New Organic Polymer Precursors: Synthesis and Electronic Structure of Thienylpyridines and Thienylethynylpyridines

Igor Novak,* Siu-Choon Ng,* Chup-Yew Mok, Hsing-Hua Huang, Jiye Fang and Kevin Kek-Tsong Wang
Department of Chemistry, National University of Singapore, Singapore 0511, Singapore

He I and He II UV photoelectron spectra (UPS) of isomeric thienylpyridines and thienylethynylpyridines have been recorded. Their electronic structures were analysed and spectra assigned on the basis of He II/He I intensity variations, comparison with UPS of pyridine, thiophene and ethyne and semiempirical MO calculations. The spectra indicate that there is considerable interaction between π orbitals of thiophene, pyridine and ethynyl moieties. The relationship between electronic structure and formation of novel polymer materials is discussed.

The conjugated polymers (CP) *i.e.* those with delocalised π states have been studied extensively over the last two decades, primarily because they are a basis for new technological materials with applications in the fields of electrochemical energy storage (rechargeable batteries), electrochromic devices (displays), photovoltaic cells and various sensors. The applicability is a direct consequence of their physicochemical properties, in particular nonlinear optical susceptibility, optical dichroism and highly anisotropic electrical conductivity. Whilst it has been recognised for some time that the electronic structure influences such properties,[1] their exact relationship remains to be elucidated. Several new polymer materials derived from thiophene, pyridine and ethyne monomer units have recently been prepared as thin films. They do not show outstandingly high electrical conductivity (when compared with polythiophene) but exhibit interesting electrochemical and optical properties.[2-5]

To analyse the electronic structure of these polymers one may initially study the electronic structure of their oligomeric precursors (*e.g.* by high resolution gas phase UPS) and then infer the polymer results by extrapolation and analogy. This allows one not only to work with better resolved spectra (compared with solid-state UPS or XPS) but also clearly to discern the role of electronic structure in the polymer properties.

In this work we attempted to analyse the electronic structure of thienylpyridines and thienylethynylpyridines; 'building blocks' for a polymer consisting of (–thiophene–pyridine–) or (thiophene–C≡C–pyridine) repeating units.

Experimental

General—M.p.s were determined on a Thomas–Hoover capillary melting point apparatus and are uncorrected. Spectral characterisation studies were carried out with the following instruments: ¹H NMR, Bruker AF–F300 spectrometer using CDCl₃ as the solvent and tetramethylsilane as an internal reference; mass spectrum, Micromass 7035E or 5988A GC/MS spectrometer under electron impact; UV, Hewlett Packard Model 8452A Diode-array spectrophotometer. Microanalyses were performed with a Perkin-Elmer CHN instrument whilst sulfur contents were determined by the oxygen flask method.

Ultraviolet Photoelectron Spectroscopy (UPS).—The He I and He II UPS were recorded on a UPG-200 Leybold-Heraeus spectrometer using Ar^+ $^2P_{3/2}$ and $^2P_{1/2}$ calibration lines and achieving a resolution of 30–35 meV. The individual sample inlet temperatures varied in the range 30–200 °C. The ionisation energies (E_i) quoted in Figs. 1–4 and Table 1 refer to adiabatic
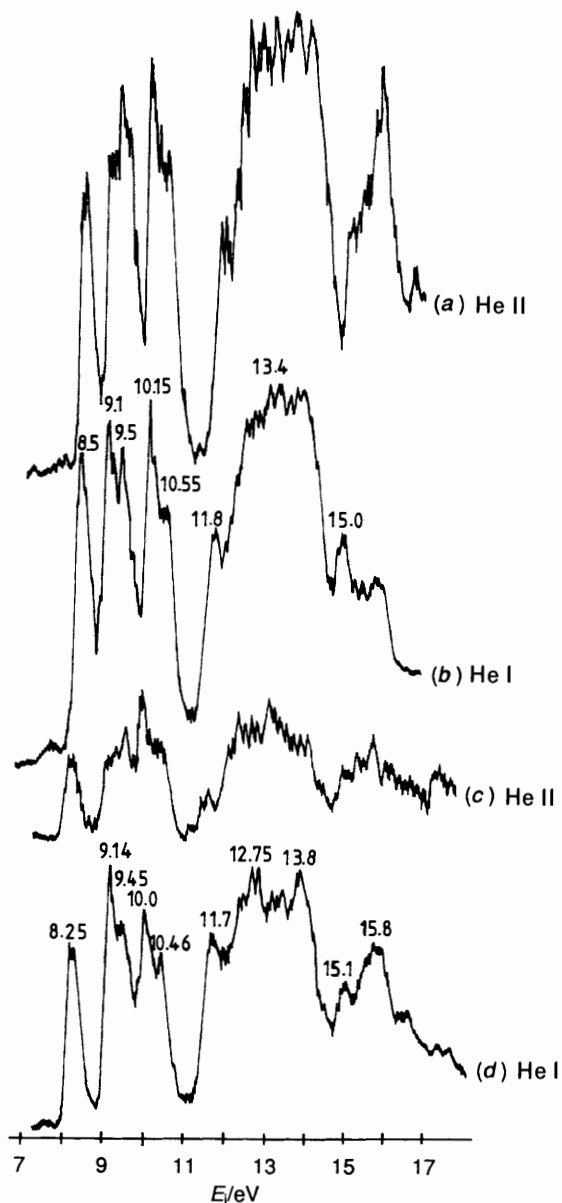

