Synthesis of 1,4-di(*n*-pyridyl)buta-1,3-diyne and formation of charge-transfer complexes. X-Ray structure of 1,4-di(3-pyridyl)buta-1,3-diyne

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Ethynylpyridines have been satisfactorily prepared by two different routes: (a) the Wittig reaction between chloromethylene(triphenyl)phosphine ylide and a pyridinecarbaldehyde, followed by elimination of hydrogen chloride; (b) from the 2-methyl-4-(*n*-pyridyl)but-3-yn-2-ol intermediate, by elimination of acetone. 1,4-Di(*n*-pyridyl)buta-1,3-diynes are obtained by oxidative dimerization in good yield. An X-ray structure of the 3-substituted dimer is reported. Mono- and di-methyl salts of the 3-substituted diyne have been obtained and the charge-transfer complexes with tetramethyl-*p*-phenylenediamine (TMPD) are formed.

Introduction

The use of molecular organic materials for conductor and nonlinear optics applications is an area of considerable recent activity. Interest in these materials is due to their inherent synthetic flexibility which permits the 'design' of molecular properties.[1] Solid-state polymerization of 1,3-diynes to form crystalline conjugated polydiynes has attracted much attention.[1,2] Some of the recent interest in poly-1,3-diynes is related to their large and fast nonlinear optical response, making them good potential materials in ultrafast optical applications.[3] Although the electronic and optical properties of poly-1,3-diynes are primarily dominated by the π-conjugated backbone, the substituent groups markedly influence the topopolymerization behaviour of the 1,3-diynes and the physical and chemical properties of the crystalline conjugated poly-1,3-diynes. An aspect of the substituent effect that has received little attention is the influence of formally π-conjugated substituents on the electronic properties of poly-1,3-diynes, because many of them are unreactive in the solid state,[4–6] although they may undergo liquid-crystalline polymerization to form polymers distinct from the solid-state polymers. However, preliminary studies show that 4-amino-4′-nitrodiphenyl-1,3-diyne is solid-state reactive.[6]

The discovery of a one-dimensional metallic state in the ion-radical solid formed from the π-donor tetrathiafulvalene and the acceptor tetracyanoquinodimethane has stimulated interest in the structure–properties relationships of novel donors and acceptors.[7]

Metallic conductivity and superconductivity are the most important properties in these organic charge-transfer salts. Recently, attention has also been directed to the novel magnetic and optical properties which they can display.

Here we report the synthesis of the 1,4-di(*n*-pyridyl)buta-1,3-diynes **12**, **13** and **14**, and the methylation of the 3-substituted derivative **13**, to give molecules with acceptor characteristics which allow them to form charge-transfer complexes with donors.

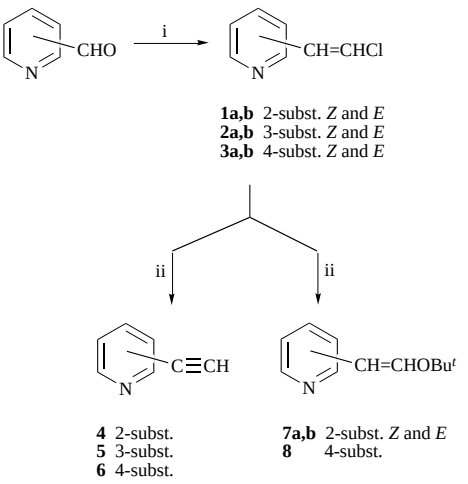
Results and discussion

Synthesis of *n*-ethynylpyridines

(*a*) By elimination of hydrogen chloride from the chlorovinyl derivatives. The starting acetylene derivatives **4**–**6** were prepared in good yields from a mixture of the corresponding (*E*)- and (*Z*)-2-chlorovinylpyridines **1**–**3** by dehydrochlorination with potassium *tert*-butoxide in tetrahydrofuran (THF) at different temperatures. In this elimination reaction we observed that the temperature had an influence on the yield and the reaction products. Furthermore, the position of the vinyl group on the pyridine ring determined some of the necessary reaction conditions (Table 1, Scheme 1).

Table 1 Dehydrochlorination of **1**–**3** with $Bu^tO^-K^+$ in THF at different temperatures

Chlorovinyl	*T*/°C	Elimination (%)	Substitution (%)
1a	25	48	
1a	70		50, *E* : *Z* = 1 : 1
1b	50	45	
1b	70		40, *E*
2a + **2b**	60	54	
2a + **2b**	70	25	
3a + **3b**	25	40	
3a + **3b**	70		20



Scheme 1 *Reagents and conditions:* i, $Ph_3P{=}CHCl$; ii, $Bu^tO^-K^+$, 25 °C (**4**–**6**) or 70 °C (**7a**,**b**; **8**)

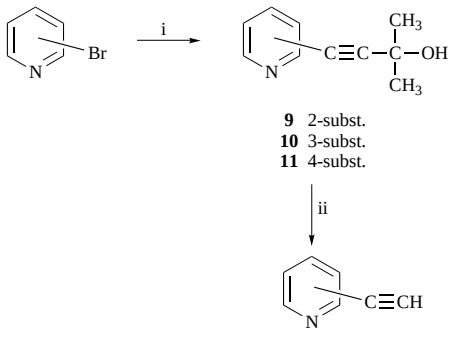
The chlorovinyl derivatives were prepared by the Wittig reaction between chloromethylene(triphenyl)phosphine ylide[8] and

