92. *Absorption Spectra and Structure of Organic Sulphur Compounds. Part III. Vulcanisation Accelerators and Related Compounds.*

By H. P. Koch.

Ultraviolet-absorption curves have been obtained for tetramethylthiourea, methyl dimethyldithiocarbamate, tetramethylthiuram mono- and di-sulphides, methyl, sodium, and zinc diethyldithiocarbamates, 2-mercaptobenzthiazole and its sodium and zinc derivatives, benzthiazolyl *N'-cyclo*hexyl 2-sulphenamide, and dibenzthiazolyl 2-di- and -tetra-sulphides. The resonance properties of these molecules are discussed.

Both tetramethylthiuram disulphide and dibenzthiazolyl 2-disulphide in solution give rise to thermochromasy, attributable to reversible thermal dissociation into coloured free radicals. Cyclic intramolecular interaction of non-bonded groups is suggested to account for some peculiar spectrographic and chemical properties of tetramethylthiuram disulphide. The absorption curves and structures of 2-mercaptobenzthiazole and its various derivatives can be divided into two distinct constitutional types arising from thioketo–thioenol mesomerism of the ion or radical of the parent compound. Varying degrees of co-ordination complex formation are apparent from the spectra of zinc diethyldithiocarbamate and bis-2-mercaptobenzthiazolezinc.

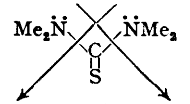
ULTRAVIOLET-ABSORPTION spectroscopy probably constitutes one of the most powerful methods of identification and analysis in the study of rubber vulcanisation accelerators and their transformation products, but little work has been published in this field (cf. Jarrijon, *Rev. Gen. du Caoutchouc*, 1943, **20**, 155). The majority of accelerator mixes in modern use contain various derivatives of the conjugated benzthiazolyl or dialkyldithiocarbamyl groups, both of which give rise to characteristic high-intensity absorption in the ultraviolet. The spectra of some typical members of these two classes have now been measured and recorded, together with those of certain structurally related molecules which are of assistance in the interpretation of bands. The practical application of such measurements to problems of rubber vulcanisation has already been referred to elsewhere (Jarrijon, *loc. cit.*; Koch, *India Rubber J.*, 1946, **61**, 145), and the following more fundamental account represents an attempt at correlation between ultraviolet absorption and the molecular structure and reactivity of sulphur-containing accelerators.

Tetramethylthiourea.—The absorption spectrum of tetramethylthiourea (I), one of the products of thermal decomposition of the accelerator TMT (see below), provides a valuable clue to the effect of conjugation between a thiocarbonyl group and a lone pair of electrons on an adjacent nitrogen atom. Intense absorption is displayed at 2555 A. ($\varepsilon = 17,000$; curve 1, Fig. 1), presumably associated with the presence of the polar structures (I*a*) in the excited state. Owing to the symmetry of the crossed-conjugated molecule, electric vectors oriented in two perpendicular directions in the plane of the chromophore (I) should be active in the absorption.

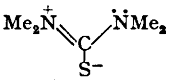
Methyl Dimethyldithiocarbamate.—In the carbamic ester molecule (II), the thiocarbonyl group is placed in crossed conjugation with a nitrogen and a sulphur atom, and two different polar excited structures (II*a* and *b*) may now be written corresponding to the two equivalent forms (I*a*) above. In resemblance with the chromophoric behaviour of other unsymmetrical crossed-conjugated systems (*e.g.*, benzoyl sulphides, see Part I), two separate absorption regions may be recognised in the ultraviolet spectrum of methyl dimethyldithiocarbamate (curve 2, Fig. 1). The 2480 A. maximum ($\varepsilon = 8500$) is evidently due to conjugation with nitrogen (II*a*), being only slightly shifted from, and about half as intense as, the 2555 A. peak of tetramethylthiourea; and the new absorption at 2740 A. ($\varepsilon = 11{,}000$) must involve the sulphur conjugation (II*b*). Since the latter band occurs at lower frequencies than the former, it may be inferred that the excited structure (II*b*) lies nearer to the ground state than does (II*a*). This conclusion is in harmony with Pauling's electronegativity scale (" The Nature of the Chemical Bond ", p. 60), according to which the sulphur atom is more positive than nitrogen. The two characteristic electronic transitions have electric moments approximately at right angles to each other, and the respective light vectors active in the absorption may be visualised in two perpendicular directions in the plane of the molecule as shown in (II).

