Thiophen-containing Radicals. Anions of Isomeric Dithienylethylenes

By **L. Lunazzi,* A. Mangini, G. Placucci, P. Spagnolo,** and **M. Tiecco,*** Laboratorio del C.N.R. dei Composti del carbonio contenenti eteroatomi, Istituto di Chimica organica e Industriale, University of Bologna, Viale Risorgimento 4, 40136 Bologna, Italy

Alkali-metal reduction of some thienylethylene derivatives at −80° yields the corresponding radical anions whose e.s.r. spectra have been interpreted by the use of deuteriated derivatives. The results indicate that phenyl and thienyl groups are locked in a definite position. on the e.s.r. time scale; rotational isomers were detected in the case of the 1.2-di-(2-thienyl)ethylene. The experimental hyperfine splitting constants could be reproduced satisfactorily by molecular orbital calculations. assuming. in the *p*-model framework. twisting angles of 40° for the 3-thienyl. and 0° for the 2-thienyl and phenyl groups. An analogous theoretical approach. which takes into account the participation of the 3*d* orbitals of sulphur. was found to disagree with the experimental results.

THIOPHEN-CONTAINING radicals have recently attracted attention both from the experimental and the theoretical point of view. However most of the radicals so far investigated contain functional groups, such as nitro [1] and carbonyl,[2-4] and are not therefore perfectly suited to theoretical investigations, owing to the presence of heteroatoms other than sulphur. Radicals without this drawback have only recently been detected, *e.g.* the neutral radicals thenyl [5] and trithienylmethyl [6,7] and the negative bithienyl and phenylthiophen radicals.[8]

The anions of the *trans*-thienylethylenes and acetylenes reported here belong to the latter class. Because of the large number of non-equivalent hydrogen atoms, these radicals give complicated e.s.r. spectra. Moreover rotational isomerism may occur, in view of the appreciable barrier to internal rotation observed in the analogous diphenylethylenes.[9] Nevertheless they offer the great advantage of giving a large number of independent data, which provides a good framework for testing theoretical and structural models.

To avoid the errors that may occur [4,7,10-13] with theoretical methods, the assignment of hyperfine splitting constants was carried out by means of selective deuteriation except when the occurrence of large differences allowed unambiguous attribution on the basis of computed spin densities. These experimental assignments are particularly advisable for sulphur-containing radicals because two electronic models, which either involve or neglect the sulphur *d* orbitals, may be used.[14]

RESULTS

The compounds whose e.s.r. spectra have been studied were *trans*-1,2-di-(2-thienyl)ethylene (Ia), *trans*-1,2-di-(3-thienyl)ethylene (IIa), and *trans*-1-(2-thienyl)-2-(3-thienyl)-ethylene (III). Two other compounds, *trans*-1-(2-thienyl)-2-phenylethylene (IVa) and 1-(2-thienyl)-2-phenylacetylene (V), were investigated in order to compare the results with

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those for the corresponding radicals of stilbene and diphenylacetylene.[9] The spectra were fully analysed by use of deuterium and t-butyl derivatives.

The dithienylethylenes were obtained by condensation of a thienyl phosphonate with a thiophencarbaldehyde in the presence of sodium hydride or potassium t-butoxide. The same reaction was employed to synthesize the deuteriated dithienylethylenes from the appropriate deuteriated aldehydes. During the condensation hydrogen–deuterium exchange took place to a certain extent, so that mixtures of deuteriated and protiated compounds were obtained.

