Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 1021–1032

TETRAHEDRON

π-Extended conjugate phenylacetylenes. Synthesis of 4-[(*E*) and (*Z*)-2-(4-ethenylphenyl)ethenyl]pyridine. Dimerization, quaternation and formation of charge–transfer complexes

J. Gonzalo Rodríguez,* Rosa Martín-Villamil and Antonio Lafuente

Departamento de Química Orgánica, Universidad Autónoma de Madrid, Cantoblanco, 28049-Madrid, Spain

Received 24 September 2002; revised 20 November 2002; accepted 12 December 2002

Abstract—The conjugate (*E*)- and (*Z*)-(4′-pyridylethenyl)-4-phenylethyne (*E*-**4** and *Z*-**4**) has been satisfactorily prepared by two different routes: (a) by dehydrohalogenation of 4′-pyridylethenyl-4-phenyl-β-chloroethene; (b) by the Wittig reaction between *p*-(iodobenzyl)-(triphenyl)phosphine ylide and 4-pyridinecarboxaldehyde, *E*/*Z* isomer separation, and cross-coupling with 2-methyl-but-3-yn-2-ol followed the propanone elimination. The Glaser oxidative dimerization of (*Z*)-**4** yields (*Z*,*Z*)-1,4-di[(4′-pyridylethenyl)-4-phenyl]-buta-1,3-diyne in good yield, (*Z*,*Z*)-**5**. (*E*,*E*)-**5** was obtained by phase transfer oxidative dimerisation of (*E*)-**4** in presence of their *N*-methyl salt (*E*)-**10**. Mono- and di-N-methylated salts of conjugate (*E*,*E*)-**5** and (*Z*,*Z*)-**5**, were obtained by quaternation with iodomethane. The (*Z*,*Z*)-**5** di-N-methylated salt forms charge–transfer complexes with TCNE, TCNQ and TMPD.

1. Introduction

The use of molecular organic materials for conductor and non-linear 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 architectures with important properties. Compounds containing the conjugate molecular fragment type bistyryl are applied as carrier transport agents and electrophotographic photoreceptors.[1a] Molecules showing π-extended conjugation, in general exhibit high thermal stability and can present electroconductive, magnetic and optical properties.[1b]

Solid state polymerisation of 1,3-diynes to form crystalline conjugated poly(1,3-diynes) has attracted much attention.[1b,2] Some of the recent interest is related to their large and fast non-linear 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 acetylene substituents markedly influence the topopolymerisation behaviour and the physical and chemical properties of the crystalline conjugated poly(1,3-diynes) because, many of them, are inactive in the solid state,[4,5] although undergo liquid crystal polymerisation. However, preliminary studies show that 4-nitro, 4′-amino diphenyl-1,3-diyne is solid state reactive.[6]

The discovery of the one-dimensional metallic state in the ion–radical solid formed from the π-donor tetrathiofulvalene (TTF) and the acceptor tetracyanoquinodimethane (TCNQ) has stimulated the interest for structure–properties relationship of novel donor 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 can display.[8]

In this paper we report the synthesis of (*E*)- and (*Z*)-(4′-pyridylethenyl)-4-phenylethyne, the oxidative homocoupling to 1,3-butadiynes and the quaternation to give molecules with strong acceptor character, which enables to prepare charge–transfer complexes with donor and acceptor molecules.

2. Results and discussion

2.1. Synthesis of π-extended conjugate phenylacetylene derivatives

Synthesis of (*E*)- and (*Z*)-(4′-pyridylethenyl)-4-phenylethyne (*E*-**4** and *Z*-**4**) was outlined in two ways: (a) by dehydrohalogenation of the appropriate halovinylarene derivative, (*E*,*E*) or (*Z*,*E*) or the mixture[9] and; (b) by cross-coupling reaction of the corresponding haloarene with 2-methyl-but-3-yn-2-ol, catalysed by palladium, followed of propanone elimination.[10]

Keywords: charge–transfer complex; oxidative dimerization; dehydrohalogenation.

* Corresponding author. Tel.: +34-1397-4715; fax: +34-1397-3966; e-mail: gonzalo.rodriguez@uam.es

0040–4020/03/$ - see front matter
PII: S0040-4020(02)01628-9

2.2. (*E*)- and (*Z*)-(4′-pyridylethenyl)-4-phenylethyne (4), by dehydrohalogenation of the halovinylarene derivatives

The synthesis of the conjugate (*E*)- and (*Z*)-(4′-pyridylethenyl)-4-phenylethyne (*E*-**4** and *Z*-**4**) was carried out by dehydrohalogenation of (*E*,*Z*)-**3** and (*E*,*E*)-**3** (X=chloro- or bromo-) with potassium *tert*-butoxide in THF at room temperature and sunlight exposure during 24 h: (*E*,*Z*)-**3** gives (*Z*)-(4′-pyridylethenyl)-4-phenylethyne (*Z*)-**4**, (66%, X=Br); and (*E*,*E*)-**3** gives (*E*)-(4′-pyridylethenyl)-4-phenylethyne, (*E*)-**4** (75%, X=Br). The reaction products and yield in this elimination are temperature dependent.[11] The dehydrohalogenation in toluene, at the reflux temperature, results unsuccessful.

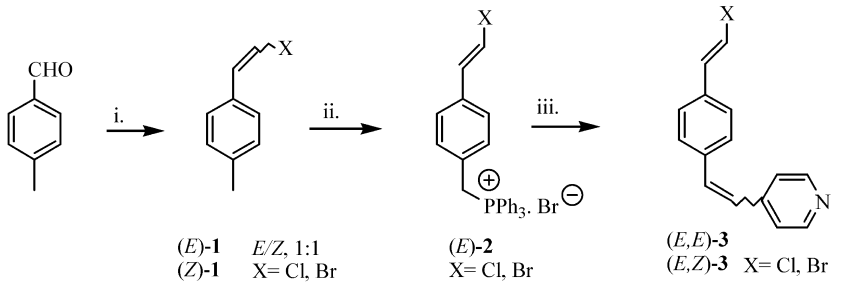
The β-haloethene **3** was obtained starting of *p*-(2′-halovinyl)toluene (**1**), which was prepared by reaction of the halomethylene(triphenyl)phosphine ylide[9,12] (X=Cl or Br) and *p*-tolualdehyde in THF, yielding a *E*/*Z* mixture (1:1) (X=Cl, 61%; X=Br, 52%), Scheme 1. The mixture (*E*/*Z*)-**1** was transformed in the phosphonium salt (*E*)-(β-haloethenyl)-benzyl(triphenyl)phosphonium bromide (*E*)-**2** (X=Cl, Br), by treatment with NBS and a little amount of benzoyl peroxide allowing only to the *E*-isomer of the bromobenzyl derivative in moderate yield. Hence, during the reaction, a complete *Z*→*E* isomerization takes place, probably through an addition–elimination mechanism of the bromine radical.[13] Some amount of the starting product **1** was recovered but also only as the *E*-isomer. The bromobenzyl derivative was transformed in the phosphonium bromide salt *E*-**2** with triphenylphosphine in toluene at the reflux temperature, (X=Cl, Br), in excellent yield. The phosphonium salt (*E*)-**2** permits the preparation in situ of the corresponding ylide with potassium *tert*-butoxide in toluene, which with 4-pyridinecarboxaldehyde gives 4′-(pyridylethenyl)-4-phenyl-β-haloethene (**3**) in good yield, as a mixture of the (*E*,*Z*)-**3** and (*E*,*E*)-**3** isomers: X=Cl, 60:40, 84%; X=Br, 53:47, 63%, Scheme 1.

Compounds **4** show structural evidence of the electronic effect produced by the pyridine ring on the ethylene bridge (^{1}H NMR, (*Z*)-**4**; 6.71 and 6.52 ppm, *J*=12.3 Hz) and (*E*)-**4**; 7.28 and 7.03 ppm, *J*=16.1 Hz). Both isomers exhibit conjugation of the aromatic rings through the double bond but this effect is more relevant in the *E* isomer probably due to steric hindrance of the aromatic rings in the *Z* isomer.

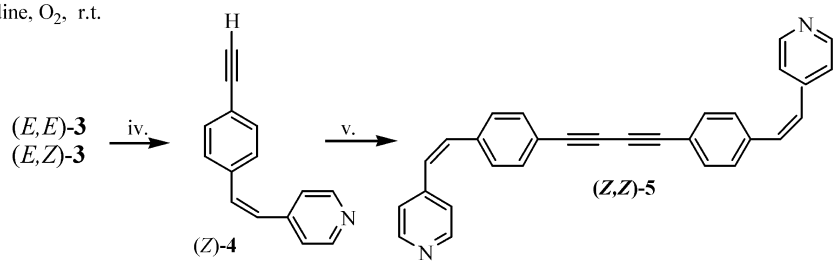
2.2.1. From the appropriate haloarene with 2-methyl-but-3-yn-2-ol catalysed by palladium. Because of the difficulty in the dehydrohalogenation of the halovinyl derivatives **3** in toluene, an alternative synthesis of the stereoisomers of the acetylene **4** has been also outlined. Hence, the heterocoupling reaction between *p*-(iodophenylethenyl)-4-pyridine (*E*-**6** and *Z*-**6**) and 2-methyl-but-3-yn-2-ol, catalysed by palladium, was applied. However, (*E*)-4-[4′-(pyridylethenyl)-4-phenyl]-4-(2-methyl-but-3-yn-2-ol) (**7**) was only obtained from the iodo derivative (*E*/*Z*)-**6**, in good yield (71%); for X=Cl or Br, the cross-coupling reaction was not observed, Scheme 2.

The *E*/*Z* mixture of compound **7** was treated with a catalytic amount of powdered sodium hydroxide, in toluene at reflux temperature, to give (*E*/*Z*)-**4** (1:1) in good yield (70%). Both isomers (*E*)-**4** and (*Z*)-**4** were isolated by chromatographic methods.

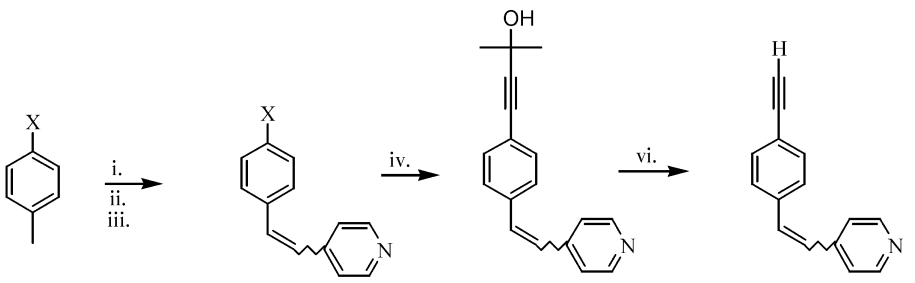
The isomers mixture of the haloarene *E*/*Z*-**6** (1:1) was obtained by the Wittig reaction of the appropriate *p*-halobenzyl(triphenyl)phosphonium ylide, prepared in situ from the corresponding phosphonium salt, and 4-pyridinecarboxaldehyde. The phosphonium salt results in good yield by reaction of the *p*-halotoluene with NBS to give the corresponding *p*-bromomethylhalobenzene, which



i. halomethyl(triphenyl)phosphonium ylide, KOtBu.
ii. NBS/ benzoylperoxide, PPh_3;
iii. KOtBu, 4-pyridinecarboxaldehyde;
iv. KOtBu;
v. Cu_2Cl_2, pyridine, O_2, r.t.



