

Valence-shell Expansion in Sulphur Heterocycles

By W. G. Salmond

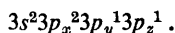
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Valence-shell expansion in the sulphur atom, though implicit in earlier studies of thiazole derivatives,¹ was first postulated explicitly in connection with thiophen.² Much of the subsequent evidence for this phenomenon has come, however, from work on open-chain compounds. A review³ of this area covers most of the literature to the end of 1959. The purpose of this Review is to survey the evidence accruing from studies of the heterocyclic systems, particularly aromatic systems, in which the *d* orbitals of the sulphur atom have been thought to be important in the bonding. It is not intended to present an exhaustive bibliography but to trace the developments which have proved most fruitful. Work on acyclic systems has been ignored, except where it has been of particular relevance in a generalised treatment of the bonding of sulphur. Inorganic cyclic compounds such as thiazyl halides and the sulphur nitrides will not be discussed.

1 The Bonding Possibilities of Sulphur

Although recent publications^{3, 4} have considered in some detail the bonding possibilities of sulphur, it will still be advantageous to present a brief outline here.

Sulphur belongs to the second short period and to the sub-group VI_B of the Periodic Table. Its valence electrons are contained in the *M* shell and in its ground state the sulphur atom has the electronic configuration



If, following the lead of Craig and his school,⁵ we assume that the angular functions of *s*, *p*, and *d* orbitals are the same as in the free atom, that is, bond formation leaves these functions virtually unchanged, then a preliminary discussion of the atomic orbitals associated with sulphur will lead naturally to a discussion of the bonding in molecules containing sulphur.

The *K* and *L* shells of the sulphur atom are completely filled and the electrons contained therein are assumed to play no part in the bonding. The atomic

¹ H. Erlenmeyer and H. M. Weber, *Helv. Chim. Acta*, 1938, **21**, 863; H. Erlenmeyer, H. M. Weber, and P. Wiessmar, *ibid.*, p. 1017.

² V. Schomaker and L. Pauling, *J. Amer. Chem. Soc.*, 1939, **61**, 1769.

³ G. Cilento, *Chem. Rev.*, 1960, **60**, 147.

⁴ J. Nys and A. van Dormael, *Ind. chim. belge*, 1961, 1109; A. B. Burg in 'Organic Sulphur Compounds', ed. N. Kharasch, vol. I, pp. 30-40, Pergamon Press, New York, 1961; C. C. Price and S. Oae, 'Sulphur Bonding', Ronald Press, New York, 1962.

⁵ D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 1954, 332.

orbital of lowest energy in the valence shell is the $3s$. This orbital, which is spherically symmetrical and is completely filled is also normally assumed to play no part in bonding except, of course, where sp or spd hybrid orbitals are involved. The orbitals of next higher energy are the three mutually perpendicular and orthogonal $3p$ orbitals, $3p_x$, $3p_y$, and $3p_z$. These orbitals, of equal energy, are those employed most commonly in organic sulphur compounds since they can be used with neighbouring ligands in the formation of σ bonds (Figure 1a) or π bonds (Figure 1b). In this Review we are concerned with sulphur bound to first-row elements (carbon, nitrogen, oxygen) so that the π bond formed will be of the $2p\pi-3p\pi$ type (Figure 1c). Owing to inner-shell repulsions this type of bond can be expected to be weaker than a bond of the $2p\pi-2p\pi$ type, which is of course the double bond normally met in organic chemistry.

Of even higher energy are the five $3d$ orbitals. These orbitals are mutually orthogonal and in the isolated atom are degenerate. This degeneracy is lost in a ligand field, however. In an octahedral field, for instance, those of highest energy are the $3d_{z^2}$ and the $3d_{x^2-y^2}$. The remaining three orbitals are of equal energy and are of the correct symmetry to be able to participate in π -bonding. They are the $3d_{xy}$, $3d_{yz}$, and $3d_{zx}$ orbitals. A π bond arises if one of these orbitals is appropriately oriented with its positive and negative lobes equally inclined to the line of nuclear centres and requires a $p\pi$ (or $d\pi$) orbital at the other centre (Figure 1d). This $p\pi-d\pi$ bonding is of particular relevance here.

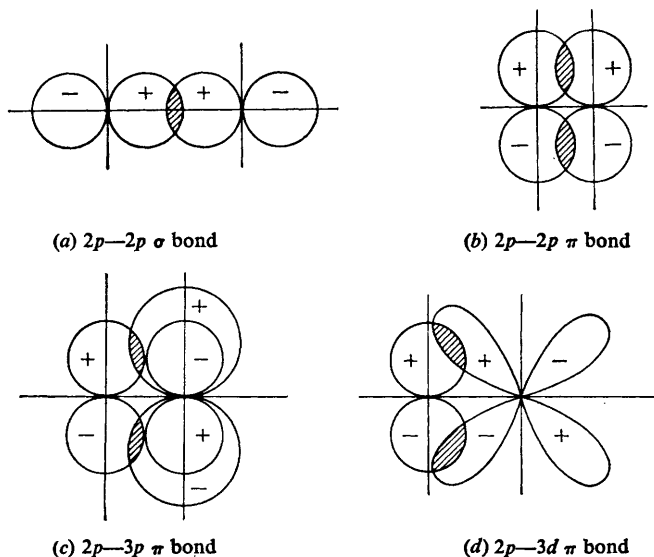


Figure 1

In an important paper Craig and his co-workers⁵ have discussed theoretically the conditions necessary for the formation of chemical bonds involving d orbitals. They calculated overlap integrals for a series of different types of bond (for

example bonds involving different spd hybrid orbitals) and used these integrals as criteria of bond strength.

Calculations based on the Slater rules⁶ indicate that the d orbitals associated with the sulphur atom would be far too diffuse for bonding purposes and Craig points out that for dealing with the valence states of atoms use of Slater's rules may be inadequate. Certainly comparison with S.C.F. (self-consistent field) functions in some cases shows that the Slater d -orbital functions are too diffuse; but the same is found to hold for s and p functions when the same type of comparison is made. It was concluded, therefore, that results obtained by use of Slater's rules would still be expected to be at least qualitatively correct in unsophisticated comparative studies. Consequently it was assumed that, when employed for bonding purposes, d orbitals contract as a result of perturbation by the ligands.

This idea was developed in later papers⁷ and applied to compounds such as sulphur hexafluoride where σ bonds are involved and whose structure is usually interpreted in terms of the configuration $3s3p^33d^2$ for the sulphur atom. One of the ways in which this contraction can be brought about is by the development of a formal positive charge on the central atom by partial ionisation of the outer d electrons into the ligand orbitals. This positive charge causes the more polarisable $3d$ orbitals to contract and thus increases their ability to hybridise effectively with the $3s$ and $3p$ orbitals. This approach has been criticised by some workers⁸ who computed S.C.F. functions for the sulphur atom in various spectroscopic states arising from the electronic configuration sp^3d^2 and found the radial maxima of the d functions to be within the bonding region and that therefore it was not necessary to invoke this type of orbital contraction. The view that d orbitals are of a favourable size for bonding has had support from others⁹ but more recent work still favours the requirement of orbital contraction.¹⁰ Indeed, at the other end of the scale, it has been claimed¹¹ that the contraction required (in aromatic sulphides for example) is too great to allow the use of d orbitals in bonding at all.

In situations involving π bonding, however, the necessity for such perturbing effects is not so critical. In a $p\pi-d\pi$ bond, overlap is better when the d orbital is considerably more diffuse than the p orbital, than when the two orbitals (p and d) are of the same size. Put another way, in a σ bond or in a π bond involving two p orbitals, overlap is most highly developed between the nuclei and so will be greatest if the two orbitals are the same size; however $d\pi$ and $p\pi$ orbitals overlap most efficiently when the lobes of the d orbital are almost above and below the nucleus of the other atom as indicated in Figure 1*d*. This asymmetric overlap would be expected to give rise to a polar bond.

⁶ J. C. Slater, *Phys. Rev.*, 1930, **36**, 57.

⁷ D. P. Craig and E. A. Magnusson, *J. Chem. Soc.*, 1956, 4895; D. P. Craig, *Chem. Soc. Special Publ. No. 12*, 1958, p. 343.

⁸ D. W. J. Cruikshank, B. C. Webster, and D. F. Mayers, *J. Chem. Phys.*, 1964, **40**, 3733.

⁹ R. S. Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 4493; H. H. Jaffe, *J. Phys. Chem.*, 1954, **58**, 185.

¹⁰ D. P. Craig and T. Thirunamachandran, *J. Chem. Phys.*, 1965, **43**, 4183.

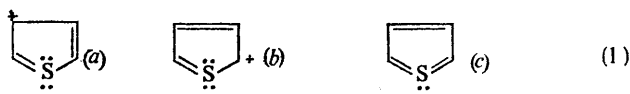
¹¹ G. L. Bendazzoli and C. Zauli, *J. Chem. Soc.*, 1965, 6827.

For the C-S bond Craig found overlap values much larger than normal but this need not infer greater bond strength since, by virtue of the low electronegativities of carbon and sulphur, overlap occurs in a region of weak nuclear field. It does, however, imply that in compounds such as thiophen such $p\pi-d\pi$ bonding may be considerable despite the low electronegativity of carbon and despite the non-development of a formal positive charge on the sulphur atom.

