Condensed Five-membered Heterocycles with Potentialities as Conducting Polymers: *ab initio* Electronic Structures and Theoretical Valence *X*-Ray Photoelectron Spectra

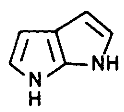
R. Lazzaroni, J. P. Boutique, J. Riga, and J. J. Verbist *
Laboratoire de Spectroscopie Electronique, Facultés Universitaires Notre-Dame de la Paix, Rue de Bruxelles 61, B-5000 Namur, Belgium
J. G. Fripiat and J. Delhalle
Laboratoire de Chimie Théorique Appliquée, Facultés Universitaires Notre-Dame de la Paix, Rue de Bruxelles 61, B-5000 Namur, Belgium

The electronic structures of pyrrolo-[2,3-*b*]- and -[3,2-*b*]-pyrroles, and the equivalent thienopyrroles and thienothiophenes have been investigated by MNDO and STO-3G *ab initio* calculations on model molecules. In agreement with previously reported u.v. photoelectron spectral data and semiempirical calculations, the [3,2-*b*] derivatives display lower ionization potentials than their [2,3-*b*] homologues. For two compounds, a discrepancy regarding the nature of the HOMO is found between these theoretical results and ours. As experimental *X*-ray photoelectron spectral data have to be obtained, simulated valence *X*-ray spectra based on the molecular intensity model proposed by Gelius have been calculated.

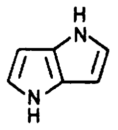
The preparation of air-stable compounds is one of the key features in the development of conducting polymers. Polythiophene and doped polypyrrole are among the few existing systems which exhibit such stability; this explains the present interest in these and related systems. Also, polypyrrole and polythiophene can easily be prepared by a one-pot procedure using electrochemical methods,[1–11] and their organic nature opens up possibilities for applying chemical modifications to enhance favourable trends in their properties. For example, substitution of thiophene in the β-position dramatically affects both the electrical and mechanical behaviour of the polymer.[9,10] Similar attempts on polypyrrole are subject to preparation difficulties for β-substituted pyrroles.[9,12,13] More elaborate changes can also be envisaged such as condensation of the basic building blocks, pyrrole, thiophene, selenophene, either with themselves or with other compounds. Recently, Wellinghoff *et al.*[14] have obtained conducting films of a chemically doped *N*-methyl-3,6-dibromocarbazole polymer.

Quantum mechanical calculations on model molecules and polymers (extended and/or short-chain systems), doped[15,16] and undoped,[17] not only provide a description of their electronic structure, but also guidance in what are the most probable phenomena occurring at the atomic level. *X*-Ray photoelectron spectroscopy (XPS) provides an ideal tool for an experimentally based description of core and valence energy regions of both pristine and doped systems. From careful analyses, it is even possible to speculate on the response modes of the system upon doping.[18,19]

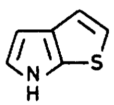
We are interested in a series of heterocyclic molecules, pyrrolo[2,3-*b*]pyrrole (**1**), thieno[2,3-*b*]pyrrole (**3**), thieno[2,3-*b*]thiophene (**5**), and analogues, which, from the viewpoint of the above comments, are logical candidates for new conducting polymers. The measurement of their u.v. photoelectron (UPS) spectra and interpretations based on semiempirical calculations have already been published.[20,21] However, UPS probes topmost levels only and other techniques, *e.g.* XPS, should be used to obtain access to the deeper valence states. In previous work, we have demonstrated the capability for the STO-3G minimal basis set calculations to predict reliably the essential features, shape, intensity, nature, and location of peaks of valence XPS spectra.[22]



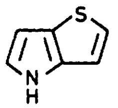
(1)



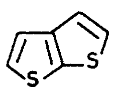
(2)



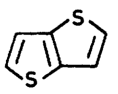
(3)



(4)



(5)



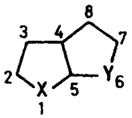
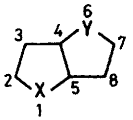
(6)

We report here the results of *ab initio* calculations on the electronic structure and theoretically constructed valence XPS spectra of the aforementioned molecules.

