The Stereochemistry of Polysulphides

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The existence of linear chains of sulphur atoms and also rings of such atoms, *e.g.* S_8, has been known for a long time. The discovery of restricted rotation about the —S—S— bond had obvious stereochemical implications, but examples of this isomerism were rare until recent years. Similarly, the asymmetry of quadrivalent sulphur was appreciated at the time of the discovery of methionine sulphoxide but further examples were described only this year, and the implication of such stereochemistry to the controversy about the existence of branched, *i.e.* $—\mathrm{S}—\underset{\underset{\mathrm{S}}{\downarrow}}{\mathrm{S}}—$, sulphur compounds has not been explored. Recently, a few natural products having asymmetric polysulphide moieties have been isolated, and improved methods of synthesis have enabled other asymmetric polysulphides to be secured. The availability of these compounds has enabled n.m.r. studies to be made, and these investigations have shown that the chemical shift of atomic nuclei adjacent to a sulphur group depends on its asymmetry. In addition, these compounds exhibit different circular dichroism. These advances have led to an increase in our knowledge of the stereochemistry of sulphur compounds and it therefore seems appropriate to present a review of the subject at this time. We have divided the review into four sections dealing with sulphur, acyclic polysulphides, organic cyclic polysulphides, and inorganic cyclic polysulphides, merely to aid access to particular information.

1 Elemental Sulphur

A sulphur melt contains innumerable forms of molecular sulphur which exist as a complex equilibrium mixture. Thirty different allotropic forms of sulphur have been described, but the precise structure of only a few of these is known. From a stereochemical and molecular point of view two distinct classes of sulphur allotropes have been defined: those allotropic forms which differ in their stereochemical assemblage of atoms, *i.e.* intramolecular allotropy; and those which differ in the assembly of their molecules, *i.e.* intermolecular allotropy. In this review we are concerned with the intramolecular allotropes.[1]

The three most common intramolecular allotropes of naturally-occurring sulphur are cyclo-octasulphur (S_λ), cyclohexasulphur (S_ρ), and a complex mixture of non-cyclic polymeric forms. The structure and properties of poly-

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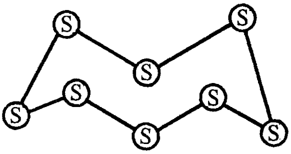
[1] B. Meyer, *Chem. Rev.*, 1964, **64**, 429; 'Elemental Sulfur', John Wiley, New York, 1965.

sulphur (or fibrous sulphur) vary with the conditions under which it is formed. It invariably occurs, and is produced, in liquid sulphur melts, together with many other allotropes. Many other molecular forms of sulphur have been detected; at least ten different molecular species have been detected in sulphur vapour[2] and some have recently been identified mass spectrometrically.[3] Several authors have reported S_2, S_3, S_4, and S_5 but their extreme instability has prevented detailed study.[4] Cyclododeca-, cyclodeca-, and cyclohexa-sulphur have recently been synthesised by Schmidt and his co-workers.[5]



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A. Cyclo-Octasulphur, (S_λ, 1).—Cyclo-octasulphur (S_λ) is the most common intramolecular allotrope of sulphur and the orthorhombic (S_α) crystalline modification is the most stable form. The *X*-ray crystallographic structure determination of S_α has been reported by several groups of workers[6] and the following molecular constants have been obtained: 16 S_8 molecules in the unit cell; average S—S bond length 2·048 Å; S—S—S bond angle 107° 54′; and S—S—S—S dihedral angle 98° 42′. As suggested by Pauling,[7] the structure depends on the two latter constants.

Monoclinic sulphur (S_β) is a second modification of cyclo-octasulphur and it is the stable form at temperatures greater than 95·4°. *X*-Ray crystallographic studies[8] have shown 48 atoms in the unit cell having an average bond distance of 2·06 Å.

Some structural information has been reported[9] on a third modification of cyclo-octasulphur (S_λ) and de Haan has proposed a structure based on the packing of only four S_8 molecules in the unit cell. Several other allotropes of

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[2] H. Staudinger and W. Kreis, *Helv. Chim. Acta*, 1925, **8**, 71.

[3] J. Berkowitz and J. R. Marquart, *J. Chem. Phys.*, 1963, **39**, 275; J. Berkowitz and W. Chupka, *ibid.*, 1964, **40**, 287; J. Berkowitz and C. Lifshitz, *ibid.*, 1968, **48**, 4346; D. Cubicciotti, *J. Phys. Chem.*, 1963, **67**, 1385.

[4] K. Ikenoue, *J. Phys. Soc. Japan*, 1953, **8**, 646; H. Lux and E. Bøhm, *Chem. Ber.*, 1965, **98**, 3210; J. A. Poulis and W. Derbyshire, *Trans. Faraday Soc.*, 1963, **59**, 559.

[5] M. Schmidt and E. Wilhelm, *Angew. Chem. Internat. Edn.*, 1966, **5**, 964.

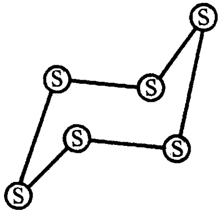
[6] S. C. Abrahams, *Acta Cryst.*, 1955, **8**, 661; A. S. Cooper, W. L. Bonds, and S. C. Abrahams, *ibid.*, 1961, **14**, 1008; A. Caron and J. Donohue, *ibid.*, 1965, **18**, 562.

[7] L. Pauling, *Proc. Nat. Acad. Sci. U.S.A.*, 1949, **35**, 495.

[8] J. T. Burwell, *Z. Krist.*, 1937, **97**, 123; D. E Sands, *J. Amer. Chem. Soc.*, 1965, **87**, 1395.

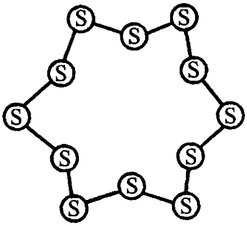
[9] J. Donohue, A. Caron, and E. Goldish, *J. Amer. Chem. Soc.*, 1961, **83**, 3748; Y. M. de Haan, *Physica*, 1950, **24**, 855.

cyclo-octasulphur have been described but few structural details reported. The major variations are intermolecular allotropes prepared either by crystallisation from a variety of organic solvents, *e.g.*, α-pinene, fenchenone, and *o*-xylene,[10] by irradiation,[11] or by controlled generation of sulphur in a chemical reaction.[5, 12]



(2)

B. Cyclohexasulphur, (S_ρ, 2).—Cyclohexasulphur occurs naturally and has been synthesised, but little data has been given about the synthetic material. The naturally-occurring S_ρ exists as a staggered six-membered ring with the following molecular constants: S—S bond length 2·059 Å; S—S—S bond angle 102° 12′; and S—S—S—S dihedral angle 74°; three S_6 molecules were found in the unit cell.[13]



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[10] M. G. Wolf, *J. Chem. Educ.*, 1951, **28**, 427.

[11] (*a*) P. D. Bartlett and G. Meguerian, *J. Amer. Chem. Soc.*, 1956, **78**, 3710; P. D. Bartlett, E. F. Cox, and R. E. Davis, *ibid.*, 1961, **83**, 103; (*b*) F Fehér and D. Kurz, *Z. Naturforsch.*, 1969, **24b**, 1089; (*c*) F. Fehér and W. Becker, *ibid.*, 1965, **20b**, 1125; F. Fehér, B. Degen, and B. Söhngen, *Angew. Chem.*, 1968, **80**, 320.

[12] W. A. Pryor, in 'Mechanisms of Sulphur Reactions', McGraw-Hill Co., New York, 1962.

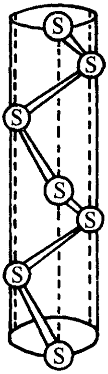
[13] J. Donohue, A. Caron, and E. Goldish, *Nature*, 1958, **182**, 518; A. Caron and J. Donohue, *J. Phys. Chem.*, 1960, **64**, 1767; S. H. Goodman and J. Donohue, *ibid.*, 1964, **68**, 2363; C. Frondel and R. E. Whitfield, *Acta Cryst.*, 1950, **3**, 242; J. D. H. Donnay, *ibid.*, 1955, **8**, 245.

C. Cyclododecasulphur, (3).—Schmidt and his co-workers[5] have developed a new and promising synthetic method for the preparation of specific sulphur molecules, *viz*:

$$S_yCl_2 + H_2S_x = 2HCl + S_{(x+y)} \, .$$

Thus condensation of dihydro-octasulphide ($x = 8$) and tetrasulphur dichloride ($y = 4$) in carbon disulphide gave a stable cyclododecasulphur, S_{12}. *X*-Ray crystallographic analysis[14] gave the following molecular constants: 2 molecules/unit cell; S—S bond distance 2·055 Å; S—S—S bond angle 106° 30′. The ring exists as a zig-zag conformation with the sulphur atoms lying in three planes. This approach to sulphur chemistry seems to be of great versatility since cyclohexa- and cyclodeca-sulphur have been prepared by the method.

The reaction of triarylphosphines with cyclic sulphur compounds has received some attention.[11a, b] Thus it has been shown that the rate of the reaction of diphenyl-*o*-tolylphosphine with S_6, S_7, S_{12}, and S_8 decreases in the order given; the rate difference between the reaction of S_6 and S_8 with the nucleophilic reagent is at least 10,000 and this has been attributed to the strain in the six-membered ring, shown by the value of the dihedral angle (74°) as compared to 98° 42′ in S_8.



