

91. *Absorption Spectra and Structure of Organic Sulphur Compounds.*
Part II. Disulphides and Polysulphides.

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Existing physical data point to a stabilised static non-planar configuration of the two valencies attached to the sulphur-sulphur bond and offer a possible explanation for the anomalous failure of *di-tert.*-butyl disulphide to display characteristic absorption near 2500 Å. The spectra of diallyl and dibenzyl disulphides suggest hyperconjugation between C=C and C-S bonds (cf. Part I). Ultraviolet-absorption curves obtained for dialkyl and diphenyl disulphides, sulphur, thionyl chloride, sulphur mono- and di-chlorides, dialkyl and diphenyl tetrasulphides, two representative thiokols, and a dialkyl hexasulphide provide strong evidence in favour of the straight-chain formulation of polysulphide structure. The resonance properties and reactivities of S-S bonds in their dependence on intramolecular environment are discussed. Some reserve is expressed with regard to Fuller's cyclic structure of tetrasulphide thiokols incorporating co-ordinately linked sulphur.

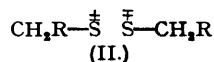
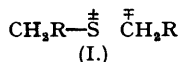
By further application of the general method of approach outlined in Part I (preceding paper), it is proposed now to consider the molecular structure and some of the resonance properties of organic disulphides and polysulphides. A representative number of ultraviolet-absorption spectra have been obtained, and these will be discussed together with such related structural information as is obtainable from other physical and chemical data in the field.

Saturated Dialkyl Disulphides.—The straight-chain bond-structure of hydrogen disulphide,

dimethyl disulphide, and dichlorine disulphide (sulphur monochloride) has been established by Raman spectra and electron-diffraction investigations (Palmer, *J. Amer. Chem. Soc.*, 1938, **60**, 2360; Stevenson and Beach, *ibid.*, p. 2872; Feher and Baudler, *Z. Elektrochem.*, 1941, **47**, 844), and no evidence has hitherto come to light in support of the possible existence of structural isomers of the branched-chain type containing a co-ordinated sulphur atom in the side chain. The chemical properties of organic disulphides are also in full accord with the "linear" formulation analogous to the structure of organic peroxides. Direct information regarding the possibility or otherwise of free rotation about the S-S bonds in simple dialkyl disulphide molecules is lacking. Penney and Sutherland (*Trans. Faraday Soc.*, 1934, **30**, 898) have, however, shown theoretically that interaction of the unsymmetrical electron clouds of two oxygen or nitrogen atoms should stabilise a non-planar skew arrangement of groups about the O-O or N-N linkages in hydrogen peroxide and hydrazine, and similar considerations presumably apply to the disulphide bond. In confirmation of these ideas, Zumwalt and Giguère (*J. Chem. Physics*, 1941, **9**, 458) obtained evidence for the static non-planar character of the hydrogen peroxide molecule from infra-red analysis, and exact correspondence has been noted between the Raman frequencies of this molecule and its sulphur analogue, hydrogen disulphide (Feher and Baudler, *loc. cit.*). Analogous non-planar configurations of the two structures may therefore be regarded as highly probable. The observed azimuthal angle between the two hydroxyl groups in hydrogen peroxide is about 105° (cf. model shown in *Ann. Reports*, 1942, **39**, 104), and virtually identical azimuthal angles around the S-S linkages have recently been found in the accurately determined structures of *pp'*-dibromodiphenyl disulphide, dimethyl trisulphide, and elementary sulphur (see below). Thus, all the available evidence suggests that a non-planar and almost right-angled skew distribution of valencies about the sulphur-sulphur bond is energetically preferred.

