Conformational Isomerism in Cation Radicals of Alkylthiothiophens

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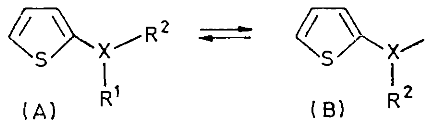
Radical cations containing a thiophen ring substituted by 2,5-bisalkylthio-groups have been obtained and their e.s.r. spectra interpreted in terms of unequally populated rotational isomers. Assignment of their structures has been achieved by examining the effect of steric hindrance caused by bulky substituents on the ratio of conformers. The hyperfine splitting constants have been assigned experimentally to the asymmetric conformers, the results being in agreement with the conclusions of theoretical methods. Theoretical calculations (CNDO/2) indicate that, for these derivatives, the most populated conformation of the radical cation corresponds to the most stable rotational isomer of the neutral molecule.

ASYMMETRICALLY substituted thiophens are expected, in principle, to exist as rotational isomers of the types (A) and (B). Many investigations have been reported on this subject but unambiguous evidence for the existence of these conformers has seldom been obtained in the case of neutral molecules. However, several indications of restricted rotation have been collected for a relatively large number of derivatives by means of dipole moment investigations,[1] and i.r. spectral,[2] ultrasonic relaxation,[3] and n.m.r. spectral measurements.[4] Unfortunately, whereas for some furan [5] and pyrrole [6] derivatives it was possible to slow down the internal rotation rate and therefore to detect the rotational isomers by n.m.r. spectroscopy at low temperatures, this could never be achieved for the analogous thiophen derivatives. This would indicate either that only one conformer is present or that the lifetimes of the isomers are lower than $\Delta\nu^{-1}$, $\Delta\nu$ being the difference between the resonance frequencies of the conformers. Owing to this situation the assignment of structure to the more stable isomer is not always satisfactory, although the advent of n.m.r. spectroscopy in liquid crystalline solvents seems quite promising for this purpose.[7]



(A) (B)

The situation is more promising for negative radicals of thiophen derivatives, as many cases have already been reported where rotational isomers could be unambiguously detected by e.s.r. spectroscopy.[8] Recently rotational isomers were also found in neutral radicals containing a nitroxide group bonded to thiophen,[9] so that, to complete our survey of rotational isomerism in thiophen radicals, we have investigated thiophen derivatives bearing a positive charge. The main difficulty originates from the fact that positive radicals of thiophen-containing molecules are more unusual than the corresponding anions. For many years the only report of such a species was that of tetraphenylthiophen cation;[10] however it was not completely unambiguous as the lack of an appreciable fine structure prevented a definite identification by e.s.r. spectroscopy. Recently, however, unambiguous proof of the existence of positive radicals in the thiophen series [11] has been obtained. In searching for a positive thiophen radical which also exhibited rotational isomerism we investigated 2,5-bis(methylthio)thiophen (I), as the phenomenon had been observed in the analogous benzene derivative.[12]

RESULTS AND DISCUSSION

The positive radical of 2,5-bis(methylthio)thiophen (I) was obtained by reaction with a Lewis acid ($AlCl_3$) in nitromethane. The e.s.r. spectrum (Figure) of (I) shows two superimposed groups of signals which have been interpreted as due to two of the three possible

