Synthesis, Electrical Conductivity and Electron Paramagnetic Resonance Spectroscopy of Polymers derived from $NOPF_6$-Doped XYZ-Triheterocycles Based on Pyrrole, Furan and Thiophene

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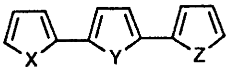
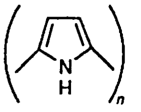
A series of triheterocycles;



for X, Y, Z = OOO, SSS, SOS, SSO, OSO, SOO, O(N-Me)O, S(N-Me)O and S(N-Me)S have been synthesised; of these O(N-Me)O, SOO and S(N-Me)O are new. The triheterocycles were chemically polymerised and oxidised with $NOPF_6$. Only the polymers derived from SSS, SOS and SSO show appreciable conductivities. EPR studies indicate the presence of polarons in SSS, SOS, SSO and, at lower concentrations, in OOO. All the samples appear to show an easily saturable EPR signal assigned to localised radicals. In OSO, SOO, O(N-Me)O, S(N-Me)O and S(N-Me)S this signal displays considerable asymmetry, and *g*-values significantly above the free electron value. S(N-Me)S shows a higher *g*-value consistent with a loss of planarity.

Since the discovery of electrical conductivity in polyacetylene, conjugated polymers of many types have continued to attract considerable interest. Polyacetylene is extremely oxygen-sensitive, and is also subject to a long-term (> 6 months) degradation through mechanisms that are not yet fully understood. Polypyrrole **1** and polythiophene **2** are great practical improvements on polyacetylene, in that they are air-stable conductors. One can think of **1** and **2** as heterosubstituted polyacetylenes, with



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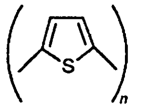

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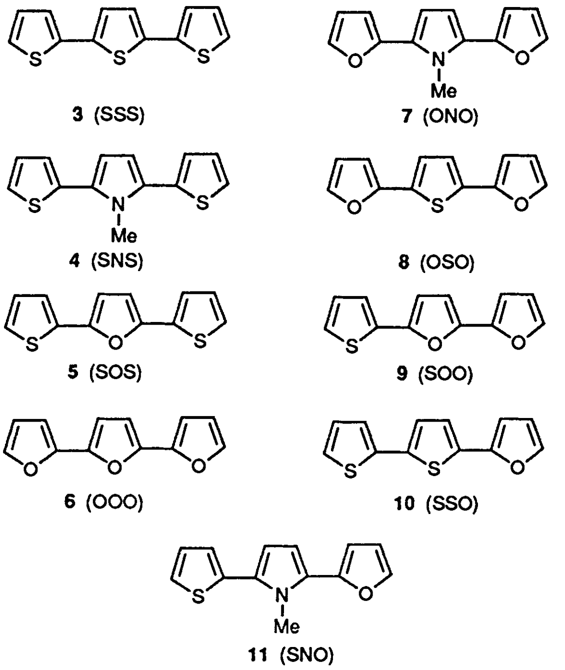
some degree of involvement of the hetero atom in the conductivity. However, the presence of a five-membered aromatic ring makes polymerisation possible not only at the 2 and 2′-positions (α), but also at the 3 and 3′ positions (β). This can lead to branching and off-chain coupling with a resultant reduction in the degree of conjugation of the polymer. The presence of the hetero atom can cause successive monomer units to be tilted out of plane relative to one another. If the tilt is sufficient the π system is interrupted. Therefore one speaks of 'effective conjugation lengths', *i.e.* the effective 'idealised' polyacetylene strand that may exist in the polymer. Both types of flaw in the π system would be expected to lead to a reduction in electrical conductivity. It is difficult to control *a priori* the amount of β branching or the degree of tilt of monomer units.

One synthetic tool available to control partially some of these variables is the use of polyheterocycles of known structure as oligomers. This approach has been taken by Ferraris and Skiles,[1] and extended broadly in the present study. We have prepared a number of α,α′-linked triheterocycles containing thiophene, furan, or *N*-methylpyrrole chemically, and then oxidatively polymerised them using $NOPF_6$, in the hope of forming new conducting polymers with PF_6^- as the gegenion.