The ultraviolet absorption of saturated organic disulphides is characterised by a relatively weak and rather broad maximum near 2500 Å., together with intense absorption near the edge of the quartz-ultraviolet region. These general features are illustrated by the spectra of diisooamyl and dicyclohexyl disulphides recorded in Fig. 1, as well as by the previously reported diethyl disulphide spectrum (Ley and Arends, *Z. physikal. Chem.*, 1932, *B*, **15**, 311), the cysteine absorption curve due to Anslow and Lyman (*J. Opt. Soc. Amer.*, 1941, **31**, 114), and the absorption of disulphide thiokol (see below). It seems rather remarkable, then, that no selective absorption near 2500 Å. should be displayed by di-*tert.*-butyl disulphide (curve 3, Fig. 1). In view of the entirely normal spectral properties of the dicyclohexyl derivative containing sulphur linked to a secondary carbon atom, the anomalous behaviour of the *tert.*-butyl compound appears to be associated with steric rather than inductive electronic effects. If, in fact, the 2500 Å. absorption region is in some way related to the electron-cloud interaction responsible for the energetically preferred skew configuration of disulphides, then the suppression of this absorption in di-*tert.*-butyl disulphide would be expected as a result of steric hindrance. Scale models indicate that spatial interference between the two *tert.*-butyl groups would strongly militate against the conformation of the disulphide valencies at an azimuthal angle near 100°.

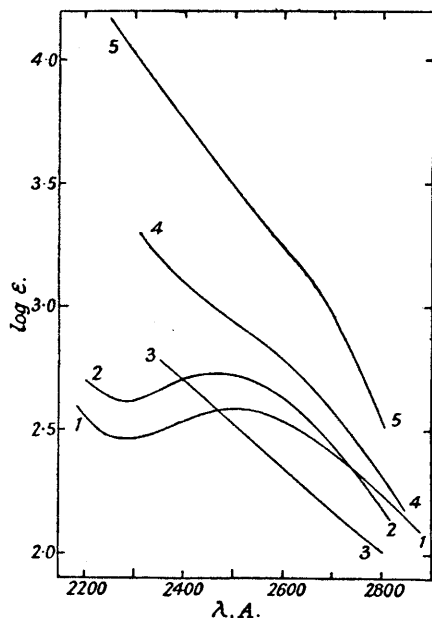
It was suggested in the preceding paper that polar excited structures of the type (I) are important in the intense absorption of saturated dialkyl monosulphides near 2000 Å. If this hypothesis is correct, similar polarisation of both C-S and presumably even more markedly of S-S bonds (II) should arise in the analogous high-intensity short-wave absorption of dialkyl disulphides. Independent evidence of the relative weakness or polarisability of the covalent disulphide linkage is probably provided by its propensity for symmetrical radical dissociation (Waters, *Trans. Faraday Soc.*, 1946, **42**, 189), and by the well-known facile hydrative fission observed in the presence of alkali. It will also appear below that the concept of partial ionic bond character affords a satisfactory explanation of the interesting conjugation phenomena arising in aromatic disulphides and in polysulphides.



βγ-Unsaturated Disulphides.—The absorption curve of diallyl disulphide (III; curve 4, Fig. 1) exhibits an inflection near 2450 Å. which probably corresponds to the characteristic 2500 Å. region of saturated disulphides, but this has now become merged into the increased absorption displayed by all allylic sulphide groupings (cf. this vol., p. 388). According to resonance theory, the polar excited level (I) should be stabilised in the *βγ*-unsaturated compounds because of allylic resonance of the formal charge on the carbon atom, and this circumstance

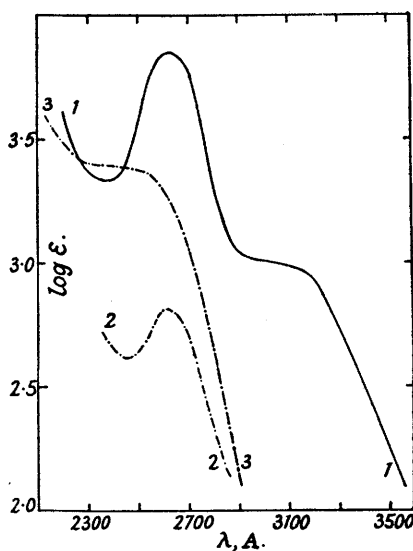
would result in the observed red shift and enhancement of the absorption. Thus, both (IV) and (V) probably contribute to the excited states associated with the observed ultraviolet-absorption properties of diallyl disulphide (III). With regard to the postulated hyperconjugated form (IV), which implies fractional bond order for the C-S linkage, it may well be significant that the bond in question is chemically weaker in allylic than in saturated disulphides (Bloomfield, private communication).

