The Prevalence of Unbranched Sulphur Chains in Polysulphides and Polythionic Compounds

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Divalent sulphur is apparently unable to add sulphur to any of its lone electron pairs to form branched groupings of the type $\text{>S}\rightarrow\text{S}$ or $\text{>S}=\text{S}$ (with coordinate or double sulphur-sulphur bonds). Thus, sulphur compounds such as disulphides, polysulphides and polythionic compounds are apparently all built up of unbranched, zigzag sulphur chains. The purpose of this article is to demonstrate that earlier arguments, on chemical basis, against the existence of unbranched sulphur chains in polythionic compounds and polysulphides are fallacious in view of recent work on the reactivity of these compounds. Furthermore, the purpose is to discuss the prevalence of unbranched sulphur chains on the basis of the following considerations.

Sulphur may be expected to add to an atom A to form a coordinate bond $\text{>A}\rightarrow\text{S}$ or $\text{>A}=\text{S}$ only in cases where A is the less electronegative element, since such a bond implies that sulphur becomes the negative end of the polar bond. In the case where A is sulphur, a stable coordinate grouping $\text{X}_2\text{A}\rightarrow\text{S}$ or $\text{X}_3\text{A}\rightarrow\text{S}$ is accordingly probable only if the atoms or groups, X, bonded to A are able to decrease the effective electronegativity of A to a sufficient degree. Such cases do apparently not exist. In polythionic compounds X_2A where A is sulphur and the groups X are thio groups, A has in most cases a partial positive charge, as evidenced by the chemical reactions of the compounds. In such cases the groups X increase the effective electronegativity of A. Coordinate structures $\text{X}_2\text{S}\rightarrow\text{S}$ of the next higher polythionic compounds are therefore improbable.

A double bond $\text{>A}=\text{S}$ or $\text{>A}=\text{S}$ where A is sulphur, requires an expanded valency shell (beyond the octet) of A. Divalent sulphur is apparently unable to expand its valency shell for double bonding to additional sulphur atoms.

THE STRUCTURE AND REACTIVITY OF DISULPHIDES, POLYSULPHIDES AND POLYTHIONIC COMPOUNDS

In these compounds there are, generally, two structural possibilities, *viz.*, that of unbranched sulphur chains, and that of branched structures. The following compounds have been subjected to detailed structure investigation, by electron or X-ray diffraction methods: Rhombic sulphur¹, sulphur (S_8) vapour², disulphur dichloride³, dihydrogen disulphide⁴, dimethyl disulphide⁴, di(*p*-bromophenyl) disulphide⁵, dimethyl trisulphide⁶, and di(2-iodoethyl) trisulphide^{7,8}. The compounds are all built up of unbranched chains (8-membered unbranched rings in the case of rhombic sulphur and sulphur vapour). Lattice dimensions and space group are reported⁷ for di(2-chloroethyl) trisulphide, and for two pentathionic compounds, *viz.*, monosulphur di(benzenethiosulphonate) and di(*p*-toluenethiosulphonate). A twofold axis of symmetry was found for these compounds, thus limiting the possibility of branched structures. Preliminary results⁹ of an X-ray structure analysis of di(methanesulphonyl) disulphide, a tetrathionic compound, reveal an unbranched structure. Plastic or elastic sulphur consists of long, unbranched chains^{10,11}. X-ray crystal studies of potassium trithionate¹², barium trisulphide¹³, di(benzenesulphonyl) sulphide^{7,14} and di(*p*-toluenesulphonyl) sulphide⁷ are in accordance with unbranched chains; however, in these cases there is hardly any possibility for branched structures.

Dihydrogen disulphide and the dihydrogen polysulphides (tri, tetra, penta, hexa) are built up of unbranched sulphur chains, with terminal hydrosulphide groups, according to their Raman spectra^{15,16}. The sensitivity of these sulphides towards basic substances is probably due to a base-catalysed prototropic change to unstable, branched structures¹⁷. Raman spectra of disulphur dimethoxide and *bis*(dimethylamide) indicate unbranched structures^{18,19}, and so do the Raman spectra of disulphur dichloride and dimethyl disulphide^{20,21}. The ultraviolet absorption spectra of the following compounds provide strong evidence in favour of unbranched chains²²: A series of organic disulphides, disulphur dichloride, diethyl tetrasulphide, diphenyl tetrasulphide, di(2-benzthiazolyl) tetrasulphide, polyethylene tetrasulphide, and dicyclohexyl hexasulphide. For di(*n*-hexadecyl) trisulphide and tetrasulphide the ultraviolet absorption curves were not interpreted as giving definite results²³.