Calculations

To our knowledge, neither *X*-ray diffraction nor microwave spectroscopy measurements have been made available on the series of compounds we are dealing with. To keep computational expenses at a reasonable level, we have determined a model structure through MNDO geometry optimization; this technique[23,24] is known to yield reliable structural parameters for series of similar compounds. In so doing we have mainly attempted to take into account differences between configurations, *e.g.* between pyrrolo[2,3-*b*]- and pyrrolo[3,2-*b*]-pyrrole, as well as relative variations due to the nature of the heteroatoms involved, N and/or S. Results are listed in Table 1.

Table 1. MNDO-optimized bond lengths (Å) and angles (°)

 	Pyrrole*	Thiophene*	Pyrrolo[2,3-*b*]-pyrrole	Thieno[2,3-*b*]-pyrrole	Thieno[2,3-*b*]-thiophene	Pyrrolo[3,2-*b*]-pyrrole	Thieno[3,2-*b*]-pyrrole	Thieno[3,2-*b*]-thiophene
Bond lengths[c]								
1—2	1.398 (1.370)[a]	1.693(1.714)[a]	1.418	1.408	1.703	1.404	1.402	1.700 (1.72)[b]
2—3	1.393 (1.382)	1.367 (1.370)	1.394	1.398	1.371	1.401	1.402	1.372 (1.36)
3—4	1.440 (1.417)	1.454 (1.423)	1.437	1.431	1.449	1.431	1.424	1.442 (1.41)
4—5			1.434	1.425	1.404	1.436	1.423	1.404 (1.36)
5—1			1.379	1.375	1.668	1.387	1.385	1.676 (1.74)
5—6			1.379	1.673	1.668			
6—7			1.418	1.713	1.703	1.404	1.705	1.372
7—8			1.394	1.368	1.371	1.401	1.371	1.700
8—4			1.437	1.447	1.449			
5—8						1.431	1.445	1.442
4—6						1.387	1.676	1.676
Angles[c]								
C(2)X(1)C(5)	109.4 (109.8)	93.3 (92.2)	106.4	107.9	92.1	108.7	108.4	92.7 (91.2)
[2,3-*b*] C(5)Y(6)C(7)			106.4	91.2	92.1			
[3,2-*b*] C(4)Y(6)C(7)						108.7	92.8	92.7 (91.2)

[a,b] Experimental data from refs. 30 and 35.[c] Non-systematic numbering.

* It should be noted that our results on pyrrole and thiophene are close to those obtained using *ab initio* optimization.[36]

These optimized geometries have been utilized as input data in STO-3G minimal basis set[25] calculations using the Gaussian 80 package.[26] All integrals larger than 10^{-6} were explicitly retained and convergence on density matrix elements was always satisfied within a maximum threshold of 5×10^{-5}.

All calculations made in this work were carried out on a DEC 2060 computer.

As one of our future aims is to record XPS spectra of these compounds, special attention has been paid to theoretical simulations of the valence region using the molecular orbital intensity model proposed by Gelius.[27] Previously made simulations on related compounds have come very close to the shape of experimental spectra;[22,28] a similar agreement is hoped for this series of molecules. In another context, such theoretical simulations have also been revealed as a potential means for detecting undesirable photoelectron contributions to the valence XPS spectra originating from the metallic support [29] (even though no contamination could actually be observed in the core region).

The frozen orbital approximation is the basic assumption on those theoretical simulations which consist of peaks centred at rescaled one-electron energies, ε_i (multiplication factor 0.72).[22] Each peak is represented by a linear combination of one Lorentzian and one Gaussian both having the same height and the same width (1.5 eV) over the energy range considered.

Results

(1) *One-electron and Total Energy Mulliken Analysis.*—As mentioned previously, almost no experimental information is available on the geometries besides an early *X*-ray structure on

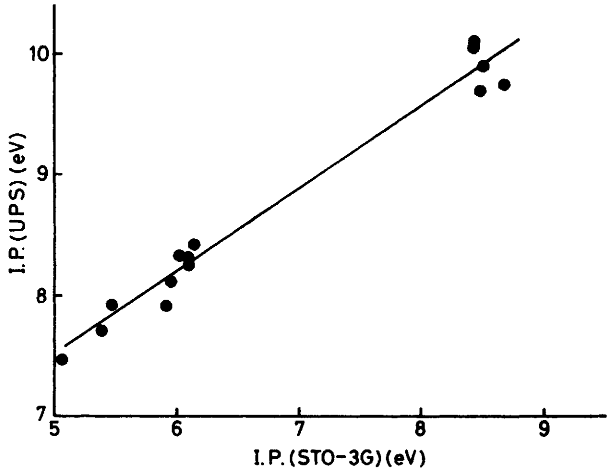


Figure 1. Relation between theoretical (*ab initio* STO-3G) and experimental (UPS) ionization potentials (I.P.)