Table 2 Synthesis of **1**–**3** *via* Wittig reaction

	Isomer	*Z* (%)	*E* (%)	Yield (%)
	1	84	16	77
	2	50	50	90
	3	50	50	84

the corresponding pyridinecarbaldehyde derivative in THF in good yield as a mixture of *E* : *Z* isomers (Scheme 1, Table 2). In the case of the 2-substituted derivative the main product is the *Z* isomer, because the *cis*-1,2-oxaphosphetane precursor of this isomer is more stable. The ylide reacts on the face of the carbonyl group to give the oxaphosphetane intermediate with the dipolar moment of the C–Cl bond in the opposite direction to that of the N–C dipole in the pyridine, and this stereodisposition is the most stable.

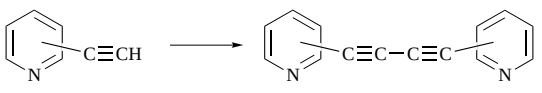
(*b*) From the *n*-halogenopyridines by insertion of the acetylene group catalysed by palladium. The low yield in the hydrogen chloride elimination step prompted us to carry out an alternative synthesis of the acetylene derivatives of pyridine using the coupling reaction between the bromopyridine and 2-methylbut-3-yn-2-ol;[9] the reaction is catalysed by palladium and the 2-methyl-4-(*n*-pyridyl)but-3-yn-2-ol derivatives **9**–**11** were obtained in excellent yields. Finally, the elimination of acetone gave the acetylene derivatives in moderate yield (Scheme 2, Table 3).



Scheme 2 *Reagents and conditions:* i, 2-methylbut-3-yn-2-ol, $Cl_2Pd(PPh_3)_2$, Cu_2I_2, $HNEt_2$; ii, NaOH, reflux

Synthesis of 1,4-di(*n*-pyridyl)buta-1,3-diynes 12–14

The title compounds were synthesized in good yield by oxidative dimerization[10] of the corresponding acetylene derivative with oxygen in pyridine in the presence of copper(I) iodide at 40 °C as solids which are stable to sunlight (Scheme 3).



4 2-subst.
5 3-subst.
6 4-subst.

12 2-subst.
13 3-subst.
14 4-subst.

Scheme 3 *Reagents:* Cu_2CI_2, O_2, pyridine

A single crystal of the 1,4-di(3-pyridyl)buta-1,3-diyne **13** was used for X-ray crystallographic analysis. The crystal was stable to Cu-Kα X-radiation and no topopolymerization to the monocrystalline poly-1,3-diyne was observed.

Crystal structure analysis

Compound **13** consists of a buta-1,3-diyne chain with 1,4-substitution at position 3 in both pyridine rings.

Fig. 1 shows a view of the molecule with the atom numbering scheme. A table of fractional atomic coordinates has been deposited as supplementary material,† and in Table 4 are listed (a) the bond distances and (b) the bond angles. The molecule has a symmetry centre which coincides with a crystallographic one.

Table 3 Yields of **9**–**11** and **4**–**6**

Bromopyridine	Alcohol (%)	Acetylene (%)
2-subst.	93	84
3-subst.	98	55
4-subst.	90	50

Table 4 Bond distances and angles for **13**

(a) Bond distances (Å)

N(1)–C(2)	1.338(3)	C(5)–C(6)	1.394(3)
N(1)–C(6)	1.325(3)	C(5)–C(7)	1.431(3)
C(2)–C(3)	1.375(3)	C(7)–C(8)	1.199(3)
C(3)–C(4)	1.371(3)	C(8)–C(8′)[a]	1.371(3)
C(4)–C(5)	1.392(3)		

(b) Bond angles (°)

C(2)–N(1)–C(6)	117.3(2)	C(4)–C(5)–C(6)	117.4(2)
N(1)–C(2)–C(3)	123.1(2)	C(6)–C(5)–C(7)	121.4(2)
C(2)–C(3)–C(4)	119.2(2)	N(1)–C(6)–C(5)	123.9(2)
C(3)–C(4)–C(5)	119.0(2)	C(5)–C(7)–C(8)	178.1(2)
C(4)–C(5)–C(7)	121.2(2)	C(7)–C(8)–C(8′)[a]	179.7(2)

[a] C(8′) is related to C(8) by the symmetry operation $(1 - x, -1 - y, 2 - z)$.

Bond distances and angles are within the expected values (Table 4). The pyridine ring is planar, C(7) and C(8) deviating by 0.031(2) and 0.086(2) Å above this plane.

The distances N(1)–C(2) and N(1)–C(6) of 1.338(3) and 1.325(3) Å respectively are similar to those found in pyridine.

Bond distances of the buta-1,3-diyne chain show normal values,[11] with a C(7)–C(8) triple bond distance of 1.199(3) Å. This chain is practically linear with a C(7)–C(8)–C(8′) angle of 179.7(2)°.

The crystal packs with the molecules in parallel columns (see Fig. 2) along the *c*-axis which defines the distance between the centroids of consecutive rings as being 3.87 Å, forming with the *c*-axis an angle of 10°. It can be seen in Fig. 2 that along the *a*-axis there are zones of neighbouring intermolecular rings and zones of intramolecular –C≡C–C≡C– linear chains, producing a so called 'segregation', the overall least-squares planes through each molecule in the cell are parallel and within each column a stack is produced. Along the *b*-axis there are also chains of molecules in the so called 'edge-to-edge' mode with parallel molecules within a column but forming an angle of almost 90° between molecules of two neighbouring columns.

