The Chemistry of Homonuclear Sulphur Species

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1 Introduction

The occurrence of sulphur is widespread, and both the element and its compounds find a wide range of applications, *e.g.* in agriculture, in the glass/ceramics industry, and as insulators and lubricants. The present glut of sulphur on the world market results largely from the processing of natural gas and is certain to increase when stricter emission control standards come into effect. This situation has led to an intensive search for new technological applications of sulphur, *e.g.* in concrete, for road paving, and as insulators. In view of this activity a review of the extensive chemistry of homonuclear sulphur species seems timely. It has recently been established that the colours produced in liquid sulphur above 250 °C, by sulphur in highly acidic media, and by sulphur in basic solvents are due to small sulphur allotropes (S_3 and S_4), sulphur cations, and sulphur radical anions, respectively. Furthermore, the synthesis of sulphur rings other than S_8 has been achieved. This Review will focus attention on these new facets of the chemistry of elemental sulphur, particularly as they relate to sulphur chemistry generally. An earlier Review described the more than thirty solid allotropes of sulphur,[1] and three recent books give an account of various aspects of the chemistry of elemental sulphur.[2-4]

2 Atomic Sulphur

Photolysis of carbonyl sulphide either in the gas phase[5,6] or in solution[7] is the most useful source of singlet sulphur atoms, $S(^1D)$, while photolysis of carbon disulphide produces sulphur atoms in their ground state, $S(^3P)$. The spin-forbidden conversion $S(^1D) \rightarrow S(^3P)$ is catalysed by all solvents.[7] A unique feature of the extensively studied reactions of sulphur atoms with olefins is the stereospecific addition of $S(^3P)$,[8] which occurs in reactions with the following three pairs of olefins, *cis-* and *trans-*but-2-ene, *cis-* and *trans-*1,2-dichloro- and -1,2-

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[1] B. Meyer, *Chem. Rev.*, 1964, **64**, 429.
[2] 'Elemental Sulphur', ed. B. Meyer, Interscience, New York, 1965.
[3] 'Inorganic Sulphur Chemistry', ed. G. Nickless, Elsevier, Amsterdam, 1968.
[4] 'Sulphur Research Trends', Advances in Chemistry Series, No. 110, American Chemical Society, Washington D.C., 1972.
[5] H. E. Gunning and O. P. Strausz, *Adv. Photochem.*, 1966, **4**, 143.
[6] O. P. Strausz in 'Organosulphur Chemistry', ed. M. J. Janssen, Interscience, New York, 1967, p. 11.
[7] K. Gollnick and E. Leppin, *J. Amer. Chem. Soc.*, 1970, **92**, 2217, 2221.
[8] O. P. Strausz, I. Safarik, W. B. O'Callaghan, and H. E. Gunning, *J. Amer. Chem. Soc.*, 1972, **94**, 1828.

difluoro-ethylene. Unlike $S(^1D)$ atoms, triplet sulphur atoms do not undergo insertion reactions with paraffins either in solution or in the gas phase at 25 °C,[5] but recombine to form S_2 molecules which polymerize to elemental sulphur.[7,9]

3 Small Sulphur Allotropes—S_2, S_3, S_4, S_5

S_2 is an important constituent of sulphur vapour, especially at high temperatures and low pressures. The purple solid obtained by quenching hot sulphur vapour in liquid nitrogen probably contains S_2,[10] but the expected Raman-active band at 668 cm^{-1} is not observed.[11] Like O_2, S_2 has a triplet ground-state configuration $^3\Sigma_g^-$.[12] The value of 422.6 ± 4.2 kJ mol^{-1} for $D_0{}^0(S_2)$ obtained by spectroscopic, thermochemical, and photoionization measurements is indisputable.[13] The weakly paramagnetic solutions of sulphur in carbon disulphide have been attributed to S_2,[14] although the free S_2 molecule does not exist at room temperature. It can, however, be stabilized by co-ordination to a transition metal, *e.g.* $(\pi\text{-}C_5H_5)_2Nb(S_2)X$ (X = halogen),[15] $[Ir(S_2)(Ph_2PCH_2CH_2PPh_2)_2]Cl,CH_3CN$.[16] The iridium complex is prepared under mild conditions from cyclo-S_8 and the *X*-ray structure shows that the S_2 ligand occupies a side-on position at an equatorial site in an approximately trigonal-bipyramidal configuration, nearly isostructural with the analogous O_2 complex.[17] Although the S—S distance in the niobium complex (0.173 nm) is the shortest known for a S—S bond, the S—S distance (0.207 nm) in the iridium complex is much longer than in free S_2 (0.189 nm).[18] The Ir—S_2 bonding may be rationalized in terms of a π-bonding scheme involving $p_\pi(S_2) \rightarrow d(Ir)$ σ-bonding complemented by $d_\pi(Ir) \rightarrow p_\pi{}^*(S_2)$ back donation. The mild conditions used for the preparation of S_2 complexes suggest that the catalysis of reactions of cyclo-S_8 with organic compounds by transition-metal complexes is a potentially fruitful area of research. It should be noted, however, that dioxygen does not displace S_2 from the iridium complex in solution, so that the complex is not a reversible S_2 carrier.[16]

The best preparative route to small sulphur allotropes S_n (n = 2—4) is photolysis of the corresponding dihalogenosulphane XS_nX (X = Cl or Br) in an organic glass at 77 K or rare-gas matrix at 20 K.[19] In this way S_2 is obtained in over 90%

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[9] N. Basco and A. E. Pearson, *Trans. Faraday Soc.*, 1967, **63**, 2684.
[10] L. Brewer and G. D. Brabson, *J. Chem. Phys.*, 1966, **44**, 3274.
[11] R. E. Barletta and C. W. Brown, *J. Phys. Chem.*, 1971, **75**, 4059.
[12] D. J. Meschi and A. W. Searcy, *J. Chem. Phys.*, 1969, **51**, 5134.
[13] J. Drowart and P. Goldfinger, *Quart. Rev.*, 1966, **20**, 545; P. Budininkas, R. K. Edwards, and P. G. Wahlbeck, *J. Chem. Phys.*, 1968, **48**, 2859, 2867, 2870; J. M. Ricks and R. F. Barrow, *Canad. J. Phys.*, 1969, **47**, 2423; J. Berkowitz and W. A. Chupka, *J. Chem. Phys.*, 1969, **50**, 4245.
[14] C. Courty and L. Néel, *Compt. rend.*, 1971, **273**, *C*, 193.
[15] P. M. Treichel and G. P. Werber, *J. Amer. Chem. Soc.*, 1968, **90**, 1753.
[16] A. P. Ginsberg and W. E. Lindsell, *Chem. Comm.*, 1971, 232; A. P. Ginsberg, W. E. Lindsell, and W. E. Silverthorn, *Trans. N.Y. Acad. Sci.*, 1971, 303.
[17] W. D. Bonds and J. A. Ibers, *J. Amer. Chem. Soc.*, 1972, **94**, 3413.
[18] K. Ikenoue, *J. Phys. Soc. Japan*, 1953, **8**, 646; G. Herzberg, 'Molecular Spectra and Molecular Structure', Vol. 1, Van Nostrand, Princeton, N.J., 1950, p. 566.
[19] B. Meyer, T. Stroyer-Hansen, D. Jensen, and T. V. Oommen, *J. Amer. Chem. Soc.*, 1971, 93, 1034; B. Meyer, T. V. Oommen, and D. Jensen, *J. Phys. Chem.*, 1971, **75**, 912

