

Steric Effects on the Optical and Electrochemical Properties of *N*-Substituted Pyrrole–Thiophene Monomers and Polymers

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Monomers consisting of *N*-alkyl-substituted-2,5-bis(2-thienyl)pyrroles and their electro-oxidatively generated polymers display electrochemical and optical properties which reflect the steric demands of the alkyl substituents.

Much of the recent interest in heteroaromatic polymers stems from their novel electrical and optical properties, their enhanced environmental stability (compared to polyacetylene and its analogues) and the relative ease with which self-supporting films may be produced by electro-oxidative polymerization of a wide variety of monomer types.¹ These films provide a convenient form for transport and optical measurements, but remain, until recently,² intractable once produced. In principle, pyrroles substituted at *N* comprise a large family of potentially useful monomers. Unfortunately, once polymerized these derivatives invariably afford materials whose electrical conductivities are many orders of magnitude inferior

to the parent system even though alkyl substitutions on *N* impart only minor electronic perturbations to the pyrrole (as evidenced by the similarities in electrochemical oxidation potentials). The greatest effect of such groups is steric interference with the achievement of coplanarity by contiguous rings in the polymer (especially in the oxidized state), a configuration which must be maintained to within 40° for high electrical conductivity.³ The effect, most pronounced for homopolymers with bulky substituents, is attenuated in copolymers such as pyrrole-*co*-*N*-methylpyrrole.⁴

We have observed a similar attenuation for the thiophene-pyrrole copolymers derived from monomers (1) (SNS) and (2) (SMS).^{5,6} For comparably doped polymers, the room temperature conductivities differed by a factor of ~10³, whereas the analogous difference between polypyrrole and poly(*N*-methylpyrrole) was ~10⁷.¹ The intervening thiophene rings in SMS may be serving as 'steric diluents' in the polymer, partially relaxing the constraints on inter-ring coplanarity. This comparatively moderate reduction in electrical conductivity for an (*N*-substituted)pyrrole (co)polymer, coupled with the ease with which such groups may be introduced onto the pyrrole nitrogen and the advantageous effects on mechanical (solubility) properties of polythiophenes upon alkyl-substitution,² encouraged us to examine several SN(R)S derivatives (1)–(6).

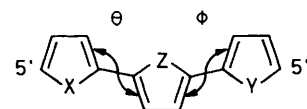
Table 1 gives the peak anodic potentials (E_{pa}) and long wavelength absorption for the monomers and derived polymers. The peak oxidation potentials fall into three groups depending on the substituent on the pyrrole. The most easily oxidized is the unsubstituted SNS, in which all rings can readily achieve coplanarity. Straight chain alkyl substituents raise this potential by *ca.* 70–100 mV over SNS's and the α -branched isopropyl group raises it by an *additional* 70 mV over the *n*-alkylated derivatives. Although counter to the electron donating abilities of the various alkyl groups, this trend is consistent with the relative steric requirements of these substituents in the vicinity of the aromatic rings.

To assess further the steric effects of *N*-alkyl substitution, we conducted molecular mechanics calculations (MMX),⁷ including π -interactions, on SNS and SMS model compounds (Figure 1, X = Y = O, Z = NH or NMe) where furans

Table 1. Peak anodic potentials (E_{pa})^a and long wavelength absorption^b for the monomers and derived polymers.

System	Monomer		Polymer $h\nu_{min}/eV$
	E_{pa}/V vs. SCE	$h\nu_{min}/eV$	
SNS	0.620	3.65	2.62
SMS	0.685	3.89	2.98
SN2S	0.706	3.97	3.02
SN7S	0.712	3.92	3.18
SN18S	0.738 ^c	3.94	—
SNIPS	0.807	4.13	3.42

