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Possible Effect of Charge Transfer Complexation on the Dihedral Angle of Dialkyl Disulfides¹

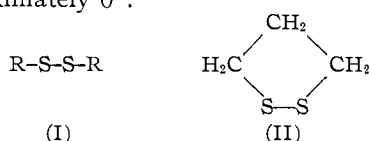
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It is shown by some simple molecular orbital considerations that when a dialkyl disulfide functions as an electron donor in a charge transfer complex one expects the dihedral angle of the disulfide group to increase. A concomitant red shift of the characteristic -S-S- absorption band at *ca.* 2500 Å. is predicted. Efforts to observe this red shift in solutions of di-*n*-amyl disulfide and diethyl disulfide with iodine are not completely conclusive. A maximum shift of 70 Å. has been observed, and the deduced shift for the pure diethyl disulfide-iodine complex has been calculated to be 2000 cm.⁻¹. Using this latter number, the dihedral angle in the complex may be shown to be 104 or 76°, the former being preferred for steric reasons. The theoretical considerations presented are dependent on some unverified assumptions, foremost among which is the assignment of the 2500 Å. absorption band of the disulfide group as an *n* → *σ** transition. Efforts to verify this assignment using solvent techniques suggest it to be correct but cannot be accepted as a final proof.

Introduction

The importance of the disulfide linkage in biological chemistry,² as well as the fact that most reactions of disulfides depend on the ready fission of the -S-S- bond, make physico-chemical study of this moiety imperative. It has been established³ that the dihedral angle between the 3pπ_⊥ orbitals of the two sulfur atoms in a normal disulfide (I) is about 90°, whereas in dithiolane (II) this angle is approximately 0°.



In this latter case the steric requirements of the five-membered ring necessitate approximate coplanarity of the 3pπ_⊥ orbitals of the two sulfurs, and the resultant removal of the 3pπ_⊥ orthogonality which exists in the 90° case (I) leads both to a destabilization of the -S-S- bond in dithiolane and a shift of the electronic absorption characteristic of the disulfide group from 2500 Å. in (I) to 3300 Å. in (II). This shift has been explained by Bergson³ in terms of a simple molecular orbital (m.o.) theory, in which the rotational barrier⁴ of 12 ± 2 kcal./mole for normal disulfides is attributed to the net antibonding character of the four 3pπ_⊥ electrons of the two sulfurs.

The purpose of this note is to point out that if electron occupancy of the 3pπ_⊥ orbitals be decreased, as for example when a normal disulfide functions as a π electron donor in a charge transfer complex, one may expect the dihedral angle to change, and, dependent on the amount of electron transfer, to have a value different from 90°. It is the further aim of this note to attempt to demonstrate the reality of this angular change by observation of the characteristic electronic absorption band of the -S-S- group in iodine complexes of various normal disulfides. To the extent

that these purposes are realized, a corresponding stabilization of the -S-S- linkage is predicted.

Theory.—An effective Hamiltonian for the disulfide bond region of a normal disulfide might be assumed to have C₂ symmetry. As a particular consequence of this symmetry, it is no longer strictly meaningful to draw a distinction between π and σ electrons. However, the lone pair 3p and 3s electrons can still be sharply differentiated and retention of the π,σ nomenclature is perhaps justified at least for these orbitals.

Let φ₁ and φ₂ represent 3pπ_⊥ atomic orbitals on sulfurs 1 and 2, respectively. Because of the rotational symmetry (at least within the -S-S- region) we may immediately specify for a disulfide and independent of the dihedral angle

$$\phi_{\pm} = (\varphi_1 \pm \varphi_2) / (2 \pm 2S)^{1/2}$$

Solution of the appropriate secular equation yields

$$E_{\pm} = (E + \beta) / (1 + S)$$

where

$$E = \int \varphi_1^* H \varphi_1 d\tau = \int \varphi_2^* H \varphi_2 d\tau, \beta = \int \varphi_1^* H \varphi_2 d\tau$$