2 Thiophen

A. Theoretical Studies.—For many years the electronic structure of thiophen was considered to be entirely analogous to that of furan. In this conception the $3s$, $3p_x$, and $3p_y$ orbitals of sulphur are mixed to form three sp^2 hybrid orbitals, of which two serve to establish two σ bonds with the ring carbon atoms and the third, non-bonding, contains the two electrons with antiparallel spin of the lone pair. There remain two electrons in the $2p_z$ orbital capable of entering into conjugation with the $2p_z$ electrons of the carbon atoms of the heterocycle. This gives rise to the situation illustrated on Figure 2a which is identical with that for furan except that $3p$ orbitals for sulphur are used in place of $2p$ orbitals in the oxygen case. In a pioneering extension of the Hückel molecular orbital (M.O.) theory¹² to include heterocyclic systems, this scheme was employed by Wheland and Pauling¹³ and later its use was implicit in an early valence-bond (V.B.) treatment of the chemical reactivity of thiophen.¹⁴

Schomaker and Pauling,² comparing bond lengths, resonance energy values, and dipole moments in pyrrole, furan, and thiophen, concluded that in thiophen the sulphur appeared to admit, to some extent, ten electrons into its valence shell in place of the usual octet in oxygen or nitrogen. The value of the C-S bond length in thiophen (obtained from electron diffraction) is 1.74 Å compared with the sum of the single-bond covalent radii of 1.81 Å, a shortening of 0.07 Å. The corresponding decrease in furan is only 0.03 Å. In a similar fashion the dipole moment of thiophen in benzene is 0.54 D and that of tetrahydrothiophen is 1.87 D, a difference of 1.33 D. The corresponding difference for furan to tetrahydrofuran is 1.01 D. Further evidence for the stronger conjugation of the sulphur atom with the ring in thiophen than the oxygen atom with the ring in furan comes from thermochemical data. The resonance energies of the two compounds were found to be 31 and 23 kcal. mole⁻¹ respectively. These results were held as evidence that in a valence-bond description of the molecule the structures (1) are important contributors to the resonance hybrid of thiophen,



the added stabilisation resulting from this increased delocalisation accounting for the closer similarity of this compound to benzene.

¹² E. Hückel, *Z. Physik*, 1931, 70, 204.

¹³ G. W. Wheland and L. Pauling, *J. Amer. Chem. Soc.*, 1935, 57, 2086.

¹⁴ P. Daudel, R. Daudel, Buu-Hoi, and M. Martin, *Bull. Soc. Chim. France*, 1948, 1202.

This essentially qualitative valence-bond representation of thiophen was translated into a quantitative study by Longuet-Higgins¹⁵ in 1949 with the aid of the M.O. method. He demonstrated that the $3p_z$ orbital and two $3d$ orbitals (the $3d_{xz}$ and $3d_{yz}$) of sulphur could be mixed to give three hybrid pd^2 orbitals, two of which have the proper energy and symmetry characteristics required for entering into conjugation with the $2p_z$ orbitals of the neighbouring ring carbon atoms. Since, moreover, these two sulphur hybrid orbitals are defined to be mutually non-orthogonal, the analogy with benzene becomes clear: both are systems in which six electrons are associated with six atomic orbitals (instead of a system in which six electrons are associated with five orbitals, as in the other scheme). The third pd^2 orbital, which is orthogonal to the other two is mainly $3d$ in character and is of too high an energy for it to be occupied in the ground state. The projection of the carbon $2p_z$ orbitals and the three sulphur pd^2 hybrid orbitals on the molecular plane is shown in Figure 2b.

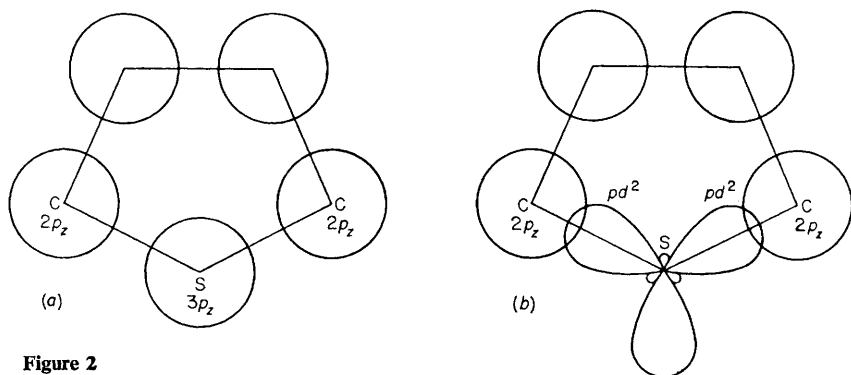


Figure 2

Longuet-Higgins concluded that with the use of pd^2 hybrid orbitals each atomic orbital contains unit charge, as in benzene, and in this way the pronounced aromatic character of thiophen compared with furan or pyrrole is readily explained. Since the overlap integrals for the C-S bond (which determine the degree of conjugation with the sulphur atom) are about 20% lower than the corresponding integrals for the C-C bond in benzene, the ability of thiophen to show the characteristics of a diene, albeit weakly, is readily understood. Arising from this, for example, is a greater reactivity at the α rather than the β carbon atoms. Finally he concluded that the dipole moment of thiophen is due predominantly to the unsymmetric character of the pd^2 orbitals.

This mode of reasoning, with various and minor modifications, has been applied to thiophen, its substituted derivatives, and its ring homologues.¹⁶

¹⁵ H. C. Longuet-Higgins, *Trans. Faraday Soc.*, 1949, 45, 173.

¹⁶ M. G. Evans and J. de Heer, *Acta Cryst.*, 1949, 2, 363; J. de Heer, *J. Amer. Chem. Soc.*, 1954, 76, 4802; J. Metzger and F. Ruffler, *J. Chim. phys.*, 1954, 51, 52; L. Melander, *Arkiv Kemi*, 1955, 8, 361; 1957, 11, 397; *Acta Chem. Scand.*, 1955, 9, 1400; K. Kikuchi, *Sci. Reports Tôhoku Univ.*, First Ser., 1956, 40, 133; 1957, 41, 35; K. Maeda, *ibid.*, 1959, 43, 203; *Bull. Chem. Soc. Japan*, 1960, 33, 304; J. Koutecky, R. Zahradnik, and J. Paldus, *J. Chim. phys.*, 1959, 455; G. Milazzo and G. De Alti, *Gazzetta*, 1959, 89, 2479; R. Zahradnik, C. Parkanyi, V. Horak, and J. Koutecky, *Coll. Czech. Chem. Comm.*, 1963, 28, 776.

Much controversy concerning whether the d orbitals of sulphur should be used in quantum-mechanical calculations remains, however. Their use has proved useful in many cases but many workers feel that thiophen and related compounds can still be treated adequately without their inclusion.¹⁷ Indeed, subsequent to a V.B. treatment of thiophen it has been averred that calculations based on the Longuet-Higgins model are fallacious.¹⁸ Treatment of thiophen by the Free Electron method has also been claimed¹⁹ to give reasonable correlation with experiment.

A notable recent paper²⁰ set out to examine the possibility of inclusion of the d orbitals of sulphur in a quantum-mechanical treatment of thiophen and avoided the unsatisfactory approach of making an apparently arbitrary choice between their inclusion or exclusion. The S.C.F.M.O. method was extended to include more than one atomic orbital per atomic site and in this manner three models differing in the orbitals used on the sulphur atom were studied: the first model used only the $3p_z$ orbital, the second included the $3d_{xy}$ and $3d_{yz}$ orbitals, and the last included also the $4p_z$ orbital. It was concluded that the d orbitals do participate in the π bonding to a small extent and although this participation is small, it nevertheless affects the calculated properties (charge densities and electronic absorption spectrum) markedly.

In spite of the many startling results obtained from theoretical calculations there exists still the doubt as to whether they have any real chemical meaning. Do theoretical calculations provide any real chemical information? Does it necessarily mean anything that in one case a p -model gives better correlation with experiment or in another case a d -model? Until questions such as these can be answered, the results of theoretical calculations as reliable predictive aids will be treated with considerable reserve.

B. Experimental Studies.—In order to elucidate the rôle of the d orbitals of the sulphur atom, thiophen and its derivatives have been subjected to various experimental studies, often with conflicting results. The technique most extensively used has been ultraviolet (u.v.) absorption spectrophotometry. The difference in the u.v. spectrum of the azine (2) and its carbocyclic analogues was held up as evidence for valence-shell expansion of the sulphur atom in the thiophen rings.²¹ Conversely the u.v. spectrum of the dibenzothiophen derivatives (3) seemed to indicate non-involvement of the d orbitals.²² In a short review of the u.v. absorption spectra of aromatic sulphur compounds it was

¹⁷ G. Berthier and B. Pullman, *Compt. rend.*, 1950, **231**, 774; S. Nagakura and T. Hosaya, *Bull. Chem. Soc. Japan*, 1952, **25**, 179; M. M. Kreevoy, *J. Amer. Chem. Soc.*, 1958, **80**, 5543; F. L. Pilar and J. R. Morris, *J. Chem. Phys.*, 1961, **34**, 389; D. S. Sappenfield and M. M. Kreevoy, *Tetrahedron*, 1963, Suppl. 2, 1963, 157; A. J. H. Wachtors and D. W. Davies, *Tetrahedron*, 1964, **20**, 2841; N. Solony, F. W. Birss, and J. B. Greenshields, *Canad. J. Chem.*, 1965, **43**, 1569; D. T. Clark, *Tetrahedron Letters*, 1967, 2889.

¹⁸ A. Mangini and C. Zauli, *J. Chem. Soc.*, 1960, 2210.

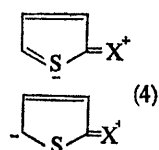
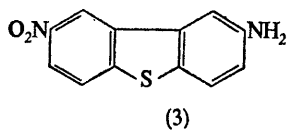
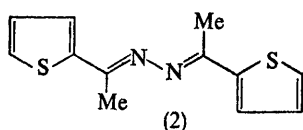
¹⁹ T. N. Rekaseva, *Optika i Spektroskopija*, 1961, **11**, 284.

²⁰ M. J. Bielefield and D. D. Fitts, *J. Amer. Chem. Soc.*, 1966, **88**, 4804.

²¹ H. H. Szmant and H. J. Planinsek, *J. Amer. Chem. Soc.*, 1950, **72**, 4981.