3 (SSS) **7** (ONO) **4** (SNS) **8** (OSO) **5** (SOS) **9** (SOO) **6** (OOO) **10** (SSO) **11** (SNO)

Fig. 1 Triheterocycles used in this study and abbreviations employed

Results

Synthetic Studies.—The nine triheterocycles **3–11** prepared for this study are shown in Fig. 1, along with a simple reference code which we will employ for convenience in this paper (SSS, SNS, *etc.*, where N = N-Me). Compounds **3**, **4** and **5** are known triheterocycles, the electrochemical and chemical oxidation of which have been reported previously.[1,2] We have included them in our work to obtain comparative values under our conditions. Compounds **6**, **8** and **10** have been reported previously, by

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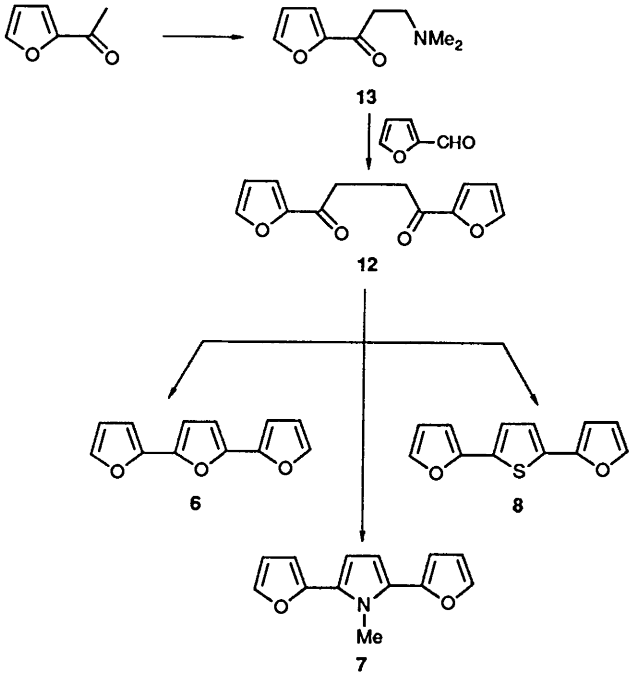
different synthetic routes,[3-5] but they have not been employed as oligomer substrates. Compounds **7**, **9** and **11** are new triheterocycles, and their syntheses are described below.

1,4-Di(2-furyl)butan-1,4-dione **12** has been prepared previously from furfural and divinyl sulfone using a modified Stetter procedure, and subsequently dehydrated to give α-terfuryl **6** (OOO). We prepared diketone **12** from furfural and 2-acetylfuran *via* Mannich base **13** using the original Stetter protocol. In addition to giving **6** on acid dehydration, **12** afforded **8** (OSO) on treatment with Lawesson's reagent, while its reaction with methylamine yielded the pyrrole **7** (ONO). A previous synthesis of **8** employed a diacetylenic intermediate.[4] These reactions are outlined in Scheme 1.

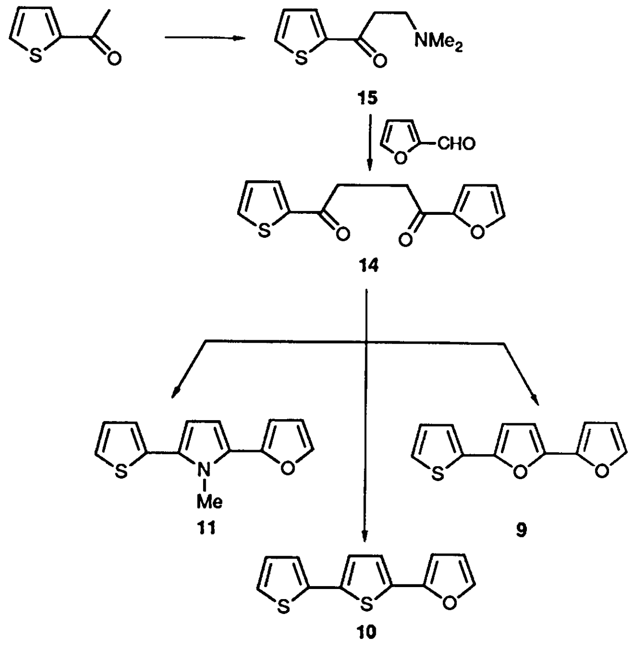


Scheme 1

No triheterocycles of the SXO type (*i.e.* **9**, **10** and **11**) have been prepared previously, with the exception of **10**, which was prepared *via* a diacetylenic precursor.[5] The key intermediate was 1-(2-furyl)-4-(2-thienyl)butane-1,4-dione **14**, which was obtained by a Stetter synthesis *via* Mannich base **15** starting with 2-acetylthiophene and furfural. Dione **13** was converted to the triheterocycles **9**, **10** and **11** by reaction with acid, Lawesson's reagent, or methylamine, respectively (Scheme 2).