Scheme 1.



i. NBS, benzoylperoxide; ii. PPh_3, toluene;
iii. KOtBu, toluene; 4-pyridinecarboxaldehyde;
iv. 2-methyl-but-3-yn-2-ol, $Cl_2Pd(PPh_3)_2$, Cu_2Cl_2, $HNEt_2$;
v. (E/Z)-7, EtOH, sunligh exposure for 48 h.,
vi. NaOH, toluene.

Scheme 2.

was finally treated with triphenylphosphine in toluene at reflux temperature.

2.3. 1,4-Di[(4-pyridylethenyl)-4-phenyl]-buta-1,3-diyne, (*Z*,*Z*)-5

The conjugate 1,3-butadiyne (*Z*,*Z*)-**5** was purely obtained by oxidative homocoupling of the conjugate acetylene (*Z*)-**4**, catalysed by cuprous chloride in pyridine under oxygen atmosphere,[12] in moderate yield (43%), Scheme 1. (*Z*,*Z*)-**5** was obtained as a white powder stable to the sunlight.

In contrast, the *E*-**4** isomer, under the same Glaser conditions used for *Z*-**4**, or with different bases as diethylamine, piperidine, pyridine or TMEDA, at variable temperatures does not transform to the corresponding 1,3-diyne (*E*,*E*)-**5**.

2.4. Charge–transfer complex between (*Z*,*Z*)-1,4-di[(4-pyridylethenyl)-4-phenyl]-buta-1,3-diyne, (*Z*,*Z*)-5, and tetracyanoethene, TCNE, 8

2.4.1. Donor molecules. The presence of the pyridine ring in the structure invites to the preparation of charge–transfer complex with donor molecules. However, the isolation of a pure charge–transfer complex between (*Z*,*Z*)-1,4-di[(4-pyridylethenyl)-4-phenyl]-buta-1,3-diyne, (*Z*,*Z*)-**5**, with donor molecules such as *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylendiamine (TMPD) results unsuccessful.

2.4.2. Acceptor molecules. In contrast, a charge–transfer complex between (*Z*,*Z*)-**5** and tetracyanoethene (TCNE) as acceptor was obtained by slow addition of a solution of the acceptor in acetonitrile to a solution of the 1,3-diyne (*Z*,*Z*)-**5**, in nearly boiling acetonitrile. The starting yellow solution turned orange and by slow evaporation of the solvent only the charge–transfer complex **8** was isolated as a green solid as little spheres. On the basis of the elemental analysis and spectral data, the acceptor/donor molar ratio (A/D) was 1:1.

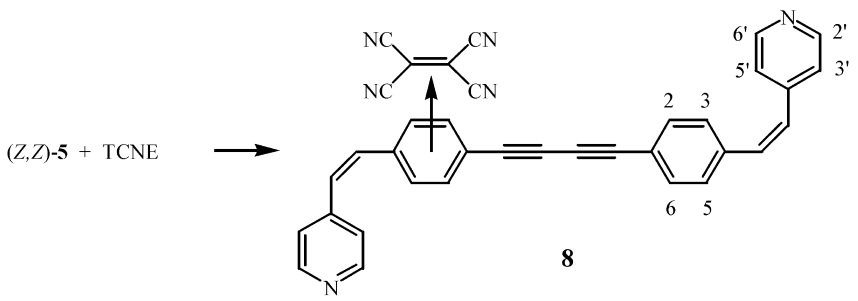
2.4.3. Structure of (*Z*,*Z*)-1,4-di[4-pyridylethenyl)-4-phenyl]-buta-1,3-diyne–TCNE molecular complex. The IR spectrum (KBr) of **8** shows a broad stretching vibration band of C≡N and C≡C bonds at 2200 cm^{-1}, while the free TCNE shows two bands at 2260 and 2220 cm^{-1} and the free 1,3-diyne at 2190 cm^{-1}. The C=C bond of the 1,3-diyne moiety exhibits a new band at 1460 cm^{-1}, which corresponds to the molecular complex. Moreover, the C–H bending vibration of the benzene and pyridine rings and the double bond shows some differences in the frequencies, at 950 and 890 cm^{-1} (830 and 820 cm^{-1} in the free diyne) and at 715 cm^{-1} due to the *Z*-isomer, (750 cm^{-1} in the free diyne).

The ^1H NMR spectrum of complex **8** in acetone-d_6 shows a strong deshielding effect on the pyridine protons pairs H-3′, H-5′ and H-2′, H-6′, diminishing in this order, with respect to the free 1,3-diyne. This effect was also observed with strong intensity on the phenyl proton pairs H-2, H-6 and H-3, H-5 and also on the conjugated vinyl protons of the complex part of the molecule. Moreover, the uncomplexed part also exhibits a deshielding effect on the phenyl and the vinyl protons of the molecule but in very lowest intensity; H-3′, H-5′ and H-2′, H-6′ on the pyridine ring are practically not affected, Table 1. The net deshielding effect for the phenyl protons were not well observed because the grouping of the signals in the spectrum. Hence, the deshielding effect diminishes with the distance to the complex site and is less intense through the 1,3-triple bond conjugation. On the basis of the deshielding effect, the TCNE–(*Z*,*Z*)-**5** binding site must be close to the C3–C5 phenyl bond and the TCNE double bond parallel to the 1,3-diyne axis,[14] Scheme 3.

The UV–visible spectrum of complex **8** shows a new charge–transfer band at 419 nm (ϵ, 655 l mol^{-1} cm^{-1}).

Table 1. ^1H NMR of (*Z*,*Z*)-**5** and the charge–transfer complex **8**

	(*Z*,*Z*)-**5**	Complex ring	Uncomplex ring
H-2′ and H-6′ Py	8.49	9.02	8.49
H-3′ and H-5′ Py	7.13	8.40	7.21
H-2 and H-6 Ph	7.41	7.9–7.4	7.51
H-3 and H-5 Ph	7.19	7.9–7.4	7.31
Py–CH=C*H*	6.75	7.9–7.4	6.90
Py–C*H*=CH	6.55	7.9–7.4	6.71



Scheme 3.

Table 2. ^{1}H NMR of (*Z*,*Z*)-**5** and the charge–transfer complex **9**

	(*Z*,*Z*)-**5**	Complex **9**
H-2′ and H-6′ Py	8.49	8.68
H-3′ and H-5′ Py	7.13	7.82–7.42
H-2 and H-6 Ph	7.41	7.82–7.42
H-3 and H-5 Ph	7.19	7.82–7.42
Py–CH=C*H*	6.75	6.95
Py–C*H*=CH	6.55	6.87

2.5. Complex between (*Z*,*Z*)-1,4-di[(4-pyridylethenyl)-4-phenyl]-buta-1,3-diyne, (*Z*,*Z*)-5, and 7,7′,8,8′-tetracyanoquinodimethane, TCNQ, 9

Some charge–transfer complexes between conjugated systems and the acceptor TCNQ showing conductive properties are ready known.[15]

The charge–transfer complex between (*Z*,*Z*)-**5**, and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) was prepared by slow addition of a solution of the acceptor in acetonitrile to a solution of the 1,3-butadiyne in nearly boiling acetonitrile giving **9** as a green solid after complete evaporation of the solvent. On the basis of the elemental analysis and the spectral data, the A/D molar ratio of the complex was 2:1.

The IR spectrum (KBr) of the complex **9** shows a broad stretching vibration band of C≡N and C≡C bonds at 2150 cm^{-1}, while the free TCNQ shows a band at 2210 cm^{-1} and the free diyne at 2190 cm^{-1}. The C–H bending vibration due to the phenyl substitution appears at 810 cm^{-1} (830 and 820 cm^{-1} in the free diyne) and at 705 cm^{-1} due to the *Z*-isomer (750 cm^{-1} in the free diyne).

The ^{1}H NMR spectrum in DMSO-d_6 of the complex **9** shows a strong deshielding effect on the pyridine and phenyl protons of the conjugate 1,3-diyne part with respect to the free diyne (*Z*,*Z*)-**5**, Table 2. The net deshielding effect on each proton was not well observed because the grouping of the signals of the phenyl ring. However, the double bond is polarised towards the phenyl ring due to the electron demand of the acceptor molecule on the phenyl ring, Table 2.

On the basis of the deshielding effect, the TCNQ–(*Z*,*Z*)-**5** binding site must be close to the C3–C5 phenyl bond and TCNQ the double bonds orthogonal to the 1,3-diyne axis, Scheme 4.

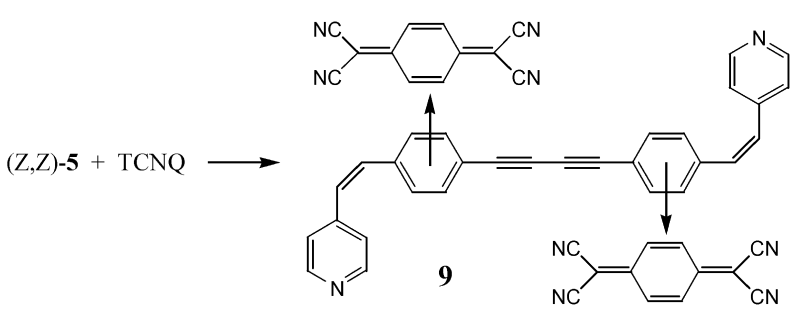
The UV–visible spectrum of the complex **9** shows a new absorption band at 506 nm (ε, 710 l mol^{-1} cm^{-1}).