²² A. Mangini and R. Passerini, *Gazzetta*, 1954, **84**, 635.

concluded that although involvement of the d orbitals in open-chain compounds is unlikely, it is nevertheless probable in heterocyclic systems.²³



Recent infrared and Raman studies²⁴ of 2-halogenated thiophenes favour the contribution of the structures (4) to the resonance hybrid of the molecule as postulated in earlier studies²⁵ to explain the magnitudes of the dipole moments of these compounds. The high nuclear quadrupole resonance frequency of the chlorine atom in 2-chlorothiophen has been interpreted in terms of similar structures.²⁶ However, recent e.s.r. work on the radical anions derived from dibenzothiophen and its oxygen and selenium analogues, together with the u.v. absorption spectra and the polarographic reduction potentials of these compounds, are in firm disagreement with a model which incorporates valence-shell expansion of the hetero-atom.²⁷

Convincing evidence for through-conjugation *via* a sulphur atom seems to emerge from n.m.r. studies. The coupling constant between the 2- and the 5-hydrogen atoms (J_{25}) in furan derivatives is 1.5 c./sec.²⁸ The corresponding J_{25} in thiophen compounds is 2.7 c./sec.,²⁹ suggesting more through-conjugation *via* the sulphur atom by means of structures such as (1c). Such structures (5) involving hyperconjugation of the methyl group with the d orbitals of sulphur have been invoked to explain the coupling of the methyl protons with the β -olefinic protons in methyl vinyl sulphide.³⁰ No coupling occurs with the α protons. Similar structures may also explain the coupling between the 2- and 6-protons in benzo[*b*]thiophen which is *ca.* 0.5 c./sec.³¹ The coupling J_{26} in benzo[*b*]furan has not been resolved.³² It is significant perhaps that in indolizine J_{26} is of the order of 0.5 c./sec.³³ Through-conjugation of the 2- and 6-protons in a manner analogous to benzo[*b*]thiophen is possible with indolizine but not with benzo[*b*]furan (cf. structures 6a, b, c).

²³ A. I. Kiss, *Acta Phys. et Chem. Szeged*, 1960, 45.

²⁴ M. Horak, I. J. Hymans, and E. R. Lippincott, *Spectrochim. Acta*, 1966, 22, 1355.

²⁵ M. T. Rogers and T. W. Campbell, *J. Amer. Chem. Soc.*, 1955, 77, 4527.

²⁶ M. J. S. Dewar and E. A. C. Lucken, *J. Chem. Soc.*, 1959, 426.

²⁷ R. Gerdil and E. A. C. Lucken, *J. Amer. Chem. Soc.*, 1965, 87, 213; 1966, 88, 733.

²⁸ R. J. Abraham and H. J. Bernstein, *Canad. J. Chem.*, 1961, 39, 905.

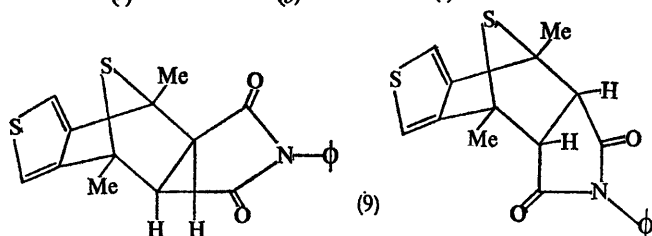
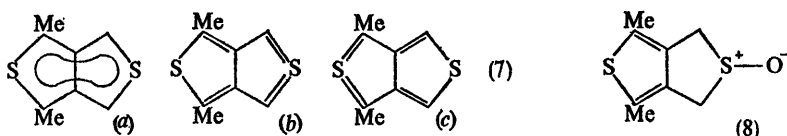
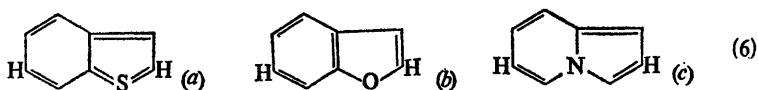
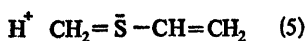
²⁹ S. Gronowitz and R. A. Hoffman, *Arkiv Kemi*, 1958, 13, 279; C. A. Reilly, *Analyt. Chem.*, 1961, 32, 221; D. M. Grant, R. C. Hirst, and H. S. Gutowsky, *J. Chem. Phys.*, 1963, 38, 470.

³⁰ R. T. Hobgood, G. S. Reddy, and J. H. Goldstein, *J. Phys. Chem.*, 1963, 67, 110; M. C. Caserio, R. E. Pratt, and R. J. Holland, *J. Amer. Chem. Soc.*, 1966, 88, 5747.

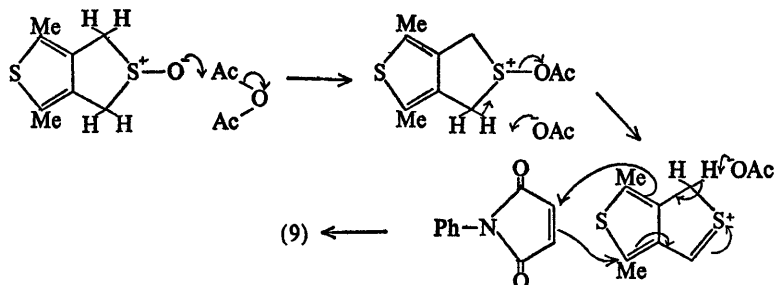
³¹ K. Takahashi, T. Kanda, F. Shoji, and Y. Matsuki, *Bull. Chem. Soc. Japan*, 1965, 38, 508.

³² P. J. Black and M. L. Heffernan, *Austral. J. Chem.*, 1965, 18, 353.

³³ P. J. Black, M. L. Heffernan, L. M. Jackman, Q. N. Porter, and G. R. Underwood, *Austral. J. Chem.*, 1964, 17, 1128.



A transient existence for the fully delocalised structure (7a) of which structures (7b, c) are contributors to the resonance hybrid has been claimed.³⁴ It is tempting certainly to write such a formulation for this compound but its high reactivity has also been attributed to a triplet ground state³⁵ (calculations based on a *p*-model). But more important in such situations is the necessity for care in the interpretation of the experimental results. Sulphoxide (8) when dehydrated in presence of acetic anhydride and *N*-phenylmaleimide yields the



adduct (9) where the dienophile has attacked the ring which was originally aromatic and which holds methyl substituents. Since methyl groups are known to increase the rate of some Diels-Alder reactions this behaviour was deemed evidence for the intervention of (7) as an intermediate. However, such a dehydration and addition might easily follow the concerted Scheme 1 which does not require an intermediate involving *d* orbitals or a triplet ground state. Without a more thorough investigation of the reaction such a sequence cannot be dismissed.

³⁴ M. P. Cava and N. M. Pollack, *J. Amer. Chem. Soc.*, 1967, **89**, 3639.

³⁵ D. T. Clark, *Tetrahedron Letters*, 1967, 5257.

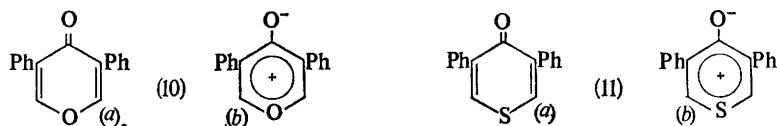
From the conflicting nature of the experimental results it appears that the use of *d* orbitals may not be universal; that there may be situations where for some reason their use is favoured and other situations where they are not.

3 Other Systems with Sulphur as the Sole Hetero-atom

In a discussion of aromaticity in carbocyclic systems it is a logical step from benzene to tropylium, so here the thiopyrylium ion follows thiophen. In a theoretical treatment of this compound it has been found useful to include the *d* orbitals of the sulphur atom.³⁶ However, calculations based on a *p*-model also agree well with the observed u.v. and n.m.r. results of various thiopyrylium ions.³⁷ A similar analogy with tropone is found in γ -thiopyrone which has been studied extensively in its anomalous relation to γ -pyrone-anomalous, that is, in regard to the relation of acyclic ethers to sulphides.

Evidence for the ability of sulphur to conjugate with a carbonium centre is manifest in the very high rate of hydrolysis of α -chloro-sulphides³⁸ compared with the rate of hydrolysis of alkyl halides. This reaction proceeds *via* a carbonium-ion intermediate³⁹ which is presumably stabilised by delocalisation of the positive charge, the $3p\pi$ orbital of the sulphur atom overlapping with the vacant $2p\pi$ orbital of the adjacent carbon atom to give a $2p\pi$ - $3p\pi$ bond. Were this interpretation correct, α -chloro-ethers would be expected to hydrolyse⁴⁰ even more quickly since the $2p\pi$ orbital of the oxygen atom would give rise to a $2p\pi$ - $2p\pi$ bond where overlap would be more substantial. This is the case, and numerous examples of this greater electron-releasing power of oxygen than sulphur⁴¹ are to be found in the literature.

The two compounds γ -pyrone and γ -thiapyrone, however, provide a notable exception to this behaviour. The dipole moment (3.82 D) of the γ -pyrone (10) indicates a large contribution from the polar structure (10*b*) to the resonance hybrid.⁴² The absence of a normal carbonyl frequency from the i.r. spectrum,⁴³ the lack of normal carbonyl reactivity and the basicity of the compound⁴⁴



³⁶ J. Koutecky, *Coll. Czech. Chem. Comm.*, 1959, **24**, 1608.

³⁷ T. E. Young and C. J. Ohnmacht, *J. Org. Chem.*, 1967, **32**, 444, 1558.

³⁸ R. A. Peters and E. Walker, *Biochem J.*, 1923, **17**, 260; H. Mohler and J. Hartnagel, *Helv. Chim. Acta*, 1941, **24**, 564; 1942, **25**, 859; H. Böhme and K. Sell, *Chem. Ber.*, 1948, **81**, 123.

³⁹ F. G. Bordwell, G. D. Cooper, and H. Morita, *J. Amer. Chem. Soc.*, 1957, **79**, 376.

⁴⁰ H. Böhme, H. Fischer, and R. Frank, *Annalen*, 1949, **563**, 54.

⁴¹ C. K. Ingold and E. H. Ingold, *J. Chem. Soc.*, 1926, 1310; E. L. Holmes and C. K. Ingold, *ibid.*, 1328.

⁴² E. C. E. Hunter and J. R. Partington, *J. Chem. Soc.*, 1933, 87; F. Arndt, G. T. O. Martin, and J. R. Partington, *ibid.*, 1935, 602.

