Thiothiophthene No-bond Resonance Compounds*

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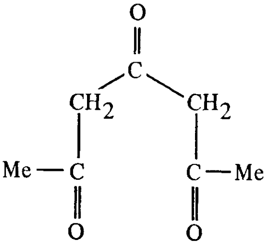
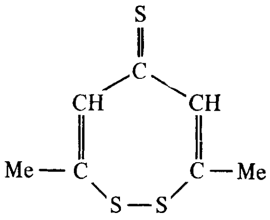
The story of the thiothiophthene no-bond resonance compounds began in 1925, when Arndt, Nachtwey, and Pusch[1] ascribed the 1,2-dithiepine structure (2) to the reaction product of diacetylacetone (1) and phosphorus pentasulphide.

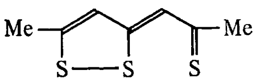


(1)



(2)

Apparently the compound attracted little further attention for *ca.* 30 years, until very unexpected results of an *X*-ray structure determination were reported by Mammi, Bezzi, and Garbuglio.[2] They found that the sulphur atoms are all on a straight line, equally spaced at a distance of 2·36 Å, which is considerably greater than the normal S—S bond distance of 2·04 Å. These results are of course utterly incompatible with the Arndt structure (2), but can be explained by two equivalent resonance structures (3, 3a). Only a few weeks earlier, an i.r.



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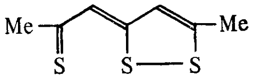
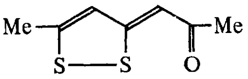


(3a)



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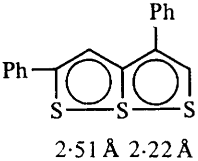
*Based on a lecture at the Third International Organic Sulphur Symposium, University of Caen, May 21—24, 1968.

[1] F. Arndt, P. Nachtwey, and J. Pusch, *Ber.*, 1925, **58**, 1633; *cf.* F. Arndt and C. Martius, *Rev. Fac. Sci. Univ. Istanbul*, 1948, **13**, 70; *Chem. Zentr.*, 1950, II, 767.

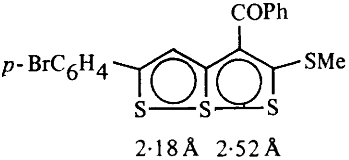
[2] S. Bezzi, M. Mammi, and G. Garbuglio, *Nature*, 1958, **182**, 247; *cf.* S. Bezzi, C. Garbuglio, M. Mammi, and G. Traverso, *Gazzetta*, 1958, **88**, 1226.

analysis had led Guillouzo[3] to propose structure (3), but without any suggestion of the (3a) resonance. Valuable supporting evidence was provided by n.m.r.,[4] which shows the expected equivalence both of the methyl protons and the nuclear protons. In the corresponding carbonyl compound (4) (C=O instead of C=S), neither the methyl protons nor the nuclear protons are equivalent; this result is of course required by the thiothiophthene structure (3) but not the Arndt structure (2). In a more recent n.m.r. study, Dingwall, McKenzie, and Reid have found evidence for ring current, *i.e.*, aromaticity, in the strong deshielding of the ring protons.[5] Sanesi and Traverso[6] have used dipole moment measurements to compare the aromaticity of (3) and (4).

It has since been found that in unsymmetrical thiothiophthene derivatives (5) and (6) the S—S spacing is not equal, and it has been suggested that even in a symmetrical derivative such as (3), the reported equality of S—S bond lengths is not significant but simply due to random packing of the molecules or to an ordered superstructure.[8,9] However, Leung and Nyburg, in a re-examination of (3), found no evidence of statistical disordering.[9a] Furthermore, Hordvik [10] has now shown that in the symmetrical diphenyl derivative (17), the S—S distances are almost equal (2·30 and 2·36 Å); the small difference may reflect a true molecular symmetry slightly disturbed by the intermolecular environment. It does seem clear that no-bond resonance or some equivalent structural notion is needed to account not only for the bond lengths of these compounds but also for their chemistry. Thus it has been shown that an S—S bonding isomer of (5) (*i.e.*, with bond lengths reversed) does not exist. It is also known that, contrary to expectation, the more tightly bound of the two terminal S atoms is the more reactive: in reactions requiring cleavage of one or the other S—S bond (desulphuration, *S*-methylation), it is not the weaker bond that is cleaved as might be expected, but the stronger, with concurrent normalization of the weaker bond.[11,12]



(5)≡(13)
(ref. 7)



(6) (ref. 8)