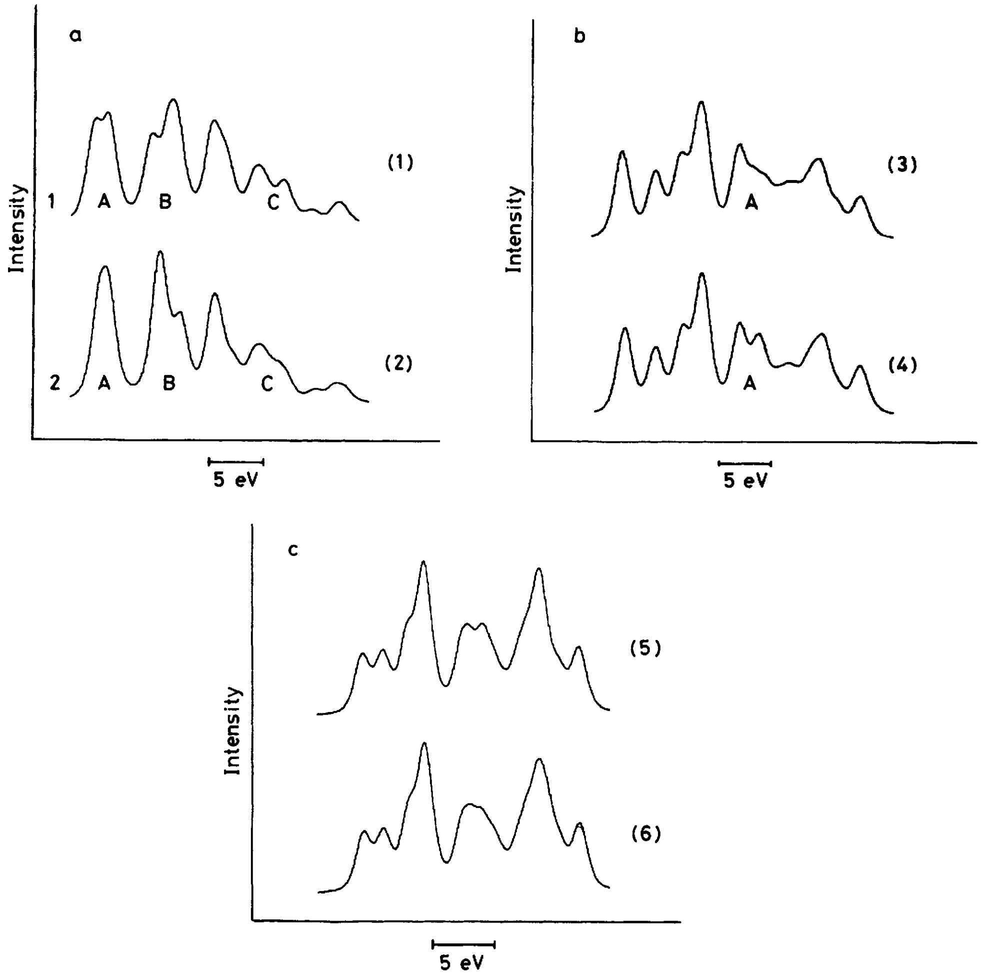


Figure 2. a, Simulated XPS valence spectra of pyrrolo-[2,3-*b*]- (**1**) and [3,2-*b*]-pyrrole (**2**); b, simulated XPS valence spectra of thieno-[2,3-*b*]- (**3**) and [3,2-*b*]-pyrrole (**4**); c, simulated XPS valence spectra of thieno-[2,3-*b*]- (**5**) and [3,2-*b*]-thiophene (**6**)

Table 2. Total energy (a.u.), electron densities, and Mulliken π overlap populations