Physical Studies.—Table 1 contains the electrochemical oxidation potentials (E_{p} for the peak in the cyclic voltammogram that corresponds to the polymer growth), conductivities of the polymers, rings per positive charge of the polymers, and, from EPR spectroscopy, the *g*-value and the number of rings per unpaired electron. The polymers that show significant conductivity are SSS, SOS and SSO. From comparison with Table 1, these are also the polymers with the lowest EPR linewidths. Particularly with SSS and SOS, the linewidth decreases at lower temperature. All the *g*-values are somewhat above the free electron *g*-value, with that of the SNS polymer (2.0038) being significantly higher than that of the other polymers.

Table 2 gives the effect of temperature and time after preparation of the EPR linewidth of the various samples. With the exceptions of SSS, OSO and SOS, the linewidth did not change substantially with time. For SSS, OSO and SOS the linewidth narrowed with time, in the case of OSO by 30%. This suggests that some reaction, *e.g.* further oxidation, occurs. It is unlikely that this narrowing is due to escape of residual NO, as all samples were treated identically, and the other samples do not show similar changes in linewidth. The lineshapes showed no Dysonian character, indicating that there is no significant surface conductance. Since the conductivities are low and the samples were ground, it would be expected that these samples would not show Dysonian character. For ONO, SOO, SNO, SSO and OSO the curves were asymmetric, and did not fit well to either a single Lorentzian or a single Gaussian curve.



Scheme 2

To gain insight into the nature of the specie or species giving the EPR signal, curve fitting of the type described by Schärli *et al.*[6] was carried out. Specifically, a Lorentzian curve and a Gaussian were simultaneously fitted to each spectrum. As would be expected, in each case this produced a better fit than either a Gaussian or Lorentzian curve by itself. For SSS and SOS the Lorentzian curve predominated in the fitted spectra, whereas for OOO the fitted curve was predominantly Gaussian. The other samples had approximately equal contributions from both Gaussian and Lorentzian components.

Power dependence. It was found that the EPR signals of the different heterocycles showed significantly different microwave power dependencies. In all cases but SOS, SSO and SSS, the EPR signal was substantially saturated by 20 dB (*ca.* 2 mW); SOS showed indications of saturation above 17 dB (*ca.* 4 mW), whereas SSS did not shown appreciable saturatation at 10 dB (*ca.* 20 mW). Significant changes in spectra were also observed as the microwave power was changed. This is illustrated in Fig. 2(*a*) for OOO and Fig. 2(*b*) for SNS. SNO, ONO showed similar behaviour to that for SNS, *i.e.* as the EPR line begins to saturate the high field portion of the spectrum saturates first, leading to increasing asymmetry. OOO clearly shows two components, a broader component which saturates readily, and a narrow component which does not. For SSS there were only small changes in lineshape with power, although at above 13 dB (*ca.* 10 mW) the ratio of Lorentzian to Gaussian began to change significantly, suggesting that the Gaussian component was beginning to saturate at this power. SSO showed similar changes in the ratio of Lorentzian to Gaussian components.

Doping dependence. Studies of the effect of doping level on samples of polythiophene (SSS) over the range 0.5 to 3.0 equivalents of $NOPF_6$ did not show any significant correlations with linewidth or spin concentration.

Table 1 Oxidation potentials, conductivity, *g*-values and rings per polaron for the polymers from chemical oxidation of XYZ-triheterocycles

Sample	Oligomer oxidation^a potential/V	Polymer oxidation^a potential/V	Conductivity^b/S cm^{-1}	*g*-Value^c	Rings per polaron^d	Rings per charge^e
ONO	0.78	0.50	$<10^{-5}$	2.0029	1200	11
OSO	1.11	0.57	$<10^{-5}$	2.0030	1500	31
SNO	0.82	0.62	$<10^{-5}$	2.0028	900	85
SSO	1.09	0.64	10^{-5}	2.0026	300	32
SOO	1.03	0.66	$<10^{-5}$	2.0029	1000	18
SNS	0.96	0.7	$<10^{-5}$	2.0038	960	36
SOS	1.10	0.72	0.2	2.0024	40	18
OOO	1.11	0.75	$<10^{-5}$	2.0028	500	12
SSS	1.14	0.75	2.4	2.0024	40	32

[a] Volts *versus* standard calomel electrode. [b] Measured at 300 K by four-probe DC method. [c] Measured against DPPH, estimated error ±0.0006. [d] Measured at 0.01 mW, calculated as the number of thiophene/pyrrole/furan rings per unpaired electron. Estimated error for one measurement relative to another is 50%, estimated absolute error is factor of three. In a preliminary account of this work 0.2 mW microwave power and an incorrect value for the DPPH standard were used. [e] Based on elemental phosphorus analysis, assuming all phosphorus is present as PF_6^-.

