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# Synthesis and structural analysis of 1,4-bis[*n*-(*N,N*-dimethylamino)phenyl]buta-1,3-diynes and charge-transfer complexes with TCNE

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ABSTRACT: *n*-(*N,N*-Dimethylamino)phenylethynes were satisfactorily prepared by a Wittig reaction between chloromethylene(triphenyl)phosphine ylide and the appropriate *n*-(*N,N*-dimethylamino)benzaldehyde, followed by dehydrochlorination with a strong base. The conjugate dimers 1,4-bis[*n*-(*N,N*-dimethylamino)phenyl]buta-1,3-diyne were obtained by oxidative dimerization with copper(I) chloride. X-ray molecular structure analysis of the dimer 1,4-bis[*2*-(*N,N*-dimethylamino)phenyl]buta-1,3-diyne corroborated the resonance contribution of the *o*-dimethylamino substituent, which was confirmed in the solid state by the molecular crystalline packing. Both *o*- and *p*-(*N,N*-dimethylamino) conjugate dimers develop 1:1 charge-transfer complexes with TCNE and their structure was identified by NMR, IR and UV–visible spectroscopic data. Differential scanning calorimetric analyses of the 1,3-diynes showed an irreversible transformation to a thermopolymer as a unimolecular reaction. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: 1,4-bis[*n*-(*N,N*-dimethylamino)phenyl]buta-1,3-diynes; TCNE; charge-transfer complexes; synthesis; structural analysis

## INTRODUCTION

The use of molecular organic materials as conductors and in nonlinear optics is of considerable interest since such materials have inherent synthetic flexibility which permits the design of specific molecular properties.[1]

Solid-state polymerization of 1,3-diynes to form crystalline conjugated polydiynes has attracted much attention,[1,2] often because of the large and fast non-linear optical response of the latter, which suggests that they can have potential applications.[3] Although the electronic and optical properties of poly-1,3-diynes are primarily dominated by the $\pi$-conjugated backbone, the substituent groups markedly influence both their topopolymerization behaviour and physical and chemical properties. An aspect of the substituent effect that has received little attention is the influence of formally $\pi$-conjugated substituents on the electronic properties of poly-1,3-diynes. This is because many of them are unreactive in the solid state,[4–6] although they do undergo liquid crystal polymerization. Moreover, 4-aminophenyl-4-nitrophenylbuta-1,3-diyne is solid-state reactive.[6]

The discovery of a one-dimensional metallic state in the ion-radical solid formed from the $\pi$-donor tetrathiofulvalene and the acceptor tetracyanoquinodimethane has stimulated interest in the structure–property relationships of novel donors and acceptors.[7] Although the metallic conductivity and superconductivity of these organic charge-transfer salts are the most important properties, recently attention has also been directed to the novel magnetic and optical properties which they can display (review[8]).

Here we describe an efficient synthesis of *o*-, *m*- and *p*-(*N,N*-dimethylamino)phenylacetylene units (**3a–c**), the oxidative dimerization to 1,4-bis[*n*-(*N,N*-dimethylamino)phenyl]buta-1,3-diynes (**4a–c**) and the synthesis of charge-transfer complexes with acceptors, as well as preliminary results concerning their conductive properties. The acetylene derivatives (**3**) were also obtained for the synthesis of $\pi$-conjugated polyenes, and furthermore serve for the synthesis of nanostructural molecules containing these useful units (J. Gonzalo Rodríguez *et al.*, in preparation).

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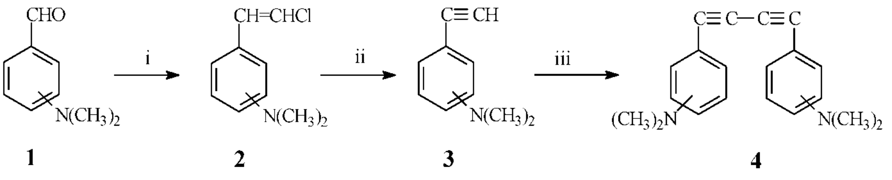


i. Ph$_3$P=CHCl; ii. K$^{+t}$BuO$^-$; iii. Cu$_2$Cl$_2$, py, O$_2$

**Scheme 1**

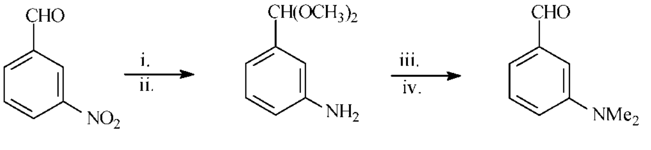
## RESULTS AND DISCUSSION

### Synthesis of 1,4-bis[*n*-(*N,N*-dimethylamino)phenyl]buta-1,3-diynes, 4a–c (*n* = 2, 3 and 4)

Compounds **4a–c** were synthesized from *n*-(*N,N*-dimethylamino)benzaldehyde (**1**) and chloromethylene(triphenyl)phosphine ylide to isolate the *n*-(2-chlorovinyl)-*N,N*-dimethylaminobenzene (**2**) which, by dehydrochlorination with a strong base, gives the corresponding *n*-(*N,N*-dimethylamino)phenylethyne (**3**) (Scheme 1). Finally, the oxidative dimerization of **3** gives the 1,4-bis[*n*-(*N,N*-dimethylamino)phenyl]buta-1,3-diyne (**4**) in good yield.

**Preparation of *o*- and *m*-(*N,N*-dimethylamino)benzaldehyde.** The preparation of *o*-(*N,N*-dimethylamino)-benzaldehyde was carried out from *o*-fluorobenzaldehyde by nucleophilic substitution with dimethylamine in dimethyl sulfoxide.[9]

The synthesis of *m*-(*N,N*-dimethylamino)benzaldehyde, was carried out from *m*-nitrobenzaldehyde, in a modification of the Cocker method (Scheme 2).[10] In this way, *m*-nitrobenzaldehyde was first transformed into the dimethyl acetal and then the nitro group was satisfactorily reduced to the amino group with sodium sulfide and transformed into the *N,N*-dimethylamino derivative by treatment with dimethyl sulfate in an aqueous solution of sodium carbonate; the monomethyl derivative was isolated in low yield and re-used in the methylation step. The *m*-(*N,N*-dimethylamino)benzaldehyde was finally obtained by hydrolysis of the acetal with dilute sulfuric acid (Scheme 2).



i. CH$_3$OH/H$^+$, SO$_4$Me$_2$; ii. SNa$_2$, HCl/H$_2$O;
iii. SO$_4$Me$_2$/ether, Na$_2$CO$_3$/H$_2$O; iv. H$^+$/H$_2$O, Δ

**Scheme 2**

**Synthesis of 2-chloro-1-[2-(*N,N*-dimethylamino)phenyl]ethene (2a).** Compound **2a** was prepared by the Wittig reaction between chloromethylene(triphenyl)-phosphine ylide and *n*-(*N,N*-dimethylamino)benzaldehyde in THF as a mixture of the *E*- and *Z*-isomers in good yield.[11]

Good yields in the 2-chloroethenyl derivative were obtained in all cases, as a mixture of the *E*- and *Z*-isomers, which depends of the ylide stability, the solvent and the base used for the preparation.[12] Table 1 shows the *E/Z* diastereoisomeric ratio of compounds **2a–c** obtained under the same reaction conditions (solvent and temperature). For *o*- and *p*-(*N,N*-dimethylamino)benzaldehyde the *Z*-(2-chloroethenyl) form predominates whereas for *m*-(*N,N*-dimethylamino)benzaldehyde the *E*-(2-chloroethenyl) form predominates slightly in the mixture of the two isomers.