and

$$S = \int \varphi_1^* \varphi_2 d\tau$$

E may further be written as

$$E - E_0 = \int \frac{e^2}{r_{12}} \varphi_1^2 d\tau$$

and is more or less independent of the angle of twist, θ. β and *S*, however, are θ dependent; thus if θ be the dihedral angle we may immediately specify

$$\varphi_2 = \varphi_{\parallel} \cos \theta + \varphi_{\perp} \sin \theta$$

where φ_∥ and φ_⊥ signify those 3pπ atomic orbitals (a.o.) of the second sulfur atom which are mutually parallel and perpendicular, respectively, to φ₁. Because of symmetry φ_⊥ will not interact with φ₁, and consequently the parameter θ enters into the subject in a particularly simple manner. Indeed, the energies at angle θ become approximately

$$E_{\pm} = (E \pm \beta \cos \theta) / (1 \pm S \cos \theta)$$

where the new β and *S* are now independent of twist.

It is further presumed that the lowest energy unfilled molecular orbital of the -S-S- bond region is the σ* antibonding orbital formed from the out of phase combination of the two 3pσ a.o.'s, one on each sulfur atom, and given by

$$\phi_{\sigma^*} = (\varphi_{3p\sigma 1} + \varphi_{3p\sigma 2}) / (2 + 2S\sigma)^{1/2}$$

(1) This research was supported by a National Science Foundation Grant G-7390 and a Research Corporation Grant to the Louisiana State University.

(2) J. A. Barltrop, P. M. Hayes and M. Calvin, *J. Am. Chem. Soc.*, **76**, 4348 (1954).

(3) G. Bergson, *Arkiv Kemi*, **12**, 233 (1957).

(4) D. W. Scott, H. L. Finke, M. E. Gross, G. B. Guthrie and H. M. Huffman, *J. Am. Chem. Soc.*, **72**, 2424 (1950). D. W. Scott, H. L. Finke, J. P. McCullough, M. E. Gross, R. E. Pennington and G. Waddington, *ibid.*, **74**, 2478 (1952).

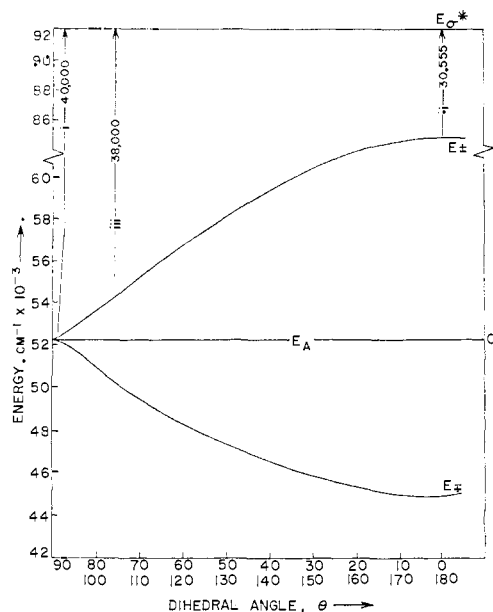


Fig. 1.—The m.o. energies E_{σ^*} , E_+ and E_- as a function of angular twist θ : (i) the characteristic $-S-S-$ absorption band in a free dialkyl disulfide, (ii) in dithiolane and (iii) in the complex $Et_2S_2 \cdot I_2$. The upper of the two symbols \pm which are suffixed to E corresponds to the range $90-0^\circ$, the lower to the range $90-180^\circ$.

In a $C_{\infty v}$ or $D_{\infty h}$ potential region the energy of this orbital, E^* , would be independent of twist but not so in actual disulfides. However, the twist dependence should not be too great even in a real disulfide, and it is for this reason that in Fig. 1 E^* is shown independent of θ .