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[3] G. Guillouzo, *Bull. Soc. chim. France*, 1958, 1316.
[4] H. G. Hertz, G. Traverso, and W. Walter, *Annalen*, 1959, **625**, 43.
[5] J. G. Dingwall, S. McKenzie, and D. H. Reid, *J. Chem. Soc.(C)*, 1968, 2543; see also ref. 36*a*.
[6] M. Sanesi and G. Traverso, *Chem. Ber.*, 1960, **93**, 1566.
[7] A. Hordvik, E. Sletten, and J. Sletten, *Acta Chem. Scand.*, 1966, **20**, 2001.
[8] S. M. Johnson, M. G. Newton, I. A. Paul, R. J. S. Beer, and D. Cartwright, *Chem. Comm.*, 1967, 1170.
[9] J. H. van den Hende and E. Klingsberg, *J. Amer. Chem. Soc.*, 1966, **88**, 5045.
[9a] F. Leung and S. C. Nyburg, *Chem. Comm.*, 1969, 137.
[10] A. Hordvik, *Acta Chem. Scand.*, 1968, **22**, 2397; private communication.
[11] E. Klingsberg, *J. Amer. Chem. Soc.*, 1963, **85**, 3244.
[12] E. Klingsberg, *J. Org. Chem.*, 1968, **33**, 2915.

This is readily enough rationalized as a consequence of steric hindrance of the more weakly bound sulphur atom, but it remains clear that the system is a delicately poised one, with a high degree of interaction between the two S—S bonds, and, apparently, no significant barrier to change of bond-length. This being the case, molecular symmetry in (3) and (17) is at least a reasonable expectation on resonance grounds.[13] All of these results are in striking agreement with very recent calculations of Gleiter and Hoffman: when 3*d*-orbitals are included, the potential energy of the system shows a very flat minimum at a configuration which is almost but not quite symmetrical.[14] These calculations seem to militate against the suggestion that forms (3) and (3a) are not contributing resonance structures but valence tautomers, interconverting too rapidly to be distinguished.[15]

An *X*-ray determination of bond-length for every new compound is hardly feasible and thus secondary experimental criteria are needed. Two such have already been mentioned: the first is the use of n.m.r. to test the symmetry of derivatives such as (3).[4,15,16,16a] The second is the synthetic demonstration that the same thiothiophthene is formed from isomeric starting materials. This has been applied in various ways to products substituted by aryl[11,17,18] or methylthio-groups[16,19a] and to nitrogen isosteres.[20] In principle, of course, synthesis cannot provide information about abnormality of S—S bonding; in other words, there well might be cases where the single product that is obtained is a perfectly normal compound. Therefore this method, though it leads to striking results, can never be conclusive in itself.

Another useful criterion is provided by electronic absorption characteristics, as pointed out by Behringer: the longest wavelength maximum of thiothiophthenes (10), as compared with their precursors (9), is shifted to higher wavelength and reduced in intensity, while a second and much stronger peak appears at 200—250 nm in the u.v.[18,20]

This pattern has been repeatedly recognized in various structural contexts,[21-23] but has been called into question as lacking specificity.[15] The force of the criticism is difficult to judge, since it seems to be based entirely on the position of the longest wavelength maximum, without regard to other features of the spectrum.

When sulphur is replaced by selenium, the observed pattern is continued in the visible region (still weaker absorption maximum at still higher wavelength)

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[13] G. W. Wheland, 'Resonance in Organic Chemistry', Wiley, London, 1955.

[14] R. Gleiter and R. Hoffman, *Tetrahedron*, 1968, **24**, 5899.

[15] D. Leaver and D. M. McKinnon, *Chem. and Ind.*, 1964, 461.

[16] C. Portail and J. Vialle, *Bull. Soc. chim. France*, 1966, 3187.

[16a] E. J. G. Brown, D. Leaver, and T. J. Rawlings, *Chem. Comm.*, 1969, 83.

[17] G. Pfister-Guillouzo and N. Lozac'h, *Bull. Soc. chim. France*, 1963, 153; 1964, 3252.

[18] H. Behringer, M. Ruff, and R. Wiedenmann, *Chem. Ber.*, 1964, **97**, 1732.

[19] R. J. S. Beer, R. P. Carr, D. Cartwright, D. Harris, and R. A. Slater, *J. Chem. Soc.(C)*, 1968, 2490.

[19a] F. Clease and H. Quiniou, *Compt. rend.*, 1969, **268**, *C*, 637.

[20] H. Behringer and D. Weber, *Chem. Ber.*, 1964, **97**, 2567.

[21] E. Klingsberg, *J. Org. Chem.*, 1966, **31**, 3489.

[22] H. Behringer and D. Bender, *Chem. Ber.*, 1967, **100**, 4027.

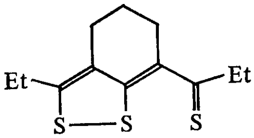
[23] E. Klingsberg, *Chem. and Ind.*, 1968, 1813.

but not in the u.v., where the selenium compound (39) is intermediate between the oxygen and sulphur compounds.[9]

I.r. spectroscopy, although it led to a partial anticipation of the thiothiophthene structure,[3] apparently does not have diagnostic value.[24]

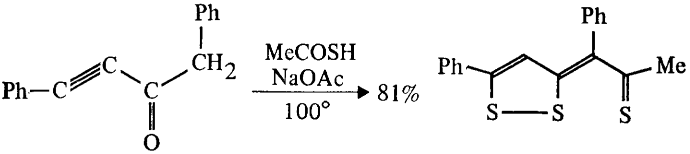
1 Preparation

The first known thiothiophthene derivative, the dimethyl (3), was obtained by Arndt, Nachtwey, and Pusch[1] in 40% yield from diacetylacetone and phosphorus pentasulphide. Later authors have reported yields of 15%[17] and 28—33%.[25] In the most recent and extensive study of the reaction, yields obtained from 23 different ketones averaged 24% and exceeded 30% in only three instances.[26] Behringer, Ruff, and Wiedenmann[18] used the reaction to synthesize the interesting bridged thiothiophthene (7) in 59% yield from 2,6-dipropionylcyclohexanone.



