

3d-ORBITAL RESONANCE IN DIVALENT SULPHIDES—VI

ABSORPTION SPECTRA OF SOME MERCAPTALS IN THE NEAR ULTRAVIOLET REGION^{1,2}

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Abstract—The UV spectra of open chain mercaptals ($(R_1R_2C(SR_3)_2)$), cyclic mercaptals

$(R_1R_2C \begin{array}{c} \diagup S \diagdown \\ \diagdown S \diagup \end{array} (CH_2)_n, n = 2,3,4)$, orthothioformate and a bicyclic trisulphide have been investigated.

The results indicate that the spectra of these compounds can be classified into four groups which have λ_{max} near: 235 $m\mu$, acyclic compounds; 230 ~ 250 $m\mu$, 7-membered compounds; 246 $m\mu$, 5-membered compounds; 250 $m\mu$, 6-membered compounds, and there is a remarkable similarity of λ_{max} within each of these four groups. These observations are interpreted in terms of the non-bonding interaction between two sulphur atoms involving their 3d orbitals, where a singlet radical structure is suggested for the photoexcited state.

AVAILABLE chemical and physical evidence relating to sulfoxides, sulphones and sulphonium compounds has suggested a ready acceptance of electron(s) into the 3d orbitals of the positively charged sulphur atom in each of these compounds.⁴⁻⁸ This view, however, has not been accepted in the cases of uncharged divalent sulphides. Recently, strong evidence for the possible 3d orbital resonance has been found in the base-catalysed deuterium-hydrogen exchange reactions of substituted mercaptals.⁹ Since the earlier study suggested an apparent correlation between the rate of the base-catalysed hydrogen exchange reactions and the red-shift of absorption maxima of UV spectra,¹⁰ and since spectral data available for both acyclic and cyclic mercaptals is limited,^{4,11} the present investigation has been undertaken in order to study

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² A part of this work has been done at the Radiation Center of Osaka Prefecture.

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⁴ C. C. Price and S. Oae, *Sulfur Bonding* Ronald Press, New York (1962).

⁵ G. Cilento, *Chem. Revs.* **60**, 147-167 (1960).

⁶ W. A. Pryor, *Mechanism of Sulfur Reactions* McGraw-Hill, New York (1962).

⁷ R. C. Passerini, *Organic Sulfur Compounds* (Edited by N. Kharasch) Vol. 1; Chapt. 7. Pergamon Press (1961).

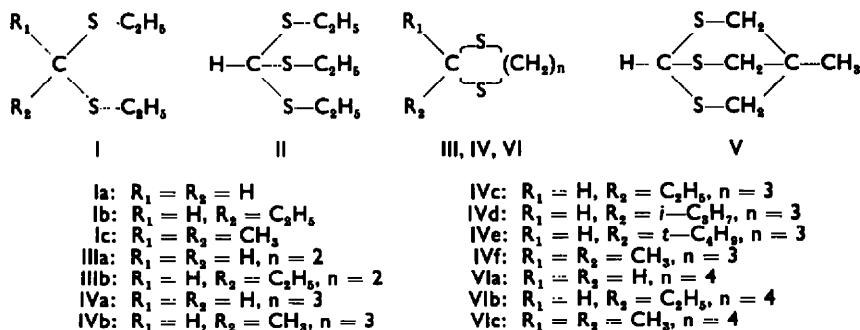
⁸ H. H. Jaffé and M. Orchin, *Theory and Application of Ultraviolet Spectra* John Wiley, New York (1962).

⁹ S. Oae, W. Tagaki and A. Ohno, *Tetrahedron* Preceding papers.

¹⁰ S. Oae, W. Tagaki and A. Ohno, *J. Amer. Chem. Soc.* **83**, 5036 (1961).

¹¹ S. Oae, *3d Orbital Resonance involving the Sulfur Atom in Organic Sulfides in Organic Sulfur Compounds*, (Edited by N. Kharasch) Vol. 4, in press.

the spectra of a number of mercaptals (I–VI) of varying ring size and to examine the effects of ring formation and of ring size on the spectra.