Tetramethylthiuram Monosulphide.—The bright yellow compound (III), known as " Thionex " or MS, displays a strong and rather broad absorption band at 2770 A. ($\varepsilon = 17{,}500$) whose tail reaches into the visible. On careful inspection of the recorded curve, a distinct inflection was also revealed in the neighbourhood of 2500 A. (curve 3, Fig. 1). By reference to the light-absorption properties of the two related molecules (I) and (II), it would seem that the intense maximum is due to sulphur conjugation (two equivalent polar excited structures, III*b*), and the partly masked short-wave band associated with the crossed conjugation of the dimethylamino-groups (III*a*). These excited levels require a coplanar configuration of the two NC=S groups, with an energy barrier opposing rotation about the central sulphide bonds. Three distinct stereoisomeric forms, (III), (IV), and (V), might then occur (cf. *cis*- and *trans*-butadiene), but only one stable modification of tetramethylthiuram monosulphide is actually known.

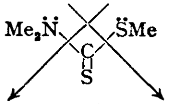
Tetramethylthiuram Disulphide.—The ultraviolet-absorption spectrum of the technically important " direct " vulcanisation accelerator generally known as TMT or " Tuads " (VI) is recorded as curve 4 in Fig. 1. In contrast with tetramethylthiuram monosulphide (III), the disulphide is almost colourless, but its solutions turn yellow on heating, reverting to colourless in the cold (thermochromasy). An absorption band is indicated near 2850 A. ($\varepsilon \sim 10{,}000$), but this merges into a second very intense short-wave region without any intervening minimum, the curve passing through an inflection near 2700 A. By comparison with the reported spectra of the monosulphide and of the related methyl dimethyldithiocarbamate, the relatively low intensity and ill-defined character of the long-wave absorption, and the greatly increased extinction at shorter wave-lengths appear anomalous in the spectrum of tetramethylthiuram disulphide. Reference to the chromophoric behaviour of diphenyl disulphide (this vol., p. 397) and of dibenzthiazolyl disulphide (see below) would suggest that the absorption of TMT should not be substantially different from twice the absorption of the " half "-chromophore represented by the ester molecule (II), but this expectation is not borne out by the curves 2 and 4 of Fig. 1. It seems as if some peculiar resonance process distinguishes the structure of TMT from that of other conjugated disulphides.



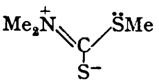
(I.)



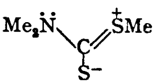
(I*a*.)



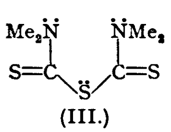
(II.)



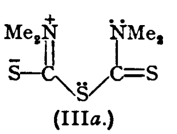
(II*a*.)



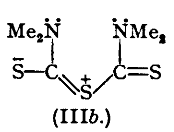
(II*b*.)



(III.)

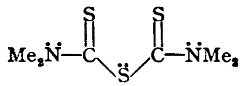


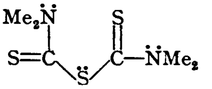
(III*a*.)



(III*b*.)

(IV.)



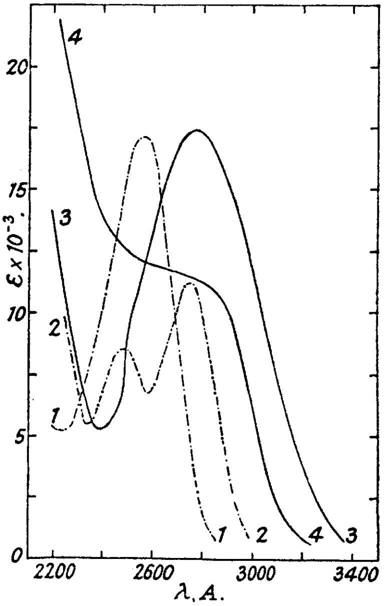


(V.)