	Pyrrole	Thiophene	Pyrrolo[2,3-*b*]-pyrrole	Thieno[2,3-*b*]-pyrrole	Thieno[2,3-*b*]-thiophene	Pyrrolo[3,2-*b*]-pyrrole	Thieno[3,2-*b*]-pyrrole	Thieno[3,2-*b*]-thiophene
Total energy	−206.221 56	−545.087 06	−335.332 89	−674.211 37	−1 013.084 38	−335.337 13	−674.214 49	−1 013.086 84
Electron densities[a]								
X(1)	7.31	15.72	7.33	15.73	15.71	7.31	15.73	15.72
C(2)	5.98	6.19	5.98	6.19	6.19	5.97	6.18	6.18
C(3)	6.10	6.08	6.09	6.08	6.08	6.11	6.09	6.08
C(4)			6.06	6.05	6.04	5.94	5.93	6.15
C(5)			5.80	6.04	6.27	5.94	6.16	6.15
Y(6)			7.33	7.32	15.71	7.31	7.32	15.72
C(7)			5.98	5.98	6.19	5.97	5.97	6.18
C(8)			6.09	6.10	6.08	6.11	6.10	6.08
Mulliken π overlap[a] populations								
1—2	0.060	0.044	0.045	0.032	0.37	0.056	0.040	0.041
2—3	0.139	0.154	0.146	0.159	0.157	0.137	0.154	0.153
3—4	0.077	0.062	0.064	0.053	0.056	0.070	0.058	0.060
4—5			0.109	0.115	0.125	0.108	0.114	0.124
5—1			0.054	0.037	0.056	0.049	0.033	0.037
5—6			0.054	0.058	0.040			
6—7			0.045	0.052	0.037	0.056	0.057	0.041
7—8			0.146	0.142	0.157	0.137	0.137	0.153
8—4			0.064	0.069	0.056			
4—6						0.049	0.053	0.037
5—8						0.070	0.075	0.060

[a] The atoms are numbered as in Table 1.

thieno[3,2-*b*]thiophene.[30] According to this determination, the MNDO C–S bond length appears too short by *ca.* 0.05 Å while the CSC angle is slightly overestimated (Table 1). This corroborates the results on thiophene oligomers obtained by Brédas *et al.*[31]

Total energies, atomic, and overlap populations are listed in Table 2. From these calculations the [3,2-*b*] derivatives are predicted to be more stable than the [2,3-*b*] ones, mainly because of smaller nuclear repulsions due to larger internuclear distances between heteroatoms in the former series. The energy difference increases with the nitrogen content in the molecule. In the case of pyrrolo-[2,3-*b*]- and -[3,2-*b*]-pyrrole, *e.g.*, this interaction should be evidenced by the width of the N2*s* peaks as revealed by XPS valence band spectra.

Gross atomic charges are little affected by the molecular configuration, except those for α-carbons which strongly depend on the neighbouring heteroatoms.

Overlap populations indicate that double- and single-bond alternation is less pronounced in (i) the [3,2-*b*] than in the [2,3-*b*] derivatives, and (ii) in the nitrogen rather than the sulphur molecules. The stronger alternation in the sulphur-containing heterocycles is somewhat puzzling in view of the reported higher resonance energy for thiophene (28.7 kcal mol^{-1}) than for pyrrole (21.2 kcal mol^{-1}).[32] Suitable analysis of the aromatic character of heterocycles would require sophisticated calculations which go beyond the simple one-electron picture used here. MNDO and *ab initio* potentials are compared in Table 3 with UPS data.[20,21,34] The ordering of the levels is similar in both methods, but, in the absolute, MNDO values come closer to the the experimental ionization potentials. Nonetheless STO-3G results correlate reasonably well with UPS values as shown in Figure 1.

In the case of pyrrolo[2,3-*b*]pyrrole and thieno[2,3-*b*]-pyrrole, our assignment of the two highest occupied levels differs from the proposition by Gleiter *et al.*[21] For both systems our MNDO and *ab initio* calculations predict the HOMO as being a b_1 state for pyrrolo[2,3-*b*]pyrrole and an a'' state for thieno[2,3-*b*]pyrrole. Accordingly, in the whole series of the [2,3-*b*] compounds, the HOMO is characterized by weak p_z contributions from the heteroatoms and large $2p_z$ contributions from C(4) and C(5). This disagreement would result from the use of different methods of calculation and/or geometries (in our case MNDO optimized geometries). Published UPS measurements are unfortunately insufficient to clarify this point, as intensity criteria are not invoked in the assignments. In future measurements, use of $\mathrm{He^{I}}$ and $\mathrm{He^{II}}$ radiations could certainly help in solving this problem of identifying unambiguously the nature of the first ionization potential, *e.g.* by watching changes in the relative intensity of the first two lines.