yields from S_2Cl_2, and photolysis of S_3Cl_2 or S_4Cl_2 yields green S_3 or red S_4, characterized by broad visible absorption bands at 410 and 530 nm, respectively.[20] S_4 was also obtained by annealing S_2 in krypton matrices.[20] Meyer and Spitzer have reported extended Hückel calculations for S_3, S_4, and various cyclic sulphur allotropes which fit the spectral data very well and allow the prediction of the colour and spectra of undiscovered allotropes.[21] The structure of S_3 is not known but is likely to be bent like O_3. Calculations on seven S_4 isomers and conformers suggest the following order of stability: branched > chain > zigzag > *cis* > helical > cyclic > planar > puckered cyclic > tetrahedron. The predicted stability of the branched structure is of considerable interest (*cf.* SO_3) although the S_4 spectrum in matrices and the gas phase is more compatible with a chain. S_5 and longer chains are expected to absorb to the red of S_4, but S_5 has not yet been identified. There is a suggestion that an absorption centred at 625 nm which appears when S_2 is annealed in a krypton matrix is due to S_6 chains.[20,21]

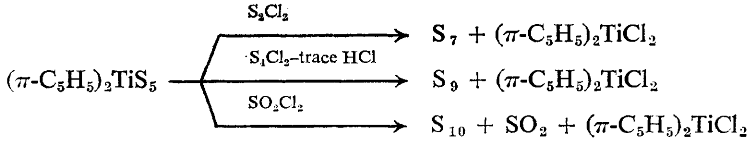
4 Cyclic Sulphur Allotropes

The thermodynamically stable form of elemental sulphur at ordinary temperatures consists of S_8 molecules in a crown configuration of D_{4d} symmetry.[22] Recently a number of other sulphur rings S_n ($n = 6, 7, 9, 10, 12$, or 18), including the well-known cyclo-S_6, have been synthesized using kinetically controlled reactions.[23] For example, the reaction of dichlorosulphanes with polysulphanes in *very dilute solutions* has been used in the synthesis of cyclo-S_6,[24] -S_{10},[24] and -S_{12}.[25]

$$H_2S_x + S_yCl_2 \rightarrow S_{x+y} + 2HCl$$

($x = 4, y = 2$;[24] $x = 6, y = 4$;[24] $x + y = 12$.[25])

The related cyclic compound S_5CH_2 is formed from methanedithiol using a similar approach.[26] The pentasulphide $(\pi\text{-}C_5H_5)_2TiS_5$[27] (Section 7B) is a versatile reagent for the preparation of the odd-numbered rings S_7[28] and S_9.[29]



$$(\pi\text{-}C_5H_5)_2TiS_5 \xrightarrow{S_2Cl_2} S_7 + (\pi\text{-}C_5H_5)_2TiCl_2$$

$$(\pi\text{-}C_5H_5)_2TiS_5 \xrightarrow{S_4Cl_2\text{–trace HCl}} S_9 + (\pi\text{-}C_5H_5)_2TiCl_2$$

$$(\pi\text{-}C_5H_5)_2TiS_5 \xrightarrow{SO_2Cl_2} S_{10} + SO_2 + (\pi\text{-}C_5H_5)_2TiCl_2$$

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[20] B. Meyer, T. Stroyer-Hansen, and T. V. Oommen, *J. Mol. Spectroscopy*, 1972, **42**, 335.

[21] B. Meyer and K. Spitzer, *J. Phys. Chem.*, 1972, **76**, 2274.

[22] G. A. Ozin, *J. Chem. Soc.* (*A*), 1969, 116.

[23] M. Schmidt, *Inorg. Macromol. Rev.*, 1970, **1**, 101.

[24] M. Schmidt and E. Wilhelm, *Inorg. Nuclear Chem. Letters*, 1965, **1**, 39.

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

[26] F. Fehér and W. Becher, *Z. Naturforsch.*, 1965, **20b**, 1125; F. Fehér, B. Degen, and B. Söhngen, *Angew. Chem. Internat. Edn.*, 1968, **7**, 301.

[27] H. Köpf, B. Block, and M. Schmidt, *Chem. Ber.*, 1968, **101**, 272; H. Köpf and B. Block, *ibid.*, 1969, **102**, 1504; H. Köpf, *ibid.*, 1969, **102**, 1509.

[28] M. Schmidt, B. Block, H. D. Block, H. Köpf, and E. Wilhelm, *Angew. Chem. Internat. Edn.*, 1968, **7**, 632.

[29] M. Schmidt and E. Wilhelm, *Chem. Comm.*, 1970, 1111.

The identification of these unusual cyclic molecules relies heavily on molecular weight determinations, particularly by mass spectrometry,[30] since in solution they are often thermodynamically unstable with respect to the formation of cyclo-S_8. At low ionizing potentials parent ions can be observed, but the spectra are several orders of magnitude less intense than the superimposed spectrum of cyclo-S_8. The conversion of cyclo-S_7, and probably of other sulphur rings, to cyclo-S_8 apparently occurs *via* a ring-scission → polymerization → depolymerization sequence. The relatively high melting point (148 °C) of cyclo-S_{12} and its greater stability compared to cyclo-S_6 or -S_{10} was unexpected,[31] but is in accord with recent calculations on sulphur rings by strain-energy minimization methods.[32] In its activity as a Lewis acid, *e.g.* towards Ph_2(*o*-tolyl)P, cyclo-S_{12} is intermediate between cyclo-S_6 and -S_8.[33] A single-crystal *X*-ray structure determination of cyclo-S_{12} reveals[34] that the sulphur atoms lie in three planes with average S—S bond distances and $\widehat{SSS}$ angles similar to those found for cyclo-S_6[35] and -S_8[36] (Table 1). A very recent structural determination of cyclo-S_8[37] is in basic agreement with the older results but shows small, but significant, differences in S—S bond distances and $\widehat{SSS}$ bond angles, possibly due to intermolecular effects. Such differences geometrically must occur in the odd-numbered rings S_7 and S_9, except in the very unlikely planar configuration, and will result in differences in electron density (and thus energy content) around these rings.[38] The structural data for cyclo-S_7 are not very reliable, and only the projection on to the *xy* plane, suggesting a seven-membered ring in a chair configuration, is known.[39]