The chemical properties of tetramethylthiuram disulphide likewise exhibit some rather unexpected features which cannot be explained in terms of normal disulphide reactivity alone. For instance, in the presence of cyanide ion in solution, one of the sulphur atoms forming part of the disulphide linkage is smoothly eliminated with the production of monosulphide (von Braun and Stechele, *Ber.*, **1903**, **36**, 2275); and when heated to its melting point, tetramethylthiuram disulphide dissociates irreversibly and in good yield into tetramethylthiourea, carbon disulphide, and elementary sulphur (cf. Bloomfield, *J. Polymer Sci.*, **1946**, **1**, 316). No explanation of these reactions has as yet been proposed.

FIG. 1.

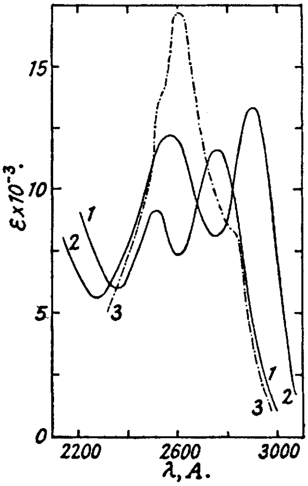
Dimethyldithiocarbamyl compounds.



1. *Tetramethylthiourea.*
2. *Methyl dimethyldithiocarbamate.*
3. *Tetramethylthiuram monosulphide.*
4. *Tetramethylthiuram disulphide.*

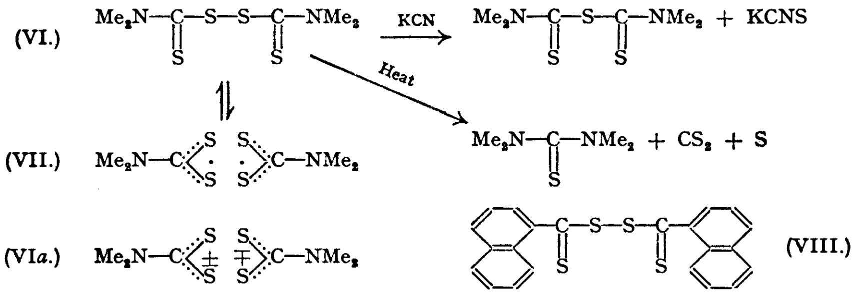
FIG. 2.

Diethyldithiocarbamic acid derivatives (in EtOH).



1. *Methyl ester.*
2. *Sodium salt trihydrate.*
3. *Zinc salt* (ε *per* Zn/2).

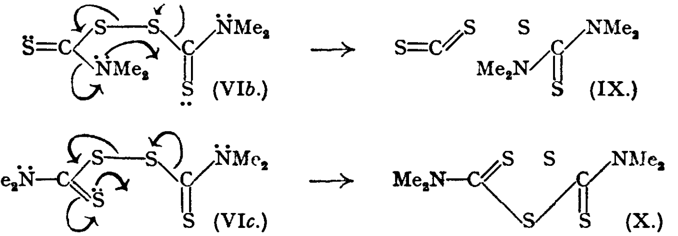
In view of the conventional mode of preparation by oxidative linking of two dimethyldithiocarbamic acid molecules, there can be little doubt about the normal straight-chain nature of the disulphide linkage in TMT. This assumption is in agreement with the above-mentioned thermochromatic properties, which accord with the corresponding behaviour of straight-chain diphenyl and dibenzthiazolyl disulphides, being attributable to reversible thermal dissociation of the disulphide link into coloured free radicals. Radical dissociation of the disulphide structure (VI) should be expected to occur very readily owing to extensive resonance stabilisation of the resulting dithiocarbamyl (VII). Similar dissociation takes place in the related molecules of dibenzoyl peroxide and di-α-dithionaphthoyl disulphide (VIII) (Schönberg *et al.*, *Ber.*, **1933**, **66**, 1932). As a corollary of such facile bond fission, polar structures like (VI*a*) may be expected to be significant in the excited levels responsible for the observed spectrum of TMT. None of


(VI.) (VII.) (VI*a*.) (VIII.)