2.6. Quaternation of the pyridine ring

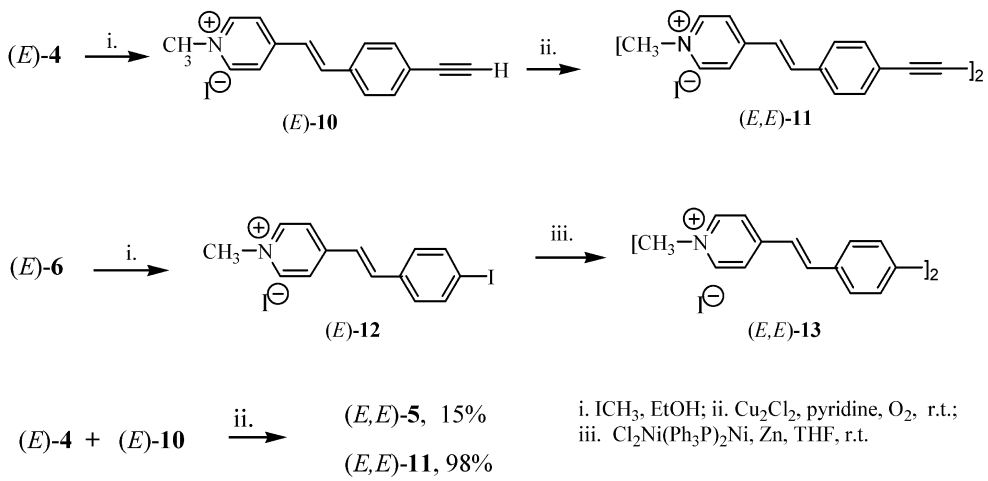
2.6.1. Methyl quaternation of (*E*)-4. Preparation of (*E*)-10 and dimerisation to (*E*,*E*)-11. The π-electronic effect of the pyridine rings and the π-extended conjugation to the 1,3-diyne chain, in 1,4-di(*n*-pyridyl)-buta-1,3-diyne derivatives, seems not sufficient to prepare charge–transfer complexes with some donors. In contrast, we reported that the mono- and di-methylated salts of the 1,4-di(*m*-pyridyl)-buta-1,3-diyne gives a charge–transfer complex with the donor molecule *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD).[15b]

Moreover, a plus extended π-conjugated family compounds containing the pyridine and phenyl rings are now prepared and charge–transfer complexes with acceptor and donor molecules investigated.

Compound *E*-**10** was obtained by quaternation of *E*-**4** with iodomethane in ethanol at 70–75°C in good yield. The salt *E*-**10** was transformed in the dimer (*E*,*E*)-**11** in excellent



Scheme 4.



Scheme 5.

yield (98%), by oxidative homocoupling in presence of cuprous chloride in pyridine, Scheme 5. However, the preparation of (*E*,*E*)-**5** under the same conditions results unsuccessful. An argument about the different behaviour, found in the oxidative coupling of (*Z*)-**4** and (*E*)-**4** isomers, can be due to the deactivation of the copper(I) catalyst by coordination with the N-electron pair of the pyridine ring, more effective for the (*E*)-isomer. To prove this premise, the coupling reaction of (*E*)-**4** was carried out in presence of the salt (*E*)-**10**, in 0.5 molar ratio giving the mixture (*E*,*E*)-**5** (yellow solid, mp 113–115°C) and the disalt (*E*,*E*)-**11** (brown solid, mp 158–159°C), in 15 and 98%, respectively; the mono-salt was not detected. Hence, on the basis of the stoichiometry of the reaction, a plausible interpretation of this fact must be related to the enhanced transfer phase produced by the salt *E*-**10**. Moreover, a Cu(I)/Cu(III) redox pair mechanism for the oxidative dimerisation of the acetylenes has been recently reported.[16]

2.6.2. Methyl quaternation of (*E*)-6. Preparation of (*E*)-12 and dimerisation to (*E*,*E*)-13. The saline compound (*E*)-**12** was isolated by quaternation of *E*-**6** with iodomethane in ethanol at the reflux temperature, as a yellow solid, in excellent yield (92%). The salt *E*-**12** yields the homocoupling biphenyl salt (*EE*)-**13**, in the presence of zero-valent nickel complexes, prepared in situ, with dichlorobis(triphenyl)phosphine nickel (II) in THF and zinc powder, in good yield (68%), as a yellow solid, Scheme 5. In contrast, the synthesis of the non-saline biphenyl derivative starting of *E*-**6**, under the same method was unsuccessful.

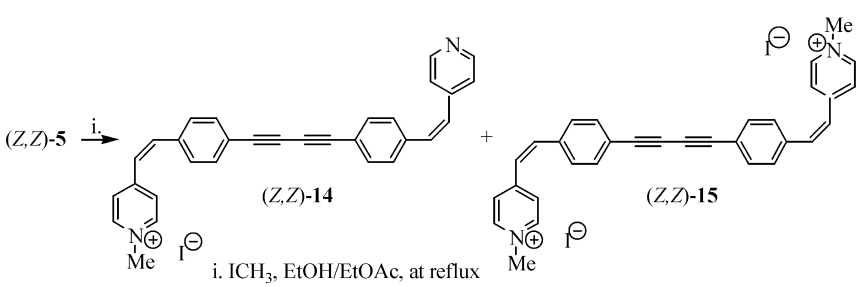
2.6.3. Mono- and di-methylated salts of (*Z*,*Z*)-1,4-di[(4-pyridylethenyl)-4-phenyl]-buta-1,3-diyne, (*Z*,*Z*)-5, (*Z*,*Z*)-14 and (*Z*,*Z*)-15. The 1,3-butadiyne (*Z*,*Z*)-**5** shows some difficulty to form charge–transfer complexes with some acceptors as TMPD. The quaternation of the nitrogen atom of the pyridine rings was outlined to increase the acceptor character of the compound, Scheme 6.[15b]

The methylated salts of the 1,3-diyne (*Z*,*Z*)-**5**, were obtained by treatment with iodomethane in a mixture of ethanol/ethyl acetate as solvent at reflux temperature. Two products were isolated as solids in a 1:1 ratio (94% of yield); an orange solid partially soluble in ethanol (*Z*,*Z*)-**14** identified as the mono- and an insoluble yellow solid (*Z*,*Z*)-**15** as the di-methylated salt.

By DSC, both (*Z*,*Z*)-**14** and (*Z*,*Z*)-**15** exhibit an irreversible endothermic peak up to 125°C which corresponds with the decomposition of the respective compound.

In the IR spectrum (KBr) the mono- (*Z*,*Z*)-**14** and di-methylated salt (*Z*,*Z*)-**15** exhibit two characteristic bands of the CH_3-N bond at 1330, 1185 and 1320, 1180 cm^{-1}, respectively. The stretching frequencies C=C and C=N and the bending C–H phenyl and pyridine show important differences with the free diyne (*Z*,*Z*)-**5** (see Section 3).

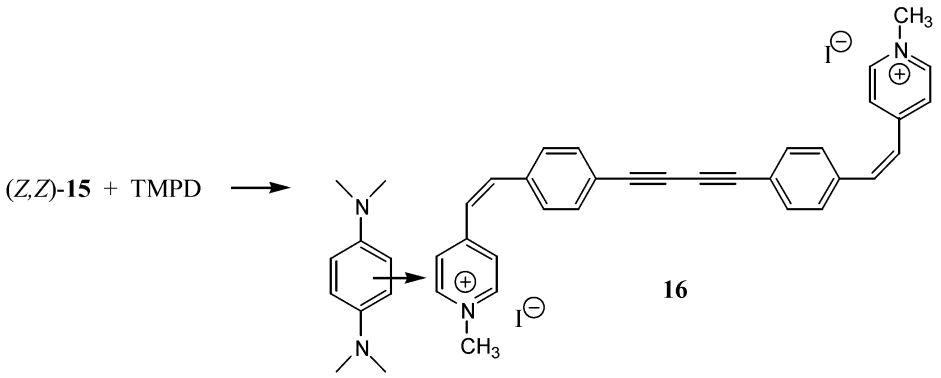
The ^1H NMR spectrum of the mono-salt (*Z*,*Z*)-**14** in methanol-d_4, shows a strong deshielding effect on the protons of N-methylated pyridine, double bond and phenyl ring in this order of intensity, by reference with diyne



Scheme 6.

Table 3. ^{1}H NMR of (*Z*,*Z*)-**5**, and the saline compounds (*Z*,*Z*)-**14** and (*Z*,*Z*)-**15**

	(*Z*,*Z*)-**5**	(*Z*,*Z*)-**14** Saline moiety	(*Z*,*Z*)-**14** Non-saline moiety	(*Z*,*Z*)-**15**
H-2′ and H-6′ Py	8.49	8.91	8.46	8.78
H-3′ and H-5′ Py	7.13	7.99	7.19	7.83
H-2 and H-6 Ph	7.41	7.54	7.49	7.57
H-3 and H-5 Ph	7.19	7.39	7.30	7.34
Py–CH=C*H*	6.75	7.40	6.89	7.23
Py–C*H*=CH	6.55	6.97	6.78	6.89



Scheme 7.

(*Z*,*Z*)-**5**. In contrast, in the non-saline moiety the deshielding effect through the diyne conjugation is significant in the phenyl and double bond protons but pyridine protons are practically unperturbed. The *N*-methyl salt protons appear as a singlet at 4.50 ppm.

The ^{1}H NMR spectrum of the di-N-methylated salt (*Z*,*Z*)-**15** in DMSO-d_6, shows a strong deshielding effect on all the protons of the conjugate system but in slightly lowest intensity than the saline moiety of the mono-methylated salt, Table 3. The *N*-methyl protons appear at 4.28 ppm.

2.7. Charge–transfer complex between (*Z*,*Z*)-15 and *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD), 16

The charge–transfer complex **16** was prepared by addition of TMPD acetone solution into a (*Z*,*Z*)-**15** acetone/water solution by slow evaporation. Complex **16** was isolated as a blue–black solid with metallic shine. On the basis of the elemental analysis and spectral data, the A/D molar ratio was 1:1.

The IR spectrum (KBr) of the complex **16** shows a broad C=N and C=C stretching band at 1610, 1590, 1540, 1510 and 1460 cm^{-1}. The N^+–CH_3 bond shows two absorption bands at 1185 and 1170 cm^{-1} (Scheme 7).

The ^{1}H NMR spectrum of complex **16** in DMSO-d_6 exhibits a strong shielding effect on the pyridinium ring, and double bond protons of the 1,3-diyne derivative. The phenyl protons appear within a multiplet at 7.4–7.9 ppm but the net effect of each proton was not well observed, Table 4. In contrast, the uncomplexed ring moiety shows a deshielding effect with respect to the free dimethylated salt (*Z*,*Z*)-**15**.

In the DSC diagram of **16** was observed a broad irreversible endothermic peak up to 125°C, which coincides with the decomposition of the compound (*Z*,*Z*)-**15**.

In the UV–visible spectrum of complex **16**, were observed two bands at 533 (ε, 660) and 639 nm (ε, 905 l mol^{-1} cm^{-1}), probably due to the two different electronic transfer absorption band, which from the ^{1}H NMR spectrum, show a symmetric overlapping of the donor molecule on the pyridinium salt.