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D. Polysulphur, (4).—Polysulphur is a complex mixture of non-cyclised sulphur chains, and several allotropic forms have been described. Very little structural data has been reported but the proposition has been made that they consist of helices of sulphur atoms, as found in metallic selenium and tellurium.[15] It should be noted that chain elongation occurs by *trans* addition of sulphur atoms.

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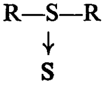
[14] A. Kutoglu and E. Hellner, *Angew. Chem. Internat. Edn.*, 1966, **5**, 965.

[15] J. A. Prins, J. Schenk, and L. H. J. Wachters, *Physica*, 1957, **23**, 746; J. A. Prins, *ibid.*, 1954, **20**, 124; J. A. Prins and F. Tuinstra, *ibid.*, 1963, **29**, 329, 884; C. W. Thompson and N. S. Gingrich, *J. Chem. Phys.*, 1959, **31**, 1598.

E. Charge Transfer Complexes of Sulphur.—Charge transfer complexes of sulphur are well known, and *X*-ray crystallographic determination of the structures of the iodine[16]– and iodoform[17]– sulphur complexes have been reported. The average bond distances and bond angles (2·043 Å, and 107° 42′ respectively) for the iodoform–tricyclo-octasulphur complex are comparable to the data obtained for S_8; the slightly smaller S—S bond distances of the complex are undoubtedly due to charge transfer interactions.

2 Inorganic and Organic Linear Polysulphides

The structure and stereochemistry of acyclic polysulphides has been the subject of a large number of investigations. There has been particular controversy on the question of whether or not the chains of sulphur atoms are branched (*i.e.* 5 or 6). The chemical evidence can be interpreted to support either type of



$$\underset{\displaystyle S}{\overset{\displaystyle R{-}S{-}R}{\downarrow}}$$

(5)

$$R{-}S{-}S{-}R$$

(6)

structure. Thus, those sulphur atoms bonded only to other sulphur atoms are extremely reactive. This may be illustrated by the reaction of a nucleophile[18], *e.g.* CN^-, *viz*:

$$\begin{gathered} R{-}SSSS{-}R + CN^- \rightarrow R{-}SSS{-}CN + S{-}R^- \\ R{-}SSS{-}CN + CN^- \rightarrow R{-}SS{-}CN + SCN^- \\ R{-}SSS{-}CN + RS^- \rightarrow R{-}SS{-}R + SCN^- . \end{gathered}$$

It has been suggested that a branched sulphur chain would react more readily with the nucleophile and hence account for the fast reaction of trisulphides and higher sulphides. The reaction of triphenylphosphine with trisulphides[19] to give disulphides is formally analogous to its reaction with sulphoxides, when the sulphide is the principal product.[20] Another analogy with sulphoxide chemistry is the reaction of diphenyl disulphide with dihydrogen disulphide to give polysulphides,[21] in the same way that the sulphides give sulphoxides when treated with hydrogen peroxide.

Recent studies by Barnard and his co-workers[22] describe the facile thermal racemisation of di-allyl polysulphides (7, 9). Because the racemisation of (7) does not take place with disproportionation or allylic rearrangement, and rate studies indicate the absence of homolytic side reactions, the authors believe the

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[16] J. Jander and G. Turk, *Chem. Ber.*, 1964, **97**, 25.

[17] T. Bjorvatten, *Acta Chem. Scand.*, 1962, **16**, 749.

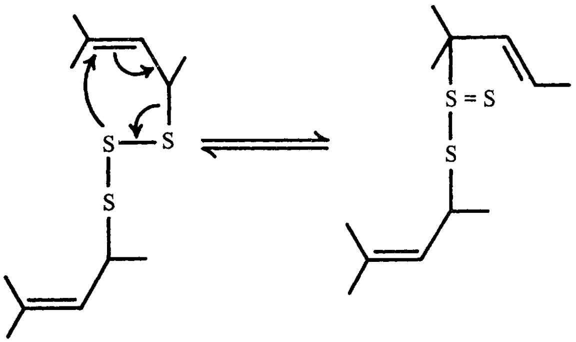
[18] O. Foss, in 'Organic Sulfur Compounds', vol. 1, Pergamon Press, Oxford, 1961, p. 83; J. L. Kice, *Accounts Chem. Res.*, 1968, **1**, 58.

[19] C. G. Moore and B. R. Trego, *Tetrahedron*, 1962, **18**, 205; 1963, **19**, 1251.

[20] H. H. Szmant and O. Cox, *J. Org. Chem.*, 1966, **31**, 1595.

[21] S. Safe and A. Taylor, *J. Chem. Soc.* (*C*), 1970, 432.

[22] D. Barnard, T. H. Houseman, M. Porter, and B. K. Tidd, *Chem. Comm.*, 1969, 371.



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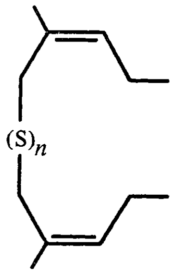
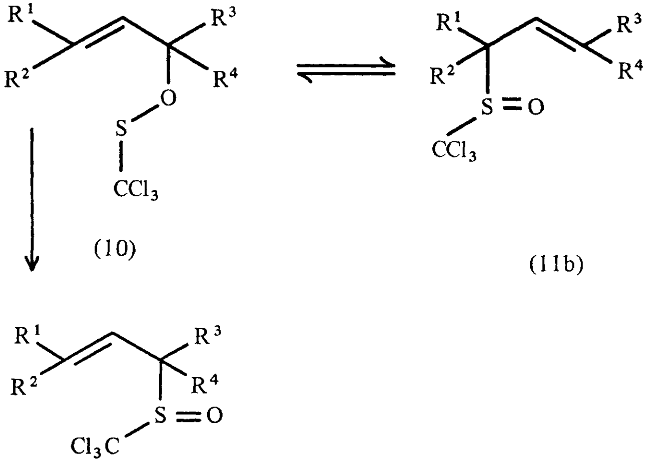


(9)

branched compound (8) to be an intermediate. The similarity of this reaction with the sulphenate (10)–sulphoxide(11) rearrangement[23] is clear and is illustrated in the following scheme.



(11a)

When disulphides prepared from a ^{35}S-labelled thiol and a different unlabelled thiol are reduced, both of the thiols obtained are equally radioactive. Wieland and Schwahn[24] propose an equilibrium between the linear disulphide and its branched isomer, *i.e.*:

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[23] S. Braverman and Y. Stabinsky, *Chem. Comm.*, 1967, 270; *Israel J. Chem.*, 1967, **5**, 125.
[24] T. Wieland and H. Schwahn, *Chem. Ber.*, 1956, **89**, 422.

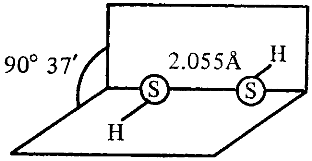
$$\begin{array}{cccc} R^1SS^*R^2 \rightleftharpoons & R^1S^*R^2 & \rightleftharpoons R^1SR^2 & \rightleftharpoons R^1S^*SR^2, \\ & \downarrow & \downarrow & \\ & S & S^* & \end{array}$$

to account for this phenomenon. Thus, all of this chemical evidence supports the view that disulphides (and presumably polysulphides) exist in solution in equilibrium with their branched isomers.

Physical measurements (that is dipole moment studies[25], Raman[26], and i.r. spectroscopic results[27]) all favour unbranched sulphur chains and these conclusions are supported by *X*-ray crystallographic data. In the following sections some of this physical evidence will be presented.

A. Disulphides.—(i) *Inorganic disulphides.* Linear disulphides are non-planar with an X—S—S—X dihedral angle of about 90°, although there are, understandably, considerable deviations from this average value. The 90° dihedral angle affords the molecule a configuration in which the repulsion between the sulphur lone pairs of electrons is at a minimum. There are thus two possible enantiomorphic forms of a disulphide.

Winnewasser and Haase[28] have recently reported electron diffraction measurements of dihydrogen disulphide (12). The data are typical of many disulphides. The compound disulphur difluoride[29] (13) has a comparable dihedral angle but a much shorter S—S bond length (1·888 Å) which is similar to that found for S_2 (1·889 Å); disulphur dichloride and disulphur dibromide also have short S—S bond lengths (1·97 Å and 1·98 Å respectively).[30] Kuczkowski[29] has suggested that this phenomenon may be due to efficient *pd* orbital overlap (possible with a dihedral angle of 90°) to give π bonding. This bonding might occur in the dihalogen disulphides, since the electronegative substituents may distort the sulphur 3*d* orbitals. A second isomer (14), which represents the stable branched form, can be isolated from the preparation of disulphur difluoride.



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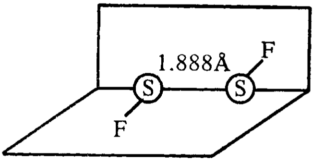

(13)

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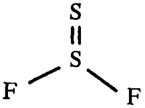
[25] C. C. Woodrow, M. Carmack, and J. G. Miller, *J. Chem. Phys.*, 1951, **19**, 951.
[26] F. Feher, G. Krause, and K. Vogelbruch, *Chem. Ber.*, 1957, **90**, 1570.
[27] L. Schotte, *Arkiv Kemi*, 1956, **9**, 361.
[28] M. Winnewasser and J. Haase, *Z. Naturforsch.*, 1968, **23a**, 56.
[29] R. L. Kuczkowski, *J. Amer. Chem. Soc.*, 1964, **86**, 3617.
[30] E. Hirota, *Bull. Chem. Soc. Japan*, 1958, **31**, 130.