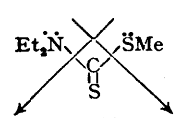
these considerations offers any clue, however, to the peculiar spectroscopic and chemical characteristics which have been described above.

Additional electronic stabilisation may result from the special steric relationships in the thiuram disulphide structure, depicted by the two-dimensional diagrams (VI*b*) and (VI*c*). Such interaction would involve the intramolecular donation of a lone pair of electrons from one dimethylaminothiocarbonyl group towards the other, facilitated both by spatial proximity and by the possibility of further electron shifts completing the cyclic conjugation process indicated by the curved arrows. In view of the symmetry properties of the system, either half of the molecule could donate a bond to the other. It may, perhaps, be pointed out that the peculiar electron donation across space which is formulated in (VI*b*) merely represents the first step of the well-known addition of amino-groups to carbonyl or thiocarbonyl compounds, while the analogous interaction of double-bonded sulphur (VI*c*) should involve no special difficulty in view of the more strongly electropositive nature of sulphur as compared with nitrogen.

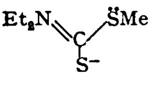
The cyclic intramolecular interaction hypothesis does not explain the rather featureless spectrum of TMT, but it does at least provide qualitative justification for the observed departure from the expected normal type. Moreover, the new postulate suggests a simple and rational overall mechanism for the peculiar chemical reactions of this compound. When carried to their extreme limit, the incipient electron shifts depicted by the curved arrows in (VI*b* and *c*) lead to the fragmentary structures (IX) and (X) respectively; and it has already been noted that at high temperatures TMT does in fact break down to (IX) (tetramethylthiourea, carbon disulphide, and free sulphur), while the presence of cyanide ion even in the cold promotes the formation of (X) (tetramethylthiuram monosulphide, and sulphur as thiocyanate). Although the detailed mechanism and the number of successive steps involved in these transformations have not been elucidated, they seem to suggest that the quasi-bonds donated across space as proposed in (VI*b* and *c*) are of real significance in the reactivity of TMT. The relative importance of the alternative conformations (VI*b* and *c*) of a given molecule may be a complex function of the comparative donor properties of nitrogen and sulphur and of the relative probabilities of attaining the requisite geometrical conditions for intramolecular bond formation in the two cases.

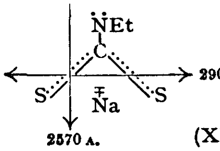

(VI*b*.) (IX.)
(VI*c*.) (X.)

Diethyldithiocarbamic Acid Derivatives.—In correspondence with the slightly more basic character of the diethyl- as compared with the dimethyl-amino-group (cf. Lewis, *J. Amer. Chem. Soc.*, 1945, **67**, 771), it was found that the absorption of methyl *N*-diethyldithiocarbamate (XI) occurred at slightly lower frequencies than that of the dimethyl compound (II) (cf. Figs. 1 and 2). The nitrogen conjugation band was displaced by 600 cm.$^{-1}$ from 2480 A. ($\varepsilon = 8500$) to 2520 A. ($\varepsilon = 9000$), whereas the sulphur conjugation maximum suffered a smaller shift of 300 cm.$^{-1}$ from 2740 A. ($\varepsilon = 11{,}000$) to 2760 A. ($\varepsilon = 11{,}500$). The relative magnitude of these two shifts suggests that both excited (XI*a*) and ground (XI) states of the molecule are affected

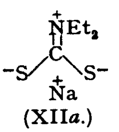


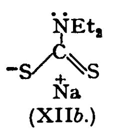
(XI.)

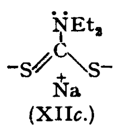

(XI*a*.)



(XII.)


(XII*a*.)