Table 2 Effect of temperature and time after sample preparation on the EPR linewidth^a

Sample	Room temp.^{b}	Room temp.^{c}	77 K^b	12 K^b
ONO	6.2	6.0	6.9	7.6
SNO	5.7	5.8	6.6	6.7
SNS	7.5	6.5	7.0	6.4
SOO	5.2	4.9	6.2	5.8
SSO	2.0	2.1	3.5	5.2
SOS	2.6	1.9	2.7	1.6
OOO	5.5	5.1	6.5	5.7
OSO	7.5	4.5	7.5	6.4
SSS	3.1	2.2	0.9	0.9

[a] All linewidths are peak-to-peak in Gauss, at 0.1 mW microwave power, doping level of 2 equiv. of $NOPF_6$. [b] For freshly prepared samples. [c] For three month old samples, held at room temperature, exposed to air.

Discussion

The conductivities for SSS and SOS are both higher than those found by Ferraris and Skiles,[1] who also used $NOPF_6$ as oxidant. In contrast no discernible conductivity ($< 10^{-5}$ S cm^{-1}) was measured for SNS, for which Ferraris and Skiles reported a conductivity of 2.7×10^{-2} S cm^{-1}. It seems possible that the different conductivities may result from differences in procedure: we used two equivalents of $NOPF_6$ and a methanol wash rather than one equivalent of $NOPF_6$ and a methylene dichloride wash used by Ferraris and Skiles. We found that when a methylene dichloride wash was used all our samples deliquesced and gave approximately the same conductivities, suggesting that there was some residual acid. After methanol washes the samples were much more stable.

The minimal conductivity of SSO and the absence of measurable conductivities from the other polymers was disappointing. The EPR studies were carried out to gain further insight into why the conductivities of ONO, SNO, SNS, SOO, OOO and OSO were so low.

EPR signals in organic conductors normally result from either localised radicals or polarons.[7] The identitity of the charge carrier in polymers based on heterocycles such as were studied in this work is still a matter of some debate. However from work on polythiophene,[7] and polypyrrole[8] it appears that at low dopant concentrations the polaron is the charge carrier, while at higher dopant concentrations the bipolaron predominates and is the primary charge carrier.

A comparison of the conductivity and the rings per polaron in Table 1 shows clearly that the conductivity is correlated to the number of spins, and also to the *g*-value which is closest to 2.0023, the free electron value, for the polymers showing the highest conductivity and the higher spin concentrations. The rings per polaron for polythiophene and SOS are similar to the results of Kaneto *et al.*[9] who found a maximum for spin concentration of 33 rings per spin at 3% doping in electrochemically grown polythiophene, and are comparable to that found for poly(3-methylthiophene) by Schärli *et al.*[6]

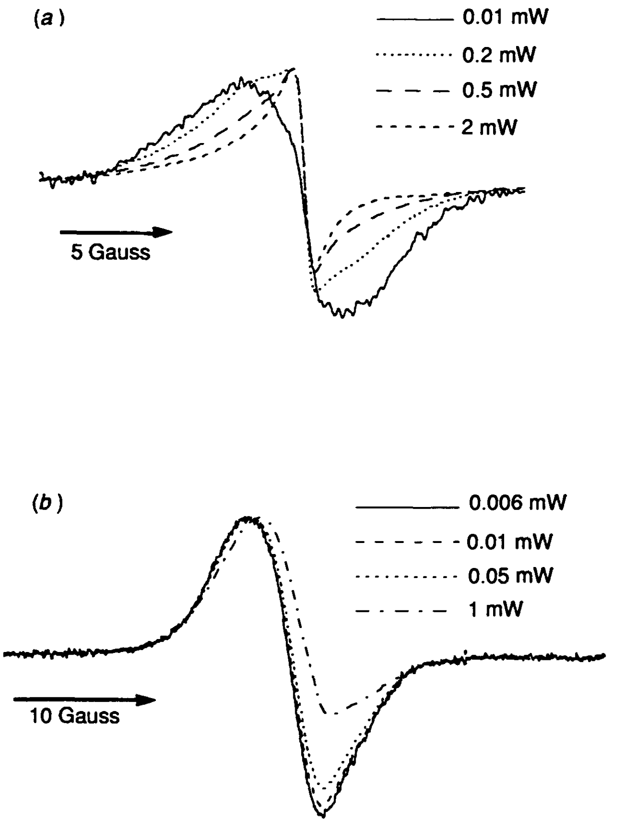


Fig. 2 EPR spectra of (*a*) OOO and (*b*) SNO, showing the effect of microwave power. The spectra have been scaled relative to one another to highlight the change in lineshape.