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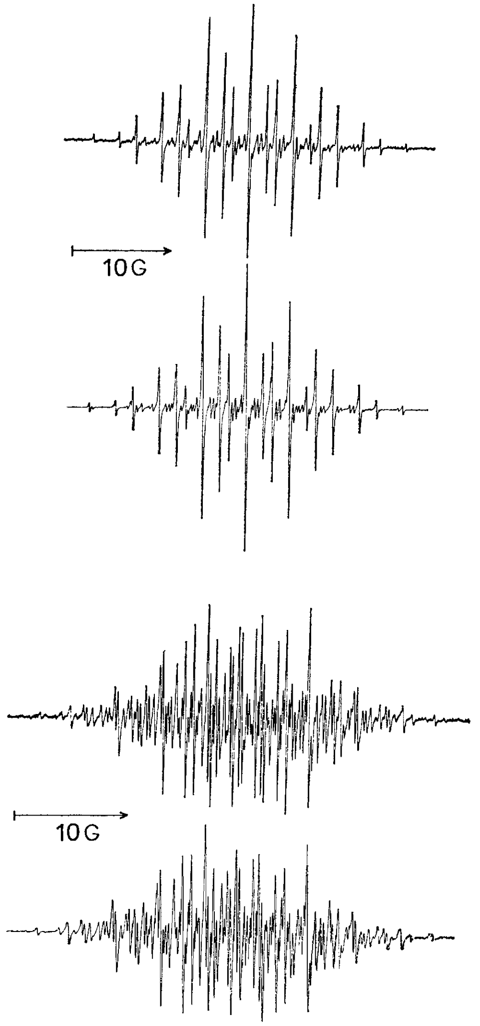
TABLE 1

Hyperfine splitting constants (G) of cation radicals (I)—(VI)

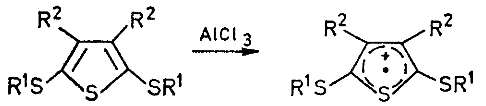
Compound		$a_{3\text{-H}}$	$a_{4\text{-H}}$	$a_{syn\text{-SR}'}$	$a_{anti\text{-SR}'}$	$a_{3\text{-Me}}$	$a_{4\text{-Me}}$
(Ia)	(75%)	2·60	2·60	4·30			
(Ib)	(25%)	3·48	2·16	4·40	3·82		
(IIa)	(80%)	2·62$_5$	2·62$_5$	3·48$_5$			
(IIb)	(20%)	2·95	2·30	3·70	3·12$_5$		
(IIIa) *	(*ca.* 100%)	2·62$_5$	2·62$_5$	2·50			
(IIIb)							
(Va)	(100%)			3·90		2·25	2·25
(Vb)							
(VIa)	(80%)		1·96	3·94 and 4·20		2·74	
(VIb)	(20%)		1·60	4·30	3·70 or 3·60	3·60 or 3·70	

* An additional splitting (0·13 G) corresponding to the 12 protons of the two isopropyl groups was also detected.

rotational isomers *S-cis-cis* (Ia), *S-cis-trans* (Ib), *S-trans-trans* (Ic). The less intense signals (*ca.* 25%) could be unambiguously assigned to the asymmetric conformer (Ib) because of the different hyperfine splittings (see Table 1) for the 3- and 4-hydrogen atoms and for the two SMe groups which are *syn* or *anti* with respect to the heterocyclic sulphur atom. On the other hand the more intense signals (75%) belong to a symmetric isomer, but one cannot directly assign it to structure (Ia) or (Ic).

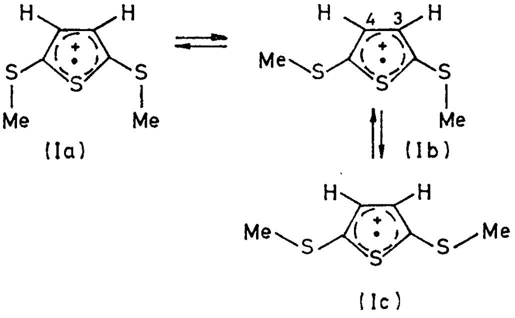


Upper traces: experimental and simulated e.s.r. spectrum of the cation radical of 2,5-bis(methylthio)thiophen (I) at 0 °C in nitromethane. The *S-cis-cis* isomer (Ia) (75%) has a *g* factor smaller than the *S-cis-trans* (Ib) (25%) ($\Delta g = 5 \times 10^{-5}$). The hyperfine splitting constants are reported in Table 1 and the line-width is 0·1 G for both conformers. Lower traces: experimental and simulated e.s.r. spectrum of the cation radical of 3-methyl-2,5-bis(methylthio)thiophen(VI) at −40 °C in nitromethane. The *S-cis-cis* isomer (VIa) (80%) has a *g* factor smaller than the *S-cis-trans* (VIb) (20%) ($\Delta g = 6 \times 10^{-5}$). The hyperfine splitting constants are in Table 1 and the line-width is 0·15 G for both conformers