The m.o. energies, E_{\pm} , may be calculated from a knowledge of the parameters E , β and S . At a distance of 2.08 \AA , the normal $-S-S-$ distance, the overlap $S = \int \phi_1 \phi_2 ds \sim 0.129$.⁵ Since there are four electrons involved in bonding, the difference in ground state energies between the molecules with $\theta = 90^\circ$ and $\theta = 180^\circ$ may be equated⁶ with Penney and Sutherland to the rotational barrier about the $-S-S-$ bond. This yields

$$\Delta E = 2(E + \beta)/(1 + S) + 2(E - \beta)/(1 - S) - 4E = (4197 \pm 699) \text{ cm.}^{-1}$$

Since ϕ_{σ^*} is presumed independent of θ , and since the characteristic $-S-S-$ electronic transition is (in orbital notation) $\phi_{\pm} \rightarrow \phi_{\sigma^*}$, the energy difference between this transition in dithiolane and in a normal disulfide³ ($\sim 9445 \text{ cm.}^{-1}$) is to be attributed entirely to variation of E_- with θ . One may then equate

$$E_-(0^\circ) - E_{\pm}(90^\circ) = (ES - \beta)/(1 - S) = 9445 \text{ cm.}^{-1}$$

From these latter two equations one may then deduce $E = 52328 \text{ cm.}^{-1}$ and $\beta = -1475 \text{ cm.}^{-1}$, and thus plot the curves E_+ and E_- of Fig. 1.

It is at this point pertinent to introduce the results of the present work. It has been found that the characteristic $-S-S-$ electronic transition of

(5) R. S. Mulliken, C. A. Rieke, D. Orloff and C. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

(6) W. G. Penney and G. B. M. Sutherland, *Trans. Faraday Soc.*, **30**, 898 (1934).

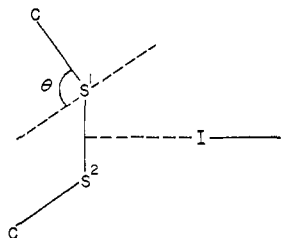


Fig. 2.—The structure of a 1:1 complex of a dialkyl disulfide and iodine which one might expect by extrapolation of the X-ray work of Hassel (ref. 9 of text) on monosulfide complexes to disulfide complexes.

diethyl disulfide is red-shifted by $\sim 2000 \text{ cm.}^{-1}$ in the complex $(C_2H_5)_2S_2 \cdot I_2$, which would imply from consideration of Fig. 1 that if the dihedral angle in $(C_2H_5)_2S_2$ is 90° , then θ in the complexed ethyl disulfide is 104° or 76° . It may be presumed, with some reservations (*vide infra*), that this angular change occurs because an amount of charge $(1 - x)e$, where e is the electronic charge, is transferred from the donor orbital of the $-S-S-$ group, ϕ_{\pm} , to the acceptor orbital of iodine. If this be the case then for $\theta = 104^\circ$

$$(3 + x)E_A \geq (3 + x)E_A - 2E_+ + (1 + x)E_-$$

where E_+ and E_- are evaluated at 104° ; in other words the value of x must be such as to render the conformation with $\theta = 104^\circ$ the most stable. The calculated value of x is 0.85, implying a charge-transfer from the $-S-S-$ region of $0.15e$; at a distance of separation of donor-acceptor centers of about 3 \AA . this would produce an additive dipole moment increment parallel to the DA bond of about 2 debye, which would seem to be a reasonable order of magnitude.⁷ Exactly similar conclusions apply for $\theta = 76^\circ$. However, henceforth we will consider the value of 104° more probable for steric reasons (*vide infra*).