2.8. Charge–transfer complex between the di-salt (*Z*,*Z*)-15 and TCNQ, 17

The charge–transfer complex between the di-salt (*Z*,*Z*)-**15** and TCNQ was obtained by slow addition of a solution of TCNQ in hot acetonitrile to a solution of the salt (*Z*,*Z*)-**15** in hot acetonitrile and after complete evaporation of solvent, the complex **17**, was isolated as a black-green solid with metallic shine.

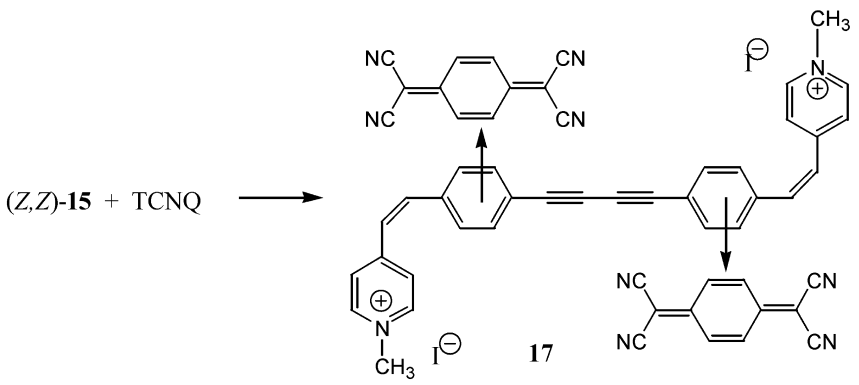
The IR spectrum (KBr) of the complex **17** shows a broad C=N and C=C stretching vibration band at 1610, 1590,

Table 4. ^{1}H NMR of (*Z*,*Z*)-**15**, and charge–transfer complex **16**

	(*Z*,*Z*)-**15**	**16**, Complexed ring	**16**, Uncomplexed ring
H-2′ and H-6′ Py	8.78	8.25	8.90
H-3′ and H-5′ Py	7.83	7.9–7.4	8.05
H-2 and H-6 Ph	7.57	7.9–7.4	7.9–7.4
H-3 and H-5 Ph	7.34	7.9–7.4	7.9–7.4
Py–CH=C*H*	7.23	6.90	7.36
Py–C*H*=CH	6.89	6.72	7.22

Table 5. ^{1}H NMR of (*Z*,*Z*)-**15**, and charge–transfer complex **17**

	(*Z*,*Z*)-**15**	Complex **17**
H-2′ and H-6′ Py	8.78	8.90
H-3′ and H-5′ Py	7.83	8.25
H-2 and H-6 Ph	7.57	7.9–7.5
H-3 and H-5 Ph	7.34	7.9–7.5
Py–CH=C*H*	7.23	7.39
Py–C*H*=CH	6.89	7.08



Scheme 8.

1540, 1510 and 1460 cm^{-1}. The $N^{+}-CH_3$ bond show two absorption bands at 1185 and 1170 cm^{-1}.

The ^1H NMR spectrum of **17** in DMSO-d_6 shows a strong general deshielding effect on the protons with respect to the free di-salt (*Z*,*Z*)-**15**, Table 5.

On the basis of the elemental analysis and the spectral data, was determined a stoichiometric ratio of 2:1 of the components, Scheme 8.

The DSC diagram of **17** shows an irreversible broad exothermic peak (160–225°C) corresponding to the decomposition of the complex, but no melting peaks of the components were detected.

In the UV–visible spectrum of the complex **17**, was observed a weak band at 644 nm (ε, 780 l mol^{-1} cm^{-1}) due to the electronic transfer absorption band.

3. Experimental

Melting points were determined in open capillary tubes or in a Reichert hot stage microscope and are uncorrected. Infrared spectra were recorded using a Bruker Vector 22 spectrophotometer. NMR spectra were recorded at 200 or 300 MHz using a Bruker Aspect spectrometer. Chemical shifts are given in ppm, using TMS as internal reference. UV–visible spectra were recorded using a Hewlett–Packard 8453 spectrophotometer. Mass spectra were recorded using electronic impact technique at 70 eV, in a VG AutoSpec spectrometer. The DSC analyses were carried out in a Perkin–Elmer calorimeter. Elemental analyses were performed with a LECO CHN-600. All solvents and chemicals were reagent grade.

3.1. (*E*)- and (*Z*)-(4′-pyridylethenyl)-4-phenylethyne (4), by dehydrohalogenation of the halovinylarene derivatives

3.1.1. *p*-(2-Bromoethenyl)toluene, 1. A solution of triphenylphosphine (60 g, 228 mmol) and dibromomethane (89.2 g, 460 mmol) in dry toluene (500 ml) was warmed at the reflux temperature for 24 h. The mixture was cooled at 0°C and the precipitated of bromomethyl(triphenyl)-phosphonium bromide was filtered and washed with toluene. The filtered solution was warmed at the reflux temperature for 24 h, giving a new precipitate of the phosphonium salt. The precipitate fractions were finally dried at reduced pressure giving the phosphonium salt as a white solid, 77.4 g. (75%), mp 238–240°C (lit.[9] 241–242°C).

Wittig reaction between bromomethyl(triphenyl)phosphonium ylide and 4-methylbenzaldehyde. To a solution of bromomethyl(triphenyl)phosphonium bromide (18.69 g, 42.88 mmol) in dry THF (100 ml), under argon atmosphere at 0°C, was added potassium *tert*-butoxide (5.23 g, 42.88 mmol). The yellow solution was stirred for 30 min and then was slowly added 4-methylbenzaldehyde (5.15 g, 42.88 mmol) and stirred at room temperature for 6 h. After, solvent was removed and the residual oil was washed with water (30 ml) and extracted with dichloromethane, dried on magnesium sulfate, filtered and solvent removed giving an oil which was purified by silica gel column chromatography (hexane/dichloromethane, 4:1). The *p*-(2-bromoethenyl)-toluene (**1**) was obtained, (4.32 g, 52%), as a yellow oil as an *E*/*Z* isomer mixture (1:1, by NMR).

(*E*)-*p*-(2-*Bromoethenyl*)*toluene*, (*E*)-**1**. IR (film): 2920 and 2860 (C–H); 1620 and 1520 (C=C, conj.); 950 (CH=CHBr, *E*); 820 and 805 (*p*-disubst.). ^1H NMR ($CDCl_3$): 7.7–7.1 (m, 4H, Ar); 7.05 (d, 1H, *J*=14.0 Hz, C*H*=CHBr, *E*); 6.65 (d, 1H, *J*=14.0 Hz, CH=C*H*Br, *E*); 2.33 (s, 3H, CH_3). Calcd for C_9H_9Cl: C, 70.83; H, 5.94; N, 23.23. Found: C, 70.66; H, 6.24; N, 23.07%.

(*Z*)-*p*-(2-*Bromoethenyl*)*toluene*, (*Z*)-**1**. IR (film): 2920 and 2860 (C–H); 1620 and 1520 (C=C, conj.); 820 and 805 (*p*-disubst.); 720 (CH=CHBr, *Z*). ^1H NMR ($CDCl_3$): 7.7–7.1 (m, 4H, Ar); 7.00 (d, 1H, *J*=8.2 Hz, C*H*=CHBr, *Z*); 6.32 (d, 1H, *J*=8.2 Hz, CH=C*H*Br, *Z*); 2.35 (s, 3H, CH_3). Calcd for C_9H_9Cl: C, 70.83; H, 5.94; N, 23.23. Found: C, 70.52; H, 5.75; N, 23.12%.

3.1.2. *p*-(2-Bromoethenyl)benzyl(triphenyl)phosphonium bromide, 2. *p*-(2-*Bromoethenyl*)*bromomethylbenzene*. To a solution of (*E*/*Z*)-*p*-(2-bromoethenyl)toluene (**1**) (4.2 g, 21.33 mmol) in tetrachloromethane (10 ml), was added *N*-bromosuccinimide (3.39 g, 19.04 mmol) and benzoyl peroxide (100 mg). The mixture was warmed at the reflux temperature for 16 h and after cooling, was filtered and solvent removed, giving a residual oil that was

purified by pressurised silica gel column chromatography (hexane/toluene, 16:1). The (*E*)-*p*-(2-bromoethenyl)bromomethylbenzene was isolated, as a yellow oil, 2.95 g (56%); the starting product was recovered as the *E* isomer (**1**) and reused, 1.68 g (40%). ^{1}H NMR ($CDCl_3$): 7.7–7.1 (m, 4H, Ar); 7.07 (d, 1H, *J*=13.8 Hz, C*H*=CHBr, *E*); 6.77 (d, 1H, *J*=13.8 Hz, CH=C*H*Br, *E*); 4.45 (s, 2H, CH_2).

p-(2-*Bromoethenyl*)*benzyl*(*triphenyl*)*phosphonium bromide*, **2**. A solution of triphenylphosphine (2.8 g, 10.68 mmol) and *p*-(2-bromoethenyl)bromomethylbenzene (2.95 g, 10.68 mmol) in dry toluene (60 ml), was warmed at the reflux temperature for 12 h. After, the mixture was cooled and the precipitated phosphonium salt **2**, was filtered and dried at vacuum, giving a white solid, 5.27 g (92%), mp 213–216°C.

3.1.3. (*E*,*E*)-(4′-Pyridylethenyl)-4-phenyl-β-bromoethene, 3. To a suspension of the phosphonium salt **2** (X=Cl, Br) (9.8 mmol) in dry toluene (10 ml), at 0°C was added potassium *tert*-butoxide (1.19 g, 9.8 mmol) and stirred for 30 min. Then, pyridine-4-carboxaldehyde (1.05 g, 9.8 mmol), was added and stirred at room temperature for 4 h. Finally, solvent was removed at reduced pressure and the residual oil was washed with water (10 ml) and extracted with dichloromethane. After, solvent was removed and the residual oil was purified by silica gel column chromatography (hexane/THF, 1:1). Compound **3** was isolated as a mixture of isomers, (*E*,*E*)-(4′-pyridylethenyl)-4-phenyl-β-bromoethene, 0.82 g (30%), yellow solid, mp 117–120°C and (*E*,*Z*)-(4′-pyridylethenyl)-4-phenyl-β-bromoethene, 0.92 g (33%), as a yellow oil.