The non-linear least squares procedure fits the EPR spectra of all samples with some Lorentzian component and some Gaussian component. The presence of such a Gaussian component is also observed in polythiophene and in poly(3-methylthiophene), where this signal is usually assigned to localised spins. However the fitting must be treated with some caution, as a non-linear least squares would be expected to fit some amount of Lorentzian and Gaussian component to any arbitrary curve. For example, in the case of a localised cation radical with significant anisotropy, the non-linear least squares fit would still fit two components. This said, it is certainly clear from the power dependence for OOO that in this case there are indeed two components: a small amount of a delocalised species with lower *g*-value, and a larger quantity of a localised species with a longer relaxation time. The power dependences of SNO, SNS, ONO, SOO and OSO indicate that, although the non-linear least squares fits about equal amounts of Lorentzian and Gaussian components, there is in fact only one asymmetric line, corresponding to a localised species. The asymmetry results from anisotropy of the *g*-value and/or hyperfine tensors. In the case of SSS, SOS and SSO it is clear that there is a significant Lorentzian component of the lineshape attributable to a polaron, which is certainly consistent with the power dependence and the conductivity. However the difference in *g*-values for the two fitted components in SSS is only about 0.0001, which would give a *g*-value for the localised species in SSS of 2.0025, lower than the *g*-value for the localised species in the other polymers.

The *g*-values for conducting polymers are consistent with those observed for electrochemically grown polythiophene,[9] although lower than those found for poly(3-methylthiophene).[6] The *g*-values of the localised radicals are lower than those reported for electrochemically grown polythiophene (2.0039) and poly(3-methyl-thiophene) (*ca.* 2.0035). Apart from SNS none of the polymers have *g*-values above 2.0030. The value of 2.0038 for SNS is consistent with a localised radical in which there is significant loss of planarity due to the steric interaction between the methyl group and thiophene rings.[10,11] It is not possible to compare our linewidths, as the doping level of our chemically polymerised polythiophene is uncertain, and the linewidth of polythiophene ranges from 0.4 to *ca.* 9 G. It is interesting that at 12 K the EPR lines for SSS and SOS are narrower than at room temperature, whereas for SSO it is the opposite: this suggests that in SSO there may be an activation barrier to hopping.

Linear regression analysis of the spin concentration against the oxidation potential of the polymers (Table 1) gives a weak correlation (correlation coefficient = 0.74). There is little apparent correlation with the oxidation potential of the oligomer. It appears also that the conducting polymers tend to have somewhat higher oligomer oxidation potentials. Likewise OOO, which appears to have a (low) concentration of polarons also has a high oligomer oxidation potential. There appears to be no correlation between the rings per charge and any of the other properties measured.

Despite the EPR studies it is still not clear why SSS, SOS and SSO show appreciable conductivity while ONO, SNO, SNS, SOO, OOO and OSO do not. EPR spectroscopy has shown the presence of radicals at moderately high concentrations in all these samples. The saturation behaviour and spectral shape of the radicals in ONO, SNO, SNS, SOO and OSO are consistent with localised radicals, such as are often observed in thiophene and polypyrrole. There is little evidence of any polarons. The presence of a difficult to saturate, Lorentzian component in OOO implies that this polymer has traces of a charge carrier which is at least locally mobile, and suggests that this polymer might be made measurably conducting.

From a consideration of the rings per charge for the various polymers, it is clear that even in the polymers with no measurable conductivity, and very low spin concentration there is still substantial stored charge. This argues strongly that in these systems the charge is stored as bipolarons, which are EPR silent. $NOPF_6$ is a strong oxidising agent which could easily lead to the formation of bipolarons. The absence of conductivity cannot be attributed solely to the presence of most of the charge as bipolarons, since bipolarons can also act as charge carriers in polythiophene and other systems.[8,12,13]

The low conductivities overall compared to polythiophene produced by other methods are consistent with earlier work[14] on the effect of oligomer chain length on the conductivity of polythiophene prepared electrochemically. As the length of the oligomer increases the stability of the oligomer radical cation increases, with a resultant decrease in reactivity.[14,15] Thus shorter polymers are favoured. This should be especially so for chemical polymerisation, where the total concentration of radical cations is much higher than in electrochemical oxidation and so shorter polymers will be kinetically favoured. Further, as the oligomer length increases the relative reactivities of the α and β positions become similar,[16,17] so that the amount of β branching and off-chain coupling increases as the length of the oligomer increases.