The structures of the barium[31] and sodium salts[32] of tetrathionic acid (15) have been determined by *X*-ray crystallography. The barium salt crystallises in enantiomorphous space groups with only one enantiomorph/unit cell. The length of the middle S—S bond is 2·02 Å; the bond angle of the two divalent sulphur atoms is 103° and the dihedral angle is 90°. A related derivative, dimethanesulphonyl disulphide,[33] has similar structural properties.



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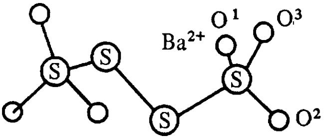

(15)

(ii) *Organic disulphides.* The structures of a large number of organic disulphides, including diphenyl disulphide,[34] 5,5′-dithiobis-(2-nitrobenzoic acid),[35] 2,2′-biphenyl disulphide,[36] L-cystine hydrochloride[37] and hydrobromide,[38] *NN*′-diglycyl-L-cystine dihydrate,[39] L-cystine,[40] formamidinium disulphide di-iodide monohydrate[41], and tetramethylthiuram disulphide,[42] have been determined by *X*-ray crystallography. The S—S bond distances, in all cases, lie between 2·03 and 2·05 Å, and the —C—S—S—C— dihedral angles vary from 74° to 105°. Distortion of the structures from the 90° dihedral angle is usually due to steric or electronic effects, *e.g.* the dihedral angle in di-t-butyl disulphide is larger than normal, due to some extent to the steric interactions of the bulky t-butyl groups.[43]

The n.m.r. spectra of the diphenyl disulphides (16, 17) change with temperature;[44] *o*-alkyl groups become magnetically non-equivalent at −27° in the case of (16) and at −55° for (17). These experimental results show that at low temperatures the rotation about the S—S bond is restricted, and hence the n.m.r. spectrum of each of the two enantiomers is observed. This explanation recalls the suggestion of Strem *et al.*,[45] that the unusually large specific rotation

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[31] O. Foss, S. Furberg, and H. Sachariasen, *Acta Chem. Scand.*, 1953, **7**, 230; 1954, **8**, 459

[32] O. Foss and A. Hordvik, *Acta Chem. Scand.*, 1958, **12**, 1700; 1964, **18**, 662.

[33] O. H. Sorum, *Acta Chem. Scand.*, 1953, **7**, 1.

[34] I. M. Dawson, A. McL. Mathieson, and J. M. Robertson, *J. Chem. Soc.*, 1948, 322.

[35] E. Shefter and T. I. Kalman, *Chem. Comm.*, 1969, 1027.

[36] I. Bernal and J. Ricci, *Acta Cryst.*, 1966, **21**, Suppl., A105.

[37] L. K. Steinrauf, J. Peterson, and L. H. Jensen, *J. Amer. Chem. Soc.*, 1958, **80**, 3835.

[38] J. Petersen, L. K. Steinrauf, and L. H. Jensen, *Acta Cryst.*, 1960, **13**, 104.

[39] H. L. Yakel, jun., and E. W. Hughes, *Acta Cryst.*, 1954, **7**, 291.

[40] B. M. Oughton and P. M. Harrison, *Acta Cryst.*, 1959, **12**, 396.

[41] O. Foss, J. Johnsen, and O. Tvedten, *Acta Chem. Scand.*, 1958, **12**, 1782.

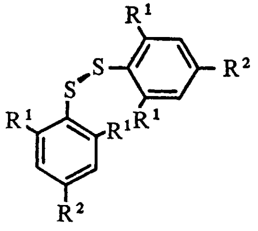
[42] K. Marøy, *Acta Chem. Scand.*, 1965, **19**, 1509.

[43] H. P. Koch, *J. Chem. Soc.*, 1949, 394.

[44] H. Kessler, A. Rieker, and W. Rundel, *Chem. Comm.*, 1968, **475**.

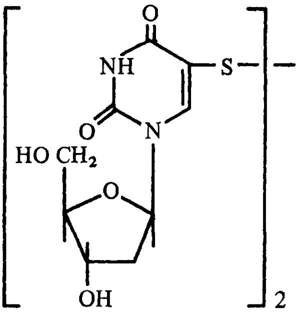
[45] J. Strem, Y. S. R. Krishna-Prasad, and P. J. A. Schellman, *Tetrahedron*, 1961, **13**, 176.

of L-cystine was due to the presence of relatively stable geometrical isomers. Similarly, the optical rotations of the anomeric deoxynucleosides (18, 19) vary



(16) $R^1 = R^2 = Pr^i$

(17) $R^1 = Et, R^2 = H$

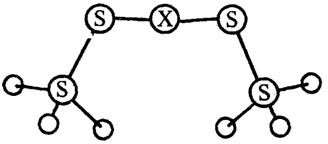


(18,19)

inversely with temperature, and *X*-ray crystallographic analysis indicates that rotation about the S—S bond is hindered by both the sugar and base moieties. The presence of thionucleotides has been reported in certain soluble ribonucleic acids, and, whilst the biological function of such nucleotides is unknown, the results discussed above suggest that they may introduce another element of asymmetry into these complex molecules.[46]

B. Trisulphides.—(i) *Inorganic trisulphides.* Trisulphides of the general formula X—SSS—X can exist as two stable rotational isomers. The X groups are rotated approximately 90° out of the plane of the sulphur atoms; rotation of the X groups on the same side of the plane gives the *cis* form, whereas rotation of these groups on the opposite side of the plane gives the *trans* isomer. The latter configuration exists in two enantiomorphous forms.

The pentathionate ion and the isomorphous monoseleno- and monotelluro-derivatives have been extensively investigated, and show both *cis* (20, X = S,



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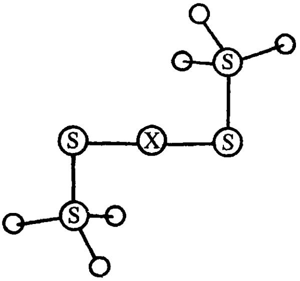

(21)

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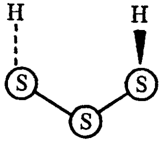
[46] C. Szantay, M. P. Kotick, E. Shefter, and T. J. Bardos, *J. Amer. Chem. Soc.*, 1967, **89**, 713; M. N. Lipsett, *J. Biol. Chem.*, 1967, **242**, 4067, and references cited therein.

Se, or Te) and *trans* (21, X = S, Se, or Te) isomers in the solid state. The nature of the cation and its bonding with the pentathionate ion largely determine the preferred configuration. Barium pentathionate[47] (20, X = S), its seleno (20, X = Se),[49] and telluro (20, X = Te)[48] analogues exist in the *cis* configuration, whereas the corresponding potassium salt exists in the *trans* form.[50] Cyanogen trisulphide[51] and the isomorphous cyanogen triselenide[52] are neutral and both occur in the *cis* configuration in the crystalline form. A detailed study of the i.r. and Raman spectra of dihydrogen trisulphide (22) by



(22)

Weiser and his co-workers,[53] resulted in the conclusion that the most stable conformer in solution is *cis*. The assigned conformation of (22) accounts for the hydrogen bonding which occurs in solution.

(ii) *Organic trisulphides.* The structures of di-2-iodoethyl trisulphide,[54] dibenzenesulphonyl and -toluene-*p*-sulphonyl trisulphides,[34] and perchlorodimethyl trisulphide[55] have been determined by *X*-ray crystallography. In all cases the sulphur chains are unbranched and in the *trans* configuration. Dipole moment (μ) and theoretical studies by Woodrow and his co-workers[25] concluded that the μ value for hexadecyl trisulphide ($\mu = 1{\cdot}63$) was indicative of a mixture of linear rotational isomers.

C. Tetra- and Poly-sulphides.—Tetrasulphides of the general structure X—S—S—S—S—X can exist in six non-superimposable forms, or three different pairs of enantiomers (*i.e.*, 23, 24, and 25). Woodrow, Carmack, and Miller[25] suggested their presence to account for the dipole moment of di-n-hexadecyl tetrasulphide. They concluded that the observed dipole moment ($\mu = 2{\cdot}16$) could be accounted for by assuming that equal proportions of the enantiomers were present in solution, but it is conceivable that unequal enantiomer

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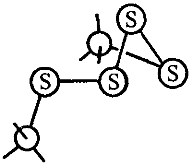
[47] O. Foss and O. Tjomsland, *Acta Chem. Scand.*, 1956, **10**, 424; 1958, **12**, 44.
[48] O. Foss and O. Tjomsland, *Acta Chem. Scand.*, 1958, **12**, 52.
[49] O. Foss and O. Tjomsland, *Acta Chem. Scand.*, 1954, **8**, 1701.
[50] K. Marøy, *Acta Chem. Scand.*, 1969, **23**, 338.
[51] F. Fehér and K. H. Linke, *Z. anorg. Chem.*, 1964, **327**, 151.
[52] O. Aksnes and O. Foss, *Acta Chem. Scand.*, 1954, **8**, 1787.
[53] H. Wieser, P. J. Kreuger, E. Muller, and J. B. Hyne, *Canad. J. Chem.*, 1969, **47**, 1633.
[54] I. M. Dawson and J. M. Robertson, *J. Chem. Soc.*, 1948, 1256.
[55] H. J. Berthold, *Z. anorg. Chem.*, 1963, **325**, 237.