FIG. 1.
Dialkyl disulphides, $R \cdot S_2 \cdot R$ (in EtOH).



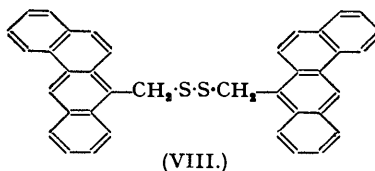
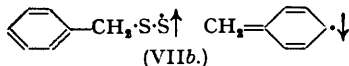
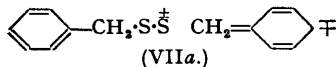
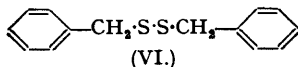
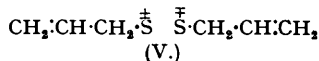
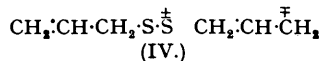
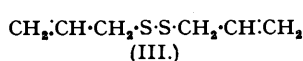
1. R = isoAmyl.
2. R = cycloHexyl.
3. R = tert.-Butyl.
4. R = Allyl.
5. R = Benzyl.

FIG. 2.
Sulphur chlorides (in n-hexane).



1. Sulphur monochloride, S_2Cl_2 .
3. Thionyl chloride, $SOCl_2$.
2. Sulphur dichloride, SCl_2 .

Analogous hyperconjugation in the corresponding $\beta\gamma$ -unsaturated dibenzyl disulphide molecule (VI) may be deduced from the strong and general ultraviolet extinction recorded as curve 5 of Fig. 1. This absorption is even greater than that of the related monosulphide (see



Part I) which it otherwise resembles in the complete masking of fine-structure aromatic bands. Again, Trotter and Thompson (*J.*, 1946, 481) found that the characteristic stretching-frequency of the C-S bond was lowered from 631 cm^{-1} in dipropyl to 570 cm^{-1} in dibenzyl disulphide, a reduction which would appear to be attributable at least in part to a diminution of the force constant involved. Thus, the C-S bond is apparently weakened even in the ground state of the

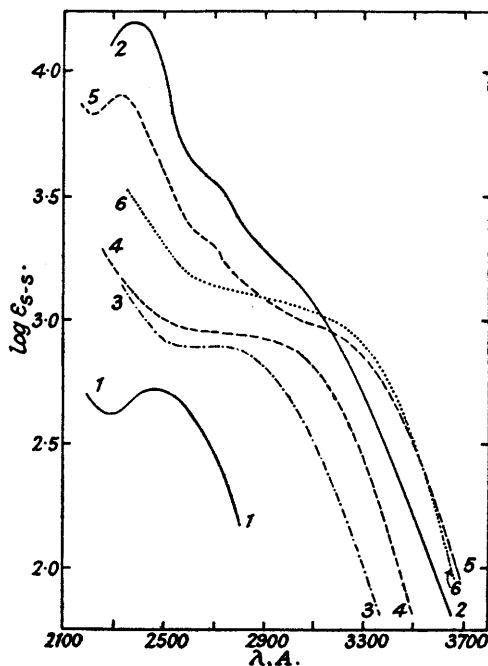
molecule, and hyperconjugation, formally expressed by excited structures like (VIIa or b), may be recognised.

