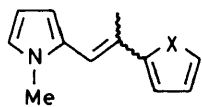


## Di-heteroarylethylenes: Synthesis and Donor Properties

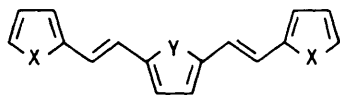
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The Wittig-Horner condensation of *N*-methylpyrrole-2-, and 2,5-dicarbaldehydes with diethyl heteroarylmethylphosphonates (heteroary = *N*-methylpyrrol-2-yl or 2-thienyl and the corresponding 2,5-diyl) leads to the (*E*)-1,2-diheteroarylethylenes (1) and (2), and the triheteroaryl derivatives respectively. A new entry into diethyl pyrrolylmethylphosphonates is described starting from the pyrrol-2-ylmethyltrimethylammonium iodide and the sodium salt of diethyl phosphite: the rate and the regiochemistry of the reaction is solvent dependent. The heteroarylethylenes (1)–(5) are electron-rich substrates affording charge transfer (c.t.) complexes with iodine and TCNQ (tetracyano-1,4-quinodimethane): the d.c. conductivities of the c.t. complexes are relatively low and fall in the range of semiconductors. I.r. frequencies of the CN stretching relative to the TCNQ moiety are used to evaluate the degree of charge transfer between the donor and the acceptor. It is believed that the radical cation of (5) arising by mono-electron transfer to TCNQ is the most stable charged species among the series considered.

Electron-rich heterocycles can be constituent partners of charge transfer (c.t.) complexes, potentially endowed with high electric conductivity.<sup>1</sup> One of the requirements they should fulfil is easy mono-electron transfer to stable carbenium ion radicals: this situation is usually met with non-aromatic systems (e.g. tetrathiofulvalene) which evolve to aromaticity in the charged species.<sup>2</sup> In principle, however, any  $\pi$ -excessive heteroaromatic compound could be a good candidate if sufficient opportunities are provided to the carbenium ion radical for being largely delocalized and thus stabilized. In view of our previous results<sup>3</sup> that showed that the pyrrole ring has a propensity to give c.t. complexes with iodine and in view of the fact that poly-*p*-phenylenevinylene<sup>4</sup> affords, with iodine, a conductive material, we decided to couple the ingredients of these two methods by focusing the investigation on ethylenic compounds substituted by heterocyclic units, especially pyrrole and thiophene, compounds designed to have chances of undergoing easy mono-electron transfer to delocalized carbenium ion radicals. Prototypes of such systems are compounds (1)–(5), the synthesis and c.t. complexes of which will be described herein.



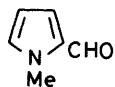
(1a) X = S, (*Z*)-isomer  
 (1b) X = S, (*E*)-isomer  
 (2) X = NMe



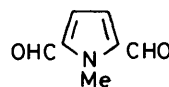
(3) X = S, Y = NMe  
 (4) X = NMe, Y = S  
 (5) X = Y = NMe

### Results and Discussion

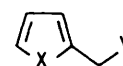
**Synthesis of Heteroarylethylenes.**—Preliminary experiments of the condensation of *N*-methylpyrrole-2-carbaldehyde (6) with 2-thienylmethyltriphenylphosphonium chloride according to Wittig conditions afforded only mixtures of the (*Z*)- and (*E*)-1,2-diheteroarylethylene (1). This finding was subsequently confirmed by others.<sup>5</sup> We decided not to investigate the (*Z*)-isomers because we suspected that their geometrical arrangements would be detrimental for the coplanarity of the systems we required. In order to obtain only the (*E*)-isomer we reverted to the Horner reaction. Indeed the condensation of the *N*-methylpyrrole-2-carbaldehyde (6) with the diethyl 2-thienyl-



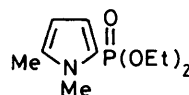
(6)



(7)



(8) X = S, Y = PO(OEt)<sub>2</sub>  
 (9) X = NH, Y = NMe<sub>3</sub><sup>+</sup>I<sup>-</sup>  
 (10) X = NMe, Y = NMe<sub>3</sub><sup>+</sup>I<sup>-</sup>  
 (11) X = NH, Y = PO(OEt)<sub>2</sub>  
 (12) X = NMe, Y = PO(OEt)<sub>2</sub>



(13)