**Synthesis of *n*-(*N,N*-dimethylamino)phenylethynes (3a–c).** Compounds **3a–c** were prepared by dehydrochlorination of the corresponding 2-chloro-1-[*n*-(*N,N*-dimethylamino)phenyl]ethene, by treatment with *n*-butyllithium (>3 equiv.) at room temperature in good yield.[13,14] A one-step synthesis of **3c** starting from **1c** has recently been described.[15]

**Synthesis of 1,4-bis[*n*-(*N,N*-dimethylamino)phenyl]-buta-1,3-diynes (4a–c).** The synthesis of the 1,3-diynes **4a–c** was carried out by an oxidative homocoupling reaction of the appropriate *n*-(*N,N*-dimethylamino)-phenylethyne (**3a–c**), catalysed by copper(I) chloride in pyridine at 40 °C, in good yield. Compounds **4a–c** were isolated as crystalline yellow solids which are stable to sunlight.

The 1,4-bis[*n*-(*N,N*-dimethylamino)phenyl]buta-1,3-diynes (**4a–c**) were analysed by differential scanning calorimetry (DSC). The diagrams show an endothermic

**Table 1.** Wittig reaction of **2a–c**: *Z/E* chlorovinyl stereoisomer ratio

| Isomer | *Z* (%) | *E* (%) | Yield (%) |
|---|---|---|---|
| **2a** *ortho* | 58 | 42 | 96 |
| **2b** *meta* | 48 | 52 | 86 |
| **2c** *para* | 60 | 40 | 90 |

**Table 2.** Arrhenius equation from the DSC broad exothermic peak for **4a–c**

| Compound | m.p. (°C) | Exo-range | $\Delta H$ (J g$^{-1}$) | Ln$Z$ (s$^{-1}$) | $E_a$ (kJ mol$^{-1}$) | $n$ |
|---|---|---|---|---|---|---|
| **4a** | 53.8 | 276–329 | −632.5 | 29.9(5) | 167(2) | 1.23(2) |
| **4b** | 173.2 | 241–302 | −510.4 | 20.8(2) | 118(1) | 0.96(1) |
| **4c** | 244.0 | 260–313 | −619.8 | 25.0(1) | 139(5) | 1.20(5) |

peak corresponding to the melting of the compound followed by an irreversible broad exothermic peak. Analysis of the Arrhenius equation of the broad range of the exothermic peak in the DSC diagram indicated an irreversible and practically unimolecular reaction (Table 2). In the solid state, the 1,3-diynes transform, under the effect of the temperature, into an insoluble black solid.

A single crystal of the 1,3-diyne **4a** was exposed to Cu K$\alpha$ x-radiation and the diffracted reflections were recovered for crystallographic structure analysis. The crystal was stable to the radiation and no topopolymerization of the diyne **4a** was observed.

## Crystal structure of 1,4-bis[2-(*N,N*-dimethylamino)phenyl]buta-1,3-diyne (4a)

Some selected bond lengths and angles for the buta-1,3-diyne **4a** are given in Table 3 and a view of the molecule with the numbering scheme is shown in Fig. 1.

In contrast to the isomer **4c** the molecule is not centrosymmetric, but the bond lengths and angles are in agreement with those found there.[16] The bond distances in the benzene rings are in the range 1.36–1.42 Å, the shortest being C-21—C-22 = 1.357(6), C-14—C-15 = 1.362(6) and C-20—C-21 = 1.372 (6) Å.

Moreover, in this molecular structure C-11—C-1 = 1.424(4), C-17—C-4 = 1.421(4), C-2—C-3 = 1.379(4) and N-5—C-18 and N-8—C-12 = 1.399(4) Å show important double bond character. The benzene rings are nearly planar, with a maximum deviation of 0.016 (3) Å and a dihedral angle between the two rings of 8.2 (1)°. The diyne unit shows small deviations from linearity with C-2—C-1—C-11 = 177.5 (4), C-3—C-4—C-17 = 176.1 (4) and C-2—C-3—C-4 = 178.0 (4)°.

The molecular packing is governed by polar interactions between $NMe_2$ and —C≡C— that give rise firstly to parallel layers to the *ab* plane which are assembled through its respective opposed dipole $(CH_3)_2N \rightarrow Ph$ (Fig. 2).

## Charge-transfer complexes of 1,4-bis[*n*-(*N,N*-dimethylamino)phenyl]buta-1,3-diynes (4a–c) with TCNE

Some linear conjugated systems are already known to give charge-transfer complexes with the acceptor TCNQ having conductive properties.[17] Compounds **4a** and **4c** also yield charge-transfer complexes with TCNQ (J. Gonzalo Rodríguez *et al.*, in preparation). The $\pi$-donor character of 1,4-bis[*n*-(*N,N*-dimethylamino)phenyl]buta-1,3-diyne (**4a** and **4c**) was evaluated by cyclic voltammetry in acetonitrile with lithium perchlorate, giving oxidation potentials of 0.79 mV for the *ortho*- and 0.72 mV for the *para*-dimer compound, while TCNE has a potential of 0.15 mV.[18]

The preparation of the molecular complex between

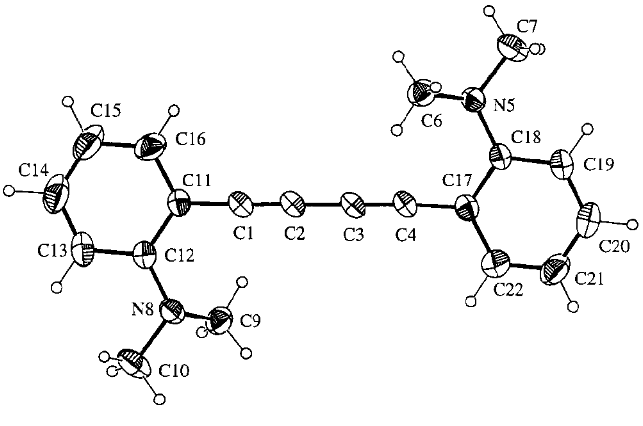


**Figure 1.** Atomic numbering and the ellipsoids at 30% probability for **4a**

**Table 3.** Some bond lengths and angles for **4a**

| Bond length (Å) | | Bond length (Å) | | Bond angle (°) | |
|---|---|---|---|---|---|
| N-5—C-18 | 1.399 (4) | C-1—C-2 | 1.204 (4) | C-2—C-1—C-11 | 177.5 (4) |
| N-5—C-7 | 1.452 (4) | C-1—C-11 | 1.424 (4) | C-1—C-2—C-3 | 178.4 (3) |
| N-5—C-6 | 1.447 (5) | C-2—C-3 | 1.379 (4) | C-4—C-3—C-2 | 178.0 (3) |
| N-8—C-12 | 1.399 (4) | C-3—C-4 | 1.179 (4) | C-3—C-4—C-17 | 176.1 (4) |
| N-8—C-10 | 1.452 (4) | C-4—C-17 | 1.421 (4) | | |
| N-8—C-9 | 1.450 (5) | | | | |

1,4-bis[2-(*N*,*N*-dimethylamino)phenyl]buta-1,3-diyne (**4a**) and TCNE as the acceptor molecule was carried out in a solution of acetonitrile. On the basis of the elemental analysis and powder diffraction techniques, the *ortho*-1,3-diyne **4a** forms only a 1:1 molecular complex with TCNE that was isolated as a dark-violet solid with a strong, bright metallic appearance, which showed semiconductor properties. The electrical resistivity for **4c** was measured on compacted pellets by a standard four-probe method under an argon atmosphere at room temperature, the conductivity being $\sigma = 1.5 \times 10^{-5}\ \Omega^{-1}\,\text{cm}^{-1}$.