The absorption maxima are shown in Table 1. The spectra conveniently divide into four groups, i.e., the first group includes the acyclic compounds, I and II, having λ_{max} near 235 $m\mu$; the second the five-membered ring compounds, III, showing the λ_{max} near 246 $m\mu$; the third the six-membered ring compounds, IV and V,

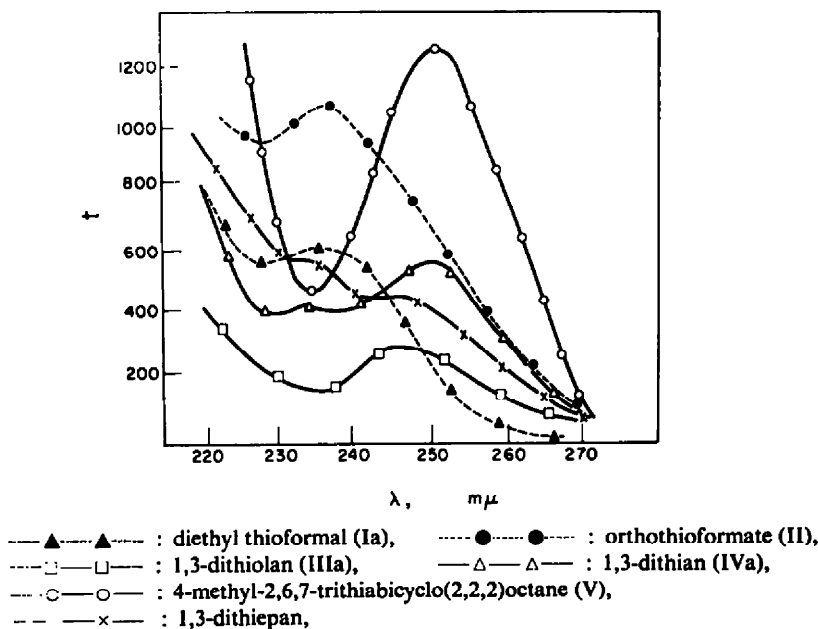
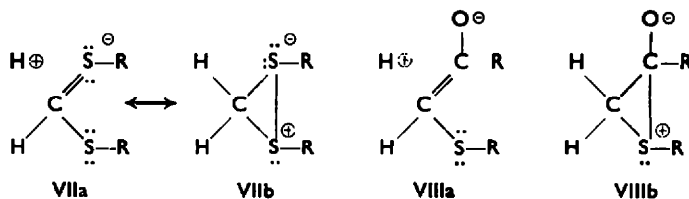


FIG. 1. Absorption spectra in the near ultraviolet region (in ethanol).

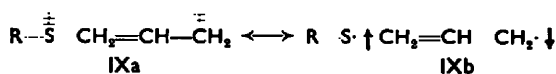
showing λ_{max} near 250 $m\mu$; and the fourth the seven membered ring compounds, VI, showing an intermediate spectra of the first and of the third. The change of solvent from ethanol to cyclohexane increases both λ_{max} and ϵ but this increase is small. The spectra of the six-membered ring compounds are particularly interesting. They all show small shoulders near 230 $m\mu$, except for α, α -dimethyl compound, IVf, and the cage compound, V. The representative spectra of the above four groups are shown in Fig. 1.

Some years ago, Fehnel and Carmack¹² suggested that the contribution of three membered ring structures, VIIb and VIIIb and also the non-bonding hyper-conjugation of the types, VIIa and VIIIa, are partly responsible for the big chromophoric change in mercaptals and β -mercaptoketones as compared with the saturated alkyl mono-sulphides which have λ_{\max} near 210 m μ .



But, since there is only a very small difference between the spectra of α, α -dimethyl compounds, Ic, IVf and VIc, and those of the other unsubstituted compounds, Ia, IVa and VIa, the contribution of hyperconjugation, if any, should be of very minor importance.¹³

The non-bond structures of the types, IXa and IXb, were also proposed by Koch¹⁴ as probable contributing factors in the photoexcitations of allyl and benzyl sulphides. These structures alone cannot explain the sharp differences between oxygen and



sulphur compounds, the absorption maxima of which shift substantially towards longer wavelengths, particularly as the structures exist for allyl and benzyl ethers or α -keto ethers.

Meanwhile the three membered ring structure is quite conceivable as a contributing factor in the photoexcitation of these sulphur compounds, because the sulphur atom can expand its valence shell beyond the octet.

Moreover, the smaller bond angles of sulphides as compared with ethers,¹⁵ the longer bond length of the C—S linkages,¹⁶ the much greater van der Waals radius of sulphur as compared with the oxygen atom, the big neighbouring group effect of sulphur atom in solvolysis reactions¹⁷ and the larger polarizability of the sulphur atom, all point strongly in favour of a three membered ring structure as contributing to the photoexcited state.