^a Cyclic voltammetric experiments used an EG&G PARC Model 173 Potentiostat (equipped with a EG&G PARC Model 176 Current Follower) coupled to an EG&G PARC Model 175 programmer. A three compartment cell was used. The working electrode consisted of a Pt disc (*ca.* 100 μ m diam.) separated by a frit from a carbon counter electrode. The reference electrode consisted of a silver wire suspended in the electrolyte solution [0.5 M LiClO₄ in propylene carbonate (PC) or 1.0 M tetra-*n*-butylammonium tetrafluoroborate (TBATFB) in tetrahydrofuran (THF)] which was saturated with AgNO₃. This was separated from the electrolysis compartment by a 3 mm length of unfused Vycor. All potentials were referenced to standard calomel electrode (S.C.E.) by measuring the ferrocene/ferrocenium couple (taken as +0.31 V vs. S.C.E.) in these media. The voltammograms were collected on a Nicolet 2090 Digital Oscilloscope which was interfaced to a Zenith Model 159 microcomputer (IEEE 488). The waveforms were analysed using commercially available software ('Waveform Basic,' Blue Feather Software, Inc.). ^b Thin films were grown galvanostatically at ≈ 0.5 mA/cm² onto indium–tin oxide (ITO) anodes from 10 mM solutions of the monomers in nitrobenzene containing 0.1 M TBATFB. All film growth was conducted in a Vacuum Atmospheres, Inc. glove box filled with high purity helium gas. Once grown, the films were rinsed with propylene carbonate (PC), stored in this solvent for several days, and then placed in a one-compartment electrochemical doping cell. The ITO/polymer slide served as the anode while a Pt wire onto which a strip of clean Li was affixed served as the cathode and pseudo-reference electrode. The cell was filled with electrolyte (0.25 M LiBF₄ in PC) and sealed in the glove box. It was then removed and placed in the sample beam of the u.v.–visible–n.i.r. spectrophotometer. A cuvette containing electrolyte and a clean ITO electrode was placed in the reference beam. ^c Determined in THF/1.0 M TBATFB owing to solubility constraints; all others in PC/0.5 M LiClO₄.



X = Y = S, Z = N–H	SNS	(1)
X = Y = S, Z = N–Me	SMS	(2)
X = Y = S, Z = N–Et	SN2S	(3)
X = Y = S, Z = N–(CH ₂) ₆ Me	SN7S	(4)
X = Y = S, Z = N–(CH ₂) ₁₇ Me	SN18S	(5)
X = Y = S, Z = N–Pr ⁱ	SNIPS	(6)

Figure 1. Structure of and acronyms for monomers studied.

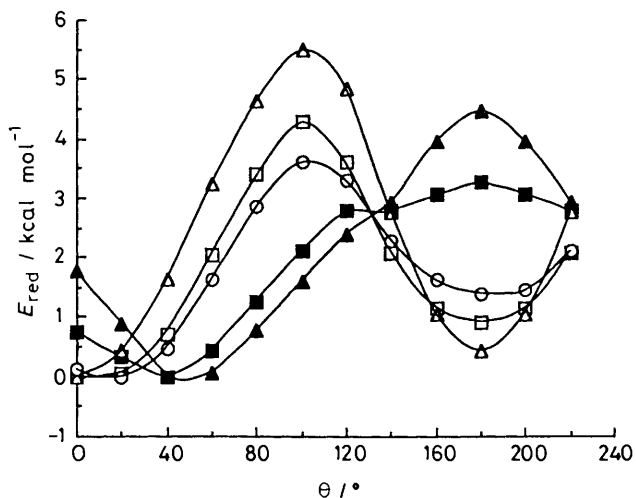


Figure 2. Calculated energy vs. dihedral angle, θ , for biaryls consisting of the X and Z rings *only* of Figure 1. The 'reduced' energy (E_{red}) is the difference between the energy of a particular conformation and the minimum calculated energy for that molecule (1 cal = 4.184 J). See text for X and Z designations. \square C1ON; \blacksquare IPON; \triangle ON; \blacktriangle TBON; \circ C2ON.