Fig. 1 He II and He I photoelectron spectra of thienylpyridines; (*a*), (*b*) 23TP; (*c*),(*d*) 22TP

or vertical energies whichever could be measured more accurately. Band overlap made in some cases accurate
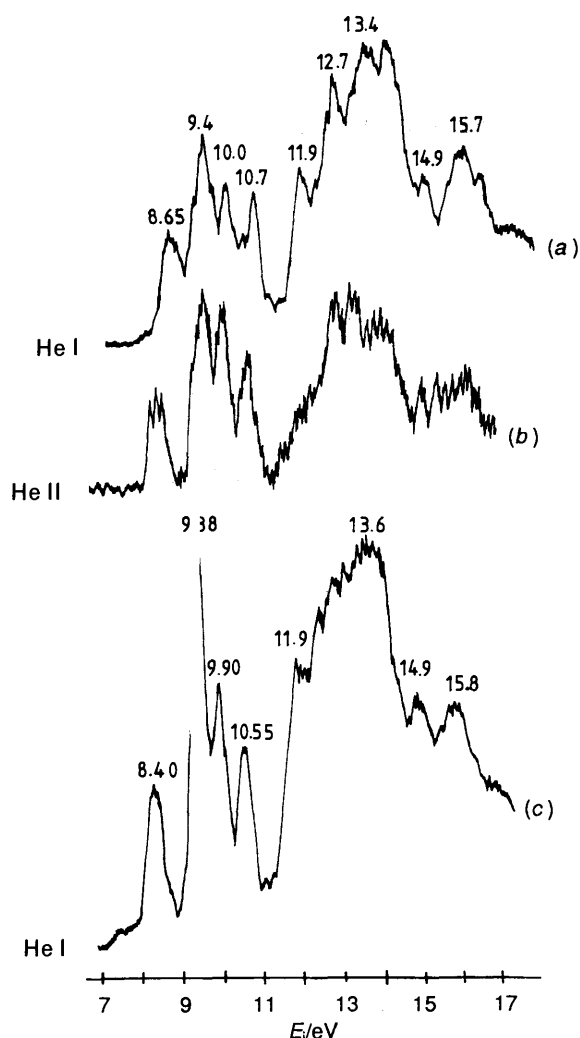
Fig. 2 He II and He I photoelectron spectra of thienylpyridines; (a) 33TP; (b),(c) 32TP
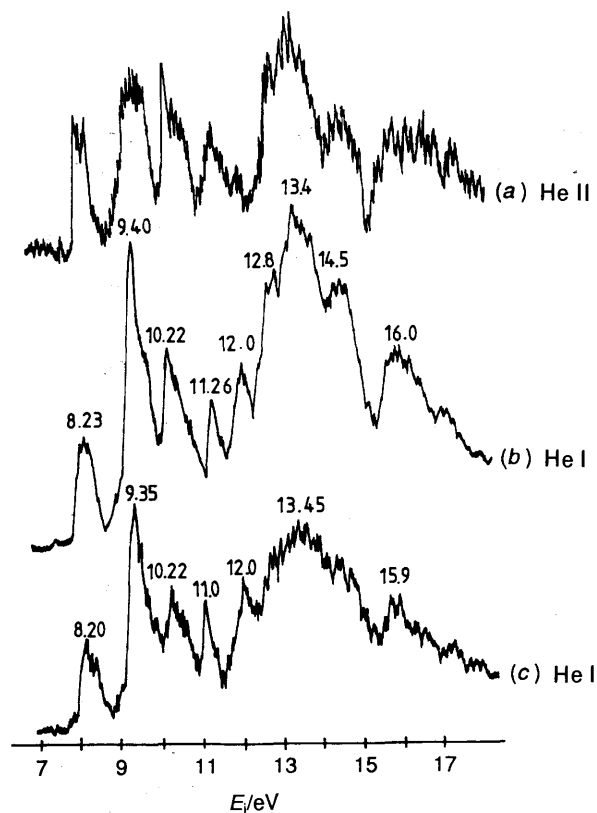