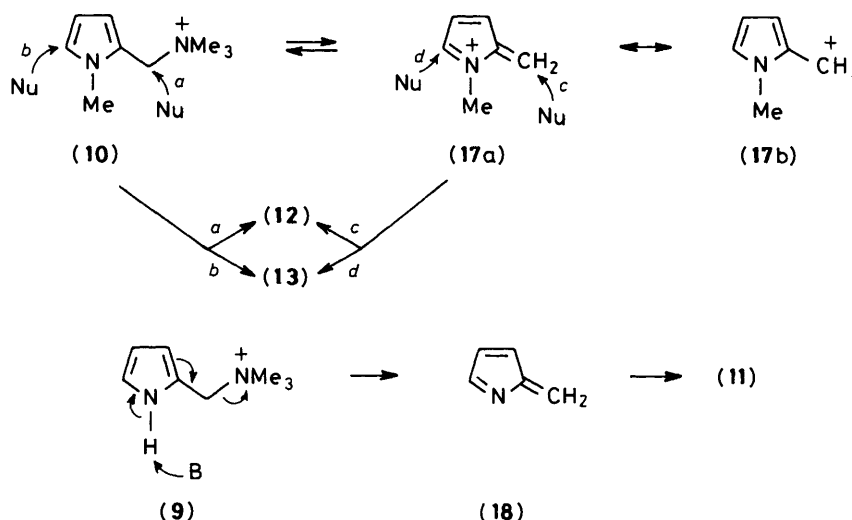
(14) X = S, Y = PO(OEt)<sub>2</sub>  
 (15) X = NMe, Y = NMe<sub>3</sub><sup>+</sup>I<sup>-</sup>  
 (16) X = NMe, Y = PO(OEt)<sub>2</sub>

methylphosphonate (8) in tetrahydrofuran (THF) afforded the pure (*E*)-isomer (1b) in good yield, a configuration confirmed both by the size of the coupling constant of the two olefinic protons and by the presence of a strong band in the i.r. spectrum at ca. 930 cm<sup>-1</sup>, attributable to the out-of-plane CH deformation of an (*E*)-disubstituted ethylene. Analogous condensation of *N*-methylpyrrole-2,5-dicarbaldehyde (7) with diethyl 2-thienylmethylphosphonate (8) gave the triheteroaryl derivative (3). Conversely compound (4) was obtained on condensing the *N*-methylpyrrole-2-carbaldehyde (6) with tetraethyl thiophene-2,5-diylbismethylphosphonate (14), in turn obtained by the action of triethyl phosphite on the known 2,5-bis(chloromethyl)thiophene. For compounds (3) and (4), both the i.r. absorption in the region of 900 cm<sup>-1</sup>, and the olefinic coupling constants are conclusive evidence for the (*E*)-isomer. The synthesis of the pyrrol-2-ylethylenes (2) and (5) by the same Horner procedure required the preparation of diethyl pyrrol-2-ylmethylphosphonate (12)\* and the bis-analogue (16). These compounds

\* Simultaneously with the submission of this work for publication, Jones independently published a paper<sup>6</sup> concerning the preparation both of the phosphonate (12) and the products described herein as compounds (1b) and (2).

Table 1. Physical, i.r., and analytical data for the ethylenes (1)–(5)

Compound	Yield	M.p. (°C)	Solvent	$\nu_{\max}$ . CH out-of-plane deformation ( $\text{cm}^{-1}$ )	Found (%) (required)		
					C	H	N
(1b) ( $\text{C}_{11}\text{H}_{11}\text{NS}$ )	75	65	Sublimed at 55 °C at 0.5 mmHg	935	70.0 (69.8)	5.85 (5.8)	7.2 (7.4)
(2) ( $\text{C}_{12}\text{H}_{14}\text{N}_2$ )	55	146–147	EtOH	935	77.1 (77.4)	7.6 (7.5)	15.0 (14.9)
(3) ( $\text{C}_{17}\text{H}_{15}\text{NS}_2$ )	60	175	AcOEt	925	68.1 (68.7)	5.1 (5.05)	4.6 (4.7)
(4) ( $\text{C}_{18}\text{H}_{18}\text{N}_2\text{S}$ )	66	115	EtOH	930	73.55 (73.5)	6.2 (6.1)	9.4 (9.5)
(5) ( $\text{C}_{19}\text{H}_{21}\text{N}_3$ )	40	185–186	EtOH	935	77.9 (78.3)	7.2 (7.3)	14.2 (14.4)