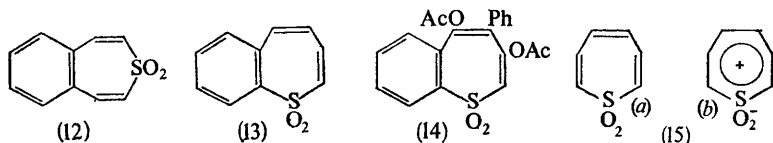
⁴³ A. Ross, *Proc. Roy. Soc.*, 1926, *A*, **113**, 213; L. Kahovec and K. W. F. Kohlrausch, *Chem. Ber.*, 1942, **75**, 627.

⁴⁴ D. S. Tarbell and P. Hoffman, *J. Amer. Chem. Soc.*, 1954, **76**, 2451.

are consistent with this polarisation. By analogy with the examples of acyclic compounds just given, the γ -thiapyrone should be less polarised in view of the suggested smaller electron-releasing ability of the sulphur atom. In fact the strong absorption in the double-bond region of the i.r. spectrum of the γ -thiapyrone (11) is even lower⁴⁴ and the dipole moment (4.40 D) is higher than the value for the corresponding γ -pyrone. In this instance, therefore, the electron-releasing ability of sulphur is greater than that of oxygen and there appears to be a considerable contribution of the polarised structure (11b) to the resonance hybrid, an assumption which is further supported by the remarkable resonance energy of γ -thiapyrone estimated at 33 kcal. mole⁻¹.⁴⁵ Although electron-releasing conjugation of this type does not *prima facie* involve the use of *d* orbitals of the sulphur atom, this remarkable change in the order of events may well be explicable in terms of more *d* orbital interaction in a ring than in open-chain compounds, perhaps because of more favourable geometry.

Arguments of this nature have also been called upon to rationalise the n.m.r. spectra of pyrone and thiapyrone.⁴⁶ The midpoint of the spectra of these compounds is found to shift downfield on the replacement of oxygen by sulphur (contrary to the normal upfield shift in acyclic compounds), and this has been interpreted in terms of an increased ring current in the sulphur-bearing ring brought about by the increased ability of sulphur to conjugate *via* the *d* orbitals. In further support of this proposition the J_{26} coupling in thiapyrones (*ca.* 4.0 c./sec.) is in general greater than J_{26} in pyrones (*ca.* 1.2 c./sec.).⁴⁷

Further more distant analogues of troponone are provided by the isomeric benzothiepin dioxides (12)⁴⁸ and (13).⁴⁹ The compound (12) possesses no aromatic property and loses sulphur dioxide readily on heating; its isomer seems to be somewhat more stable but details of its properties are not yet available. However a highly substituted derivative of this system, compound (14), seems to have no aromatic delocalisation in the seven-numbered ring as judged from its n.m.r. spectrum⁵⁰ and the parent compound (15) appears to be completely non-aromatic.⁵¹ It is stable at ordinary temperatures but its n.m.r. spectrum is reminiscent of that of a conjugated olefin, its u.v. spectrum is similar to that



⁴⁵ L. Lorenz-Oppan and H. Sternitzke, *Z. Elektrochem.*, 1934, **40**, 501.

⁴⁶ J. Jonas, W. Derbyshire, and H. S. Gutowsky, *J. Phys. Chem.*, 1965, **69**, 1.

⁴⁷ The couplings J_{26} and J_{35} are wrongly assigned in ref. 46 but the arguments presented here are not changed; see R. E. Mayo and J. H. Goldstein, *Spectrochim. Acta*, 1967, **23A**, 55.

⁴⁸ W. E. Truce and F. J. Lotspeich, *J. Amer. Chem. Soc.*, 1956, **78**, 848.

⁴⁹ V. J. Traynelis and F. F. Love, *Chem. and Ind.*, 1958, 439; *J. Org. Chem.*, 1961, **26**, 2728.

⁵⁰ H. Hoffman and H. Westmeyer, *Angew. Chem. Internat. Edn.*, 1966, 958.

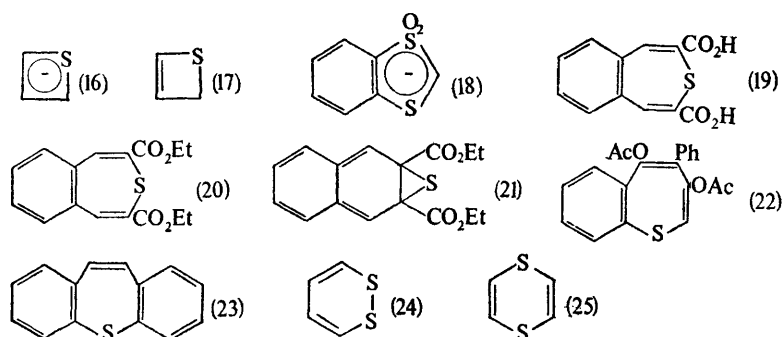
⁵¹ W. L. Mock, *J. Amer. Chem. Soc.*, 1967, **89**, 1281.

of cycloheptatriene, and it is readily hydrogenated. All of these properties together with its thermal instability argue against any contribution of the structure (15b).

The analogue of cyclopentadienide, the four-membered ring system (16) in which the *d* orbitals of the sulphur atom would be involved in any cyclical delocalisation, has not yet been prepared and is predicted to be quite unstable.⁵² The thiete (17),⁵³ the conjugate acid of this system, has been prepared but preliminary experiments indicate its non-acidic character. It is perhaps not surprising, therefore, that a system incorporating both the thiepin dioxide and the thietide systems, namely compound (18), was found to possess no aromatic stabilisation.⁵⁴

Sulphur-containing analogues of cyclo-octatetraene are known and as expected are somewhat unstable. For example the dicarboxylic acid (19) loses sulphur very readily to yield naphthalene-2,3-dicarboxylic acid.⁵⁵ Strangely the diester (20) seems to be much more stable and was attributed some degree of resonance stabilisation,⁵⁶ but this structure has been contested⁵⁷ and in its place structure (21) was suggested. The n.m.r. spectrum of the benzothiepin derivative (22) is also consistent with lack of aromatic delocalisation in the heterocyclic ring.⁵⁰ The double bond in derivatives of dibenzothiepin (23) is stated to be less 'olefinic' than that in dibenzocyclo-octatetraene.⁵⁸ Nevertheless, e.s.r. studies of compound (23) itself suggest that more conjugation is still transmitted *via* the double bond than *via* the sulphur bridge.⁵⁹ In addition these compounds lose sulphur thermally to give phenanthrene derivatives.⁶⁰

Similarly, 1,2-dithiin (24)⁶¹ loses sulphur readily to yield thiophen derivatives,



⁵² R. Zahradnik and C. Parkanyi, *Coll. Czech. Chem. Comm.*, 1965, 30, 3016.

⁵³ D. C. Dittmer, K. Takahashi, and F. A. Davis, *Tetrahedron Letters*, 1967, 4061.

⁵⁴ R. Breslow and E. Mohacsi, *J. Amer. Chem. Soc.*, 1962, 84, 684.

⁵⁵ G. P. Scott, *J. Amer. Chem. Soc.*, 1953, 75, 6332.

⁵⁶ K. Dimroth and G. Lenke, *Chem. Ber.*, 1956, 89, 2608.

⁵⁷ A. Schonberg and M. B. E. Fayez, *J. Org. Chem.*, 1958, 23, 104.

⁵⁸ E. D. Bergmann and M. Rabinovitz, *J. Org. Chem.*, 1960, 25, 828.

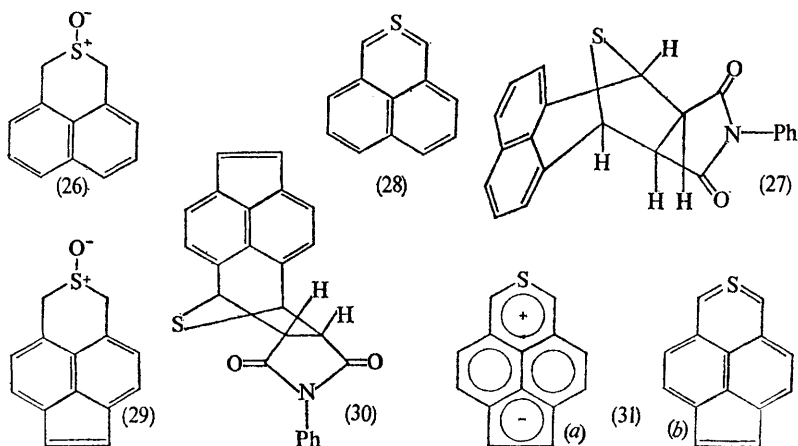
⁵⁹ M. M. Urberg and E. T. Kaiser, *J. Amer. Chem. Soc.*, 1967, 89, 5931.

⁶⁰ J. D. Loudon, A. D. B. Sloan, and L. A. Summers, *J. Chem. Soc.*, 1957, 3814.

⁶¹ W. Schroth, F. Billig, and G. Reinhold, *Angew. Chem. Internat. Edn.*, 1967, 6, 698.

nor does it display any properties consistent with cyclical delocalisation. 1,4-Dithiin, however, is a stable compound and its benzo-derivative has been attributed some degree of aromatic character.⁶² The parent compound, although not exhibiting these aromatic properties, nevertheless is not affected in many procedures which cause reaction in vinyl sulphides. The added stabilisation in this molecule has been put down to the involvement of *d* orbitals of the sulphur atom, especially as the ring is known to be puckered⁶³ and *p*-orbital delocalisation therefore impossible (unless of course some σ -overlap of *p* orbitals is admitted).⁶⁴ A large resonance energy has been calculated for 1,4-dithiin in terms of a *p*-model though in a more sophisticated treatment, still neglecting *d*-orbitals, much of this resonance energy is lost. Lucken in his e.s.r. work on 1,4-dithiin radical cations and their derivatives⁶⁵ has shown that a *d*-model gives a quantitatively better description than a *p*-model. He does point out, however, that the involvement of the *d*-orbitals of the sulphur atom may only be apparent owing to the probable non-planarity of the ring system allowing the interaction of the C-S antibonding orbital with the carbon $2p_z$ orbitals,⁶⁶ which would have a similar effect as the use of the *d*-orbitals.