The DSC analysis of the molecular complex **4a**–TCNE exhibited a broad, irreversible exothermic peak at 178 °C but melting of the components was not detected.

On the basis of the elemental analysis and powder diffraction results, the *para*-1,3-diyne **4c** forms a 1:1 molecular complex with TCNE which was isolated as a black solid with a strong, bright metallic appearance, which showed conductor properties (as a pellet, $\sigma = 2.0 \times 10^{-2}\ \Omega^{-1}\,\text{cm}^{-1}$).

The DSC analysis of the molecular complex **4c**–TCNE showed a broad, irreversible exothermic peak at 203 °C, but melting of the components was not observed.

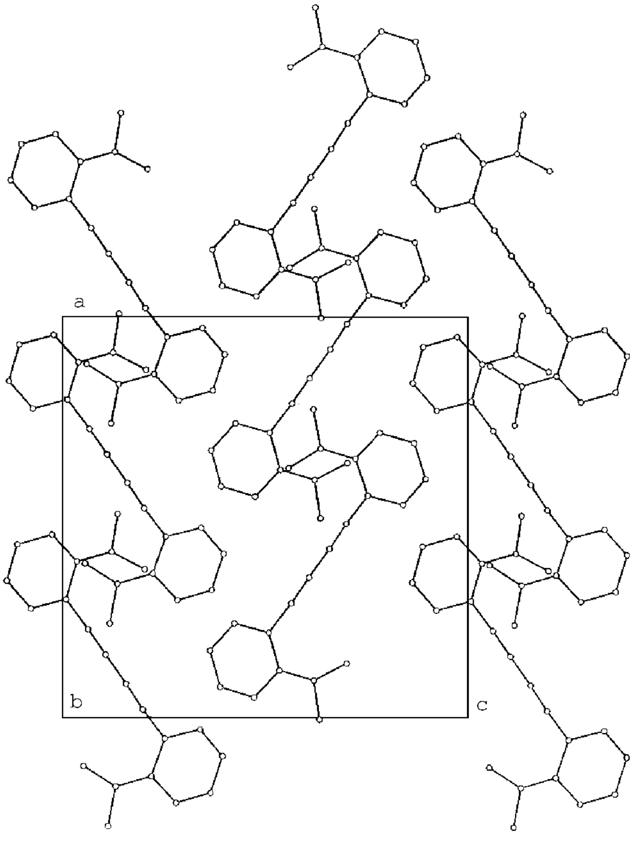


**Figure 2.** Packing of the molecules for **4a**, showing the intermolecular *N*,*N*-dimethyl contact

**Table 4.** $^1$H and $^{13}$C NMR data for **4a** and **4a**–TCNE complex ($\delta$, ppm)

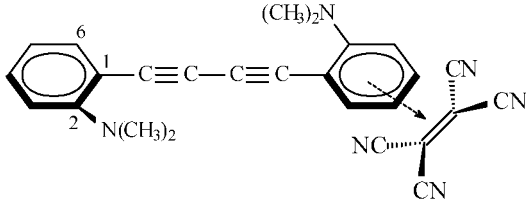
| Proton/carbon | **4a** | **4a**–TCNE (complexed ring) | **4a**–TCNE (uncomplexed ring) |
|---|---|---|---|
| H-3 | 6.89 | 7.35 | 6.85 |
| H-5 | 6.89 | 7.35 | 6.85 |
| H-4 | 7.25 | 7.78 | 7.35 |
| H-6 | 7.48 | 7.78 | 7.35 |
| $Me_2N$ | 2.98 | 3.08 | 2.76 |
| C-1 | 113.2 | 112.7 | 112.1 |
| C-2 | 155.8 | 153.4 | 155.6 |
| C-3 | 116.8 | 119.1 | 116.3 |
| C-4 | 129.9 | 133.7 | 133.0 |
| C-5 | 120.2 | 124.4 | 121.4 |
| C-6 | 135.3 | 136.9 | 135.5 |
| Ph—C≡ | 82.0 | 87.7 | 84.6 |
| ≡C—C | 79.4 | 92.2 | 84.4 |
| $Me_2N$ | 43.6 | 44.5 | 43.5 |

## Structure of the 1,4-bis[2-(*N*,*N*-dimethylamino)phenyl]buta-1,3-diyne–TCNE molecular complex

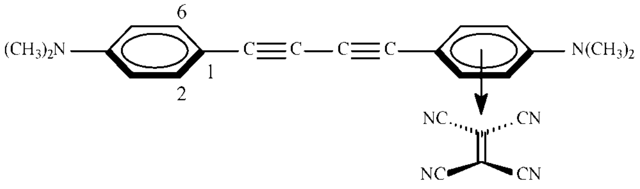
The $^1$H NMR spectrum of the **4a**–TCNE complex in solution of chloroform shows a general deshielding effect on the protons of the TCNE complexed benzene ring (Table 4). Thus, H-4 and H-6 appear at 7.78 ppm (7.25 and 7.48 ppm in the free diyne) as multiplets and H-3 and H-5 at 7.35 ppm (6.89 ppm in the free diyne) as multiplets. The deshielding effect for the uncomplexed ring is more moderate; H-4 and H-6 appear at 7.35 and H-3 and H-5 at 6.85 ppm. The methyl groups appear at 3.08 and 2.76 ppm as two singlets for the complexed and uncomplexed rings, respectively (2.98 ppm as a singlet in the free diyne).

The $^{13}$C NMR spectrum of the **4a**–TCNE complex in a solution of chloroform shows an important deshielding effect for the carbons of the complexed ring. Thus, C-5 and C-4 appear at 124.4 and 133.7 ppm for the complexed and at 121.4 and 133.0 ppm for the uncomplexed ring (120.2 and 129.9 ppm for the free diyne). Moreover, a shielding effect was observed on C-2 and C-1 (153.4 and 112.7 ppm and 155.6 and 112.1 ppm for the complexed and uncomplexed rings, respectively (155.8 and 113.2 ppm for the free diyne). This effect is probably due to the resonance of the dimethylamino group, which on the complexed ring has a deshielding effect on the methyl substituents (44.5 ppm) whereas the uncomplexed ring are practically unaffected (43.5 vs 43.6 ppm in the free diyne) (Table 4).