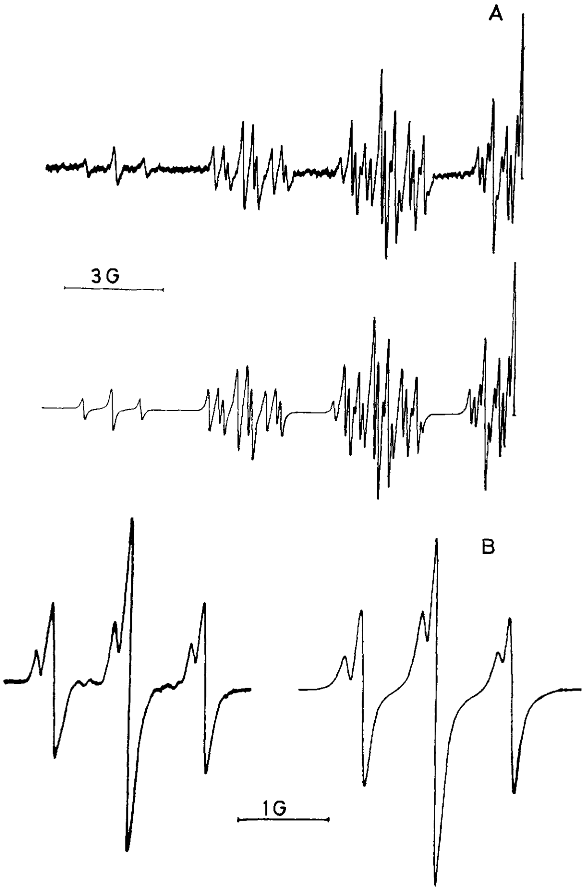


FIGURE 1 A, experimental (top) and computer-simulated half e.s.r. spectrum of radical anion of (Ia); B, enlarged high field section ($M_I = +3$) of the spectrum of the radical of (Ia) at −75° showing the presence of two rotational isomers. The simulated spectrum (right) was obtained by assuming a 4 : 1 ratio of the two rotamers

The e.s.r. spectrum of compound (Ia) is shown in Figure 1A, together with the results of a computer simulation performed using the hyperfine splitting constants of Table 1.

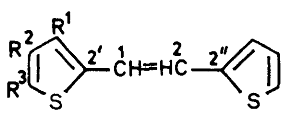
TABLE 1

Experimental and calculated[a] hyperfine splitting constants (G) for the radicals from (Ia) and (IIa)

			Calc.			
			p-Model[c]		*d*-Model[d]	
		Exper.[b]	θ = 0°		θ = 0°	
(Ia)	3′-H	3·76	3·67		2·84	
	4′-H	0·86	−1·32		−0·83	
	5′-H	4·18	4·55		3·97	
	1-H	4·05	3·93		4·17	
			θ = 40°	θ = 0°	θ = 40°	θ = 0°
(IIa)	2′-H	5·25	6·90	7·92	3·49	4·05
	4′-H	0·21	−0·34	−0·20	0·40	0·84
	5′-H	0·0	−0·04	−0·56	0·00	−0·39
	1-H	4·85	4·95	4·58	4·985	4·72

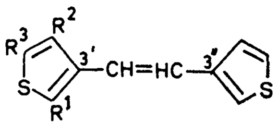
[a] The Q value of the McConnell equation was set at 23·7 and the parameter λ of the McLachlan method at, as customary, 1·2. [b] These data were obtained from the low field half spectrum and thus represent the average splittings of the rotational isomers; this is however not relevant since their a_H values are almost identical. [c] Coulomb and resonance integrals of ref. 21 were used ($h_S = 1{\cdot}2$, $k_{CS} = 0{\cdot}65$). [d] Coulomb and resonance integrals of ref. 24 were used ($h_S = 0{\cdot}0$, $k_{SS} = 1{\cdot}0$, $k_{CS} = 0{\cdot}8$).

The e.s.r. signals of compound (Ib) are due to a mixture of deuteriated and undeuteriated derivatives (4 : 1) and the overlapping of these two spectra prevented direct measurement of the hyperfine splittings. Nonetheless the values of the two overall splittings [25·71 and 22·82 G for the protiated (Ia) and deuteriated isomers (Ib), respectively] allow the assignment of the splitting constant of 4·18 G to 5′-H, since the substitution of one hydrogen having this splitting constant with a deuterium atom, is expected to reduce the overall splitting by the same amount (2·90 G) as experimentally observed.*



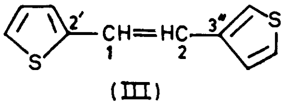
(I)

a; R¹ = R² = R³ = H
b; R¹ = R² = H, R³ = D
c; R¹ = D, R² = R³ = H

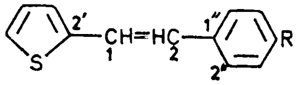


(II)

a; R¹ = R² = R³ = H
b; R² = R³ = H, R¹ = D
c; R¹ = R² = H, R³ = D
d; R¹ = R³ = H, R² = D
e; R¹ = R² = H, R³ = CMe₃

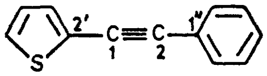


(III)