Fig. 3 He II and He I photoelectron spectra of thienylethynylpyridines; (a),(b) 23TPE; (c) 22TPE
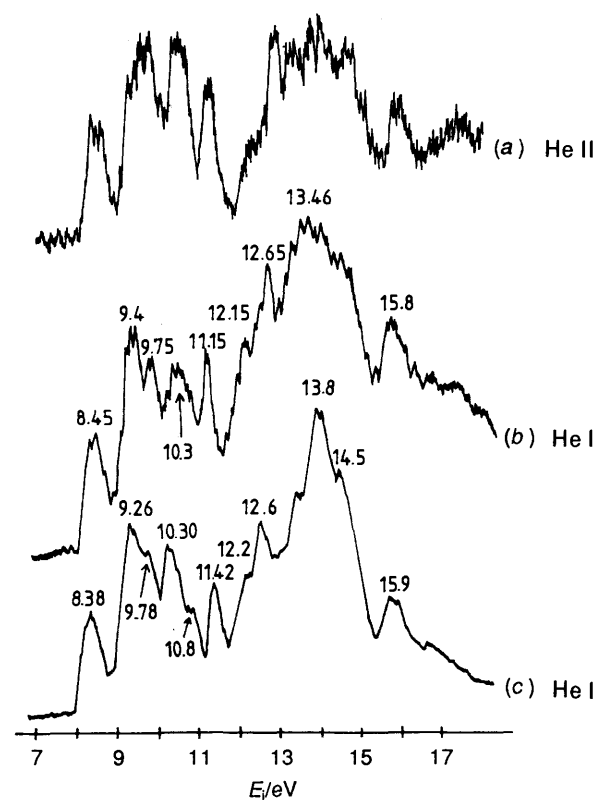
Fig. 4 He II and He I photoelectron spectra of thienylethynylpyridines; (a),(b) 32TPE; (c) 33TPE

measurement of adiabatic E_i preferable to an unreliable estimate of vertical E_is. He II spectra could not be measured for some compounds due to low or unstable vapour pressures.

Theoretical Calculations.—MO eigenvalues and eigenvectors were calculated at the semiempirical level (AM1 and PM3 Hamiltonians) with MOPAC 6.0 package[6] running on Silicon Graphics Iris platform. Experimental bond lengths for thiophene, pyridine and ethyne moieties were used initially after which all geometries were fully optimised.

Syntheses of Compounds.—The isomeric thienylpyridines: 2-(2'-thienyl)pyridine (22TP), 3-(2'-thienyl)pyridine (32TP), 2-(3'-thienyl)pyridine (23TP) and 3-(3'-thienyl)pyridine (33TP) were prepared by regioselective cross-coupling reactions of thienylmagnesium bromides with the respective bromopyridines in the presence of catalytic amounts of NiCl₂·dppp (dppp = bis-1,3-diphenylphosphinopropane),[7] whilst the series of isomeric thienylethynylpyridines: 2-[2-(2-thienyl)ethynyl]-pyridine (22TPE), 3-[2-(2-thienyl)ethynyl]pyridine (23TPE), 2-[2-(3-thienyl)ethynyl]pyridine (32TPE) and 3-[2-(3-thienyl)-ethynyl]pyridine (33TPE) were synthesised by the procedure of Rossi *et al.*[8] Of these, the compounds 23TPE, 32TPE and 33TPE are novel.

