[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

The Ultraviolet Absorption Spectra of Organic Sulfur Compounds. I. Compounds Containing the Sulfide Function[1]

BY EDWARD A. FEHNEL[2] AND MARVIN CARMACK

In connection with a study of the chemistry of certain organic sulfur compounds in this Laboratory, we have frequently had occasion to determine the ultraviolet absorption spectra of compounds containing the sulfide or sulfone functions. Since surprisingly little has been published concerning the absorption spectra of simple organic compounds of this type,[3] we have undertaken an extensive investigation of the absorption spectra of model compounds containing these functions for the purpose of providing data which should prove useful in structure determinations. The present paper describes the results obtained with aliphatic and aromatic sulfides, mercaptals and mercaptoles, alkoxysulfides, ketosulfides and carbalkoxysulfides. Further data on sulfones, nuclearly-substituted aromatic sulfides and sulfones, and heterocyclic sulfur compounds will appear in subsequent publications.

On the basis of the limited information heretofore available on the spectroscopic properties of the sulfide function, it has been stated that $-\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}-$ is a resonance insulator with properties much like those of $-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-$ and $-CH_2-$.[4] We have now observed an unusual type of conjugation between chromophores in compounds in which the sulfide function and another function such as a carbonyl, carbalkoxyl, vinyl, phenyl or second sulfide function are both attached to the same carbon atom. These observations lead to some interesting conclusions regarding the correlation of absorption spectra with structure in these types of compounds. A discussion of the theoretical aspects of the problem has been reserved until after a description of the spectra themselves.

Aliphatic Sulfides.—Alkyl sulfides in ethanol solution exhibit a narrow absorption band of rather high intensity (log $\epsilon \sim 3$) in the neighborhood of 210 mμ (Figs. 1–3). A gradual displacement of the maximum toward longer wave lengths and higher intensities is observed as the α-hydrogen atoms are successively replaced by methyl groups in the series: methyl sulfide, ethyl sulfide, isopropyl sulfide and *t*-butyl sulfide (Fig. 1). A shoulder which appears on the long wave length side of the curves for methyl sulfide, ethyl sulfide (Figs. 1 and 2), *n*-butyl sulfide (Figs. 3 and 4) and pentamethylene sulfide (Fig. 5) in the region 225–235 mμ is considerably reduced in the curve for isopropyl sulfide and disappears in the curve for *t*-butyl sulfide. This shoulder is shifted 10 mμ toward longer wave lengths in the spectrum of tetramethylene sulfide, while the peak at 210 mμ is broadened and reduced in intensity as compared with the next higher homolog, pentamethylene sulfide (Fig. 5). The differences between the spectra of the latter two compounds presumably have a stereochemical basis and will be considered further in connection with our study of the spectra of heterocyclic sulfur compounds.

Mercaptals and Mercaptoles.—The marked optical interaction exhibited by compounds in which two sulfide functions are attached to a common carbon atom is illustrated in Figs. 2 and 3. In the spectra of the mercaptals a new peak (log $\epsilon \sim 2.8$) appears in the region 235–240 mμ. Alkylation of the central carbon atom, as in 2,2-bis-(*n*-butylmercapto)-propane (Fig. 3), has only the effect of intensifying this new absorption band somewhat. As might be expected from the multiplicity of functional units, *sym*-trithiane (Fig. 2) has a spectrum similar to, but uniformly more intense than, those of the simple mercaptals. In contrast to these results, ethanol solutions of trioxane, the oxygen analog of *sym*-trithiane, are completely transparent throughout the region observable with the instrument and solvent used (down to ~208 mμ).

The spectra of bis-(*n*-butylmercapto)-methane and *sym*-trithiane were determined in both ethanol and anhydrous dioxane, and the results, shown in Fig. 6, indicate only a very slight influence of the solvent on the position of the new peak in the region 235–240 mμ. This band is not, therefore, attributable to dissociation or to chemical reaction with a hydroxylated solvent.

That there exists a profound difference in the spectral behavior of sulfur and oxygen was shown by replacing one of the sulfur atoms of a mercaptal with an oxygen atom in the monothioacetal, $n\text{-}C_4H_9SCH_2OC_2H_5$ (Fig. 4). It will be noted that the replacement of sulfur with oxygen not only results in the disappearance of the peak at 236 mμ but suppresses the intensity of absorption below that of even the simple alkyl

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[2] American Chemical Society Postdoctoral Fellow, 1946–1948. Present address: Department of Chemistry, Swarthmore College, Swarthmore, Pa.

[3] Absorption data for a few simple aliphatic and aromatic thioethers have been reported previously, but much of this is of a semiquantitative nature and permits little more than a rough comparison between the compounds studied in a given investigation. References to the earlier data are included in Table I.

[4] See, for example, Brode, "Chemical Spectroscopy," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 221. Lewis and Calvin (ref. 9a, p. 284) have, however, suggested that sulfur atoms may sometimes join chromophoric groups into single chromophoric units.

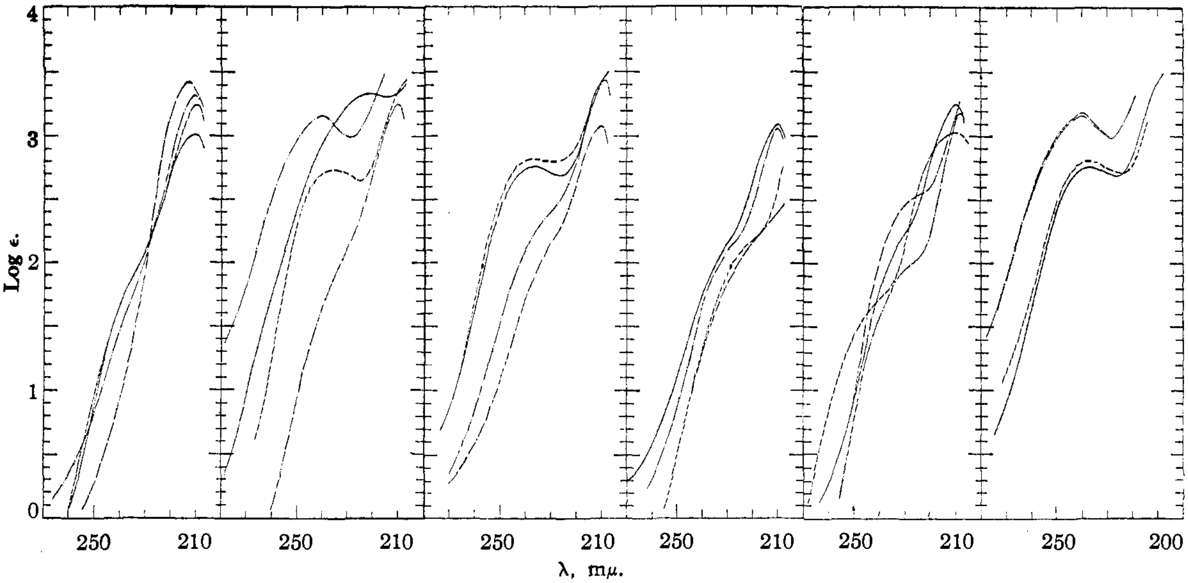

Fig. 1. Fig. 2. Fig. 3. Fig. 4. Fig. 5. Fig. 6.

Fig. 1.—Absorption spectra of $(CH_3)_2S$, —; $(C_2H_5)_2S$, ------; $[(CH_3)_2CH]_2S$, —·—; $[(CH_3)_3C]_2S$, — — —.