(IV)

a; R = H
b; R = D



(V)

For compound (Ic) a 4 : 1 deuteriation ratio was obtained. Here both the direct measurement of the a_D value (0·57 G) and that of the overall splitting (23·13 G) agree in indicating that an a_H splitting of 3·72 G has been altered by substitution by deuterium. Accordingly the splitting of 3·76 G measured for compound (Ia) may be unambiguously assigned to 3′-H. The great difference between the two remaining a_H splittings (0·86 and 4·05 G) allows assignment to 4′- and 1-H respectively, either by analogy with similar substituted thiophen derivatives[7] or by means of MO calculations (see later).

The spectrum of (IIa) (Figure 2) can be interpreted straightforwardly by means of the hyperfine splitting constants reported in Table 1.

Compound (IIb), as indicated by its e.s.r. spectrum, has 50% isotopic purity. One of the two hydrogens with the

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* Throughout this paper the ratio $a_D : a_H$ 0.1535:1 has been used.

greatest splitting has been substituted by deuterium with $a_D = 0{\cdot}81$ G (Figure 2) so that $a_H = 5{\cdot}25$ G may be assigned to 2′-H.

The e.s.r. spectrum of compound (IIc) is the same as that observed for compound (IIb), although there is a much lower degree of deuteriation ($\leqslant 10\%$). This means that 5′-D exchanges completely with the adjacent hydrogen atom and also attacks C-2′ to some degree. The opposite interpretation, namely that in compound (IIb) 2′-D exchanges completely, giving in part the 5′-D derivative (IIc), is considered unlikely on the grounds of the greater isotopic purity observed. To provide further experimental proof two more substituted derivatives were examined. To prove that we did not observe the spectrum of compound (IIc) because of complete deuterium–hydrogen exchange, the spectrum of compound (IIe) was investigated. Owing to the overlap caused by the presence of the t-butyl group, all the hyperfine splittings could not be observed; but the spectrum (Figure 2) unambiguously shows that the four hydrogens with the greatest splittings (about 5 G) are still present. It follows that the t-butyl group at C-5′ has substituted one of the two hydrogens with the smallest couplings (either 0·215 or 0·0). A definite assignment was finally reached by analysing the spectrum of compound (IId), which was 100% isotopically pure. From Figure 2 it is apparent that the first triplet of compound (IIa) is now a doublet with the same splitting (0·21 G). The assignment of $a_H = 0{\cdot}21$ G to 4-H′ is thus straightforward, and this allowed us to assign the smallest splitting to 5-H′; the remaining constant (4·85 G) is assigned to the ethylenic hydrogen atom.

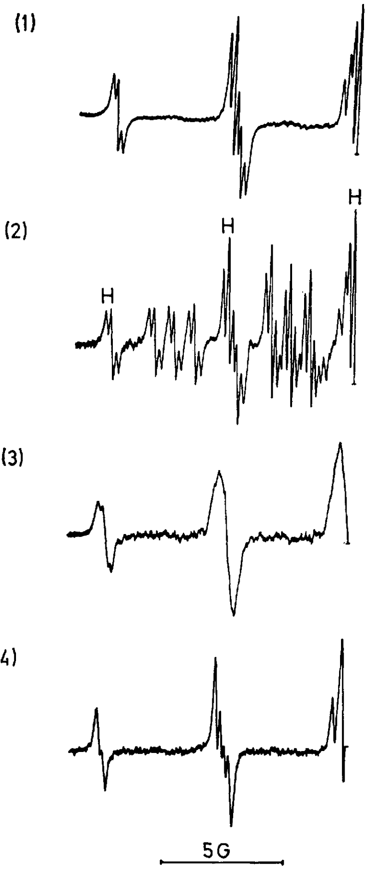

FIGURE 2 Half e.s.r. spectra of (1) radical anion of (IIa); (2) radical anion of (IIb). The groups of bands labelled with H are those of the undeuteriated radical of (IIa) (see text); (3) radical anion of (IIe); and (4) radical anion of (IId)