(7)

Simultaneous introduction of all three sulphur atoms also occurs in a surprisingly simple synthesis of (8).



(8)

Under similar conditions, other acetylenic ketones or 1,3-diketones gave thiothiophthenes such as (3) in yields of 9—39%.[25] Addition of sodium disulphide to the triple bond gives derivatives of (9) in nearly quantitative yields.[27]

In most other syntheses of the system, a 1,2-dithiole derivative is condensed with a thiocarbonyl or carbonyl compound. The former gives the thiothiophthene directly; the latter gives a product (9) which is converted to thiothiophthene (10) by reaction with phosphorus pentasulphide. Inasmuch as this step rarely presents any difficulty, interest centres on the condensation reaction. [When needed for some other purpose, (9) is sometimes prepared from the thiothiophthene (10) by desulphuration with mercury(II) acetate,[12] but this reaction

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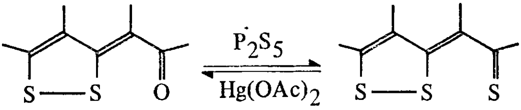
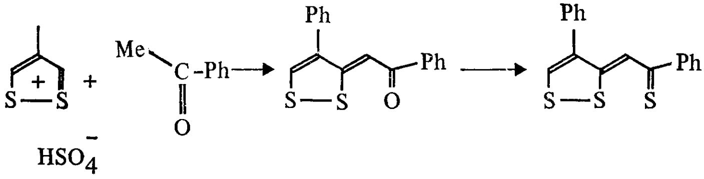
[24] R. Pinel, Y. Mollier, and N. Lozac'h, *Bull. Soc. chim. France*, 1966, 1049.
[25] H. Behringer and A. Grimm, *Annalen.*, 1965, **682,** 188.
[26] M. Stavaux and N. Lozac'h, *Bull. Soc. chim. France*, 1967, 2082.
[27] R. Bohlmann and E. Bresinsky, *Chem. Ber.*, 1967, **100,** 107.



(9) (10)

obviously has no value in the present context.] In our own work, 4-phenyl-1,2-dithiolium hydrogen sulphate (11), which is very readily prepared in any desired quantity from 4-phenyl-1,2-dithiole-3-thione,[28] has proved extremely useful for preparative purposes. The condensation with acetophenone, for example, is well suited for the preparation of 100—500 g quantities of the diphenylthiothiophthene (13); other aromatic ketones react similarly.[11]



(11) (12) (13)

With aliphatic ketones such as acetone, the reaction is slightly more complex but also useful for preparative purposes.[21] 3-Phenyl-1,2-dithiolium salts do not, unfortunately, give satisfactory yields in this reaction: the resulting void is filled partially by the reaction with ethyl benzoylacetate (30% yield)[24] and partially by the condensation reactions of 5-phenyl-1,2-dithiol-3-one (14), an intermediate which is easily prepared in any desired quantity simply by boiling sulphur and ethyl cinnamate in an open flask.[28] It condenses with certain methylenic compounds in phosphorus oxychloride, probably *via* formation of the 3-chloro-1,2-dithiolium salt. Simple ketones such as acetophenone are too weakly activated to condense, but benzoylacetonitrile reacts smoothly; the product (15) gives a thiothiophthene (16) which smoothly eliminates the cyano-group in refluxing hydrobromic–acetic acid to give (17).[11] Malononitrile condenses with (14) in satisfactory yield under the same conditions.[21]

Aroylacetonitriles also condense with dithiolethiones[29] and, more successfully, with 'trithionium salts' such as (18) to give, ultimately, the benzothiothiophthene (19).[18] Bond-length determination would be particularly interesting here, since no-bond resonance is presumably disfavoured by the *o*-quinonoid character of structure (19a).