In general, in the reactive crystals of buta-1,3-diyne compounds, the molecules are packed in a ladder-like fashion such that the ends of one triple-bond system approach an adjacent triple-bond system to a distance d <4 Å, and the inclination angle formed with the translation axis is about 45°.[12]

Charge-transfer complexes

The π-electronic defect of the pyridine rings and the π-extended conjugation to the diyne chain in 1,4-di(3-pyridyl)-buta-1,3-diyne **13** allowed it to take part in charge-transfer complexation with *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) as donor. However, the 1,4-di(*n*-pyridyl)buta-1,3-diyne derivative does not form charge-transfer complexes with

† *Supplementary material:* Tables of fractional atomic coordinates and thermal parameters, and full bond lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/78.

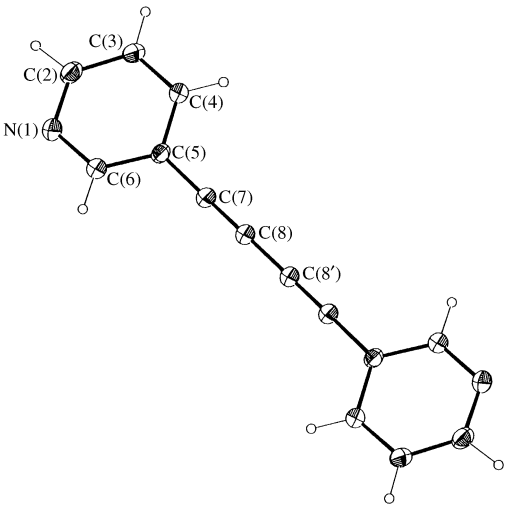
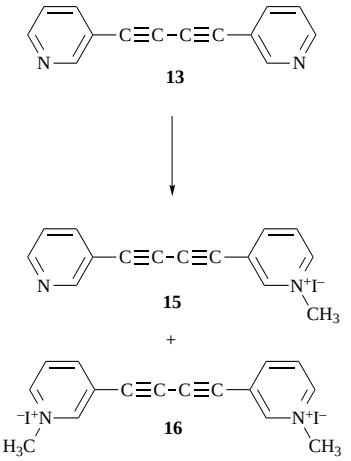


Fig. 1 View of molecule **13** with the atom numbering scheme

some acceptors or donors, so we carried out methylation of the pyridine rings to increase the acceptor character of these compounds (Scheme 4).



Scheme 4 *Reagent:* MeI

The mono- and di-methylated salts of the *meta* diyne derivative were isolated pure and used to prepare charge-transfer complexes with the donor molecule TMPD. Thus, slow evaporation of an equimolar mixture of the mono- or di-salt and TMPD in hot acetonitrile gave in both cases a metallic bright solid (black or green) (Fig. 3).

UV-Visible spectroscopy of the molecular complex of the monomethylated salt **15** and TMPD shows three charge-transfer bands, at 543, 565 and 615 nm. In the case of the molecular complex of the dimethylated salt **16** and TMPD the UV-visible spectrum also shows three charge-transfer bands, at 594, 617 and 642 nm. The IR spectra showed some differences between the complexes with TMPD and the free salts, such that the intensity of the absorption for the C=C conjugated bonds in the complexes is lower than that in the free salts.

Experimental

Mps were determined using a Reichert stage microscope and are uncorrected. IR Spectra were recorded using a Perkin-Elmer 681 spectrophotometer. NMR Spectra were recorded at 200 MHz using a Bruker WM-200-SY spectrometer; chemical shifts are given in δ units, using $SiMe_4$ as internal reference; J values are given in Hz. UV–Visible spectra were recorded using a Perkin-Elmer Lambda 6 spectrophotometer. Mass spectra were recorded using a Hewlett-Packard SP85 spectrometer.

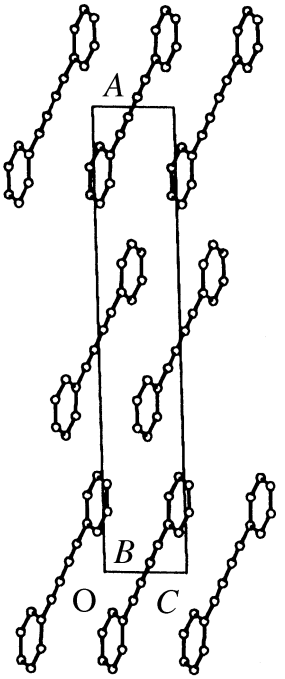


Fig. 2 Packing of the molecular crystal unit cells viewed down the *b*-axis

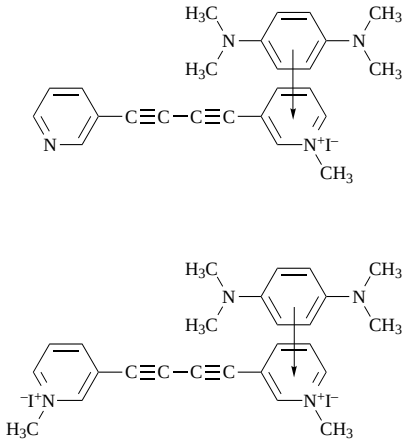


Fig. 3

Preparation of ethynylpyridines by elimination of hydrogen chloride from the chlorovinyl derivatives