In contrast with dibenzyl disulphide itself, the very intense ultraviolet spectrum of its polynuclear derivative bis-(1:2-benz-10-anthrylmethyl) disulphide (VIII) has been reported to resemble that of the parent hydrocarbon 1:2-benzanthracene (Jones, *J. Amer. Chem. Soc.*, 1941, **63**, 151). The apparent absence of C-S bond hyperconjugation effects in this spectrum is presumably due to the relatively much greater stability of electronic levels derived from resonance within the highly conjugated aromatic nucleus.

Sulphur Monochloride.—Reference to the absorption spectrum and structure of this disulphide is pertinent to the succeeding discussion. Lorenz and Samuel (*Z. physikal. Chem.*, 1931, *B*, **14**, 219) inferred from the similarity of their published spectra of thionyl chloride (SOCl_2) and sulphur monochloride (S_2Cl_2) that the latter compound must resemble the former with respect to its branched type of structure. In the present work, however, the absorption of thionyl chloride was found to be markedly different from that reported by Lorenz and Samuel, and from the sulphur monochloride spectrum. The three new absorption curves recorded in Fig. 2 are clearly differentiated from one another, and furthermore in good accord with the vapour-absorption data subsequently published by Asundi and Samuel (*Proc. Physical Soc.*, 1936, **48**, 28). Although the possible existence of the branched type of sulphur monochloride structure as a transient and reactive unstable isomeric species cannot be altogether excluded (cf. Spong, *J.*, 1934, 485), electron-diffraction data (Ackermann and Mayer, *J. Chem. Physics*, 1936, **4**, 377; Palmer, *loc. cit.*), Raman spectra (Morino and Mizushima, *Sci. Papers Inst. Phys. Chem. Res.*, 1937, **32**, 220) and dipole-moment measurements (Scheibe and Stoll, *Ber.*, 1938, **71**, 1571) all point to the straight-chain disulphide formulation and moreover seem to support the static non-planar right-angled structure. Again, the observed ultraviolet absorption step-out in the region of 3000 Å. ($\log \epsilon = 3.0$; curve 1, Fig. 2) will be recognised below as a characteristic feature of the electronically activated straight-chain disulphide linkage. As regards the more intense absorption maximum occurring at 2630 Å., this must in some way be related to the resonance properties of the S-Cl bonds in the molecule.

Diphenyl Disulphide.—*X-Ray* crystallographic analysis of the *pp'*-dibromo-derivative of diphenyl disulphide (Toussaint, *Bull. Soc. chim. Belg.*, 1945, **54**, 319) revealed a non-planar arrangement of substituents (azimuthal angle, 103°) about an unusually long S-S bond (2.15 Å.) in the molecule; the C-S bond distances were apparently normal but probably not determined with a significant degree of accuracy in the crystal structure. The most characteristic chemical property of diphenyl disulphide is the reversible symmetrical dissociation into coloured free radicals, which takes place on heating in solvents (Schönberg, Rupp, and Gumlich, *Ber.*, 1933, **66**, 1932). The thermochromatic behaviour of solutions of both diphenyl disulphide and its *pp'*-dibromo-derivative was confirmed in the present work, the ready occurrence of free-radical dissociation being apparent even from the yellow colour of the pure melt in equilibrium with colourless solid diphenyl disulphide at 61° . The ultraviolet absorption spectrum of undissociated diphenyl disulphide (curve 2, Fig. 3; cf. also Chaix, *Bull. Soc. chim.*, 1933, **53**, 700) is characterised by a very intense maximum ($\log \epsilon = 4.2$) at 2380 Å., preceded by two

FIG. 3.
Disulphides and polysulphides.