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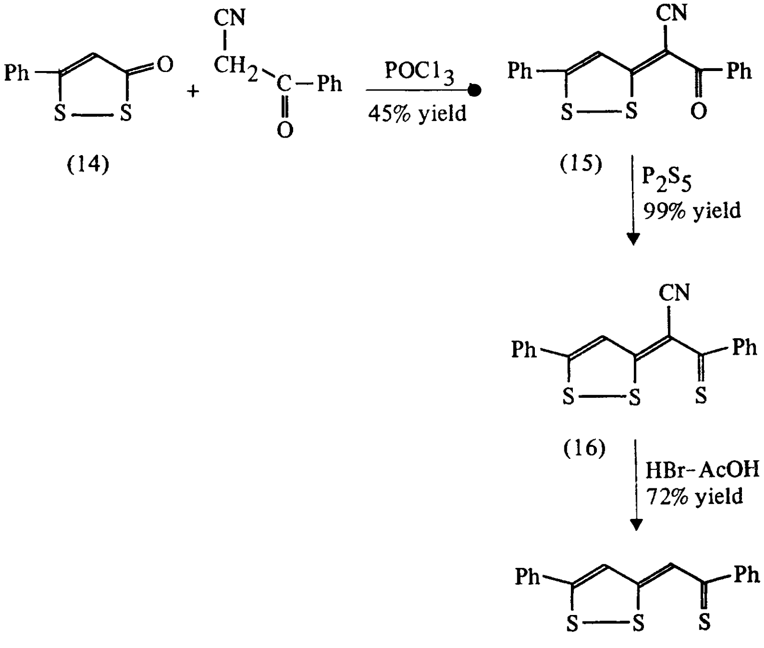
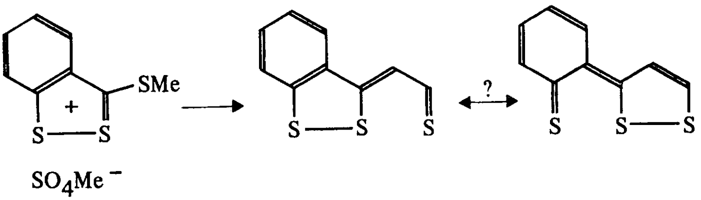
[28] E. Klingsberg, *J. Amer. Chem. Soc.*, 1961, **83**, 2934.

[29] Y. Mollier and N. Lozac'h, *Bull. Soc. chim. France*, 1963, 157.



(14) (15) (16) (17)



(18) (19) (19a)

Except for the interesting cationoid species recently described by Brown, Leaver, and Rawlings,[16a] no other thiothiophthenes fused to an aromatic ring seem to have been reported, although closely related systems such as (20) and (21) are known.[30,31] Oxygen attached to a phenyl ring is resistant to the action of phosphorus pentasulphide.[26,31,32]

In another interesting synthesis of the system (9), dithiolethiones are condensed with diazoketones, but yields are poor.[15,31] Better yields are reported in a base-induced rearrangement of 4*H*-thiapyran-4-thiones.[32a]

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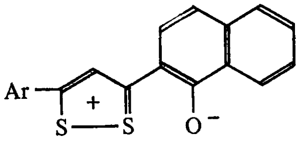
[30] Y. Poirier and N. Lozac'h, *Bull. Soc. chim. France*, 1967, 865.

[31] Y. Poirier and N. Lozac'h, *Bull. Soc. chim. France*, 1967, 2090.

[32] R. Pinel, Y. Mollier, and N. Lozac'h, *Bull. Soc. chim. France*, 1967, 856.

[32a] J. G. Dingwall, D. H. Reid, and J. D. Symon, *Chem. Comm.*, 1969, 466.



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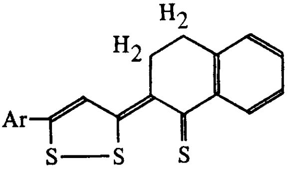
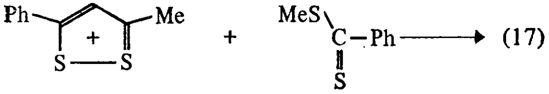


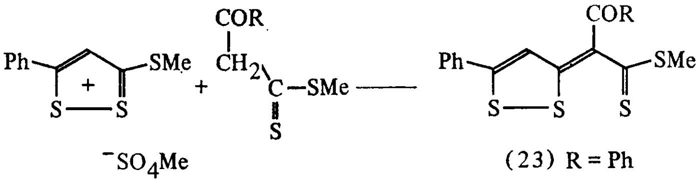
(21)

Thiocarbonyl compounds and dithioles gives thiothiophthenes directly. In the first synthesis of this type, reported by Leaver and McKinnon,[15] the dithiolium ring in (22) provides the necessary activation; yields are not stated.



(22)

In more recent syntheses, the roles of the reactants are reversed: the dithioester is the activated methylene compound, giving products (23, 24) substituted by a methylthio-group.



(23) R = Ph

(24) R = OEt

Yields are excellent; the thiothiophthene structure assignment is based on u.v. spectra.[19,19a]

Thiothiophthenes substituted by two methylthio-groups have also been prepared in various ways; in one interesting synthesis, the same product (29) is obtained from the isomeric dithiolethiones (25) and (27) in yields of 65% and 69%, respectively.[16,19] Evidently the dianionoid addition products (26) and (28) are interconverted by no-bond resonance.