2-(2-Chlorovinyl)pyridine 1. To a suspension of chloromethyl(triphenyl)phosphonium chloride (18.7 g, 57 mmol) in dry THF (60 cm^3) was slowly added a solution of butyllithium (1.6 M in hexane; 35.6 cm^3, 57 mmol) under argon at −10 °C. The solution acquired a red colour and after being stirred for 30 min was treated with pyridine-2-carbaldehyde (2 g, 19 mmol). The mixture was stirred at room temperature for 10 h and then the solvent was removed to give a brown oil. Chromatography on silica gel with hexane–ethyl acetate afforded (*Z*)-2-(2-chlorovinyl)pyridine, ν_{max}(film)/cm^{-1} 3055 (=C−H), 1620 (C=C, conj.), 1580 and 1560 (C=C and C=N) and 670 (*Z*); δ_H(200 MHz; $CDCl_3$) 6.49 (1 H, d, *J* 8.3, C*H*=CHCl), 6.86 (1 H, d, *J* 8.3, CH=C*H*Cl), 7.19 (1 H, dd, *J* 7.9 and 6.0, 5-H), 7.70 (1 H, t, *J* 7.9, 4-H), 8.02 (1 H, d, *J* 7.9, 3-H) and 8.62 (1 H, d, *J* 6.0, 6-H); *m*/*z* 141 (9%), 139 (M^+, 22), 104 (100), 84 (13), 78 (30) and 51 (27); and (*E*)-2-(2-chlorovinyl)pyridine, ν_{max}(film)/cm^{-1} 3070 (=C−H), 1620 (C=C, conj.), 1580 and 1560 (C=C and C=N) and 970 (*E*); δ_H(200 MHz; $CDCl_3$) 6.67 (1 H, d, *J* 13.3, C*H*=CHCl), 7.20 (2 H, m, 3- and 5-H), 7.43 (1 H, d, *J* 13.3, CH=C*H*Cl), 7.63 (1 H, m, 4-H) and 8.53 (1 H, br s, 6-H); *m*/*z* 141 (9%), 139 (M^+, 27), 104 (100), 78 (25) and 51 (18).

3-(2-Chlorovinyl)pyridine 2. The same procedure was followed to prepare the 3-substituted derivative, but with pyridine-3-carbaldehyde. After purification by chromatography on silica gel the chlorovinyl derivative **2** was obtained as an oily mixture of *E* : *Z* isomers (1 : 1) (2.38 g, 90%); ν_{max}(film)/cm^{-1} 3050 (=C−H), 1610 and 1605 (C=C, conj.), 1580 and 1560 (C=C and C=N), 970 (*E*) and 730 (*Z*); δ_H(200 MHz; $CDCl_3$) 6.29 (1 H, d, *J* 8.2, C*H*=CHCl, *Z*), 6.69 (1 H, d, *J* 13.9, C*H*=CHCl, *E*), 6.74 (1 H, d, *J* 8.2, CH=C*H*Cl, *Z*), 6.85 (1 H, d, *J* 13.9, CH=C*H*Cl, *E*), 7.25 (1 H, d, *J* 8.0, 5-H, *E*), 7.32 (1 H, dd, *J* 8.0 and 5.4, 5-H, *Z*), 7.60 (1 H, d, *J* 8.0, 4-H, *E*), 8.13 (1 H, d, *J* 8.0, 4-H, *Z*), 8.49 (1 H, br s, 6-H, *E*), 8.52 (1 H, d, *J* 5.4, 6-H, *Z*), 8.53 (1 H, br s, 2-H, *E*) and 8.76 (1 H, br s, 2-H, *Z*); *m*/*z* 141 (8%), 139 (M^+, 29), 104 (100), 86 (10), 77 (46) and 51 (64).

4-(2-Chlorovinyl)pyridine 3. Following the same procedure we obtained the chlorovinyl derivative **3**, from pyridine-4-carbaldehyde, as an oily mixture of *E* : *Z* isomers (1 : 1) (2.22 g, 84%); ν_{max}(film)/cm^{-1} 3060 (=C−H), 1610 (C=C, conj.), 1590 and 1540 (C=C and C=N), 960 (*E*) and 720 (*Z*); δ_H(200 MHz; $CDCl_3$) 6.48 (1 H, d, *J* 8.2, C*H*=CHCl, *Z*), 6.60 (1 H, d, *J* 8.2, CH=C*H*Cl, *Z*), 6.69 (1 H, d, *J* 13.8, C*H*=CHCl, *E*), 6.77 (1 H, d, *J* 13.8, CH=C*H*Cl, *E*), 7.16 (2 H, d, *J* 4.8, 3- and 5-H, *E*), 7.52 (2 H, d, *J* 4.6, 3- and 5-H, *Z*), 8.56 (2 H, d, *J* 4.8, 2- and 6-H, *E*) and 8.62 (2 H, d, *J* 4.6, 2- and 6-H, *Z*); *m*/*z* 141 (8%), 139 (M^+, 29), 112 (29), 104 (38), 86 (84), 77 (36), 63 (16) and 51 (100).