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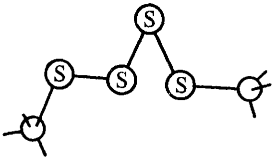

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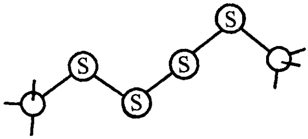
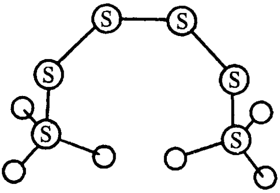


(25)

populations would also be possible. Examination of models shows that (23) is in the *cis,cis* configuration, (24) in the *trans,cis* (or *cis,trans*), and (25) in the *trans,trans* configuration. The former configuration is present in cyclo-octasulphur whilst the latter is the configuration of the helices of fibrous sulphur.

X-Ray crystallography of potassium barium hexathionate[56] shows that the molecule exists in the *cis,cis* form (26), presumably due to the bonding influence of the barium cation. By contrast, *trans*-dichlorobis-(ethylenediamine)cobalt(III) hexathionate dihydrate (27)[57] crystallises in the *trans,trans* configuration similar to fibrous sulphur and caesium hexasulphide.[58]



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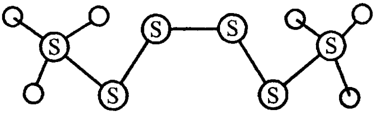
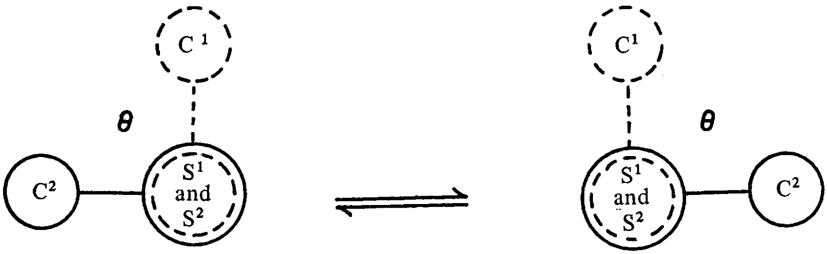


(27)

3 Organic Cyclic Polysulphides

A. Disulphides.—Cyclic disulphides of the general formula —C—SS—C— are composed of equimolar concentrations of the two enantiomeric forms (28)



(28) (29)

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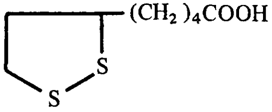
[56] O. Foss and K. Johnsen, *Acta Chem. Scand.*, 1965, **19**, 2207.
[57] O. Foss and K. Marøy, *Acta Chem. Scand.*, 1965, **19**, 2219.
[58] S. C. Abrahams and E. Grison, *Acta Cryst.*, 1953, **6**, 206.

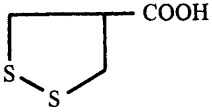
and (29). The two conformers are optical isomers, which are in equilibrium. The rate of interconversion of the two conformers depends on the height of the barrier hindering rotation about the S—S bond; in most cases the $\Delta G\dagger$ for the process is 10—15 kcal./mole.[59] This value is too small to allow separation of the enantiomers. The height of the barrier to free rotation varies with ring size, degree of unsaturation, substitution pattern, and the size of the angle θ (when $\theta = 90°$ the energy barrier has a minimum value).[60]

Lipoic acid (30), a substituted 1,2-dithiolan derivative, is the coenzyme



(30)

required for oxidative decarboxylation of pyruvate.[61] Its discovery prompted considerable interest in the dithiolan ring system. Calvin and his co-workers[62] showed that the disulphide was unbranched, thus negating previous work where a branched structure was proposed. The strain energy in dithiolan derivatives is considerable and has been estimated to be as high as 27 kcal/mole. Bergson and Schotte[63] calculated a minimum value of 16 kcal/mole, based on the *X*-ray diffraction analysis of the structure of 1,2-dithiolan-4-carboxylic acid (31).[64] The dihedral angle of this compound (31) was shown to be 26° 36′, which is



(31)

considerably less than the value (90°) for unstrained disulphides. Calvin has attributed this high strain to be a major factor in the mode of action of lipoic acid (30), which undergoes ready photolysis and reduction; the formation of the dithiol is essential for coenzyme activity.

The structures of several unsaturated five-membered cyclic disulphides, *e.g.*

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[59] G. Claeson, G. Androes, and M. Calvin, *J. Amer. Chem. Soc.*, 1961, **83**, 4357.

[60] M. Calvin, *Fed. Proc.*, 1954, **13**, 697.

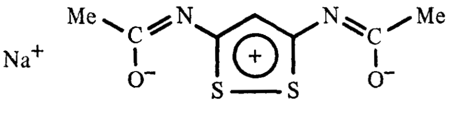
[61] L. J. Reed, in 'Advances in Enzymology', Interscience Publishers, New York, 1957, **18**, p. 319.

[62] J. A. Barltrop, P. M. Hayes, and M. Calvin, *J. Amer. Chem. Soc.*, 1954, **76**, 4348; M. Calvin and J. A. Barltrop, *ibid.*, 1952, **74**, 6153.

[63] C. Bergson and L. Schotte, *Acta Chem. Scand.*, 1958, **12**, 367.

[64] O. Foss and O. Tjomsland, *Acta Chem. Scand.*, 1957, **11**, 1426.

(32)[65] and (33),[66] have been determined by *X*-ray crystallography. These compounds are planar, with a high degree of stability, typical of aromatic systems; the aromaticity of these unsaturated rings is also dependent on the ring substituents. A recent review[67] discusses this aspect of valence-shell expansion in sulphur heterocycles.



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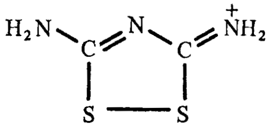
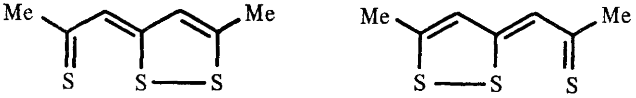


(33)

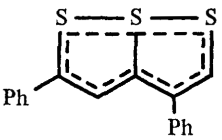
An interesting example of planar disulphides is found in the thiothiophthene system (34).[68] This compound is prepared by the reaction of a diacylacetone, *e.g.* diacetylacetone, with phosphorus pentasulphide. The structure of (34) was



(a) (b)

(34)

established by *X*-ray crystallography[69] and showed the two S—S distances are nearly equal with the S—S bond lengths, being about 2·36 Å. However, in the phenyl-substituted thiathiophthens (35 and 36) the S—S bond lengths are no longer equidistant, *e.g.* in the compound (35)[70] values of 2·297 and 2·355 Å were found and in (36)[71] the distances were 2·233 and 2·433 Å. It is possible



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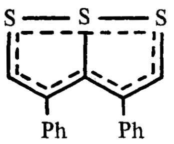

(36)

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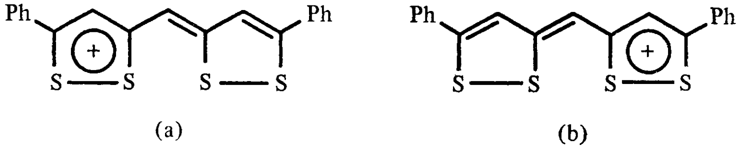
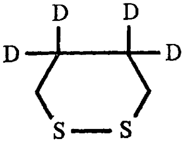
[65] A. Hordvik and E. Sletten, *Acta Chem. Scand.*, 1966, **20,** 2043.
[66] A. Hordvik and J. Sletten, *Acta Chem. Scand.*, 1966, **20,** 1907.
[67] W. G. Salmond, *Quart. Rev.*, 1968, **22,** 253.
[68] F. Arndt, P. Nacktwey, and J. Push, *Ber.*, 1925, **58,** 1638.
[69] S. Bezzi, M. Mammi, and C. Carbuglio, *Nature*, 1958, **182,** 247.
[70] A. Hordvik, *Acta Chem. Scand.*, 1968, **22,** 2397.
[71] P. L. Johnson and I. C. Paul, *Chem. Comm.* 1969 1014.

that the latter result is due to the non-planarity of the phenyl substituents with the thiathiophthen nucleus. The kind of resonance hybrid found in the substituted thiathiophthens also occurs in the system containing four thioketone groups, (*e.g.* 37a, 37b).[72]



(37)

From the foregoing discussion concerning five-membered ring disulphides, it will be gathered that only small deviations from planarity occur, and that the resulting strain accounts for some of the interesting chemistry of these compounds. Turning now to six-membered ring disulphides, it is apparent from an examination of models that the S—S dihedral angle is about 60° and hence the ring system can exist in two enantiomorphic forms. The existence of such enantiomers was first shown by Calvin; interconversion between the optical antipodes of [4,4,5,5-$^2H_4$]-1,2-dithian (38) and 3,3,6,6-tetramethyl-1,2-dithian (39) was studied by the n.m.r. technique. The n.m.r. spectra of both (38) and (39)



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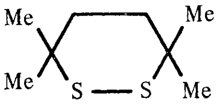

(39)

were temperature dependent (Figure 1). At room temperature the methylene protons of (38) appear as a singlet; on cooling, the signal broadens, and at temperatures below −50° the signal appears as an AB quartet. The AB pattern is typical of the coupling of magnetically non-equivalent methylene protons. This data was plausibly interpreted to support the notion that these molecules exist as enantiomeric conformers with their interconversion at −65° being slow. The interconversion rate constant (k) can be calculated from the n.m.r. data[73] since $k = \pi \Delta\nu_{AB}\sqrt{2}$, and substitution of this value into Eyring's equation gives a free energy of inversion of 11·6 kcal/mole. For the dimethyl compound (39), the methyl resonances appear as a singlet at room temperature but at lower temperatures the chair–chair interconversion is slow and two singlets for

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[72] E. Klinsberg, *J. Heterocyclic Chem.*, 1966, **3**, 243.

