer absorption is predominantly due to complexes of finite stability.

In simple disulfides the dihedral angle (θ) is approximately 90°.[33] *t*-Butyl disulfide has an anomalous absorption spectrum[34] and a smaller dipole moment than other alkyl disulfides[35] which have been ascribed to a larger than normal angle between the bulky *t*-butyl groups. The five-membered ring disulfide, thioctic acid, is generally accepted to have $\theta \approx 0°$.[36,37] From the most elementary point of view, the bonds in divalent sulfur compounds involve only the sulfur 3p orbitals.[36] It is clear that *any* change of θ from 90° (increase or decrease) will *decrease* the angle between the perpendicular 3p orbitals on adjacent sulfur atoms. The data in Table I indicate that the diminution of the charge-transfer transition energy and the growth of K_c and ϵ are associated with a decrease in the sulfur 3p(1)–3p(2) angle. Inductive effects probably play only a very minor role.[38]

In the theoretical treatment, we concern ourselves only with the extreme cases $\theta \approx 90°$ and $\theta \approx 0°$. Pertinent data are available for the ethyl disulfide and thioctic acid complexes. The acid is more stable than trimethylene disulfide, and the spectra of these two cyclic compounds and of their complexes are virtually identical[10,18] (Table II). Of the numerous theoretical approaches[39] we have adopted a modification of the simple, semiempirical, one-electron MO theory developed by Nagakura[40] for intramolecular charge-transfer spectra. The method involves calculation of the energy levels of the disulfide and of TCNE, and then computing the energies of the mixed orbitals constructed from those molecular orbitals of the donor and acceptor for which interaction is allowed by symmetry considerations. The charge-transfer transition is considered to occur between the highest occupied, and the lowest empty, mixed orbital.

In monosulfide–iodine complexes a linear S–I–I arrangement appears to be firmly established,[41] and a perpendicular orientation of the iodine molecule to the S–S bond has been assumed in disulfide complexes. With TCNE we utilize Mulliken's principle of maximum overlap[42] to arrive at the structures shown in Figure 6a and 6b for the alkyl and cyclic disulfide complexes, respectively. Confining symmetry considerations to the disulfide bond region, we may assign symmetry C_2 to the alkyl disulfide ($\theta \approx 90°$) and symmetry C_{2v} ($\theta \approx 0°$) to the cyclic disulfide. Since TCNE belongs to point group D_{2h}, the symmetries of the complexes become C_2 and C_s, respectively.[43] The π molecular orbitals of the disulfide may be expressed as linear combinations of the 3p orbitals (χ_1 and χ_2) on the two sulfur atoms

$$\Phi_\pm = c_\pm(\chi_1 \pm \chi_2) \tag{2}$$

where + and − designate the bonding and antibonding orbitals, respectively.[5,37] When $\theta = 90°$, these become degenerate, perpendicular 3p orbitals. For TCNE, with the ten atoms labeled A through J, the molecular orbitals are expressed as linear combinations of the atomic 2p orbitals.

$$\Phi_i = c_{iA}\chi_A + \ldots + c_{iE}\chi_E + c_{iF}\chi_F + \ldots + c_{iJ}\chi_J \tag{3}$$

Consideration of the dimensions of the donor and acceptor molecules, shown in Figure 7 as a top view of the structures of Figure 6, suggests that as a first approximation the intermolecular interactions involve primarily the orbital pairs χ_1 and χ_F, and χ_2 and χ_E.[44]

For a given pair of donor and acceptor molecular orbitals, Φ_D and Φ_A, two new perturbed wave functions may be specified as[40]

$$\chi_{1,2} = a_{1,2}\Phi_D + b_{1,2}\Phi_A \tag{4}$$

with the definitions, $H_{AA} = \langle\Phi_A|H_{eff}|\Phi_A\rangle$, $H_{DD} = \langle\Phi_D|H_{eff}|\Phi_D\rangle$, and $\beta_{DA} = \langle\Phi_A|H_{eff}|\Phi_D\rangle$, and neglect of

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[31] L. E. Orgel and R. S. Mulliken, *J. Am. Chem. Soc.*, **79**, 4839 (1957).