2-Ethynylpyridine 4. *From the* (Z)-2-(2-*chlorovinyl*)*pyridine isomer* **1a**.—To a solution of the (*Z*)-chlorovinyl derivative **1a** (3 g, 21 mmol) in dry THF (30 cm^3) was slowly added potassium *tert*-butoxide (6 g, 54 mmol) under argon at 0 °C. The mixture was stirred for 45 min at room temperature. Then the solution was poured onto ice–water (150 cm^3) and made alkaline (pH 8) with saturated aq. ammonium chloride. The mixture was extracted with dichloromethane; the extract was dried with magnesium sulfate and after filtration the solvent was removed to give a brown oil. Chromatography on silica gel with hexane–ethyl acetate (1 : 2) as eluent yielded the acetylene derivative **4** (1.04 g, 48%) as an orange oil, bp 91–92 °C/15 mmHg (lit.,[9] 85–86 °C/12 mmHg); ν_{max}(film)/cm^{-1} 3260 (=C−H) and 2114 (C≡C); δ_H(200 MHz; $CDCl_3$) 3.25 (1 H, s, C≡CH), 7.21 (1 H, dd, *J* 7.7 and 5.1, 5-H), 7.40 (1 H, d, *J* 7.7, 3-H), 7.60 (1 H, t, *J* 7.7, 4-H) and 8.54 (1 H, d, *J* 5.1, 6-H); δ_C(200 MHz; $CDCl_3$) 77.0 (Py−C≡*C*), 82.5 (Py−*C*≡C), 123.1 (C-5), 127.1 (C-3), 135.8 (C-4), 148.4 (C-2) and 149.5 (C-6); *m*/*z* 103 (M^+, 100%), 76 (46) and 50 (36).

From the (E)-2-(2-*chlorovinyl*)*pyridine isomer* **1b**.—To a solution of the (*E*)-chlorovinyl derivative **1b** (1 g, 7.2 mmol) in dry THF (15 cm^3) was slowly added potassium *tert*-butoxide (2 g, 18 mmol), under argon at 0 °C. The mixture was stirred for 90 min at 50 °C. Then the solution was poured onto ice–water (60 cm^3) and made alkaline (pH 8) with saturated aq. ammonium chloride. The mixture was extracted with dichloromethane; the extract was dried with magnesium sulfate and after filtration the solvent was removed to give a brown oil. Chromatography on silica gel with hexane–ethyl acetate (1 : 2) as eluent yielded the acetylene derivative **4** (0.33 g, 45%) as an orange oil.

3-Ethynylpyridine 5. To a solution of the (*Z*,*E*)-chlorovinyl derivative **2** (3 g, 21 mmol) in dry THF (30 cm^3) was slowly added potassium *tert*-butoxide (6 g, 54 mmol) under argon at 0 °C. The mixture was stirred for 60 min at 60 °C. Then the solution was allowed to cool and was poured onto ice–water (150 cm^3) and made alkaline (pH 8) with saturated aq. ammonium chloride. The mixture was extracted with dichloromethane; the extract was dried with magnesium sulfate and after filtration the solvent was removed to give a brown oil. Chromatography on silica gel with hexane–ethyl acetate (1 : 2) as eluent yielded the acetylene derivative **5** (1.17 g, 54%) as a yellow solid, mp 35–37 °C (lit.,[13] 39–40 °C); ν_{max}(film)/cm^{-1} 3280 (=C−H) and 2120 (C≡C); δ_H(200 MHz; $CDCl_3$) 3.30 (1 H, s, C≡CH), 7.25 (1 H, ddd, *J* 7.8, 5.0 and 0.9, 5-H), 7.70 (1 H, dt, *J* 7.8 and 2.0, 4-H), 8.56 (1 H, dd, *J* 5.0 and 2.0, 6-H) and 8.70 (1 H, dd, *J* 2.0 and 0.9, 2-H); δ_C(200 MHz; $CDCl_3$) 80.0 (Py−*C*≡C), 80.6 (Py−C≡*C*), 118.7 (C-3), 122.3 (C-5), 138.3 (C-4), 148.3 (C-6) and 151.9 (C-2); *m*/*z* 103 (M^+, 100%), 76 (38) and 50 (30).

4-Ethynylpyridine 6. Following the same procedure described to prepare 2-ethynylpyridine from the (*Z*)-chlorovinyl isomer, 4-ethynylpyridine was obtained (40%) as a solid from the 4-(chlorovinyl)isomer, mp 63–65 °C; ν_{max}(film)/cm^{-1} 3270 (=C−H) and 2100 (C≡C); δ_H(200 MHz; $CDCl_3$) 3.40 (1 H, s, C≡CH), 7.35 (2 H, d, *J* 6.8, 3- and 5-H) and 8.60 (2 H, d, *J* 6.8, 2- and 6-H); δ_C(200 MHz; $CDCl_3$) 80.6 (Py−*C*≡C), 81.8 (Py−C≡*C*), 129.9 (C-4), 125.7 (C-3 and -5) and 149.4 (C-2 and -6); *m*/*z* 103 (M^+, 100%), 76 (52) and 50 (41).