Fig. 2.—Absorption spectra of $(CH_2{=}CHCH_2)_2S$, —; $CH_3SCH_2SCH_3$, ------; *sym*-trithiane, —·—; $(C_2H_5)_2S$, — — —.

Fig. 3.—Absorption spectra of *n*-$C_4H_9SCH_2SC_4H_9$-*n*, —; *n*-$C_4H_9SC(CH_3)_2SC_4H_9$-*n*, ------; *n*-$C_4H_9SCH_2CH_2SC_4H_9$-*n* —·—; (*n*-$C_4H_9)_2S$, — — —.

Fig. 4.—Absorption spectra of (*n*-$C_4H_9)_2S$, —; *n*-$C_4H_9SCH_2OC_2H_5$, ------; *n*-$C_4H_9SCH_2CH_2OC_2H_5$, —·—; $(CH_3OCH_2)_2S$, — — —.

Fig. 5.—Absorption spectra of $(CH_2)_5S$, —; $(CH_2)_4S$, ------; 1,4-thioxane, —·—; 1,4-dithiane, — — —.

Fig. 6.—Absorption spectra of *n*-$C_4H_9SCH_2SC_4H_9$-*n* in ethanol, —, and in dioxane, ------; *sym*-trithiane in ethanol, —·—, and in dioxane, — — —.

sulfides. A similar effect is observed in the spectra of the dimethoxysulfide, $CH_3OCH_2SCH_2OCH_3$, and of *n*-$C_4H_9SCH_2CH_2OC_2H_5$ (Fig. 4).

When two sulfide functions are separated by two methylene groups, as in 1,2-bis-(*n*-butylmercapto)-ethane (Fig. 3), the chromophores are effectively insulated from each other, and the spectrum is similar to that calculated for a simple monosulfide at twice the molar concentration.

A comparison of the relative effect of $—CH_2—$, $—\ddot{\underset{..}{O}}—$, and $—\ddot{\underset{..}{S}}—$ in six-membered rings is shown in Fig. 5 in the spectra of pentamethylene sulfide, 1,4-thioxane and 1,4-dithiane. Little difference is observed in the effect of sulfur and oxygen when either of these is separated from a sulfide function by two carbon atoms, in marked contrast to the unique behavior observed when only a single carbon atom intervenes between two sulfide functions.

Allyl Sulfide.—An example of the effect of having a vinyl group and a sulfide function attached to the same carbon atom is provided by the spectrum of allyl sulfide (Fig. 2). The curve, which consists of a broad absorption band having a maximum at 221 mμ, differs markedly from those of both non-conjugated alkadienes[5] (*e.g.*, 1,5-hexadiene, $\lambda_{max.} < 200$ mμ) and simple sulfides.

Aromatic Sulfides.—The ultraviolet absorption spectra of a number of typical aryl and aralkyl sulfides are illustrated in Figs. 7–11. Considerable interaction between sulfur and an attached benzene ring is evident in the spectra of phenyl sulfide (Fig. 9), benzyl phenyl sulfide (Fig. 9) and the phenyl alkyl sulfides (Figs. 7 and 8), all of which differ markedly from the spectra of simple benzenoid hydrocarbons such as toluene (Fig. 8). A smoothing out of the benzenoid fine structure and a great intensification of the absorption throughout are features which appear to be characteristic of the phenylmercapto group. However, a progressive change in the position of the long wave length maximum is noted when the α-hydrogen atoms in the phenyl alkyl sulfides (Fig. 7) are replaced stepwise by alkyl groups in the series: phenyl methyl sulfide ($\lambda_{max.}$ 254 mμ), phenyl ethyl sulfide ($\lambda_{max.}$ 256 mμ), phenyl isopropyl sulfide ($\lambda_{max.}$ 258 mμ), and phenyl *t*-butyl sulfide ($\lambda_{max.}$ 266 mμ). Simultaneously with the shift of the maxima toward longer wave lengths, a downward trend in intensities is observed (log ε: 3.98, 3.90, 3.75, 3.19, resp.). Progressive changes are likewise noted in the shoulder in the region 270–290 mμ and in the short wave length peaks at 200–220 mμ.

The effect of interposing one or more methylene

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(5) Spectra of these and most other comparison compounds mentioned in this paper may be found in the "International Critical Tables," Vol. V, McGraw-Hill Book Co., New York, N. Y., 1929, pp. 359 ff.

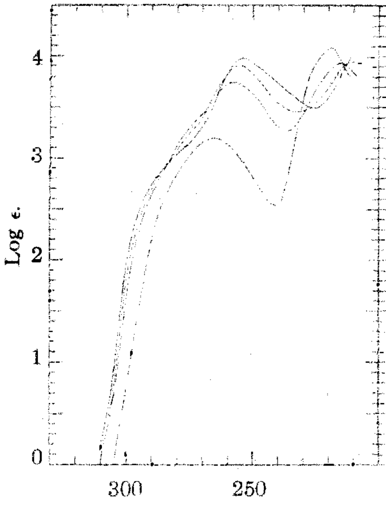

Fig. 7.

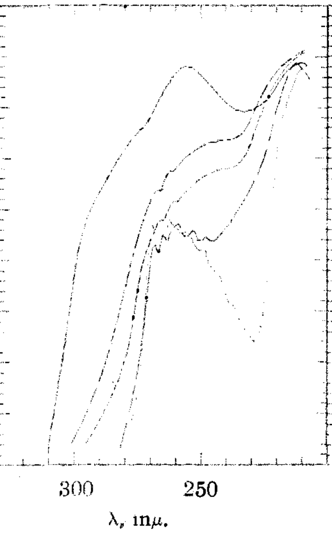

Fig. 8.

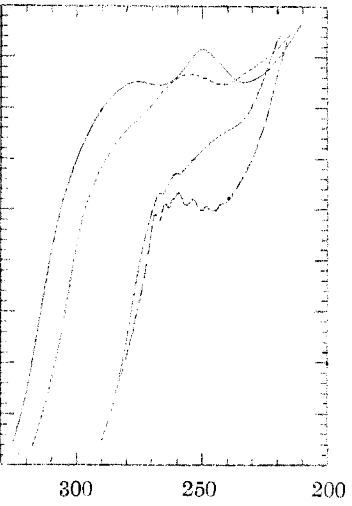

Fig. 9.

Fig. 7.—Absorption spectra of $C_6H_5SCH_3$, —; $C_6H_5SC_2H_5$, - - - - - -; $C_6H_5SCH(CH_3)_2$, –·–·–; $C_6H_5SC(CH_3)_3$, — — —.

Fig. 8.—Absorption spectra of $C_6H_5SC_2H_5$, —; $C_6H_5CH_2SC_2H_5$, - - - - - -; $C_6H_5CH_2CH_2SC_2H_5$, –·–·–; $C_6H_5CH(SCH_3)_2$, — — —; $C_6H_5CH_3$, ...

Fig. 9.—Absorption spectra of $(C_6H_5)_2S$, —; $C_6H_5SCH_2C_6H_5$, - - - - - -; $(C_6H_5CH_2)_2S$, –·–·–; $(C_6H_5CH_2CH_2)_2S$, — — —.

groups between the sulfide function and the benzene ring is illustrated in the curves for the homologous series: phenyl ethyl sulfide, benzyl ethyl sulfide, and phenethyl ethyl sulfide (Fig. 8). Although the spectrum of benzyl ethyl sulfide is less intense than that of phenyl ethyl sulfide, considerable interaction between the sulfur atom and the aromatic nucleus in the former compound is indicated by the development of a prominent shoulder at 235–240 mμ (log ε ~2.9). In this same region a minimum appears in the curve for phenethyl ethyl sulfide, which is essentially a summation of the spectra of an alkyl benzene and an alkyl sulfide. Analogous relationships, on a somewhat higher level of absorption, are observed with the corresponding series of symmetrical aryl-substituted sulfides: phenyl sulfide, benzyl sulfide and phenethyl sulfide (Fig. 9).