Phenylacetylene condenses with 5-aryl-1,2-dithiole-3-thiones to give thiothiophthenes in yields up to 50%.[33]

Dingwall, McKenzie, and Reid have shown that the 'Vilsmeier salts' (30), obtained in good yield from dithiolium salts and dimethylthioformamide, react

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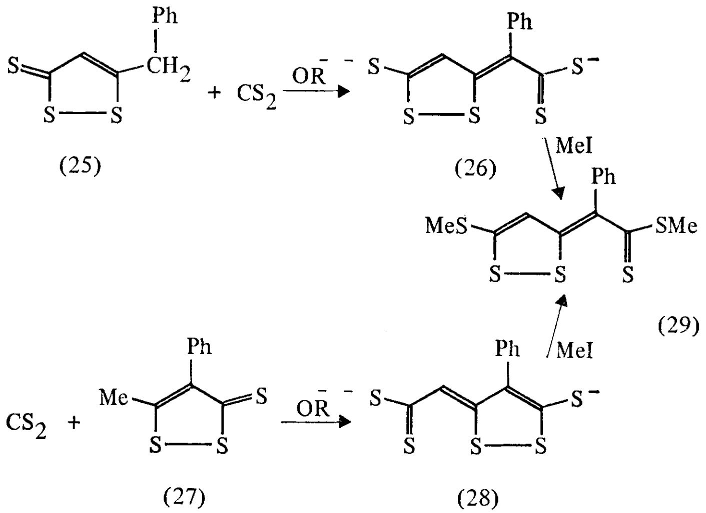
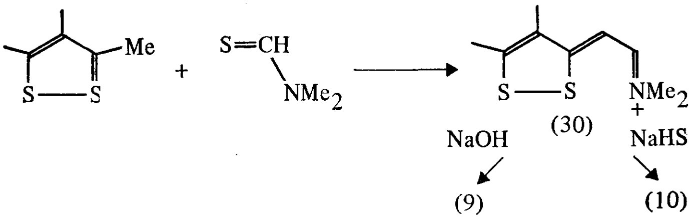
[33] H. Davy, M. Demuynck, D. Paquer, A. Rouessac, and J. Vialle, *Bull. Soc. chim. France* 1966, 1150; 1968, 2057.





smoothly with sodium hydrogen sulphide to give thiothiophthenes.[5] This recent paper is noteworthy for its careful description of the preparation of a number of difficultly accessible thiothiophthenes, including the unsubstituted parent compound and several monosubstitution products; for the former, however, *cf.* ref. 32*a*.

Other preparative reactions are reviewed by Lozac'h[34] and Beer.[34a]

2 Reactions

Nomenclature and numbering are conveniently based on the simple bicyclic representation of 6*a*-thiothiophthene as (31), with expanded octet at the central sulphur atom. In the term 'trithiapentalene', preferred in the French literature, numbering is fortunately the same. Formula (31) is of course more concise than the dual resonance structures (3, 3*a*), but the latter are perhaps more useful in representing important chemical features of the system, its thiocarbonyl character and vinylogous relationship to the 1,2-dithiole-3-thiones (32).

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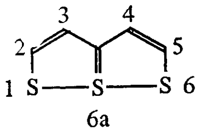
[34] N. Lozac'h, in 'Organosulfur Chemistry; Reviews of Current Research', ed. M. J. Janssen, Interscience, New York, 1967, pp. 179—201.

[34a] R. J. S. Beer, 'Annual Reports on the Mechanisms of Reactions of Sulfur Compounds', Intrascience Research Foundation, Santa Monica, California, 1968, vol. 2, p. 121.



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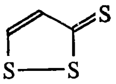


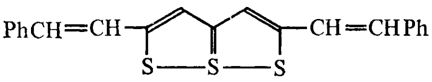
(32)

A more cumbersome system of nomenclature based on the carbon skeleton has found some use in the German[4] and American[11,12] literature. In Chemical Abstracts the system is named as a dithiolodithiole, but this does not seem to be used in the primary literature. 'Thiathiophthene' should also be noted as an alternative to 'thiothiophthene'; different spellings can sometimes be found in different articles in the same issue of the same journal.

A number of 2,5-disubstituted thiothiophthenes have been brominated in the 3-position. Nitration and nitrosation also occur at the 3-position, sometimes with loss of a sulphur atom. These results are in agreement with the results of charge-density calculations,[35] but the blocking of the 2- and 5-positions robs the experiments of selective character and may even be necessary to stabilize the system against the reaction conditions; sulphuryl chloride converts thiothiophthenes with an open 2-position to intractable pitch.[21]

The diphenylthiothiophthene (17) reacts with dimethylformamide and phosphorus oxychloride to give a good yield of the 3-aldehyde.[36] Dimethylthioformamide has also been recommended in formylation.[36a]

The positive charge at the 2-position, found by the calculations of Beer and his colleagues,[35] is confirmed by nucleophilic displacement reactions[19] and by activation of alkyl side-chains; Stavaux and Lozac'h find that (3) condenses readily with two molecules of benzaldehyde to give a high yield of the distyrylthiothiophthene (33), whereas the methyl group in (34) is inert.[37]



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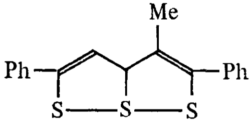

(34)

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[35] R. J. S. Beer, D. Cartwright, R. J. Gait, R. A. W. Johnstone, and S. D. Ward, *Chem. Comm.*, 1968, 688.