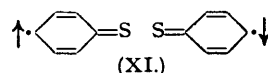
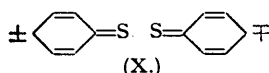
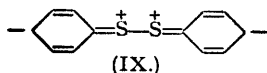
$$\epsilon_{\text{S-S}} = \frac{\text{Molar extinction coefficient}}{\text{Number of S-S bonds in molecule}}$$

1. Dicyclohexyl disulphide (in EtOH).
2. Diphenyl disulphide (in EtOH).
3. Sulphur (in CHCl_3).
4. Diethyl tetrasulphide (in EtOH).
5. Diphenyl tetrasulphide (in EtOH).
6. Dicyclohexyl hexasulphide (in CHCl_3).

distinct inflections near 2700 and 3000 Å. *pp'*-Dichloro- and *pp'*-dibromo-diphenyl disulphides give the same type of absorption curve, although displaced towards greater wave-lengths and intensities (maxima at 2420 Å., $\log \epsilon = 4.3$, and at 2480 Å., $\log \epsilon = 4.4$, respectively).

By analogy with the polar excited structures postulated for the related phenyl alkyl monosulphides (this vol., p. 392), *o*- and *p*-quinonoid resonance forms such as (IX) might be invoked to account for the intense absorption maximum of diphenyl disulphide, but this view is open to serious objections. Canonical structures containing like formal charges on adjacent atoms are regarded as intrinsically improbable (cf. Pauling, "The Nature of the Chemical Bond", p. 184), and the structure (IX) moreover requires the benzene planes to be coplanar with the S-S bond, whereas in fact they are inclined at 36° to the latter in the crystal structure examined by Toussaint (*loc. cit.*).

If, on the other hand, the previously recognised polarisation (II) is involved in the light absorption, it follows at once that in diphenyl disulphide the opposite formal charges on the two sulphur atoms can migrate to the benzene rings with which they are conjugated, and stabilised structures like (X) become plausible in the upper state. This kind of excited structure may be expected to lead to neutral radical dissociation of the central bond (cf. Mulliken, *J. Chem. Physics*, 1939, 7, 20), and similar structures such as (XI) participating in the ground state probably play a part in causing the extra length of the disulphide bond quoted above, and its facile thermal dissociation. It seems likely, then, that the 2380 Å. absorption is associated with a continuous system of quasi-conjugation of the benzene rings through the disulphide linkage. The 2700 Å. shoulder, resembling the corresponding region of phenyl monosulphides, is doubtless due to the partial benzenoid chromophore (see Part I), and the step-out near 3000 Å. may be compared with the corresponding shoulder in the spectrum of sulphur monochloride, attributable to the activated disulphide bond (see below).



Sulphur.—Before proceeding to a discussion of polysulphides, it is of interest to consider the structure and light absorption properties of the stable sulphur molecule which exists as a symmetrical puckered eight-membered ring, S_8 , both in the orthorhombic or the monoclinic crystalline form (Warren and Burwell, *J. Chem. Physics*, 1935, 3, 6) and in the vapour at ordinary temperatures (Lu and Donohue, *J. Amer. Chem. Soc.*, 1944, 67, 818). The preference shown for the octagonal size of the ring is presumably related to the fact that this is characterised by the favoured azimuthal angle of 103° occurring around each of the constituent bonds. The ultraviolet spectrum of crystalline sulphur in solution is plotted in Fig. 3. In this graph, all molecular extinction coefficients have been divided by the number of sulphur-sulphur linkages per molecule in order to permit a significant comparison between the absorption characteristics of the S-S bond in disulphides, polysulphides, and sulphur itself. Curve 3 shows that quite strong absorption takes place in elementary sulphur, intermediate between that of a saturated dialkyl disulphide (curve 1) and the conjugated diphenyl disulphide (curve 2). Some kind of mesomerism evidently occurs in the sulphur molecule. A formal extension of the resonance concepts applied in the formulations (II) and (X) or (XI) would lead to the hypothesis of two equivalent excited "Kekulé" forms of alternating no-bonds and double bonds (XII) participating in the structure, in addition to the conventional single-bond and various intermediate polar or formal-bonded excited canonical forms. The existence of appreciable resonance energy in the sulphur molecule has previously been inferred from thermal data by Powell and Eyring (*ibid.*, 1943, 65, 648), but they suggested that each bond acquired some degree of double-bond character through donation of lone-pair non-bonding electrons to unfilled $3d$ orbitals. The observed normal single-bond distances of 2.1 Å. (Warren and Burwell; Lu and Donohue; *loc. cit.*) and the non-planar configuration of the molecule would appear to favour no-bond-double-bond resonance rather than Powell and Eyring's multiple-bond formulation.