In contrast to the striking changes brought about in the absorption spectra of the alkyl sulfides by the attachment of a second alkylmercapto group to an α-carbon atom, there appears to be little evidence of interaction between the sulfide functions in the bis-(phenylmercapto)-methanes, $C_6H_5SCH_2SC_6H_5$ and $C_6H_5SC(CH_3)_2SC_6H_5$ (Fig. 10). The spectrum of the first compound is approximately that of phenyl ethyl sulfide at twice the molar concentration, and the spectrum of the second is similarly related to the curve for phenyl *t*-butyl sulfide. When one of the hydrogen atoms on the central carbon atom of a bis-(alkylmercapto)-methane is replaced by a phenyl group, as in $CH_3SCH(C_6H_5)SCH_3$ (Fig. 8), the resultant spectrum closely resembles that of benzyl ethyl sulfide except that the molar extinction values are uniformly about twice as large (0.3 log unit higher) in the case of the mercaptal.

The effect of substitution of oxygen in the alkyl portion of the aromatic sulfides is shown in the curves for $C_6H_5SCH_2OCH_3$ and $C_6H_5CH_2SCH_2OCH_3$ (Fig. 11). Here again oxygen exerts a suppressive effect on the absorption similar to that observed with the aliphatic alkoxysulfides.

Ketosulfides.—The aliphatic β-ketosulfides, ethylmercaptoacetone and α-ethylmercaptoisopropyl methyl ketone (Fig. 12), exhibit absorption maxima in approximately the same regions of the spectrum ($\lambda_{max.}$ 295–300 mμ and 240–245 mμ) as the aliphatic α,β-unsaturated ketones ($\lambda_{max.}$ 310–350 mμ and 230–250 mμ).[6] This conjugative effect disappears when the sulfide function and the carbonyl function are separated by two methylene groups, as in β-ethylmercaptoethyl methyl ketone (Fig. 12), the spectrum of which is essentially a summation of the spectra of a simple ketone and an alkyl sulfide. The presence of a well-developed peak at 235 mμ in the spectrum of tetrahydro-1,4-thiapyrone (Fig. 12) is somewhat surprising, but the absorption curve for this compound is very similar to that of an acyclic γ-ketosulfide at longer wave lengths.

The absorption spectra of several typical phenyl-substituted ketosulfides are shown in Figs. 13 and 14. Attachment of an alkylmercapto group to the α-carbon atom of a phenyl alkyl ketone, as in ω-ethylmercaptoacetophenone (Fig. 13), causes a pronounced bathochromic and hyperchromic displacement of the long wave length

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[6] For a discussion of the spectra of the α,β-unsaturated ketones see Woodward, THIS JOURNAL, **63**, 1123 (1941); **64**, 76 (1942).

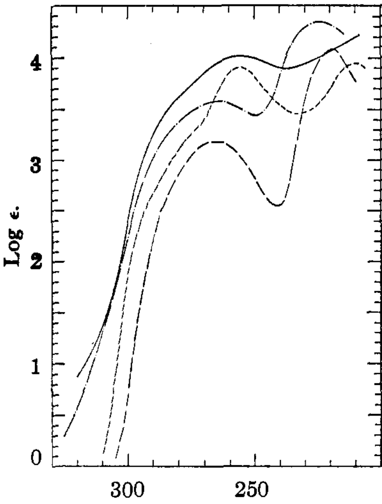


Fig. 10.

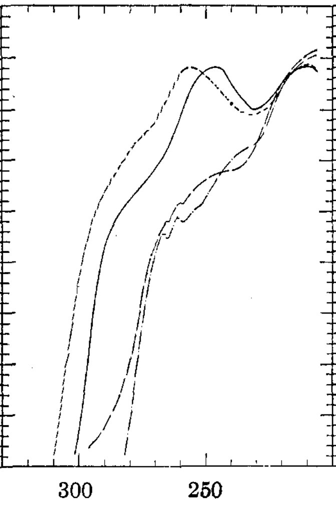


Fig. 11.

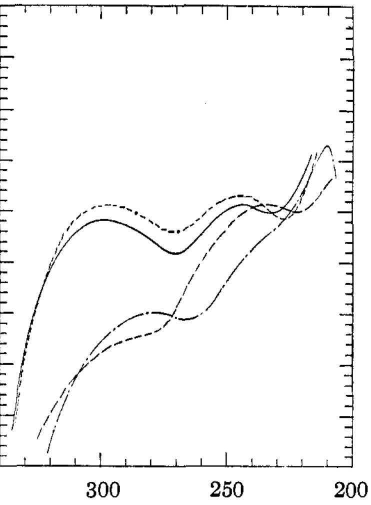


Fig. 12.

Fig. 10.—Absorption spectra of $C_6H_5SCH_2SC_6H_5$, —; $C_6H_5SC_2H_5$, ------; $C_6H_5SC(CH_3)_2SC_6H_5$, -·-·-; $C_6H_5SC(CH_3)_3$, — — —.

Fig. 11.—Absorption spectra of $C_6H_5SCH_2OCH_3$, —; $C_6H_5SC_2H_5$, ------; $C_6H_5CH_2SCH_2OCH_3$, -·-·-; $C_6H_5CH_2SC_2H_5$, — — —.

Fig. 12.—Absorption spectra of $C_2H_5SCH_2COCH_3$, —; $C_2H_5SC(CH_3)_2COCH_3$, ------; $C_2H_5SCH_2CH_2COCH_3$, -·-·-; tetrahydro-1,4-thiapyrone, — — —.

portion of the curve. Substitution of an alkylmercapto group on a β-carbon atom, as in β-ethylmercaptopropiophenone (Fig. 13), has little effect upon the characteristic absorption of the benzoyl chromophore, and the resultant spectrum is almost identical with that of a phenyl alkyl ketone. The spectra of the α-phenylmercaptoketones, phenylmercaptoacetone and α-phenylmercaptoisopropyl methyl ketone (Fig. 14), appear to be approximately summations of the spectra of an aliphatic ketone and an appropriately substituted phenyl alkyl sulfide (phenyl ethyl sulfide and phenyl *t*-butyl sulfide, respectively).

Carbalkoxysulfides.—The spectra of several α- and β-carbalkoxysulfides are shown in Fig. 15. Strong interaction between the sulfide func-

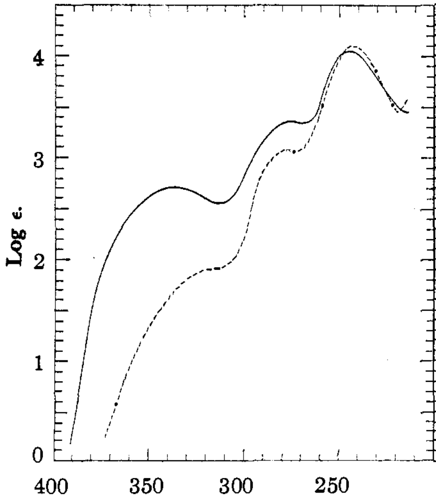


Fig. 13.

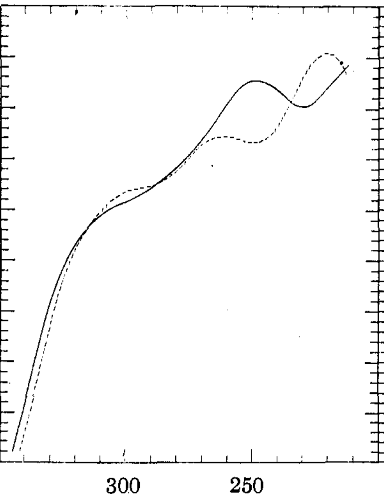


Fig. 14.