On the basis of the deshielding effect determined by the difference in the carbon frequencies between the complexed, uncomplexed and free diyne, the structure of the charge-transfer complex **4a**–TCNE can be defined as an overlapping of the double bond of TCNE which is closely parallel to the C-4—C-5 and C-3—C-6 bonds but nearest to the former. The C-4—C-5 bond shows a



**Scheme 3**



**Scheme 4**

significant electron donor effect (important double bond character) in the x-ray molecular structure of the free diyne. Furthermore, in the $^{13}$C NMR spectrum, the TCNE acceptor effect is higher than the donor effect of the *N,N*-dimethylamino group, which was observed on the $-C\equiv C-$Ph bonds of the 1,3-diyne chain, 92.2 and 87.7 ppm, respectively, for the complexed ring, but this effect is of low intensity in the conjugate $Ph-C\equiv C-$ bond that show these two carbon atoms at 84.6 and 84.4 ppm, respectively. The same effects were observed by $^{1}$H NMR, despite the grouping of the H-4,H-6 and H-3,H-5 signals (Scheme 3).

The IR spectrum of the **4a**–TCNE complex shows the $C\equiv N$ group at 2220 cm$^{-1}$ as a unique peak, whereas in the free TCNE it appears at 2260 and 2220 cm$^{-1}$; the $C\equiv C$ bond appears at 2140 cm$^{-1}$ for the complex and 2100 cm$^{-1}$ in the free diyne; the conjugated $C=C$ bond shows three absorption bands at 1590, 1535 and 1485 cm$^{-1}$ whereas in the free diyne only one is observed, at 1590 cm$^{-1}$; finally, the $C-H$ vibration due to *ortho* substitution shows two bands at 780 and 765 cm$^{-1}$, whereas in the free diyne only one appears, at 745 cm$^{-1}$.

The UV–visible spectrum in $CH_2Cl_2$ (dark blue–violet solution) shows a charge-transfer band at 559 nm ($\varepsilon = 730\,l\,mol^{-1}\,cm^{-1}$).

All the data indicated a $\pi$-complexed association of a TCNE molecule with only one of the rings in the 1,3-diyne donor, which shows an important resonance contributions to the *N,N*-dimethylamino group to the complexation.

## Structure of the 1,4-bis[4-(N,N-dimethylamino)-phenyl]-1,3-butadiyne–TCNE molecular complex

The structure of the **4c**–TCNE molecular complex was analysed by $^{1}$H and $^{13}$C NMR spectroscopy (Table 5). In solution the complex exhibits a general deshielding effect on the phenyl rings of the diyne derivative. Two signals for methyl groups at 3.19 and 3.12 ppm for the complexed and uncomplexed ring (2.98 ppm for the free diyne) shows the $\pi$-bonding association of a molecule of TCNE to only one of the aromatic rings in the diyne, which involves a resonance contribution of the *N,N*-dimethyl group to the complexation. This effect is more evident when the aromatic protons are considered. Thus, H-2,H-6 and H-3,H-5 are deshielded at 7.80 and 6.75 ppm (*meta* and *ortho* to the *N,N*-dimethyl group, respectively), as doublets in the complexed ring, and at 7.51 and 6.68 ppm, respectively, in uncomplexed ring (7.40 and 6.63 ppm, respectively, in the free diyne) (Table 5).

On the basis of the proton symmetry in the NMR spectrum of the **4c**–TCNE complex, and the deshielding effect determined by the difference in the proton frequencies between the complexed, uncomplexed and free diyne, the structure of the charge-transfer complex can be defined as a parallel molecular overlapping of the double bond of TCNE on C-5—C-4 and C-3—C-6 bonds on the diyne ring, forming an orthogonal angle with the C-2—C-5 axis (Scheme 4).

The IR spectrum of the **4c**–TCNE complex, in the solid state (KBr), shows the $C\equiv N$ group at 2210 cm$^{-1}$ as a unique peak, whereas the free TCNE exhibits two bands at 2260 and 2220 cm$^{-1}$; the $C\equiv C$ bond appears at 2120 cm$^{-1}$ in the free diyne; the conjugated $C=C$ bonds show four absorption bands at 1600, 1535, 1505 and 1480 cm$^{-1}$ (only two at 1600 and 1505 cm$^{-1}$ in the the free diyne) owing to the resonance of the dimethylamino groups which are observed at 1380 cm$^{-1}$ and assigned to the greatest double bond character for the $C-N$ bond (1350 cm$^{-1}$ in the free diyne). Finally, the $C-H$ vibration shows a new absorption band at 825 cm$^{-1}$. Two signals at 815 and 810 cm$^{-1}$ are attributed to *para* substitution in the complex (810 and 800 cm$^{-1}$ in the free diyne).

Moreover, the UV–visible spectrum in $CH_2Cl_2$ (dark

**Table 5.** $^{1}$H and $^{13}$C NMR data for **4c** and **4c**–TCNE complex

| Proton/carbon | **4c** | **4c**–TCNE (complexed ring) | **4c**–TCNE (uncomplexed ring) |
|---|---|---|---|
| H-2 | 7.40 | 7.80 | 7.51 |
| H-6 | 7.40 | 7.80 | 7.51 |
| H-3 | 6.63 | 6.75 | 6.68 |
| H-5 | 6.63 | 6.75 | 6.68 |
| $Me_2N$ | 2.98 | 3.19 | 3.12 |
| C-1 | 108.4 | 112.6 | 111.4 |
| C-2,C-6 | 133.5 | 136.1 | 132.5 |
| C-3,C-5 | 111.6 | 111.9 | 111.7 |
| C-4 | 150.2 | 148.2 | 150.0 |
| $Ph-C\equiv$ | 82.2 | 92.3 | 83.9 |
| $\equiv C-C$ | 72.5 | 89.9 | 75.8 |
| $Me_2N$ | 39.9 | 40.9 | 40.1 |

violet solution) shows a charge-transfer band at 524 nm ($\varepsilon = 749\ 1\ \mathrm{mol}^{-1}\ \mathrm{cm}^{-1}$).

All the data revealed a $\pi$-complexed association of a TCNE molecule with only one of the rings in the 1,3-diyne **4c**, which exhibits an important resonance contribution of its *N,N*-dimethyl group to the complexation.

The conjugation of the donor N,N-dimethylamino group is necessary for the complexation of **4a** and **4c** because, under the same conditions of preparation of the **4a** and **4c** complexes, the **4b**–TCNE complex was not isolated.

## CONCLUSION

The *N,N*-dimethylamino conjugated diynes **4a–c** can be satisfactorily obtained by the Wittig reaction between the appropriate aldehydes and chloromethylene(triphenyl)-phosphine ylide, followed by elimination of hydrochloric acid and oxidative dimerization of the corresponding acetylene. DSC analysis of the 1,3-diynes **4a–c** showed an irreversible transformation to a thermopolymer as a unimolecular reaction. The conjugated 1,3-diynes show electronic donor character and give 1:1 charge-transfer complexes with TCNE as acceptor. The association of the TCNE with only one benzene ring of the diyne is determined by the presence of the N,N-dimethylamino group on the ring.