(*E*,*E*)-(4′-*Pyridylethenyl*)-4-*phenyl*-β-*bromoethene*, (*E*,*E*)-**3**. IR (KBr): 1590 (Py); 1550 (C=C, conj.); 990 (Py); 970 (CH=CHBr, *E*); 955 (CH=CH, *E*); 830 (*p*-disubst.). ^{1}H NMR ($CDCl_3$): 8.59 (d, 2H, H-2 and H-6, Py); 7.8–6.8 (m, 6H, Ar); within of the multiplet was identified at 7.28 (d, 1H, *J*=16.1 Hz, Py–CH=C*H*, *E*); 7.03 (d, 1H, *J*=16.1 Hz, Py–C*H*=CH, *E*); 7.04 (d, 1H, *J*=14.0 Hz, C*H*=CHBr, *E*); 6.83 (d, 1H, *J*=14.0 Hz, CH=C*H*Br, *E*). ^{13}C NMR ($CDCl_3$): 150.0 (C-2 and C-6, Py); 144.4 (C-4, Py); 136.6 (*C*H=CHBr); 136.1 (C-4, Ph); 132.1 (C-1, Ph); 128.7 (C-2 and C-6, Ph); 127.3 (*C*H=CH); 126.8 (C-3 and C-5, Ph); 126.4 (*C*H=CH); 120.7 (C-3 and C-5, Py); 107.1 (CH=*C*HBr). MS (70 eV): 287 (M^++2, 61); 285 (M^+, 66); 204 (100); 176 (36); 151 (26); 126 (15); 102 (61); 76 (43).

(*E*,*Z*)-(4′-*Pyridylethenyl*)-4-*phenyl*-β-*bromoethene*, (*E*,*Z*)-**3**. IR (film): 3020 (=C–H); 1590 (Py); 1565 (C=C, conj.); 970 (CH=CHBr, *E*); 840 (*p*-disubst.); 710 (CH=CH, *Z*). ^{1}H NMR ($CDCl_3$): 8.46 (d, 2H, *J*=5.7 Hz, H-2 and H-6, Py); 7.43 (d, 2H, *J*=8.4 Hz, H-2 and H-6, Ph); 7.19 (d, 2H, *J*=8.4 Hz, H-3 and H-5, Ph); 7.09 (d, 2H, *J*=5.7 Hz, H-3 and H-5, Py); 7.03 (d, 1H, *J*=14.0 Hz, C*H*=CHBr, *E*); 6.75 (d, 1H, *J*=14.0 Hz, CH=C*H*Br, *E*); 6.71 (d, 1H, *J*=12.3 Hz, Py–CH=C*H*, *Z*); 6.52 (d, 1H, *J*=12.3 Hz, Py–C*H*=CH, *Z*). ^{13}C NMR ($CDCl_3$): 149.7 (2C, C-2 and C-6, Py); 144.7 (C-4, Py); 136.3 (*C*H=CHBr); 136.1 (C-4, Ph); 131.8 (C-1, Ph); 129.1 (*C*H=CH); 128.7 (C-2 and C-6, Ph); 128.3 (C-3 and C-5, Ph); 127.7 (*C*H=CH); 123.2 (C-3 and C-5, Py); 107.0 (CH=*C*HBr). MS (70 eV): 287 (M^++2, 57); 285 (M^+, 59); 204 (100); 176 (42); 151 (29); 126 (12); 102 (65); 76 (38).

3.1.4. (*E*) and (*Z*)-(4′-Pyridylethenyl)-4-phenylethyne, 4. (*Z*)-(4′-*Pyridylethenyl*)-4-*phenylethyne* (*Z*-**4**). To a solution of (*E*,*Z*)-(4′-pyridylethenyl)-4-phenyl-β-bromoethene, (*E*,*Z*)-**3**, (0.38 g, 1.34 mmol) in dry THF (10 ml), at 0°C was added potassium *tert*-butoxide (0.16 g, 1.34 mmol). The mixture was stirred under sunlight exposure at room temperature for 24 h and then was hydrolysed with a saturated solution of ammonium chloride and extracted with dichloromethane. The organic layer was dried on magnesium sulfate, filtered and solvent removed to give a residual brown oil, which was purified by silica gel column chromatography (THF/hexane, 2:1). (*Z*)-(4′-pyridylethenyl)-4-phenylethyne (*Z*-**4**), was obtained as a yellow oil, 180 mg (66%). IR (film): 3290 (≡CH); 2260 (C≡C); 1590 (Py); 1540 (C=C, conj.); 990 (Py); 830 (*p*-disubst.); 720 (CH=CH, *Z*). ^{1}H NMR ($CDCl_3$): 8.46 (d, 2H, *J*=5.2 Hz, H-2 and H-6, Py); 7.31 (d, 2H, *J*=8.2 Hz, H-2 and H-6, Ph); 7.12 (d, 2H, *J*=8.2 Hz, H-3 and H-5, Ph); 7.09 (d, 2H, *J*=5.2 Hz, H-3 and H-5, Py); 6.72 (d, 1H, *J*=12.2 Hz, Py–CH=C*H*, *Z*); 6.51 (d, 1H, *J*=12.2 Hz, Py–C*H*=CH, *Z*); 3.12 (s, 1H, ≡CH). ^{13}C NMR ($CDCl_3$): 149.5 (C-2 and C-6, Py); 144.7 (C-4, Py); 136.3 (C-1, Ph); 133.0 and 131.9 (C-2 and C-6, Ph); 128.6 and 128.2 (C-3 and C-5, Ph); 125.4 (2C, CH=CH); 123.4 (C-3 and C-5, Py); 120.8 (C-1, Ph); 80.0 (Ph–*C*≡CH); 77.1 (Ph–C≡*C*H). MS (70 eV): 205 (M^+, 95); 204 (100); 176 (31); 151 (13); 126 (11); 102 (12); 76 (17). Calcd for $C_{15}H_{11}N$: C, 87.78; H, 5.40; N, 6.82. Found: C, 87.49; H, 5.38; N, 6.52%.

(*E*)-(4′-*Pyridylethenyl*)-4-*phenylethyne* (*E*-**4**). To a solution of (*E*,*E*)-(4′-pyridylethenyl)-4-phenyl-β-chloroethene (0.2 g, 0.699 mmol) in dry THF, at 0°C was added potassium *tert*-butoxide (85 mg, 0.699 mmol). The mixture was stirred under sunlight exposure at room temperature for 24 h and then, hydrolysed with a saturated solution of ammonium chloride and extracted with dichloromethane. The organic layer was dried on magnesium sulfate, filtered and solvent removed to give a residual brown oil, which was purified by silica gel column chromatography (THF/hexane, 2:1). The (*E*)-(4′-pyridylethenyl)-4-phenylethyne (*E*-**4**), was isolated, 108 mg (75%), as a yellow solid, mp 187–190°C. IR (KBr): 1630 (C=N); 1590, 1530 and 1490 (C=C); 995 (Py), 950 (*E*-isomer); 830 (*p*-subst. ArH). ^{1}H NMR ($CDCl_3$): 8.58 (d, 2H, *J*=6.8 Hz, H-3 and H-5 Py); 7.50 (s, 4H, Ph); 7.35 (d, 2H, *J*=6.8 Hz, H-2 and H-6 Py); 7.25 (d, 1H, *J*=16.3 Hz, PhCH=); 7.02 (d, 1H, *J*=16.3 Hz, PyCH=); 3.20 (s, 1H, C≡CH). ^{13}C NMR ($CDCl_3$): 149.8 (C3, C5, Py); 144.0 (C1, Py); 136.2 (C1, Ph); 132.3 (C3, C5, Ph); 131.9 and 126.8 (CH=CH); 126.7 (C2, C6, Ph); 122.0 (C4, Ph); 120.7 (C2, C6, Py); 83.2 (–C≡); 78.5 (≡CH). MS (70 eV): 205 (M^+, 98); 204 (100); 180 (7); 176 (27); 151 (16); 126 (9); 102 (21); 76 (16). UV–visible (CH_2Cl_2): 233 (ε, 5833); 299 (ε, 7035); 456 (ε, 11). Calcd for $C_{15}H_{11}N$: C, 87.78; H, 5.40; N, 6.82. Found: C, 87.58; H, 5.23; N, 6.66%.

3.2. From the appropriate haloarene with 2-methyl-but-3-yn-2-ol catalysed by palladium

3.2.1. (*E* and *Z*)-1-(*p*-iodophenyl)-2-(4-pyridyl)ethene, 6. 4-(*Bromomethyl*) *iodobenzene*. To a solution of 4-iodotoluene (5.0 g, 22.9 mmol) in tetrachloromethane (10 ml), was added *N*-bromosuccinimide (3.73 g, 20.0 mmol) and

benzoyl peroxide (30 mg) and the mixture was warmed at the reflux temperature for 16 h. After cooling, the mixture was filtered and the solvent removed providing a residual oil, which was purified by pressurised silica gel column chromatography (hexane/dichloromethane, 5:1). The *p*-(bromomethyl)iodobenzene was isolated, as a white–rose solid, 4.76 g (70%), mp 63–65°C. ^{1}H NMR ($CDCl_3$): 7.68 (d, 2H, *J*=8.7 Hz, H-2 and H-6); 7.10 (d, 2H, *J*=8.7 Hz, H-3 and H-5); 4.45 (s, 2H, CH_2).

4-*Iodobenzyl*(*triphenyl*)*phosphonium bromide*. A solution of triphenylphosphine (3 g, 11.5 mmol) and 4-(bromomethyl)iodobenzene, (2.25 g, 11.5 mmol) in dry toluene (40 ml), was warmed at reflux temperature for 12 h. After cooling, the precipitate of phosphonium salt was filtered and dried at reduced pressure. The 4-iodobenzyltriphenylphosphonium bromide was obtained as a white solid, 3.33 g (78%), mp 255–256°C.