Semi-empirical MO calculations on the bonding in cyclo-S_6 and -S_8 show that inclusion of 3*d* orbitals in the basis sets has very little effect on the ground-state properties of the molecules.[40] The energy of the highest filled MO of S_6 without inclusion of *d*-orbitals is -868 kJ mol^{-1}, in excellent agreement with the experimental ionization potential of 871 kJ mol^{-1}.[41] On the other hand the 3*d* orbitals make an important contribution to the excited state in S_6 and S_8 and must be included in the basis sets to obtain reasonable correlations with known spectral transitions. Extended Hückel calculations on cyclic sulphur allotropes, S_6, S_7,

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[30] U. I. Záhorszky, *Angew. Chem. Internat. Edn.*, 1968, **7**, 633; J. Buchler, *ibid.* 1966, **5**, 965.
[31] L. Pauling, *Proc. Nat. Acad. Sci. U.S.A.*, 1949, **35**, 495.
[32] F. Lin, *Diss. Abs.*, 1971, **31**, *B*, 7222.
[33] F. Fehér and D. Kurz, *Z. Naturforsch.*, 1969, **24b**, 1089.
[34] A. Kutoglu and E. Hellner, *Angew. Chem. Internat. Edn.*, 1966, **5**, 965.
[35] A. Caron and J. Donohue, *Acta. Cryst.*, 1965, **18**, 562; S. C. Abrahams, *ibid.*, p. 566; J. Donohue, in ref. 2, p. 13.
[36] S. C. Abrahams, A. S. Cooper, and W. L. Bond, *Acta Cryst.*, 1961, **14**, 1008; A. Caron and J. Donohue, *ibid.*, p. 548.
[37] W. F. Cooper and P. Coppens, personal communication.
[38] F. Tuinstra, *J. Chem. Phys.*, 1967, **46**, 2741.
[39] I. Kawada and E. Hellner, *Angew. Chem. Internat. Edn.*, 1970, **9**, 379.
[40] D. J. Miller and L. C. Cusachs, *Chem. Phys. Letters*, 1969, **3**, 501.
[41] J. Berkowitz and C. Lifshitz, *J. Chem. Phys.*, 1968, **48**, 4346.

Table 1 *X-ray structural data for some cyclic sulphur allotropes*

S_n	d(S—S) (nm)	*Average* $\widehat{\mathrm{SSS}}$ (°)	*Dihedral angle* (°)
S_6[a]	0.2057 ± 0.0018	102.2 ± 1.6	74.5 ± 2.5
S_8[b]	0.2048 ± 0.0002	107.9 ± 0.6	98.6 ± 0.5
S_{12}[c]	0.2055 ± 0.001	106.5 ± 0.5	107

[a] A. Caron and J. Donohue, *Acta Cryst.*, 1965, **18**, 562.
[b] S. C. Abrahams, A. S. Cooper, and W. L. Bond, *Acta Cryst.*, 1961, **14**, 1008; A. Caron and J. Donohue, *ibid.*, p. 548.
A. Kutoglu and E. Hellner, *Angew. Chem. Internat. Edn.*, 1966, **5**, 965.

A more recent *X*-ray structure determination of cyclo-S_8 gives the following parameters (W. F. Cooper and P. Coppens, personal communication). The numbering of atoms is indicated in footnote *b* above.

d(S—S) (nm)		$\widehat{\mathrm{SSS}}$ (°)	
S(1)—S(1′)	0.2042 (1)	S(1′)—S(1)—S(3)	108.42 (4)
S(1)—S(3)	0.2050 (1)	S(1)—S(3)—S(2)	107.33 (3)
S(3)—S(2)	0.2048 (1)	S(3)—S(2)—S(4)	107.97 (3)
S(2)—S(4)	0.2048 (1)	S(2)—S(4)—S(4′)	108.99 (3)
S(4)—S(4′)	0.2046 (1)		

$R = 2.7\%$; $R_w = 3.2\%$.

S_8, S_{12}, assuming known *X*-ray structural data, give results which are in good agreement with electronic spectra, except for S_7.[21]

5 Sulphur Vapour

It is well known that sulphur vapour contains measurable quantities of several species S_n ($n = 1, 2 \ldots 10$); the smaller allotropes S_2, S_3, S_4, S_5 become more important with increasing temperature (Figure 1).[42] Various sources of sulphur vapour, *e.g.* orthorhombic sulphur,[43] mercuric sulphide,[41,43] or an electrochemical Knudsen cell Pt,Ag|AgI|Ag_2S,Pt[44] in the temperature range 200—400 °C have been used to measure the ionization potentials of sulphur allotropes S_n (n = 2—8) by electron impact and by photoionization. The photoionization results are uniformly 48—58 kJ mol^{-1} lower than those from electron-impact studies,[41] but the value obtained for S_2 by photoionization is in excellent agreement with the value determined from the electronic spectrum of S_2,[45,46] and with that previously predicted by Barrow *et al.*[47] (Table 2). The use of an electrochemical cell allows one to vary the sulphur activity and temperature inde-

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[42] J. Berkowitz, Chapter 7 in ref. 2.
[43] J. Berkowitz and W. A. Chupka, *J. Chem. Phys.*, 1964, **40**, 287.
[44] J. Drowart, P. Goldfinger, D. Detry, H. Rickert, and H. Keller, *Adv. Mass Spectrometry*, 1968, **4**, 449.
[45] R. F. Barrow, Chapter 13 in ref. 2.
[46] R. J. Donovan, D. Husain, and C. D. Stevenson, *Trans. Faraday Soc.*, 1970, **66**, 1.
[47] R. F. Barrow, R. P. du Parcq, and J. M. Ricks, *J. Phys.* (*B*), 1969, **2**, 413.

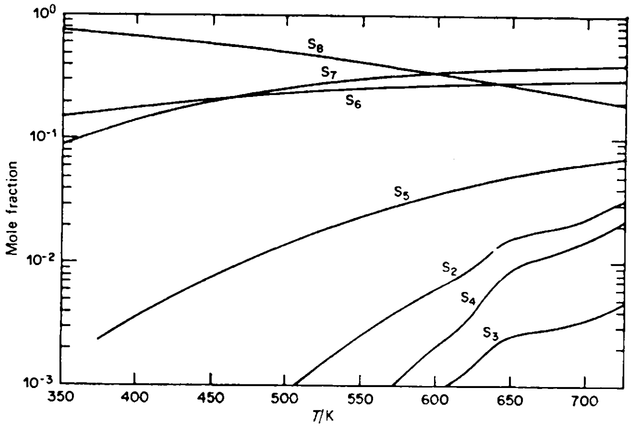

Figure 1 *Equilibrium composition of saturated sulphur vapour*
(Reproduced by permission, from J. Berkowitz, in 'Elemental Sulphur', ed. B. Meyer, Interscience, New York, N.Y., 1965, p. 125)

Table 2 *Ionization potentials of sulphur allotropes* S_n (n = 2—8) *in sulphur vapour* (kJ mol^{-1})