Since the order of mesomeric stabilization involving electron release ($O > S > Se$) is the opposite to that involved in stabilizing the photoexcited state ($Se > S > O$), it seems reasonable to suppose that a different type of mesomeric stabilization may be involved. It is possible that the photoexcited state is more radical than ionic. The polarized structures which have been conventionally suggested appear to be replaced by free radical ones in which one electron of a non-bonded or π -electron pair is

¹² E. A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.* **71**, 84 (1949).

¹³ Similar observations have been made for the acyclic mercaptals, D. Welti and D. Whittaker, *J. Chem. Soc.* 4372 (1962).

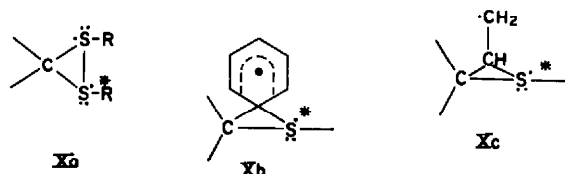
¹⁴ H. P. Koch, *J. Chem. Soc.* 387 (1949).

¹⁵ *Interatomic Distances* (Edited by L. E. Sutton) Special Publication No. 11, The Chemical Society, London (1958).

¹⁶ L. Pauling, *The Nature of Chemical Bond*, (3rd Edition) Cornell Univ. Press, 235 (1960).

¹⁷ S. Winstein, E. Grunwald, *J. Amer. Chem. Soc.* **70**, 828 (1948).

excited to a higher energy level, essentially unparing them, but not changing the spin and not having undergone the transition to a triplet state. The singlet radical structure of the types of Xa, Xb and Xc, all involving the possible expansion of the sulphur valence shell beyond eight electrons, thus seem to offer the most reasonable explanation for the remarkable difference between the spectra of these compounds and those of their oxygen analogs.¹⁸



In Table 1 small λ_{\max} shifts are recorded for various compounds. Since this variation is small within the range of 231–252 $m\mu$ ($\Delta\gamma = 21 m\mu$), the principal chromophore represented by the structure Xa seems to be essentially the same for all the mercaptals and even for the orthothioformate, and the variation is presumably

TABLE I. ABSORPTION MAXIMA AND MOLAR EXTINCTION COEFFICIENTS IN THE NEAR ULTRAVIOLET REGION

Compound	b.p. (m.p.)	in Ethanol		in Cyclohexane	
		λ_{\max} , $m\mu$.	ϵ	λ_{\max} , $m\mu$.	ϵ
Ia	182–183	237	553	—	—
Ib	106/36 mm	231	834	—	—
Ic	85/21 mm	239	707	—	—
II	136/16 mm	235	954	237	1022
IIIa	76/23 mm	246	285	248	267
IIIb	68/10 mm	246	314	—	—
IVa	95/17 mm (53)	250 (232) ^a	469 (364) ^a	251	494
IVb	108/42 mm	252 (232) ^a	449 (383) ^a	—	—
IVc	112/21 mm	250 (231) ^a	619 (510) ^a	—	—
IVd	133.5/35 mm	249 (229) ^a	690 (660) ^a	250	692
IVe	129/22 mm	249 (229) ^a	767 (730) ^a	—	—
IVf	102/24 mm	252	657	—	—
V	(131)	251	1242	252	1363
VIa ^b	—	230–250 ^a	—	230–250 ^a	—
VIb	94/7 mm	230 ^a	554 ^a	—	—
		245 ^a	428 ^a	—	—
VIc ^b	—	235 ^a	—	—	—
		250 ^a	431 ^a	—	—

^a These correspond to shoulders and are approximate values. For the values in parentheses, see the spectra of IVa in Fig. 1. ^b These are oils and were obtained in small quantities, see Experimental.

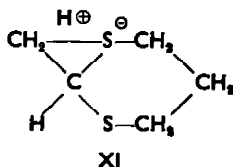
caused mainly by such factors as the inductive effects of alkyl groups, the ring size and the conformations. It is interesting to note that the λ_{\max} are apparently classified into four groups and within each of them there is a remarkable similarity of λ_{\max} , although somewhat varied in the open chain compounds. This seems to indicate that

¹⁸ A similar idea has been suggested by Jaffe and Orchin that the promotion of an electron from one of the lone pairs of the S atom is possible to MO's formed from 3d orbitals of the two S atoms. See ref. 8.