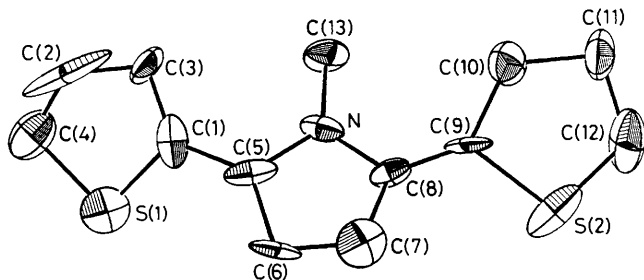


Figure 3. Molecular structure of SMS. Selected bond lengths (\AA): S(1)–C(1) 1.69(1); S(1)–C(4) 1.80(1); S(2)–C(9) 1.79(1); S(2)–C(12) 1.63(1); N–C(5) 1.40(2); N–C(8) 1.39(2); C(9)–C(1) 1.47(2); C(10)–C(11) 1.52(2); C(11)–C(12) 1.49(2).

replaced thiophene since the current version of this program does not accommodate S as a π -atom. The former compound's minimum energy conformation is at $\theta = \phi = 0^\circ$, the latter's at $\theta, \phi \sim 20^\circ$. We designate the conformation $\theta, \phi = 0^\circ$ as *syn* and $\theta, \phi = 180^\circ$ (*i.e.*, as drawn in Figure 1) as *anti*. To probe this effect further, we conducted similar calculations on the biaryls consisting of the X and Z rings of Figure 1, by driving the dihedral angle θ and observing the total energy of the system for different Z groups.

Energy diagrams for the biaryls with X = O and Z = NH (ON), Z = NMe (C1ON), Z = NEt (C2ON), Z = NPrⁱ (IPONO), or Z = NBut (TBON) are displayed in Figure 2.

The unsubstituted ON again displays its minimum energy for coplanar rings. C1ON displays minima when the rings are about $\approx 20^\circ$ out of coplanarity with a small energy preference for conformations that are generally *syn* (with respect to the heteroatoms). The greater steric demands of the substituents on IPON and TBON force the rings out of coplanarity to an even greater degree (E_{min} at $\theta \geq 40^\circ$). Although the conformational trends derived from the MMX computations on these models are consistent with the relative steric requirements of the substituents, an exact prediction of the minimum energies or dihedral angles for the SN(R)S polymers is not expected from them because (i) they are on molecules in the gas phase (hence ignoring possible crystal packing considerations) and (ii) they model furans instead of thiophenes.

A more instructive picture of the bonding arrangements in the polymer might be inferred from the single crystal X-ray structure of the monomers. We chose to examine SMS first. Its molecular structure is shown in Figure 3.[†] The large thermal parameters for some of the ring carbons, especially C(2), may be due to the fact that the number of observed reflections/refined variables (4.4) is not particularly large although slight disorder in the thiophene rings cannot be ruled out. Similar disorder has been noted before in thiophenes.⁸ The most significant feature of the structure with regard to the present discussion are the dihedral angles between the thiophenes and the pyrrole ring. The angles between the pyrrole and thiophene (1) [S(1)/C(1)/C(2)/C(3)/C(4)] and thiophene (2) [S(2)/C(9)/C(10)/C(11)/C(12)] are 31.3(6) and 34.2(6)°, respectively. These values agree remarkably well with those from the MMX-calculations both in magnitude [$\approx 20^\circ$ (calc.)] and conformation (*anti*), given the approximations discussed above.