Molecule	*Photo-ionization*[a]	*Electron impact*[b]	*Knudsen cell*[c]	*Spectroscopic*[d]
S_2	903 ± 2	955 ± 29	926 ± 19	907 ± 5
S_3	934 ± 3	1013 ± 29	955 ± 39	
S_4	[e]	1003 ± 29	936 ± 39	
S_5	830 ± 5	897 ± 29	916 ± 39	
S_6	868 ± 3	945 ± 29	916 ± 19	
		897 ± 29		
S_7	836 ± 3	897 ± 29	839 ± 19	
		878 ± 10		
S_8	872 ± 3	926 ± 29	926 ± 19	

[a] J. Berkowitz and C. Lifshitz, *J. Chem. Phys.*, 1968, **48**, 4346.
[b] J. Berkowitz and W. A. Chupka, *J. Chem. Phys.*, 1964, **40**, 287.
[c] J. Drowart, P. Goldfinger, D. Detry, H. Rickert, and H. Keller, *Adv. Mass Spectrometry*, 1968, **4**, 499.
[d] R. J. Donovan, D. Husain, and C. D. Stevenson, *Trans. Faraday Soc.*, 1970, **66**, 1.
[e] The S_4^+ ion has been demonstrated to be due to fragmentation.

pendently so that, in conjunction with a mass spectrometer, it is possible to study selectively the electron-impact behaviour of different sulphur molecules and to obtain accurate thermodynamic data.[44] The gas-phase Raman spectrum of sulphur at 180 and 250 °C shows a polarized band at 237 cm^{-1} attributed to S_7, in addition to bands due to cyclo-S_6 and -S_8.[48] Smaller sulphur allotropes were

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[48] I. R. Beattie, G. A. Ozin, and R. O. Perry, *J. Chem. Soc.* (A), 1970, 2071; G. A. Ozin, *Chem. Comm.*, 1969, 1325.

not identified, as expected in this temperature range, and at higher temperatures the spectra were dominated by resonance effects.

6 Liquid Sulphur

The molecular composition of equilibrium liquid sulphur is exceedingly complex. A theoretical model of this system must explain *inter alia* the following experimental facts:

(*i*) At the melting point (112.8 °C) liquid sulphur is transparent and has the same yellow colour as the crystals; at the boiling point (444.6 °C) it is deep red and opaque.[4]

(*ii*) The viscosity decreases to a minimum at 155 °C, rises slightly to 159 °C, and then increases rapidly to a maximum at *ca.* 185 °C.[49]

(*iii*) The heat capacity rises to a maximum at 159 °C and then decreases.[50]

(*iv*) E.s.r.[51] and magnetic susceptibility data[52] indicate the absence of free radicals below the polymerization temperature and the presence of appreciable concentrations of unpaired electrons at higher temperatures.

(*v*) Quenching of liquid sulphur yields CS_2-insoluble sulphur (S_μ) in amounts which depend on the temperature of equilibration of the liquid.[53]

Harris has summarized theoretical attempts to explain these experimental observations.[53b] At the melting point, the liquid is almost pure cyclo-S_8 with *ca.* 5.5% S_π.[1] S_π refers to the sulphur which dissolves in carbon disulphide at −80 °C in excess of the solubility of cyclo-S_8, after quenching of liquid sulphur at any temperature.[54] The identity of S_π is still in doubt. Wiewiorowski and Touro have attempted to explain the absence of free radicals at low temperatures in liquid sulphur in terms of an acid–base complex between sulphur chains (S_π) and the acidic S_8 ring, which can accept electron density from the radical chain and facilitate the pairing of free spins in these chains.[40,55] The formation of an acid–base complex would also considerably reduce the net free-energy change involved in the formation of a chain species. Extended Hückel calculations, assuming an S_2 molecule sandwiched between two S_8 rings, confirm the ability of cyclo-S_8 to participate in charge-transfer complexes.[21] Harris has concluded, however, that S_π is a mixture of sulphur rings. As yet there is no good model to predict the amount of S_μ in quenched liquid sulphur, but it is known that S_π decays on ageing to S_μ and cyclo-S_8.

The observed changes in viscosity have been explained by a model which assumes chain scission and polymerization of catena-S_8 with cyclo-S_8[56] to give

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[49] E. D. West, *J. Amer. Chem. Soc.*, 1959, **81**, 29.

[50] R. F. Bacon and R. Fanelli, *J. Amer. Chem. Soc.*, 1943, **65**, 639.

[51] D. M. Gardner and G. K. Fraenkel, *J. Amer. Chem. Soc.*, 1956, **78**, 3279; J. A. Poulis and W. Derbyshire, *Trans. Faraday Soc.*, 1963, **59**, 559; D. C. Koningsberger and T. De Neef, *Chem. Phys. Letters*, 1970, **4**, 615.

[52] J. A. Poulis, C. H. Massen, and P. v. d. Leeden, *Trans. Faraday Soc.*, 1962, **58**, 474.

[53] (*a*) J. C. Koh and W. Klement jun., *J. Phys. Chem.*, 1970, **74**, 4280; (*b*) R. E. Harris, *ibid.*, p. 3102.

[54] A. H. W. Aten, *Z. Phys. Chem.*, 1914, **86**, 1.

[55] T. K. Wiewiorowski and F. J. Touro, *J. Phys. Chem.*, 1966, **70**, 3528.

[56] J. A. Poulis, C. H. Massen, A. Eisenberg, and A. V. Tobolsky, *J. Amer. Chem. Soc.*, 1965, **87**, 413.

diradical chains with up to 500000 S_8 units. Above 250 °C the average polymer chain length and hence the viscosity decreases until at the normal boiling point sulphur again forms a thin liquid. However, the polymeric S_n chain is dark yellow in the liquid and yellow at room temperature, although extended Hückel calculations predict that linear S_n diradical chains should be dark red or black.[21] These calculations and the unexpectedly weak e.s.r. signals raise doubts concerning the generally accepted diradical model for polymeric sulphur. Meyer and Spitzer suggest that polymeric sulphur may be a long sulphane chain, arising from reaction of elemental sulphur with hydrocarbon impurities above 160 °C, a very large ring, or a charge-transfer complex of the type (cyclo-S_8–catena-S_n–cyclo-S_8)$_n$.[21] The temperature dependence of the Raman spectrum of liquid sulphur (particularly above 160 °C) has been attributed to the formation of S_n chains in addition to the presence of cyclo-S_8.[57]

Meyer and co-workers[19] have demonstrated that the colour change of liquid sulphur below 250 °C is due to a shift of the absorption edge towards the red, but above 250 °C it is mainly due to the formation of S_3 and S_4. The presence of S_3 and S_4, although not as major constituents (*ca.* 0.5—2% at 450 °C), explains why hot sulphur is decoloured by traces of organic impurities and implies the presence of other sulphur rings S_n ($n > 4$). Indeed cyclo-S_{12} has been isolated in *ca.* 0.1% yields from quenched sulphur that has been melted at various temperatures (120—370 °C).[58] The molecular composition of liquid sulphur will change during cooling, and it is likely that only a small portion of the S_{12} rings will survive transition to the thermodynamically more stable cyclo-S_8. The presence of significant amounts of cyclo-S_{12}, and probably other sulphur rings, in the equilibrium mixture of liquid sulphur therefore seems certain.