(I) $R^1 = Me$; $R^2 = H$
(II) $R^1 = Et$; $R^2 = H$
(III) $R^1 = Pr^i$; $R^2 = H$
(IV) $R^1 = Bu^t$; $R^2 = H$
(V) $R^1 = Me$; $R^2 = Me$

A way to determine the conformation experimentally is to examine derivatives having large R^1 groups because the greater their steric effect the lower is the proportion of species (Ic) and the larger that of (Ia). Accordingly, an increase in the ratio symmetric : asymmetric would require that the more stable isomer is (Ia) whilst a decrease of the ratio would support structure (Ic).



The ethyl derivative (II) gives a different isomer ratio (4 : 1 symmetric : asymmetric) than (I) but this, though indicative that (Ia) has the greater stability, is not large enough to allow an unambiguous conclusion. For the isopropyl derivative (III) only the symmetric radical was detected, although the complicated spectral patterns due to the additional splitting (0·13 G) of the four methyl groups, make it impossible to exclude the presence of a second rotamer with a relatively small concentration.

This result permits a firm assignment of the *S-cis-cis* structure (a) to the more stable radical as it would be unrealistic to consider the *S-trans-trans* (c) as the more stable conformation when R^1 is the bulky isopropyl group. For the case, however, with the largest steric effect ($R^1 = Bu^t$) no radical has been detected from compound (IV); although rather puzzling this may be explained by taking into account a possible distortion out of the thiophen plane of the two sulphur–alkyl bonds owing to the extreme hindrance of the substituent. If so, the conjugation path of the unpaired electron would be reduced and the stability of the radical lowered enough to prevent its detection under our experimental conditions.

To confirm the assignment in an unambiguous way the effect of a bulky substituent at the 3- and 4-positions has been examined by using 3,4-dimethyl-2,5-bis-(methylthio)thiophen (V). Here the line-width of the radical ion is sharp and only the symmetric species has been identified. Accordingly little doubt is left that the more stable of the two symmetric structures is *S-cis-cis* (a).

A point which is always difficult to solve when restricted motion makes two previously equivalent positions asymmetric is the assignment of the corresponding hyperfine splittings. As these differences are usually rather small, assignments have been either neglected or attempted only by theoretical methods. The latter have been based customarily on the so-called ' α effect '[13] which basically consists of an arbitrary modification of the coulomb integral in the framework of Hückel wave functions. The approach has been used to assign structures of rotational isomers.[8,12-15]

To test the reliability of these calculations we compared their results with those of a more sophisticated approach (*i.e.* the INDO approximation[16]) as applied to the positive radical which can be considered the simplest derivative in this series, that is the hydroquinone radical cation. In Table 2 the hyperfine splitting constants calculated from the INDO approach are reported for both the *cis*- and *trans*-isomers and compared with the experimental values and with the spin densities taken from ref. 15. The trend of the INDO computed splittings is in agreement with the previously computed values and consistent with the experimental data. Furthermore the INDO energies are almost identical for both the isomeric radicals (*trans* being more stable than *cis* only by 0·053 kcal mol^{-1}) in agreement with the 1 : 1 experimental ratio. It seems therefore that in the *trans*-isomer the *ortho*-hydrogen atoms *syn* to the conformationally fixed group (here OH) have a smaller splitting than the *ortho*-hydrogen atoms in the *anti*-position; this is also in agreement with the observation on the *trans*-isomer of terephthaldehyde radical anion.[13] This would lead to the assignment in the transoid structure (Ib) of the larger splitting to 3-H and the smaller to 4-H. To verify this conclusion we applied the McLachlan calculation of the α effect to radical (I), as the INDO method cannot be applied to sulphur-containing radicals. The approach we used is very similar to that reported in ref. 12. The details are discussed in the Calculations section. As expected the results indicate that in (Ib) $a_{3\text{-H}} = 3{\cdot}48$ and $a_{4\text{-H}} = 2{\cdot}16$ G, whereas $a_{\text{SMe}} = 4{\cdot}40$ when *syn* to the sulphur of the thiophen ring and 3·82 G when *anti* (Table 3). However, since the differences in the hyperfine splittings are rather large, we felt this was a case where an experimental assignment was worth an attempt. This was particularly important in order to ascertain the validity of the theoretical methods which have so far been the only possible way of assigning splitting constants in conformational isomers.