The e.s.r. spectral patterns of compound (IVa) could be satisfactorily simulated only by assuming different a_H values for the two *ortho*- as well as for the two *meta*-positions of the phenyl ring. It thus follows that the rotation of the benzene ring is restricted, on the e.s.r. time scale, as observed in stilbene and styrene radicals.[9,15] A complete experimental assignment of the ten different hyperfine splittings was not attempted. However, by analogy with similar derivatives [4,6,7] the hydrogen splittings of the phenyl ring are expected to be smaller than in stilbene, and those of the thienyl ring larger than in compound (I), owing to the greater efficiency of the thienyl group in delocalization of the odd electron.[4,6,7] This has been verified in the present case by labelling the *para*-position of the phenyl group with deuterium [compound (IVb)]. The deuteriation ratio was 1 : 1 and the overall splittings in the e.s.r. spectra of the two compounds [26·98 and 24·19 G for compounds (IVa) and (IVb) respectively] yielded a calculated $a_H = 3{\cdot}59$ G, which allowed the experimental splitting of 3·62 G to be assigned to the *para*-position. The latter value is smaller than the corresponding coupling for stilbene (3·89 G) and this encouraged us to extend the analogy to the other positions. Accordingly a tentative assignment is presented in Table 2 for this radical.

TABLE 2

Experimental and calculated [a] hyperfine splitting constants (G) for the radicals from (IVa) and (V)

	(IVa)			(V)	
	Exper.	Calc.		Exper.	Calc. [b]
3′-H	3·96	4·11	3′-H	4·38	3·64
4′-H	0·90	−1·45	4′-H	0·95	−1·36
5′-H	4·50	5·13	5′-H	4·90	5·62
1-H	4·20	4·43			
2-H	4·20	4·36			
2″-H	1·80, 2·75	1·98	2″-H	2·45	1·90
3″-H	0·31, 0·78	−0·68	3″-H	0·55	−0·58
4″-H	3·62	2·71	4″-H	4·38	3·13

[a] See notes *a* and *c* to Table 1. [b] For the carbon–carbon triple bond the resonance integral was set at 1·4 as in ref. 9.

The same method of comparison with the corresponding hydrocarbon (diphenylacetylene) [9] was also used in assigning the a_H values for the radical from compound (V), whose spectrum has been simulated with the hyperfine splittings of Table 2.

The e.s.r. spectrum of the radical from compound (III) has also been recorded and interpreted. As no deuteriated derivatives were examined, nor was any comparison with similar radicals possible, the assignment is not presented. The measured hyperfine splittings are 0·13, 0·31, 0·79, 3·52, 3·68, 4·50, 4·96, and 5·27 G.

DISCUSSION

The values of the hyperfine splittings for the radicals from compounds (Ia) and (IIa) show a trend which is typical for the thiophen ring. In 1,2-di-(3-thienyl)ethylene (IIa) the greatest spin density is at C-2′; that at C-4′ and C-5′ is much smaller (C-4′ > C-5′), as observed in the related ketyls [4] and trithienylmethyls.[6,7] Also in

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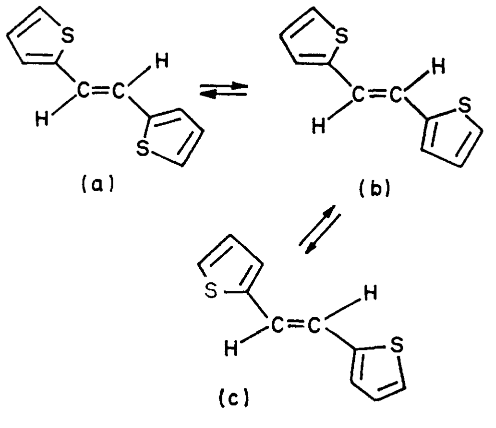
[15] A. R. Buick, T. J. Kemp, G. T. Neal, and T. J. Stone, *Chem. Comm.*, 1970, 282.