[73] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, 1956, **25**, 1228.

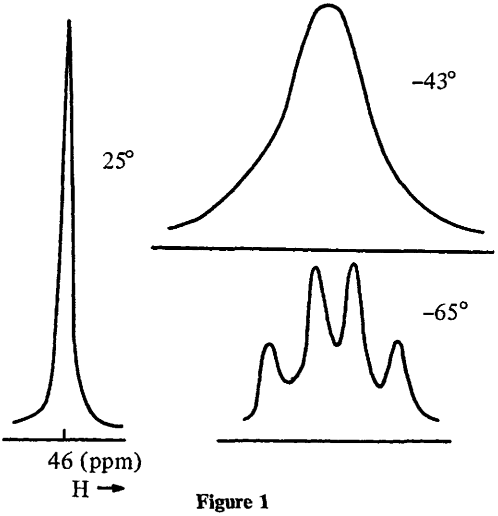
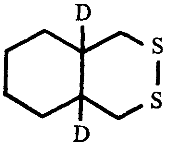


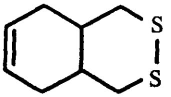
Figure 1

the axial and equatorial methyl groups are observed. The $\Delta G^{\dagger}$ for conformer interconversion for (39) is 13·8 kcal/mole.

This n.m.r. procedure has been extensively used (notably by Lüttringhaus and his colleagues[74]) in studies of a large number of cyclic disulphides (and polysulphides) in order to determine the effect of structure on the conformational inversion process. The $\Delta G^{\dagger}$ values obtained for the bicyclic compounds (40) and (41) were 14·4 and 12·5 kcal/mole respectively whereas the monocyclic



(40)



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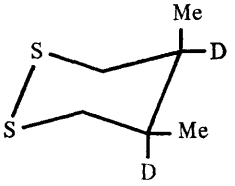

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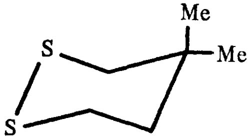

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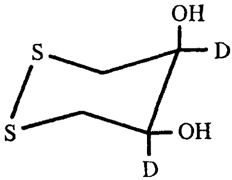

(44)

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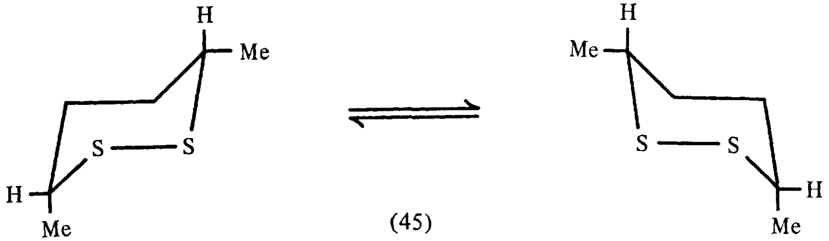
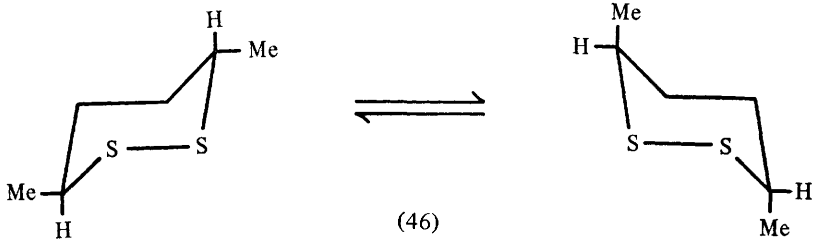
[74] (*a*) A. Lüttringhaus, S. Kabuss, W. Maier, and H. Friebolin, *Z. Naturforsch.*, 1961, **16b**, 761; (*b*) S. Kabuss, Dissertation, University of Freiburg, 1962; (*c*) H. Freibolin, Dissertation, University of Freiburg, 1963; (*d*) U. Hess, Dissertation, University of Freiburg, 1965.

disulphides (42), (43), and (44) had $\Delta G^\dagger$ values of 12·3, 12·6, and 12·5 kcal/mole respectively. The effect of substituents on the free energy of conformer inversion is illustrated by the n.m.r. studies of *cis*- and *trans*-3,6-dimethyl-1,2-dithians.[74d] At 25° the *cis* isomer (45), with an axial and equatorial methyl group, gives a


(45)

sharp doublet at τ 7·5 for the methylene protons, indicating rapid inversion, On the other hand, the *trans* isomer (46), with two equatorial methyl substituents.

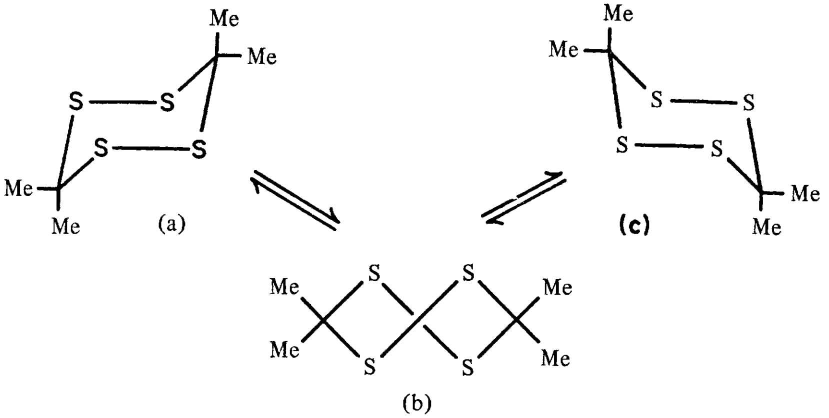

(46)

exhibits a complex pattern for the methylene signals and thus appears to be fixed into a single conformation. This would be expected since inversion would give the energetically unfavourable diaxial conformer. Bushweller[75] has examined tetramethyl-*s*-tetrathian (47), whose n.m.r. spectrum showed three methyl signals at 0°; two smaller peaks of equal area occurred at τ 8·47 and 7·97 and a larger peak at τ 8·32; only one signal was observed at higher temperatures, at τ 8·37. The data was rationalised by assigning the two smaller peaks to the axial and equatorial methyl groups of the rigid chair conformers (47a and 47c) and the larger resonance to the more flexible twist-boat conformer (47b). The substitution of four sulphur atoms for carbon in the molecule thus allows the relatively strain-free twist-boat conformer to predominate over the usually more stable chair form.

X-Ray crystallographic studies of the structure of cyclic disulphides have provided data in agreement with that obtained by spectroscopic investigations of the same compounds in solution. *X*-Ray crystallographic analysis[76] of

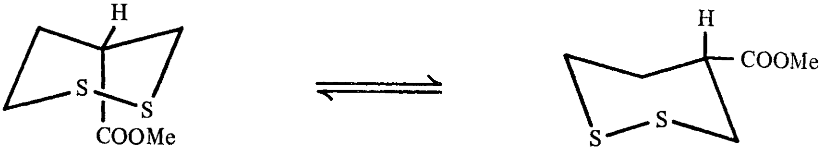
[75] C. H. Bushweller, *J. Amer. Chem. Soc.*, 1967, **89**, 5978; *ibid.*, **91**, 6019.

[76] A. Fredga, *Acta Chem. Scand.*, 1958, **12**, 891.



(47)

etramethyl-*s*-tetrathian (47) shows that the compound exists in the boat form which is energetically similar to the twist-boat conformer which predominates in solution. The structure of 1,2-dithian-3,6-dicarboxylic acid was determined by Foss and co-workers;[77] the S—S bond distance was 2·07 Å and the dihedral angle was 60°. The molecules were arranged in infinite chains held together by hydrogen bonding between the carboxyl groups. The chains consist of alternating right- and left-handed conformers, and thus the data reflect in a static sense the dynamic equilibrium in solution.



(48)

To summarise; in most of the six-membered cyclic disulphides discussed so far, the low energy barrier to rotation (~10 kcal/mole) does not allow the separation of optical antipodes, although their presence may be inferred from n.m.r. data. If, however, there is an additional asymmetric centre in the molecule it is possible that unequal populations of enantiomers exist. Thus Claeson[78] showed that at −65° the axial and equatorial carboxymethyl conformers of methyl (*R*)-(−)-1,2-dithian-4-carboxylate (48) were present in

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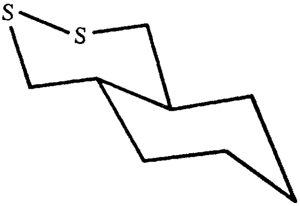
[77] O. Foss, K. Johnsen, and T. Reistad, *Acta Chem. Scand.*, 1964, **18**, 2345.

[78] G. Claeson, personal communication; Laboratory of Chemical Biodynamics Quarterly Report, Lawrence Radiation Laboratory (LCBQ-16, 1967, 5).

the ratio of 1 : 3. The more stable equatorial form predominates at low temperatures; at higher temperatures the two conformers approach equimolar concentration.