The calculations of Meyer and Spitzer on linear S_n chains and the established presence of S_3, S_4 and cyclo-S_{12} in molten sulphur necessitate a reappraisal of the generally accepted model of the molecular composition of liquid sulphur. The unusual transport properties of molten sulphur have been explained, with reference to the electronic structures of S_8, S_8^+, and S_8^-, in terms of an electron 'hopping' mechanism.[59]

7 Anionic Species

A. Sulphide Ion S^{2-}.—The u.v. absorption of aqueous sulphide was commonly accepted to have $\lambda_{max} = 364$ nm but Giggenbach has shown by careful exclusion of oxygen that $\lambda_{max}(S^{2-}) = 250$ nm and the band at 364 nm is probably due to the presence of polysulphides.[60] This assignment is supported by Nelson and Lagowski who showed that S^{2-} and HS^- have very similar absorption bands in liquid ammonia, $\lambda_{max}(S^{2-}) = 270$ nm at -77 °C.[61] Giggenbach then used this

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[57] A. T. Ward, *J. Phys. Chem.*, 1968, **72**, 4133.

[58] M. Schmidt and H. D. Block, *Angew. Chem. Internat. Edn.*, 1967, **6**, 955.

[59] D. J. Gibbons, *Mol. Cryst. Liquid Cryst.*, 1970, **10**, 137.

[60] W. Giggenbach, *Inorg. Chem.*, 1971, **10**, 1333.

[61] J. T. Nelson and J. J. Lagowski, *Inorg. Chem.*, 1967, **6**, 862.

result to estimate the second dissociation constant of H_2S and obtained a value of $pK_{a_2} = 17.1 \pm 0.2$ at 24 °C.[60] This value is some 3 units larger than the previously accepted values and has important consequences, *e.g.* although metal sulphides constitute many ore bodies, the mechanism of transport of the metal and of precipitation of the sulphide is not yet clear.* The estimation of the thermodynamic properties of aqueous sulphide ions requires accurate values of pK_{a_2} and hence the currently accepted values[62] for the free energy of formation $\Delta F_f{}^\circ[S^{2-}(aq)25\,°C] = +90.8$ kJ mol^{-1}, the heat of formation $\Delta H_f{}^\circ[S^{2-}(aq)\,25\,°C] = +37$ kJ mol^{-1}, and the entropy $S^\circ[S^{2-}(aq)25\,°C] = -17$ J mol^{-1} deg^{-1} cannot be regarded as reliable. Indeed Giggenbach studied the temperature dependence of K_{a_2} and from his data approximate values can be calculated; $\Delta F_f(25\,°C) = +109$ kJ mol^{-1}; $\Delta H_f(25\,°C) = 9.6$ kJ mol^{-1} and $S(25\,°C) = -167$ J mol^{-1} deg^{-1}. We note an empirical prediction of the entropy of -84 J mol^{-1} deg^{-1}.[63]

B. Polysulphide Ions $S_x{}^{2-}$.†—Pure crystalline samples of anhydrous Na_2S_2 and Na_2S_4 have been prepared and characterized by *X*-ray powder diffraction patterns.[64] The blue solutions of alkali-metal polysulphides in various melts and polar organic solvents are caused by dissociation and disproportionation to give sulphur radical anions (Section 7C).

The equilibria in aqueous solutions containing sulphur/sulphide are still not well characterized. One study[65] assumes the presence of only hydrosulphide (HS^-) and polysulphide ions and defines a set of formation constants:

$$iS + HS^- + OH^- \rightleftharpoons S_{i+1}{}^{2-} + H_2O$$

$$K_i = \frac{[S_{i+1}{}^{2-}]}{[S]^i\,[HS^-]\,[OH^-]}$$

If the solutions are in equilibrium with solid sulphur, the activity of sulphur is unity and the relative quantities of the various polysulphides in solution will be constant. The results of a series of experiments to determine the solubility of sulphur in sulphide solutions at various pH and the results of previous spectrophotometric work were combined to calculate K_i for a number of hypothetical equilibrium models. Another study[66] maintains that the major species in solution is the hydropentasulphide ion ($HS_5{}^-$). However, this suggestion is not in agreement with previous estimates of the acidity of the polysulphanes (H_2S_x)[67] and the study also contains several dubious experiments, *e.g.* sulphide solutions are

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* For a discussion of the geochemical implications of the higher value of pK_{a_2}, see A. J. Ellis and W. Giggenbach, *Geochim. Cosmochim. Acta*, 1971, **35**, 247.

† For a discussion of the stereochemistry of polysulphides, see R. Rahman, S. Safe, and A. Taylor, *Quart. Rev.*, 1970, **24**, 208.

[62] H. P. Stephens and J. W. Cobble, *Inorg. Chem.*, 1971, **10**, 619.

[63] R. E. Powell and W. M. Latimer, *J. Chem. Phys.*, 1951, **19**, 1139.

[64] E. Rosen and R. Tegman, *Acta Chem. Scand.*, 1971, **25**, 3329.

[65] A. Teder, *Acta Chem. Scand.*, 1971, **25**, 1722.

[66] E. M. Hauck, *Diss. Abs.*, 1972, **32**, *B*, 5671.

[67] K. W. C. Burton and P. Machmer, Chapter 10 in ref. 3.

saturated with sulphur and *then* adjusted to the desired pH so that the solutions are no longer in equilibrium with elemental sulphur, and a variation of u.v. absorbance with pH (as observed) would be expected.