[32] Aryl disulfides behave differently from the corresponding hydrocarbons. Thus the TCNE complexes of phenyl disulfide and mesityl disulfide have maxima at 515 and 430 mμ,[10] respectively, while the benzene and mesitylene complexes absorb at 384 and 461 mμ, respectively.[11]

[33] S. C. Abrahams, *Quart. Rev.* (London), **10**, 407 (1956).

[34] H. Koch, *J. Chem. Soc.*, 394 (1949).

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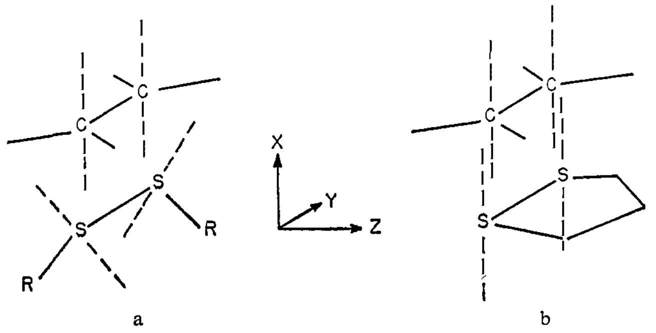

Figure 6. Structures proposed for the TCNE complexes of (a) alkyl disulfides with $\theta \approx 90°$, and (b) cyclic disulfide with $\theta \approx 0°$. The dotted lines represent the long axes of the sulfur 3p and carbon 2p orbitals.

overlap such that $a_{1,2}{}^2 + b_{1,2}{}^2 = 1$, solution of the pertinent secular equation yields the energies

$$\epsilon_{1,2} = \frac{1}{2}(H_{AA} + H_{DD}) \pm \frac{1}{2}[(H_{AA} - H_{DD})^2 + 4\beta_{DA}{}^2]^{1/2} \tag{5}$$

where ϵ_1 corresponds to the $-$ sign and ϵ_2 to the $+$ sign. If the approximation that interaction is confined to χ_1, χ_2, χ_E, and χ_F is now incorporated, β_{DA} may be expressed in terms of the two-center integral $\beta_{SC} = \langle\chi_1|H_{eff}|\chi_F\rangle = \langle\chi_2|H_{eff}|\chi_E\rangle$.

$$\beta_{DA} = c_{\pm}(c_{iE} \pm c_{iF})\beta_{SC} \tag{6}$$

In applying eq. 5 as modified by eq. 6, we identify H_{AA} with the energy of the unperturbed acceptor MO and H_{DD} with the energy of the unperturbed donor MO.[40]

The energies of the disulfide molecular orbitals $\Phi_{\pm}$ are approximately given by[5]

$$\epsilon_{\pm} = (\alpha_S \pm \beta_{SS}\cos\theta)/(1 \pm S\cos\theta) \tag{7}$$

where α_S, β_{SS}, and S represent the Coulomb, exchange, and overlap integrals, respectively. To calculate $\epsilon_{\pm}$, we equate $-\alpha_S$ to the ionization potential of ethyl disulfide (8.5 e.v.[45]). Combined with the difference in the spectral transition energies for ethyl disulfide (4.92 e.v.) and thioctic acid (3.72 e.v.), *i.e.*, 1.20 e.v. = $(\alpha_S S - \beta_{SS})/(1 - S)$ with $S = 0.129$,[48] the value $\beta_{SS} = -2.14$ e.v. is found and $\epsilon_{\pm}$ can be computed as a function of θ.[49] The results are shown in the center of Figure 8.

For TCNE, simple MO calculations were performed with the parameters[50] $\alpha_N = \alpha_C + \beta_{CC}$, $\alpha_{C'} = \alpha_C + 0.1\beta_{CC}$, $\beta_{CN} = 2.0\beta_{CC}$, and $\beta_{CC'} = 0.9\beta_{CC}$, where the subscripts indicate the atoms, with C′ designating the carbon atom bonded to nitrogen. The results pertinent to the present problem are shown in Table III.[51]

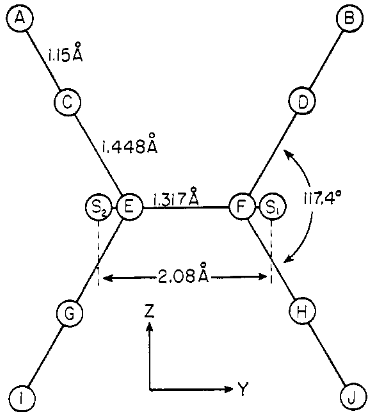

Figure 7. Projection view of the complexes of Figure 6. A–J represent the TCNE molecule, with A, B, I, and J the nitrogen atoms. S_1 and S_2 are the two sulfur atoms of the disulfide.