## EXPERIMENTAL

**General.** Melting-points were determined with a Reichert hot-stage microscope and are uncorrected. IR spectra were recorded using a Perkin-Elmer Model 681 spectrophotometer. UV–visible spectra were measured in $CH_2Cl_2$, using a Unicam 8700 spectrometer. $^1$H NMR (200 MHz) and $^{13}$C NMR (50 MHz) spectra were recorded with a Bruker WM-200-SY spectrometer; chemical shifts are given on the $\delta$ scale, using TMS as internal reference. Mass spectra were recorded using a Hewlett-Packard SP85 spectrometer. Elemental analyses were performed with a LECO CHN-900 instrument.

**2-(*N,N*-Dimethylamino)benzaldehyde.** To a solution of 2-fluorobenzaldehyde (9 g, 0.072 mol) in dry DMSO (75 ml), under an argon atmosphere was added a saturated solution of dimethylamine (40 ml) in dry THF (20 ml) and $K_2CO_3$ (20 g). The mixture was warmed at the reflux temperature for 3 h, then dimethylamine (40 ml) in dry THF (20 ml) and DMSO (15 ml) was newly added and warmed at the reflux temperature for a further 3 h. The mixture was poured on to ice to give a yellow oil, which was extracted with dichloromethane. The solvent was removed and the residual oil distilled under vacuum to obtain 2-(*N,N*-dimethylamino)benzaldehyde, 7.8 g (72%), as a yellow oil. B.p. 115–120 °C/5.0 mmHg.[9] IR (film, Nujol): 2800 (C—H, $CH_3$), 1685 (C=O), 1600 (C=C, conj.), 740 cm$^{-1}$ (*o*-disubst.). $^1$H NMR ($CDCl_3$): $\delta$ 10.22 (s, 1H, CHO), 7.75 (dd, 1H, *J* = 8.0 and 2.0 Hz, H-6), 7.45 (td, 1H, *J* = 8.0 and 2.0 Hz, H-4), 7.02 (m, 2H, H-3 and H-5), 2.9 (s, 6H, $CH_3$). $^{13}$C MNR ($CDCl_3$): $\delta$ 190.8 (C=O), 155.5 (C-2), 134.3 (C-4), 130.5 (C-6), 126.7 (C-1), 120.3 (C-5), 117.3 (C-3), 45.2 (2C, $CH_3$). MS (70 eV): *m/z* (%) 149 (70) [M$^+$], 132 (51), 120 (88), 106 (89), 91 (50), 77 (100).

**3-(*N,N*-Dimethylamino)benzaldehyde.** *m-Nitrobenzaldehyde dimethylacetal.* A mixture of *m*-nitrobenzaldehyde (5 g, 33 mmol) and dimethyl sulfite (3.96 g, 36 mmol), methanol (20 ml) and *p*-toluensulfonic acid (30 mg) was warmed at the reflux temperature for 8 h. The mixture was hydrolysed with sodium hydroxide (15%) and extracted with ethyl acetate (30 ml), washed with water and dried with magnesium sulfate. Then the mixture was filtered and the dimethylacetal derivative was distilled under vacuum giving a yellow oil, 5.8 g (90%). B.p. 159–162 °C/20 mmHg. IR (film, Nujol): 2840 (C—H) 1535 and 1350 ($NO_2$), 1060, 1120 and 1160 (C—O), 850, 750 and 680 cm$^{-1}$ (*m*-disubst.). $^1$H NMR ($CDCl_3$): $\delta$ 8.35 (s br, 1H, H-2), 8.20 (m, 1H, H-4), 7.80 (d, 1H, *J* = 6.5 Hz, H-6), 7.55 (dd, 1H, *J* = 6.5 and 6.5 Hz, H-5), 5.47 (s, 1H, *H*C—O), 3.34 (s, 6H, $CH_3$).

*m-Aminobenzaldehyde dimethylacetal.* To a mixture of sodium sulfide ($Na_2S{\cdot}9H_2O$) (15.79 g, 0.07 mol) in water (16 ml) and hydrochloric acid (36%, 5.5 ml) was slowly added the acetal prepared above (5.0 g, 25 mmol). The mixture was warmed at the reflux temperature for 8 h and finally extracted with ethyl acetate and dried with magnesium sulfate. The *m*-aminobenzaldehyde dimethylacetal was obtained as a yellow oil, 4.17 g (87%). IR (film, Nujol): 3460 and 3380 ($NH_2$), 2820 (C—H), 885, 790 and 690 cm$^{-1}$ (*m*-disubst.). $^1$H NMR ($CDCl_3$): $\delta$ 7.15 (dd, 1H, *J* = 8.0 Hz, H-5), 6.82 (m, 2H, H-2 and H-6), 6.65 (m, 1H, H-4), 5.47 [s, 1H, *H*C($OCH_3$)$_2$], 3.70 (s br, $NH_2$), 3.34 (s, 6H, $CH_3$).

*Dimethylacetal of m-(N,N-dimethylamino)benzaldehyde.* To a solution of *m*-aminobenzaldehyde dimethylacetal (2.7 g, 16 mmol) in diethyl ether (10 ml) was added a solution of sodium carbonate (7%, 50 ml) and dimethyl sulfate in four portions during 4 days, with stirring at room temperature. The mixture was hydrolysed with ammonia solution, extracted with diethyl ether and dried with magnesium sulfate. After filtration, the solvent was removed, giving a residual oil which was treated with dilute sulfuric acid (5%, 20 ml) for 1 h, with stirring at the reflux temperature, extracted with dichloromethane and dried with magnesium sulfate. After filtration, the solvent was evaporated and the residual oil chromatographed in a silica gel column using hexane–ethyl acetate (3:1) as eluent. 3-(*N,N*-Dimethylamino)benzaldehyde was isolated as a yellow oil, 1.64 g (57%). IR (film, Nujol): 2780 (C—H); 1680 (C=O), 1590 (C=C, conj.), 890, 770 and 710 $cm^{-1}$ (*m*-disubst.). $^1H$ NMR ($CDCl_3$): $\delta$ 9.93 (s, 1H, CHO), 7.38 (dd, 1H, *J* = 8.8 and 8.8 Hz, H-5), 7.27–7.12 (m, 2H, H-2 and H-6), 6.95 (dd, 1H, *J* = 8.8 and 2.2 Hz, H-4), 2.99 (s, 6H, $CH_3$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 192.9 (C=O), 150.4 (C-3), 136.9 (C-1), 129.3 (C-5), 118.3 (C-4), 117.9 (C-6), 111.2 (C-2), 39.9 (2C, $CH_3$). MS (70 eV): *m/z* (%) 149 (77) [$M^+$], 148 (100), 132 (8), 120 (5), 105 (6), 91 (5), 77 (16).

**2-Chloro-1-[2-(*N,N*-dimethylamino)phenyl]ethene (2a).** To a suspension of chloromethylene(triphenyl)-phosphine chloride[11] (10.9 g, 31 mmol) in dry THF (60 ml), under an argon atmosphere at 0 °C, was slowly added a solution of n-butyllithium (1.6 M in hexane, 22 ml, 34 mmol). The solution became red and after being stirred for 30 min, 2-(*N,N*-dimethylamino)benzaldehyde (3.19 g, 21 mmol) was added. The mixture was stirred at room temperature overnight after which the solvent was evaporated to give a brown solid which was Sohxlet extracted with hexane. The hexane was evaporated and the residual yellow oil chromatographed in a silica gel column with toluene as eluent to isolate (*E*)-**2a** and (*Z*)-**2a** (luminescent) as pale-yellow oils 3.13 g (96%) (*E:Z*, 58:42).