could not be obtained by the Arbuzov reaction because the 2-chloro- and the 2,5-bischloromethylpyrroles are unknown, presumably because they are too unstable. Thus compounds (12) and (16) were successfully prepared by treating the anion of diethyl phosphite with the methoiodide of the corresponding Mannich bases (9) or (10), and (15), respectively. Indeed, the *N*-methyl methylphosphonate (12) was cleanly prepared by exclusive *N*-methylation of the methylphosphonate (11), in turn obtained from the Mannich base methoiodide (9) and the anion of diethyl phosphite. This last reaction turned out to be somewhat sluggish; although it appears that the reaction is considerably faster when DMF is used as a solvent instead of THF, the isolation of the pure product under these last conditions is more laborious. The commercial availability of *N*-methylpyrrole allowed the preparation of the *N*-methyl methylphosphonate (12) via the *N*-methyl methoiodide of the Mannich base (10). The reaction of compound (10) with the anion of diethyl phosphite is also sluggish in THF and can be speeded up by the use of DMF as a solvent. Under these conditions, however, the reaction did not afford exclusively the *N*-methyl methylphosphonate (12) but also gave another product which proved to be difficult to separate [from (12)] and to isolate in a pure state either by distillation or chromatography. The  $^1\text{H}$  n.m.r. analysis of the crude and distilled reaction mixture, accomplished by subtracting the known peaks due to the *N*-methyl methylphosphonate (12) provides unambiguous evidence that the second product is the phosphonate (13), isomeric with (12). As in the case of the

reaction of cyanide ion with the methoiodide (10),<sup>7</sup> it seems logical to admit that the *cis*-substitution product (13) originates either from an  $\text{S}_{\text{N}}2'$  process on (10) (path *b*) or alternatively from the intermediate (17), in turn formed by an  $\text{E}_1$  elimination mechanism: it is apparent that the mechanism of substitution is sensitive to the nature of the solvent. It is not clear on which grounds the  $\text{S}_{\text{N}}2'$  process (path *b*) would be competitive with the path *a* in DMF but not in THF. It seems logical to suggest that the high dielectric constant of DMF promotes an alternative fate of (10), namely the  $\text{E}_1$  elimination of trimethylamine to form the carbenium ion (17); this intermediate, certainly better solvated by DMF than by THF, would subsequently produce both (12) and (13) via paths *c* and *d* respectively. The fact that the methoiodide (9), in contrast with the methoiodide (10), does not produce any isomeric phosphonate upon treatment with the anion of diethyl phosphite, suggests that the basic conditions used in the reaction may favour first the deprotonation at nitrogen, followed by elimination to the methylene base (18), upon which the reaction of the nucleophile at the methylene site would give exclusively the phosphonate (11). Finally, no isomeric products arise from the action of the anion of diethyl phosphite on the bis-methoiodide (15).

To accomplish the condensation of the *N*-methyl methylphosphonate (12) or of the bis-methylphosphonate (16) with pyrrole aldehydes (6) and (7) in reasonable yields, a considerable excess of both the phosphonates and the base had to be used: it appears that the carbanions of the pyrrolyl-

**Table 2.** <sup>1</sup>H N.m.r. data for compounds (1)–(5) in Me<sub>2</sub>SO

Compd.	Thiophene protons <sup>a</sup>			Pyrrole protons <sup>a</sup>			Olefinic protons <sup>b</sup> [J (Hz)]		NMe
	3 <sup>c</sup>	4 <sup>d</sup>	5 <sup>e</sup>	3 <sup>f</sup>	4 <sup>g</sup>	5 <sup>h</sup>	1	2	
(1a)	7.18dd	7.06dd	7.40dd	6.35dd	6.06dd	6.84dd	6.35 <sup>i</sup>	6.70	3.47s
(1b)	7.15dd	7.05dd	7.38dd	6.47dd	6.05dd	6.78dd	$J_{12}$ 12.1 6.83 <sup>i</sup>	7.09	3.67s
(2)				6.39dd	5.98dd	6.71dd	$J_{12}$ 16.25 6.75s		3.65s
(3)	7.18dd	7.06dd	7.42dd		6.61s		6.9 <sup>i</sup>	7.17	3.65s
(4)		6.99s		6.46dd	6.04dd	6.79dd	$J_{12}$ 16.25 6.77 <sup>i</sup>	7.0	3.68s
(5)				6.44dd <sup>j</sup>	6.01dd <sup>j</sup>	6.72dd <sup>j</sup>	$J_{12}$ 16.25 6.8s		3.62
					6.51s <sup>k</sup>				