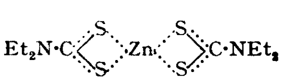

(XII*b*.)


(XII*c*.)

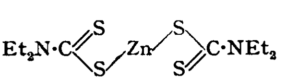
by the substitution. It may be assumed that other *N*-diethyl-substituted compounds of this class will behave in a similar manner and display absorption spectra only slightly different from those of the corresponding *N*-dimethyl derivatives. The general structural arguments advanced in this and the preceding sections are therefore regarded as relevant to dialkyldithiocarbamyl compounds generally.

Sodium diethyldithiocarbamate or SDC (XII) gives rise to the same general type of double banded spectrum as the dialkyldithiocarbamic esters ($\varepsilon = 13{,}000$ at 2900 A., and $\varepsilon = 12{,}000$ at 2570 A.; cf. Fig. 2). The ground state doubtless approximates to the resonance hybrid (XII) and the two characteristic absorption regions can be vectorially assigned in perpendicular directions as shown. Absorption at 2570 A. results in polarisation of the nitrogen conjugation as before, the extreme structure (XII*a*) now being important in the excited state; and the 2900 A. maximum must be associated with the perpendicular oscillation of charge between the two sulphur atoms (extreme polar forms XII*b* and *c*).

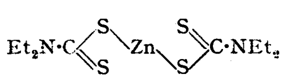
Whereas the water-soluble sodium derivative (XII) obviously represents a true ionic salt, the corresponding zinc compound ZDC, insoluble in water but soluble in organic solvents, appears to involve covalent complex formation. The ultraviolet spectrum differs characteristically from that of the sodium salt (cf. Fig. 2). The 2900 A. absorption region attributed to charge-resonance in the ionic state no longer occurs, but a new and very intense narrow band at 2605 A. ($\varepsilon = 17{,}000$) is now superimposed on two shoulders near 2540 and 2820 A. which apparently correspond to the two absorption peaks of the methyl ester. These features seem compatible with the hybrid formulation (XIII) of the ground state, symmetrically



(XIII.)



(XIII*a*.)

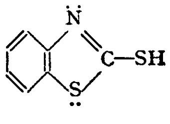


(XIII*b*.)

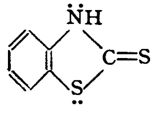
composed of two equivalent ester-analogous covalent-bond structures (XIII*a* and *b*) in resonance. The proposed constitution does not violate the known stereochemistry of either sulphur or zinc, and it probably finds an analogy in the structure of cupric dipropyldithiocarbamate, which has been shown to contain a molecular centre of symmetry (Peyronel, *Gazzetta*, **1943**, **73**, 89). The valency configurations of copper and zinc being planar and tetrahedral respectively, no molecular symmetry centre would be expected to arise in the postulated zinc complex (XIII).

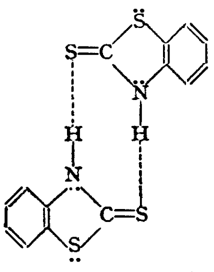
2-Mercaptobenzthiazole and Metallic Derivatives.—The vulcanisation accelerator MBT may in theory possess either of the alternative tautomeric structures (XIV) or (XV), but Morton and Stubbs have already shown that only (XV) exists in alcoholic solution, by comparing the observed spectrum with those of the sharply differentiated two stable methyl derivatives (*J.*, **1939**, 1321). The absorption curve of MBT in ethanol was redetermined in the present work, in good agreement with that reported by Morton and Stubbs (curve 1, Fig. 3; $\varepsilon = 27{,}500$ at 3250 A., and $\varepsilon = 15{,}000$ at 2360 A.). It was further observed that almost identical bands occurred in benzene or chloroform solutions, so that the greater stability of the thiocarbonyl (XV) over the thiol form (XIV) appears to be independent of the nature of the solvent. Hunter found that association takes place in concentrated solution, doubtless by way of hydrogen bonding (*J.*, **1945**, 806); and since a preliminary *X*-ray investigation by Dr. G. A. Jeffrey (private communication) has revealed that pairs of molecules are geometrically related by a centre of symmetry in the crystalline structure, it seems probable that MBT exists in the form of the symmetrical bimolecular complex (XVI) in the solid state.