Isomeric Thienylpyridines.—*General procedures.* (a) 2-Bromothiophene (8.6 g, 53 mmol) was introduced dropwise to a

mixture of magnesium turnings (1.55 g, 63 mmol) in dried diethyl ether (50 cm³) under nitrogen at such a rate as to maintain gentle reflux. On completion of addition, the mixture was heated under reflux for a further 1 h, allowed to cool and added to bromopyridine (7.0 g, 44 mmol), NiCl₂dppp (0.12 g,

Table 1 Ionisation energies (E_i), AM1 MO assignments, *anti* $\Rightarrow$ *syn* interring torsional barrier (ΔE) and HOMO-LUMO gaps (E_g) in thienylpyridines and thienylethynylpyridines[a]

Comp.	E_i/eV	MO	ΔE/kJ mol^{-1}	E_g/eV
22TP	8.25	$\pi_3 - \Pi_3$	9.79	4.13
	9.14, 9.45	π_2, n_N		
	10.0	$\pi_3 + \Pi_3$		
	10.46	Π_2		
	11.7	n_S		
32TP	8.50	$\pi_3 - \Pi_3$	8.03	4.36
	9.1	π_2		
	9.5	n_N		
	10.15	$\pi_3 + \Pi_3$		
	10.55	Π_2		
	11.8	n_S		
23TP	8.40	$\pi_3 - \Pi_3$	3.77	4.43
	9.38	π_2, n_N		
	9.90	$\pi_3 + \Pi_3$		
	10.55	Π_2		
	11.9	n_S		
33TP	8.65	$\pi_3 - \Pi_3$	6.49	4.84
	9.4	π_2, n_N		
	10.0	$\pi_3 + \Pi_3$		
	10.7	Π_2		
	11.9	n_S		
22TPE	8.20	$\pi_3 - (\pi''_{CC}) - \Pi_3$	2.0	3.90
	9.35	π_2, n_N		
	10.22	$\pi_3 + (\pi''_{CC}) + \Pi_3, \Pi_2$		
	11.0	π'_{CC}		
	12.0	n_S		
23TPE	8.23	$\pi_3 - (\pi''_{CC}) - \Pi_3$	0.96	3.87
	9.40	π_2, n_N		
	10.22	$\pi_3 + (\pi''_{CC}) + \Pi_3, \Pi_2$		
	11.26	π'_{CC}		
	12.0	n_S		
33TPE	8.38	$\pi_3 - (\pi''_{CC}) - \Pi_3$	1.09	4.05
	9.26, 9.78	π_2, n_N		
	10.30, 10.8	$\pi_3 + (\pi''_{CC}) + \Pi_3, \Pi_2$		
	11.42	π'_{CC}		
	12.2	n_S		
	12.6	π''_{CC}		
32TPE	8.45	$\pi_3 - (\pi''_{CC}) - \Pi_3$	1.63	4.10
	9.4	π_2		
	9.75	$n_{N'}$		
	10.3	$\pi_3 + (\pi''_{CC}) + \Pi_3, \Pi_2$		
	11.15	π'_{CC}		
	12.15	n_S		
	12.65	π''_{CC}		

[a] Descriptions in MO column represent LCBO of thiophene (π_3 π_2), ethyne (π'_{CC}, π''_{CC}) and pyridine (Π_3 Π_2) localised π-MOs or heteroatom lone pairs (n_N, n_S).

0.22 mmol) in diethyl ether (80 cm^3). The dark mixture was stirred at ambient temperature (25 °C) for 3 days and saturated ammonium chloride (30 cm^3) was added. The organic phase was separated and dried (MgSO$_4$), and solvent evaporated *in vacuo* to afford a crude product which was purified by vacuum distillation/sublimation.

22TP: (4.89 g, 69%), m.p. 63–64 °C (lit.,[9] 64 °C) (Found: C, 67.0; H, 4.5; N, 8.65%; M$^+$, 161. C$_9$H$_7$NS requires: C, 67.05; H, 4.4; N, 8.7%; M, 161); λ_{max}(hexane)/nm 262 (ε/dm^3 mol^{-1} cm^{-1} 8 800) and 300 (15 800); δ_H(300 MHz; CDCl$_3$), 7.10–7.16 (2 H, m, 3'-H and 4'-H), 7.39 (1 H, dd, $J_{3',5'}$ 1 and $J_{4',5'}$ 5, 5'-H), 7.58 (1 H, dd, $J_{3,5}$ 1 and $J_{3,4}$ 4, 3-H), 7.64–7.71 (2 H, m, 4-H and 5-H) and 8.57 (1 H, dd, $J_{4,6}$ 1 and $J_{5,6}$ 5, 6-H).