We do not yet have a totally satisfactory explanation for the lower or complete absence of conductivity in the pyrrole and furan containing polymers. Theoretical calculations[15] suggest that furan and pyrrole radical cations are both more reactive than the thiophene radical cation. Further, recent work[17] on SNS shows that addition to the β positions of the pyrrole ring is competitive with addition at the α position of the thiophene ring. Therefore inclusion of a pyrrole ring will increase β branching and off-chain coupling on the pyrrole rings in the mixed oligomers. It is likely also that furan rings have the same effect. In many of the mixed heterocycles that we have studied it therefore appears likely that considerable β branching and off-chain coupling occurs which would lead to the lower conductivity compared to SSS that is observed.

Conclusions

Polymers produced by chemical polymerisation of oligomers from pyrrole, furan and thiophene were studied. Only SSS, SSO and SOS showed appreciable conductivities. EPR studies showed the presence of mobile charge carriers in SSS, SOS and SSO and to a much smaller extent in OOO, consistent with the observed conductivities. The presence of localised radicals in the other polymers, particularly in the case of SNS, suggests that the absence of conductivity in these systems results primarily from the absence of mobile species in these systems. It appears likely that this results from the short conjugation lengths produced by substantial β branching and off-chain coupling.

Experimental

Synthetic.—Melting points were determined on a Thomas-Hoover capillary melting-point apparatus and are uncorrected. Infrared spectra (IR) were recorded on a Perkin-Elmer Model 781 spectrometer. NMR spectra were measured on either a Nicolet 200 or a Bruker-360 instrument. *J* Values are in Hz. Mass spectra were recorded on a Hewlett Packard 5985 GC/MS spectrometer. Elemental analyses were performed by Atlantic Microlab, Norcross, Georgia. Compounds **3** (SSS), **4** (SNS) and **5** (SOS) were prepared by minor modifications of literature procedures.

Polymer preparation. 1 equivalent of the oligomer (*ca.* 1 mmol) was dissolved in 15 cm^3 of degassed, dry methylene dichloride, under an inert atmosphere. To this, 2 equivalents of nitrosonium hexafluorophosphate ($NOPF_6$) were added. After 3 h stirring at room temperature, the black precipitate was filtered, washed with dry methylene dichloride and dried. The polymer was then heated in methanol to remove any impurities.

2,2′,5′,2″-Terfuran **6**. The diketone **12** (4.36 g, 0.02 mol) was added to 250 cm^3 of acetic anhydride. To this mixture was added slowly 20 cm^3 of conc. hydrochloric acid. After 4 h at room temperature, the reaction mixture was poured into ice water and extracted with diethyl ether. The ether layer was washed with sodium bicarbonate and water, and dried over sodium sulfate. The solvent was evaporated and the product was subjected to chromatography (silica, hexane eluent). The yellowish white solid was recrystallised from methanol; yield 2.6 g (65%), m.p. 63 °C; *m/z* 200 (100), 171 (11), 144 (11), 115 (30), 100 (11); δ_H(CDCl$_3$) 7.30–7.35 (d, 2 H, *J* 2), 6.5–6.57 (m, 4 H), 6.3–6.4 (m, 2 H).

2,5-*Di*(2-*furyl*)-N-*methylpyrrole* **7**. The diketone **12** (1.74 g, 0.008 mol), methylamine hydrochloride (10.8 g, 0.00 8 mol), and sodium acetate (13 g, 0.16 mol) were refluxed in 100 cm^3 95% ethanol overnight under an inert atmosphere. The reaction mixture was cooled and 300 cm^3 of water was added. The solid formed was filtered, dried and purified over a silica column (hexane eluent); yield 1.11 g (65%), m.p. 30 °C; *m/z* 213.5 (100), 184.5 (26.35), 156.4 (45.7), 141.3 (7.2), 128.3 (7), 115 (8), 77 (10); δ_H(CDCl$_3$) 3.8279 (s, 3 H), 6.40 (d, 2 H, *J* 9), 6.44 (s, 2 H), 6.47 (dd, 2 H, *J* 5.5, 3.6), 7.46 (d, 2 H, *J* 4.3).