TABLE 2

Experimental and computed (INDO) hyperfine splitting constants for the *cis*- and *trans*-rotational isomers of hydroquinone radical cation. In the fourth column the calculated spin densities previously employed[15] for assigning the hyperfine splitting values are reported (McLachlan method with α effect). The numbering of the protons is the same as in ref. 15

	Experimental[15]	INDO	McLachlan spin densities[15]
trans-Hydroquinone			
a_{OH}	3·294	−5·26	(ρ_{O} = 0·155)
$a_{2\text{-H}}$	2·055	−1·20	($\rho_{\text{C-2}}$ = 0·086)
$a_{3\text{-H}}$	2·456	−1·37	($\rho_{\text{C-3}}$ = 0·103)
cis-Hydroquinone			
a_{OH}	3·294	−5·26	(ρ_{O} = 0·155)
$a_{2\text{-H}}$	2·356	−1·34	($\rho_{\text{C-2}}$ = 0·099)
$a_{3\text{-H}}$	2·147	−1·23	($\rho_{\text{C-3}}$ = 0·090)

TABLE 3

Experimental and computed (McLachlan method with α effect: see Calculations section) hyperfine splitting constants for the *S-cis-cis* (Ia) and *S-cis-trans* (Ib) conformations of (I). The λ value has been kept equal to 1·2

Conformation	Position	Experimental	Computed
S-cis-cis (Ia)	$a_{3\text{-H}} = a_{4\text{-H}}$	2·60	2·93
	$a_{syn\text{-SMe}}$	4·30	4·24
S-cis-trans (Ib)	$a_{3\text{-H}}$	3·48	3·47
	$a_{4\text{-H}}$	2·16	2·61
	$a_{syn\text{-SMe}}$	4·40	4·67
	$a_{anti\text{-SMe}}$	3·82	3·98

For the SMe values it is known that couplings have the largest values when the CH axis is parallel ($\theta = 0°$) to the p-π orbitals of the conjugated systems[17,18] according to equation (1). In the *S-cis-cis* conformation (Ia) the

$$a_{\beta\text{-H}} = (B_0 + B_2 \cos^2 \theta)\rho_0^{\pi} \qquad (1)$$

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[13] E. W. Stone and A. H. Maki, *J. Chem. Phys.*, 1963, **38**, 1999.

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[17] M. C. R. Symons, *Adv. Phys. Org. Chem.*, 1963, **1**, 325; L. Lunazzi, G. F. Pedulli, G. Maccagnani, and A. Mangini, *J. Chem. Soc.* (*B*), 1967, 1072.