Table 3. Theoretical (MNDO and *ab initio*) and experimental ionization potentials (eV)

	MNDO		*Ab initio*		Experimental (UPS)[a]
Pyrrole	$1a_2$	8.57	$1a_2$	6.28	8.22
	$2b_1$	9.32	$2b_1$	7.52	9.22
	$6a_1$	13.09	$6a_1$	12.41	12.70
	$4b_2$	13.51	$4b_2$	13.14	12.95
Thiophene	$1a_2$	9.51	$1a_2$	7.02	8.90
	$2b_1$	9.95	$2b_1$	7.19	9.50
	$6a_1$	12.83	$6a_1$	7.19	12.10
	$1b_1$	13.29	$4b_2$	10.45	12.70
				12.33	
Pyrrolo[2,3-*b*]-pyrrole	$3b_1$	7.96	$3b_1$	5.07	7.46
	$2a_2$	8.22	$2a_2$	5.91	7.91
	$2b_1$	10.07	$2b_1$	8.68	9.73
	$1a_2$	12.38	$8a_1$	11.51	11.47
Thieno[2,3-*b*]-pyrrole	$5a''$	8.56	$5a''$	5.47	7.97
	$4a''$	8.86	$4a''$	6.10	8.31
	$3a''$	10.43	$3a''$	8.51	9.89
	$2a''$	12.19	$15a'$	10.32	11.45
Thieno[2,3-*b*]-thiophene	$2\mathrm{b}_1$	9.22	$3b_1$	6.02	8.32
	$2a_2$	9.37	$2a_2$	6.14	8.41
	$2b_1$	10.70	$2b_1$	8.43	10.08
	$1a_2$	12.18	$8a_1$	10.25	11.27
Pyrrolo[3,2-*b*]-pyrrole	$3a_u$	7.84	$3a_u$	4.89	
	$2a_u$	8.34	$2a_u$	6.14	
	$2b_g$	9.81	$2b_g$	8.36	
	$7a_g$	12.44	$7a_g$	11.47	
Thieno[3,2-*b*]-pyrrole	$5a''$	8.44	$5a''$	5.39	7.70
	$4a''$	8.99	$4a''$	6.11	8.24
	$3a''$	10.29	$3a''$	8.49	9.66
	$2a'$	12.27	$15a'$	10.13	11.30
Thieno[3,2-*b*]-thiophene	$3a_u$	9.10	$3a_u$	5.95	8.10
	$2a_u$	9.54	$2a_u$	6.14	8.61
	$2b_g$	10.65	$2b_g$	8.42	10.04
	$1b_g$	12.14	$8a_g$	9.84	11.50

[a] From refs. 20, 21, and 34.

(2) *Simulated XPS Valence Spectra.*—We predict theoretically the changes to be expected in the shape of the valence XPS spectra as influenced by (1) the configuration, and (2) the nature of the heteroatoms in the series of compounds.

(a) *Influence of configuration.* In pyrrolo-[2,3-*b*]- and -[3,2-*b*]-pyrroles (Figure 2a) the major differences are expected to occur in peaks A—C. Peak A splits into two components upon going from the [3,2-*b*] to the [2,3-*b*] derivative. In the latter, as already shown by the total energy results, the smaller distance between the nitrogen atoms favours more interaction between N2*s* atomic functions which, in this energy range, make large