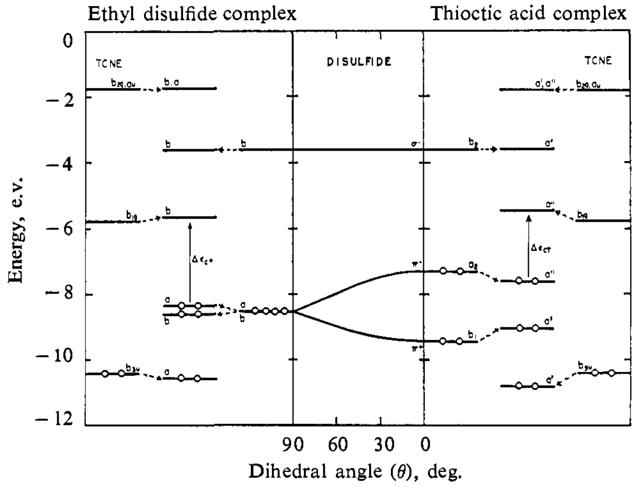

Figure 8. Orbital energies for TCNE, for the disulfide as a function of θ, and for the TCNE complexes of ethyl disulfide and thioctic acid. Labels are the symmetries of the orbitals. The –S–S– absorption of the uncomplexed disulfide corresponds to $\pi^- \rightarrow \sigma^-$ for $\theta < 90°$ and $\pi^* \rightarrow \sigma^-$ for $\theta = 90°$.

To place these levels on an absolute scale, we again equate the energy of the highest-filled MO (b_{3u}) with the ionization potential (I_p) which, in the absence of an experimental value, is estimated as 10.4 e.v.[52] The other levels are located by spectral correlation. TCNE shows a structured band with λ_{max} 266 mμ (ε 13,900) (dichloromethane) which, for present purposes, is assigned to the allowed π–π^* transition $A_{1g} \rightarrow B_{2u}$.[53]

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(45) An average was taken of the mass spectrometric value (8.85 e.v.[46]) and the photoionization value (8.27 e.v.[47]).

(46) B. G. Gowenlock, J. Kay, and J. R. Majer, *Trans. Faraday Soc.*, **59**, 2463 (1963).

(47) K. Watanabe, T. Nakayama, and J. Mottle, *J. Quant. Spectry. Radiative Transfer*, **2**, 369 (1962).

(48) The upper σ^- antibonding orbital is taken as independent of θ.[5] The value of S is for an S–S distance of 2.08 Å.

(49) McGlynn[5] attempted to calculate $\epsilon_{\pm}$ from the difference in the transition energies and the rotational barrier about the –S–S– bond (0.52 ± 0.09 e.v.). It can be easily shown that his equations can be rearranged to

$$4S(\alpha_S S - \beta_{SS})/(1 - S) = 4.68S = (1 + S)(0.52 \pm 0.09)$$

which, with $S = 0.129$ become identical and cannot be solved for α_S and β_{SS}.

(50) The relation $\beta_{CN} = 2.0\beta_{CC}$ gave good agreement between the calculated and observed spin densities for a number of cyano radicals; see P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2795 (1962).

(51) For a previous simple MO calculation, see B. R. Penfold and W. N. Lipscomb, *Acta Cryst.*, **14**, 589 (1961). These authors[1] results were approximately matched with $\beta_{CN} = 1.2\beta_{CC}$, and $\beta_{CC} = -2.55$ e.v. These levels do not, however, yield a satisfactory spectral correlation (see text).