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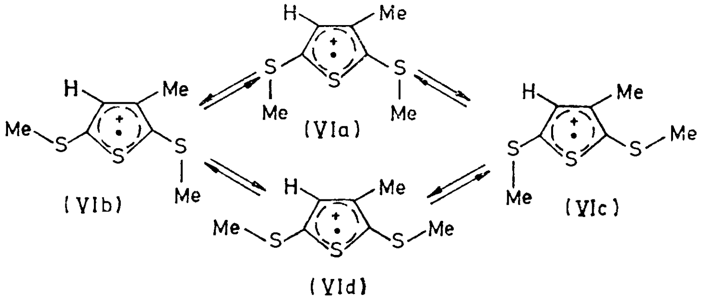
two methyl groups experience a relatively small steric effect (even their mutual repulsion is probably not very significant) and therefore the hydrogen atoms can populate almost all the conformations, including those which give large contributions to the $\alpha_{\beta\text{-H}}$ value of equation (1). When one or two of the hydrogen atoms are replaced by one or two methyl groups [as in the ethyl and isopropyl derivatives (IIa) and (IIIa)] conformations with CH parallel or nearly parallel to the p–π orbitals are much less probable as the additional methyl groups would force the CH bond to lie closer to the plane containing the thiophen ring ($\theta = 90°$). This explains the decrease in the $a_{\rm SCH}$ values from 4·30 in (Ia) to $3{\cdot}48_5$ in (IIa) to 2·50 in (IIIa). In an analogous way for the *S-cis-trans* conformation (Ib), the methyl group *anti* to the heterocyclic sulphur atom is expected to have a smaller $a_{\rm SMe}$ value than in (Ia), as it now experiences the steric influence of 4-H, which makes conformations with the CH bonds parallel to the p–π system less likely than before. On the other hand $a_{\rm SMe}$ for the group *syn* to the heterocyclic sulphur atom in (Ib) would increase slightly with respect to the value for (Ia) since the second methyl group is now far away and its steric effect, small as it was, is now completely absent. This analysis of the experimental data thus confirms the theoretical calculations in assigning to the SMe group *anti* to the heterocyclic sulphur atom a smaller hyperfine splitting value than to the group in the *syn*-position. Also the data for the ethyl derivative (II) agree with such an assignment, as in (IIb) we observe an $a_{\rm SCH_2}$ value smaller than and one larger than the corresponding value in (IIIa). Furthermore, the decrease of the splitting for $\rm SCH_2$ *anti* to the heterocyclic sulphur atom is smaller than that observed for the analogous SMe value in (I) (0·36 instead of 0·48 G), whilst the increase for $\rm SCH_2$ *syn* to the hetero-atom is larger ($0{\cdot}21_5$ with respect to 0·10 G). Actually in the *S-cis-cis* conformation of the ethyl derivative (IIa) the mutual repulsion of the two ethyl groups is by no means larger than in the methyl analogue (Ia) and, accordingly, in the asymmetric form (IIb) the steric hindrance of 4-H will be less dramatic, as it is measured with respect to the already hindered conformation (IIa); on the contrary $\rm SCH_2$ *syn* to the hetero-atom in (IIb) will be less hindered than in (IIa) and the increase of its hyperfine splitting constants will therefore be larger than for the analogous situation experienced by (Ib) with respect to (Ia).



The experimental assignment of the thiophen CH splittings (there is the decision whether 3·48 G belongs to 3-H or to 4-H) cannot be made, as for the SMe splitting, only on the basis of the radicals dealt with so far. For this purpose the e.s.r. spectrum (Figure) of the cation radical of 3-methyl-2,5-bis(methylthio)thiophen (VI) was investigated. Two species were found in *ca.* 4 : 1 ratio; the more stable isomer can be regarded as the *S-cis-cis* form (VIa) whereas the less stable can only have conformation (VIb), as compound (V) demonstrated that the SMe group cannot exist close to a methyl group on the thiophen ring, as required by conformations (VIc) and (VId). It is known that the introduction of a methyl group only slightly affects the $a_{\rm H}$ aromatic splittings[19] and furthermore the $a_{\rm Me}$ value itself remains close to that of the substituted proton. Accordingly, since in (VIb) $a_{\rm H} = 1{\cdot}60$ G (Table 1) it is straightforward to assign the value 2·16 G to $a_{4\text{-H}}$ in (Ib); this leaves the 3·48 G splitting to $a_{3\text{-H}}$. The assignment is further supported by the fact that the $a_{\rm Me}$ splitting in (VIb), although it cannot easily be distinguished from the $a_{\rm MeS}$ value, is obviously much closer to 3·48 than to 2·16 G as its value must be chosen between 3·60 and 3·70 G.

The experimental assignment of the $a_{\rm SMe}$ splittings as well as of $a_{3\text{-H}}$ and $a_{4\text{-H}}$ in (Ib) fully confirms, therefore, the predictions made on theoretical grounds.