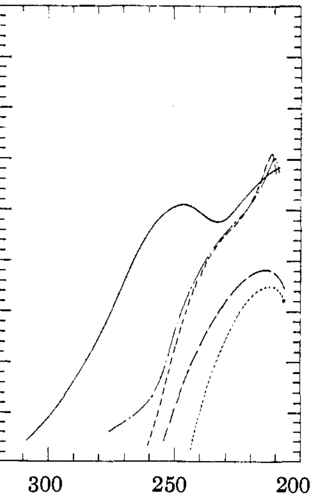


Fig. 15.

Fig. 13.—Absorption spectra of $C_2H_5SCH_2COC_6H_5$, —; $C_2H_5SCH_2CH_2COC_6H_5$, ------.

Fig. 14.—Absorption spectra of $C_6H_5SCH_2COCH_3$, —; $C_6H_5SC(CH_3)_2COCH_3$, ------.

Fig. 15.—Absorption spectra of n-$C_4H_9SCH_2CO_2C_2H_5$, —; n-$C_4H_9SCH_2CH_2CO_2CH_3$, ------; $S(CH_2CH_2CO_2CH_3)_2$, -·-·-; $C_2H_5OCH_2CO_2C_2H_5$, — — —; $CH_3CO_2C_2H_5$, ...

tion and the carbalkoxyl group in α-carbalkoxysulfides is indicated by the appearance of an absorption band at 247 mμ (log ε 2.54) in the spectrum of ethyl *n*-butylmercaptoacetate. The interpolation of a second methylene group between the sulfide and carbalkoxyl functions, as in methyl β-*n*-butylmercaptopropionate and methyl β-thiodipropionate, effectively insulates the chromophores from each other, with the result that the spectra of β-carbalkoxysulfides differ only slightly from those of simple alkyl sulfides. An ethoxyl group in the α-position of an ester has only a slight bathochromic effect on the absorption of the weakly chromophoric carbalkoxyl group, as shown in the comparison of the spectra of ethyl acetate and ethyl ethoxyacetate (Fig. 15).

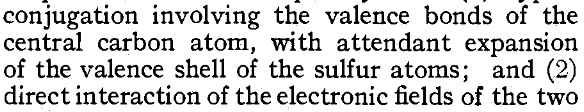
Discussion

The absorption of visible and near-ultraviolet radiation (800–200 mμ) by organic compounds is usually associated with a separation of electrical charge arising from the polarization of the π-orbital electrons of a system of multiple bonds.[7] A closely related phenomenon is the absorption of radiation in the far-ultraviolet region of the spectrum by molecules containing atoms with unshared pairs of valence electrons, which, like one of the electron pairs in a double bond, enter a π orbital in the molecule and interact more or less readily with electromagnetic vibrations of sufficiently high energy. Although absorption bands due solely to this process can generally be observed only at wave lengths below 200 mμ, the near-ultraviolet bands in the spectra of alkyl derivatives of such highly polarizable atoms as sulfur, bromine and iodine have been attributed to the excitation of these non-bonding electrons.[8] The displacement of these bands toward longer wave lengths with increasing alkyl substitution on the α-carbon atom has been ascribed to the accumulation on the sulfur and halogen atoms of a negative charge induced by the electron-releasing alkyl groups.[8b]

While this interpretation accounts satisfactorily for the absorption bands of the simple alkyl sulfides in the neighborhood of 210 mμ it fails to explain the extensive optical interaction which we have observed in the case of the alkylmercaptals and alkylmercaptoles. The appearance of a new long wave length band in the spectra of these compounds cannot be due to an inductive effect acting through the central carbon atom, since the −*I* effect of each sulfur atom would be expected to put the π electrons of the other sulfur atom under additional constraint, thereby decreasing the normal absorption associated with each sulfide function. This is the observed result when one of the sulfur atoms is replaced by oxygen in the monothioacetals. The disappearance of the long wave length band and the return of the spectrum to the alkyl sulfide type when a second carbon atom is introduced into the molecule between the two sulfide functions also argues against an interpretation in terms of an inductive effect.

When absorption of visible or ultraviolet light by a polyfunctional molecule differs markedly from a summation of the spectra of the individual chromophores (*i.e.*, by exhibiting large bathochromic and hyperchromic displacements of the absorption bands characteristic of the component chromophores, or by the appearance of entirely new bands), the effect is generally regarded as evidence for the conjugation of the chromophoric groups. Since many of the polyfunctional sulfides show the optical behavior characteristic of conjugated systems, it is of interest from the theoretical point of view to deduce what modes of polarization are possible and probable in these compounds and to evaluate their effects on the optical properties of the system.

Two types of electronic interaction appear to be possible in the mercaptal system: (1) hyperconjugation involving the valence bonds of the central carbon atom, with attendant expansion of the valence shell of the sulfur atoms; and (2) direct interaction of the electronic fields of the two sulfur atoms through space. The hyperconjugation of C–H and C–C bonds with other groups has been discussed in connection with a number of physico-chemical problems, including its effect on absorption spectra.[9] It has been specifically suggested in connection with mercaptals by Rothstein[10] to account for the observed mobility of hydrogen attached to the central carbon atom in these compounds, as for example, in the spontaneous elimination of hydrogen bromide from 2-bromo-1,1-bis-(ethylmercapto)-propane, where the apparent proton-releasing



$$\mathrm{CH_3{-}\overset{\overset{Br}{|}}{C}H{-}CH(SC_2H_5)_2 \longrightarrow CH_3{-}CH{=}C(SC_2H_5)_2 + HBr}$$

effect of sulfur is attributed to resonance forms in which sulfur has an expanded valence shell.[11]

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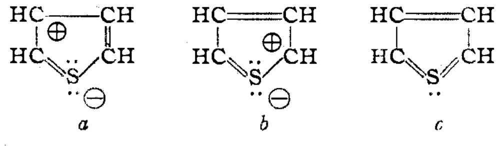
(7) (a) Lewis and Calvin, *Chem. Revs.*, **25**, 273 (1939); (b) Maccoll, *Quart. Revs.* (*London*), **1**, No. 1, 16 (1947).

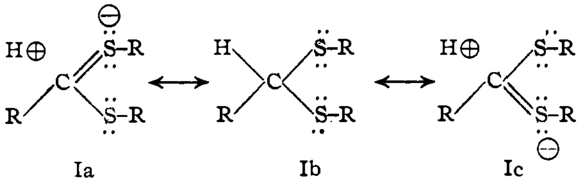
(8) (a) Mulliken, *J. Chem. Phys.*, **3**, 506 (1935); (b) Price, *ibid.*, **4**, 539, 547 (1936); *Ann. Reports Chem. Soc.* (*London*), **36**, 47 (1939); *Chem. Revs.*, **41**, 257 (1947).

(9) (a) Pauling, Springall and Palmer, THIS JOURNAL, **61**, 927 (1939); (b) Mulliken, *J. Chem. Phys.*, **7**, 339 (1939); (c) Mulliken, Rieke and Brown, THIS JOURNAL, **63**, 41 (1941).

(10) Rothstein, *J. Chem. Soc.*, 1550, 1553, 1558 (1940).

(11) An expansion of the valence shell of sulfur in the sulfide function has also been proposed by Schomaker and Pauling [THIS JOURNAL, **61**, 1769 (1939)] to account for the observed value of the dipole moment of thiophene. It was found necessary to assume approximately a 10% contribution by structures of types a, b, and c, in which the sulfur atom expands its valence shell to a decet.