Wittig reaction between 4-*iodobenzyl*(*triphenyl*)*phosphonium ylide and pyridine*-4-*carboxaldehyde*, **6**. To a solution of 4-iodobenzyltriphenylphosphonium bromide (2.52 g, 4.8 mmol) in dry toluene (10 ml), under argon atmosphere at 0°C, was added potassium *tert*-butoxide (0.54 g, 4.8 mmol). The orange solution was stirred for 30 min and then 4-pyridinecarboxaldehyde (0.46 ml, 4.8 mmol) was slowly added. The mixture was stirred at room temperature for 12 h and after, solvent was removed and the residual oil was washed with water (10 ml) and extracted with dichloromethane, dried on magnesium sulfate. After, the mixture was filtered and solvent removed giving a solid, which was purified by pressurized silica gel column chromatography (hexane/THF, 2:3). The 1-(*p*-iodophenyl)-2-(4-pyridyl)ethene, (**6**) was obtained as a yellow solid, 1.1 g (79%), as a mixture of the *E*/*Z* isomers (10:1), by NMR. A solution of the mixture of isomers in ethanol was completely transformed to (*E*)-1-(*p*-iodophenyl)-2-(4-pyridyl)ethene, by sunlight exposure for 48 h. Compound (*E*)-**6** was purely isolated as a yellow solid, mp 194–197°C, 1.1 g (80%). IR (KBr): 3040 (ArC–H); 1625 (C=N); 1590 and 1475 (C=C, conj.); 1065 (C-I); 990 (CH=CH, *E*); 815 (*p*-disubst.); 745 (CH=CH, *Z*). ^{1}H NMR ($CDCl_3$): 8.58 (d, 2H, *J*=6.8 Hz, H-3 and H-5 Py); 7.71 (d, 2H, *J*=8.4 Hz, H3 and H-5 Ph); 7.35 (d, 2H, *J*=6.8 Hz, H-2 and H-6 and H-6 Py); 7.30 (d, 2H, *J*=8.4 Hz, H-2 and H-6 and H-6 Ph); 7.22 (d, 1H, *J*=16.3 Hz, PhCH=); 7.00 (d, 1H, *J*=16.3 Hz, PyCH=). ^{13}C NMR ($CDCl_3$): 150.2 (C3, C5, Py); 144.1 (C1, Py); 137.9 (C3, C5, Ph); 135.6 (C1, Ph); 132.1 and 131.9 (CH=CH); 126.7 (C2, C6, Ph); 120.7 (C2, C6, Py); 94.3 (C–I). Calcd for $C_{13}H_{10}NI$: C, 50.84; H, 3.28; N, 4.56. Found: C, 51.18; H, 3.43; N, 4.65%.

3.2.2. (*E*)-4-[4′-(Pyridylethenyl)-4-phenyl]-4-(2-methyl-but-3-yn-2-ol (7), (*E*)-7. To a solution of 2-(4-iodophenyl)-1-(4-pyridyl)ethene (180 mg, 0.58 mmol) and 2-methyl-but-3-yn-2-ol (58 mg, 0.69 mmol) in freshly distilled diethylamine (7 ml), under argon atmosphere was added dichlorobis(triphenyl)phosphine palladium (4.1 mg) and a little amount of cuprous iodide. The mixture was stirred at room temperature for 15 h. After, diethylamine was removed at reduced pressure and the residual solid was washed with water (10 ml) and extracted with dichloromethane. The organic layer was dried on magnesium sulfate, filtered and solvent removed giving a brown solid that was purified by silica gel column chromatography (hexane/THF, 4:1). The (*E*)-4-[4′-(pyridylethenyl)-4-phenyl]-4-(2-methyl-but-3-yn-2-ol (**7**), (*E*-**7**), was obtained, 110 mg (71%), as a white solid, mp 165–167°C. ^{1}H NMR ($CDCl_3$): 8.50 (d, 2H, *J*=6.8 Hz, H3 Py); 7.657.45 (m, 6H, ArH and H2 Py); 7.52 (d, *J*=16.3 Hz, CH=); 7.21 (d, *J*=16.3 Hz, CH=); 1.60 (s, 6H, CH_3); 1.20 (broad s, 1H, OH). MS (70 eV): 263 (M^+, 69); 262 (41); 248 (100); 205 (18); 204 (29); 180 (10).

3.2.3. (*E*)-(4′-Pyridylethenyl)-4-phenyl)ethyne, (*E*)-4. A solution of the propargylic derivative (*E*)-**7** (110 mg, 0.42 mmol) in dry toluene (5 ml) was heated under reflux temperature with a little amount of pulverised sodium hydroxide for 2 h. Then, the solution was decanted and the solvent was evaporated under reduced pressure giving a brown residual solid that was purified by silica gel column chromatography (hexane/THF, 4:1). The ((*E*)-(4′-pyridylethenyl)-4-phenyl)ethyne, *E*-**4**), was obtained as a yellow solid, 60 mg (70%), mp 187–189°C. Spectral data are given above.

3.2.4. (*Z*,*Z*)-1,4-Di[(4-pyridylethenyl)-4-phenyl]-buta-1,3-diyne, (*Z*,*Z*)-5. To a dispersion of Cu_2Cl_2 (116 mg, 1.17 mmol) in dry pyridine (4 ml), under oxygen atmosphere, was added a solution of (*Z*)-**4** (240 mg, 1.17 mmol) in pyridine (6 ml). The mixture was stirred overnight and after pyridine was removed. The residual solid was purified by silica gel column chromatography (THF/hexane, 3:2) giving the 1,3-diyne (*Z*,*Z*)-**5** as a yellow solid, which was crystallised from ethanol to provide a white solid, 102 mg (43%), mp 200–202°C. IR (KBr): 2190 (C≡C); 1590, 1540 and 1495 (C=C, conj.); 990 (subst. Py); 830 and 820 (*p*-disubst.); 750 (CH=CH, *Z*). ^{1}H NMR ($CDCl_3$): 8.49 (d, 4H, *J*=5.9 Hz, H-2 and H-6 Py); 7.41 (d, 4H, *J*=8.2 Hz, H-2 and H-6 Ph); 7.19 (d, 4H, *J*=8.2 Hz, H-3 and H-5 Ph); 7.13 (d, 4H, *J*=5.9 Hz, H-3 and H-5 Py); 6.75 (d, 2H, *J*=12.7 Hz, Py–CH=C*H*, *Z*); 6.55 (d, 2H, *J*=12.7 Hz, Py–C*H*=CH, *Z*). ^{13}C NMR ($CDCl_3$): 149.7 (4C, C-2 and C-6 Py); 144.5 (2C, C-4 Py); 137.0 (2C, C-4 Ph); 132.8 (4C, C-2 and C-6 Ph); 132.5 (4C, C-3 and C-5 Ph); 128.8 (C=C); 126.9 (2C, C-1 Ph); 121.0 (4C, C-3 and C-5 Py); 81.7 (Ph–*C*≡C); 74.7 (*C*≡C–Ph). MS (70 eV): 408 (M^+, 100), 204 (9). UV–visible (CH_2Cl_2): 235 (ε, 5800); 342 (ε, 7300 l mol^{-1} cm^{-1}). Calcd for $C_{30}H_{20}N_2$: C, 88.21; H, 4.94; N, 6.86. Found: C, 88.27; H, 4.77; N, 6.55%.

3.2.5. Charge–transfer complex of (*Z*,*Z*)-1,4-di[(4-pyridylethenyl)-4-phenyl]-buta-1,3-diyne, (*Z*,*Z*)-5 with TCNE, 8. A hot solution of tetracyanoethene (TCNE) (25 mg (0.19 mmol) in acetonitrile (20 ml) was added to a nearly boiling solution of *Z*,*Z*-**5** (80 mg (0.19 mmol) in acetonitrile (60 ml). The resulting orange solution was allowed to cool and then to evaporate slowly to provide a brown–green solid (**8**), which was continuously extracted with hexane for 48 h in a soxhlet, giving a green solid as little spheres, with a 1:1 stoichiometry between the components. IR (KBr): 2200 (br, C≡N and C≡C); 1590, 1540, 1500 and 1460 (C=C, conj.); 1335 (C–N); 990, 950 and 890 (susbt. Py); 835 and 820 (*p*-disubst.); 750 and 715 (CH=CH, *Z*). ^{1}H NMR (acetone-d_6): 9.02 (d, 2H, *J*=5.7 Hz, H-2 and H-6, Py, complex); 8.49 (d, 2H,

J=5.7 Hz, H-2 and H-6, Py); 8.40 (d, 2H, J=5.7 Hz, H-3 and H-5, Py, complex); 7.9–7.4 (m, 4H, Ph and 2H, CH=CH, complex ring); 7.51 (d, 2H, J=8.7 Hz, H-2 and H-6, Ph); 7.31 (d, 2H, J=8.7 Hz, H-3 and H-5, Ph); 7.21 (d, 2H, J=5.7 Hz, H-3 and H-5, Py); 6.90 (d, 1H, J=11.6 Hz, Py–CH=C*H*, *Z*); 6.71 (d, 1H, J=11.6 Hz, Py–C*H*=CH, *Z*). UV–visible (CH_2Cl_2): 234 (5750); 347 (7240); 419 (655 l mol^{-1} cm^{-1}). DSC: >210°C, dec. Calcd for $C_{36}H_{20}N_6$: C, 80.58; H, 3.76; N, 15.66. Found: C, 80.88; H, 3.43; N, 15.45%.

3.2.6. Charge–transfer complex between (*Z*,*Z*)-1,4-di[(4-pyridylethenyl)-4-phenyl]-buta-1,3-diyne, (*Z*,*Z*)-5 and TCNQ, 9. A hot solution of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) (100 mg, 0.48 mmol) in hot acetonitrile (25 ml) was added to a nearly boiling solution of 1,4-di((*Z*)-1-(4-phenyl)-2-(4-pyridyl)ethenyl(-1,3-butadiyne (*Z*,*Z*-**5**) (100 mg, 0.24 mmol) in acetonitrile (50 ml). The mixture was stirred at reflux temperature for 3 h. The resulting brown solution was allowed to cool and then to evaporate slowly to provide **9**, which was continuously extracted with hexane for 60 h in a soxhlet, giving as a green solid, with 2:1 stoichiometry ratio between the components. IR (nujol): 2150 (C≡N); 1580 and 1550 (C=C, conj.); 950 (Py); 810 (*p*-disubst.); 705 (CH=CH, *Z*). ^{1}H NMR (DMSO): 8.68 (m, 4H, H-2 and H-6 Py); 8.10 (m, 4H, TCNQ); 7.82–7.42 (m, 12H, H-3 and H-5 Py, H-2, H-3, H-5 and H-6 Ph); 6.92 (m, 4H, CH=CH). UV–visible (CH_2Cl_2): 233 (5860); 361 (6700); 396 (7200); 506 nm (710 l mol^{-1} cm^{-1}). Calcd for $C_{54}H_{28}N_{10}$: C, 79.40; H, 3.45; N, 17.15. Found: C, 79.63; H, 3.67; N, 16.82%.

3.3. Quaternation of the pyridine ring

3.3.1. Methyl quaternation of (*E*)-4. Preparation of (*E*)-10 and dimerisation to (*E*,*E*)-11. (*E*)-**10**. In a previously flamed three-necked flask were placed under argon atmosphere a solution of (*E*)-**4** (150 mg, 0.73 mmol) and of iodomethane (0.45 ml, 0.73 mmol) in ethanol (25 ml). The solution that takes initially a dark-orange colour, was stirred overnight at 70–75°C. Finally, the solvent was evaporated and chloroform (25 ml) was added and the solution filtered to give (*E*)-**10**, 227 mg (89%) as a brown solid, mp 197–198°C (darkness at 195°C). IR (KBr): 3424 (≡C–H); 1620 (C=N); 1598 and 1517 (C=C); 1334 (N–CH_3); 1185 ($^+$N–CH_3); 981 (*E*-isomer); 840 (*p*-subst. ArH). ^{1}H NMR (MeOD): 8.76 (d, 2H, J=6.8 Hz, H-3 Py); 8.20 (d, 2H, J=6.8 Hz, H-2 Py); 7.95 (d, 1H, J=16.3 Hz, PhCH=); 7.77 (d, 2H, J=8.4 Hz, H-2 Ph); 7.57 (d, 2H, J=8.4 Hz, H-3 Ph); 7.49 (d, 1H, J=16.3 Hz, PyCH=); 4.35 (s, 3H, $^+$N–CH_3); 3.71 (s, 1H, –C≡CH). UV–visible (EtOH), λ_{max} (nm): 206 (31000); 250 (16180); 295 (10175); 360 (13565). Calcd for $C_{16}H_{14}NI$: C, 55.35; H, 4.06; N, 4.03. Found: C, 55.11; H, 4.25; N, 3.73%.