Despite the last equation, which would tend to indicate that the value of $0.15e$ is a minimal value, it is perhaps better to regard it as a sort of maximum. In the above conclusions it has been presumed that angular opening of θ is occasioned only by charge transfer; no regard was given to the extent which donor-orbital acceptor-orbital overlap (*i.e.* stability of the complex) might determine the final value of θ in the complex. It is to be concluded that S_{DA} overlap maximization considerations should in all cases lead to increase of θ : if we presume with Mulliken⁸ that

$$S_{DA} = \int \phi_+(-S-S-)\phi_{\sigma^*u}(5p_z)(I_2) d\tau$$

where $\phi_{\sigma^*u}(5p_z)(I_2)$ denotes the antibonding orbital formed from the two $5p_z$ orbitals of the iodine atoms (where z is defined perpendicular to the I-I axis) in I_2 , one would expect maximum overlap when the I_2 molecule lies above the $-S-S-$ bond, and with the I_2 axis parallel or closely parallel to the S-S axis. However, one might expect from the X-ray work of Hassel⁹ on monosulfide complexes of iodine that the actual structure is that shown in Fig. 2 and that the dominant feature

(7) S. P. McGlynn, *Chem. Revs.*, **58**, 1113 (1960).

(8) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

(9) O. Hassel, *Proc. Chem. Soc. (London)*, 250 (1957).

of iodine complexes is a tendency on the part of one of the iodines to increase its coordination number using either its 5p, 5d or 4f orbitals as acceptance centers, with the 5d orbital being the most likely choice. In this case $S_{DA} = \int \phi_+ (-S-S-) \phi_{5d}(I_2) d\tau$, and again maximization of S_{DA} will tend to increase θ . In other words, to the extent that we neglect the effects of maximization of the stability of the complex in increasing θ , we obtain a delocalization of charge ($\sim 0.15e$) out of the $-S-S-$ bond region; on the other hand when we include such effect we conclude that this value is probably somewhat too high.

Experimental Results

The only chemicals used were iodine, diethyl disulfide and diamyl disulfide and the solvent was *n*-heptane; the purification and origin of these materials is described elsewhere.¹⁰ All absorption spectra were recorded on a Beckmann DK spectrophotometer at 27° using pairs of matched 0.1 mm. and 1 mm. cells obtained from Aminco. Small path lengths were used so that large concentrations of both components (*i.e.*, the disulfide and the iodine) could be used and thus ensure a reasonable concentration of complex. This expedient was necessary because of the small effects which were to be observed and solutions in which the ratio of complexed disulfide to free disulfide was as large as possible were desirable.

A series of solutions of amyl disulfide and iodine in heptane were prepared and their spectra recorded. The results are given in Fig. 3. It is evident from this figure and from Table I that even though the absolute and relative concentrations of both components vary over a fairly wide range that as X , a measure of the ratio (complexed disulfide)/(total disulfide), increases, the characteristic $-S-S-$ absorption band at *ca.* 2500 Å. undergoes a red shift much as expected. The quantity X was measured by simply taking the ratio of optical density at the charge transfer maximum at 3030 Å. and is proportional to the ratio: (complex)/(total disulfide), as long as we presume the extinction coefficient $\epsilon_{\text{complex}}$ to be independent of concentration and ϵ_{-S-S-} to be but slightly dependent on angular twist for $\Delta\theta \leq 20^\circ$. It may be argued that the red shift observed is merely a consequence of the intensification of the charge transfer band; as this CT band becomes more intense its additive intensity contribution to the long wave length edge of the $-S-S-$ band will tend to shift the $-S-S-$ absorption maximum toward the red. Such an effect has been investigated by drawing in the presumed exponential tail of the short wave length edge of the CT band with no effect on the results of column 4 Table I.

TABLE I
CHARACTERISTICS OF THE AMYL DISULFIDE IODINE SOLUTIONS STUDIED

(Am ₀ S ₂), M	(I ₂), M	X	$\nu_{\text{max}}(-S-S-)$ cm. ⁻¹	Solution no. ^a
0.179	0	0.11 ^b	39,900	I
.09	0.92×10^{-4}	.38	39,700	II
.06	1.25×10^{-4}	.55	39,600	III
.009	1.05×10^{-3}	.66	39,000	IV
.0067	1.25×10^{-3}	.83	39,200	V
.223	5.9×10^{-3}	1.2	39,300	VI
.179	7.9×10^{-3}	1.6	39,000	VII

^a These numbers correspond to those of Fig. 3. ^b The characteristic $-S-S-$ absorption band has itself a finite intensity at 3030 Å.