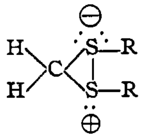




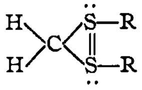
Ia Ib Ic

Woodward and Eastman[12] have recently pointed out that Rothstein's mechanism would also account for the formation of 2-carbomethoxy-3-ketotetrahydrothiophene as the major product in the Dieckmann cyclization of α,β'-dicarbomethoxymethylethyl sulfide at low temperatures.

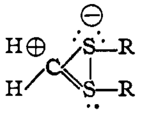
The type of polarization represented by structures Ia and Ic might be considered to afford an adequate explanation for the development of a new peak in the region 235–240 mμ in the spectra of the alkylmercaptals and alkylmercaptoles. It is of interest to note, however, that the possibilities for polarized resonance forms are not exhausted by the structures postulated by Rothstein if one accepts the original assumption that the sulfide function can behave as either a donor or an acceptor of electrons. For example, there seems to be no reason for excluding the possibility of direct interaction of the electronic systems of the two sulfur atoms, involving a transfer of charge from one sulfur atom to the other and giving rise to polarizations along the line of centers of these atoms. Such interactions, illustrated in formulas II and III, imply the existence of transient three-membered rings. In addition, still other resonance forms (formula IV) can be written which involve the simultaneous operation of this effect and the hyperconjugative effect proposed by Rothstein.[13]



(two forms)
II



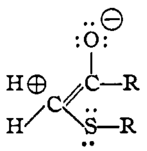
III



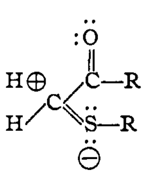
(four forms)
IV

That direct interaction may occur between the two sulfur atoms in the alkylmercaptals and alkylmercaptoles seems to be supported by the resemblance of the spectra of these compounds to those of the alkyl disulfides, RSSR, in which two sulfur atoms are joined by primary valence bonds.[14] The marked difference in the optical behavior of the mercaptals and monothioacetals is also consistent with this interpretation; while the oxygen atom can exert an inductive effect upon the sulfur atom, it cannot be considered to participate in resonance involving expansion of its valence shell to accommodate more than eight electrons.

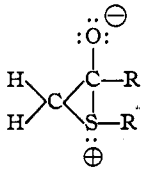
Resonance forms embodying similar assumptions can be written for the β-ketosulfides, α-carbalkoxysulfides, benzyl sulfides, and allyl sulfides. Thus, contributions from structures such as V–VIII might account for the characteristic absorption spectra of the β-ketosulfides.



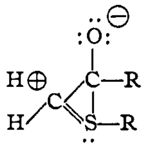
V



VI



VII



VIII

In 1,2-bis-(alkylmercapto)-ethanes and γ-ketosulfides, little, if any, direct interaction between the functional groups would be anticipated, since these groups would, on the average, be widely separated in space. Possible exceptions might be found in cyclic compounds, such as 1,4-dithiane and tetrahydro-1,4-thiapyrone, in which the 1,4-atoms are restricted to relatively feeble oscillations between the positions corresponding to "chair" and "boat" forms of the rings and, as a result, are always in close proximity to each other.[15] It is interesting to note that the spectra of 1,4-dithiane and tetrahydro-1,4-thiapyrone differ from those of their acyclic analogs, and it is very probable that these differences are attributable to direct interaction between the 1,4-atoms.

When the sulfide function is attached directly to a benzene ring, a much larger number of modes of polarization are possible than in the case of the aliphatic sulfides. By analogy with the corresponding phenyl ethers, structures in which sulfur behaves as an electron donor with respect to the benzene ring would be expected to contribute heavily to the resonance in all phenylmercapto derivatives. If, however, the sulfur atom is also capable of accepting electrons from the aromatic nucleus, additional resonance structures can be

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(12) Woodward and Eastman, THIS JOURNAL, **68**, 2229 (1946).

(13) The possible participation of cyclic structures such as II, III and IV depends not only upon the ability of sulfur to donate *and accept* electrons, but also upon the ability of the two sulfur atoms to approach each other sufficiently closely to interact. That such three-membered rings are not a stereochemical impossibility is indicated by considerable recent work on the role of neighboring groups in nucleophilic displacement reactions [*cf.* Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 176–178; Winstein and Buckles, THIS JOURNAL, **64**, 2780 (1942), and succeeding papers; Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 242]. Studies on the mechanism of replacement of halogen in mustard gas have shown specifically that the sulfur atom may be involved in three-membered rings [*cf.* Gilman and Philips, *Science*, **103**, 409 (1946); Fuson, Price and Burness, *J. Org. Chem.*, **11**, 475 (1946)].

(14) Ethyl disulfide has an absorption band with a maximum at 249 mμ (log ϵ 2.63) [Ley and Arends, *Z. physik. Chem.*, **B15**, 311 (1932)].

(15) The close approach of the 1,4-atoms of these compounds in all possible configurations of the rings is only fully appreciated after an examination of the scale models: *e. g.*, Stuart or Fisher-Hirschfelder molecular models.

written which are not possible with the analogous oxygen compounds. The progressive changes observed in the spectra of the phenyl alkyl sulfides with increasing alkylation of the α-carbon atom might result either from changes in the relative importance of resonance contributions by structures of these two types, or from steric effects, or from a combination of both these factors. A study of the absorption spectra of various nuclearly-substituted phenyl sulfides is being undertaken to provide additional data on this aspect of the problem, and the results will be described in a subsequent communication.

Regardless of the directional character of the polarization within the phenylmercapto group, it is evident that the resonance within this system is considerable, and it is not surprising, therefore, to find that the sulfur atom in this combination shows little or no tendency to interact with other functional groups attached to the α-carbon atom. We can thus account for the fact that the attachment of a second phenylmercapto group or an acetyl group in this position on a phenyl alkyl sulfide fails to give rise to new absorption bands or to cause any appreciable displacement of the maxima characteristic of the parent sulfide.

An obvious implication of these concepts is that the unique properties postulated for the sulfide function on spectroscopic grounds should be reflected in the chemical reactivity of compounds containing this function. Several examples of the activation of methylene groups by adjacent alkylmercapto groups have been referred to[10,12] above, and other unusual properties of thio compounds have been reported which might be satisfactorily explained on the basis of these concepts. Further work is planned along chemical and physico-chemical lines suggested by the spectroscopic data.

Experimental[16]

Ultraviolet Absorption Measurements.—The ultraviolet absorption spectra were determined with a Beckman quartz spectrophotometer, Model DU, using an approximately constant spectral band width of *ca.* 1 mμ down to wave lengths in the neighborhood of 220 mμ. Readings at shorter wave lengths were obtained by using the 0.1 switch position and balancing the galvanometer for 100% transmission with the solvent in position before the phototube. The wave lengths and logarithms of the molar extinction coefficients at the absorption maxima and at prominent points of inflection are listed in Table I.