1,4-*Di*[(*E*)-4-(*p-ethenylphenylethynyl*)*pyridinium iodide*], (*E*,*E*)-**11**. In a previously flamed three-necked flask, under argon atmosphere, were placed a solution of cuprous chloride (13.6 mg, 0.068 mmol) in anhydrous pyridine (10 ml) and then oxygen was bubbled through the solution. The mixture was heated at 40°C and a solution of (*E*)-**10** (65 mg, 0.181 mmol) in anhydrous pyridine (5 ml) was added. The mixture was stirred for 4 h and after, solvent was removed, to give a residual solid that was washed with ammonium hydroxide and extracted with dichloromethane. The organic layer was dried on anhydrous magnesium sulphate and after filtration and solvent evaporation a brown solid was obtained that was purified by crystallisation in warmed n-hexane to give 1,4-di[(*E*)-4-(*p*-ethenylphenylethynyl)pyridinium iodide], (*E*,*E*)-**11**, 63 mg (98%) as a brown solid, mp >300°C. IR (KBr): 3418 (≡C–H); 1617 (C=N); 1593 and 1517 (C=C); 1181 ($^+$N–CH_3); 986 (*E*-isomer); 834 (*p*-subst. ArH). ^{1}H NMR ($(CD_3)_2SO$): 8.87 (d, 4H, J=6.8 Hz, H-3 Py); 8.24 (d, 4H, J=6.8 Hz, H-2 Py); 8.03 (d, 2H, J=16.6 Hz, PhCH=); 7.82 (d, 4H, J=8.7 Hz, H-2 Ph); 7.56 (d, 2H, J=16.6 Hz, PyCH=); 7.54 (d, 4H, J=8.7 Hz, H-3 Ph); 4.26 (s, 6H, $^+$N–CH_3). Calcd for $C_{32}H_{26}N_2I_2$: C, 55.51; H, 3.79; N, 4.05. Found: C, 55.66; H, 3.48; N, 3.78%.

(*E*,*E*)-1,4-*Di*[(4-*pyridylethenyl*)-4-*phenyl*]-*buta*-1,3-*diyne*, (*E*,*E*)-**5**. To a dispersion of Cu_2Cl_2 (66 mg, 0.67 mmol) in dry and freshly distilled pyridine (5 ml), at 40°C under oxygen atmosphere, a solution of the acetylene derivatives (*E*)-**4** (88 mg, 0.43 mmol) and (*E*)-**10** (336 mg, 0.97 mmol) in dry pyridine (10 ml) was added. The mixture was stirred for 12 h and after, pyridine was removed and the residual solid was dissolved in dichloromethane and filtered. After solvent elimination a brown solid was obtained which was crystallised in hot ethanol, giving the saline 1,3-diyne (*E*,*E*)-**11** (328 mg, 98%), as a brown solid, mp 158–159°C. The filtered dichloromethane solution was washed with ammonium hydroxide and extracted with dichloromethane. The organic layer was dried with $MgSO_4$ and after filtration and solvent elimination a residual solid was obtained and purified by silica gel column chromatography (dichloromethane). The 1,3-diyne (*E*,*E*)-**5** was isolated as a yellow solid, 13 mg (15%). IR (KBr): 1595 and 1485 (C=C, conj.), 995 (subst. Py); 973 (C=CH, *E*), and 828 (*p*-disubst.). ^{1}H NMR ($CDCl_3$): 8.60 (d, 4H, J=6.3 Hz, H-2 and H-6 Py), 7.66 (d, 4H, J=7.8 Hz, H-3 and H-6, Ph), 7.47 (d, 4H, J=7.8 Hz, H-2 and H-6, Ph), 7.28 (d, 2H, J=15.8 Hz, PhC*H*=CH, *E*), 7.05 (d, 2H, J=15.8 Hz, Py–C*H*=C*H*, *E*). ^{13}C NMR ($CDCl_3$): 149.5 (4C, C-2 and C-6 Py), 144.8 (2C, C-4 Py), 136.8 (2C, C-1, Ph), 132.8 (4C, C-2 and C-6 Ph), 132.6 (2C, Ph*C*H=CH, *E*), 127.1 (2C, Py*C*H=CH, *E*), 127.0 (4C, C-2 and C-6, Ph), 121.9 (2C, C-4, Ph), 121.1 (4C, C-3 and C-5, Py), 82.1 (2C, Ph–*C*≡C), 75.3 (2C, PhC≡*C*). MS (70 eV): 408 (M^+, 100), 204 (9). UV–visible (CH_2Cl_2) λ_{max} (nm): 230 (15630); 361 (22705 l mol^{-1} cm^{-1}). Calcd for $C_{30}H_{20}N_2$: C, 88.21; H, 4.94; N, 6.86. Found: C, 87.87; H, 4.64; N, 6.75%.

3.3.2. Methyl quaternation of (*E*)-6. Preparation of (*E*)-12 and dimerisation to (*E*,*E*)-13. 4-[*p*-(2-*Ethenyl*)-*iodophenyl*]*pyridinium iodide* (*E*)-**12**. In a three-necked flask were placed *E*-**6** (200 mg, 0.65 mmol) and iodomethane (0.40 ml, 0.65 mmol) in ethanol (25 ml). The mixture that takes initially a dark brown colour was heated at reflux temperature and stirred overnight. Then, after ethanol evaporation, chloroform (25 ml) was added and the solution was filtered, to isolate (*E*)-**12**, 270 mg (92%) as a yellow solid, mp 210–212°C (darkness at 200°C). IR (KBr): 1619 (C=N); 1576 and 1516 (C=C); 1231 (N–CH_3); 1180 ($^+$N–CH_3); 1055 (C–I); 1000 (*E*-isomer); 816 (*p*-subst. ArH). ^{1}H NMR (MeOD): 8.75 (d, 2H, J=6.8 Hz, H-3 Py);

8.21 (d, 2H, *J*=6.8 Hz, H-2 Py); 7.90 (d, 1H, *J*=16.3 Hz, PhCH=); 7.89 (d, 2H, *J*=8.4 Hz, H-3 Ph); 7.55 (d, 2H, *J*=8.4 Hz, H-2 Ph); 7.50 (d, 1H, *J*=16.3 Hz, PyCH=); 4.38 (s, 3H, N–CH_3). UV–visible (EtOH), λ_{max} (nm): 223 (80225); 284 (27500); 355 (1260). Calcd for $C_{14}H_{13}NI_2$: C, 37.44; H, 2.92; N, 3.12. Found: C, 37.18; H, 3.20; N, 2.94%.

Di-{4-[*p*-(2-*ethenylphenyl*)]*pyridinium iodide*}, (*E*,*E*)-**13**. A solution of dichlorobis(triphenyl)phosphine nickel (II) (245.1 mg, 0.377 mmol) in anhydrous THF (25 ml), tetrabutylammonium iodide (139.4 mg, 0.377 mmol) and zinc powder (36.6 mg, 0.56 mmol), under argon atmosphere, was stirred for 30 min. The solution turns to red colour and then a solution of (*E*)-**4** (170 mg, 0.377 mmol) in anhydrous THF (10 ml) was added. The mixture was stirred overnight at room temperature. Finally, dichloromethane (25 ml) was added, and the catalyst was filtered. Solvent was removed, and compound **13** was obtained as a yellow solid, 82 mg (68%). IR (KBr): 1624 (C=N); 1597 and 1516 (C=C); 1184 ($^+$N–CH_3); 997 (*E*-isomer); 838 (*p*-subst. ArH); 724 (*Z*-isomer). ^{1}H NMR (MeOD): 8.86 (d, 4H, *J*=6.7 Hz, H-3 Py, *E*-isomer); 8.82 (d, 4H, *J*=6.7 Hz, H-3 Py, *Z*-isomer); 8.30 (d, 4H, *J*=6.7 Hz, H-2 Py, *E*-isomer); 8.17 (d, 4H, *J*=6.7 Hz, H-2 Py, *Z*-isomer); 8.10 (d, 2H, *J*=16.0 Hz, Ph–CH=, *E*-isomer); 8.00–7.72 (m, 18H, Biph and Py–CH= (*E*-isomer)); 7.31 (d, 2H, *J*=11.6 Hz, *Z*-isomer); 7.09 (d, 2H, *J*=11.6 Hz, *Z*-isomer); 4.41 (s, 6H, $^+$N–CH_3, *E*-isomer); 4.37 (s, 6H, $^+$N–CH_3, *Z*-isomer). UV–visible (EtOH), λ_{max} (nm): 196 (ε=71460); 223 (ε= 22085); 333 (ε=16500). Calcd for $C_{28}H_{26}N_2I_2$: C, 52.19; H, 4.07; N, 4.35. Found: C, 52.44; H, 3.93; N, 4.57%.

3.3.3. Mono- and di-methylated salts, (*Z*,*Z*)-14 and (*Z*,*Z*)-15, of (*Z*,*Z*)-1,4-di[(4′-pyridylethenyl)-4″-phenyl]-buta-1,3-diyne, (*Z*,*Z*)-5. To a solution of (*Z*,*Z*)-**5** (100 mg, 0.24 mmol) in ethanol (25 ml) and ethyl acetate (5 ml), was added iodomethane (0.06 ml, 0.96 mmol). The mixture was heated at reflux temperature and stirred overnight. After cooling, a yellow precipitate was filtered and identified as the dimethylated salt (*Z*,*Z*)-**15**, 70 mg (44%), mp 230°C (dec.). The filtered solution was evaporated yielding an orange solid identified as the monomethylated salt (*Z*,*Z*)-**14**, 70 mg (53%), mp 180°C (dec.).

Monomethylated salt (*Z*,*Z*)-**14**. IR (KBr): 1610, 1500 and 1460 (C=C and C=N, conj.); 1330 (N–CH_3); 1185 (Py^+–CH_3); 980, 890 and 880 (Py sust.); 835 (*p*-disust.).