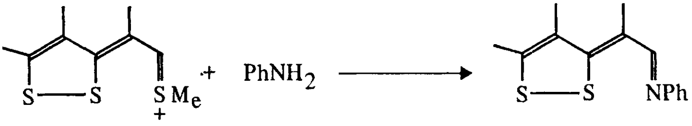
[36] J. Bignebat and H. Quiniou, *Compt, rend.*, 1968, **267**, *C*, 180.

[36a] J. G. Dingwall, D. H. Reid, and K. Wade, *J. Chem. Soc.* (*C*), 1969, 913.

[37] M. Stavaux and N. Lozac'h, *Bull. Soc. chim. France*, 1968, 2077.

Nucleophilic attack by hydrosulphide at the 2-position probably initiates the very interesting rearrangement to 4*H*-thiapyran-4-thiones, recently described by Dingwall and Reid.[38]

Although 2,4-dinitrophenylhydrazones and anils are given by some[4,12] (but not all[11]) derivatives of (9), thiothiophthenes are inert to carbonyl reagents.[6] Anils (36) are, however, readily given by the *S*-methylated thiothiophthenes (35),[12,38a] which are vinylogues of the 'trithionium salts' (37), just as thiothiophthenes are vinylogues of the 'trithiones' (1,2-dithiole-3-thiones).



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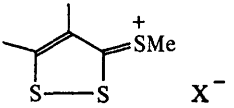


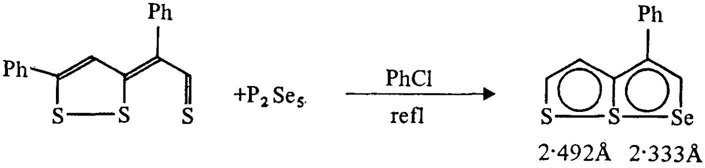
(37)

Normal thiocarbonyl character is also shown in the desulphuration of (10) to (9) with mercury(II) acetate.[12] Beer and his associates have observed cases in which this replacement is accompanied by other elimination reactions.[19]

The effect of alcoholic alkali on (3) is to cause isomerization to a dimercaptan which has been shown to be a thiophene derivative.[39]

3 Isosteres of Thiothiophthene

Selenium and oxygen isosteres differ strikingly in their bonding characteristics. The selenium derivative (39) was made from (38) and phosphorus selenide,[9] a reagent which is much more limited than phosphorus pentasulphide in its utility but gives satisfactory results in the present case. The same compound has been obtained from 'Vilsmeier salt' (30) and sodium hydrogen selenide.[5] *X*-Ray



(38) (39)

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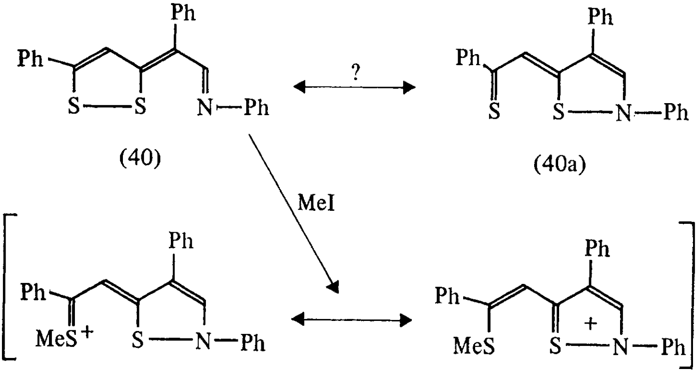
[38] J. G. Dingwall and D. H. Reid, *Chem. Comm.*, 1968, 863.
[38a] H. Behringer and J. Falkenberg, *Chem. Ber.*, 1969, **102**, 1580.
[39] F. Arndt and W. Walter, *Chem. Ber.*, 1961, **94**, 1757.

crystallography shows that the corresponding S—S bond-lengths in (13) and (39) are almost identical.[9] In other words, selenium replaces sulphur without disturbing the system. This is also borne out by the S—Se bond length of 2·33 Å, appreciably higher than the sum of the covalent bond radii for S and Se (2·21 Å); experimental values for comparable S—Se bonds are apparently not available in the literature.