(52) For acrylonitrile the reported ionization potentials are 10.75 e.v. (mass spectrometric value, J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, 20, 1021 (1952)) and 10.91 e.v. (photoionization value[47]). In arriving at the estimated value for TCNE, it was noted that although the introduction of additional electronegative groups is expected to raise I_p, increased conjugation has the opposite effect.[47]

(53) This band is at 254 mμ for the vapor[54] and thus appears to show the red-shift behavior characteristic of π–π^* (N → V) transitions.[55] However, on the basis of polarized ultraviolet and infrared spectral measurements with crystals of TCNE, this absorption has been ascribed to a Rydberg N → R transition ($A_{1g} \rightarrow B_{3u}$) superimposed on an N → V transition.[54] (Note that owing to a different choice of axes, B_{3u} here corresponds to B_{1u} in ref. 54.) The Rydberg orbital has symmetry a_{1g}, which is not an irreducible representation for the π-MO's of TCNE in D_{2h} and is not amenable to the MO treatment developed here. Vacuum ultraviolet measurements, currently in progress in this laboratory (J. L. Roebber), should clarify the nature of the transition.

(54) J. Prochorow and A. Tramer, *Bull. Acad. Polon. Sci., Ser. Sci. Math. Astron. Phys.*, **12**, 429 (1964).

(55) H. McConnell, *J. Chem. Phys.*, 20, 700 (1952).

Table III. Molecular Orbitals and Energy Levels for TCNE

MO[a]	Symmetry	Energy
$\Phi_8 = 0.312(\Phi_A + \Phi_B - \Phi_I - \Phi_J) - 0.390(\Phi_C + \Phi_D - \Phi_G - \Phi_H)$	b_{2g}	$\alpha_C - 1.50\beta_{CC}$
$\Phi_7 = 0.312(\Phi_A - \Phi_B - \Phi_I + \Phi_J) - 0.390(\Phi_C - \Phi_D - \Phi_G + \Phi_H)$	a_u	$\alpha_C - 1.50\beta_{CC}$
$\Phi_6 = 0.278(\Phi_A - \Phi_B + \Phi_I - \Phi_J) - 0.188(\Phi_C - \Phi_D + \Phi_G - \Phi_H) - 0.524(\Phi_E - \Phi_F)$	b_{1g}	$\alpha_C - 0.36\beta_{CC}$
$\Phi_5 = 0.268(\Phi_A + \Phi_B + \Phi_I + \Phi_J) - 0.597(\Phi_E + \Phi_F)$	b_{3u}	$\alpha_C + 1.00\beta_{CC}$

[a] Φ_1 is the lowest and Φ_5 the highest occupied MO. The accidental degeneracy of Φ_7 and Φ_8 was also obtained for the Φ_3 and Φ_4 orbitals which have the same symmetries (a_u and b_{2g}).

Table IV. Calculated and Observed Spectra of Some Cyanoethylenes

Compound	$x_{i+1} - x_i$[a]	Transition energy, e.v. Calcd.	Obsd.	$\epsilon \times 10^3$	Solvent
Acrylonitrile	1.76	6.05	6.11[b]	6.0	Ethanol
1,2-Dicyanoethylene	1.57	5.40	5.58[c]	~13–16	Ethanol
Tricyanoethylene	1.46	5.02	5.23[d]	13.1	Ether
Tetracyanoethylene	1.36	(4.66)	4.66[e]	13.9	Dichloromethane

[a] In units of β_{SS}; $\epsilon_i = \alpha_C + x_i\beta_{SS}$. [b] R. Heilman, J. Bonnier, and G. de Gaudemaris, *Comp. rend.*, **244**, 1787 (1957). [c] The *cis* and *trans* compounds have the same λ_{max}, with the lower ϵ for the *cis* compound: R. L. Webb, S. Frank, and W. C. Schneider, *J. Am. Chem. Soc.*, **77**, 3491 (1955). [d] C. L. Dickinson, D. W. Wiley, and B. C. McKusick, *ibid.*, **82**, 6132 (1960). [e] This study.

This leads to the rather high value $\beta_{CC} = -3.44$ e.v. To check whether this value indeed provides a spectral correlation for cyanoethylenes, MO calculations using the same parameters were performed for three compounds, with the reassuring results given in Table IV.