When the rings in the monomers and corresponding α -linked polymers are not sterically restricted from achieving coplanar arrangements, a linear relationship between their respective E_{pa} values is observed.⁶ The greater oxidation potential of SMS monomer compared to SNS is consistent with some steric inhibition to coplanarity in the former, which would attenuate the resonance stabilization of the oxidized form by the adjacent thiophene rings. The polymer solid should be even more sensitive to this effect and, indeed, E_{pa} for poly(SMS) is disproportionately higher.⁶ The gradual increase in peak anodic potentials of monomers (2)—(5) suggests that (all other factors being equal) there are no dramatic differences in the steric demands of the n-alkyl substituents proximal to the pyrrole ring once they are one carbon removed from the N. The step increases in the peak anodic potentials in going from SNS to the n-alkylated SNS derivatives or from the latter to SNIPS, however, are fully consistent with the dramatic differences in size between H and Me or between a normal and α -branched alkyl substituent. (Some caution must be exercised with this interpretation, however, since the redox behaviour of these systems is irreversible.) Closer examination of Figure 2 also reveals that the relative energy difference between the *syn*- and *anti*-conformations for the modelled monomers increases as the size of the substituent increases. This trend could influence the relative ratio of linear to helical polymer. Others have observed a similar effect in 3-alkyl substituted thiophenes.⁹

When the coplanar arrangement in the propagating radical cation is sufficiently disfavoured owing to these steric interactions, the spin density on the 5' and 5'' positions may be reduced and the resultant polymer could be affected structurally and/or electronically. For example, the proportion of 'mislinked', (α - β or β - β) polymer could increase; the rate of polymerization could be retarded (or even halted in favour of reactions with adventitious nucleophiles), or the degree of polymerization could decrease. Even if the polymer is predominantly α -linked, the facility in producing (bi)polarons

[†] Crystal data for SMS: $C_{13}H_{11}NS_2$, $M = 245.37$, orthorhombic, space group $Pca2_1$, $a = 6.965(7)$, $b = 7.89(5)$, $c = 23.879(6)$ \AA , $U = 1195.7$ \AA^3 , $Z = 4$, $D_c = 1.36$ g cm^{-3} . The structure was solved by direct methods and refined by full-matrix least-squares using 627 reflections with $I > 33\sigma(I)$ measured on an Enraf-Nonius CAD-4 diffractometer. Hydrogen atoms were located and added to the structure factor calculations but their positions were not refined. The final residuals were $R = 0.059$ and $R_w = 0.064$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

upon oxidation and/or their mobility would certainly be sensitive to these deviations. We are currently studying the evolution of the bipolaron spectra as a function of oxidation level for these systems.¹⁰

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References

1 T. A. Skotheim, ed., 'Handbook of Conductive Polymers,' Marcel Dekker, New York, 1986.

- 2 K. Y. Yen, R. Oboodi, and R. L. Elsenbaumer, *Polym. Materials: Sci. Eng.*, 1985, **53**, 79; M. Sato, S. Tanaka, and K. Kaeriyama, *J. Chem. Soc., Chem. Commun.*, 1986, 873; S. Hotta, S. D. D. V. Rughooputh, A. J. Heeger, and F. Wudl, *Macromolecules.*, 1987, **20**, 212.
 - 3 J. L. Bredas, G. B. Street, B. Themans, and J. M. Andre, *J. Chem. Phys.*, 1985, **83**, 1323.
 - 4 K. K. Kanazawa, A. F. Diaz, M. T. Krounbi, and G. B. Street, *Synth. Metals*, 1981, **4**, 1190.
 - 5 J. P. Ferraris and G. D. Skiles, *Polymer*, 1987, **28**, 179.
 - 6 J. P. Ferraris and T. R. Hanlon, *Polymer*, 1989, **30**, 1319.
 - 7 MMX (an expanded version of MM2), Serena Software, Inc., Bloomington, Indiana.
 - 8 G. J. Visser, G. J. Heeres, J. Walters, and A. Vos, *Acta Crystallogr., Sect. B.*, 1968, **24**, 467; T. J. Giordano and P. G. Rasmussen, *Inorg. Chem.*, 1975, **14**, 1628.
 - 9 J. Roncali, R. Garreau, A. Yassar, P. Marque, F. Garnier, and M. Lemaire, *J. Phys. Chem.*, 1987, **91**, 6706.
 - 10 J. P. Ferraris and R. G. Andrus, unpublished results.
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