(XIV.)



(XV.)



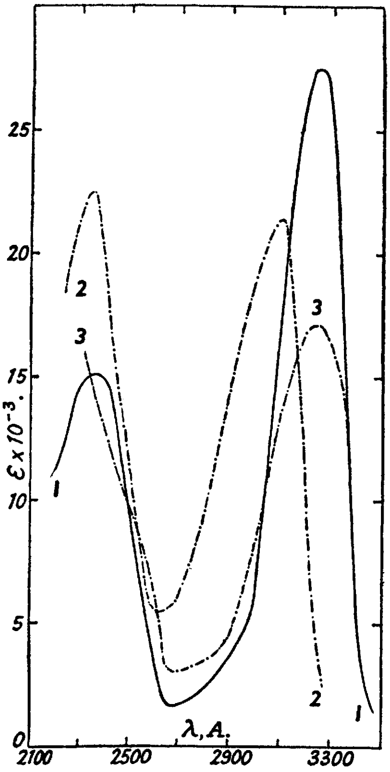


(XVI.)

No complete interpretation of the 2-mercaptobenzthiazole spectrum will be attempted here in view of the paucity of further reference data, but it would seem that (XV*a*, *b*, *c*, and *d*) represent the most obvious polar excited structures. Accordingly, it is suggested that the very intense long-wave absorption band which constitutes such a unique feature of MBT may be correlated with the formal oscillation of negative charge between the two ends of the molecule. Deep colour is known to result from this type of charge-resonance involving a large transition moment (Pauling, Gilman's " Organic Chemistry ", 2nd edtn., 1943, p. 1982). A similar band is observed in the anion (XVII) (curve 2; ε = 21,500 at 3090 A., and ε = 22,500 at 2340 A.),

FIG. 3.

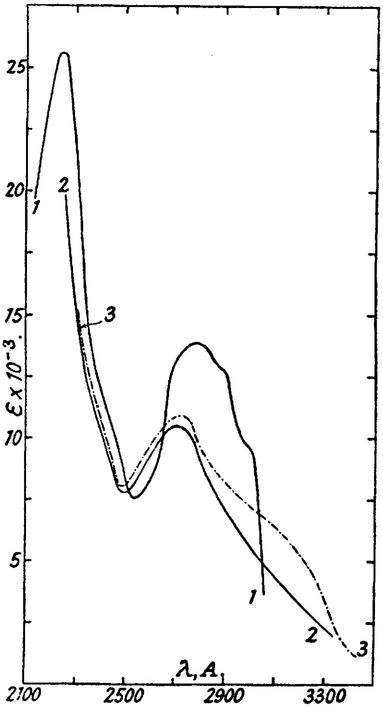
2-*Mercaptobenzthiazole.*



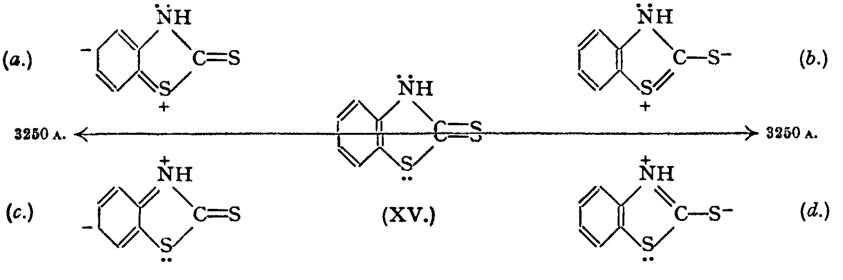
1. *In* EtOH.
2. *In* 2N *aq.* NaOH.
3. *Zinc salt* (*in* CHCl$_3$; ε *per* Zn/2).

FIG. 4.