The X-ray emission spectra of the potassium polythionates are in accordance with unbranched chain formulae²⁴.

The chemical reactions of a series of polythionic compounds SX_2 show^{25,26} that in those compounds a divalent sulphur atom forms a bridge between the thio sulphur atoms of two thio groups X. These considerations apply to the

following compounds, which, therefore, are built up of unbranched sulphur chains:

Monosulphur

di(thiocyanate)	$S(SCN)_2$
bis(dimethylthiophosphate)	$S(SPO(OCH_3)_2)_2$
di(ethanethiosulphonate)	$S(S_2O_2R)_2$
di(<i>p</i> -toluenethiosulphonate)	
di(thiosulphate)	$S(S_2O_3)_2^{--}$

The space group ⁷ of monosulphur di(*p*-toluenethiosulphonate) crystals is in accordance with this structure.

The investigations referred to above are thus unequivocally in favour of unbranched sulphur chains. Physico-chemical evidence reported in support of branched structures, such as the dipole moment of disulphur dichloride ²⁷ and the parachor ²⁸ and viscosity ²⁹ of diethyl tetrasulphide, seems less conclusive.

The unbranched sulphur chain formulae for the polythionic acids were first proposed by Blomstrand ³⁰ and Mendelejeff ³¹. The arguments against these formulae are mostly of chemical nature. Thus, pentathionate and hexathionate in presence of small amounts of basic substances readily liberate sulphur, to give tetrathionate (for literature, see Ref. 26). So do organic polysulphides, to give disulphides ³²⁻³⁴. Tetrathionate, pentathionate and hexathionate with sulphite give trithionate and thiosulphate; organic polysulphides ³⁴⁻³⁶ give disulphide and thiosulphate. The argument is ^{32,33,37-43} that the sulphur atoms which are thus easily removable, are bonded differently from the others, and that they therefore cannot be part of unbranched chains. The validity of this view, in the case of organic polysulphides, has recently been questioned by Farmer and Shipley ³⁴ and Bloomfield ³⁶, on the ground that diethyl tetrasulphide, as prepared from ethylthiol and disulphur dichloride, should have an unbranched structure, and yet it gives off two sulphur atoms to sulphite.

In view of recent work ^{25,44} on the chemistry of polythionic compounds the reactions with sulphite are, in fact, consistent with unbranched sulphur chain structures.

Thus, it was predicted some time ago ²⁵, on the basis of the general reactivity of tetrathionate, pentathionate and hexathionate, that the reactions with sulphite are ionic displacements of thiosulphate by sulphite, as follows:

This theory has recently been confirmed by Christiansen and Drost-Hansen ⁴⁵ by experiments with sulphite labelled with radioactive sulphur.

At the same time ²⁵, the first steps of the analogous reactions with cyanide were formulated as ionic displacements of thiosulphate by cyanide. *E.g.*, hexathionate is assumed to react with excess cyanide in the following way:

The catalytic decompositions of pentathionate and hexathionate into sulphur and tetrathionate are, likewise, compatible with unbranched sulphur chain formulae ^{25,26}.

Now, the reactions of organic polysulphides with sulphite ^{34,36} and cyanide ^{46,47} probably take place by analogous ionic displacement mechanisms. It seems reasonable to assume that the first steps are ionic displacements of mercaptide by sulphite or cyanide. Thus, for tetrasulphides and sulphite:

The analogous mechanism for tetrasulphides and cyanide is:

In the last steps, the formed sulphenyl thiosulphate and thiocyanate react with the mercaptide, displaced in the first steps, to give disulphide. The electrophilic properties of the sulphenyl sulphur of sulphenyl thiosulphates and thiocyanates are well known ^{44,48}.