Several transition-metal complexes containing chelated polysulphides have been prepared. These include $Pt(S_5)_2^{2-}$ prepared from $Pt(S_5)_3^{2-}$[68] and the bis-π-cyclopentadienyl compounds $(\pi\text{-}C_5H_5)_2TiS_5$,[69] $(\pi\text{-}C_5H_5)_2VS_5$,[70] $(\pi\text{-}C_5H_5)_2MoS_4$,[71] and $(\pi\text{-}C_5H_5)WS_4$.[72] Crystals of all these compounds are air-stable but the solutions of the cyclopentadienyl compounds are oxygen-sensitive. A preliminary crystal structure of $(NH_4)_2Pt(S_5)_3,2H_2O$ has been published[73] showing an octahedrally co-ordinated Pt with three PtS_5 rings in the chair conformation. The crystal structure of $(\pi\text{-}C_5H_5)_2TiS_5$[69] also shows a six-membered TiS_5 ring in the chair conformation; thus the two cyclopentadienyl rings are not equivalent (Figure 2). This structure provides an explanation for the two singlet resonances in the ^1H n.m.r. spectrum at room temperature which coalesce at 120 °C owing to rapid inversion of the chair-shaped ring. The crystal structure of $(\pi\text{-}C_5H_5)_2WS_4$[72] reveals that the WS_4 ring is non-planar but symmetrically placed with respect to the cyclopentadienyl rings, in accord with the lack of splitting of the single ^1H n.m.r. signal even at -95 °C. A noteworthy feature of this structure is the variation in the three S—S bond distances. The two outer S—S bonds have an average value of 0.2101(5) nm while the central S—S bond is shorter, 0.2017(6) nm. In contrast, the aromatic tetrasulphide, $C_{20}H_{24}O_4S_8$, shows an alternation of S—S bond lengths in the reverse order,[74] and a redetermination of the structure of the piezoelectric BaS_4,H_2O reveals *no significant difference* in S—S bond distances in the S_4^{2-} ion.[75]

C. Sulphur Radical Anions S^-, S_2^-, S_3^-, S_x^-.—The S^- (and HS) radicals have been produced in aqueous solution by the oxidation of HS^- with hydrogen peroxide in the presence of titanium(III) salt at pH 9 (HS at pH 2).[76] The radical was not detected directly but the radicals formed by trapping with acrylic acid or acrylonitrile were identified by their e.s.r. spectra. The formation and subsequent reactions of S^- in various binary mixtures ($ClCN/CS_2$; $ClCN/H_2S$; ClCN/COS; $ClCN/CH_3SH$) have been studied in the gas phase using a time-of-flight mass spectrometer.[77] The main products were the CN^- and CNS^- ions. The electron affinity of the sulphur atom has been measured as 200.45 ± 0.05 kJ

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[68] A. E. Wickenden and R. A. Krause, *Inorg. Chem.*, 1969, **8**, 779.
[69] E. F. Epstein, I. Bernal, and H. Köpf, *J. Organometallic Chem.*, 1971, **26**, 229.
[70] H. Köpf, A. Wirl, and W. Kahl, *Angew. Chem. Internat. Edn.*, 1971, **10**, 137.
[71] H. Köpf, *Angew. Chem. Internat. Edn.*, 1969, **8**, 375.
[72] B. R. Davis and I. Bernal, *J. Cryst. Mol. Struct.*, 1972, **2**, 135.
[73] P. E. Jones and L. Katz, *Chem. Comm.*, 1967, 842.
[74] J. S. Ricci jun. and I. Bernal, *J. Chem. Soc. (B)*, 1971, 1928.
[75] S. C. Abrahams and J. L. Bernstein, *Acta Cryst.*, 1969, **B25**, 2365.
[76] R. O. C. Norman and P. M. Storey, *J. Chem. Soc. (B)*, 1971, 1009.
[77] A. Di Domenico, D. K. Sen Sharma, J. L. Franklin, and J. G. Dillard, *J. Chem. Phys.*, 1971, **54**, 4460.

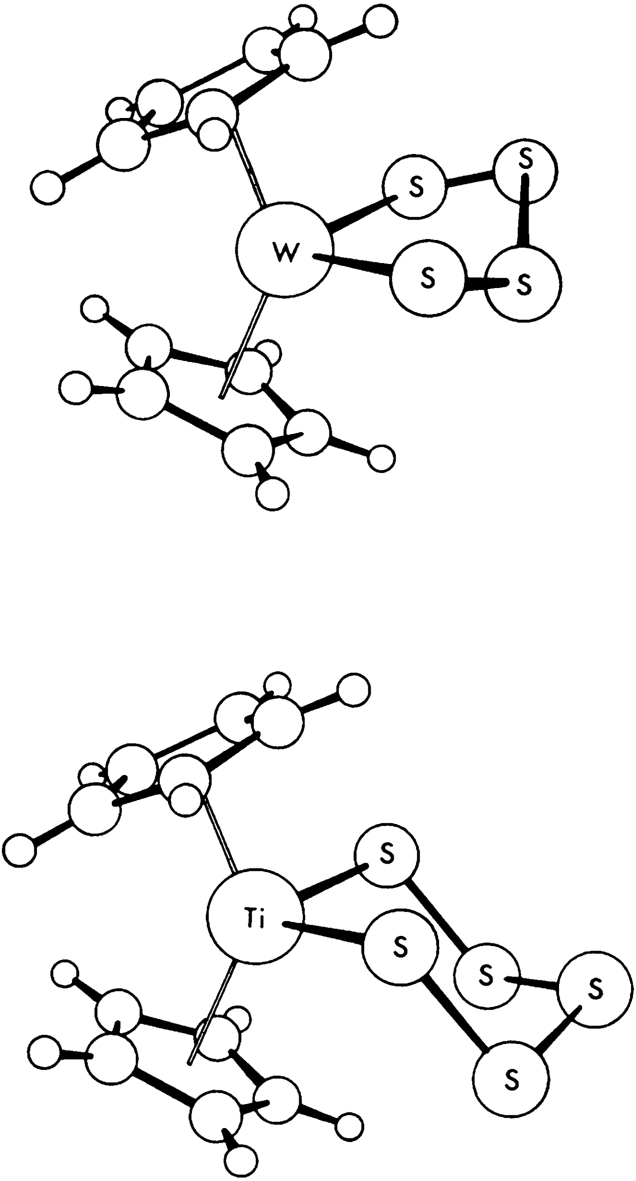

Figure 2 *Structures of* (π-$C_5H_5)_2WS_4$ *and* (π-$C_5H_5)_2TiS_5$

mol^{-1} by using a tunable dye laser to excite the photodetachment process $S^-(^2P_{3/2}) + h\nu \rightarrow S(^3P_2) + e^-$ in a molecular beam experiment.[78]

Both S_2^- and S_3^- have been well characterized in sulphur-doped alkali halide crystals by e.s.r., ENDOR, u.v.–visible, i.r., resonance Raman, and fluorescence spectra.[79] In a KI host lattice S_2^- has $\lambda_{max} \approx 400$ nm while S_3^- has λ_{max} 610 nm. A study of the equilibria between sulphur and sulphide in LiCl/KCl melts showed absorption bands at 595 nm and 385 nm ascribed to S_3^- and S_2^- respectively.[80] Solutions of either cyclo-octasulphur or alkali-metal polysulphides in the basic solvent hexamethylphosphoramide are blue due to the presence of S_3^-.[81] The visible spectra of S_3^- solutions show a characteristic vibrational structure. In view of this body of evidence, reports that the blue species (λ_{max} 617 nm) formed by alkali-metal polysulphides in dimethylformamide, high-temperature water, and various melts and glasses[82] is S_2^- must be treated with great reserve. Earlier suggestions that the blue colour is due to neutral sulphur molecules S_x, $2 \leq x \leq 4$, are incorrect.[83] A report of the formation of S_8^- in the electrochemical reduction of cyclo-S_8 in dimethyl sulphoxide[84] has been shown to be erroneous.[85] The optical absorption band (λ_{max} 618 nm) associated with the blue product formed in the first reduction step reaches a maximum when the number of electrons passed per S_8 is equal to 8/3. This is interpreted in terms of a *two-electron* reduction to give S_8^{2-} followed by disproportionation,