1,2-di-(2-thienyl)ethylene (Ia) the spin density at C-3′ and C-5′ is much greater than at C-4′, as observed in related radicals.[1,4,6-8]

As regards the structure of the radicals, the possibility of rotational isomerism has to be taken into account, since in related molecules groups linked to the central double bond do not rotate freely. It has been observed that in the radical anions of styrene,[15] stilbene, and 1,2-di-(4-pyridyl)ethylene [9] the two *ortho*- and the two *meta*-positions are not equivalent; in the present case the asymmetry of the thiophen ring would lead to the existence of rotational isomers. The splitting constants of the ethylenic hydrogens in 1,2-di-(2-thienyl)ethylene, stilbene, and 1,2-di-(3-thienyl)ethylene are 4·05, 4·37, and 4·85 G, respectively, and this indicates that the delocalization power of the rings is in the order 2-thienyl > phenyl > 3-thienyl. Since it is reasonable to assume that the double bond character of the aromatic–ethylenic linkage follows the same trend, rotational isomers should be detected at least in the case of 1,2-di-(2-thienyl)ethylene. Actually in the high field region ($M_I = +3$) of the spectrum of compound (Ia), two triplets were detected whose relative intensity was found to be solvent- and temperature-dependent (Figure 1B). This is clearly due to the presence of two rotamers, the less stable one having a smaller overall splitting (0·1 G) but a greater g factor ($\Delta g = 5 \times 10^{-3}$) than the more stable one. Inspection of the whole spectrum indicates that the more intense signals (80%) are those of a symmetrical radical (a), while the others (20%) belong to an asymmetrical one (b); on the basis of a four-jump model [16,17] a third conformer (symmetrical) is expected to be present in small amounts (*ca.* 1%), which explains why it was not detected. It is difficult to decide whether the *S-cis-cis* (a) or the *S-trans-trans* (c) is the symmetrical rotamer observed, although by analogy with results for similar compounds [18,19] the former is tentatively preferred.



The theoretical approach used to rationalize the electronic distribution and the rotational structures is that of McLachlan,[20] which has been succesfully applied to a great number of π-radicals. From the series of k_{CS} and h_S integrals suggested for bivalent sulphur we chose the values suggested by Sullivan [21] ($h_S = 1{\cdot}2$ and $k_{CS} = 0{\cdot}65$) which have been used successfully [13,22] although never for thiophen-containing radicals. A survey of the results yielded by other values [1,23] suggests that they give the most satisfactory agreement with our data (Table 3), *e.g.* the pairs of integrals 1·0 and 0·7 [23] and 1·0 and 0·8 [1] give the wrong value for $a_{5'-H}$ relative to the ethylenic splitting, while the parameters 1·0 and 0·566 [1] do not give the correct prediction for the values of $a_{3'-H}$ and the ethylenic coupling.

Hindered rotation has been taken into account by setting the resonance integral $\beta = \beta_0 \cos \theta$ for the aryl–ethylene bond. The best fit with the experimental data (see Tables 1 and 2) was obtained by assuming, for compounds (Ia) and (IVa), a planar arrangement ($\theta = 0°$) of the phenyl and 2-thienyl rings and a twisting angle of 40° for the 3-thienyl group in compound (IIa). This agrees with the trend of the aryl–ethylene double bond character expected on the basis of the relative values of the ethylenic splittings.

TABLE 3

Experimental ($Q = 23{\cdot}7$) and calculated [a] McLachlan spin densities for the radical from (Ia) as function of different pairs of coulomb (h) and resonance (k) integrals

	Exper.	$h_S = 1{\cdot}2$, $k_{CS} =$ 0·65 [b]	$h_S = 1{\cdot}0$, $k_{CS} =$ 0·7 [c]	$h_S = 1{\cdot}0$, $k_{CS} =$ 0·8 [d]	$h_S = 1{\cdot}0$, $k_{CS} =$ 0·566 [d]
3′-H	0·159	0·155	0·146	0·139	0·157
4′-H	0·037	−0·056	−0·053	−0·048	−0·056
5′-H	0·176	0·192	0·166	0·140	0·200
1-H	0·172	0·166	0·184	0·209	0·155

[a] Planar situation. [b] Ref. 21. [c] Ref. 23. [d] Ref. 1.

For theoretical purposes these radicals are also very suitable systems for investigating the validity of *p*- and *d*-models since they contain only one type of heteroatom (sulphur) and, because of the asymmetry of the thiophen fragment, are very sensitive to the parameters employed. As regards the *d*-model the approach proposed by Longuet-Higgins [24] and extensively used by many authors [1,13,22,25,26] was tested but the results disagree with the experimental assignments (Table 1). It is worth noting that, without the experimental assignment, the *d*-model would have appeared as good as the *p*-model and, at some θ values, even better, since the assignment could have been reversed to match the theoretical results.