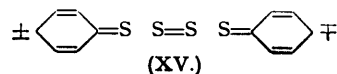
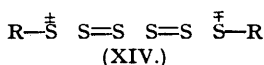
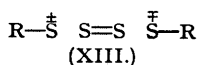
In plastic or elastic sulphur, the eight-membered rings are found to have broken down to give rise to long chains of sulphur atoms (Powell and Eyring, *loc. cit.*; Meyer and Go, *Helv. Chim. Acta*, 1934, 17, 1081).

Polysulphides.—When allowance is made for additional bands due to the presence of phenyl groups, it emerges from Figs. 2 and 3 that the sulphur-sulphur bonds of sulphur monochloride, diphenyl disulphide, sulphur, diethyl tetrasulphide, diphenyl tetrasulphide, and dicyclohexyl

hexasulphide all display characteristic absorption of the same spectral type, resembling the dialkyl disulphide spectrum displaced towards greater wave-lengths and intensities. In view of the known "linear" structure of dialkyl disulphides, sulphur monochloride, diphenyl disulphide, and sulphur, the close correspondence of all these curves may be taken as very strong evidence that the tetrasulphide and hexasulphide molecules are likewise composed of straight chains of sulphur atoms. No additional spectral features which might be ascribed to the presence of co-ordinated sulphur are discernible.

Some authors still seem to favour polysulphide formulations containing side-chain sulphur co-ordinately attached to a main di- or tri-sulphide chain, but with the possible exception of the X-ray data on thiokol (see below), all the more reliable evidence appears to be in support of the conclusion reached from ultraviolet spectra. The Raman frequencies of tri- and tetrasulphides are reported to resemble those observed in elementary sulphur, none of which occur in the region to be expected for a co-ordinate sulphur-sulphur double bond (Hibben, "The Raman Effect and its Chemical Applications", Reinhold, 1939, p. 259). Recent electron-diffraction results have established the linear character of the dimethyl trisulphide molecule (Donohue and Schomaker, *J. Chem. Physics*, 1948, 16, 92). Similarly, unpublished X-ray data obtained by Mr. S. C. Nyburg (cf. also Dawson, Mathieson, and Robertson, *J.*, 1948, 322) indicate that the straight-chain but apparently not the hypothetical side-chain form of the *pp'*-dichloro-derivative of diphenyl tetrasulphide can be fitted into the observed unit-cell dimensions of the crystalline structure. By way of chemical evidence, spectrographically identical samples of diethyl tetrasulphide could be independently synthesised either from sodium tetrasulphide and ethyl bromide, or from sulphur monochloride and ethylthiol, a result which it is difficult to interpret on any but the straight-chain hypothesis of tetrasulphide structure (cf. Bloomfield, *J.*, 1947, 1547).

The observed shifts between the various sulphur-sulphur bond spectra recorded in Fig. 3 can be qualitatively accounted for by simple extension of the concept of S-S bond polarisation (II). The enhanced absorption of the saturated dialkyl tetrasulphide (curve 4) over the disulphide (curve 1) may be correlated with the fact that, in addition to the polar forms (II), further plausible conjugated polar structures (XIII) with a central double bond and two adjacent no-bonds would be expected to stabilise the excited level of the tetrasulphide. There may well be some connection between this type of excited structure and the observed chemical properties of diethyl tetrasulphide, in which two sulphur atoms can be removed rather easily to furnish the disulphide under a variety of conditions. Again, the still greater light absorption of a dialkyl hexasulphide (curve 6) follows from the possibility of yet further more highly conjugated polar structures (XIV) participating in the excited state. It should, perhaps, be pointed out that the great similarity of the eight-atom sulphur molecule absorption to that of the dialkyl tetrasulphide does not conflict with the proposed explanation of the observed chain-length effects, since special factors are known to come into play in cyclic resonators.