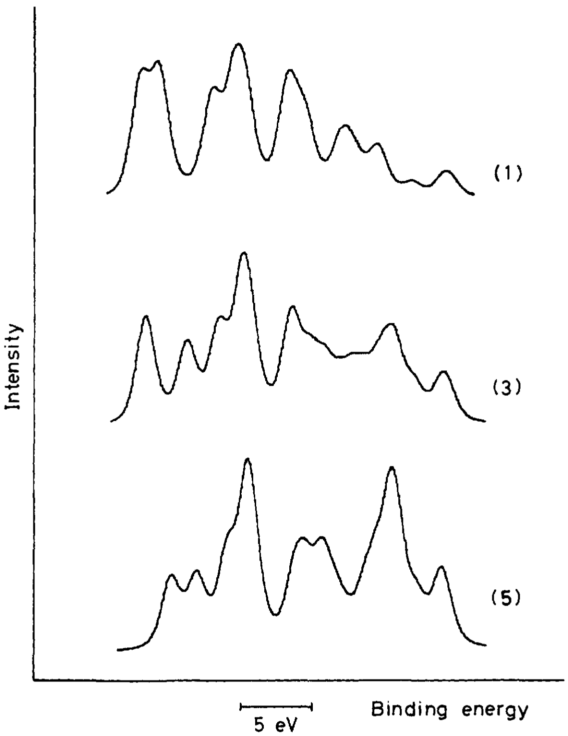


Figure 3. Simulated XPS valence spectra of the [2,3-*b*] derivatives: pyrrolo[2,3-*b*]pyrrole (**1**); thieno[2,3-*b*]pyrrole (**3**); thieno[2,3-*b*]-thiophene (**5**)

contributions to the LCAO expansion of the one-electron states. On the basis of previous experience this is likely to be observed as a broadening of peak A in the measured spectra.

A drastic change is observed in peak B; it results from a nearly 1 eV shift of the $2b_2$ orbital whose composition is mainly 2*s* and originates from atoms in positions 1, 3, 6, and 8. Changes in peak C are small and will probably be experimentally unobservable.

As can be seen in Figure 2b, both thienopyrroles exhibit similar spectral shapes. However, we note the appearance of a new feature, (A), in the [3,2-*b*] compound; it can be related to the nature of the $19a'$ orbital whose S3*s* contribution is significantly more important than in the [2,3-*b*] configuration.

In the case of thieno-[2,3-*b*]- and -[3,2-*b*]-thiophenes, the simulated spectra are quite comparable. As the differences between these two simulations (Figure 2c) are small, it may be inferred that these isomers will remain indistinguishable in their valence XPS spectra.

(b) *Influence of the heteroatoms*. A comparison of the three [2,3-*b*] derivatives (Figure 3) can serve as a way to follow the influence of the nature of the heteroatoms on the shape of the spectra. The most noticeable feature is a progressive lowering of the intensity of the innermost valence levels, characterized by a strong N2*s* nature, balanced by an intensity increase of the lines related to the sulphur lone pairs which arise at lower binding energies. Other differences exist, but are less marked, and to some extent not very significant for experimental measurements.

Conclusions

The *ab initio* calculations carried out on pyrrolopyrroles, thienopyrroles, and thienothiophenes (**1**)—(**6**) have brought additional information on their electronic structure, especially in relation to the potential valence XPS measurements.

In all cases, except when it comes to the comparison between the two thienothiophenes (**5**) and (**6**), significant differences driven by configuration and nature of heteroatoms are expected in their experimental spectra. Work is currently in progress to check these predictions.

Acknowledgements

We are very grateful to the IRSIA (R. L.) and NFSR (J. P. B.) for financial support.

References

1 A. Dall'Olio, G. Dascola, V. Varacca, and V. Bocchi, *Compt. Rend. Acad. Sci.* (*Paris*), 1968, **C267**, 433.

2 A. F. Diaz, K. K. Kanazawa, and G. P. Gardini, *J. Chem. Soc., Chem. Commun*, 1979, 635.

3 K. K. Kanazawa, A. F. Diaz, R. H. Geiss, W. D. Gill, J. F. Kwak, J. A. Logan, J. F. Rabolt, and G. B. Street, *J. Chem. Soc., Chem. Commun.*, 1979, 854.

4 K. K. Kanazawa, A. F. Diaz, W. D. Gill, P. M. Grant, G. B. Street, G. P. Gardini, and J. F. Kwak, *Synth. Metals*, 1979, **1**, 329.