With $\theta \approx 90°$ in ethyl disulfide, the orbitals on the sulfur atoms are inclined 45° to the plane defined by the long axes of the orbitals (χ_E and χ_F) on the central atoms of TCNE (*cf.* Figure 6a). Let β_{SC} represent the exchange integral for the cyclic disulfide complex in which the orbitals χ_1, χ_2, χ_E, and χ_F are essentially coplanar (Figure 6b). Then, if the intermolecular separation remains constant, the exchange integral (β'_{SC}) for the structure of Figure 6a is, to a good approximation, given by $\beta'_{SC} = \beta_{SC} \cos \theta = 0.707\beta_{SC}$. Using eq. 5 and 6 with $\beta_{SC} = -0.92$ e.v. ($\beta'_{SC} = -0.65$ e.v.), the energy levels shown in Figure 8 were computed. Typical mixing parameters for the new donor levels in the complexes are $\beta_{DA} = -0.73$ e.v., $a_1 = 0.932$, and $b_1 = 0.367$ for b_{1g} and a_2 levels; and $\beta_{DA} = -0.48$ e.v., $a_1 = 0.987$, and $b_1 = 0.168$ for the b_{1g} and b levels.

The calculated and observed spectral data are summarized in Table V. The model predicts a red-shifted –S–S– absorption for the ethyl disulfide complex (second a level → third b level) without recourse to a changed dihedral angle which has been postulated to accompany charge transfer in the ground state.[5] Judging by the mixing parameters quoted above, the extent of ground-state charge transfer is extremely small for this complex. None the less, a slight structural adaptation of the disulfide cannot be excluded, and may well accompany the orbital perturbations. The –S–S– absorption of the complexed cyclic disulfide (lowest a″ level → third a″ level) is predicted to be blue-shifted as observed. For thioctic acid, θ is undoubtedly greater than 0° as we have assumed,[38] but any further diminution would probably be strongly opposed by the geometrical requirements of the ring. Thus in this complex, orbital perturbation is the predominant factor responsible for the absorption shift.

Table V. Calculated and Observed Transitions for Disulfide–TCNE Complexes

Transition	Energy, e.v.[a] Calcd.	Obsd.
Thioctic Acid Complex		
Charge transfer	2.14	2.13
Complexed RSSR	4.01	4.00
Complexed TCNE	5.34	*b*
Ethyl Disulfide Complex		
Charge transfer	2.70	2.76
Complexed RSSR	4.77	4.82, 4.94
Complexed TCNE	4.89	

[a] Observed values for free RSSR are 4.92 (thioctic acid) and 3.72 e.v. (ethyl disulfide). [b] No measurements were made in this spectral region.

The empirical equation of McConnell, Ham, and Platt may be utilized[56] to estimate the ionization potentials of some disulfides which lack experimental values. Based on spectral data from Table I and photoionization potentials of 8.46 and 8.27 e.v.[47] for methyl and ethyl disulfides, respectively, this takes the form[57]

$$h\nu_{CT} = 0.85I_p - 4.3 \text{ e.v.} \tag{8}$$

Since only two close points were used, the error in this equation could be large. Some illustrative values are 7.78 and 7.57 e.v. for *t*-butyl and trimethylene disulfides, respectively. For the latter compound the estimate is much lower than a previous one of 8.53 e.v.[5]

Acknowledgments. This study was sponsored by the U. S. Air Force Cambridge Research Laboratories, Office of Aerospace Research, under Contracts AF 19(604)-7358 and AF 19(628)-3836. We are grateful to Drs. J. L. Roebber, R. N. Wiener, and K. H. Bar-Eli for many fruitful discussions. Samples of several sulfur compounds were kindly furnished by the U. S. Bureau of Mines, Laramie, Wyo. We also wish to thank Mr. Eric Reid for his aid with the computation work which was carried out at the MIT Computation Center.

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(56) H. McConnell, J. S. Ham, and J. R. Platt, *J. Chem. Phys.*, 21, 66 (1953).

(57) This equation is almost identical with the equation given for substituted benzene-TCNE complexes by E. M. Voigt and C. Reid, *J. Am. Chem. Soc.*, **86**, 3930 (1964).