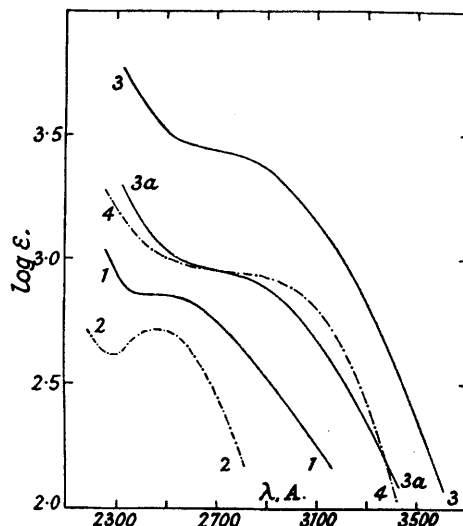


Replacement of alkyl by phenyl substituents in disulphides results in a very marked red shift and intensification of the first absorption region characteristic of the disulphide linkage (curves 1 and 2, Fig. 3). The origin of this strong activation may be sought in conjugation arising from contributions of the structures (X), which have already been postulated above in order to account for the high-intensity region of the diphenyl disulphide spectrum. A further long-wave displacement of the S-S bond absorption occurs in diphenyl tetrasulphide (curve 5), which resembles the disulphide at shorter wave-lengths, except that greater extinction values are shown in this region by the tetrasulphide when it is compared on the absolute molecular scale. Additional conjugation and contributions from the polar form (XV) in the excited state are plausible in correspondence with the related formulations above. Some significance may be attached to the fact that at 100°, when the saturated dicyclohexyl tetrasulphide is quite stable, diphenyl tetrasulphide displays a tendency to decompose, giving rise to disulphide together with free sulphur or higher polysulphides (Bloomfield, *loc. cit.*).

Thiokols.—A typical disulphide thiokol of the polymeric ethylene-formal structure $[(\text{CH}_2)_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{O} \cdot (\text{CH}_2)_2 \cdot \text{S}_2]_n$ furnished a spectrum akin to that of a simple dialkyl disulphide, as illustrated by curves 1 and 2 of Fig. 4. Similarly, polyethylene-tetrasulphide, $[(\text{CH}_2)_2 \cdot \text{S}_4]_n$, was found to be virtually indistinguishable from monomeric diethyl tetrasulphide with respect to its ultraviolet-absorption properties (curves 3a and 4).

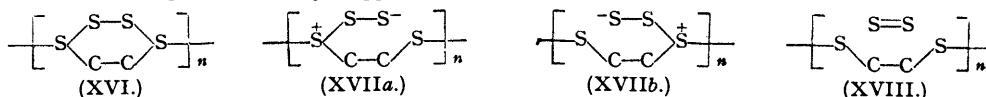
This result appears surprising in view of the common assumption that the latter thiokol contains two sulphur atoms co-ordinated to a disulphide chain in the repeat-unit structure, thereby differing from the straight-chain nature of diethyl tetrasulphide which is implicit in all the evidence outlined above. Although chemical arguments adduced in support of the co-ordinated structure of the polymeric tetrasulphide are not altogether convincing (cf. Bloomfield, *loc. cit.*), it has been stated on the basis of X-ray fibre diagrams (Fuller, *Chem.*

FIG. 4.
Thiokols.



1. Polyethyleneformal disulphide (in dioxan).
2. Dicyclohexyl disulphide (in EtOH).
3. Polyethylene tetrasulphide (in ethylene dichloride).
- 3a. do. ϵ values per S-S linkage.
4. Diethyl tetrasulphide (in EtOH; ϵ values per S-S linkage).