2,5-*Di*(2-*furyl*)*thiophene* **8**. A mixture of diketone **12** (2.15 g, 0.01 mol) and Lawesson's reagent (2.43 g, 0.006 mol) were refluxed overnight in 20 cm^3 toluene. The toluene was evaporated and the black residue was subjected to column chromatography over neutral alumina, using light petroleum (b.p. 60–70 °C) CH$_2$Cl$_2$ (1 : 1) as eluent. The product was recrystallised from methanol to give a white solid; yield 1.51 g (70%); m.p. 61 °C; *m/z* 216.5 (100), 187.5 (21.0), 159 (29), 134 (9), 115 (20), 108 (11), 79 (6.7), 69 (7.3); δ_H(CDCl$_3$) 6.45 (dd, 2 H, *J* 5.4), 6.50 (d, 2 H, *J* 9), 7.16 (s, 2 H), 7.41 (d, 2 H, *J* 4).

2-(2-*Thienyl*)-5-(2-*furyl*)*furan* **9**. Diketone **14** (4.68 g, 0.02 mol) was added to 250 cm^3 of acetic anhydride. To this mixture was added slowly 20 cm^3 of conc. hydrochloric acid. The reaction mixture was stirred for 4 h at room temperature, and then poured into ice water and extracted with ether. The organic layer was dried with sodium sulfate, the solvent was evaporated, and the product was purified by flash column chromatography over silica gel (hexane eluent). The yellowish white solid was recrystallised from methanol; yield 3.0 g (70%), m.p. 34 °C; *m/z* 216 (100), 187 (11), 160 (8), 159 (13), 134 (5), 115 (14), 111 (8), 95 (7); δ_H(CDCl$_3$) 6.47 (dd, 1 H, *J* 4.7, 4.4), 6.54 (d, 1 H, *J* 10), 6.59 (d, 1 H, *J* 10), 6.62 (d, 1 H, *J* 10), 7.04 (dd, 1 H, *J* 3, 10), 7.23 (dd, 1 H, *J* 240), 7.29 (dd, 1 H, *J* 2, 10), 7.42 (d, 1 H, *J* 3) (Found: C, 66.5; H, 3.75; S, 14.86. Calc. for C$_{12}$H$_8$O$_2$S: C, 66.64; H, 3.73; S, 14.8).

2-(2-*Thienyl*)-5-(2-*furyl*)*thiophene* **10**. Diketone **14** (2.34 g, 0.01 mol) and Lawesson's reagent (2.43 g, 0.006 mol) were refluxed overnight in 20 cm^3 toluene. The toluene was evaporated and the black cake was purified using silica flash column with hexane/CH$_2$Cl$_2$ (1 : 1) as eluent. The product was recrystallised from methanol; yield 1.77 g (75%), m.p. 75 °C; *m/z* 232 (100), 204 (8), 203 (50), 171 (39), 127 (7), 116 (10), 115 (6), 69 (13); δ_H(CDCl$_3$) 6.45 (m, 1 H), 6.5 (d, 1 H, *J* 9), 7.00–7.22 (m, 5 H), 7.41 (s, 1 H) (Found: C, 62.1; H, 3.5; S, 27.55. Calc. for C$_{12}$H$_8$OS$_2$: C, 62.04; H, 3.47; S, 27.6).

2-(2-*Thienyl*)-5-(2-*furyl*)-N-*methylpyrrole* **11**. Diketone **14** (1.87 g, 0.008 mol) was placed in a round bottom flask, methylamine hydrochloride (10.8 g, 0.008 mol), and sodium acetate (13 g, 0.16 mol) were added, and the reaction mixture was refluxed in 100 cm^3 of 95% ethanol overnight under an inert atmosphere. The mixture was cooled and 300 cm^3 of water was added. The solid was filtered and subjected to column chromatography using hexane as eluent. Yield 1.6 g (86%), m.p. 53 °C; *m/z* 229 (100), 214 (6), 200 (47), 199 (9), 186 (14), 167 (9), 115 (8), 97 (3), 89 (4), 86 (3), 77 (5), 69 (5); δ_H(CDCl$_3$) 3.76 (s, 3 H), 6.34 (d, 1 H, *J* 3), 6.40 (d, 1 H, *J* 9), 7.46–7.44 (m, 2 H), 7.07–7.09 (m, 2 H), 7.28 (dd, 1 H, *J* 3, 10), 7.44 (d, 1 H, *J* 4) (Found: C, 68.15; H, 4.85; N, 6.05; S, 13.9. Calc. for C$_{13}$H$_{11}$NOS: C, 68.09; H, 4.83; H, 6.10; S, 13.98).