Departures from this general scheme must be expected to occur depending upon the relative amounts of reagents present. Since sulphenyl thiosulphates and thiocyanates

react readily with sulphite and cyanide ⁴⁴, the following reactions might, in presence of excess of the last ions, take the place of (10) and (13):

If insufficient amounts of sulphite and cyanide are employed, one might have, instead of (9), (10) and (12), (13):

The trisulphides thus formed should react with sulphite and cyanide as follows:

with (10) or (14) and (13) or (15) as subsequent steps. According to the experiments reported by Farmer and Shipley ³⁴ and Bloomfield ³⁶, the reactions of tetrasulphides with sulphite in some cases do not proceed to the disulphide stage.

The first steps, (8), (11), (18) and (19), require some comments. Sulphite and cyanide have no effect on disulphides; thus, mercaptides displace the sulphite of sulphenyl sulphites ⁴⁹, to give disulphides. These are displacements opposite to those of Eqs. (8), (11), (18) and (19). However, the course of the displacements, if only slightly reversible, evidently depends upon the possibilities for subsequent, more rapid reactions, like (9), (10) and (12), (13) in the present case; for disulphides, there are no such possibilities.

The above considerations apply to dialkyl and diaryl disulphides and polysulphides. Carbonic acid derivatives, such as dixanthyl, di(thiocarbamyl) and diaroyl disulphides, react with cyanide * to give thiocyanate and monosulphides ^{47, 50}. These reactions involve ionic displacements, as follows ^{25, 51}:

The corresponding polysulphides, in presence of basic substances like alkalies and thio-carbonyl anions, liberate sulphur to give disulphides, not monosulphides ^{26, 52, 53}. The reactions of the disulphides with cyanide thus lend support to the hypothesis that corre-

* Preliminary experiments have shown that di(ethylxanthyl) and bis(diethylthiocarbamyl) disulphide react also with sulphite, to give one equivalent of thiosulphate.

sponding reactions of polysulphides are displacement reactions, and not base-catalysed liberations of sulphur, which afterwards reacts with cyanide to give thiocyanate.

Thus, the reactions with sulphite and cyanide, of compounds containing unbranched sulphur chains, are explainable on the basis of ionic displacement mechanisms. Arguments to the contrary, *i. e.*, that such compounds should not react readily with sulphite and cyanide, are untenable also from the fact that sulphur itself, which is built up of unbranched rings or chains, does so. This reasoning leads, from the established mechanism of the reactions of tetrathionate, pentathionate and hexathionate with sulphite, to the following theory concerning the mechanism of the reactions of sulphur with sulphite and cyanide.

The first step is the attachment of a sulphite or cyanide group to one end of a sulphur chain. This process might take place as a consequence of an ionic opening of the 8-membered ring of rhombic sulphur, *i. e.*, as an ionic displacement, by sulphite or cyanide, of electronegatively polarized sulphur from its electropositively polarized ring neighbour:

The next steps are successive ionic displacements of thiosulphate by sulphite, and of thiocyanate by cyanide:

The last steps are, thus, the following:

The sulphur chains bearing sulphite or cyanide groups (or thiosulphate or thiocyanate groups) at one end must, of course, be pictured as unstable intermediates only.

Also the reactions of sulphinates and of dialkylphosphites⁵⁴ with sulphur, to give thiosulphonates and dialkylthiophosphates, respectively, fit into this scheme.

COORDINATE AND DOUBLE SULPHUR-SULPHUR BONDS

The structural and chemical data thus pointing to the nonexistence of branched sulphur chains, one may inquire why such groupings are, apparently, unstable.

The sulphur-sulphur bond of a 'branch' may be coordinate, $\text{>S}\rightarrow\text{S}$, or double, $\text{>S}=\text{S}$. In a *coordinate bond*, both electrons of the shared pair are contributed by one of the atoms linked, the donor. The chemical evidence indicates that a sulphur atom acts as an acceptor for the formation of a coordinate bond only when the donor is less electronegative than sulphur. The same applies to selenium as an acceptor; in stable compounds the donor is always the more electropositive element. Consider as donors, the oxygen of ethers, R_2O , sulphur of sulphides, R_2S , nitrogen of amines, R_3N , and phosphorus of phosphines, R_3P . The electronegativity values, after Pauling⁵⁵, are: O, 3.5; N, 3.0; S, 2.5; Se, 2.4; P, 2.1. Whereas sulphoxides, R_2SO , selenoxides, R_2SeO , amine oxides, R_3NO , phosphine oxides, R_3PO , sulphides, R_3PS , and selenides, R_3PSe , are stable compounds, amine sulphides, R_3NS , selenides, R_3NSe , and analogous compounds like R_2OS , R_2OSe and R_2SSe are not known. Thus, sulphur and selenium do add to donors only which are less electronegative. In compounds with elements which are more electronegative, sulphur is always linked to (at least) two of these atoms. Examples are mono-sulphur and disulphur alkoxides, $\text{RO}-\text{S}-\text{OR}$ and $\text{RO}-\text{S}-\text{S}-\text{OR}$, and amides, $\text{R}_2\text{N}-\text{S}-\text{NR}_2$ and $\text{R}_2\text{N}-\text{S}-\text{S}-\text{NR}_2$.