5 A. F. Diaz and J. I. Castillo, *J. Chem. Soc., Chem. Commun.*, **1980**, 397.

6 G. Tourillon and F. Garnier, *J. Electroanal. Chem.*, 1982, **135**, 173.

7 K. Kaneto, K. Yoshino, and Y. Inuishi, *Jpn. J. Appl. Phys.*, 1982, **21**, L567.

8 K. Kaneto, Y. Kohno, K. Yoshino, and Y. Inuishi, *J. Chem. Soc., Chem. Commun.*, 1983, 382.

9 R. J. Waltman, J. Bargon, and A. F. Diaz, *J. Phys. Chem.*, 1983, **87**, 1459.

10 F. Garnier, G. Tourillon, M. Gazard, and J. C. Dubois, *J. Electroanal. Chem.*, 1983, **148**, 299.

11 G. Tourillon and F. Garnier, *J. Phys. Chem.*, 1983, **87**, 2289.

12 R. A. Jones and G. P. Bean, in 'The Chemistry of Pyrroles,' Academic Press, New York, 1977.

13 A. F. Diaz, A. Martinez, K. K. Kanazawa, and M. Salmon, *J. Electroanal. Chem.*, 1981, **130**, 181.

14 T. Wellinghoff, T. Kedrowski, S. Lenekke, and H. Ishida, *J. Phys.* (*Paris*), 1983, **44-C3**, 677.

15 J. Delhalle, J. L. Brédas, and J. M. André, *Chem. Phys. Lett.*, 1981, **78**, 93.

16 J. L. Brédas, R. R. Chance, and R. Silbey, *J. Phys. Chem.*, 1981, **85**, 756.

17 J. L. Brédas, J. M. André, and J. Delhalle, *J. Mol. Struct.*, 1982, **87**, 237.

18 W. R. Salaneck, R. Erlandsson, J. Prejza, I. Lundström, and O. Inganäs, *Synth. Metals*, 1983, **5**, 125.

19 P. Pfluger and G. B. Street, *J. Chem. Phys.*, in the press.

20 P. A. Clark, R. Gleiter, and E. Heilbronner, *Tetrahedron*, 1973, **29**, 3085.

21 R. Gleiter, M. Kobayashi, J. Spanget-Larsen, S. Gronowitz, A. Konar, and M. Farnier, *J. Org. Chem.*, 1977, **42**, 2230.

22 J. P. Boutique, Ph.D. Thesis, Facultés Universitaires N.D. de la Paix, Namur, 1982.

23 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899, 4907.

24 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1978, **100**, 777.

25 (*a*) W. J. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 1970, **52**, 2769; (*b*) J. B. Collins, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Chem. Phys.*, 1976, **64**, 5142.

26 J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Sieger, D. J. Defrees, H. B. Schlegel, S. Topiol, L. R. Kahn, and J. A. Pople, *QCPE*, 1981, **13**, **406**.

27 U. Gelius, *J. Electron Spectrosc. Relat. Phenom.*, 1974, **5**, 985.

28 J. P. Boutique, J. Riga, J. J. Verbist, J. Delhalle, J. G. Fripiat, R. C. Haddon, and M. L. Kaplan, *J. Am. Chem. Soc.*, 1984, **106**, 312.

29 J. Riga, J. P. Boutique, J. J. Verbist, J. Delhalle, and J. G. Fripiat, *J. Electron Spectrosc. Relat. Phenom.*, 1984, **33**, 263.

30 E. G. Cox, R. J. Gillot, and G. A. Jeffrey, *Acta Crystallogr.*, 1949, **2**, 356.

31 J. L. Brédas, R. Silbey, D. S. Boudreaux, and R. R. Chance, *J. Chem. Phys.*, to be published.

32 N. L. Allinger, M. P. Cava, D. C. De Jongh, C. R. Johnston, N. A. Lebel, and C. S. Stevens, in 'Organic Chemistry,' McGraw Hill, New York, 1975.

33 G. Marino, *Adv. Heterocycl. Chem.*, 1971, **13**, 235.

34 A. D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, *Anal. Chem.*, 1970, **42**, 1064.

35 L. Nygaard, J. Tormod Nielsen, J. Kirchleiner, G. Maltesen, J. Rastrup-Andersen, and G. Ole Sorensen, *J. Mol. Struct.*, 1969, **3**, 491.

36 F. R. Cordell and J. E. Boggs, *J. Mol. Struct. Theochem.*, 1981, **85**, 163.

Received 21*st March* 1984; *Paper* 4/458