32TP: (5.03 g, 71%), bp 36 °C 0.01 mmHg (lit.,[7] 95 °C 1 mmHg) (Found: C, 66.9: H, 4.4; N, 8.8%; M$^+$, 161. C$_9$H$_7$NS requires: C, 67.05; H, 4.4; N, 8.7%; M, 161); λ_{max}(hexane)/nm 260 (ε/dm^3 mol^{-1} cm^{-1} 9 400) and 284 (13 000); δ_H(300 MHz; CDCl$_3$) 7.11–7.14 (1 H, m, 4'-H), 7.28–7.37 (3 H, m, 5-H, 3'-H

and 5'-H), 7.84–7.88 (1 H, m, 4-H), 8.52 (1 H, dd, $J_{4,6}$ 1.5 and $J_{5,6}$ 5, 6-H) and 8.88 (1 H, d, $J_{2,4}$ 2, 2-H).

(*b*) Butyllithium (40 mmol) was added to a stirred solution of bromothiophene (6.2 g, 38 mmol) in dried diethyl ether (40 cm^3) at -78 °C under a nitrogen atmosphere. After 30 min, MgBr$_2$·OEt$_2$ (42 mmol) in ethyl ether (50 cm^3) was added and the resulting mixture stirred for 30 min at ambient temperature (25 °C). The solution was added to a mixture of bromopyridine (32 mmol), NiCl$_2$·dppp (0.12 g, 0.22 mmol) in dried diethyl ether (30 cm^3) and stirring was allowed to continue at ambient temperature for 3 days whereupon saturated ammonium chloride (30 cm^3) was added. Subsequent work-up procedures then followed (*a*), as above.

23TP: b.p. 48 °C/0.01 mmHg (lit.,[10] 93–95 °C/0.45 mmHg) (Found: C, 66.5; H, 4.3; N, 8.3%; M$^+$, 161. C$_9$H$_7$NS requires: C, 67.05; H, 4.4; N, 8.7%; M, 161); λ_{max}(hexane)/nm 228 (ε/dm^3 mol^{-1} cm^{-1} 12 800), 256 (12 600) and 280 (9 200, shoulder); δ_H(300 MHz; CDCl$_3$) 7.14–7.19 (1 H, m, 5-H), 7.39 (1 H, dd, $J_{2',5'}$ 3 and $J_{4',5'}$ 5, 5'-H), 7.60–7.73 (3 H, m, 3-H, 4-H and 4'-H), 7.90 (1 H, dd, $J_{2',4'}$ 1 and $J_{2',5'}$ 3, 2'-H) and 8.60–8.63 (1 H, m, 6-H).

33TP: m.p. 71.0–72.5 °C (lit.,[11] 73–74 °C) (Found: C, 66.7; H, 4.4; N, 8.4%; M$^+$, 161. C$_9$H$_7$NS requires: C, 67.05; H, 4.4; N, 8.7%; M, 161); λ_{max}(hexane)/nm 224 (ε/dm^3 mol^{-1} cm^{-1} 15 700) and 256 (15 600); δ_H(300 MHz; CDCl$_3$) 7.30–7.47 (3 H, m, 5-H, 4'-H and 5'-H), 7.53 (1 H, dd, $J_{3',5'}$ 1 and $J_{3',4'}$ 3, 3'-H), 7.85–7.89 (1 H, m, 4-H), 8.53 (1 H, dd, $J_{5,6}$ 1.5 and $J_{4,6}$ 5, 6-H) and 8.88 (1 H, d, $J_{2,6}$ 2, 2-H).

Isomeric Thienylethynylpyridines.—General procedure. Nitrogen-deaerated aqueous NaOH (5.5 mol dm^{-3}; 30 cm^3) was added to a stirred mixture containing 2-methylbut-3-yn-2-ol (3.53 g, 42 mmol), bromothiophene (6.85 g, 42 mmol), benzyltriethylammonium chloride (0.28 g, 1.3 mmol), copper(I) iodide (0.38 g, 1.9 mmol) and Pd(Ph$_3$P)$_4$ (1.1 g, 0.94 mmol); the progress of reaction was monitored by TLC. When the first coupling stage was completed, bromopyridine (6.7 g, 42 mmol) in benzene (10 cm^3) was added and the mixture heated under reflux for 4 days. Saturated NH$_4$Cl (100 cm^3) was added and the mixture extracted with diethyl ether. The organic phase was separated and dried (MgSO$_4$), and solvent evaporated off *in vacuo* to afford a crude product which was purified by flash chromatography using chloroform–hexane mixtures as the eluent and thereafter by vacuum distillation/sublimation.