Systems with seven π -electrons formally associated with the ring have been invoked as intermediates in the dehydration of the sulphoxides (26) and (29) in the presence of *N*-phenylmaleimide and acetic anhydride.⁶⁷ Sulphoxide (26) gives rise to the adduct (27) but for reasons given earlier this need not imply the separate existence of the intermediate (28). Likewise, although the formation



⁶² See W. E. Parham in 'Organic Sulphur Compounds', ref. 4, p. 248.

⁶³ P. A. Howell, R. M. Curtis, and W. N. Lipscomb, *Acta Cryst.*, 1954, 7, 498.

⁶⁴ See, e.g., K. G. Untch, *J. Amer. Chem. Soc.*, 1963, 85, 345.

⁶⁵ E. A. C. Lucken, *J. Chem. Soc.*, 1962, 4963; *Theor. Chim. Acta*, 1963, 1, 397.

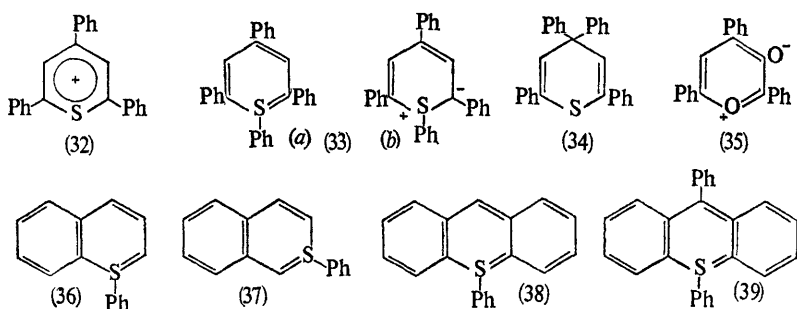
⁶⁶ J. F. A. Williams, *Trans. Faraday Soc.*, 1961, 57, 2089.

⁶⁷ M. P. Cava, N. M. Pollack, and D. A. Repella, *J. Amer. Chem. Soc.*, 1967, 89, 3640; R. H. Schlessinger and I. S. Ponticello, *ibid.*, p. 3641; *Tetrahedron Letters*, 1967, 4057.

of the adduct (30) from sulphoxide (29) may argue against the structure (31a) for the intermediate, it does not imply the validity of the structure (31b) as the intermediate.

4 Thiabenzene Derivatives

When phenyl-lithium and the thiapyrylium salt (32) are allowed to react the thiabenzene (33) is produced. This has been isolated as a deep purple amorphous solid which isomerises slowly to the isomeric thiapyran (34). Attempts to prepare *S*-alkylthiabenzene derivatives gave only the isomeric thiapyrans. When solutions of the thiabenzene (32) are treated with oxygen and then acidified, the betaine (35) and thiophenol are produced, indicating no doubt that the phenyl group from phenyl-lithium has become attached to sulphur and thus establishing the structure of the compound. The ring homologues of thiabenzene (36—39) are much more stable to heat, to light, and to oxygen. Nor do they revert to the isomeric thiapyrans. They are also less highly coloured than the parent compound (red rather than violet).⁶⁸



The dipole moments of all five compounds in benzene lie in the range 1.50—1.88 D indicating a larger contribution from the covalent structure to the resonance hybrid than the ylide structure. [The dipole moment of the ylide (40) is 6.2 D].⁶⁹ Moreover n.m.r. data support an aromatic structure. Similarly the low basicities⁷⁰ compared with acyclic ylides and the resistance of compounds (37) and (39) to desulphurisation with Raney nickel suggest marked stabilisation by through-conjugation in the six-membered ring.

Commenting on the electronic structure of the S atom in these compounds, Price has suggested that instead of a p^3 arrangement for the σ -framework around the sulphur atom, the hybridisation changes to sp^2 so that the thiabenzene ring and the *S*-phenyl ring become coplanar leaving the $3p_x$ orbital of the sulphur atom to conjugate with the $2p_z$ orbitals of the neighbouring

⁶⁸ G. Suld and C. C. Price, *J. Amer. Chem. Soc.*, 1961, **83**, 1770; 1962, **84**, 2090; 2094; C. C. Price, M. Flori, T. Parasaran, and M. Polk, *ibid.*, 1963, **85**, 2278.

⁶⁹ G. M. Phillips, J. S. Hunter, and L. E. Sutton, *J. Chem. Soc.*, 1945, 146.

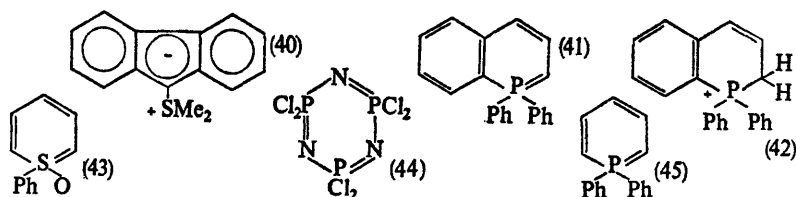
⁷⁰ E. A. Blair, *Diss. Abs.*, 1965, **26**, 1912.

Valence-shell Expansion in Sulphur Heterocycles

carbon atoms. The lone pair would then occupy a $3d$ orbital. In the monocyclic compound such a planar array would be hindered by the adjacent phenyl groups, the p^3 geometry being maintained. The lone pair would then occupy the $3s$ orbital and any through-conjugation with the ring would have to take place *via* a $p\pi-d\pi$ bond, this conceivably being the source of the relative instability of this system.

The u.v. spectra of thiabenzenes are similar to those of the related benzenoid systems so Price's theory⁶⁸ concerning the electronic structure of the sulphur atom is supported by the additional absorption in the visible region, causing excitation of one electron from a low-lying d orbital into a higher d orbital; especially is this so if the lone pair is contained in a d orbital. This hypothesis is supported by comparison of these thiabenzenes with the analogous phosphabenzenes.⁷¹

In the phosphabenzenes all the valence electrons associated with the phosphorus atoms are involved in the bonding so that any aromatic delocalisation in the ring must be transmitted *via* a $p\pi-d\pi$ bond. It is perhaps significant, therefore, that the phosphabenzenes are much less stable and that thiabenzenes are highly coloured compounds whereas the phosphabenzenes are pale yellow. Moreover the phosphabenzene (41) is protonated readily in aqueous media to the conjugate acid phosphonium salt (42). The thiabenzenes are not protonated at all under these conditions. However thiabenzene S -oxides,⁷² for example compound (43), a remarkably stable substance, exchange the ring protons readily in acidic media, behaviour consistent with 'ylide-character'.



Four main views are held on the bonding in phosphorus-containing compounds. Treating the electronic structure of phosphorus in phosphates, Fukui and his school⁷³ considered one $d\pi$ orbital (a d^3s hybrid) and one electron for the phosphorus atom and Mason⁷⁴ in his work on phosphabenzene chose a model similar to that Craig uses for phosphonitrilic compounds, for example compound (44).⁷⁵ Craig⁷⁶ believes that the $3d_{xz}$ orbital of the adjacent nitrogen atoms

⁷¹ G. Märkl, *Angew. Chem. Internat. Edn.*, 1963, 2, 153.

⁷² A. G. Hortmann, *J. Amer. Chem. Soc.*, 1965, 87, 4972; Y. Kishida and J. Ide, *Chem. and Pharm. Bull. (Japan)*, 1967, 15, 360.

⁷³ K. Fukui, K. Morokuma, and C. Nagata, *Bull. Chem. Soc. Japan*, 1960, 33, 1214.

⁷⁴ S. F. Mason, *Nature*, 1965, 205, 495.

⁷⁵ N. L. Paddock, *Quart. Rev.*, 1964, 18, 168; D. P. Craig and N. L. Paddock, *Nature*, 1958, 181, 1052.

⁷⁶ D. P. Craig, *J. Chem. Soc.*, 1959, 997.

(Figure 3a) to give a system in which there is complete cyclic delocalisation. In this type of delocalisation the 'aromatic sextet' loses its significance since the interactions of the d_{xz} orbital with the $2p_z$ orbitals on either side are of opposite sign. This leads to the result that the lower filled energy levels are degenerate (whereas in benzene of course the highest filled energy level is degenerate), and the delocalisation energy rises slowly with the number of π electrons (provided there is an even number) in the (AB) system. (A is a first row element which gives rise to a $p\pi$ orbital and B is a second row element providing a $d\pi$ orbital).

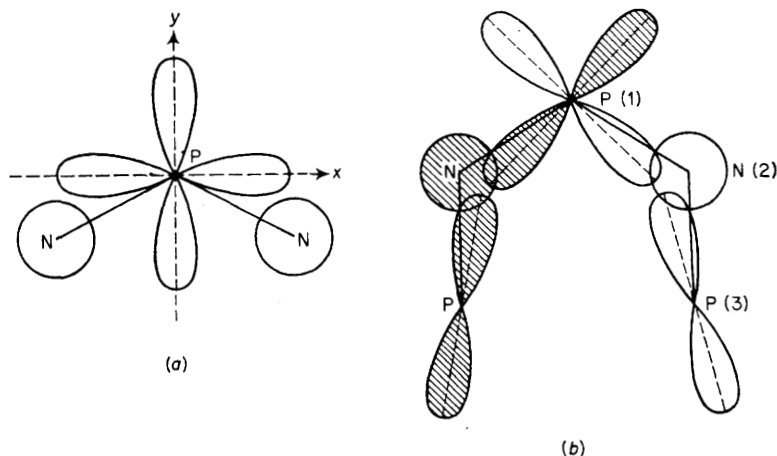


Figure 3

Dewar and his collaborators,⁷⁷ however, point out that the d_{yz} orbital ought to be included in the discussion. Assuming that the electronegativities of the d_{xz} and d_{yz} orbitals are equal and the orbitals thus being equivalent any linear combination of these orbitals would be suitable for this valence problem. Dewar suggested the sum and the difference. This gives rise to another two hybrid orbitals (designated d^+ and d^-) which are simply as if the previous two had been rotated in a clockwise direction through an angle of 45° . This brings them into a much more favourable position for overlap with the adjacent $2p_z$ orbitals of the nitrogen atoms. In this scheme the $2p_z$ orbital of N(2) overlaps strongly with the d^- orbital at P(1) and the d^+ orbital at P(3) (Figure 3b). Now the d_{xz} and d_{yz} orbitals are orthogonal; so also, therefore, are d^+ and d^- . Delocalisation, therefore, takes place over three-centre (P-N-P) 'islands' and not over the complete cyclic structure as in benzenoid chemistry, since conjugation is effectively interrupted at each phosphorus atom.