The oxygen isosteres of thiothiophthenes are of course their precursors (8). *X*-Ray crystallographic analysis shows that the S—S distance of 2·36 Å in (3) falls to the nearly normal value of 2·12 Å in (4).[40] Clearly oxygen is much less effective than selenium as a replacement for sulphur in the system. The S—O distance in (4) (2·41 Å) is far greater than the normal S—O bond length of 1·69 Å. It is, however, less than the sum of the van der Waals radii (3·2 Å), and partial bonding has been proposed as an explanation for the abnormal i.r. absorption of the carbonyl group:[34] 1520—1620 cm.$^{-1}$ instead of 1620—1720 cm.$^{-1}$ Hückel calculations, however, suggest that S—O overlap is slight.[40a] In (12) the S—S and S—O distances are 2·11 and 2·38 Å, respectively.[10] A very short S—O distance of 2·03 Å has been reported for a related nitroso-compound.[40b]

The anils or S—N isosteres (40) have recently been obtained in several different ways.[12,38a] No evidence is yet available as to possible S—N bonding (40a).



(40) (40a)

(41) (41a)

Methyl iodide reacts at sulphur to give what is believed to be the isothiazolium salt (41); its reaction with aniline did not introduce a second arylamino residue as hoped, but simply demethylated to regenerate (40)[12].

Isosteres are also known in which ring carbon is replaced by nitrogen. No-bond resonance structure assignments are based on the spectroscopic and synthetic criteria.[21,22,41]

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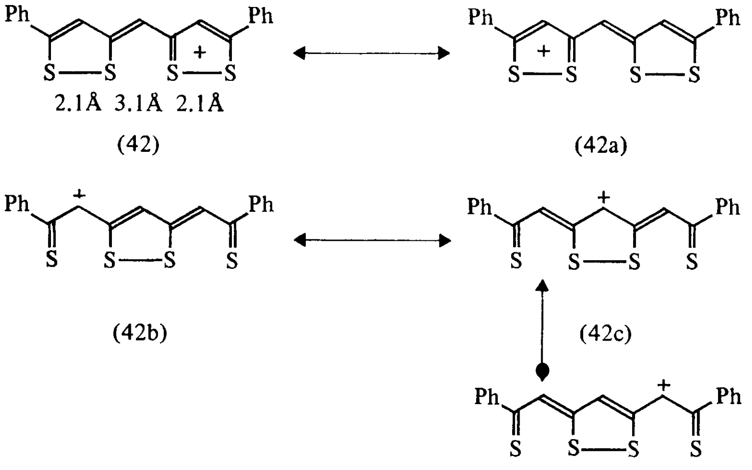
[40] M. Mammi, R. Bardi, G. Traverso, and S. Bezzi, *Nature*, 1961, **192**, 1282.
[40a] J. A. Kapecki and J. E. Baldwin, *J. Amer. Chem. Soc.*, 1969, **91**, 1120.
[40b] P. L. Johnson and I. C. Paul, *J. Amer. Chem. Soc.*, 1969, **91**, 781.
[41] J. Derocque, M. Perrier, and J. Vialle, *Bull. Soc. chim. France*, 1968, 2062.

4 Other Variations

The thiothiophthene structural principle is capable of indefinite extension: just as conjugated polyenes are built up by repetition of vinylene units, higher and higher no-bond resonance systems could be built up by repetition of vinylene thio units. Examination of the structures shows that charge type alternates: systems with an odd number of sulphur atoms (*e.g.*, thiothiophthene itself) are neutral, whereas systems with an even number of sulphur atoms are cationic. The first such cation contains four sulphur atoms and has been reported; it is a symmetrical methincyanine in the 1,2-dithiole series (42, 42a).



(42) (42a)

(42b) (42c)

(42d)

The terminal S—S bonds in (42) (2·1 Å) are essentially normal, and the suggestion that (42b), (42c), and (42d) also make some contribution was based on the collinearity of all four sulphur atoms and the fact that the central S—S distance of 3·1 Å is well below the van der Waals distance (3·7 Å).[42,43] However, an even shorter S—S distance (2·95 Å) has since been reported[43a] for a phosphamethincyanine of the benzothiazole series, in which there is no indication of S—S bonding. Still more recently, an *X*-ray study has found a three-sulphur thiothiophthene system little affected by a fourth sulphur in the row.[43b] A thiocarbonyl derivative of a four-sulphur system has been briefly reported, as well as two different five-sulphur systems.[23,44]

The no-bond resonance principle can be extended not only upward, but also downward to the 1,2-dithiolium cation (43); *i.e.*, (43a) might be a contributing form.

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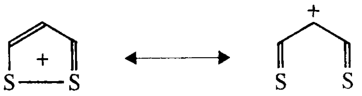
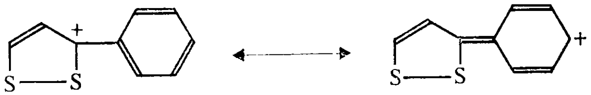
[42] E. Klingsberg, *J. Heterocyclic Chem.*, 1966, **3**, 243.
[43] A. Hordvik, *Acta Chem. Scand.*, 1965, **19**, 1253.
[43a] R. Allmann, *Chem. Ber.*, 1966, **99**, 1332.
[43b] J. Sletten, *Chem. Comm.*, 1969, 688.
[44] M. Stavaux and N. Lozac'h, *Bull. Soc. chim. France*, 1967, 3557; 1968, 4273.