Turning to sulphur, the same element, as a donor for sulphur, it seems reasonable to predict, on the basis of the above evidence, that stable coordinate groupings $\text{X}_2\text{S}\rightarrow\text{S}$ are possible only if the atoms or groups, X, are able to reduce the effective electronegativity of the donor sulphur to a sufficient degree. Take the series:

In the three first compounds the sulphur atom has a partial positive charge, due to the higher electronegativity of the atoms bonded to it, and in dimethyl sulphide it has a partial negative charge, from dipole measurements. Since positive charge increases and negative charge decreases the effective electronegativity of an atom⁵⁵, dimethyl sulphide should have the highest tendency to add sulphur to form a coordinate sulphur-sulphur bond. Apparently, it does not do so, and the chance for the other compounds to add sulphur to from such bonds should consequently be very small. Thus, the structure

$\text{Cl}_2\text{S} \rightarrow \text{S}$ discussed by Smyth *et al.*²⁷ to account for the dipole moment of disulphur dichloride, is improbable on this basis.

Next, consider the polythionic compounds:

In reactions with nucleophilic reagents, such as piperidine or thiocarbonyl anions, the middle sulphur atom of these compounds is the electrophilic part of the molecule²⁵, like the sulphur atom of monosulphur dichloride. This atom has therefore, presumably, a partial positive charge, there being resonance between covalent bonds and ionic bonds like:

The effective electronegativity of the middle sulphur atom of the above polythionic compounds is thus higher than that of electroneutral sulphur, and the structure $\text{>S} \rightarrow \text{S}$ is therefore improbable in the next higher polythionic compounds.

The nonexistence of structures $\text{R}_2\text{A} \rightarrow \text{S}$ or $\text{R}_3\text{A} \rightarrow \text{S}$ where A is more electronegative than sulphur, is understandable from considerations of the nature of the coordinate bond. Such a bond implies that A impart a negative charge to sulphur and, itself, acquires a positive charge. The energy required to produce this dipole must oppose the energy of the bonds (electrostatic plus single covalent) thereby made possible, and, unless the first-named amount of energy is substantially lowered through a favourable electronegativity difference between sulphur and the donor, it is apt to reduce the strength of the resultant bond considerably. Even if the acceptor is more electronegative than the donor, as in amine oxides, the N—O bond is nearly of the length to be expected for a normal single covalent bond between the two elements, and is accordingly supposed to have nearly the same strength⁵⁶. That is, there is no resultant electrostatic strengthening of the bond. Therefore, when the participants in a coordinate bond have the same electronegativity, it is not surprising that the bond is too weak for a stable compound to exist.

The analogous statement, that the stability of $\text{>S} \rightarrow \text{O}$ bonds, as contrasted with $\text{>S} \rightarrow \text{S}$ bonds, is attributable to the higher electronegativity of oxygen as compared with sulphur, has recently been made by Vogel-Högler⁵⁷ and Eucken and Wagner⁵⁸.

The argument concerning the necessity for the donor to be less electro-negative than the acceptor is apparently not valid if the acceptor is the positive end of a dipole, like boron in the boron halides, especially if the donor, at the same time, is the negative end of a dipole. The elements of the sulphur group are unique in the sense that they, as atoms, are electroneutral and nonpolar, univalent acceptors.