<sup>a</sup> Protons are numbered within each single heterocycle and not according to the numbering of the whole molecule. <sup>b</sup> For compounds (1), (3), and (4) the present arbitrary numbering assigns number 1 to olefinic protons bonded to the carbon at position  $\alpha$  of the pyrrole ring and number 2 to protons bonded to the carbon at position  $\alpha$  of the thiophene ring. <sup>c</sup>  $J_{34}$  3 Hz. <sup>d</sup>  $J_{45}$  5.4 Hz. <sup>e</sup>  $J_{35}$  1.2 Hz. <sup>f</sup>  $J_{34}$  3.63 Hz. <sup>g</sup>  $J_{45}$  2.7 Hz. <sup>h</sup>  $J_{35}$  1.85 Hz. <sup>i</sup> AB System. <sup>j</sup> Values referred to the outer pyrrole rings. <sup>k</sup> Values referred to the 3-H,4-H protons of the internal pyrrole ring.

**Table 3.** Conductivity, analytical, and i.r. data of charge transfer complexes obtained from compounds (1)–(5)

Compound	Dopant	Solvent	$\sigma_{298}/S\text{ cm}^{-1}$	Formula	Found (%) (required)				$\nu_{\text{CN}}$
					C	H	N	I	
(1b)	I <sub>2</sub>		$1.05 \times 10^{-9}$	(C <sub>11</sub> H <sub>11</sub> NS)I	41.6 (41.7)	3.4 (3.5)	4.2 (4.4)		
(2)	I <sub>2</sub>		$8.86 \times 10^{-9}$	(C <sub>12</sub> H <sub>4</sub> N <sub>2</sub> )I <sub>3.1</sub>	24.8 (24.9)	2.4 (2.4)	4.8 (4.8)	68.2 (68.4)	
(3)	TCNQ	THF	$3.55 \times 10^{-6}$	(C <sub>17</sub> H <sub>15</sub> NS <sub>2</sub> )(C <sub>12</sub> H <sub>4</sub> N <sub>4</sub> )	69.7 (69.4)	3.8 (3.8)	13.9 (14.0)		2 203
(3)	I <sub>2</sub>		$5.7 \times 10^{-5}$	(C <sub>17</sub> H <sub>15</sub> NS <sub>2</sub> )I <sub>2.5</sub>	33.6 (33.2)	2.5 (2.4)	2.2 (2.3)		
(4)	TCNQ	THF	$2.6 \times 10^{-9}$	(C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> S)(C <sub>12</sub> H <sub>4</sub> N <sub>4</sub> )	71.9 (72.3)	4.4 (4.45)	16.4 (16.85)		2 214
(4)	I <sub>2</sub>		$6 \times 10^{-6}$	(C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> S)I <sub>2</sub>	39.1 (39.4)	3.3 (3.3)	4.9 (5.1)		
(5)	TCNQ	CH <sub>3</sub> CN	$1.08 \times 10^{-4}$	(C <sub>19</sub> H <sub>21</sub> N <sub>3</sub> )(C <sub>12</sub> H <sub>4</sub> N <sub>4</sub> )	75.35 (75.15)	4.9 (5.05)	19.6 (19.8)		2 186
(5)	I <sub>2</sub>		$7.9 \times 10^{-7}$	(C <sub>19</sub> H <sub>21</sub> N <sub>3</sub> )I <sub>4</sub>	28.1 (28.6)	2.5 (2.65)	5.1 (5.3)	63.2 (63.5)	

methylphosphonates are formed sluggishly and are somewhat unstable.