the λ_{\max} is determined by the extent of the non-bonding interaction between two sulphur atoms and the interaction is dependent on the structure of the cyclic mercaptal. In an open chain compound, two mercapto groups are not held in a fixed geometry and the most stable form will assume a conformation in which the two mercapto groups twist the two C—S—C planes out of symmetry which is presumably important for an efficient hybridization of 3p and 3d orbitals for non-bonding interaction. On the other hand, the cyclic five- and six-membered compounds are confined in relatively more rigid ring systems, and their conformations would be unchanged by the change of the alkyl substituents. This seems to be the reason for the relatively large variations of λ_{\max} in the open chain compounds as compared with other ring systems, and also for the longer wavelength of the λ_{\max} of the least hindered compound, Ia, than that of the ethyl substituted compound, Id. Moreover, the five- and six-membered compounds would have planes of symmetry with respect to the two C—S—C planes, and the symmetry character seems to be quite important for the non-bonding interaction in the photoexcitation and the situation seems to be more favoured for six-membered than for five- and seven-membered compounds.

The dependency of the UV spectra on the ring size was also observed for the cyclic monosulphides.¹⁹ In this case, however, the absorption maxima concerned are of very low intensities (near 260 m μ , $\epsilon \sim 50$), and the order of the position of the λ_{\max} is $4 > 3 > 5 > 6$, is opposite to that of the present work, e.g. $6 > 5 > 7 >$ for acyclic compounds and for the cyclic mercaptals. For the cyclic monosulphides, the explanations made were based on the electron density of the sulphur atom and the interactions between the orbitals of sulphur and the other atoms. For the cyclic mercaptals, however, these interactions appear to be outweighed by the interaction between the non-bonded sulphur atoms.

One also finds some anomaly in the effects of alkyl substituents. Namely, the substitution of a methyl group in all the mercaptals tested, i.e., open chain, Ic, six-, VIId and IVf, and seven-membered compounds, VIc, shifts the UV maxima distinctly toward longer wavelengths and the bathochromic effect does not follow the well-known sequence of the inductive effects of alkyl substituents, although the molar extinction coefficients seem to follow the usual order of the inductive effect. Although no satisfactory explanation is available at present, it would be possible that the larger bathochromic effect of the methyl substituted compounds is caused partly through the non-bonding hyperconjugation between the methyl group and the sulphur atom involving either of its 3p or vacant 3d orbitals as represented by a structure, XI, as was suggested for the abnormal slow rate of the base-catalysed tritium-hydrogen exchange reaction of the same compound.⁹ A similar interpretation is also supported by the NMR spectra of the six-membered cyclic mercaptals.⁹



The base-catalysed D—H or T—H exchange reactions of these compounds has

¹⁹ R. E. Davis, *J. Org. Chem.* **23**, 216, 1380 (1958).

been extended⁹ as a continuation of the previous work.¹⁰ However, the direct correlation between the rate of exchange reaction and the spectra has not been observed.⁹ This may in part be due to the fact that the photoexcited state is different from the intermediate of the exchange reaction, since the latter and not the former involves the α -C-H bond rupture.

EXPERIMENTAL

Recording of the spectra. Absorption spectra were recorded with a Hitachi Photo-Electric Spectrophotometer Model EPU-2A, a manual type, in anhydrous ethanol and cyclohexane which were carefully purified. Concentrations were adjusted so as to make the optical densities at λ_{max} fall in a range of 0.5–1.0, usually 10^{-1} g/l. Recording was made with an interval of 2–4 μ and 1 μ near λ_{max} .

Materials. All of the compounds listed in Table 1 were prepared by previous methods.⁹ The exchange reactions of orthoformate and aldehyde diethylacetals with mercaptans were employed using either zinc chloride or *p*-toluenesulfonic acid as the catalyst for the compounds, Ib, II, IIIa, IIIb, IVa, IVb, IVc, IVd, V, VIa and VIb. The compounds, Ia, Ic, IVe, IVf and VIc, were obtained by the reaction of aldehydes and ketones directly with mercaptans by saturating the reaction mixture with hydrogen chloride gas. The reaction products were purified by distillation or recrystallization and finally by vapour-phase chromatography in the case of oils. Nitrogen was used as the carrier gas. Hydrogen gas should be avoided because of the considerable hydrogenolysis. The compounds, VIa, VIb and VIc, were obtained in low yields with a large amount of high boiling solids, hence special care was taken in the purification of these compounds. The purities were checked by elementary and IR analyses.⁹ The b.ps and m.ps are shown in Table 1.