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In compound (III) the same angles used in the symmetrical radicals (I) and (II) were used for the corresponding fragments (0 and 40° for the 2- and 3-thienyl groups, respectively). The computed a_{H} values are in reasonable agreement with the measured ones but no assignment was made, since, as previously mentioned, the results were not checked experimentally. The calculated spin densities are as follows: 0·222(5′-H), −0·061(4′-H), 0·149(3′-H), 0·097(1-H), 0·307(2-H), 0·213(2″-H), 0·002(4″-H), and −0·023(5″-H). The calculations for 1-(2-thienyl)-2-phenylacetylene (V) were made by using the same h_{S} and k_{CS} parameters of the other radicals and, for the carbon–carbon triple bond, the k_{CC} parameter (1·4) employed in diphenylacetylene.[9] Once more agreement with the experimental values is satisfactory, both for absolute values and for the relative trend.

The results lead us to conclude that, by using the *p*-model for the sulphur atom with the parameters reported for very different radicals [13,21,22] it is possible to rationalize the results for all the compounds investigated here without invoking the participation of 3*d* orbitals.

EXPERIMENTAL

Radicals were obtained by reduction of the substrates on a potassium mirror in 1,2-dimethoxyethane at $\leqslant -80°$. The spectra were recorded at −80° on a pre-cooled Varian 4502 spectrometer. Computer-simulated spectra were obtained with an IBM 7094 machine assuming a Lorentzian shape with a line-width of 80 mG.

trans-1,2-Di-(2-thienyl)ethylene [27] (Ia), *trans*-1,2-di-(3-thienyl)ethylene [27] (IIa), *trans*-1-(2-thienyl)-2-(3-thienyl)-ethylene [27] (III), *trans*-1-(2-thienyl)-2-phenylethylene [28] (IVa), and 1-(2-thienyl)-2-phenylacetylene [29] (V) were prepared by reported procedures. The following deuteriated derivatives: [5′-^{2}H]*trans*-1,2-di-(2-thienyl)ethylene (Ib), [3′-^{2}H]*trans*-1,2-di-(2-thienyl)ethylene (Ic), [2′-^{2}H]*trans*-1,2-di-(3-thienyl)ethylene (IIb), [5′-^{2}H]*trans*-1,2-di-(3-thienyl)-ethylene (IIc), [4′-^{2}H]*trans*-1,2-di-(3-thienyl)ethylene (IId) were prepared by use of the appropriate deuteriated thiophencarbaldehydes. Their n.m.r. spectra, as well as those of the intermediate compounds, were in agreement with those expected.[30] The deuterium content of the products was established by analysing the e.s.r. spectra of the corresponding radical anions.

[5-^{2}H]*Thiophen*-2-*carbaldehyde*.— To n-butyl-lithium [from lithium (0·15 g)] in ether (100 ml) [2,5-^{2}H$_2$]thiophen [31] (4·5 g) was added and the solution was stirred at room temperature for 20 min. Dimethylformamide (8·5 ml) was added dropwise and the resulting mixture was stirred for 2 h then poured into water. The ethereal layer was separated, dried, and evaporated and the residue was distilled to give [5-^{2}H]thiophen-2-carbaldehyde (2·4 g), b.p. 83—84° at 14 mmHg.

[3-^{2}H]*Thiophen*-2-*carbaldehyde*.— To n-butyl-lithium [from lithium (0·5 g)] in ether (100 ml) cooled at −70°, 3-bromothiophen-2-carbaldehyde ethylene acetal [32] (8 g) was added dropwise, and the resulting mixture was stirred for 20 min. Acetic [^{2}H]acid in deuterium oxide, prepared by refluxing acetic anhydride (9 ml) with deuterium oxide (3·5 ml) for a few min, was added dropwise, and the resulting mixture was stirred overnight. Excess of hydrochloric acid (2N) was added, stirring was continued for a further 30 min, and the two layers were separated. The ethereal solution was separated, washed with water, dried, and evaporated. The residue was distilled to give [3-^{2}H]thiophen-2-carbaldehyde (2·2 g), b.p. 84° at 14 mmHg.