Synthesis of ethynylpyridines by insertion of the acetylene group catalysed by palladium

2-Methyl-4-(2-pyridyl)but-3-yn-2-ol 9. Bis(triphenylphosphine)palladium(II) dichloride (220 mg, 0.3 mmol) and copper(I) iodide (32 mg, 0.2 mmol) were added successively to a solution of 2-bromopyridine (5 g, 31.6 mmol) and 2-methylbut-3-yn-2-ol (3.62 ml, 37.3 mmol) in diethylamine (freshly distilled; 25 cm^3) under argon at 0 °C. The mixture was stirred for 15 h at room temperature and then the diethylamine was removed under reduced pressure. The crude mixture was washed with water and extracted with dichloromethane; the extract was dried with magnesium sulfate and after filtration the solvent was removed to give a brown solid. Chromatography on silica gel with hexane–ethyl acetate as eluent yielded 2-methyl-4-(2-pyridyl)but-3-yn-2-ol **9** (4.76 g, 93%) as a yellow solid, mp 60–62 °C (lit.,[9] 61–63 °C); ν_{max}(film)/cm^{-1} 3300 (O−H), 2980 (C−H), 2230 (C≡C), 1585 (C=C, conj.), 1380 and 1360 (CH_3), 1170 (C−O), 970 (Py) and 780 (Py−H, 2-subst.); δ_H(200 MHz; $CDCl_3$) 1.70 (6 H, s, CH_3 × 2), 5.29 (1 H, s, OH), 7.20 (1 H, dd, *J* 6.7 and 5.0, 5-H), 7.39 (1 H, d, $J_{3,4}$ 6.7, 3-H), 7.62 (1 H, td, $J_{4,3} = J_{4,5}$ 6.7 and $J_{4,6}$ 0.8, 4-H) and 8.59 (1 H, br s, 6-H); δ_C(200 MHz; $CDCl_3$) 30.9 (CH_3), 64.5 (C−OH), 80.6 (Py−*C*≡C), 94.9 (Py−C≡*C*), 122.5 (C-5), 126.7 (C-3), 136.0 (C-4), 142.6 (C-2) and 149.2 (C-6).

2-Methyl-4-(3-pyridyl)but-3-yn-2-ol 10. Following the same procedure the 3-substituted derivative **10** was obtained (5 g, 98%) as a yellow solid, from 3-bromopyridine, mp 52–54 °C; ν_{max}(film)/cm^{-1} 3300 (O−H), 2980 (C−H), 2240 (C≡C), 1590 (C=C, conj.), 1380 and 1360 (CH_3), 1170 (C−O), 970 (Py) and 810 and 705 (Py−H, 3-subst.); δ_H(200 MHz; $CDCl_3$), 1.58 (6 H, s, CH_3 × 2), 5.78 (1 H, s, OH), 7.15 (1 H, dd, $J_{5,4}$ 8.0, $J_{5,6}$ 6.4, 5-H), 7.09 (1 H, d, $J_{4,5}$ 8.0, 4-H), 8.38 (1 H, s, 6-H) and 8.60 (1 H, s, 2-H); δ_C(200 MHz; $CDCl_3$) 31.1 (CH_3), 64.3 (C−OH), 77.6 (Py−*C*≡C), 98.6 (Py−C≡*C*), 120.2 (C-3), 122.9 (C-5), 138.7 (C-4), 147.4 (C-6) and 151.3 (C-2).

2-Methyl-4-(4-pyridyl)but-3-yn-2-ol 11. The preparation of the 4-substituted derivative **11** was carried out, following the same procedure, from 4-bromopyridine hydrochloride. Compound **11** was obtained (3.72 g, 90%) as a yellow solid, mp 96–98 °C; ν_{max}(film)/cm^{-1} 3350–3040 (O−H), 2980 (C−H), 2230 (C≡C), 1600 (C=C, conj.), 1370 and 1360 (CH_3), 1170 (C−O), 970 (Py) and 840 (Py−H, 4-subst.); δ_H(200 MHz; $CDCl_3$) 1.62 (6 H, s, CH_3 × 2), 3.10 (1 H, s, OH), 7.29 (2 H, d, *J* 8.1, 3- and 5-H) and 8.59 (2 H, s, 2- and 6-H); δ_C(200 MHz; $CDCl_3$) 31.0 (CH_3), 64.5 (C−OH), 78.6 (Py−*C*≡C), 100 (Py−C≡*C*), 125.6 (C-3 and -5) and 148.8 (C-2 and -6).

General procedure to prepare the ethynylpyridines from the 2-methyl-4-(*n*-pyridyl)but-3-yn-2-ols

A solution of the alkynol (5 g, 31 mmol) in dry toluene (30 cm^3) was heated under reflux with pulverized sodium hydroxide (0.90 g) for 2 h. Then, the solution was decanted and the solvent was evaporated under reduced pressure to give a brown solid.

Chromatography on silica gel with hexane–ethyl acetate (1:2) yielded the ethynyl derivative 2-Ethynylpyridine (84%) as an orange oil, bp 90–92 °C/15 mmHg; 3-ethynylpyridine (55%) as a yellow solid, mp 37–39 °C and 4-ethynylpyridine (50%) as a solid, mp 63–65 °C.