**Charge Transfer Complexes.**—Compounds (1)–(5) react with iodine vapour to give black, powdery, c.t. complexes whose analytical and electrical properties are reported in Table 3. [The stoichiometry of the iodine dopant is widely variable ranging from 1 for compound (1) to 4 for compound (5)]. Compounds (3)–(5) show a distinctive increase in conductivity upon doping and afford c.t. complexes in the range of semiconductors. Even more interestingly, compounds (3)–(5) give black insoluble c.t. complexes with TCNQ. Analytical, conductivity, and i.r. data relative to the CN stretching frequency of the TCNQ moiety are reported in Table 3. It has been suggested<sup>8</sup> that in c.t. complexes in which TCNQ acts as the electron-acceptor, the frequency of the CN group in TCNQ is linearly related to the degree of charge transfer from the donor. If such a diagnostic tool is applied to the TCNQ complexes of compounds (3)–(5), the c.t. complex formed by (5) should be 100% ionic with total charge transfer, the complex formed by (4) would be ca. 50% ionic, while the complex of (3) should be practically neutral. Results show that the conductivity of the c.t.

complexes increases on decreasing the  $\nu_{\text{CN}}$ , i.e. on increasing the degree of charge transfer, reaching a maximum in the complex of (5) with TCNQ, the conductivity of which is of the same order of magnitude as that shown by alkaline salts of the TCNQ radical anion. According to a recent proposal,<sup>9</sup> highly conductive c.t. complexes, in order to satisfy their mixed valence structure, must occur in a narrow range of  $\Delta E_{\text{redox}}$  values (difference of oxidation potential of the donor and reduction potential of the acceptor); this lies between the ionic Mott insulators and the neutral insulators. Although from the  $\Delta E_{\text{redox}}$  criterion the complex formed by compound (5) with TCNQ should lie in the mixed valence region,<sup>9b</sup> it appears to behave as a Mott insulator in which the donor is present exclusively as a radical cation. The nature of radical ion species for all the c.t. complexes described is supported by the presence of an intense peak in the e.p.r. spectra of the compounds. In the case of the c.t. complex of compound (5) with TCNQ, the signal has a peak-to-peak linewidth of ca. 5 G and lacks fine structure, suggesting an odd electron delocalized over a very large frame of atoms. Further studies will investigate whether compound (5) or structurally varied analogues undergoes electrochemical oxidation simultaneous with crystal deposition of radical cationic salts at the anode (electrocrystallization).

### Experimental

<sup>1</sup>H N.m.r. spectra were recorded on VARIAN XL-200 and XL-300 instruments, operating at 200 MHz and 300 MHz respectively. I.r. spectra of the heteroarylethylenes were recorded on a Perkin-Elmer Model 298 instrument, while the i.r. spectra of the c.t. complexes were obtained using a Perkin-Elmer Model 1700-FTIR instrument.

**Materials.**—Pure and anhydrous tetrahydrofuran (THF) was obtained by long reflux and final distillation under nitrogen over sodium diphenylketyl. Drying of the solvents was performed over Na<sub>2</sub>SO<sub>4</sub>. Thiophene-2-carbaldehyde (Fluka) and *N*-methylpyrrole (Fluka) were commercial products. *N*-Methylpyrrole-2-carbaldehyde,<sup>10</sup> *N*-methylpyrrole-2,5-dicarbaldehyde,<sup>11</sup> diethyl 2-thienylmethylphosphonate,<sup>12</sup> and tetraethyl thiophene-2,5-diylbismethylphosphonate<sup>13</sup> were prepared according to known procedures.

**Diethyl Pyrrol-2-ylmethylphosphonate (11).**—A suspension of sodium hydride in oil (55% by weight; 6.29 g corresponding to 3.46 g, 0.144 mol) was thoroughly washed with anhydrous THF, and finally suspended in THF (100 ml). To this stirred suspension maintained at -10—-20 °C, under nitrogen, a solution of diethyl phosphite (19.92 g, 0.144 mol) in THF (20 ml) was slowly added; when hydrogen evolution had ceased, pyrrol-2-ylmethyltrimethylammonium iodide<sup>14</sup> (12 g, 0.045 mol) was added portionwise. The mixture was refluxed for 16—18 h until the evolution of trimethylamine ceased. After being cooled, the mixture was poured onto ice (100 g), extracted with ether (3 × 200 ml), and the extracts were dried and evaporated under reduced pressure to give the crude product (9 g, 91%) as an oil, b.p. 125 °C/0.05 mmHg (Found: C, 49.5; H, 7.3; N, 6.2. C<sub>9</sub>H<sub>15</sub>NO<sub>3</sub>P requires C, 49.8; H, 7.4; N, 6.25%); δ<sub>H</sub> (90 MHz, CDCl<sub>3</sub>) 1.20 (6 H, m, Me), 3.25 [2 H, d, *J*(P—CH<sub>2</sub>) 18 Hz, CH<sub>2</sub>], 4.0 (4 H, m, OCH<sub>2</sub>CH<sub>3</sub>), 6.0 (2 H, m, pyrrole H<sub>β</sub>), 6.7 (1 H, m, pyrrole H<sub>α</sub>), 9.2 (1 H, s, NH).