22TPE: m.p. 52–54 °C (lit.,[8] 50–54 °C) (Found: C, 71.6; H, 3.8; N, 7.4%; M$^+$, 185. C$_{11}$H$_7$NS requires: C, 71.3; H, 3.8; N, 7.6%; M, 185); λ_{max}(hexane)/nm 284 (ε/dm^3 mol^{-1} cm^{-1} 13 100), 304 (21 600), 310 (20 000) and 318 (19 500); δ_H(300 MHz; CDCl$_3$) 7.03 (1 H, dd, $J_{3',4'}$ 4 and $J_{4',5'}$ 5, 4'-H), 7.21–7.26 (1 H, m, 5-H), 7.35 (1 H, dd, $J_{3',5'}$ 1 and $J_{4',5'}$ 5, 5'-H), 7.39 (1 H, dd, $J_{3',4'}$ 4 and $J_{3',5'}$ 4, 3'-H), 7.49–7.52 (1 H, m, 3-H), 7.65–7.71 (1 H, m, 4-H) and 8.62 (1 H, d, $J_{5,6}$ 5, 6-H).

23TPE: m.p. 41.0–41.5 °C (Found: 71.3; H, 3.8; N, 7.4%; M$^+$, 185. C$_{11}$H$_7$NS requires: C, 71.3; H, 3.8; N, 7.6%; M 185); λ_{max}(hexane)/nm 286 (ε/dm^3 mol^{-1} cm^{-1} 15 000), 302 (19 100), 308 (16 500) and 320 (16 300); δ_H(300 MHz; CDCl$_3$) 7.04 (1 H, dd, $J_{3',4'}$ 4 and $J_{4',5'}$ 5, 4'-H), 7.28–7.34 (3 H, m, 5-H, 3'-H and 5'-H), 7.77–7.81 (1 H, m, 4-H), 8.55 (1 H, dd, $J_{4,6}$ 1.5 and $J_{5,6}$ 5, 6-H) and 8.75 (1 H, d, $J_{2,4}$ 1.6, 2-H).

32TPE: m.p. 56–58 °C (Found: C, 71.2; H, 3.7; N, 7.55%; M$^+$, 185. C$_{11}$H$_7$NS requires: C, 71.3; H, 3.8; N, 7.6%; M, 185); λ_{max}(hexane)/nm 200, 230, 288, 296 and 304; δ_H(300 MHz, CDCl$_3$) 7.21–7.26 (2 H, m, 4'-H and 5-H), 7.31 (1 H, dd, 5'-H), 7.48–7.52 (1 H, m, 3-H), 7.64 (1 H, dd, $J_{2',4'}$ 1 and $J_{2',5'}$ 3, 2'-H), 7.67–7.71 (1 H, m, 4-H) and 8.61 (1 H, dd, $J_{4,6}$ 1.5 and $J_{5,6}$ 4.5, 6-H).

33TPE: m.p. 63.5–64 °C (Found: C, 71.2; H, 3.7; N, 7.6%, M$^+$, 185. C$_{11}$H$_7$NS requires: C, 71.3; H, 3.8; N, 7.6%; M, 185); λ_{max}(hexane)/nm 282 (ε/dm^3 mol^{-1} cm^{-1} 21 700), 292 (18 100)
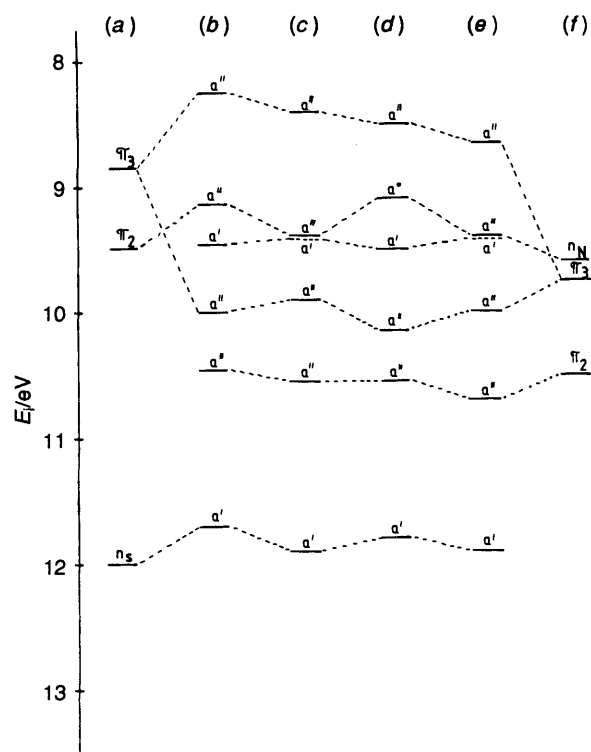
Fig. 5 Correlation energy level diagram of thienylpyridines (T = thiophene, P = pyridine); (a) T; (b) 22TP; (c) 32TP; (d) 23TP; (e) 33TP and (f) P