This is also reflected in the optical rotatory dispersion properties of (49), which vary markedly with temperature. Its c.d. dispersion curve has a Cotton effect at 286 nm coincident with the u.v. absorption maximum associated with the disulphide group.[79] When the c.d. of a series of disulphides is examined [open chain (λ_{max} 250 nm; θ = dihedral angle = 90°), 1,2-dithians (λ_{max} 255 nm; θ = 60°), 1,2-dithiolans (λ_{max} 330 nm; θ = 27°), gliotoxin (52; λ_{max} 340 nm; θ = 14°)[82a]], a relationship between θ and the lowest energy transition in the u.v. is observed. C.d. data on three cyclic disulphides [(9*S*,10*S*)-*trans*-2,3-dithiadecalin (49), (4*R*,5*R*)-4,5-isopropylidenedioxy-1,2-dithian (50), and the corresponding diol (51)] have been reported.[80] Using the Cahn, Ingold, Prelog[81] rules, compound (49) has left-handed helicity whilst the other two compounds are right-handed. The c.d. and u.v. absorption of the lowest energy disulphide absorption band occurs at 285—290 nm for all, but the dithiadecalin (49) has a negative c.d. band whereas the two dithians (50, 51) have positive c.d. bands. It was concluded that 'in simple 1,2-dithian ring systems a positive c.d. band corresponding to the lowest frequency u.v. absorption band of the disulphide



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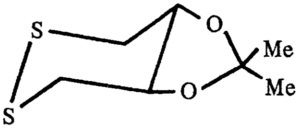

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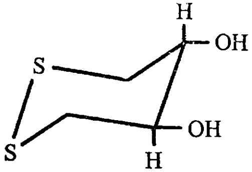

(51)

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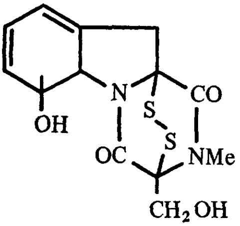
[79] G. Bergson, G. Claeson, and L. Schotte, *Acta Chem. Scand.*, 1962, **16**, 1159.
[80] M. Carmack and L. A. Neubert, *J. Amer. Chem. Soc.*, 1967, **89**, 7134.
[81] R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem. Internat. Edn.*, 1966, **5**, 385.
[82] (*a*) A. F. Beecham, J. Fridrichsons, and A. McL. Mathieson, *Tetrahedron Letters*, 1966, 3131; (*b*) J. Fridrichsons and A. McL. Mathieson, *Acta Cryst.*, 1967, **23**, 429.

group (in the case of 1,2-dithians in the range 280—290 nm) is associated with a right-handed (*P*) screw sense of the helix containing the atoms C—S—S—C, and a negative c.d. band is associated with a left-handed (*M*) screw sense of the helix'.

The structures of the naturally-occurring epidithiadioxopiperazines have been determined by *X*-ray crystallography. The absolute stereochemistry of gliotoxin (52),[82b] sporidesmin (53, $x = 2$),[83] and acetylaranotin (54)[84] is the same at the asymmetric centres of the dioxopiperazine rings. The conformation of the piperazine ring in gliotoxin (52) and sporidesmin (53, $x = 2$) is the boat form, due to the constraint imposed by the sulphur bridge; in acetylaranotin the skewed-boat conformation is preferred as a result of the additional strain imposed by the fused pyrrolidine rings. The circular dichroic dispersion of several of these compounds[85] shows a negative band at about 340 nm, thus indicating a



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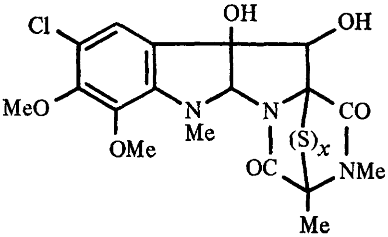

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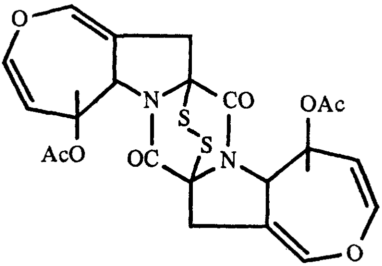

(54)

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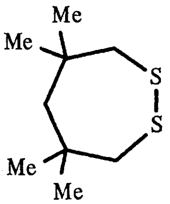
[83] J. Fridrichsons and A. McL. Mathieson, *Acta Cryst.*, 1965, **18**, 1043.

[84] D. B. Cosulich, N. R. Nelson, and J. H. van den Hende, *J. Amer. Chem. Soc.*, 1968, **90**, 6519.

[85] H. Herrmann, R. Hodges, and A. Taylor, *J. Chem. Soc.*, 1964, 4315; A. F. Beecham and A. McL. Mathieson, *Tetrahedron Letters*, 1966, 3139; R. Nagarajan, N. Neuss, and M. M. Marsh, *J. Amer. Chem. Soc.*, 1968, **90**, 6518.

left-handed helicity of the disulphide-bridged system. Thus the c.d. results and the *X*-ray data are in complete accord.

N.m.r. studies of the conformations of seven-membered rings containing a vicinal disulphide group have been reported.[86] The n.m.r. spectrum of the disulphide (55) at 25° shows a singlet for the methylene protons at positions 3 and 7. At −110° the signal appears as an AB quartet, indicating the magnetic non-equivalence of the methylene hydrogens. In the deuteriated compound (56) at −110° the 5-*gem*-dimethyl group and the 4- and 6-methylene protons appear as 2 singlets and a quartet respectively. However, an additional signal is also present at low temperatures and this has been attributed to a twist-boat form of the seven-membered ring. The $\Delta G^\dagger$ values for (55) and (56) are 11 and about 9 kcal/mole respectively, which are significantly higher than those for the corresponding cycloheptane analogues.



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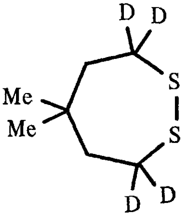
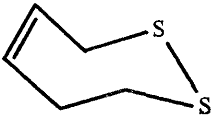


(56)

In cycloheptene vicinal disulphides, three main conformations are present, the chair form (57), the boat form (58), and the twist-boat form (59). The chair conformer is rigid whereas the boat and twist-boat forms are interconvertible. The n.m.r. spectrum of (60, R = H) below 0° shows a quartet for the



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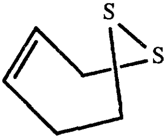

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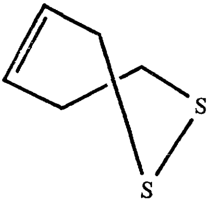

(59)

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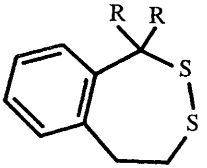
[86] S. Kabuss, A. Lüttringhaus, H. Friebolin, and R. Mecke, *Z. Naturforsch.*, 1966, **21b**, 320; H. Friebolin and S. Kabuss, in 'Nuclear Magnetic Resonance in Chemistry', ed. Biagio Pesce, Academic Press, New York, 1965, p. 125; K. von Bredow, Dissertation, University of Freiburg, 1968.



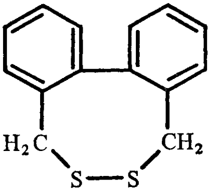
(60)

3-methylene group as well as a singlet in the ratio 7 : 3. The former signal corresponds to the axial–equatorial protons of the chair conformer whereas the singlet is attributed to the more flexible conformers. The overall equilibrium process may proceed as shown:

$$\begin{tikzcd}
 & \text{twist-boat} \arrow[dl, shift left] \arrow[dr, shift left] & \\
\text{chair} \rightleftharpoons \text{boat} \arrow[ur, shift left] \arrow[dr, shift left] & & \text{boat} \rightleftharpoons \text{chair} \arrow[ul, shift left] \arrow[dl, shift left] \\
 & \text{twist-boat} \arrow[ul, shift left] \arrow[ur, shift left] &
\end{tikzcd}$$

The $\Delta G^{\dagger}$ for inversion for (60) was 13·5 kcal/mole, whereas the $\Delta G^{\dagger}$ for pseudorotation (boat $\rightleftharpoons$ twist-boat) was 10·4 kcal/mole. When the 3-methylene protons are replaced with a *gem*-dimethyl group (60, R = Me) a $\Delta G^{\dagger}$ for inversion of 12·1 kcal/mole is observed. This value is about 1·4 kcal/mole less than (60, R = H) but about 1 kcal/mole greater than the comparable effect of methyl-group substitution in the corresponding carbocyclic analogues.

The preparation and properties of 4,5,6,7-dibenzo-1,2-dithiacyclo-octadiene (61) have been described.[87] Its n.m.r. spectrum showed an AB quartet at τ 6·13 (J_{AB} = 14 Hz, $\Delta\nu_{AB}$ = 60 Hz) at 25° and even at 130°. The estimated $\Delta G^{\dagger}$ of inversion (28·8 kcal/mole) was of sufficient magnitude to allow the first



(61)

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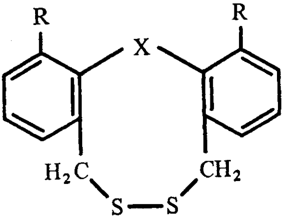
[87] A. Lüttringhaus, U. Hess, and H. J. Rosenbaum, *Z. Naturforsch.*, 1967, **22b**, 1296; A. Lüttringhaus and H. J. Rosenbaum, *Monatsh.*, 1967, **98**, 1323; H. J. Rosenbaum, Dissertation, University of Freiburg, 1968.

separation of the optical isomers of a vicinal disulphide. The right-handed (*P*) form had a positive c.d. band at 244 nm, whilst the left-handed (*M*) form had a negative band, in accord with the conclusions of Carmack and Neubert (see above).