**Diethyl *N*-Methylpyrrol-2-ylmethylphosphonate (12).**—A suspension of sodium hydride in oil (55% by weight; 0.827 g corresponding to 0.45 g, 19 mmol) was thoroughly washed with anhydrous THF, and finally suspended in it (30 ml). To this suspension maintained under nitrogen and magnetically stirred, diethyl pyrrol-2-methylphosphonate (11) (4.10 g, 19 mmol) in THF (10 ml) was slowly added. After the evolution of hydrogen had ceased, methyl iodide (2.68 g, 21 mmol) in THF (6 ml) was added and the mixture stirred for 15 h. Since the starting material was still present, a slurry of sodium hydride (50% in oil; 0.18 g, 3.8 mmol) in THF (5 ml) was added, followed by more methyl iodide (0.5 g, 3.5 mmol); the mixture was then heated at 50 °C for 3 h, cooled, poured onto ice, and extracted with diethyl ether (2 × 100 ml). The organic phase was washed with water, dried, and the solvent was evaporated off at reduced pressure to leave a residue which, upon distillation, gave the *title compound* (1.4 g, 32%), b.p. 110 °C at 0.1 mmHg (Found: C, 51.7; H, 7.7; N, 6.0. C<sub>10</sub>H<sub>18</sub>NO<sub>3</sub>P requires C, 51.95; H, 7.8; N, 6.1%); δ<sub>H</sub> (90 MHz, CDCl<sub>3</sub>) 1.3 (6 H, m, Me), 3.2 [2 H, d, *J*(P—C—H) 18 Hz], 3.8 (3 H, s, NMe), 4.05 (4 H, m, OCH<sub>2</sub>), 6.05 (2 H, m, pyrrole H<sub>β</sub>), and 6.55 (1 H, m, pyrrole H<sub>α</sub>).

**Reaction of *N*-Methylpyrrol-2-ylmethyltrimethylammonium Iodide with the Sodium Salt of Diethyl Phosphite: Formation of Diethyl *N*-methylpyrrol-2-ylmethylphosphonate (12) and Diethyl 1,5-Dimethylpyrrol-2-ylphosphonate (13).**—(A) **In THF.** A suspension of sodium hydride in oil (55% by weight; 1.67 g, corresponding to 0.92 g, 38 mmol) was thoroughly washed with THF and suspended in THF (50 ml). To this suspension maintained under nitrogen, cooled to -15—-20 °C, and magnetically stirred, a solution of diethyl phosphite (5.32 g, 38.5

mmol) was slowly added: once the evolution of hydrogen had ceased, the temperature was raised to room temp. and the methoiodide (10)<sup>7</sup> (3.27 g, 11.7 mmol) was added; the mixture was then refluxed for 15 h, cooled, and poured onto water. The mixture was extracted with diethyl ether (3 × 30 ml), and the organic phase washed with water, dried, and evaporated at reduced pressure to leave an oily residue which was distilled to give the compound (12) (1.2 g, 44%), b.p. 130 °C at 1 mmHg. The <sup>1</sup>H n.m.r. of the product showed it to be a slightly impure (<5%) sample of compound (13).