None the less a more quantitative study was desirable and for this purpose ethyl disulfide-iodine solutions in heptane were used. The reason for this choice was that knowledge of ϵ_0 and K_0 for the complex Et₂S₂-I₂ were available from other sources^{10,11} from experimentation in dilute

(10) M. Good, A. Major, J. Nag-Chaudhuri and S. P. McGlynn, *J. Am. Chem. Soc.*, **83**, 4329 (1961).

(11) H. Tsubomura and R. Lang, *ibid.*, **83**, 2085 (1961).

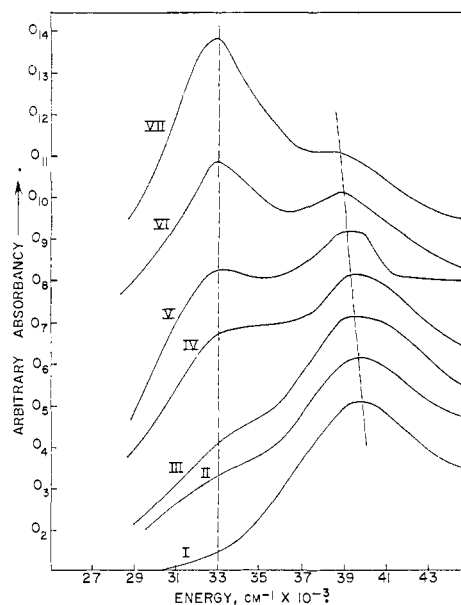


Fig. 3.—The absorbance of various diamyl disulfide, iodine solutions in heptane, illustrating the increasing red shift of the $-S-S-$ absorption band with X . The vertical axis is arbitrary; all absorbances at 2500 Å. have been normalized to an identical value and curves have been displaced vertically one from the other, in order to prevent confusion of lines. Numbers of curves correspond to those of Table I.

solutions of such relative concentrations in ethyl disulfide and iodine that it was possible to apply Benesi-Hildebrand considerations.¹² In the present work the concentrations used were such as to necessitate use of the Drago method.¹³ The results obtained by use of the data of Table II are

TABLE II
CHARACTERISTICS OF THE ETHYL DISULFIDE-IODINE SOLUTIONS STUDIED

(Et ₂ S ₂), M	(I ₂), M	X	Log I ₀ /I _a	ν^b	Solution no.
0.098	8.4×10^{-3}	0.66	0.34	40500	I
.078	1.01×10^{-2}	.93	.42	40200	II
.065	1.12×10^{-2}	.94	.445	39400	III

^a The optical density at the maximum of the $-S-S-$ absorption band, from which by use of X , that at the maximum of the CT band may be calculated. ^b The position in cm.⁻¹ of the $-S-S-$ absorption band. Its gradual red shift with increasing X should be noted.

$\epsilon_0 = 8000$ and $K_0 = 5.71/\text{m.}(27^\circ)$ and are to be compared with values $\epsilon_0 = 15,000$ and $K_0(1/\text{m.}) = 5.62(20^\circ)$ obtained by Lang¹¹ and a value of $K_0 = 5.6(20^\circ)$ obtained in dilute solution work done in the Laboratories.¹⁰ The agreement is reassuring. Knowing the equilibrium constant K_0 and the extinction coefficient, it then was possible to take a given mixture and from its absorbance calculate individually the amounts of complex and of free disulfide present; knowing the extinction curves for these species, it then was possible to calculate that for the $-S-S-$ absorption band of the complexed disulfide. The results of these calculations are shown in Fig. 4, wherein it is seen that a total red shift of approximately 2000 cm.⁻¹ has occurred.