Preparation of Compounds.—Most of the previously known compounds were prepared by methods described in the literature or were obtained from commercial supply houses; source references are given in Table I. With several exceptions which are noted below, all compounds were purified by two or more redistillations or recrystallizations immediately before determination of the spectra. The physical constants for all previously known compounds except phenethyl sulfide (see below) checked those recorded in the literature.

bis-(Phenylmercapto)-methane,[17] 2,2-bis-(phenylmercapto)-propane,[18] and α,α-bis-(methylmercapto)-toluene,[19] decomposed so readily on heating that it was not found possible to purify the crude products by distillation, even at very low pressures. To obtain the pure compounds, large excesses of the sulfhydryl intermediates were employed in the preparations, and the crude oils

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF ORGANIC SULFIDES[a]

		Maxima[c]	
Compound	Source[b]	λ (mμ)	Log ε
A. Alkyl Sulfides			
Methyl sulfide[d]	1	(229)	2.14
		210	3.01
Ethyl sulfide[e,f]	2	(229)	2.14
		210	3.25
n-Butyl sulfide	3	(229)	2.16
		210	3.09
Isopropyl sulfide	4	211	3.32
t-Butyl sulfide	5	213	3.42
Allyl sulfide	2	221	3.33
Pentamethylene sulfide[g]	6	(229)	2.26
		210	3.25
Tetramethylene sulfide	7	(239)	1.73
		210	3.04
B. Mercaptals and Mercaptoles			
bis-(Methylmercapto)-methane	8	235	2.73
bis-(*n*-Butylmercapto)-methane	9	236	2.76
bis-(*n*-Butylmercapto)-methane[h]	9	236	2.81
2,2-bis-(*n*-Butylmercapto)-propane	9	237	2.82
bis-(Phenylmercapto)-methane	5	255	4.03
2,2-bis-(Phenylmercapto)-propane	5	265	3.58
		224	4.36
α,α-bis-(Methylmercapto)-toluene	5	(266)	2.69
		(260)	2.88
		(240)	3.17
sym-Trithiane	10	240	3.16
sym-Trithiane[h]	10	240	3.19
C. 1,2-bis-(Alkylmercapto)-ethanes			
1,2-bis-(*n*-Butylmercapto)-ethane	9	(229)	2.42
		209	3.44
1,4-Dithiane[f,g,i]	11	(225)	2.54
D. Aryl and Aralkyl Sulfides			
Phenyl methyl sulfide	12	(275)	3.15
		254	3.98
Phenyl ethyl sulfide	13	(270)	3.40
		256	3.90
		210	3.94
Phenyl isopropyl sulfide	5	258	3.75
		215	3.94
Phenyl *t*-butyl sulfide	14	266	3.19
		218	4.08
Benzyl phenyl sulfide	15	255	3.83
Phenyl sulfide[i,j,k]	16	277	3.76
		250	4.08

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[16] Microanalyses were performed by Mrs. Sarah M. Woods. All melting points are corrected.

[17] Fromm, *Ann.*, **253**, 135 (1889); *cf.* Otto and Tröger, *Ber.*, **25**, 3425 (1892).

[18] Baumann, *ibid.*, **19**, 2803 (1886).

[19] Bongartz, *ibid.*, **21**, 478 (1888).

TABLE I (*Continued*)

		Maxima[c]	
Compound	Source[b]	λ (mμ)	Log ε
Benzyl sulfide[i,l]	17	(266)	2.66
		260	2.85
		(238)	3.30
Phenethyl sulfide	5	268	2.45
		265	2.55
		259	2.65
		253	2.59
		248	2.52
		(242)	2.56
Benzyl ethyl sulfide	18	(265)	2.40
		(260)	2.58
		(240)	2.90
Phenethyl ethyl sulfide	5	268	2.15
		265	2.23
		259	2.35
		253	2.28
		248	2.22
		212	3.95
E. Alkoxysulfides			
n-Butylmercaptomethyl ethyl ether	9	(219)	2.18
β-*n*-Butylmercaptoethyl ethyl ether	5	(226)	2.19
		210	3.06
bis-(Methoxymethyl) sulfide	19	<210	>2.38
1,4-Thioxane[g,i]	20	(227)	2.00
		209	3.18
Phenylmercaptomethyl methyl ether	5	(272)	2.86
		247	3.90
		210	3.92
Benzylmercaptomethyl methyl ether	5	267	2.28
		261	2.43
		(233)	3.13
F. Ketosulfides			
Ethylmercaptoacetone	21	299	2.41
		243	2.56
α-Ethylmercaptoisopropyl methyl ketone	5	296	2.56
		244	2.66
β-Ethylmercaptoethyl methyl ketone	5	278	1.50
		(235)	2.24
		210	3.15
Tetrahydro-1,4-thiapyrone	22	(283)	1.26
		235	2.55
ω-Ethylmercaptoacetophenone	23	337	2.71
		276	3.36
		245	4.07
β-Ethylmercaptopropiophenone	5	(315)	1.91
		277	3.08
		242	4.10
Phenylmercaptoacetone	21	~(300)	2.58
		250	3.78
α-Phenylmercaptoisopropyl methyl ketone	5	(293)	2.72
		262	3.22
		220	4.03
G. Carbalkoxysulfides			
Ethyl *n*-butylmercaptoacetate	5	247	2.54
Methyl β-*n*-butylmercaptopropionate	5	(225)	2.37
		211	3.05
Methyl β-thiodipropionate	24	(225)	2.39
		210	3.01
H. Other Compounds			
Toluene[m]	2	269	2.33
		265	2.24
		262	2.40
		(260)	2.33
		256	2.27
		249	2.11
Ethyl acetate[m]	2	211	1.76
Ethyl ethoxyacetate	25	214	1.92
Trioxane	2	Transparent[n]	

[a] All spectra were determined in absolute ethanol unless otherwise indicated. [b] Source references: (1) reaction of methyl iodide and sodium sulfide in aqueous ethanol; (2) purified commercial material; (3) Grabowsky and Saizew, *Ann.*, **171**, 253 (1874); (4) Beckmann, *J. prakt. Chem.*, [2] **17**, 459 (1878); (5) see section on "Preparation of Compounds"; (6) Clarke, *J. Chem. Soc.*, 101, 1805 (1912); (7) Tarbell and Weaver, THIS JOURNAL, **63**, 2939 (1941); (8) Böhme and Marx, *Ber.*, **74**B, 1667 (1941); (9) Whitner and Reid, THIS JOURNAL, **43**, 638 (1921); (10) Bost and Constable, "Organic Syntheses," Coll. Vol. II, p. 610; (11) Masson, *J. Chem. Soc.*, **49**, 233 (1886); (12) Bourgeois and Abraham, *Rec. trav. chim.*, **30**, 413 (1911); (13) Otto, *Ber.*, **13**, 1275 (1880); (14) Ipatieff, Pines and Friedman, THIS JOURNAL, **60**, 2731 (1938); (15) Pummerer, *Ber.*, **43**, 1406 (1910); (16) Mauthner, *ibid.*, **39**, 3593 (1907); (17) Märcker, *Ann.*, **136**, 88 (1865); (18) Märcker, *ibid.*, **140**, 86 (1866); (19) Bloch and Höhn, *Ber.*, **55**B, 53 (1922); (20) Clarke, *J. Chem. Soc.*, 101, 1788 (1912); (21) Autenrieth, *Ber.*, **24**, 159 (1891); (22) Fehnel and Carmack, THIS JOURNAL, **70**, 1813 (1948); (23) Prelog, Hahn, Brauchli and Beyerman, *Helv. Chim. Acta*, **27**, 1209 (1944); (24) Gershbein and Hurd, THIS JOURNAL, 69, 241 (1947); (25) Scheibler, Marhenkel and Nikolic, *Ann.*, **458**, 36 (1927). [c] The wave lengths in parentheses refer to inflection points. [d] *Cf.* Hantzsch, *Ber.*, **52**, 1544 (1919); **58**, 612 (1925). [e] *Cf.* ref. 14. [f] *Cf.* Mohler, *Helv. Chim. Acta*, **20**, 1188 (1937); Mohler and Sorge, *ibid.*, **23**, 1200 (1940). [g] *Cf.* Houston, Canning and Graham, *J. Chem. Soc.*, 965 (1935). [h] In dioxane. [i] *Cf.* Gibson, Graham and Reid, *ibid.*, **123**, 874 (1923). [j] *Cf.* Fox and Pope, *ibid.*, **103**, 1265 (1913). [k] *Cf.* Chaix, *Bull. soc. chim.*, [4] **53**, 700 (1933). [l] *Cf.* Purvis, Jones and Tasker, *J. Chem. Soc.*, **97**, 2287 (1910). [m] *Cf.* ref. 5. [n] A 0.1 *M* solution in a 1-cm. cell gave transmission readings above 90% at all wave lengths down to limits of observation (208 mμ).

were then washed repeatedly with water, 10% sodium hydroxide and saturated sodium bisulfite solution. The oils were dried over anhydrous magnesium sulfate, treated with Norit, filtered and used at once for the determination of spectra. Since analytical data for these and several other compounds used in the present investigation have not previously been reported, we have listed our values in Table II.