(B) **In DMF.** A suspension of sodium hydride in oil (55% by weight; 0.5 g, corresponding to 0.275 g, 11.4 mmol) was thoroughly washed with hexane and then suspended in dry DMF (30 ml). To this suspension maintained at -15 °C under nitrogen, diethyl phosphite (1.5 g, 11.5 mmol) in DMF (3 ml) was cautiously added: after 15 min the temperature was gradually raised to ambience and *N*-methylpyrrol-2-ylmethyltrimethylammonium iodide (1 g, 3.57 mmol) was added portionwise. The mixture was heated at 80 °C for 3 h, cooled, and poured into water; it was then extracted with diethyl ether (2 × 50 ml). The extracts were dried and evaporated to leave an oil (0.78 g), the <sup>1</sup>H n.m.r. analysis of which showed it to be a 60:40 mixture of (12) and (13); δ<sub>H</sub> (90 MHz, CDCl<sub>3</sub>) 1.35 (6 H, m, OCH<sub>2</sub>Me), 2.3 (1.2 H, s, Me), 3.15 [1.2 H, d, *J*(H—C—P) 18 Hz, CH<sub>2</sub>PO], 3.65 (1.2 H, s, NMe), 3.8 (1.8 H, s, NMe), 4.05 (4 H, m, OCH<sub>2</sub>Me), 5.90 [0.4 H, m, 4-H of (13)], 6.05 [1.2 H, m, 3- and 4-H of (12)], 6.55 [0.6 H, m, 5-H of (12)], 6.7 [0.4 H, m, 3-H of (13)].

**Condensation of *N*-Methylpyrrole-2-carbaldehyde with Diethyl 2-Thienylmethylphosphonate.**—(A) **Mixture of (*E*)- and (*Z*)-Isomers of 1-(*N*-Methylpyrrol-2-yl)-2-(2-thienyl)ethylene.** 2-Thienylmethyltriphenylphosphonium chloride<sup>15</sup> (2 g, 5.06 mmol) was added under nitrogen to a stirred solution of potassium *t*-butoxide (0.72 g, 6.4 mmol) in *t*-butyl alcohol (9 ml) and diethyl ether (6 ml). *N*-Methylpyrrole-2-carbaldehyde<sup>10</sup> (0.66 g, 6.05 mmol) was then added portionwise to the red solution of the ylide; the reaction mixture was stirred for 3 h after which the solvent was evaporated off under reduced pressure. The residue was taken up with water and extracted with chloroform. The solution was washed with water, dried, and evaporated to a small volume submitted to chromatography on silica (50 g) to give a product (0.8 g), the <sup>1</sup>H n.m.r. of which revealed it to be a mixture of two products in the ratio 2:1 identified as the (*Z*)- and (*E*)-isomer respectively.

(B) **(*E*)-1-(*N*-Methylpyrrol-2-yl)-2-(2-thienyl)ethylene (1b).**—A suspension of sodium hydride in oil (50% by weight; 1.08 g, 22.5 mmol) was repeatedly washed with dry THF and finally suspended in THF (40 ml). To this suspension, kept under nitrogen was first added a solution in THF (5 ml) of diethyl 2-thienylmethylphosphonate<sup>12</sup> (4.8 g, 20.5 mmol) and then a solution in the same solvent (5 ml) of *N*-methylpyrrole-2-carbaldehyde<sup>10</sup> (1.86 g, 17.1 mmol). The mixture was cautiously heated on an oil-bath at 50 °C until the evolution of hydrogen had ceased, and then at reflux for 1 h. The reaction was monitored by t.l.c. using, as eluant, hexane—AcOEt (9:1). The mixture was then poured onto ice (200 g) and extracted with diethyl ether (350 ml). The organic phase was washed, dried, and evaporated under reduced pressure to leave a solid which, after chromatography on silica gel (350 g) with hexane—AcOEt (9:1) as eluant, gave the product. Yields and physical and analytical data are given in Table 1; <sup>1</sup>H n.m.r. data are given in Table 2.

(*E*)-1,2-Bis(*N*-methylpyrrol-2-yl)ethylene (2).—A solution of sodium bistrimethylsilylamide (3.66 g, 19 mmol) in THF (30 ml) was added dropwise under nitrogen to a stirred solution of

*N*-methylpyrrole-2-carbaldehyde<sup>10</sup> (1.55 g, 14 mmol) and the mixture of phosphonates (12) (80%) and (13) (20%) [a total of 5.71 g corresponding to 4.57 g, 15.8 mmol of (12)] in THF (30 ml). The mixture was heated at 40 °C for 6 h, stirred overnight, and another portion of base (0.4 g, 2 mmol) was added. The mixture was heated at 60 °C for a further 3 h, cooled, and finally poured onto ice, then extracted with ether (3 × 30 ml); the organic phase was dried and evaporated at reduced pressure to give the crude compound. Physical, i.r., and analytical data are reported in Table 1, <sup>1</sup>H n.m.r. data are in Table 2.