1,4-*Di*(2-*furyl*)*butane*-1,4-*dione* **12**. To a suspension of sodium cyanide (310 mg, 6.3 mmol) in dry DMF (4 cm^3), was added furan-2-carboxaldehyde (1.2 g, 12.5 mmol) in 4 cm^3 of dry DMF. The reaction mixture, which turned green and then brown, was stirred for 15 min, and then Mannich base **13** (1.83 g, 10 mmol) in 10 cm^3 DMF was added over 15 min. The solution was stirred overnight. Water was added and the product was extracted (×3) with chloroform. After evaporation of the solvent, the diketone was recrystallised from ethanol; yield 1.78 g (65%), m.p. 131 °C; *m/z* 218 (90), 201 (15), 19 (20); δ_H(CDCl$_3$) 3.22 (m, 4 H), 6.4–6.6 (m, 2 H), 7.13–7.28 (m, 2 H), 7.5–7.68 (m, 2 H).

3-*Dimethylamino*-1-(2-*furyl*)*propanone* **13**. A mixture of 2-acetylfuran (8.8 g, 0.08 mol), paraformaldehyde (2.7 g, 0.09 mol), dimethylamine hydrochloride (7.35 g, 0.09 mol) and 0.4 cm^3 of hydrochloric acid was refluxed for 16 h in 20 cm^3 of 95% ethanol. The reaction mixture was cooled and the precipitate was filtered, washed with ether and dried; yield 11.35 g (85%). This Mannich base hydrochloride (2 g, 10 mmol) was basified using ammonium hydroxide. The solution was extracted (×3) with diethyl ether. The organic layer was washed with water and dried over sodium sulfate. Evaporation of ether gave 1.68 g of product δ_H(CDCl$_3$) 6.47 (dd, 1 H, *J* 3, 4), 6.54 (d, 1 H, *J* 10), 7.42 (d, 1 H, *J* 3), 3.7 (s, 6 H), 3.4 (s, 2 H), 3.5 (s, 2 H).

1-(2-*Thienyl*)-4-(2-*furyl*)*butane*-1,4-*dione* **14**. A solution of furan-2-carboxaldehyde (1.2 g, 12.5 mmol) in 4 cm^3 dry DMF was added over 15 min (inert atmosphere) to a suspension of sodium cyanide (310 mg, 6.3 mmol) in 4 cm^3 dry DMF. After stirring for 15 min, the Mannich base **15** (1.83 g, 10 mmol) in 10 cm^3 DMF was added over 1 h. The solution was stirred overnight. Water was added, and the product was extracted with chloroform. The extract was washed with water, dried over sodium sulfate, and evaporated. The product was recrystallised from ethanol; yield 1.9 g, (50%), m.p. 130–131 °C; *m/z* 234 (100), 218 (30), 97 (15), 68 (10); δ_H(CDCl$_3$) 3.4 (s, 4 H), 7.14 (dd, 1 H, *J* 3, 7), 7.4 (s, 2 H), 7.2 (dd, 1 H, *J* 1, 4), 7.31 (dd, 1 H, *J* 1, 4), 6.45 (s, 1 H) (Found: C, 61.6; H, 4.3; S, 13.6. Calc. for C$_{12}$H$_{10}$O$_3$S: C, 61.53; H, 4.30; S, 13.68).

Physical Methods and Materials.—Four-probe conductivities at room temperature in air were measured on pressed pellets (10 mm diameter, about 1 mm thick, made by a Carver Press at 140 MPa pressure) by using four point probes 1 mm thick and 1.5 mm apart in a straight line; the outer probes were connected to a 200 V DC power supply, to provide a constant current of 30 μA, while the potential drop across the inner probes was measured by an Edward Morley N1a Nanovolt Amplifier. Silver dots were painted on the pellet surface to make better contact and reduce ohmic losses. The 200 V DC potential ('forward voltage') could be reversed, and the voltage drop across the inner two electrodes under reverse bias was then averaged with the drop measured with the forward voltage. The pellets were also inverted, to measure the conductivity on both sides of the pellet. The conductivities were calculated with corrections for sample size and geometry.[18]

EPR spectra were recorded at 9 GHz on a Varian E-109 bridge combined with an IBM ER 073, 10″ magnet using a Varian 4533 cylindrical cavity fitted with teflon guides. Measurements at 77 K were done in a quartz dewar. For measurements at 12 K an Oxford Products ESR 900 cryogenics system was used to blow cooled helium past the sample tube. Between 5 and 8 mg of sample was ground and placed in 4 mm o.d. quartz sample tubes. Spin concentrations were determined against α,α′-diphenyl-β-picrylhydrazyl (DPPH) at 43 dB (*ca.* 0.01 mW), and checked against samples of 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy (Tempol) and Galvinoxyl; *g*-values were determined against DPPH as the average of three measurements on two samples.

Curve fitting was done on a MacIntosh computer using the curve fitting functions of program Igor from Wavemetrics, which are based on the Numerical Recipes algorithms.[19]

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