[2-^{2}H]*Thiophen*-3-*carbaldehyde*.— 2,3-Dibromothiophen [33] (20 g), acetic anhydride (7 g), deuterium oxide (25 ml), and zinc dust (17 g) were refluxed for 16 h and then poured into water. The mixture was extracted with ether; the extract was washed with dilute sodium hydroxide solution and water, dried, and evaporated. The residue was distilled to give [2-^{2}H]-3-bromothiophen (10 g), b.p. 158—160°. It was transformed into [2-^{2}H]thiophen-3-carbaldehyde (4·4 g), b.p. 78° at 14 mmHg, following the procedure [34] for the undeuteriated aldehyde.

[5-^{2}H]*Thiophen*-3-*carbaldehyde*.— 2,4-Di-iodothiophen [35] (24 g), acetic anhydride (5 ml), deuterium oxide (15 ml), and zinc dust (11 g) were treated as described for the synthesis of 3-iodothiophen [35] to give [5-^{2}H]-3-iodothiophen (8·6 g), which, when treated as reported [36] for the undeuteriated compound, gave [5-^{2}H]thiophen-3-carbaldehyde (2·6 g), b.p. 78° at 14 mmHg.

[4-^{2}H]*Thiophen*-3-*carbaldehyde*.— 4-Iodothiophen-3-carbaldehyde [36] (4 g), benzene (50 ml), ethylene glycol (1·3 ml), and toluene-*p*-sulphonic acid (trace) were refluxed until no more water separated (6 h). The benzene layer was then washed with a dilute solution of sodium hydrogen carbonate and water, dried, and evaporated. The residue was distilled to give 4-*iodothiophen*-3-*carbaldehyde ethylene acetal* (4·5 g), b.p. 150—152° at 1 mmHg (Found: C, 29·7; H, 2·5; I, 45·2; S, 11·5. $C_7H_7IO_2S$ requires C, 29·7; H, 2·5; I, 44·85; S, 11·3%), which, when treated with n-butyl-lithium at −70°, and acetic [^{2}H]acid, gave [4-^{2}H]thiophen-3-carbaldehyde (1 g), b.p. 78° at 14 mmHg.

5-t-*Butylthiophen*-3-*carbaldehyde*.— 3-Iodo-5-t-butylthiophen [37] (10 g) was added dropwise to n-butyl-lithium [from lithium (0·7 g)] in ether (100 ml), at −70°, the solution was stirred for 30 min, and dimethylformamide (6 ml) was added. The mixture was stirred overnight and then poured into dilute hydrochloric acid. The organic layer was washed with water, dried, and evaporated. The residue was distilled to give the *product* (7·7 g), b.p. 120° at 14 mmHg (Found: C, 64·2; H, 7·0; S, 19·0. $C_9H_{12}OS$ requires C, 64·25; H, 7·2; S, 19·05%), δ 7·93 (*J* 1·55 Hz, 2-H), 7·27 (*J* 1·55 and 0·35 Hz, 4-H), 9·82 (*J* 0·35 Hz, CHO), and 1·40 p.p.m. (CMe_3).

trans-1-(5-*t*-*Butyl*-3-*thienyl*)-2-(3-*thienyl*)*ethylene* (IIe).—

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Dimethyl 3-thienyl phosphonate[27] (1·6 g), 5-t-butylthiophen-3-carbaldehyde (0·9 g), sodium hydride (0·12 g), and dimethoxyethane (8 ml) were refluxed for 2 h and then poured on water. Crystallization afforded the *product* (1·3 g), m.p. 114—115° (from ethanol) (Found: C, 67·9; H, 6·4; S, 25·9. $C_{14}H_{16}S_2$ requires C, 67·7; H, 6·5; S, 25·8%).

[4″-H]trans-1-(2-*Thienyl*)-2-*phenylethylene* (IVb).—A stirred mixture of dimethyl 2-thienyl phosphonate[27] (1·2 g), [4-^{2}H]benzaldehyde (0·5 g) (prepared from [4-^{2}H]-benzoic acid[38,39]), sodium hydride (0·12 g), and dimethoxyethane was refluxed for 2 h and then worked-up as described above to give the product (IVb) (0·8 g), m.p. 112—113° (from ethanol), mixed m.p. with the undeuteriated compound 112—113°.

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