*N*-Methyl-2,5-bis[(*E*)-2-thienylvinyl]pyrrole (3).—The compound was obtained under conditions (B) described as for (1), by condensing the *N*-methylpyrrole-2,5-dicarbaldehyde<sup>11</sup> (4.75 g, 34.7 mmol) with diethyl 2-thienylmethylphosphonate (8)<sup>12</sup> (20 g, 85.5 mmol) in the presence of sodium hydride (97.3 mmol corresponding to 4.5 g, of a 50% suspension in oil). Physical, i.r., and analytical data are reported in Table 1, <sup>1</sup>H n.m.r. data are in Table 2.

2,5-Bis[(*E*)-*N*-methylpyrrol-2-ylvinyl]thiophene (4).—The compound was obtained under conditions (B) described for (1) by condensing *N*-methylpyrrole-2-carbaldehyde (2.28 g, 20.9 mmol) with tetraethyl thiophen-2,5-diylbismethylphosphonate<sup>13</sup> (5 g, 13 mmol) in the presence of a suspension of sodium hydride in oil (50% by weight; 31.25 mmol, 1.5 g). Physical, i.r., and analytical data are given in Table 1, <sup>1</sup>H n.m.r. data are in Table 2.

Tetraethyl *N*-Methylpyrrole-2,5-diylbismethylphosphonate.—A solution of diethyl phosphite (11.52 g, 83.4 mmol) in DMF (20 ml) was slowly added to a suspension of NaH (2 g, 83.4 mmol) in DMF (80 ml) under nitrogen at −15 °C. When hydrogen evolution had ceased, the bismethiodide (15)<sup>16</sup> (9 g, 18.8 mmol) was added at room temperature and the mixture was heated at 80 °C for 8 h. After being cooled, the mixture was poured onto ice and extracted with CHCl<sub>3</sub> (150 ml); the organic layer was dried and evaporated to give an oily product which was purified by distillation at 160 °C/0.1 mmHg, yield 64% (Found: C, 47.1; H, 7.5; N, 4.1. C<sub>15</sub>H<sub>29</sub>NO<sub>6</sub>P<sub>2</sub> requires C, 47.2; H, 7.7; N, 3.7%); δ<sub>H</sub> (90 MHz, CDCl<sub>3</sub>) 1.25 (12 H, m, Me), 3.20 [4 H, d, *J*(CH–P) 18 Hz, CH<sub>2</sub>P], 3.60 (3 H, s, NMe), 4.05 (8 H, m, OCH<sub>2</sub>), 6.0 (2 H, m, pyrrole-H<sub>β</sub>).

*N*-Methyl-2,5-bis[(*E*)-*N*-methylpyrrol-2-ylvinyl]pyrrole (5).—This compound was obtained under the conditions (B) described for (1) starting from sodium bistrimethylsilylamide (2.5 g, 13.7 mmol), *N*-methylpyrrole-2-carbaldehyde (1.21 g, 11.12 mmol) and the diphosphonate (16) (2.12 g, 5.56 mmol). Physical, i.r., and analytical data are in Table 1, <sup>1</sup>H n.m.r. data are in Table 2.

*C.T. Complexes with Iodine.*—The finely ground products (1)–(5), (0.2–0.5 g) were exposed to iodine vapour in a sealed vessel with magnetic stirring, at room temperature for 48 h. The resulting black products were washed with light petroleum (b.p. 40–60 °C) until the colour of the excess of iodine had disappeared, they were then dried at room temperature *in vacuo* (0.1 mmHg) to constant weight.

*C.T. Complexes of Compounds (3), (4), and (5) with TCNQ.*—A solution of TCNQ in THF or acetonitrile (0.04M) was added to a solution of the product in the same solvent (equimolar amounts with TCNQ). The brown-black complex, which separated as a crystalline mass, was filtered off, washed with the same solvent, and dried *in vacuo* (yields 40–70%).

*Conductivity Measurements.*—The electrical conductivities were measured on pressed pellets using a two probe technique under a.c. conditions (1 KHz, autobalance bridge-Wayneker 6425). For the product (5)-TCNQ the conductivity was measured under the van der Pauw technique,<sup>17</sup> under d.c. conditions (current source: Keithley 617; high impedance voltmeter: Solartron Schlumberger 7066).

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