Oxidative dimerization of ethynylpyridines. General procedure

Oxygen was bubbled into a solution of copper(I) chloride (0.54 g, 2.73 mmol) in pyridine (12 cm^3) warmed to 40 °C, after which the acetylene derivative (0.78 g, 7.57 mmol) was added. The mixture was stirred for 3 h, after which it was cooled and concentrated by removal of the pyridine by distillation. The crude mixture was washed with ammonium hydroxide until the blue colour disappeared, after which it was extracted with dichloromethane. The extract was dried ($MgSO_4$), filtered and evaporated to give a yellow solid, chromatography of which on silica gel with hexane–ethyl acetate (1 : 2) as eluent yielded the diyne derivative. 3-Substituted product **13** (49%) was a yellow solid, mp 145–146 °C; ν_{max}(KBr)/cm^{-1} 1550 (C=C, conj.), 955 (Py), 800 and 700 (Py–H, 3-subst.); δ_H(200 MHz; $CDCl_3$) 7.30 (2 H, dd, *J* 7.9 and 5.0, 5-H), 7.82 (2 H, dt, *J* 7.9 and 1.7, 4-H), 8.61 (2 H, br s, 6-H) and 8.78 (2 H, br s, 2-H); δ_C(200 MHz; $CDCl_3$) 78.9 (C≡C), 118.5 (C-3), 122.7 (C-5), 139.1 (C-4), 149.2 (C-6) and 152.9 (C-2); *m*/*z* 204 (M^+, 100%), 177 (11), 151 (23) and 124 (8); λ_{max}(CH_2Cl_2)/nm 229 (ε/dm^3 mol^{-1} cm^{-1} 30 000), 244 (29 000), 292 (22 000), 319 (30 000) and 331 (26 000).

4-Substituted product **14** (54%) was a brown solid, mp 198–201 °C; ν_{max}(Nujol)/cm^{-1} 1580 (C=C, conj.), 980 (Py) and 810 (Py–H, 4-subst.); δ_H(200 MHz; $CDCl_3$) 7.41 (4 H, d, *J* 7.2, 3- and 5-H) and 8.67 (4 H, br s, 2- and 6-H); δ_C(200 MHz; $CDCl_3$) 76.9 (Py–C≡*C*), 79.9 (Py–*C*≡C), 125.7 (C-3 and -5), 128.9 (C-4) and 149.6 (C-2 and -6); *m*/*z* 204 (M^+, 100%), 177 (13), 151 (14) and 124 (6).

X-Ray crystallographic analysis of 1,4-di(3-pyridyl)buta-1,3-diyne 13

Yellow, transparent, plate-like crystals of 1,4-di(3-pyridyl)buta-1,3-diyne **13** were grown by slow evaporation from an acetonitrile solution. A crystal of dimensions 0.29 × 0.27 × 0.18 mm^3 was selected for X-ray diffraction analysis. Accurate cell dimensions were determined by least-squares analysis of setting angles of 40 reflections ($15 < 2\theta < 84°$) using graphite-monochromated Cu-Kα radiation ($\lambda = 1.5418$ Å) automatically located and centred on a four-circle Philips PW1100 diffractometer. $C_{14}H_8N_2$, M = 204.23, monoclinic, $a = 22.104(3)$, $b = 6.017(1)$, $c = 3.873(1)$ Å, $\beta = 91.48(1)°$, $V = 514.92(7)$ $Å^3$, $Z = 2$, space group $P2_1/n$, $D_c = 1.317(3)$ g cm^{-3}, $F(000) = 212$, $\mu = 6.253$ cm^{-1}.

Data collection. Two standard reflections were measured every 90 min to ascertain crystal stability; no significant variation was observed. The intensities were corrected for Lorentz and polarization effects. No corrections were made for absorption.

For the intensity measurement, reflections were surveyed in the range $2 < \theta < 65°$; from 975 independent reflections measured, 778 were considered as observed, satisfying the criterion $I < 2\sigma(I)$ in the range h −27/27, k 0/8, l 0/5, and were used in the subsequent calculations. The structure was solved by direct methods using SIR92,[14] and refined by anisotropic full-matrix least-squares.[15] The H-atoms were located on a difference map and refined isotropically. After several cycles of mixed refinement (89 refined parameters), convergence was reached at $R = 0.057$ and $R_w = 0.069$, with a weighting scheme[16] to prevent trends in $\langle w\Delta^2F\rangle$ *vs.* $\langle|F_o|\rangle$ and $\langle\sin\theta/\lambda\rangle$.

The atomic scattering factors and the anomalous dispersion corrections were taken from the literature.[17] Atomic coordinates, bond distances and angles were calculated using the PARST program.[18]

1,4-Di(2-pyridyl)buta-1,3-diyne 12

To a suspension of copper(I) chloride (57 mg, 0.58 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (0.11 cm^3, 0.75 mmol) in 1,2-dimethoxyethane (DME) (4 cm^3) was added a solution of 2-ethynylpyridine **4** (0.3 g, 2.9 mmol) in DME (1 cm^3), previously heated for 10 min at 35 °C, while oxygen was bubbled in. After 30 min the mixture changed in colour from green to brown and 15 min later the solvent was removed to give a brown solid, chromatography of which on silica gel with hexane–ethyl acetate (2:3) as eluent yielded the diacetylene derivative **12** (150 mg, 52%) as a solid, mp 120–122 °C (lit.,[19] 122–123 °C); ν_{max}(KBr)/cm^{-1} 1580 and 1560 (C=C, conj.), 990 (Py), 780 and 735 (Py–H, 2-subst.); δ_H(200 MHz, $CDCl_3$) 7.24 (2 H, ddd, *J* 7.6, 4.8 and 1.1, 5-H), 7.47 (2 H, d, *J* 7.7, 3-H), 7.63 (2 H, td, *J* 7.7 and 1.7, 4-H) and 8.55 (2 H, d, *J* 4.8, 6-H); δ_C(200 MHz; $CDCl_3$) 72.9 (Py–C≡*C*), 80.7 (Py–*C*≡C), 123.6 (C-5), 128.2 (C-3), 136.0 (C-4), 141.5 (C-2) and 150.2 (C-6); *m*/*z* 204 (M^+, 100%), 177 (14), 151 (14), 124 (5), 102 (6) and 78 (10); λ_{max}(CH_2Cl_2)/nm 238 (ε/dm^3 mol^{-1} cm^{-1} 23 600), 294 (18 400), 309 (24 000) and 330 (20 800).