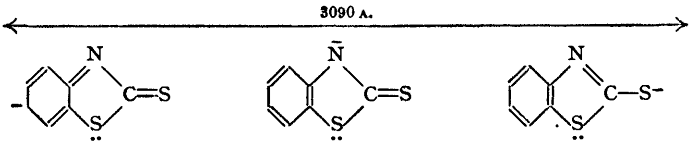
2-*Benzthiazolyl compounds* (*in* EtOH).



1. 2-*Benzthiazolyl* N'-cyclo*hexyl sulphenamide.*
2. *Di*-(2-*benzthiazolyl*) *disulphide* (ε *per mol. wt.* × ½).
3. *Di*-(2-*benzthiazolyl*) *tetrasulphide* (ε *per mol. wt.* × ½).



(XV.)

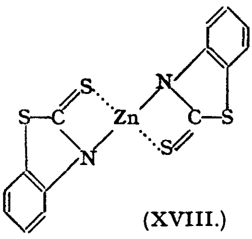


(XVII.)

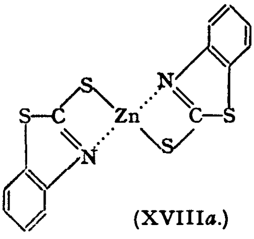
but not in the derivatives of the thiol form (XIV) (see below), in which charge-resonance is precluded.

The highly insoluble zinc derivative of MBT again exhibits the characteristic long-wave absorption (ε = 17,000 at 3240 A.; curve 3, Fig. 3), but the intensity is reduced and no second band is observed near 2350 A., although this arises in both MBT and its *N*-alkyl derivatives (Morton and Stubbs, *loc. cit.*). Some modification of the thiocarbonyl structure (XV) is therefore indicated, and it may be assumed that co-ordination complex formation occurs (XVIII). The primary valency attachment of the heavy metal is still formulated at the nitrogen atom in view of the previously identified charge-resonance band in the spectrum, but the alternative sulphur-linked structure (XVIII*a*) is thought to make some contribution. The resonance degeneracy of the metallic bonds would not be expected to be complete as it is in the dithiocarbamyl complex (XIII) on account of the non-equivalence of the two postulated extreme canonical structures (XVIII) and (XVIII*a*).

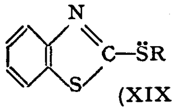
Organic Derivatives of 2-Mercaptobenzthiazole.—The spectrum of the sulphenamide known as HBS or "Santocure" (XIX; R = $NH{\cdot}C_6H_{11}$) closely resembles that of 2-methylthiobenzthiazole (XIX; R = Me) as recorded by Morton and Stubbs, so that the constitution of this compound as a derivative of the hypothetical thiol form (XIV) of MBT cannot be in doubt. Two maxima occur, one at 2245 A. (ε = 25,000), and the other at 2780 A. (ε = 13,500), with subsidiary fine-structure bands superimposed on the near-ultraviolet slope (curve 1, Fig. 4). The 2780 A. absorption region can probably be assigned to the system of conjugation depicted by the classical and polar excited forms (XIX) and (XIX*a*) respectively.



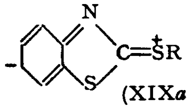
(XVIII.)



(XVIII*a*.)



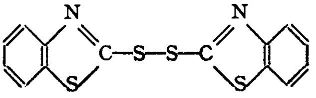
(XIX.)

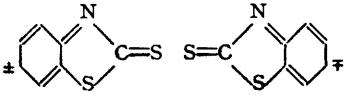


(XIX*a*.)

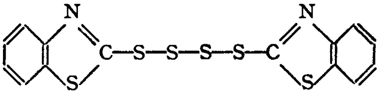
Dibenzthiazolyl 2-disulphide or MBTS (XX) again displays absorption of the same general type as that of the thiol-derived structures (XIX) (curve 2, of Fig. 4; ε/2 = 10,500 at 2710 A.). The typical long-wave tail characteristic of conjugated S–S bonds can also be recognised (this vol., p. 397), and the importance of the polar structures (XX*a*) in the excited state inferred by analogy with the case of diphenyl disulphide which has been discussed in the preceding paper. A predisposition for facile reversible dissociation into neutral free radicals may again be predicted and is evidently responsible for the observed thermochromatic properties of MBTS solutions.