Phenyl isopropyl sulfide,[20] b. p. 97° at 20 mm., phenylmercaptomethyl methyl ether,[21] b. p. 113–114° at 18 mm., and ethyl *n*-butylmercaptoacetate, b. p. 110–111° at 18 mm., which have previously been prepared by other methods, were conveniently obtained by the action of isopropyl bromide, chloromethyl ether, and ethyl bromoacetate, respectively, on the appropriate sodium mercaptide in ethanol.[22]

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(20) Table I, source ref. 14.

(21) de Lattre, *Bull. soc. chim. Belgique*, **26**, 323 (1912); *Chem. Zentr.*, **83**, II, 1192 (1912).

(22) Uyeda and Reid, THIS JOURNAL, **42**, 2388 (1920).

TABLE II

Compound	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
bis-(Phenylmercapto)-methane	$C_{13}H_{12}S_2$	67.18	67.09	5.21	5.00
2,2-bis-(Phenylmercapto)-propane	$C_{15}H_{16}S_2$	69.18	69.12	6.19	6.06
α,α-bis-(Methylmercapto)-toluene	$C_9H_{12}S_2$	58.64	58.65	6.57	6.42
bis-(*n*-Butylmercapto)-methane	$C_9H_{20}S_2$	56.18	56.25	10.48	10.27
2,2-bis-(*n*-Butylmercapto)-propane	$C_{11}H_{24}S_2$	59.94	60.09	10.98	10.91
1,2-bis-(*n*-Butylmercapto)-ethane	$C_{10}H_{22}S_2$	58.19	58.03	10.74	10.52
n-Butylmercaptomethyl ethyl ether	$C_7H_{16}OS$	56.69	56.52	10.88	10.90

t-**Butyl Sulfide.**[23]—A mixture of 225 g. of concentrated sulfuric acid and 65 g. of water was cooled in an ice-bath, and 50.4 g. (0.60 mole) of *t*-butyl alcohol was added at such a rate that the temperature of the mixture did not exceed 10°. After addition of the alcohol was complete, stirring and cooling were continued while 27.0 g. (0.30 mole) of *t*-butyl mercaptan was added dropwise over a thirty-minute period. The ice-bath was then removed and the mixture was allowed to warm to room temperature. The product was separated by pouring the reaction mixture into 500 g. of ice, extracting with ether, drying the combined extracts over anhydrous magnesium sulfate, and fractionally distilling the ether solution. After removal of the ether, a fraction boiling at 60–65° and consisting mostly of unreacted mercaptan was obtained; recovery, 7.1 g. The crude *t*-butyl sulfide boiled at 144–149°; yield, 27.9 g. (87%, taking the recovered mercaptan into account). Redistillation afforded pure material boiling at 148–149°.

Phenethyl sulfide was prepared by a modification of the method of Bermejo and Herrera,[24] using sodium sulfide nonahydrate instead of potassium sulfide. The product was a colorless oil, b. p. 190–192° at 8 mm. (yield, 67%), which crystallized when cooled in a Dry Ice–acetone mixture but remelted again below room temperature[25]; the earlier investigators[24] reported a melting point of 92°.

Anal. Calcd. for $C_{16}H_{18}S$: C, 79.27; H, 7.48. Found: C, 79.11; H, 7.35.

Phenethyl Ethyl Sulfide.—A solution of 13.6 g. (0.22 mole) of ethyl mercaptan and 8.8 g. (0.22 mole) of sodium hydroxide in 100 ml. of ethanol was heated to boiling, and 31.0 g. (0.22 mole) of phenethyl chloride was added dropwise at such a rate as to maintain refluxing without the application of external heat. The mixture was then refluxed for another thirty minutes after which most of the solvent was removed by distillation, the residue was diluted with several times its volume of water, and the layers were separated. The upper layer was washed with water, dried over anhydrous magnesium sulfate, and distilled under diminished pressure to yield 29.5 g. (81%) of colorless oil, b. p. 96–98° at 4 mm. This material was redistilled and the middle fraction, b. p. 96° at 4 mm., was taken for the spectrum determination.

Anal. Calcd. for $C_{10}H_{14}S$: C, 72.22; H, 8.49. Found: C, 72.27; H, 8.54.

β-*n*-**Butylmercaptoethyl Ethyl Ether.**—A solution of 45 g. (0.50 mole) of *n*-butyl mercaptan and 20 g. (0.50 mole) of sodium hydroxide in 200 ml. of ethanol was treated with 76.5 g. (0.50 mole) of 2-bromoethyl ethyl ether and worked up exactly as in the procedure above. Distillation of the crude product at reduced pressure gave 57.8 g. (71%) of colorless oil, b. p. 103–108° at 31 mm. The spectral sample was taken from the middle fraction of a second distillation; b. p. 105–106° at 30 mm.

Anal. Calcd. for $C_8H_{18}OS$: C, 59.20; H, 11.18. Found: C, 59.32; H, 11.34.

Benzylmercaptomethyl Methyl Ether.—A solution of 52.0 g. (0.42 mole) of benzyl mercaptan and 16.8 g. (0.42 mole) of sodium hydroxide in 200 ml. of ethanol was treated with 33.5 g. (0.42 mole) of chloromethyl methyl ether and worked up as above. Fractional distillation of the crude product afforded 11.7 g. (17%) of colorless oil, b. p. 128–133° at 19 mm. On redistillation most of this sample boiled at 128° at 18 mm.

Anal. Calcd. for $C_9H_{12}OS$: C, 64.23; H, 7.19. Found: C, 64.33; H, 7.11.

α-**Ethylmercaptoisopropyl methyl ketone** was prepared by an adaptation of the method for ethylmercaptoacetone,[26] using *α*-bromoisopropyl methyl ketone instead of chloroacetone. The crude product was obtained as a colorless oil, b. p. 64–67° at 15 mm., yield 73%. On redistillation most of this material boiled at 65–66° at 15 mm.

Anal. Calcd. for $C_7H_{14}OS$: C, 57.50; H, 9.65. Found: C, 57.51; H, 9.59.

β-**Ethylmercaptoethyl methyl ketone** was obtained by the dropwise addition of 8.7 g. (0.14 mole) of ethyl mercaptan in which a bit of sodium had been dissolved to 12.8 g. (0.18 mole) of methyl vinyl ketone, and distillation of the crude product at reduced pressure; yield, 10.9 g. (61%) of colorless oil, b. p. 78–79° at 10 mm.

Anal. Calcd. for $C_6H_{12}OS$: C, 54.51; H, 9.15. Found: C, 54.58; H, 9.01.