Methylation of the 1,4-di(3-pyridyl)buta-1,3-diyne 13

To a solution of the diyne derivative (100 mg, 0.49 mmol) in ethanol (25 cm^3) was added iodomethane (0.12 cm^3, 1.96 mmol). The mixture was stirred for 20 h at 50 °C. A yellow solid precipitated from the solution and was filtered off and identified as the dimethylated derivative **16** (92 mg, 38%), mp 190 °C (decomp.). Then, the mixture was allowed to cool and an orange solid precipitated out, which was filtered off and identified as the monomethylated derivative **15** (72 mg, 42%), mp 166 °C (decomp.).

Dimethylated product **16** had ν_{max}(KBr)/cm^{-1} 1620 and 1500 (C=C and C=N, conj.), 1290 (N–CH_3), 1150 (Py^+–CH_3), 810 and 665 (Py–H, 3-subst.); δ_H[200 MHz; $(CD_3)_2SO$] 4.37 (6 H, s, CH_3 × 2), 8.23 (2 H, t, 5-H), 8.91 (2 H, d, 4-H), 9.13 (2 H, d, 6-H) and 9.49 (2 H, s, 2-H); δ_C(200 MHz; $CDCl_3$) 48.4 (CH_3), 77.2 and 77.6 (Py–*C*≡*C*), 120.1 (C-3), 127.7 (C-5), 146.4 (C-4), 147.9 (C-6) and 149.3 (C-2); *m*/*z* (FAB^+) 234 (M^+, 25%) and 219 (52); λ_{max}(CH_2Cl_2)/nm 237 (ε/dm^3 mol^{-1} cm^{-1} 31 430), 290 (18 500), 308 (20 000), 330 (18 570), 345 (13 710), 354 (12 000) and 360 (11 430).

Monomethylated product **15** had ν_{max}(KBr)/cm^{-1} 1620, 1580 and 1500 (C=C and C=N, conj.), 1280 (N–CH_3), 1160 (Py^+–CH_3), 830, 800, 700 and 675 (Py–H, 3-subst.); δ_H[200 MHz; $(CD_3)_2SO$] 4.31 (3 H, s, CH_3), 7.50 (1 H, m, 5-H), 8.20 (2 H, m, 5-H in the methylated ring and 4-H), 8.70 (2 H, m, 2- and 6-H), 8.88 (1 H, m, 4-H in the methylated ring), 9.05 (1 H, d, 6-H in the methylated ring) and 9.42 (1 H, br s, 2-H in the methylated ring); δ_C(200 MHz; $CDCl_3$) 48.4 (CH_3), 77.2 and 77.6 (Py–*C*≡*C*), 120.1 (C-3), 127.7 (C-5), 146.4 (C-4), 147.9 (C-6) and 149.3 (C-2); *m*/*z* (FAB^+) 219 (M^+, 100%) and 205 (13); λ_{max}(CH_2Cl_2)/nm 237 (ε/dm^3 mol^{-1} cm^{-1} 40 250), 290 (17 750), 308 (22 500), 330 (24 000) and 345 (12 500).

Charge-transfer complex of 1-(*N*-methylpyridinium-3-yl)-4-(3-pyridyl)buta-1,3-diyne iodide 15 with TMPD

A hot solution of TMPD (24 mg, 0.14 mmol) in acetonitrile (10 cm^3) was added to a nearly boiling solution of the monomethylated buta-1,3-diyne derivative **15** (50 mg, 0.14 mmol) in 100 cm^3 of acetonitrile. The resulting dark violet solution was allowed to cool and then to evaporate slowly to yield a black solid with metallic lustre; ν_{max}(Nujol)/cm^{-1} 1610, 1580 and 1510 (C=C and C=N, conj.), 1160 (Py^+–CH_3), 950 (Py), 820, 810, 800, 720, 690 and 665 (Py–H, 3-subst.); λ_{max}(CH_2Cl_2)/nm 238, 309, 330, 350, 543, 565 and 615.

Charge-transfer complex of 1,4-bis(*N*-methylpyridinium-3-yl)-buta-1,3-diyne diiodide 16 with TMPD

The same procedure was followed to form the charge-transfer complex of the dimethylated buta-1,3-diyne derivative **16**.

The complex was a green solid with a metallic lustre; ν_{max}(Nujol)/cm^{-1} 1620 and 1520 (C=C and C=N, conj.), 1320 (N−CH_3), 1170 and 1150 (Py^+−CH_3), 950 (Py), 815, 720 and 665 (Py−H, 3-subst.); λ_{max}(CH_2Cl_2)/nm 264, 327, 594, 617 and 642.

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