As pointed out above, dimethyl sulphide should be more susceptible to add sulphur than the other compounds discussed, because the sulphide sulphur has a partial negative charge and therefore a smaller electronegativity than the sulphur of the remaining compounds. The same considerations apply to diaryl sulphides, and, furthermore, to the disulphides and polysulphides, since the organic groups may, likewise, induce a negative charge on one or more of the sulphur atoms of these compounds. Correspondingly, dialkyl and diaryl selenides should be the selenium compounds most susceptible to add selenium, since the selenium of the selenides is the negative end of the dipole, like the sulphur of the sulphides. It is perhaps significant that the only sulphur or selenium compounds reported, with two isomeric forms one of which may possibly have the structure $\text{>S}\rightarrow\text{S}$ or $\text{>Se}\rightarrow\text{Se}$, are di(β -naphthyl) diselenide⁵⁹ and diethyl pentasulphide²⁸.

A structure like $(\text{CH}_3)_2\text{S}\rightarrow\text{S}$, even if relatively stable with respect to dissociation into dimethyl sulphide and atomic sulphur, may still be unstable with respect to change into dimethyl sulphide and higher sulphur units such as S_2 and S_8 molecules. A slight dissociation into atomic sulphur:

is apt to lead to complete breakdown of the disulphur compound, because of the rapid process $8 \text{ S} \rightarrow \text{S}_8$. The same argument applies to corresponding double bond structures.

A *double bond* $\text{>A}=\text{S}$ where A is sulphur, requires an expanded valency shell, beyond the octet, of A.

There are indications^{60, 61} that the divalent sulphur of thioacetals is able to expand its valency shell for hyperconjugation with the carbon already bonded to the sulphur atoms. In oxygen compounds, like thionyl chloride, sulfoxides, sulphones, and sulphur-oxy ions, sulphur does seem to form partial double bonds and thus to exceed the octet, judging from bond lengths^{55, 62}, dipole moments⁵⁶, and ultraviolet and infrared absorption spectra^{63, 64}. Also, fluorine enables sulphur to exceed the octet, as in sulphur hexafluoride.

Sulphite and sulphinate ions, which both are derivatives of tetravalent sulphur, are apparently the only compounds capable of adding sulphur to give stable sulphur-sulphur compounds, where one of the sulphur atoms forms only one bond. It is a consequence of the hypothesis concerning the nonexistence of coordinate bonds $\text{>S}\rightarrow\text{S}$ and $\text{>S}\rightarrow\text{S}$ that the sulphur-sulphur bonds of thiosulphate and thiosulphonates are double bonds. That is so because the sulphite and sulphinate sulphur has, presumably, a positive charge, therefore a higher electronegativity than electroneutral sulphur, and thus cannot act as a donor for a coordinate bond with sulphur.

The Raman spectrum of thiosulphate contains no lines corresponding to a double sulphur-sulphur bond of normal strength ⁵⁸. However, if the sulphite sulphur really has a positive charge, there seems to be no other way in which to correlate the existence of thiosulphate with the nonexistence of branched sulphur chains, than to postulate double sulphur-sulphur bonds in thiosulphate.

Thus, the evidence indicates that sulphur expands its valency shell, for bonding to additional atoms, only when already bonded to strongly electro-negative elements like oxygen and fluorine, or when the new bond is formed by such atoms. According to this view, the divalent sulphur compounds most susceptible to add sulphur to form double bonds $>\text{S}=\text{S}$ should be monosulphur difluoride and dichloride, and monosulphur dialkoxides.

SUMMARY

The available physical and chemical evidence points to the nonexistence of branched structures $>\text{S}\rightarrow\text{S}$ or $>\text{S}=\text{S}$ in disulphides, polysulphides and polythionic compounds. The chemical reactivity of these compounds is consistent with formulae containing unbranched sulphur chains.

The nonexistence of branched structures is discussed in terms of the properties of coordinate and double sulphur-sulphur bonds.

A mechanism is suggested for the reactions of sulphur and of polysulphides with sulphite and cyanide.

Note added in proof: According to Backer and Evenhuis ⁶⁵, tetrakis(bromomethyl) methane reacts with alkali disulphides and tetrasulphides to give organic sulphides, which are formulated by the authors as containing sulphur-sulphur bonds of the branched type. The proposed structure has recently been accepted by Challenger and Greenwood ⁶⁶. It may be noted, though, that the chemical evidence reported by Backer and Evenhuis in support of a branched structure, such as (I):

does equally well fit with the unbranched structure (II) not discussed by Backer and Evenhuis.

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