This procedure has been criticised⁷⁸ because the d_{xz} and d_{yz} orbitals are assumed to have the same electronegativities. Since the weakly bonded d orbitals

⁷⁷ M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *J. Chem. Soc.*, 1960, 2423.

⁷⁸ D. P. Craig, M. L. Heffernan, R. Mason, and N. L. Paddock, *J. Chem. Soc.*, 1961, 1376.

are easily polarisable the degree of polarisation clearly depends closely upon the environment. The d_{xz} orbital is tangential to the ring; the d_{yz} radial, so the electronegativities are expected to differ.

In a further paper, Craig and Paddock⁷⁹ admit to the involvement of d orbitals other than d_{xz} . For example, the lone pairs of the nitrogen atoms in an sp_y orbital are allowed to overlap with the vacant $d_{x^2-y^2}$ orbital of the phosphorus atom giving rise to π' -bonding⁸⁰ around the periphery of the ring. Later the two approaches were compared and it was shown that the 'island' model was merely a special case of the cyclic model and that the delocalisation energy in the 'island' model is always less, although the differences between the two may be small.⁸¹

Extending such arguments to 1,1-diphenylphosphazene (45), this compound may be stabilised by a fully delocalised π -electron system or by an 'internal cyanine' structure stabilisation. It is important to note that the phosphabenzene (45) has very similar u.v. absorption to the linear phosphonium salt (46), suggesting that the 'island' model is more correct in this case.⁸² In agreement a recent theoretical appraisal of the four models favours the Dewar or the Fukui models.⁸³

By analogy those arguments which apply to phosphabenzenes may be extended to thiabenzenes and thence to other sulphur-containing heterocycles.

5 Mixed Systems

A. Thiazole.—While attempting to explain the base-catalysed exchange of the 4-methyl hydrogen atoms with deuterium in the thiazole (47), Erlenmeyer¹ invoked structures such as (48). This appears to be the earliest reference to such structures involving quadrivalent sulphur. From u.v. studies of isomeric 2-styryl-4-aryl- and 2-styryl-5-aryl-thiazoles, it has been concluded that valence-shell expansion may be important.⁸⁴ To add to the confusion concerning the applicability of theoretical calculations, recent studies of radical phenylation p -nitrophenylation,⁸⁵ and methylation⁸⁶ of thiazole and its methyl derivatives accord well with recent calculations based on a d -model⁸⁷ while disagreeing with a previous p -model.⁸⁸ However the same experimental results are in agreement with a later theoretical treatment based on another p -model.⁸⁹ The anomalous downfield resonance of the 2-proton in the n.m.r. spectrum of thiazole⁹⁰ may perhaps be due to feedback of the p electrons of the carbon-

⁷⁹ D. P. Craig and N. L. Paddock, *J. Chem. Soc.*, 1962, 4118.

⁸⁰ D. W. J. Cruickshank, *J. Chem. Soc.*, 1961, 5486.

⁸¹ D. P. Craig and K. E. Mitchell, *J. Chem. Soc.*, 1965, 4682.

⁸² G. Märkl, *Angew. Chem. Internat. Edn.*, 1964, 3, 147.

⁸³ R. Vîlceanu, A. Balint, and Z. Simon, *Nature*, 1968, 217, 61.

⁸⁴ E. D. Sych and L. P. Umanskaya, *J. Gen. Chem. (U.S.S.R.)*, 1963, 73.

⁸⁵ J. Vitry-Raymond and J. Metzger, *Bull. Soc. chim. France*, 1963, 1784.

⁸⁶ H. J. Dou, *Bull. Soc. chim. France*, 1966, 1678.

⁸⁷ E. Vincent and J. Metzger, *Bull. Soc. chim. France*, 1962, 2039.

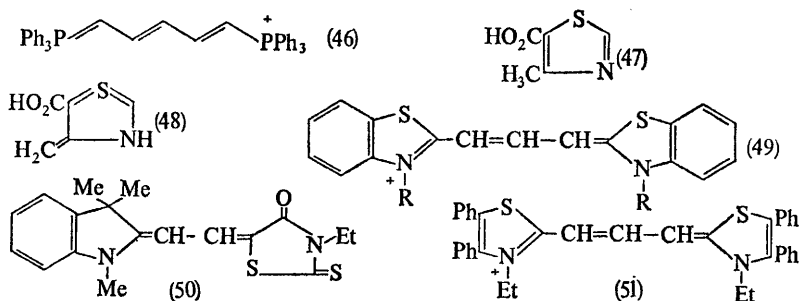
⁸⁸ J. Metzger and A. Pullman, *Compt. rend.*, 1948, 226, 898; *Bull. Soc. chim. France*, 1948, 1166; A. Pullman and J. Metzger, *ibid.*, p. 1021.

⁸⁹ R. Zahradnik and J. Koutecky, *Coll. Czech. Chem. Comm.*, 1961, 26, 156.

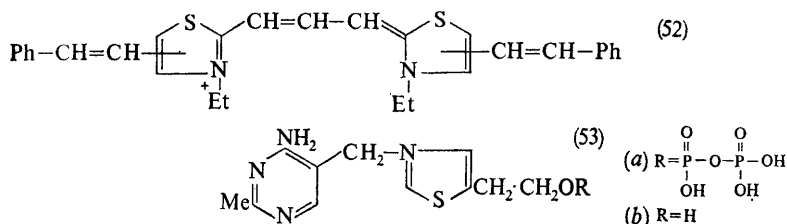
⁹⁰ A. Taurins and W. G. Schneider, *Canad. J. Chem.*, 1960, 38, 1237.

nitrogen double bond into a vacant *d* orbital. This postulation may be supported by the ^{13}C -H coupling constants observed for thiazolium salts (see below concerning thiamine) and from recent studies of the ^{13}C -H coupling constants in vinyltin compounds⁹¹ and n.m.r. studies in vinylsilicon compounds.⁹² In addition the J_{25} coupling constant in thiazole is 1.9 c./sec. and J_{24} is 0 c./sec. while the corresponding couplings in oxazole are both very small, again suggesting the involvement of the *d* orbitals of the sulphur atom in transmitting conjugation.

Considerable work has been done on the thiazolium ring system in connection with the commercially important cyanine dyes. The thiazole dyes (49—51) are



all deeper in colour than their oxygen analogues.⁹³ This uniform behaviour led Knott⁹⁴ to suggest that valence-shell expansion in the heterocyclic ring was responsible, a supposition which is supported by further u.v. studies of cyanine dyes (52) derived from 2-methyl-4-styryl- and 2-methyl-5-styryl-thiazoles where it was found that a styryl group in the 5-position of the thiazole ring is more feebly conjugated with the polymethine chromophore than one in the 4-position.⁹⁵



Coccarboxylase (53a), the pyrophosphate of thiamine (53b), is the coenzyme for a number of important biochemical processes. From deuterium exchange

⁹¹ D. J. Blears, S. S. Danyhik, and S. Cawley, *J. Organometallic Chem.*, 1966, 6, 284.

⁹² R. T. Hobgood, J. H. Goldstein, and G. S. Reddy, *J. Chem. Phys.*, 1961, 35, 2038; R. T. Hobgood and J. H. Goldstein, *Spectrochim. Acta*, 1963, 19, 321; R. Summit, J. J. Eisch, J. T. Trainor, and M. T. Rogers, *J. Phys. Chem.*, 1963, 67, 2362.

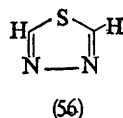
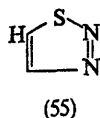
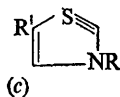
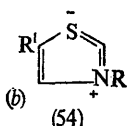
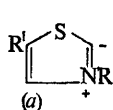
⁹³ B. Beilenson, N. I. Fisher, and F. M. Hamer, *Proc. Roy. Soc.*, 1937, B, 163, 138; L. G. S. Brooker, G. H. Keyes, R. H. Sprague, R. H. Van Dyke, E. Van Lare, G. Van Zandt, F. L. White, H. W. J. Cressman, and S. G. Dent, *J. Amer. Chem. Soc.*, 1951, 73, 5332; E. B. Knott, *J. Chem. Soc.*, 1952, 4099; R. A. Jeffreys, *ibid.*, p. 4823.

⁹⁴ E. B. Knott, *J. Chem. Soc.*, 1955, 916.

⁹⁵ E. D. Sych and E. D. Smaznaya, *J. Gen. Chem. (U.S.S.R.)*, 1963, 68.

studies on simpler model thiazolium salts the action of thiamine has been explained in terms of ionisation of the 2-hydrogen of the thiazolium ring to give the intermediate thiazolium anion (54a).⁹⁶ The exchanged deuterium was detected originally by mass spectral analysis and subsequently (unambiguously) by n.m.r. studies. Breslow stated that valence-shell expansion in the sulphur atom is an unlikely explanation for the stabilisation of the thiazolium anion owing to the unfavourable geometry required in the bent allenic structure at the 2-carbon atom (54b). It is true that such an ylide is not stabilised wholly by valence-shell expansion since imidazolium and oxazolium cations also exchange their 2-hydrogen atoms readily in the presence of base. The difference in the rates of exchange between oxazolium and thiazolium cations and the magnitudes of the ¹³C-H coupling constants of the 2-protons in the two systems, however, indicate that *d*-orbital interaction may well be occurring and the benzyne-like structure (54c), as a contributor of the resonance hybrid, of the intermediate has been postulated.⁹⁷ Calculations indicated that in the thiazolium ring a greater part of the charge (0.6) resides on the sulphur atom so that sufficient *d*-orbital contraction may occur to allow overlap with the adjacent *sp*² orbital containing the lone pair. (The overlap of two *sp*² orbitals has been suggested with respect to benzene;⁹⁸ and the overlap of an *sp*² orbital containing a lone pair with a vacant *d* orbital constitutes the important π' -bonding in phosphonitrilic compounds). However, these calculations were based on a *p*-model and it seems not altogether aesthetically satisfying to calculate the charge in the sulphur atom with such a model and then to proceed to say that the charge is sufficient to cause *d*-orbital contraction. Moreover the use of ¹³C-H coupling constants as a guide to the *s*-character of a bond has been criticised.⁹⁹

Olofson and his collaborators¹⁰⁰ have substantiated considerably the case for *d*- σ overlap by studying the rates of deprotonation of thiazole and related bases. They found an extraordinary rate enhancement when a proton is on a carbon atom adjacent to sulphur and that the position of the nitrogen (whether α or β to that proton) has little effect. Remarkably the 5-proton in isothiazole is ionised more readily than the 2-proton in thiazole. This behaviour is echoed in the thiadiazole series where H(5) in compound (55) is deprotonated more



⁹⁶ R. Breslow, *Chem. and Ind.*, 1957, 893; *J. Amer. Chem. Soc.*, 1957, 79, 1762; 1958, 80, 3719.