Several nine-membered rings containing vicinal disulphides have been synthesised by Eckhardt.[88] At low temperatures, the ether (62, R = H, X = O)



(62) (X = O, CH_2, S, SO_2)

showed signals attributable to both the chair and boat forms. At −50° an AB quartet at τ 6·07 (J_{AB} = 14 Hz, $\Delta\nu_{AB}$ = 14 Hz) and a weaker AB quartet at τ 5·91 (J_{AB} = 14 Hz, $\Delta\nu_{AB}$ = 50 Hz) were observed for the chair and boat conformers respectively. Similar results were obtained for other members of the series (62, R = H, X = CH_2, S, SO_2). The substituted compound (62, R = Me, X = SO_2) gave a considerably higher $\Delta G^\dagger$ value (19·7 kcal/mole) probably because the methyl groups cause considerable interaction in the chair form. Thus the AB quartet observed at 35° is probably due to the boat conformer.

(i) *Macrocyclic disulphides.* A large number of macrocyclic disulphide natural products are known. Those whose structures have been determined include oxytocin (*20*), vasopressin (*20*), insulin (*20*, *85*), ribonuclease (*26*, *187*), hen's egg-white lysozyme (*53*, *368*), papain, and chymotrypsinogen A.[89] (Figures in parenthesis indicate the smallest and largest numbers of atoms in the disulphide rings of the molecules.) The physiological properties of these molecules depend on the stereochemistry of the disulphide bonds since the topography of the peptide is determined by their presence. There are four disulphide bridges in hen's egg white lysozyme and their chirality has been determined. It is of interest that, whilst all the asymmetric carbon centres have the same (L) configuration, the asymmetric disulphides are present in both stereoisomeric forms; the disulphides linking amino-acid residues 64→80 and 76→94 are the mirror images of the bridges linking 6→127 and 30→115. The disulphide bridge between residues 6 and 127 is not required for biological activity; however, when

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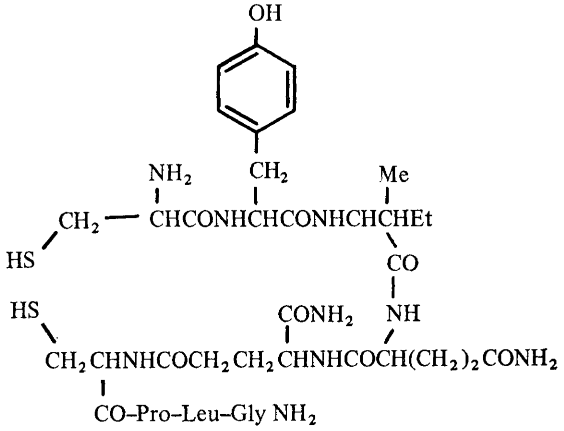
[88] P. Eckardt, Dissertation, University of Freiburg, 1968.

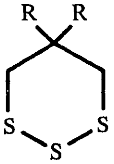
[89] D. G. Smyth, *Ann. Reports*, 1964, **61**, 507; 1965, **62**, 488.

that linking residues 30 and 115 is also broken, the molecule is no longer biologically active.[90,91] The first four polypeptides mentioned above have been synthesised. The formation of the disulphide groups from the corresponding dithiols is usually the last step of the synthesis but yields at this step have been very low. The ease of cyclisation may be dependent on the conformation of the ring, *e.g.* the cyclisation of the linear peptide (63) to give a 22-membered ring proceeds in better yield than the cyclic oxidation of reduced oxytocin, where a 20-membered ring is formed.[92]



(63)

B. Trisulphides.—Conformational equilibria in six- and seven-membered rings containing the 1,2,3-trithia-group have been studied by n.m.r. spectroscopy.[86, 93, 94] The $\Delta G^\dagger$ values for the six-membered trithians (64, R = H, Me)



(64)

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[90] C. C. F. Blake, G. A. Mair, A. C. T. North, D. C. Philips, and V. R. Sarma, *Proc. Roy. Soc.*, 1967, *B*, **167**, 372.

[91] P. Jollies, *Proc. Roy. Soc.* 1967, *B*, **167**, 350.

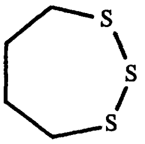
[92] C. Ressler and V. du Vigneaud, *J. Amer. Chem. Soc.*, 1957, **79**, 4511.

[93] S. Kabuss, A. Lüttringhaus, H. Friebolin, H. G. Schmid, and R. Mecke, *Tetrahedron Letters*, 1966, 719.

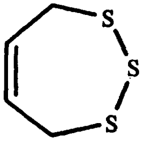
[94] B. Milligan and J. M. Swan, *J. Chem. Soc.*, 1965, 2901.

were 13·2 and 14·7 kcal/mole respectively, which is 1·6 and 1·1 kcal/mole greater than the value for the corresponding dithians. These values reflect the greater rigidity imposed on the ring when a sulphur atom is substituted for a methylene group.

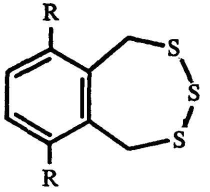
The seven-membered ring trisulphides (65, 66, 67, R = H) give $\Delta G^\dagger$ values



(65)



(66)



(67)

(6·7, 8·9, and 17·4 kcal/mole respectively) for inversion that are also higher than the values obtained for the corresponding carbocyclic compounds. The n.m.r. spectrum of the trithia-compound (67, R = H) is complex (Figure 2). At 153° a singlet is observed for the protons of the methylene groups, but at 25° the signal assigned to the methylene hydrogens appears as an AB quartet at τ 5·70

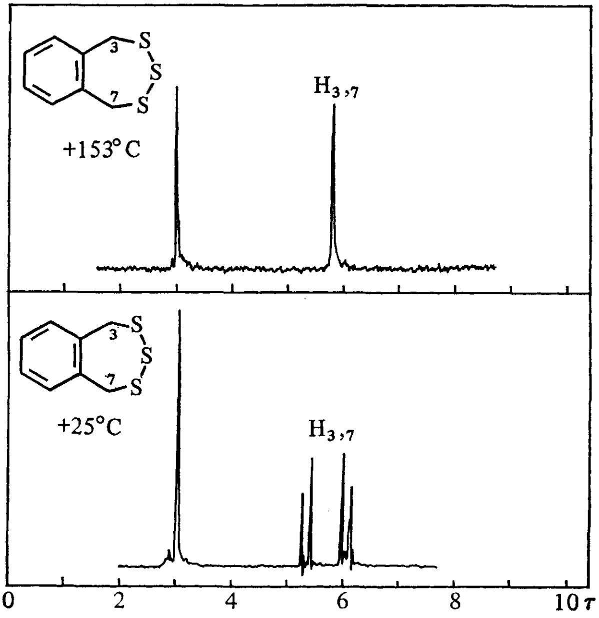


Figure 2

(chair conformer) and a singlet at τ 6·0 in the ratio 17 : 3. At $-60°$ the peak at τ 6·0 is broadened and is assigned to the flexible twist-boat or boat conformer, probably representing an average value. von Bredow[86] has prepared several substituted 1,2,3-trithia-5,6-benzocycloheptenes (67, R = OMe, Me, Ph) whose n.m.r. spectra indicate both the chair and boat forms. The $\Delta G^\dagger$ values are high ($\Delta G^\dagger$ 19·8, 20·0, and 21·2 kcal/mole for 67, R = OMe, Me, and Ph respectively). For the dimethyl derivative (67, R = Me) the resonances due to the methyl groups and aromatic protons appear as two singlets whose ratio is proportional to the conformer population.

Sporidesmin E (53, $x = 3$)[95] is a toxic metabolic product of *Pithomyces chartarum.* It can be converted into sporidesmin (53, $x = 2$) and it is probably a 3,6-epitrithia-2,5-dioxopiperazine. Its n.m.r. spectrum is complex (Figure 3a) but it is not a mixture of isomers because the relative intensity of the peaks in

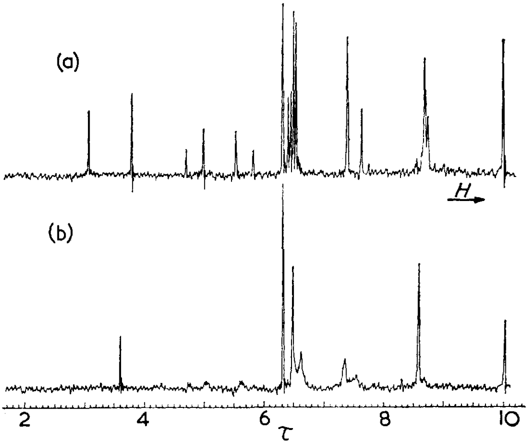


Figure 3

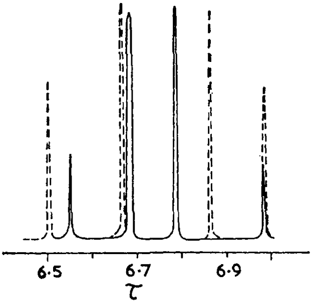


Figure 4

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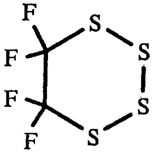
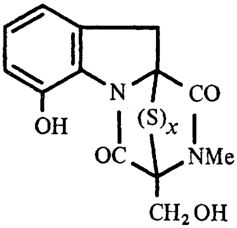
[95] R. Rahman, S. Safe, and A. Taylor, *J. Chem. Soc.* (*C*), 1969, 1665.

the spectrum depends on the solvent used (Figure 4) and also on temperature (Figure 3b). A model of an 3,6-epitrithiadioxopiperazine reveals that the unbranched sulphur bridge can exist in two conformations, depending on the position of the central sulphur atom. In one case this is towards the centre of the open-book-like molecule and in the other at the edge of the right-hand page. From the intensity of the *N*-methyl peaks in the n.m.r. spectrum, the ratio of the two principal conformers was calculated to be 2 : 3 in chloroform but 1 : 3 in methanol. This change in conformer population is also reflected in the c.d., in which the asymmetric transition at 306 nm in chloroform is shifted to 312 nm in methanol. Thiadehydrogliotoxin (69, $x = 3$) has been prepared[21] and has similar properties.