$$S_8 + 2e^- \rightleftharpoons S_8^{2-} \text{ and } 4S_8^{2-} \rightleftharpoons 4S_6^{2-} + S_8$$

which amounts to the overall process,

$$3S_8 + 8e^- \rightleftharpoons 4S_6^{2-} .$$

Although Bonnaterre and Cauquis[85] attribute the blue colour to S_6^{2-}, their results are fully consistent with the presence of S_3^-. Further reduction at the second wave gives S_4^{2-} which is still in equilibrium with the blue species and, presumably, sulphide ion, in agreement with the results found for polysulphides in hexamethylphosphoramide.[81] The catalytic effect of amines on reactions of elemental sulphur is well known, but the exact nature of the sulphur species present in amine solvents is still obscure. The blue species in ethylenediamine (λ_{max} 616 nm) has been identified as S_x^-,[86] and from the known extinction coefficient of S_3^-[81] this species accounts for only 3% of the sulphur in ethylenediamine (0.08 molar in S atoms at 25 °C).

Blue colours are also observed in other situations where sulphur anions might

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[78] W. C. Lineberger and B. W. Woodward, *Phys. Rev. Letters*, 1970, **25**, 424.

[79] (*a*) W. Holzer, W. F. Murphy, and H. J. Bernstein, *J. Mol. Spectroscopy*, 1969, **32**, 13; (*b*) W. C. Holton and M. DeWit, *Solid State Comm.*, 1969, **7**, 1099.

[80] D. M. Gruen, R. L. McBeth, and A. J. Zielen, *J. Amer. Chem. Soc.*, 1971, **93**, 6691.

[81] T. Chivers and I. Drummond, *Inorg. Chem.*, 1972, **11**, 2525.

[82] W. Giggenbach, *J. Inorg. Nuclear Chem.*, 1968, **30**, 3189; W. Giggenbach, *Inorg. Chem.*, 1971, **10**, 1306, 1308.

[83] H. Lux, S. Benninger, and E. Böhm, *Chem. Ber.*, 1968, **101**, 2485.

[84] M. V. Merritt and D. T. Sawyer, *Inorg. Chem.*, 1970, **9**, 211.

[85] R. Bonnaterre and G. Cauquis, *J.C.S. Chem. Comm.*, 1972, 293.

[86] R. MacColl and S. Windwer, *J. Phys. Chem.*, 1970, **74**, 1261.

occur, *e.g.* in sulphur freshly extracted by the Frasch process (use of superheated water),[87] in acetone solutions of sulphur containing potassium hydroxide,[88] and in hot mineral springs. However, the purple-blue colour formed by sulphur imides (*e.g.* S_7NH) in methanolic KOH and used as a sensitive spot test for these compounds is not due to S_3^- but to an isomer of cyclo-S_7N^-,[89] which is slowly converted into S_3^- in hexamethylphosphoramide solutions containing traces of dimethylamine.[89]

D. Ultramarines.—Ultramarine is a generic name for a range of compounds derived from sodalite ($6NaAlSiO_4,2NaCl$) doped with sulphur. They may be blue, green, red, or violet. The various colours arise from optical absorption bands at 590, 520, and 380 nm.[90] E.s.r. and Raman spectra identify the blue species (λ_{max} 590 nm) as S_3^-[79a,90,91] but there is still confusion over the yellow species (λ_{max} 380 nm) which may be S_2^{2-}[90,91] or S_2^-[92] and over the red species (λ_{max} 520 nm) which may be either S_2O or S_2O^-.[90] Some authors[82,93] have attributed the blue colour to S_2^- but in view of the numerous reports to the contrary[79–81,90,91] this assignment cannot be regarded as correct.

Ultramarines are efficient catalysts for many reactions of hydrocarbons, *e.g.* dehydrogenation, hydrodesulphurization, cracking, and isomerization, and the activity has been related to the number of paramagnetic centres.[94] Molecular sieves containing sulphur radicals are also reported to be catalysts in the cracking of 2,3-dimethylbutane.[95]

8 Sulphur Cations* S_{16}^{2+}, S_8^{2+}, S_4^{2+}

Sulphur dissolves in highly acidic media containing oxidizing agents, *e.g.* oleum or fluorosulphuric acid/$S_2O_6F_2$, to give highly coloured solutions. Gillespie and co-workers have recently established that the colours of these solutions are due to the presence of polysulphur cations. Red S_{16}^{2+}, blue S_8^{2+}, and yellow S_4^{2+} cations have been identified.[96] The crystal structure of $S_8(AsF_6)_2$ has been determined and reveals that the S_8^{2+} cation is an eight-membered ring with *exo–endo* configuration[97] (Figure 3). This structure can be compared with the eight-membered rings of S_8 (*exo–exo* configuration) and S_4N_4 (*endo–endo* configuration), compounds which have two more and two less valence electrons,

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* For a review of polycations of Group VI, see R. J. Gillespie and J. Passmore, *Accounts Chem. Res.*, 1971, **4**, 413.

[87] C. Pratt, *Sci. Amer.*, 1970, **222**, (5), 63.

[88] T. Urbanski, *Talanta*, 1962, **9**, 799.

[89] T. Chivers and I. Drummond, unpublished observations.

[90] S. D. McLaughlan and D. J. Marshall, *J. Phys. Chem.*, 1970, **74**, 1359.

[91] A. Wieckowski, *Phys. Stat. Sol.*, 1970, **42**, 125.

[92] O. M. Platonov, V. P. Belichenko, A. M. Tarashchan, A. K. Ziya-Zada, and O. S. Povarennikh, *Chem. Abs.*, 1972, **76**, 29266w.

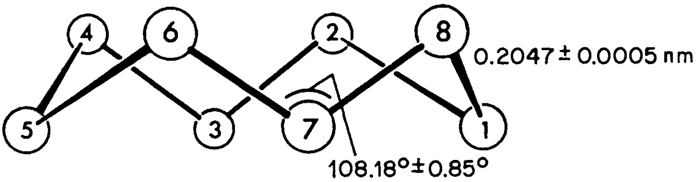
[93] M. I. Samoilovich, *Chem. Abs.*, 1971, **75**, 56493d.

[94] Z. Dudzik, *Chem. Abs.*, 1968, **68**, 108259j.

[95] Z. Dudzik and K. F. Preston, *J. Colloid Interface Sci.*, 1968, **26**, 374.