⁹⁷ P. Haake and W. B. Miller, *J. Amer. Chem. Soc.*, 1963, 85, 4044.

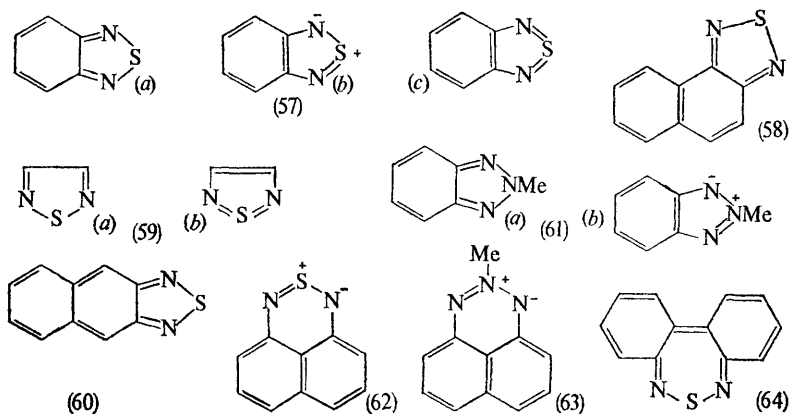
⁹⁸ J. D. Roberts, D. Semenov, H. Simmons, and L. Carlsmith, *J. Amer. Chem. Soc.*, 1956, 78, 601.

⁹⁹ G. J. Karabatsos and C. E. Orzech, *J. Amer. Chem. Soc.*, 1964, 86, 3574.

¹⁰⁰ R. A. Olofson and J. M. Landesburg, *J. Amer. Chem. Soc.*, 1967, 88, 4263; R. A. Olofson, J. M. Landesburg, K. N. Houk, and J. S. Michelman, *ibid.*, p. 4265.

quickly than H(2) in (56). All these results provide strong indications of d - σ overlap with the sulphur atom.

B. 1,2,5-Thiadiazole.—It has been claimed¹⁰¹ that the stability of the well-known thiadiazole derivatives (57) and (58) implies a significant degree of quadrivalent character in the sulphur atom of these compounds. X-Ray crystallographic data¹⁰² seem to support this claim. The reactions of the parent compound (59) itself suggest that the structure (59b) is an important contributor to the resonance hybrid.¹⁰³ However, microwave¹⁰⁴ and electron diffraction studies¹⁰⁵ suggest that the structure (59a) in which the sulphur is bivalent is more important in the ground state. These two views are, however, not incompatible since the reactions could involve excited electronic and vibrational states as well as the ground state. A recent theoretical study has indicated that the quadrivalent character of the sulphur atom increases in the series (59), (57), and (60).¹⁰⁶ It is noteworthy that the u.v. absorption spectra of (57) (λ_{\max} 310 nm).¹⁰⁷ and (61) (λ_{\max} 274 nm)¹⁰⁸ are quite different. The analogous structures (57a, b) and (61a, b) can be drawn for both compounds but no structure analogous to (57c) can be drawn for the benzotriazole. On the other hand, the u.v. spectra of the tricyclic systems (62)¹⁰⁹ and (63)¹¹⁰ which have seven π -electrons associated



¹⁰¹ M. P. Cava and R. H. Schlessinger, *Tetrahedron Letters*, 1964, 3815.

¹⁰² V. Luzzatti, *Acta Cryst.*, 1951, 4, 193.

¹⁰³ L. M. Weinstock, *Diss. Abs.*, 1959, 19, 3136; M. Carmack, L. M. Weinstock, and D. Shew, *Abstr. 136th National Meeting of Amer. Chem. Soc.*, Atlantic City, N.J., Sept. 1959, p. 37P.

¹⁰⁴ V. Dobyns and L. Pierce, *J. Amer. Chem. Soc.*, 1963, 85, 3553.

¹⁰⁵ F. A. Momany and R. A. Bonham, *J. Amer. Chem. Soc.*, 1964, 86, 162.

¹⁰⁶ N. K. Ray and P. T. Narasimhan, *Theor. Chim. Acta*, 1966, 5, 401.

¹⁰⁷ L. S. Efros and R. M. Levit, *J. Gen. Chem. (U.S.S.R.)*, 1955, 25, 183.

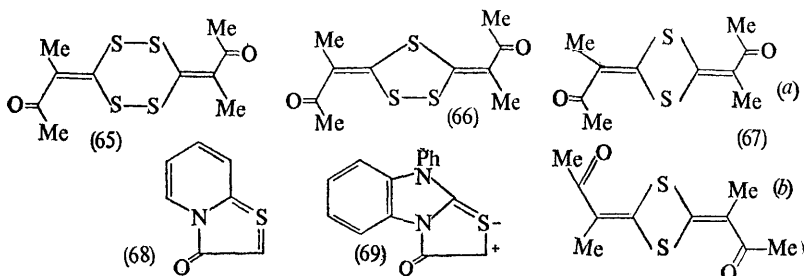
¹⁰⁸ D. Dalmonte, A. Mangini, R. Passerini, and C. Zauli, *Gazzetta*, 1958, 88, 977.

¹⁰⁹ R. Dietz, *Chem. Comm.*, 1965, 57; H. Behringer and K. Leiritz, *Chem. Ber.*, 1965, 98, 3196.

¹¹⁰ M. J. Perkins, *J. Chem. Soc.*, 1964, 3005.

with the heterocyclic ring are remarkably similar (λ_{\max} 658 and 655 nm., respectively), implying no contribution from the N=S=N bond system in the thiadiazine derivative. Also in the eight- π -heterocyclic system (64) sulphur is easily extruded to give diazaphenanthrene.¹¹¹ The properties of these compounds thus strongly suggest delocalisation *via* the *d* electrons of the sulphur in six π -systems. This may be the reason for the observed increase in conjugation observed in the series (65—67), although interaction between the oxygen and sulphur atoms (67*b*) as in furothiophthen derivatives (see later) is undoubtedly also important.¹¹² However, e.s.r. studies of the radical anion derived from (57) based on two different *d*-models suggest that *d*-orbital interaction is not important.¹¹³

C. Mesoionic Compounds.—Although a large number of mesoionic compounds have been prepared, few physical measurements have been made with a view to evaluating their electronic structures. On the basis of u.v. solvent-shift studies¹¹⁴ the structure (68) has been claimed to be important in the resonance hybrid of the molecule and the ease of nucleophilic attack at the 5-position in the thiazole ring of compound (69) has been attributed to similar structures.¹¹⁵



6 Thiothiophthens

Treatment of diacetylacetone with phosphorus pentasulphide gives a compound to which Arndt¹¹⁶ assigned the structure (70). This structure seemed to be confirmed by chemical means when it was found that potassium hydrosulphide reacted with 2,6-dimethylthiapyrone to yield the oxygenated compound (71) which on treatment with phosphorus pentasulphide gave Arndt's compound.¹¹⁷

¹¹¹ G. R. Collins, *Diss. Abs.*, 1966, 403b.

¹¹² A. K. Kirby, *Tetrahedron*, 1966, 3001; T. R. Lynch, I. P. Mellor, S. C. Nyburg, and P. Yates, *Tetrahedron Letters*, 1967, 373.

¹¹³ E. T. Strom and G. A. Russell, *J. Amer. Chem. Soc.*, 1965, **87**, 3326; N. M. Atherton, J. N. Ockwell, and R. Dietz, *J. Chem. Soc. (A)*, 1967, 771.

¹¹⁴ E. B. Knott, *J. Chem. Soc.*, 1955, 937.

¹¹⁵ G. F. Duffin and J. D. Kendall, *J. Chem. Soc.*, 1956, 361.

¹¹⁶ F. Arndt, *Rev. Fac. Sci Univ. Istanbul*, 1948, **13**, A, 57; F. Arndt, P. Nachtwey, and J. Push, *Chem. Ber.*, 1925, **58**, 1638.

¹¹⁷ G. Traverso and M. Sanesi, *Ann. Chim. (Italy)*, 1953, **43**, 795; G. Traverso, *ibid.*, 1954, **44**, 1018; *Chem. Ber.*, 1958, **91**, 1224.

Early n.m.r. work also seemed to confirm the structure (70) since two equivalent hydrogen atoms and two equivalent methyl groups were shown to be present.¹¹⁸ However, almost simultaneously both i.r.¹¹⁹ and X-ray diffraction studies¹²⁰ indicated that the trisulphurated compound had the structure (72) and the oxygenated compound structure (73).

The S-S bond length in (72) is 2.36 Å, greater than the S-S bond length of 2.00–2.10 Å in disulphides¹²¹ but still much less than the sum of the van der Waals radii of 3.70 Å between two sulphur atoms, so bonding to some extent between the two outer with the inner sulphur atom is apparent. Moreover the C-C bond distances are all in the range 1.37–1.38 Å, the bond length of 'aromatic' double bonds. The compound was stated to exhibit 'no-bond' resonance which conferred aromatic properties on the rings. In the oxygenated compound (73) the S-S bond length of 2.12 Å is much nearer normal, suggesting solely the structure (73a) without resonance interaction. However, the S-O distance is 2.41 Å, halfway between the 'normal' S-O single bond length and the sum of the van der Waals radii of the sulphur and oxygen atoms. This may be electrostatic in origin. The polarisation (73b) can be envisaged followed by an electrostatic attraction between the negative oxygen and the positive ring, perhaps with some covalent bonding by involvement of the *d* orbitals of sulphur. Where a full negative charge is available on the oxygen atom as, for example, in the amino-furothiophthen derivatives (see later), a sulphur oxygen bond does seem to be formed.