and 302 (18 400); δ_H(300 MHz; $CDCl_3$) 7.21 (1 H, dd, $J_{2',4'}$ 1 and $J_{4',5'}$ 5, 4'-H), 7.27–7.34 (2 H, m, 5-H and 5'-H), 7.57 (1 H, dd, $J_{2',4'}$ 1 and $J_{2',5'}$ 3, 2'-H), 7.77–7.81 (1 H, m, 4-H), 8.54 (1 H, dd, $J_{4,6}$ 2 and $J_{5,6}$ 5, 6-H) and 8.75 (1 H, d, J 1, 2-H).

Results and Discussion

The electronic structure of isomeric thienylpyridines has been studied previously by Knop et al.[12] using EHMO, CNDO/2 and PPP-SCF MO methods. They put forward two important predictions: (i) the most stable molecular conformations are nonplanar with torsional angles of around 30 and 150° (planar syn conformation being assigned 0°). The molecular geometries of the two conformations were calculated to be very similar. (ii) the increase in the number of carbon atoms with three nearest C-neighbours leads to the increased singlet–singlet π–π* transition energy.

Both predictions are confirmed by our results (Table 1). Thus 22TP (with no C3-neighbours) has the longest λ and 33TP (with 2 C3-neighbours) the shortest λ in the UV spectra. Our calculated torsional barriers (Table 1) are slightly different from the values obtained by Knop et al., but that can be expected in view of different parametrisation employed by different semiempirical methods. AM1 results predict syn–anti conformer energy differences in the range 0–3.6 kJmol⁻¹, with torsional angles of 0–25° and 155–180° for syn and anti conformers, respectively. The largest syn–anti energy difference was calculated for 22TP (9.8 kJ mol⁻¹), possibly reflecting the additional H-bonding stabilisation in the anti conformer. The prevalent conformation would be determined by an interplay of electronic (π-conjugation) and steric effects (H–H repulsions).

The general conclusion is that, the torsional barrier being small, a mixture of conformers can be expected to exist in the gas phase leading to possible band broadening. In further discussion we shall assume the molecules to be planar (C_s symmetry) which, due to small torsional barriers, should not affect the validity of our arguments.
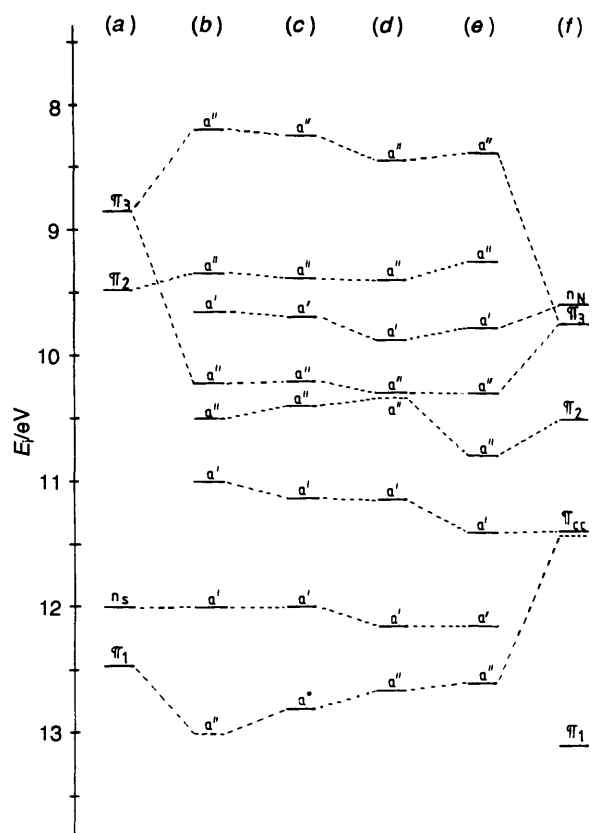