*(Z)-2-Chloro-1-[2-(N,N-dimethylamino)phenyl]ethene (**2a**).* IR (film, Nujol): 2800 (C—H), 1600 (C=C, conj.), 740 (*o*-disubst.), 660 $cm^{-1}$ (CH=CHCl, *Z*). $^1H$ NMR ($CDCl_3$): $\delta$ 7.84–7.80 (m, 1H, H-6), 7.24–7.13 (m, 1H, H-4), 7.06–6.90 (m, 2H, H-3 and H-5), 6.85 (d, 1H, *J* = 7.9 Hz, C*H*=CHCl), 6.28 (d, 1H, *J* = 7.9 Hz, CH=C*H*Cl), 2.70 (s, 6H, $CH_3$). MS (70 eV): *m/z* (%) 181 (14) [$M^+$], 166 (1), 146 (72), 131 (100).

*(E)-2-Chloro-1-[2-(N,N-dimethylamino)phenyl]ethene (**2a**).* IR (film, Nujol): 2800 (C—H), 1600 (C=C, conj.), 960 (CH=CHCl, *E*), 740 $cm^{-1}$ (*o*-disubst.). $^1H$ NMR ($CDCl_3$): $\delta$ 7.33–7.18 (m, 2H, H-4 and H-6), 7.07–6.93 (m, 2H, H-3 and H-5), 7.12 (AB, 1H, *J* = 13.7 Hz, C*H*=CHCl), 6.62 (AB, 1H, *J* = 13.7 Hz, CH=C*H*Cl), 2.73 (s, 6H, $CH_3$). MS (70 eV): *m/z* (%) 181 (5) [$M^+$], 166 (1), 146 (88), 131 (100).

**2-Chloro-1-[3-(*N,N*-dimethylamino)phenyl]ethene (2b).** Following the above method, 3-(*N,N*-dimethylamino)benzaldehyde gives a mixture of (*E*)-**2b** and (*Z*)-**2b** as a yellow oil, 2.0 g (76%) (*E:Z*, 48:52).

*(Z)-2-Chloro-1-[3-(N,N-dimethylamino)phenyl]ethene (**2b**).* IR (film, Nujol): 2790 (C—H), 1590 (C=C, conj.), 840, 760 and 690 (*m*-disubst.), 710 $cm^{-1}$(CH=CHCl, *Z*). $^1H$ NMR ($CDCl_3$): $\delta$ 7.24 (dd, 1H, *J* = 7.8 Hz, H-5), 7.09–7.07 (m, 1H, H-2), 7.03–6.99 (m, 1H, H-6), 6.60 (AB, 1H, *J* = 8.2 Hz, C*H*=CHCl, *Z*), 6.73–6.65 (m, 1H, H-4), 6.22 (AB, 1H, *J* = 8.2 Hz, CH=C*H*Cl, *Z*), 2.95 (s, 6H, $CH_3$). MS (70 eV): *m/z* (%) 181 (72) [$M^+$], 180 (100), 165 (8), 144 (6), 130 (6).

*(E)-2-Chloro-1-(3-N,N-dimethylaminophenyl)ethene (**2b**).* IR (film, Nujol): 2790 (C—H), 1590 (C=C, conj.), 990 (CH=CHCl, *E*), 840, 760 and 690 $cm^{-1}$ (*m*-disubst.). $^1H$ NMR ($CDCl_3$): $\delta$ 7.17 (dd, 1H, *J* = 7.8 Hz, H-5), 6.73–6.65 (m, 3H, H-2, H-4 and H-6), 6.80 (AB, 1H, *J* = 13.6 Hz, C*H*=CHCl), 6.61 (AB, 1H, *J* = 13.6 Hz, CH=C*H*Cl), 2.95 (s, 6H, $CH_3$). MS (70 eV): *m/z* (%) 181 (75) [$M^+$], 180 (100), 165 (10), 144 (10), 130 (8).

**2-Chloro-1-[4-(*N,N*-dimethylamino)phenyl]ethene (2c).** Following the above method, 4-(*N,N*-dimethylamino)benzaldehyde gave a brown oil which was chromatographed in a silica gel column (hexane–toluene, 1:1) to give **2c** as a mixture of *E*- and *Z*-isomers (40:60), yellow solid (13.16 g, 99%). IR ($CH_2Cl_2$): 3078, 2810, 1600 (C=C, conj.), 1360 ($NMe_2$), 960 (*E*), 830 (*p*-subst.), 700 $cm^{-1}$ (*Z*). $^1H$ NMR ($CDCl_3$): $\delta$ 7.63–6.70 (8H, m, H-2′ and H-3′, *E* and *Z*), 6.66 (1H, d, *J* = 13.5 Hz, H-2, E), 6.50 (1H, d, *J* = 8.0 Hz, H-2, Z), 6.41 (1H, d, *J* = 13.5 Hz, H-1, *E*), 6.04 (1H, d, *J* = 8.0 Hz, H-1, *Z*), 2.98 (6H, s, $NMe_2$, *E*), 2.94 (6H, s, $NMe_2$, *Z*). MS (70 eV): *m/z* (%) 183 (29), 181 (95) [$M^+$], 180 (100), 165 (91).

**2-(*N,N*-Dimethylamino)phenylethyne (3a).** To a solution of the (*E,Z*)-chloroethenyl derivative **2a** (1.25 g, 6.9 mmol) in dry THF (40 ml) under an argon atmosphere at 0 °C was slowly added a solution of n-butyllithium (1.6 M in hexane, 12.9 ml, 20.7 mmol) and the mixture was stirred for 3 h at room temperature. Then a saturated solution of ammonium chloride (25 ml) was added, extracted with dichloromethane and dried over magnesium sulfate. After filtration, the solvent was removed, giving a brown oil that was purified by silica gel column chromatography using toluene as eluent to give the acetylene derivative **3a** (0.85 g, 85%) as a yellow oil. IR (film, Nujol): 3320 (≡C—H), 2800 (C—H), 2100 (C≡C), 1600 (C=C, conj.), 760 $cm^{-1}$ (*o*-disubst.). $^1H$ NMR ($CDCl_3$): $\delta$ 7.45 (m, 1H, H-6), 7.25 (dd, d, 1H, *J* = 7.3, 7.3 and 1.7 Hz, H-4), 6.93–6.82 (m, 2H, H-3 and H-5), 3.42 (s, 1H, ≡CH), 2.93 (s, 6H, $CH_3$). $^{13}C$ MNR ($CDCl_3$): $\delta$ 155.5 (C-2), 134.8 (C-6), 129.6 (C-4), 120.6 (C-5), 117.0 (C-3), 114.5 (C-1), 83.1 (C≡), 82.3 (≡CH), 43.5 (2C, $CH_3$). MS (70 eV): *m/z* (%) 145 (50) [$M^+$], 144 (100), 129 (14), 115 (19), 101 (9). $C_{10}H_{11}N$ (145.21): calcd C, 82.71; H, 7.64; N, 9.65; found C, 82.47; H, 7.45; N, 9.30%.