Some reticence on the part of the authors in presenting extinction coefficient data may have been noted. This is not accidental. It was very difficult to standardize disulfide solutions, partly because of the varying types and degrees of impurity contamination in commercial disulfide preparations, partly because of its ease of decomposition upon exposure to light and partly because of worker repugnance.

(12) H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949).

(13) N. J. Rose and R. S. Drago, *ibid.*, **81**, 6138 (1959).

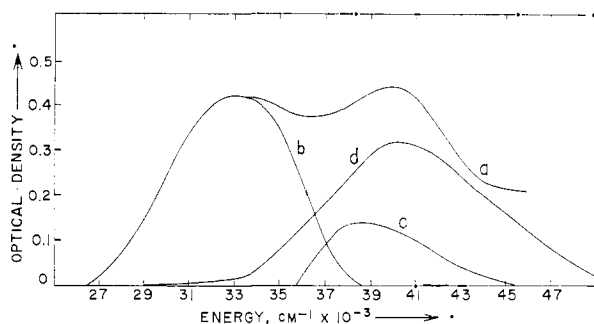


Fig. 4.—The resolution of the optical density *versus* ν (cm^{-1}) plot for solution III of Table II (curve a) into component plots for the charge transfer band of pure $\text{Et}_2\text{S}_2\text{I}_2$ complex (curve b), for the $-\text{S}-\text{S}-$ absorption band of pure $\text{Et}_2\text{S}_2\text{I}_2$ complex (curve c) and for the $-\text{S}-\text{S}-$ absorption band of free Et_2S_2 (curve d). The relative optical densities are functions of the concentrations of the various species present in solution III, and also of the relative extinctions. Curves a, b and d are experimental and from the present work (see also ref. 10 and 11 of text). Curve c is the derived absorption band.

However, the major reason for reluctance is the *extreme* degree of error which enters into determination of ϵ by either the Drago or Benesi-Hildebrand methods. Such errors affect plots of the type of Fig. 4; for this reason we consider Fig. 4 as demonstrating no more than a simple red shift of the characteristic $-\text{S}-\text{S}-$ absorption upon complexation. Another comment is that the total *observed* shift (as opposed to *deduced* shift) was only 70 \AA . and although occurring in a high dispersion region of the spectrum is still very small, particularly when one is observing a diffuse band maximum. Efforts to induce larger shifts using a stronger acceptor (tetracyanoethylene) were unsuccessful because of reaction; thus despite the considerable room for doubt in the present experimental results, it is felt that they shall have to suffice until methods of experimentation at lower temperatures (-190°) have been more thoroughly elaborated; at present the scattering of light by inhomogeneities in organic glasses is too great at 2500 \AA . to permit further study.

Conclusions

In any work as tenuous as the foregoing, it is appropriate to accurately delineate one's assumptions. The attribution of the rotational barrier about the $-\text{S}-\text{S}-$ bond to the net antibonding character of the four $3p\pi_{\perp}$ electrons is reasonable and has been used by many authors. However, since the validity of this attribution has never been truly established, it must remain questionable. Such, to a much greater degree, is true of the second equality used: namely that $E_{-}(0^\circ) - E_{\pm}(90^\circ)$ equals 9445 cm^{-1} . This equality is dependent, among other things, on the assumption that the energy of the terminal state in the absorption process occurring at $40,500 \text{ cm}^{-1}$ is independent of twist. This necessitates that this state be of species σ , at least in the region of cylindrical symmetry of the $-\text{S}-\text{S}-$ bond. The designation $\sigma^*(3p)$ seems reasonable on an m.o. basis and is substantiated to some extent by the fact that in dithiolane the characteristic $-\text{S}-\text{S}-$ band has indeed red-shifted. None the less the equality $E_{-}(0^\circ) - E_{\pm}(90^\circ) = 9445 \text{ cm}^{-1}$ is tolerable only when it is realized that factors not considered nor easily specified render it subject to considerable probable error.