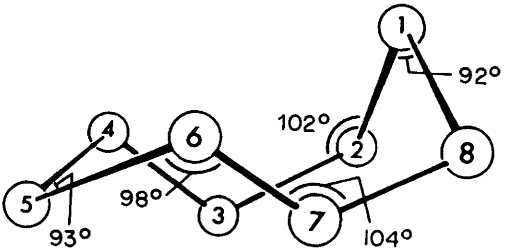
[96] R. J. Gillespie, J. Passmore, P. K. Ummat, and O. C. Vaidya, *Inorg. Chem.*, 1971, **10**, 1327.

[97] C. G. Davies, R. J. Gillespie, J. J. Park, and J. Passmore, *Inorg. Chem.*, 1971, **10**, 2781.



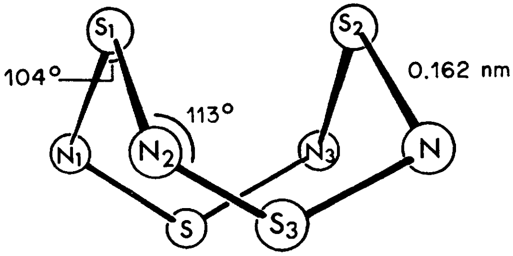
S_8

Av. S(2)—S(8) dist. = 0.333 nm
Av. S(3)—S(7) dist. = 0.468 nm



S_8^{2+}

Av. S—S dist. around ring = 0.204 — 0.001 nm
S(2)—S(8) = 0.294 nm
S(3)—S(7) = 0.286 nm
S(4)—S(6) = 0.300 nm



S_4N_4

S(1)—S(2) = 0.258 nm
S(1)—S(3) = 0.269 nm
N(1)—N12(2) = N(1)—N(3) = 0.255 nm
∠ N(2)—S(1)—S(2) = 90°

Figure 3 *Structures of cyclo-*S_8, -S_8^{2+}, *and* S_4N_4

respectively, than S_8^{2+}. The conformation of the S_8^{2+} ring is apparently not due to crystal packing effects and as yet there is no good description of the bonding which can explain the shape of these related eight-membered rings, although a novel scheme involving delocalized electron pairs has been suggested.[98] The structures of S_{16}^{2+} and S_4^{2+} are not known but the spectral similarities between Se_4^{2+} and S_4^{2+} suggest that the structures are similar, *i.e.* a symmetric square-planar cation.[99]

Solutions and solids containing the S_{16}^{2+} and S_8^{2+} cations are usually weakly paramagnetic.[100] S_{16}^{2+} is associated with a non-axially symmetric radical with $g = 2.027$ whereas S_8^{2+} is associated with a radical at $g = 2.014$ which is axially symmetric.[100] Gillespie and Ummat claim that the radicals are S_8^+ and S_4^+ respectively, arising from dissociation of the dipositive cations. Oleum solutions of sulphur enriched to over 90% ^{33}S have been examined by e.s.r. spectroscopy. One study[101] agrees that the radical with $g = 2.014$ is S_4^+, whereas other workers[102] argue that the spectra contain an *even* number of lines and, therefore, an *odd* number of S atoms (^{33}S, $I = \frac{3}{2}$); they favour S_5^+. Thus the radical cations are not yet satisfactorily identified. Significantly, the solutions and solids of S_4^{2+} are diamagnetic, showing that there is no tendency to form the S_2^+ ion, the sulphur analogue of the only known oxygen cation O_2^+.

The blue-green solutions of sulphur in fluorosulphuric acid have been studied polarographically.[103] Two well-defined oxidation waves were observed but the results need reinterpreting now that it is known these solutions contain a mixture of S_8^{2+} and S_4^{2+} cations. Sulphur cations, not antimony cations as first reported, produced by reduction of the solvent account for the colours observed when antimony dissolves in fluorosulphuric acid.[104] Likewise, the reported formation of a yellow As_4^{2+} species and a blue P_8^{2+} species in disulphuric acid is open to doubt. Except for the ready synthesis of bis(perfluoroethyl)polysulphides $(C_2F_5)_2S_x$ ($x = 2$—6) from tetrafluoroethylene and $S_8(AsF_6)_2$,[105] few reactions of sulphur cations have been studied.

9 Concluding Remarks

Table 3 compares the well-characterized homonuclear species formed by sulphur with those formed by oxygen. There are no oxygen analogues of the extensive series of sulphur rings, polysulphur dications, or polysulphide anions, and the S_3^- radical anion readily dimerizes to S_6^{2-}[89] (*cf.* isolation of ammonium and alkali-metal ozonides, MO_3[106]). Thus sulphur demonstrates a pronounced

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[98] A. J. Banister, *Nature Phys. Sci.*, 1972, **239**, 69.

[99] I. D. Brown, D. B. Crump, and R. J. Gillespie, *Inorg. Chem.*, 1971, **10**, 2319.

[100] R. J. Gillespie and P. K. Ummat, *Inorg. Chem.*, 1972, **11**, 1674.

[101] R. A. Beaudet and P. J. Stephens, *Chem. Comm.*, 1971, 1083.

[102] M. C. R. Symons and J. G. Wilkinson, *Nature Phys. Sci.*, 1972, **236**, 126.

[103] G. Adhami and M. Herlem, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1970, **26**, 363.

[104] R. J. Gillespie and O. C. Vaidya, *J.C.S. Chem.Comm.*, 1972, 40.

[105] H. L. Paige and J. Passmore, *Inorg. Chem.*, 1973, **12**, 593.

[106] 'Advanced Inorganic Chemistry', F. A. Cotton and G. Wilkinson, Wiley, New York, 1972, 3rd Edn., p. 418.

Table 3 *Homonuclear species of sulphur and oxygen*

Homonuclear Species	S	O
Cyclic Allotropes	S_6, S_7, S_8, S_9 S_{10}, S_{12}, S_{18}	None
Smaller Allotropes	S_2, S_3, S_4	O_2, O_3
Dications	S_4^{2+}, S_8^{2+}, S_{16}^{2+}	None
Radical Cations[a]	S_4^+, S_8^+	O_2^+
Dianions	S_x^{2-} (x = 1—6)	O_x^{2-} (x = 1 or 2)
Radical Anions	S_2^-, S_3^-	O_2^-, O_3^-

[a] See Section 8.

tendency to form catenated species, a trend which may result partly from the relatively high σ-bond energy (263 kJ mol^{-1}) compared to π-bond energy (423 kJ mol^{-1}) for sulphur (*cf.* O—O, 146 kJ mol^{-1}; O=O, 496 kJ mol^{-1}).

The preparation of small sulphur allotropes by photolysis of dihalogenosulphanes, the ready formation of S_3^- from polysulphides in basic solvents, and the synthesis of polysulphur dications in strongly acidic, oxidizing media are all relatively simple preparative routes to homonuclear sulphur species which are much more reactive than cyclo-S_8. The reactions of these species have scarcely been investigated and provide an interesting challenge to synthetic chemists, both inorganic and organic.