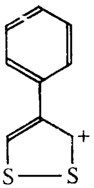


(43) (43a)

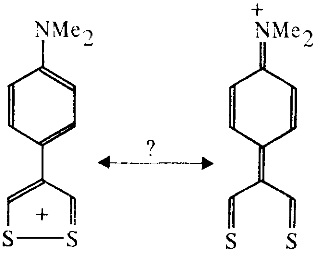
Theoretical support for (43*a*) seems to be lacking at present,[45] and the available experimental evidence is against it: u.v. absorption spectra indicate a high degree of interannular interaction in 3-phenyl-(44) but not 4-phenyl-1,2-dithiolium salts (45).[28] It might be interesting to apply a more searching test by introducing an electron-releasing group into (45); thus a bathochromic shift in (46) might indicate an important contribution from (46*a*).



(44)



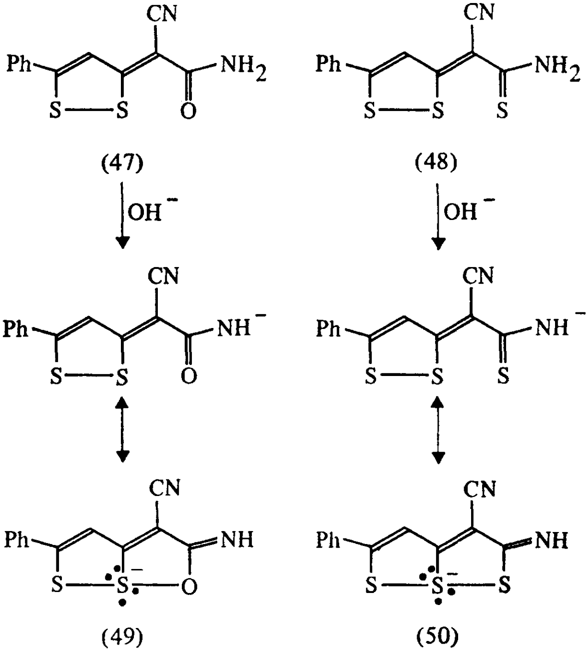
(45)



(46) (46a)

[45] G. Bergson, *Arkiv. Kemi*, 1962, **19**, 181.

No-bond resonance has also been invoked to explain the anomalous properties of certain anionoid systems: the amide (47) and the thioamide (48), when dissolved in aqueous sodium hydroxide, are remarkable both for their stability at the boil and for the close similarity of their u.v. absorption spectra, which seems to be without precedent for sulphur–oxygen isosteres of any known type. It has been suggested that these properties can be explained by sulphur octet expansion in the anions, giving a no-bond resonance system which, unlike thiothiophthene, can equally well accommodate sulphur or oxygen (49, 50).[21] I.r. data have been reported,[46] and also several benzo-substitution products of (47) and (48).[47]



Unfortunately, the prospects are not very bright for bond-length determination by *X*-ray methods, because no crystalline salts of these anions are known.

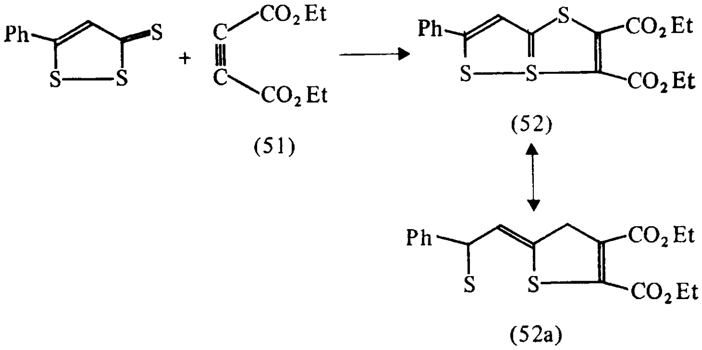
In another interesting variation, the no-bond resonance idea has been extended to the 1,3-dithiole series; the addition of 1,2-dithiole-3-thiones to acetylenes such as (51) gives a series of products which resemble thiothiophthenes in various respects and have been formulated as (52) with an indeterminate contribution from the normal thiocarbonyl form (52a). Bond lengths have not been reported.[48,49]

[46] Y. Mollier, F. Terrier, R. Pinel, and N. Lozac'h, *Bull. Soc. chim. France*, 1967, 2074.

[47] A. Rouessac and J. Vialle, *Bull. Soc. chim. France*, 1968, 2054.

[48] H. Behringer and R. Wiedenmann, *Tetrahedron Letters*, 1965, 3705.

[49] D. B. J. Easton and D. Leaver, *Chem. Comm.*, 1965, 585.



(51)

(52)

(52a)

These products can be isomerized to ordinary thiothiophthenes, which are also obtainable directly from the dithiolethione and the acetylene under suitable reaction conditions.[33] Acetylenes condense similarly with 1,2,4-dithiazole-3-thiones.[50]

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[50] H. Behringer, D. Bender, J. Falkenberg, and R. Wiedenmann, *Chem. Ber.*, 1968, **101**, 1428.