The X-ray work on these compounds was confirmed by later n.m.r. studies¹²² when it was demonstrated that the oxygenated compound (73) possessed non-equivalent methyl groups and hydrogen atoms. Moreover the proton resonances in the trisulphurated derivatives are consistently down-field from those in the furothiophthens, implying a degree of aromaticity to the thiothiophthens which is not present in the oxygen analogues.

Once the structures of these compounds had been established, the chemistry of the system developed rapidly and many thiothiophthens have been prepared by different routes and from isomeric starting materials indicating the delocalised nature of the system.¹²³ Replacement of carbon by nitrogen as in

¹¹⁸ A. Bothner-By and G. Traverso, *Chem. Ber.*, 1957, **90**, 453.

¹¹⁹ G. Guillouzo, *Bull. Soc. chim. France*, 1958, 1316.

¹²⁰ S. Bezzi, C. Carbuglio, M. Mammi, and G. Traverso, *Gazzetta*, 1958, **88**, 1226; S. Bezzi, M. Mammi, and C. Carbuglio, *Nature*, 1958, 182, 247; M. Mammi, R. Bardi, G. Traverso, and S. Bezzi, *ibid.*, 1961, **192**, 1282.

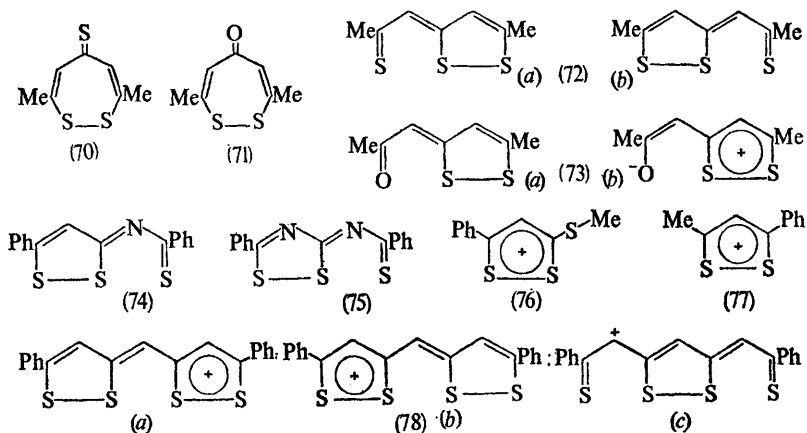
¹²¹ I. M. Dawson and J. M. Robertson, *J. Chem. Soc.*, 1948, 1256; A. Hordvik, *Acta Chem. Scand.*, 1966, **20**, 1885.

¹²² H. G. Hertz, G. Traverso, and W. Walter, *Annalen*, 1959, **625**, 43; G. Pfister-Gillouzo and N. Lozac'h, *Bull. Soc. chim. France*, 1964, 3254.

¹²³ G. Pfister-Guillouzo and N. Lozac'h, *Bull. Soc. chim. France*, 1963, 153; 1964, 3252; E. Klinsberg, *J. Amer. Chem. Soc.*, 1963, **85**, 3244; C. Portail and J. Vialle, *Bull. Soc. chim. France*, 1966, 3187; H. Behringer, H. Reimann, and M. Ruff, *Angew. Chem.*, 1960, **72**, 415; R. Pinel, Y. Mollier, and N. Lozac'h, *Bull. Soc. chim. France*, 1967, 856; Y. Poirier and N. Lozac'h, *ibid.*, p. 865; G. Duguay, H. Quiniou, and N. Lozac'h, *ibid.*, p. 2763; R. J. S. Beer, D. Cartwright, and D. Harris, *Tetrahedron Letters*, 1967, 953; G. Claeson and J. Pederson, *ibid.*, p. 3283.

compounds (74) and (75) seems to have little effect on their properties.¹²⁴

Theoretical calculations have been made by making use of *p*-models which invoke no-bond resonance.¹²⁵ However, Maeda¹²⁶ feels this type of resonance unlikely and considers the system to be truly bicyclic. He considers the central sulphur atom, by virtue of hybridisation, to be quadrivalent. The electronic configuration of the sulphur atom is then $3s^23p^33d$. One *p* orbital makes a σ bond with the central carbon atom, the second enters into the π -electron system of the molecule, and the third mixes with a *d* orbital to yield two hybrid *pd* orbitals which overlap with two *p* orbitals of the adjacent sulphur atoms to complete the σ -framework of the molecule. Such an arrangement, he claims, would explain both the S-S-C bond angles and the S-S bond lengths.



Klinsberg¹²⁷ has recently extended the thiothiophthen system to one containing four sulphur atoms. By allowing compounds (76) and (77) to react the salt (78) is obtained which can be looked upon formally as a cyanine-type structure, resonating between the forms (78a) and (78b). X-Ray structural analysis¹²⁸ indicates that the internal pair of sulphur atoms are less than 3·10 Å apart (considerably less than the sum of the van der Waals radii) so that some bonding between these atoms seems to exist. Structures such as (78c) should therefore be included in the resonance hybrid.

Selenium analogues of the thiothiophthen system have also been prepared.¹²⁹ By comparing the different S—S bond distances¹³⁰ in the unsymmetrical com-

¹²⁴ J. Derocque and J. Vialle, *Bull. Soc. chim. France*, 1967, 3079; G. Lang and J. Vialle, *ibid.*, p. 2865; H. Behringer and D. Bender, *Chem. Ber.*, 1967, 100, 4027.

¹²⁵ G. Giacometti and G. Rigatti, *J. Chem. Phys.*, 1959, 30, 1633; E. M. Shustorovich, *Zhur. obshchei Khim.*, 1959, 29, 2459.

¹²⁶ K. Maeda, *Bull. Chem. Soc. Japan*, 1960, 33, 1466; 1961, 34, 785, 1166.

¹²⁷ E. Klinsberg, *J. Heterocyclic Chem.*, 1966, 3, 243.

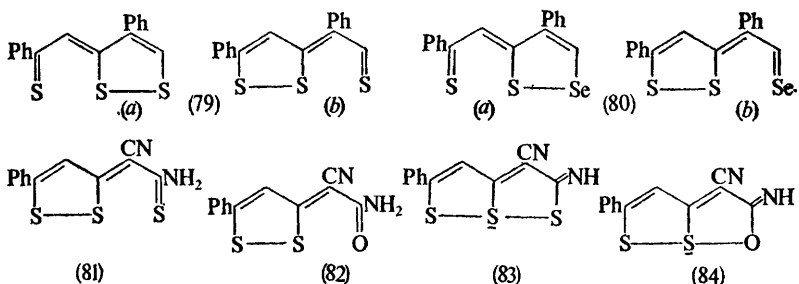
¹²⁸ A. Hordvik, *Acta Chem. Scand.*, 1965, 19, 1253.

¹²⁹ G. Traverso, *Ann. Chim. (Italy)*, 1957, 47, 3; M. Sanesi and G. Traverso, *Chem. Ber.*, 1960, 93, 1566; J. H. van den Hende and E. Klinsberg, *J. Amer. Chem. Soc.*, 1966, 88, 5045.

¹³⁰ A. Hordvik, E. Sletten, and J. Sletten, *Acta Chem. Scand.*, 1966, 20, 2001.

pound (79) with the equal S—S bond lengths in the symmetrical compound (72), Klinsberg has suggested more of a contribution of the structure (79a) to the resonance hybrid. By similar reasoning he points out that selenium is readily accommodated in this type of system and suggests that structure (80b) provides a greater contribution to the resonance hybrid of the molecule. The original X-ray work on compound (72) has been brought into question by workers who claim¹³¹ that thiothiophthens have a typical 'short' S—S bond length in the range 2.12—2.22 Å and a typical 'long' distance (2.47—2.57 Å). However, comparison of the 'long' distance with van der Waals distance between two sulphur atoms still provides evidence for one-bond-no-bond resonance.

It has been noted¹³² that the 'thioamide' (81) should be considered as a thiothiophthen and that the 'amide' (82) should be considered as having the open-chain structure since their u.v. spectra are related in the manner that appears completely characteristic for the thiophthens and furothiophthens.¹³³ Thus in neutral and acidic solutions the compounds (81) and (82) have u.v. spectra which are related in the same way as the spectra of, say, compounds (73) and (72). A remarkable feature of the compound (81) is that functionally the amino-group is acidic. The resistance of the anion to further attack by hydroxyl ion has been attributed to structures such as (83) where the *d* orbitals of sulphur are involved. Even more remarkable is the acidity of the amide (82) which is also stable to further attack by hydroxyl ion. The u.v. spectra of both compounds in alkali are so similar that the structure (84) for the oxygenated ion has been suggested



as an important contributor to the hybrid. Another remarkable feature is the accommodation of oxygen in this system without a corresponding change in the spectra. As Klinsberg points out, such an easy interchange of oxygen and sulphur in heterocyclic systems is virtually unprecedented and argues most cogently for the involvement of the *d* orbitals of the central sulphur atom in these compounds. Determination of the S—O bond lengths must constitute one of the more immediate aims in the study of these anions.

¹³¹ S. M. Johnson, M. G. Newton, I. C. Paul, R. J. S. Beer, and D. Cartwright, *Chem. Comm.*, 1967, 1170.

¹³² E. Klinsberg, *J. Org. Chem.*, 1966, **31**, 3489.

¹³³ H. Behringer and R. Wiedenmann, *Tetrahedron Letters*, 1965, 3705; H. Behringer, M. Ruff, and R. Wiedenmann, *Chem. Ber.*, 1964, **97**, 1732; H. Behringer and D. Weber, *ibid.*, 2567.