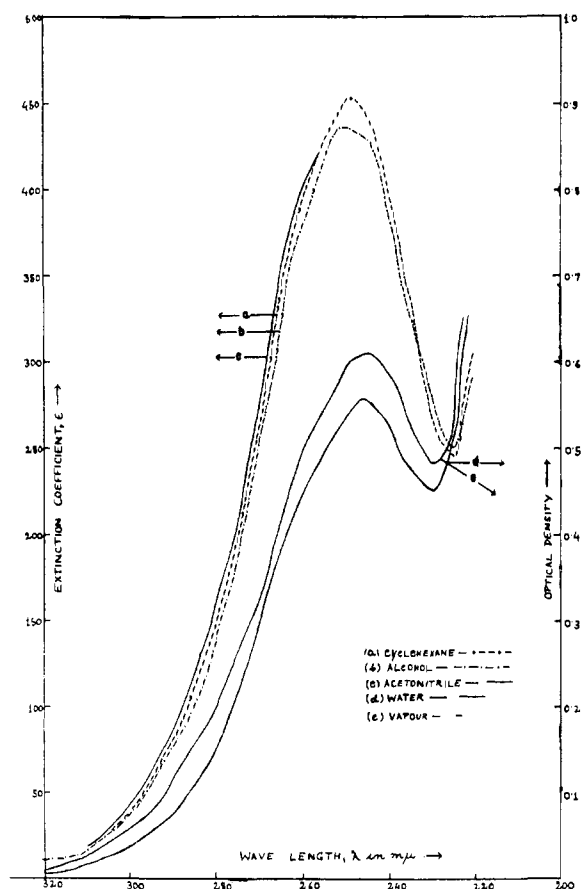


Fig. 5.—The absorption spectrum of diethyl disulfide in (a) cyclohexane, (b) acetonitrile, (c) alcohol, (d) vapor and (e) water. The observed red shifts are of the expected order of magnitude ($\sim 500 \text{ cm}^{-1}$) for a transition originating in an n -orbital but cannot be considered very obvious from these plots. Arrows indicate the ordinate to which curves should be referred. It is further to be noted that the present work does not distinguish between the two choices: $\sigma^*(3p_z)$ or $\sigma(4s)$, for the terminal state of the characteristic disulfide band.

An attempt to validate the $\phi_{\pm} \rightarrow \sigma^*$ nature of the diethyl disulfide transition has been made using the "blue-shift" techniques of Kasha.¹⁴ The ϕ_{\pm} orbital is a non-bonding orbital, and a considerable charge redistribution should occur on excitation of an electron from this orbital to the σ^* m.o. This redistribution will not be as great as that which occurs in a normal $n \rightarrow \pi^*$ transition but none the less should result in a similar effect: namely, that the characteristic $-\text{S}-\text{S}-$ absorption band should increasingly blue-shift upon solution in solvents of increasing dielectric constant. Fig. 5 illustrates the results of such an investigation; band maxima and extinction coefficients are given in Table III. It is obvious that if one considers the solvent series cyclohexane, acetonitrile, alcohol and water, a small but definite blue shift does occur. However, the vapor spectrum and that in cyclohexane are anomalous in that a red shift occurs upon solution in the latter medium. In short, the sum of evidence presented

(14) M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1950).

TABLE III
THE EFFECT OF SOLVENT ON THE 2500 Å. BAND OF DIETHYL DISULFIDE

Solvent	$\bar{\nu}_{\max}$ (cm. ⁻¹)	ϵ
Cyclohexane	39990	455
Acetonitrile	39990	455
Alcohol	40310	436
Water ^a	40803	..
Vapor	40473	..

^a Solubility was too low to permit measurement of ϵ .

in this work does seem to indicate that the genesis orbital is ϕ_{\pm} , and the ability to account for so many diverse aspects of the -S-S- absorption band using the designation $\phi_{\pm} \rightarrow \sigma^*$ is taken as support for this assignment. Under no circumstances, however, should this work be considered as "proving" such an assignment; for example, the terminal state $\sigma(4s)$ is equally probable.