^{1}H NMR (MeOD): 8.91 (d, 2H, *J*=6.7 Hz, H-2 y H-6, methylated Py); 8.46 (d, 2H, *J*=6.3 Hz, H-2 and H-6, Py); 7.99 (d, 2H, *J*=6.7 Hz, H-3 and H-5, methylated Py); 7.54 (d, 2H, *J*=8.7 Hz, H-2 and H-6, Ph near to methylated Py); 7.49 (d, 2H, *J*=8.7 Hz, H-2 and H-6, Ph); 7.39 (d, 2H, *J*=8.7 Hz, H-3 and H-5, Ph near to methylated Py); 7.40 (d, 1H, *J*=12.5 Hz, Me–Py^+–CH=C*H*); 7.30 (d, 2H, *J*=8.7 Hz, H-3 and H-5 Ph); (7.19 (d, 2H, *J*=6.3, H-3 and H-5, Py); 6.97 (d, 1H, *J*=12.5 Hz, Me–Py^+–C*H*=CH); 6.89 (d, 1H, *J*=12.0 Hz, Py–CH=C*H*); 6.78 (d, 1H, *J*=12.0 Hz, Py–C*H*=CH); 4.50 (s, 3H, CH_3). UV–visible (CH_2Cl_2): 230 (ε, 7800); 292 (ε, 4800); 340 (ε, 5130); 385 (ε, 6000 l mol^{-1} cm^{-1}). Calcd for $C_{31}H_{23}N_2I$: C, 67.64; H, 4.21; N, 5.09. Found: C, 67.47; H, 4.56; N, 5.05%.

Dimethylated salt (*Z*,*Z*)-**15**. IR (KBr): 1600, 1500 and 1450 (C=C, conj.); 1320 (N–CH_3); 1180 (Py^+–CH_3); 975 and 880 (Py sust.); 840 and 830 (*p*-disubst.). ^{1}H NMR (DMSO): 8.78 (d, 4H, *J*=6.6 Hz, H-2 and H-6, Py); 7.83 (d, 4H, *J*=6.6 Hz, H-3 and H-5, Py); 7.57 (d, 4H, *J*=8.3 Hz, H-2 and H-6, Ph); 7.34 (d, 4H, *J*=8.3 Hz, H-3 and H-5, Ph); 7.23 (d, 2H, *J*=12.3 Hz, Py–CH=C*H*, *Z*); 6.89 (d, 2H, *J*=12.3 Hz, Py–C*H*=CH, *Z*); 4.28 (s, 6H, CH_3). MS (FAB$^+$): 438 (M^+, 43); 423 (35); 219 (22). UV–visible (CH_2Cl_2): 236 (6800); 292 (5080); 396 (6520 l mol^{-1} cm^{-1}). Calcd for $C_{33}H_{26}N_2I_2$: C, 56.27; H, 3.72; N, 3.98. Found: C, 56.09; H, 3.60; N, 3.78%.

3.3.4. Charge–transfer complex between (*Z*,*Z*)-15 and *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylendiamine (TMPD), 16. A hot solution of TMPD (100 mg, 0.61 mmol) in hot acetonitrile (25 ml) was added to a nearly boiling solution of (*Z*,*Z*)-**15** (132 mg, 0.30 mmol) in acetonitrile (50 ml). The mixture was stirred at reflux temperature for 2 h. The resulting green solution was allowed to cool and then to evaporate slowly to provide the complex **16** as a green solid. The solid was continuously extracted with hexane in a soxhlet giving a green solid with metallic bright. A 1:1 stoichiometry between the components was deduced from the spectroscopic analysis. IR (KBr): 1610, 1590, 1540, 1510 and 1460 (C=C, conj.); 1340 (N–CH_3); 1185 and 1170 (Py^+–CH_3); 980, 950 and 880 (subst. Py); 840 (*p*-disubst.). ^{1}H NMR (DMSO): 8.90 (br s, 2H, H-2 and H-6, Py); 8.25 (br s, 2H, H-2 and H-6, Py, complexed ring); 8.05 (br s, 2H, H-3 and H-5, Py); 7.9–7.4 (m, 10H, Ph and H-3 and H-5, Py, complexed ring); 7.36 (br d, 1H, Py–CH=C*H*); 7.22 (br d, 1H, Py–C*H*=CH); 6.90 (br d, 1H, Py–CH=C*H*, complexed ring); 6.72 (br d, 1H, Py–C*H*=CH, complexed ring). UV–visible (CH_2Cl_2): 230 (6740), 265 (4400), 315 (5080), 401 (6600), 533 (660) and 639 nm (905 l mol^{-1} cm^{-1}). DSC: >125°C, broad endothermic peak (decomposed). Calcd for $C_{39}H_{42}N_4I_2$: C, 57.08; H, 5.16; N, 6.83. Found: C, 57.16; H, 5.52; N, 6.54%.

3.3.5. Charge–transfer complex between (*Z*,*Z*)-15 and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), 17. A hot solution of TCNQ (35 mg, 0.17 mmol) in hot acetonitrile (15 ml) was added to a hot solution of (*Z*,*Z*)-**15** (75 mg, 0.17 mmol) in acetonitrile (70 ml). The mixture was stirred at reflux temperature for 20 min. After cooling the green solution was slowly evaporated at room temperature yielding the complex as a green solid, which was continuously extracted with hexane in a soxhlet, giving the complex **17** as a black–green solid. A 2:1 stoichiometry between the components was deduced by spectroscopic and combustion analysis. ^{1}H NMR (DMSO): 8.9 (d, 4H, H-2 and H-6, Py); 8.25 (d, 4H, H-3 and H-5, Py); 8.08 (m, 4H, TCNQ); 7.9–7.5 (m, 8H, Ph); 7.39 (d, 2H, *J*=12.5 Hz, Py–CH=C*H*); 7.08 (d, 2H, *J*=12.5 Hz, Py–C*H*=CH); 4.30 (s, 6H, CH_3). UV–visible (CH_2Cl_2): 239 (6800), 400 (6520), 644 (780 l mol^{-1} cm^{-1}). DSC: >160°C, decomposed. Calcd for $C_{57}H_{31}N_{10}I_2$: C, 61.69; H, 2.82; N, 12.62. Found: C, 61.45; H, 2.56; N, 12.25%.

Acknowledgements

We are greatly indebted to CICYT of Spain for financial support (PB97-0060).

References

1. (a) Mitsui, S.; Abe, N.; Hirose, H.; Sasaki, O.; Suzuki, S.; Hayata, H. Patent application JP 91-100425 19910405. (b) Suzuki, S.; Abe, N.; Mitsui, S.; Sasaki, O.; Hirose, H.; Hayata, H. (Konica Co., Japan). Jpn. Kokai Tokkyo Koho, Patent Application JP 91-108805 19910412, 1992. For reviews: (c) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605. (d) Irie, M. *Chem. Rev.* **2000**, *100*, 1685. (e) Delaire, J. A.; Nakatani, K. *Chem. Rev.* **2000**, *100*, 1817. (f) In *Polydiacetylenes*. *NATO ASI series E, No. 102*, Bloor, D., Chance, R. R., Eds.; Matinus Nijkoff: Boston, 1985. (g) Stiegman, A. E.; Graham, E.; Perry, K. J.; Khundkard, R.; Cheng, L. T.; Perry, J. W. *J. Am. Chem. Soc.* **1991**, *113*, 1658, and references cited herein.
2. (a) Wegner, G. *Z. Naturforsch. B* **1969**, *24*, 824. (b) *Electrical and Electronic Properties of Polymers: A State of the Art Compendium*. *Encyclopedia Reprint Series*, Kroschwitz, J. I., Ed.; Wiley: New York, 1988; pp 198–213.
3. (a) Carter, G. M.; Chen, Y. J.; Rubner, M. F.; Sandman, D. J.; Thakur, M. K.; Tripathy, S. K. *Nonlinear Optical Properties of Organic Molecules and Crystals*, Chemla, D. S., Zyss, J., Eds.; Academic: New York, 1987; Vol. 2, p 85. (b) *Electronic and Photonic Applications of Polymers*. *Advances in Chemistry Series 218*, Bowden, M. J., Turner, S. R., Eds.; American Chemical Society: Washington, DC, 1988.
4. Wegner, G. *J. Polym. Sci., Part B* **1971**, *9*, 133.
5. Ozcayir, Y.; Asrar, J.; Blumstein, A. *Mol. Cryst. Liq. Cryst.* **1984**, *110*, 1424.
6. Milburn, G. H.; Wernick, A. R.; Tsibouklis, J.; Bolton, E.; Thomson, G.; Shand, A. *Polymer* **1989**, *30*, 1004.
7. Ferraris, J. P.; Cowan, D. O.; Walatka, V.; Perlstein, J. *J. Am. Chem. Soc.* **1973**, *95*, 948.
8. Bandyopadhyay, S. *Bull. Mater. Sci.* **1999**, *22*(3), 537–542.
9. (a) Köbrig, G.; Trapp, H.; Flory, K.; Drischel, W. *Chem. Ber.* **1966**, *99*, 689. (b) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, *36*, 3769.
10. (a) Hagihara, N.; Takahashi, S.; Kuroyama, Y.; Sonogashira, K. *Synth. Commun.* **1980**, 627. (b) Ames, D. E.; Bull, D.; Takundwa, C. *Synth. Commun.* **1981**, 364. (c) Rodríguez, J. G.; Martín-Villamil, R.; Cano, F. H.; Fonseca, I. *J. Chem. Soc., Perkin Trans. 1* **1997**, 709–714.
11. Bradsma, L. *Studies in Organic Chemistry: Preparative Acetylenic Chemistry*, Elsevier: Amsterdam, 1988; Vol. 34. p 220.
12. Rodríguez, J. G.; Ramos, S.; Martín-Villamil, R.; Fonseca, I.; Albert, A. *J. Chem. Soc., Perkin Trans. 1* **1996**, 541.
13. (a) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, 4th ed. Wiley: New York, 1992; pp 334–338. (b) Schmidt, G. M. J. *Reactivity of the Photoexcited Organic Molecule*, Wiley: New York, 1967; p 227.
14. *Molecular Complexes*, Foster, R., Ed.; Elek Science: London, 1973; Vol. 1, pp 178–190.
15. (a) Mazaki, Y.; Kobayashi, K. *J. Chem. Soc., Perkin Trans. 2* **1992**, 761. (b) Rodríguez, J. G.; Lafuente, A.; Martín-Villamil, R.; Martínez-Alcazar, M. P. *J. Phys. Org. Chem.* **2001**, *14*, 859.
16. Karlin, K. D.; Kaderli, S.; Zuberbühler, A. D. *Acc. Chem. Res.* **1997**, *30*, 139.