(XX.)





(XX*a*.)



(XXI.)

Finally, the constitutional type of the reaction product of MBT with sulphur monochloride was confirmed as the tetrasulphide (XXI) by comparison of its spectrum (curve 3, Fig. 4; ε/2 = 10,900 at 2730 A.) with that of the disulphide (XX). The "bulge" in the curve near 3000 A. may be identified with the enhanced absorption of linear tetrasulphides in that spectral region (this vol., p. 397).

EXPERIMENTAL.

Fig. 1.—Tetramethylthiuram mono- and di-sulphides were commercial recrystallised samples. The monosulphide was bright yellow, and the practically colourless disulphide was thermochromatic in benzene or ethanol solutions but did not turn yellow on heating in the solid state until it decomposed irreversibly at its m. p. (146°). The compound obeyed Beer's law in dilute alcoholic solution at room temperature. Tetramethylthiourea (m. p. 78°) was prepared by Dr. F. W. Shipley, and methyl dimethyldithiocarbamate (white needles, m. p. 46°) obtained in these laboratories by Mr. A. L. Morris from carbon disulphide, dimethylamine, and methyl iodide (cf. Delépine, *Bull. Soc. chim.*, 1902, **27**, 591).

Fig. 2.—Sodium and zinc diethyldithiocarbamates were purified from commercial samples by recrystallisation. The sodium salt was obtained as the trihydrate in thin irregular plates, m. p. 92—102°, from acetone (Found : C, 26·9; H, 7·45; S, 28·55; Na, 10·2. Calc. for $C_5H_{10}NS_2Na,3H_2O$: C, 26·7; H, 7·15; S, 28·45; Na, 10·2%), and the zinc salt in large transparent crystals, m. p. 177°, from benzene. *X*-Ray examination of the latter compound, kindly carried out by Mr. S. C. Nyburg, revealed the presence of four molecules in a monoclinic unit cell (a = 9·96, b = 10·62, c = 15·45 A.; β = 105°) with the space-group symmetry $P2_1/n$. The dilute alcoholic solutions were found to obey Beer's law. (No quartz-ultraviolet absorption was displayed by alcoholic solutions of zinc chloride.)

Methyl diethyldithiocarbamate (b. p. 120°/16 mm.) was prepared by reaction of the corresponding sodium salt with methyl iodide in alcoholic solution.

Fig. 3.—A commercial sample of 2-mercaptobenzthiazole gave large, ochre-yellow, monoclinic needles (cell dimensions : a = 15·2, b = 6·01, c = 8·04 A.; β = 100°), m. p. 178°, on recrystallisation from benzene. The observed space-group symmetry $P2_1/n$, with four molecules in the unit cell, requires that pairs of molecules are related by a centre of symmetry in the crystal structure (*X*-ray data by courtesy of Dr. G. A. Jeffrey). Light absorption in benzene : $\lambda_{max.}$ = 3290 A., ε = 25,000; in $CHCl_3$: $\lambda_{max.}$ = 3209 A., ε = 24,500.

The zinc derivative of 2-mercaptobenzthiazole was prepared and purified by Dr. G. F. Bloomfield.

Fig. 4.—Dibenzthiazolyl 2-disulphide was obtained in irregular white leaflets on recrystallisation from benzene. The solid compound remained colourless when heated to its m. p. (179—180°), whereat a yellow melt was produced which re-set to a white solid on cooling. Thermochromasy was displayed by the solutions in benzene and alcohol. Dibenzthiazolyl 2-tetrasulphide was prepared by Dr. F. W. Shipley from 2-mercaptobenzthiazole and sulphur monochloride.

2-Benzthiazolyl *N'-cyclo*hexyl sulphenamide (" Santocure ") was a commercial sample which furnished off-white (light ochre) needles, m. p. 102—103°, on crystallisation from aqueous ethanol (Found : S, 24·0. Calc. for $C_{13}H_{16}N_2S_2$: S, 24·3%).

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