Finally an attempt has been made to provide some indication as to whether the conformational preferences of these radical cations might be the same as in the corresponding neutral molecules. In few cases[7,8] it has been shown that the more stable radical conformer actually corresponds to the more stable isomer in the neutral molecule. Here the problem was approached by performing CNDO/2 calculations (see Calculations section) on the three possible conformations of both the radical cation and the neutral molecule. Although not completely satisfactory from a quantitative point of view owing to the uncertainties in the geometric parameters, the trend of the energies for both the neutral and

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positive species does show that (Ia) is more stable than (Ib) which in turn is more stable than (Ic).

It seems therefore not unreasonable to conclude that the *S-cis-cis* conformation, which has been experimentally proved to be the most stable form in the radical cation, should be the most stable conformer in the neutral molecule also.

CALCULATIONS

The INDO method [16] has been applied to both *cis*- and *trans*-forms of hydroquinone radical cation using standard [16] angles and bond lengths; the trend of the hyperfine splittings is satisfactory although the a_{OH} values are larger and the a_{CH} smaller than experimentally determined. We therefore tried other geometries in which the CO bonds do not bisect the corresponding benzene ring angle, as it is known from microwave studies [20] that phenol does show a deviation of the CO bond with respect to the line bisecting the $\widehat{CCC}$ angle of benzene. In this way the agreement with the experiment improved as both a_{OH} decreased and a_{CH} increased; the variations, however, were not large enough to give complete agreement with the experimental data and accordingly the values obtained with the standard geometry have been reported in Table 2.

CNDO/2 Calculations on the conformations of 2,5-bis(methylthio)thiophen (I), both as cation radical and neutral molecule, were performed by assuming for the thiophen ring the basic geometry obtained from microwave spectroscopy [21] and for the angle and bond lengths of the SMe group those reported for analogous sulphides.[22] The main uncertainty is in the value of the angle between the thiophen double bond and the sulphur–methyl bond: 2-substituted thiophens and furan have values of *ca.* 130 ± 5°.[23] We verified however that variations in this parameter of this order of magnitude do not affect the trend of the relative stability of the three isomers (Ia—c). The hydrogen atoms of the methyl groups were arbitrarily placed in the conformation with the minimum steric hindrance; there is one atom in the thiophen plane and the other two are equally displaced above and below this plane. However the relative stability of the isomers was not affected by placing the hydrogen atoms in different positions, even those with the maximum steric effect.

In the McLachlan approach [24] the coulomb and resonance integrals introduced by Sullivan [25] and successfully applied in many other thiophen-containing radicals [8,11] were employed for the heterocyclic sulphur atom ($h_S = 1{\cdot}2$ and $k_{CS} = 0{\cdot}65$). For the integrals relating to the SMe group the values of ref. 12 were employed for h_{Me}, k_{SMe}, and h_{C4} (3·0, 0·70, and 0·1 respectively) as well as for Q_{CH} and Q_{SMe} (−24 and 18·5). The values of h_S and k_{CS} for the sulphide group [12] (1·05 and 0·97), however, gave in the present case SMe splitting constants smaller than the a_H values in both (Ia) and (Ib) in obvious disagreement with the experimental evidence. Accordingly we tentatively changed these terms until the trend was reversed, the final values being $h_S = 0{\cdot}9$ and $k_{CS} = 0{\cdot}7$. It is noteworthy that the calculations leading to the wrong trend of a_{SMe} with respect to a_H also give in (Ib) $a_{3\text{-}H}$ smaller than $a_{4\text{-}H}$ whereas, when the appropriate parameters were used to provide good correspondence between the experimental and computed a_{SMe} and a_H values, the attribution of $a_{3\text{-}H}$ and $a_{4\text{-}H}$ was also reversed and matched the experimental assignment. Finally we verified that, although rather different from the values of ref. 12, the terms $h_S = 0{\cdot}9$ and $k_{CS} = 0{\cdot}7$ for the sulphide group still give the same assignment as 1·05 and 0·97 in *p*-bis(methylthio)benzene.