Fig. 6 Correlation energy level diagram of thienylethynylpyridines (T = thiophene, P + E = pyridine and ethyne fragments); (a) T; (b); 22TPE; (c) 23TPE; (d) 32TPE; (e) 33TPE and (f) P + E

Assignment of UPS spectra based on empirical arguments is given in Table 1 and Figs. 5 and 6. It can be reached by comparison with the UPS of thiophene,[13] pyridine[14] and ethyne. Consideration of spectral bandwidths (the narrower the band the more localised the MO being ionized) also supports the assignment in specific cases. He II/He I intensity variations are invaluable in assigning the thiophene localised π_2 ionisation which has considerable S 3p character. Using an atomic photoionisation cross-section as a guide[15] it appears that C 2p, N 2p and S 3p cross-sections are reduced to 31, 45 and 14%, respectively on going from He I to He II excitation. The most pronounced fall in band intensity, invariably occurs in band Ã (Figs. 1–4) which can be expected for ionisation from orbital with large S 3p character (π_2).

The X̃ and C̃ bands arise from MOs described as linear combinations (out-of-phase and in-phase) of bonding orbitals (LCBO) which are π orbitals located in pyridine, thiophene and ethyne moieties. X̃ bands are generally broad which supports their LCBO designation. A slight ambiguity arises in the assignment of Ẽ–G̃ bands with $E_i \geq 11$ eV. The correlation diagram (Fig. 6) suggests two plausible assignments: π''_{CC}(a') < n_S(a') < π''_{CC}(a'') or π''_{CC}(a') < π''_{CC}(a'') < n_S(a') for Ẽ, F̃ and G̃ bands, respectively. (n_S ⊏> sulfur lone pair, π''_{CC}, π''_{CC} ⊏> ethyne π orbitals parallel and perpendicular to the molecular plane, respectively). Semi-empirical MO calculations are unreliable for such closely spaced levels, and we prefer to use observed He II/He I intensity variations for the assignment. F̃ band intensity shows significant decrease in He II spectra and is hence assigned to the sulfur lone pair n_S(a') ionisation.

The most interesting aspect of the electronic structure of the title compounds concerns the extent of electron delocalisation (interaction) between thiophene, pyridine and ethyne moieties. In order to estimate such interactions in thienylpyridines, let us consider $8 < E_i < 11$ eV spectral region where altogether five

ionizations are found. The width of the region i.e. the difference between bands $\tilde{X}$ and $\tilde{C}$, can be taken as a measure of inter-ring π interactions. Data from Fig. 5 suggests that the largest interaction is present in 22TP and the smallest in 33TP. This conclusion is in keeping with the well established sensitivity of thiophene 2-substituent position as deduced previously by UPS.[16] Thienylethynylpyridines afford another indicator of inter-ring interactions, since a pair of ethyne bands (π_{CC}) can be distinguished in the UPS spectra. One member of the pair (π'_{CC}, a') has the wrong symmetry for π interactions (delocalisations) and may be expected to stay closer to its ethyne 11.4 eV value. The π'_{CC}–π''_{CC} splitting can then be taken as a good estimate of π-delocalisation. Fig. 6 indicates that splitting (and consequently π-interaction) is smallest in 33TPE and largest in 22TPE.

It is interesting to compare the π'_{CC}–π''_{CC} splitting observed in this work with similar aromatic systems. The value of 0.71 eV calculated from the UPS of ethynylbenzene[17] is smaller than in most TPEs indicating a smaller degree of interaction between benzene and ethyne moieties. The π_{CC} bandwidths (Franck–Condon envelopes) in ethynylbenzene are smaller than in TPEs which also indicates smaller π-delocalisation in the former.

The semiempirical MO calculations (parametrised for molecular ground states) sometimes differ from our empirical analysis in the interpretation of $\tilde{B}$ and $\tilde{C}$ bands, but in view of the closeness of levels their prediction may be unreliable.

Relation to Polymer Properties.—Our results suggest that intramolecular charge transfer between π-excessive thiophene and π-deficient pyridine rings postulated earlier[3] is brought about by strong inter-ring conjugation. The inter-ring interactions in 22TP and 22TPE are comparable, which explains why optoelectronic properties (e.g. third-order nonlinear optical susceptibility) for the two compounds also have the same order of magnitude.[2,4] Polymeric materials based on ethynylbenzene oligomers will not be expected to show useful optoelectronic properties, since ethene–benzene π-interactions (and intramolecular charge-transfer) are small.

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