β-**Ethylmercaptopropiophenone** was prepared in a similar manner from 17.5 g. (0.13 mole) of phenyl vinyl ketone and 9.3 g. (0.15 mole) of ethyl mercaptan. The crude product solidified on standing overnight and was recrystallized from aqueous ethanol (Norit) to yield 13.4 g. (53%) of colorless microcrystalline powder, m. p. 46–47°.

Anal. Calcd. for $C_{11}H_{14}OS$: C, 67.99; H, 7.26. Found: C, 68.13; H, 7.17.

α-**Phenylmercaptoisopropyl methyl ketone** was prepared by an adaptation of the method for phenylmercaptoacetone,[26] using *α*-bromoisopropyl methyl ketone instead of chloroacetone. The crude product was obtained as a colorless oil, b. p. 115–117° at 5 mm., yield 65%. On redistillation most of this material boiled at 102° at 3 mm.

Anal. Calcd. for $C_{11}H_{14}OS$: C, 67.99; H, 7.26. Found: C, 67.88; H, 7.13.

Methyl *β*-*n*-**butylmercaptopropionate** was obtained by the cautious addition of 27.9 g. (0.31 mole) of *n*-butyl mercaptan, in which a bit of sodium had been dissolved, to 25.8 g. (0.30 mole) of methyl acrylate, and distillation of the crude product at reduced pressure; yield, 42.8 g. (81%) of almost colorless oil, b. p. 118–119° at 19 mm. Redistillation of this material afforded the pure compound as a colorless oil, b. p. 118° at 19 mm.

Anal. Calcd. for $C_8H_{16}O_2S$: C, 54.50; H, 9.15. Found: C, 54.30; H, 9.10.

Summary

The ultraviolet absorption spectra are reported for forty-four organic compounds containing the sulfide function, including alkyl, aryl and aralkyl sulfides, mercaptals and mercaptoles, 1,2-bis-(alkylmercapto)-ethanes, alkoxysulfides, ketosulfides and carbalkoxysulfides. The prepara-

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[23] Jones and Reid, *ibid.*, **60**, 2452 (1938), obtained a 6% yield of this compound as a by-product in the addition of hydrogen sulfide to isobutylene at 180° in the presence of sulfur.

[24] Bermejo and Herrera, *Congr. intern. quim. pura y aplicada 9th Congr., Madrid*, **4**, 238 (1934); *C. A.*, **30**, 3418 (1936).

[25] Oxidation of this product with excess 30% hydrogen peroxide in acetic acid gave the sulfone as colorless leaflets, m. p. 99–100° after recrystallization from aqueous ethanol; reported[24] m. p. for phenethyl sulfone 101°.

[26] Table I, source ref. 21.

tion of a number of new sulfides and a greatly improved method for the preparation of *t*-butyl sulfide are described.

Considerable optical interaction is observed when the sulfide function is attached to a benzene ring or to a carbon atom bearing a carbonyl, carbalkoxyl, phenyl, vinyl or alkylmercapto group. The apparent conjugative effect of the sulfide function in these compounds is not destroyed by alkylation of the central carbon atom, but when two methylene groups intervene between the functional groups, the absorption spectra are essentially summations of the spectra of the component chromophores.

An attempt is made to account for the interaction of the sulfide function with a second similar function or with an unsaturated group attached to the same carbon atom by assuming the formation of three-membered rings stabilized by resonance among forms in which sulfur has an expanded valence shell.

PHILADELPHIA, PENNSYLVANIA RECEIVED MARCH 5, 1948

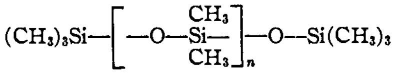
[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY]

Ultrasonic Investigation of Molecular Properties of Liquids. III.[1] Linear Polymethylsiloxanes[2]

BY ALFRED WEISSLER

Certain aspects of the relation between molecular structure and sound velocity in liquids may be studied by means of a polymer series. This has already been done (using four or five members of each series) in the cases of the polyethylene glycols,[3] polychlorotrifluoroethylene,[4] and polyisobutylenes.[5] The last is of special interest because it was in highly viscous polyisobutylenes that Mason found the first unquestionable example of sound velocity dispersion in liquids.

A polymer series in which the liquid state persists up to high molecular weights is the linear polydimethylsiloxanes,[6,7] of type formula



$$(CH_3)_3Si-\left[-O-\overset{CH_3}{\underset{CH_3}{Si}}-\right]_n-O-Si(CH_3)_3$$

where n may vary from zero up to several hundred. These materials offer an opportunity for more extensive investigations than the three series mentioned above, where members of moderate molecular weight are already solids. In the present work, the velocity of sound, density and refractive index (D light) at 30° were measured for fourteen linear polydimethylsiloxanes, and the results were used to calculate adiabatic compressibility, ratio of specific heats and molecular weight.

Experimental

The polymers used were those sold by Dow Corning under the name Silicone Fluids DC 500 and 200, viscosity grades from 0.65 to 1000 centistokes. Higher members are polymerization mixtures with the volatiles removed, but the first four fluids are chemical individuals—the dimer, trimer, tetramer and pentamer, respectively. A few measurements were also made on two partially phenylated polymethylsiloxane fluids, of the DC 700 and 702 series.

Sound velocity in these liquids was measured by means of the one-megacycle ultrasonic interferometer previously described.[1] Refractive indices were determined with an Abbe refractometer.

Results and Discussion

The values of sound velocity listed in Table I are lower than for most organic liquids, except that replacing methyl groups by phenyls raises the velocity, as in the 700 and 702 fluids. Figure 1 is a semilogarithmic plot of the data, which shows

TABLE I

PHYSICAL PROPERTIES OF LINEAR POLYMETHYLSILOXANES (DOW CORNING SILICONE FLUIDS)

Fluid	Velocity (meters/sec.) at 30.0°	Velocity (meters/sec.) at 50.7°	Temp. coeff. (meters/second/degree)	Refractive index (D)	Density, g./ml.
DC 500–0.65 cs	873.2	795.3	−3.8	1.3724	0.7535
1.0	901.3	828.5	−3.5	1.3810	.8114
1.5	919.0	849.8	−3.3	1.3856	.8434
2.0	931.3	863.0	−3.3	1.3883	.8652
3.0	942.2	875.2	−3.2	1.3916	.8874
5.0	953.8	892.1	−3.0	1.3943	.9083
10	966.5	909.4	−2.8	1.3972	.9295
20	975.2	918.0	−2.8	1.3992	.9423
50	981.6	925.3	−2.7	1.4007	.9540
200–100	985.2	929.6	−2.7	1.4015	.9579
200	985.7	931.5	−2.6	1.4017	.9611
350	986.2	932.0	−2.6	1.4018	.9628
500	986.4	932.1	−2.6	1.4019	.9632
1000	987.3	933.3	−2.6	1.4020	.9636
702–27	1236.4				
700–50	1054.0				

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[1] Weissler, Part II, THIS JOURNAL, **70**, 1634 (1948).

[2] The opinions contained herein are the private ones of the writer and are not to be construed as official or reflecting the views of the Navy Department or the navy service at large.

[3] Weissler, Fitzgerald and Resnick, *J. Appl. Phys.*, **18**, 434 (1947).

[4] Lagemann, Woolf, Evans and Underwood, THIS JOURNAL, **70**, 2994 (1948).

[5] Mason, Baker, McSkimin and Heiss, *Phys. Revs.*, **73**, 1074 (1948).

[6] Hunter, Warrick, Hyde and Currie, THIS JOURNAL, **68**, 2284 (1946).

[7] Patnode and Wilcock, *ibid.*, **68**, 358 (1946).