EXPERIMENTAL

Spectral Measurements.—The reactions to obtain the radical cations were carried out in a T-shaped vacuum sealed tubes containing freshly sublimated aluminium chloride ($AlCl_3$) in one of the arms and nitromethane solutions of (I)—(VI) in the other; the second arm can be directly introduced into the cavity of an e.s.r. spectrometer. On mixing the solutions and $AlCl_3$ at room temperature the radical cations were obtained. However, the temperature for recording the e.s.r. spectra with the best resolution was strongly dependent on the concentration and on the nature of the product, the most suitable values being found in the 0 to −40 °C range. The *g* factor of the symmetric conformer of (I) ($2{\cdot}0065_5 \pm 0{\cdot}00005$) was determined either with respect to *p*-quinone or to tetracyanoethylene radical anion (reference values 2·00509 and 2·00277 respectively). The spectra were run on Varian 4502 and JEOL JES–ME–IX spectrometers equipped with standard low temperature devices. Theoretical spectra were simulated on a CDC 6600 computer assuming Lorentzian line shapes.

Syntheses.—2,5-Bis(methylthio)thiophen (I), 2,5-bis(ethylthio)thiophen (II), and 2,5-bis(t-butyl)thiophen (IV) were prepared according to the literature [26–28] and purified by preparative g.l.c. All the compounds gave satisfactory n.m.r. spectra.

3,4-*Dichloromethyl*-2,5-*bis*(*methylthio*)*thiophen*.— 2,5-Bis(methylthio)thiophen (I) (5 g, 0·028 mol.) was slowly added to a concentrated hydrochloric acid solution (10 ml) of trioxan (7·7 g, 0·085 mol.) at *ca.* 50 °C. The mixture was stirred for 2 h, then diluted with water (40 ml), and extracted with light petroleum. On concentrating the organic layer, crystals of the *dichloro-compound* were obtained, m.p. 80—81 °C (from n-hexane) (Found: C, 35·6; H, 3·7; S, 35·0; Cl, 25·7. $C_8H_{10}Cl_2S_3$ requires C, 35·15; H, 3·7; S, 35·2; Cl, 25·95%).

3,4-*Dimethyl*-2,5-*bis*(*methylthio*)*thiophen* (V).—By reduction of the above dichloro-compound with $LiAlH_4$ in anhydrous tetrahydrofuran *crystals* of (V) were obtained, m.p. 27–29 °C (Found: C, 47·1; H, 5·95; S, 46·9. $C_8H_{12}S_3$ requires C, 47·0; H, 5·9; S, 47·1%).

3-*Methyl*-2,5-*bis*(*methylthio*)*thiophen* (VI).—To an ether solution of n-butyl-lithium [prepared from n-butyl bromide

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(13·9 ml) and lithium (1·27 g)] 3-methylthiophen (12·5 g) was added dropwise and the solution was refluxed under dry nitrogen for 1 h. The temperature was then lowered to −40 °C and dimethyl sulphide (11·3 ml) was added dropwise. After stirring the mixture overnight, 10% hydrochloric acid was added and concentration and distillation (50—66 °C, 1 mmHg) gave a mixture of 3-methyl-2-methylthio- and 5-methylthio-thiophen which was directly relithiated with n-butyl-lithium and then treated with dimethyl sulphide as above. Distillation of the mixture gave 3-*methyl*-2,5-*bis*(*methylthio*)*thiophen* (VI), b.p. 85·5—86 °C at 1 mmHg (Found: C, 44·6; H, 5·3; S, 51·2. $C_7H_{10}S_3$ requires C, 44·15; H, 5·3; S, 50·55%).

2-*Isopropylthiothiophen*, b.p. 63—65 °C at 1 mmHg (Found: C, 53·0; H, 6·4; S, 40·4. $C_7H_{10}S_2$ requires C, 53·1; H, 6·35; S, 40·5%) and 2,5-*bis*(*isopropylthio*)*thiophen* (III), b.p. 92—94 °C at 1 mmHg (Found: C, 52·1; H, 7·0; S, 41·6. $C_{10}H_{16}S_3$ requires C, 51·65; H, 6·95; S, 41·4%) were prepared according to ref. 28 starting from 2-isopropylthiothiophen, butyl-lithium, sulphur, and isopropyl iodide.

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