Reviews, 1940, **26**, 160; cf. Katz, *Trans. Faraday Soc.*, 1936, **32**, 77) that the length of the polymer repeating unit (4.32 Å) is much too short to accommodate an unbranched tetrasulphide chain. Fuller (*loc. cit.*) advanced a cyclic structure (XVI) as the most plausible model, without, however, putting forward any suggestions as to the nature of the chemical bonds involved.



Presumably, (XVIIa and b) and (XVIII) would be contributing structures, and the considerable sulphur-bond resonance involved in the hybridisation might conceivably result in the observed ultraviolet-absorption properties resembling those of a linear diethyl tetrasulphide. It should be noted, however, that the X-ray diagrams given by tetrasulphide thiokol were apparently not altogether satisfactory, and that the proposed structural interpretation raises other difficulties of a more general nature. The cyclic co-ordination hypothesis does not link up well with recent views on the straight-chain character of elastic sulphur (see above), nor is it applicable to the repeat-units of polymeric diethylene ether tetrasulphide, $[(\text{CH}_2)_2 \cdot \text{O} \cdot (\text{CH}_2)_2 \cdot \text{S}_4]_n$, or trimethylene tetrasulphide, $[(\text{CH}_2)_3 \cdot \text{S}_4]_n$, because of their different intramolecular spatial conditions, although the general properties of the latter thiokols are not reported to be different in any important respect. Considerable restrictions on free rotation of bonds, difficult to reconcile with rubbery properties, would also be imposed by the cyclic structure. It seems that further substantiation of Fuller's work must be awaited before the evidence against the linear tetrasulphide formulation of thiokol can be accepted without reserve.

EXPERIMENTAL.

Fig. 1.—Diisoamyl, dicyclohexyl, and diallyl disulphides were prepared by Dr. F. W. Shipley in these laboratories. Two samples of di-*tert.*-butyl disulphide were synthesised by independent methods by

Dr. R. F. Naylor, the two preparations being identical in ultraviolet-absorption properties. A commercial sample of dibenzyl disulphide, after recrystallisation from ethanol, had m. p. 69—70°.

Fig. 2.—The sulphur-chlorine compounds were redistilled immediately before spectrographic examination, the monochloride over free sulphur at reduced pressure. Duplicate determinations were carried out in each case as a check against loss by volatilisation or hydrolysis, concordant results being obtained. All three chlorides obeyed Beer's law in dilute *n*-hexane solution.

Fig. 3.—Diphenyl disulphide was prepared by atmospheric oxidation of commercial thiophenol and crystallised in white matted needles, m. p. 60—61°, from ethanol. An abrupt colour change takes place at the m. p., the melt being yellow but re-solidifying to a pure white solid on freezing. Both diphenyl and *pp'*-dibromodiphenyl disulphides gave yellow solutions in hot solvents, which decolorised on cooling. The *pp'*-dibromo- and -dichloro-derivatives were obtained by courtesy of Drs. J. Toussaint and G. F. Bloomfield, respectively. The sulphur was a commercial crystallised sample, and the polysulphides described were obtained and purified by fractional or molecular distillation by Dr. G. F. Bloomfield in these laboratories. Diethyl tetrasulphide samples prepared from *either* sodium tetrasulphide and ethyl bromide or sulphur monochloride and ethylthiol gave identical ultraviolet absorption and other physical properties.

Fig. 4.—The two thiokols were kindly made available by Mr. M. Gordon of the Special Products Division, Dunlop Rubber Co., Ltd. The tetrasulphide thiokol was not attacked by cold organic solvents but gradually dissolved in hot ethylene dichloride or carbon disulphide from which solvents it could be recovered apparently unchanged as a yellow rubbery solid on evaporation. Two independently prepared solutions in ethylene dichloride gave completely identical absorption curves.

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[Received, May 18th, 1948.]