C. Tetrasulphides.—Few cyclic tetrasulphides are known. The perfluoro-compound (68)[96] has a complex ^{19}F n.m.r. spectrum which showed an AB quartet, each line of which was further split into five peaks. Thus several conformers probably exist in solution. Sporidesmin G (53, $x = 4$) and dithiadehydrogliotoxin (69, $x = 4$) have been prepared from sporidesmin and dehydrogliotoxin respectively.[21] Their n.m.r. spectra suggest that only one conformation is present.



(68)



(69)

D. Penta- and Other Poly-sulphides.—The compounds S_5CH_2 and S_7CH_4 are known, but little information on their chemistry is available. Recently, compounds having two tetrasulphide bridges linking the 1,1′- and 4,4′-positions of two benzene rings have been described.[97] Such compounds, *e.g.* (70), are thought to be stabilised by charge-transfer interactions between alkoxy substituents *ortho* to the polysulphide chains.

4 Inorganic Cyclic Polysulphides

A number of cyclic compounds of sulphur are known in which none of the atoms in the ring are carbon. Some of these compounds have been known for many

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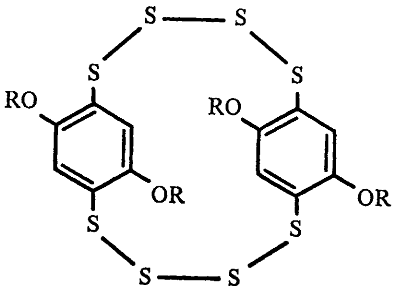
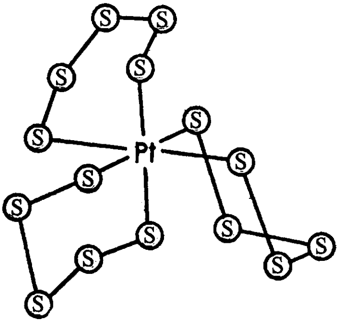
[96] C. G. Krespan and W. R. Brasen, *J. Org. Chem.*, 1962, **27**, 3995.
[97] Z. S. Ariyan and R. L. Martin, *Chem. Comm.*, 1969, 847.



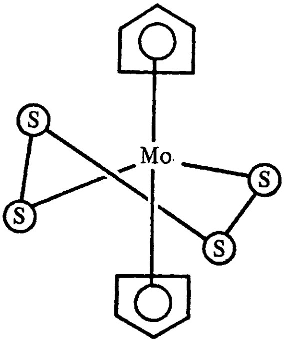
(70)

years (*e.g.* 71)[98] but their structural recognition has been the result of improved techniques of *X*-ray crystallography.

A few five-membered rings have been proposed. These compounds are the heterocyclic equivalents of the still unknown cyclopentasulphur. The product obtained[99] from the reaction of dichloro-bis-cyclopentadienylmolybdenum with ammonium pentasulphide was assigned the structure (72) on the basis of



(71)



(72)

analysis and the equivalence of the cyclopentadienyl protons in the n.m.r. spectrum. The dianil of diacetyl and cystinamine forms a tetraco-ordinated complex with Ni^{2+}, and Egen and Krause[100] pointed out that the geometry of the sulphur ligands was such that they might be expected to react with disulphur dichloride to give a five-membered 2,3,4,5-tetrathianickel(II) ring. One of the products isolated from such a reaction had the composition, $C_8H_{14}Cl_2N_2Ni^{2+}S_4$,

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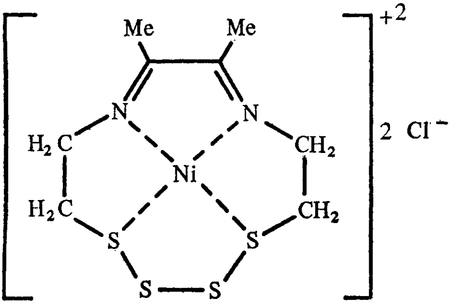
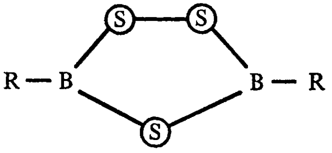
[98] K. A. Hofmann and F. Höchtlen, *Ber.*, 1903, **36**, 3090.
[99] H. Kopf, *Angew. Chem. Internat. Edn.*, 1969, **8**, 962.
[100] N. B. Egen and R. A. Krause, *J. Inorg. Nuclear Chem.*, 1969, **31**, 127.

expected for such a five-membered ring system (73). A number of 2,3,5-trithiadiboralanes (74, R = Br, I, Ph) have been prepared[101] whose ^{11}B n.m.r. spectra suggest that the boron atoms are identical and that the ring is planar.

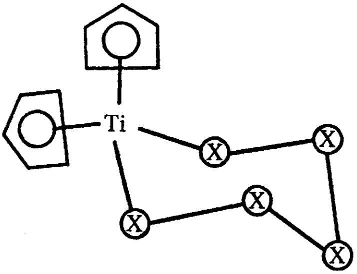


(73)

A number of six-membered ring systems have now been synthesised. Two groups of workers[102, 103] reported the preparation of a dicyclopentadienyltitanium(IV) pentasulphide (75, X = S) having a six-membered ring of five sulphur atoms and a titanium atom. The n.m.r. spectrum of this compound at 30° shows two sharp singlets at τ 3·58 and τ 3·90 for the cyclopentadienyl ligands of the chair conformer. At higher temperatures the rate of conformational inversion increases, and at 120° a single peak at τ 3·74 was observed. These results are very similar to those reported above for the organic cyclic polysulphides. An *X*-ray crystallographic analysis of the platinum complex



(74)



(75) X = S, Se

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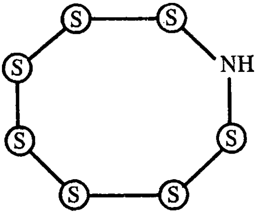
[101] M. Schmidt and W. Siebert, *Angew. Chem. Internat. Edn.*, 1964, **3**, 637; *Z. anorg. Chem.*, 1966, **345**, 87; *Chem. Ber.*, 1969, **102**, 2752.

[102] H. Kopf, B. Block, and M. Schmidt, *Chem. Ber.*, 1968, **101**, 272.

[103] R. Ralea, C. Ungurenasu, and S. Cihodaru, *Rev. Roumaine Chim.*, 1967, **12**, 861.

$(NH_4)_2PtS_{15},2H_2O$ (71)[104] has been reported. The anion is an octahedrally co-ordinated complex having S—S—S bond angles of average value 104° 48′ and S—Pt—S bond angles of 92° 48′. Thus three chains of sulphur atoms are co-ordinated to the platinum, making three six-membered rings each in a chair conformation.

Several polythiaimides have been described, prepared by the action of ammonia on a polysulphur dichloride.[105] The structures of heptathiaimide (76) and hexathiadi-imide (77) were established by *X*-ray crystallography.[106] Their structures are analogous to cyclo-octasulphur, sulphur atoms being replaced by NH groups. The di-imide studied by Weiss was the symmetrical isomer, but the other isomeric di-imides,[107] some of the tri-imides[108], and the alternating tetraimide are all known.[109] In most cases the S—S—S bond angles are about 107° and the S—NH—S angles about 120°. The bicyclic polythianitride (78) has been synthesised[110] by reaction of hexathia-1,3-di-imide with pentasulphur dichloride.



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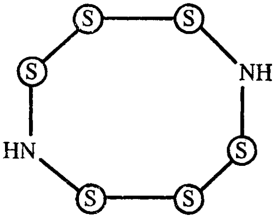

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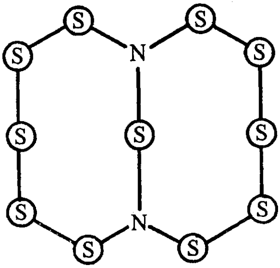

(78)

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[104] P. E. Jones and L. Katz, *Chem. Comm.*, 1967, 842.
[105] J. Weiss, *Angew. Chem.*, 1959, **71**, 246.
[106] J. Weiss, *Z. anorg. Chem.*, 1960, **305**, 190.
[107] H. G. Heal, *Nature*, 1963, **199**, 371; P. Tavs, H.-J. Schulze-Steinen and J. E. Colchester, *J. Chem. Soc.*, 1963, 2555.
[108] H. Garcia-Fernandez and H. Heal, *Compt. rend.*, 1968, **266**, *B*, 1449; H. Heal and J. Kane, *Nature*, 1964, **203**, 971.
[109] M. Goehring, *Quart. Rev.*, 1956, **10**, 437.
[110] H. G. Heal, M. S. Sahid, and H. Garcia-Fernandez, *Chem. Comm.*, 1969, 1063.

5 Conclusions

It is clear that only human ingenuity prevents the development of a chemistry of sulphur quite as subtle and complex as the better known chemistry of carbon. We might therefore extrapolate the current dogmas of astronomy and biochemistry, and suggest the thaumaturgical presence, perhaps on a remote heavenly body, of a self-replicating system based on sulphur!