**3-(*N,N*-Dimethylamino)phenylethyne (3b).** Following the above procedure, a solution of (*E,Z*)-chloroethenyl derivative **2b** gave **3b** as a pale-yellow oil, 115 mg (70%). IR (film, Nujol): 3300 (≡C*H*), 2810 (C—H), 2110 (C≡C), 1600 (C≡C, conj.), 850, 780 and 690 $cm^{-1}$ (*m*-disubst.). $^1H$ MNR ($CDCl_3$): $\delta$ 7.17 (td, 1H, $J = 8.1$ and 0.8 Hz, H-5), 6.90–6.82 (m, 2H, H-2 and H-6), 6.71 (d br, 1H, $J = 8.1$ Hz, H-4), 3.01 (s, 1H, C≡CH), 2.94 (s, 6H, $CH_3$). MS (70 eV): *m/z* (%) 145 (84) [$M^+$], 144 (100), 129 (14), 101 (22). $C_{10}H_{11}N$ (145.21): calcd C, 82.71; H, 7.64; N, 9.65; found C, 82.66; H, 7.35; N, 9.42%.

**4-(*N,N*-Dimethylamino)phenylethyne (3c).** Following the above procedure, a solution of (*E,Z*)-chloroethenyl derivative **2c** gave **3c** (60%) as a yellow solid, m.p. 51–52 °C (lit.[10] 52–53 °C). IR ($CH_2Cl_2$): 3300 (C—H), 2100 (C≡C), 1615 and 1520 (C=C, conj.), 1360 ($N(CH_3)_2$), 820 cm$^{-1}$ (*p*-subst.). $^1H$ NMR ($CDCl_3$): δ 7.37 (2H, d, $J = 8.6$ Hz, H-2′), 6.62 (2H, d, $J = 8.6$ Hz, H-3′), 3.00 (1H, s, H-1), 2.99 (6H, s, N-$Me_2$). MS (70 eV): *m/z* (%) 145 ($M^+$, 100), 144 (99), 129 (25), 101 (18). $C_{10}H_{11}N$ (145.21): calcd C, 82.71; H, 7.64; N, 9.65; found C, 82.38; H, 7.29; N, 9.66%.

**1,4-Bis[2-(*N,N*-Dimethylamino)phenyl]buta-1,3-diyne (4a).** To a solution of copper(I) chloride (0.31 g, 1.57 mmol) in pyridine (10 ml) in an oxygen atmosphere was added a solution of **3a** (0.63 g, 4.3 mmol) in pyridine (10 ml). The mixture was stirred for 4 h at 40 °C. The pyridine was removed by distillation and the crude product was washed with ammonia solution until the blue colour disappeared and then extracted with dichloromethane (30 ml) and dried with magnesium sulfate. After filtration, the solvent was removed giving a brown solid that was chromatographed in a silica gel column with hexane–ethyl acetate (6:1) as eluent to leave **4a** (0.38 g, 61%) as a yellow solid, m.p. 65 °C (decomp.). IR (film, Nujol): 2920, 2100 (C≡C), 1590 (C=C, conj.), 1370 ($NMe_2$), 745 cm$^{-1}$ (*o*-subst.). $^1H$ NMR ($CDCl_3$): δ 7.48 (dd, 2H, $J = 8.3$ and 1.8 Hz, H-6), 7.25 (td, 2H, $J = 8.3$ and 1.8 Hz, H-4), 6.89 (m, 4H, H-3 and H-5), 3.00 (s, 12H, $CH_3$). $^{13}C$ NMR ($CDCl_3$): δ 155.9 (2C, C-2), 135.3 (2C, C-6), 129.9 (2C, C-4), 120.2 (2C, C-5), 116.8 (2C, C-3); 113.4 (2C, C-1), 82.0 (2C, Ph—C≡), 79.4 (2C, ≡C), 43.6 (4C, $NMe_2$). MS (70 eV): *m/z* (%) 288 ($M^+$, 68), 287 (73), 271 (100), 200 (4), 144 (66), 143 (65). UV–visible ($CH_2Cl_2$): $\lambda_{max}$ 369 nm (ε 28 000 l mol$^{-1}$ cm$^{-1}$). Calcd for $C_{20}H_{20}N_2$: C, 83.30; H, 6.99; N, 9.71; found C, 82.92; H, 7.15; N, 9.47%.

**1,4-Bis[3-(*N,N*-Dimethylamino)phenyl]buta-1,3-diyne (4b).** Following the above procedure, the acetylene derivative **3b** gave the diyne **4b** (60%) as a pale-yellow solid, m.p. 162–165 °C. IR (KBr): 2930, 1590 and 1570 (C=C, conj.), 1370 ($NMe_2$), 830, 770 and 680 cm$^{-1}$ (*m*-subst.). $^1H$ NMR ($CDCl_3$): δ 7.19 (t, 2H, $J = 8.3$ Hz, H-5), 6.87 (m, 4H, H-2 and H-6), 6.73 (m, 2H, H-4), 2.97 (s, 12H, $NMe_2$). $^{13}C$ NMR ($CDCl_3$): δ 150.1 (2C, C-3), 129.0 (2C, C-5), 122.1 (2C, C-1), 120.5 (2C, C-6), 115.8 (2C, C-2), 113.5 (2C, C-4), 82.5 (2C, PhC≡), 72.9 (2C, H-C≡), 40.3 (4C, $CH_3$). MS (70 eV): *m/z* (%) 288 ($M^+$, 100), 287 (55), 271 (25), 258 (6), 200 (7), 144 (14), 143 (38). Calcd for $C_{20}H_{20}N_2$: C, 83.30; H, 6.99; N, 9.71; found C, 83.15; H, 6.85; N, 9.62%.

**1,4-Bis-[4-(*N,N*-Dimethylamino)phenyl]buta-1,3-diyne (4c).** Following the above procedure, the acetylene derivative **3b** gave the diyne **4c** (60%) as a yellow solid, m.p. 233 °C. IR (KBr): 2930, 2120 (C≡C), 1600 and 1505 (C=C, conj.), 1430 ($CH_3$), 1350 ($NMe_2$), 810 and 800 cm$^{-1}$ (*p*-subst.). $^1H$ NMR ($CDCl_3$): δ 7.40 (4H, d, $J = 8.2$ Hz, H-2′), 6.63 (4H, d, $J = 8.2$ Hz, H-3′), 2.98 (12H, s, $NMe_2$). $^{13}C$ NMR ($CDCl_3$): δ 150.2 (2C, C-4′), 133.5 (4C, C-2′ and C-6′), 111.6 (4C, C-3′ and C-5′), 108.4 (2C, C-1′), 82.2 (2C, C-1 and C-4), 72.5 (2C, C-2 and C-3), 39.9 (4C, $NMe_2$). MS (70 eV): *m/z* (%) 288 ($M^+$, 100), 272 (16), 144 (13); UV–visible ($CH_2Cl_2$): $\lambda_{max}$ 377 nm (ε = 55 000 1 mol$^{-1}$ cm$^{-1}$). Calcd for $C_{20}H_{20}N_2$: C, 83.30; H, 6.99; N, 9.71; found C, 83.25; H, 6.72; N, 9.55%.