If all of the foregoing assumptions are correct, a calculable red shift of the characteristic -S-S- absorption band will occur upon electron transfer from the disulfide bond region. A concomitant

opening or closing of the dihedral angle θ will occur; the authors presume that the increase of θ is more probable from steric considerations (using molecular models), but at least for smaller alkyl groups this is not an overriding conclusion, and in this case θ may very well decrease.

The experimental basis for the 2000 cm.⁻¹ red shift must now be questioned. At best, any attempt to resolve a composite two peak curve (Fig. 4a) into three contributing curves may be questioned. However, in the present instance the detailed shapes of curves b and d are known experimentally, and but for the doubt about absolute extinction values for curve b, this resolution would be straightforward. The slight shift of the 40,000 cm.⁻¹ peak cannot be accounted for by an additive contribution from curve b, and because of this a red shift such as shown in Fig. 4 is considered the more probable.

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Solvent Effects on the Energy Barrier for Hindered Internal Rotation in Some N,N-Disubstituted Amides^{1,2}

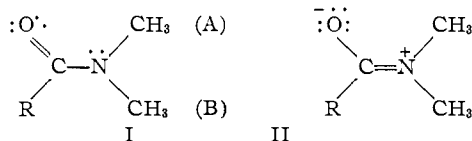
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From the temperature dependence of the proton magnetic resonance (p.m.r.) spectra of some substituted amides we have obtained values for the energy barriers restricting internal rotation about the central C-N bond. It has been found that the barrier height E_a is strongly dependent on the nature of the solvent, and on the concentration, when these substances are studied in solution. Measurements were made on N,N-dibenzylacetamide (DBA) at a single concentration and on both N,N-dimethylpropionamide (DMP) and N,N-dimethylcarbonyl chloride (DMCC) over a range of concentrations. The barrier height appears to decrease monotonically with increasing dilution in carbon tetrachloride whereas it increases initially but passes through a maximum, with increasing dilution in dibromomethane. A possible explanation for these results is suggested.

Introduction

At sufficiently low temperatures most N,N-dimethylamides (I) show a doublet in the p.m.r. spectrum of the -N(CH₃)₂ group. It was proved



by Phillips⁴ that this doublet was the result of a chemical-shift difference between the resonances for the methyl groups at A and B (I) and becomes apparent when the mean lifetime of a methyl group at one or the other of the sites is sufficiently long. Gutowsky and Holm⁵ developed a method for obtaining the mean lifetime 2τ of a methyl

group at each of the sites from the line shapes of the -N(CH₃)₂ chemical-shift doublet. Earlier methods of analyzing the data have been reviewed.⁶ Recently a method similar to that proposed by Loewenstein and Meiboom⁷ has been shown to yield more precise values of τ for the N,N-dimethylamides. The energy barriers for a series of substituted N,N-dimethylamides have been determined with fair precision by Rogers and Woodbrey⁸ from the temperature dependence of τ by use of this method.

The rather large energy barriers observed⁸ for internal rotation about the central C-N bond of amides appear to be the result of some partial double-bond character acquired by this bond through resonance between structures I and II in the ground states of the amides. Since the more polar form II should be stabilized more in polar solvents than the less polar form I, we might expect the barrier height to depend on the nature and

(1) Research supported by a grant from the National Science Foundation.

(2) Abstracted in part from a thesis submitted by J. C. Woodbrey, in partial fulfillment of the requirements for the Ph.D. degree, June, 1960.

(3) W. R. Grace and Co., Washington Research Center, Clarksville, Maryland.

(4) W. D. Phillips, *J. Chem. Phys.*, **23**, 1363 (1955).

(5) H. S. Gutowsky and C. H. Holm, *ibid.*, **26**, 1228 (1956).

(6) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

(7) A. Loewenstein and S. Meiboom, *J. Chem. Phys.*, **27**, 1067 (1957).

(8) M. T. Rogers and J. C. Woodbrey, unpublished results.