**Charge-transfer complex of 1,4-bis[2-(*N,N*-dimethylamino)phenyl]buta-1,3-diyne (4a) with TCNE (1:1).** To a hot solution of the 1,3-butadiyne **4a** (80 mg, 0.28 mmol) in acetonitrile (27 ml) was slowly added a solution of TCNE (36 mg, 0.28 mmol) in acetonitrile (3 ml). The yellow solution became violet. Slow solvent evaporation at room temperature gave a molecular charge-transfer complex **4a**-TCNE as crystalline black–violet plates with a bright metallic appearance. IR (KBr): 2220 (C≡N), 2140 (C≡C), 1590, 1535 and 1485 (C=C, conj.), 1350 ($NMe_2$), 780 and 765 cm$^{-1}$ (*o*-disubst.). $^1H$ NMR ($CDCl_3$): δ 7.78 (m, 2H, H-4 and H-6, complexed), 7.35 (m, 4H, H-3 and H-5, complexed; H-4 and H-6, uncomplexed ring), 6.85 (m, 2H, H-3 and H-5, uncomplexed ring), 3.08 (s, 6H, $NMe_2$, complexed), 2.76 (s, 6H, N-$Me_2$, uncomplexed ring). $^{13}C$ NMR ($CDCl_3$): δ 155.6 (C-2′, uncomplexed ring), 153.4 (C-2′, complexed), 136.9 (C-6′, complexed), 135.5 (C-6′, uncomplexed ring), 133.7 (C-4′, complexed), 133.0 (C-4′, uncomplexed ring), 124.4 (C-5′, complexed), 121.4 (C-5′, uncomplexed ring), 119.1 (C-3′, complexed), 116.3 (C-3′, uncomplexed ring), 112.7 (C-1′, complexed), 112.1 (C-1′, uncomplexed ring), 92.2 (C-2 and C-3, complexed), 87.7 (C-1 and C-4, complexed) and 84.6 (C1 and C-4, uncomplexed ring), 84.4 (C-2 and C-3, complexed), 44.4 (2C, $NMe_2$, complexed), 43.5 (2C, $NMe_2$, uncomplexed ring). UV–visible ($CH_2Cl_2$): $\lambda_{max}$ 559 nm (ε = 730 1 mol$^{-1}$ cm$^{-1}$). DSC: irreversible broad exothermic peak at 178 °C. Calcd for $C_{26}H_{20}N_6$: C, 74.98; H, 4.84; N, 20.18; found C, 75.36; H, 4.66; N, 19.82%.

**Charge-transfer complex of 1,4-bis[4-(*N,N*-dimethylamino)phenyl]buta-1,3-diyne (4c) with TCNE (1:1).** Following the above procedure, 1,3-butadiyne **4c** gave a black solid with a bright metallic appearance as a charge-transfer complex, which was recrystallized from hexane. IR (KBr): 2210 (CN), 2120 (C≡C), 1600, 1535, 1505 and 1480 (C=C, conj.), 1380 ($NMe_2$), 825, 815 and 810 $cm^{-1}$ (*p*-subst.). $^1H$ NMR ($CDCl_3$): $\delta$ 7.80 (2H, d, $J = 8.4$ Hz, H-2 and H-6, complexed), 7.51 (2H, d, $J = 8.4$ Hz, H-2 and H-6, uncomplexed ring), 6.75 (2H, d, $J = 8.4$ Hz, H-3 and H-5, complexed), 6.68 (2H, d, $J = 8.4$ Hz, H-3 and H-5, uncomplexed ring), 3.19 (6H, s, N-$Me_2$, complexed), 3.12 (6H, s, N-$Me_2$, uncomplexed ring). $^{13}C$ NMR ($CDCl_3$): $\delta$ 150.0 (C-4′, uncomplexed ring), 148.2 (C-4′, complexed), 136.1 (C-2′ and C-6′, complexed), 132.5 (C-2′ and C-6′, uncomplexed ring), 112.6 (C-1′, complexed), 111.4 (C-1′, uncomplexed ring), 111.9 (C-3′ and C-5′, complexed), 111.7 (C-3′ and C-5′, uncomplexed ring), 92.3 (C-2 and C-3, complexed), 83.9 (C-2 and C-3, uncomplexed ring), 89.9 (C-1 and C-4, complexed) and 75.8 (C-1 and C-4, uncomplexed ring), 40.9 (2C, $NMe_2$, complexed), 40.1 (2C, $NMe_2$, uncomplexed ring). UV–visible ($CH_2Cl_2$): $\lambda_{max}$ 524 nm ($\varepsilon = 749.1\ mol^{-1}\ cm^{-1}$). -DSC: irreversible broad exothermic peak up to 200 °C (200–250 °C). Calcd. for $C_{26}H_{20}N_6$: C, 74.98; H, 4.84; N, 20.18; found C, 74.56; H, 4.88; N, 19.91%.

**X-ray analysis of 1,4-bis[2-(*N,N*-dimethylamino)phenyl]buta-1,3-diyne (4a).** Caramel needle crystals of the diyne **4a** for x-ray analysis were obtained from slow evaporation of a dilute ethyl acetate solution. A crystal of $0.16 \times 0.10 \times 0.73$ mm dimensions was used for the crystallographic study. Accurate cell dimensions were determined by least-squares analysis of setting angles of 25 reflections ($2 < \theta < 35°$), using graphite monochromated Cu K$\alpha$ radiation ($\lambda = 1.5418$ Å) automatically located and centred on a Seifert XRD 3000S four-circle diffractometer. The crystal is orthorhombic, space group $Pca2_1$, with $a = 14.447(2)$, $b = 7.909(1)$, $c = 14.672(2)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 1.676.4(4)$ Å$^3$. The molecular formula is $C_{20}H_{20}N_2$, molecular weight 288.38, $D_c = 1.143(2)\ mg\ m^{-3}$, $Z = 4$, $F(000) = 616$. Correction by absorption was neglected, $\mu = 0.515\ (4)\ mm^{-1}$. Data collection: two standard reflections were measured every 90 min to ascertain the crystal stability, and no significant variation was observed. All the reflections were corrected for Lorentz and polarization effects, but no absorption correction was applied. For the intensity measurement, reflections were surveyed in the range $5 < \theta < 67°$; from 1471 independent reflections measured, 1059 were considered as observed, satisfying the criterion $I > 2\sigma(I)$ in the range $h$ 0–17, $k$ 0–8, $l$ 0–17, and were used in the subsequent calculations. The crystallographic data for **4a** (excluding structure factors), have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-151589. A copy of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (E-mail: deposit@ccdc.cam.ac.uk).

The crystal structure was partially elucidated by direct methods.[19] After preliminary adjustment of the heavy atoms, H-atoms were positioned from difference Fourier maps and then the coordinates were refined. Thereafter, several cycles of full-matrix least-squares calculations were carried out with anisotropic thermal parameters for heavy atoms and the H-atoms were included as fixed contributors,[20] and convergence was reached at $R = 0.036$ and $Rw = 0.084$ with a weighting scheme to prevent trends in $w\Delta^2F$ vs $\langle F_o \rangle$ and vs $\langle \sin\theta/\lambda \rangle$.[21] The final difference synthesis showed no peaks exceeding 0.11 e Å$^{-3}$. The atomic scattering factors and the anomalous dispersion correction were taken from the literature.[22]

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