

# Synthesis and X-ray structure of 1,4-bis[4-(*N,N*-dimethylamino)phenyl]buta-1,3-diyne: charge-transfer complex with acceptors

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4-(*N,N*-dimethylamino)phenylethyne has been satisfactorily prepared by the Wittig reaction between chloromethylene(triphenyl)phosphine ylide and 4-(*N,N*-dimethylamino)benzaldehyde, followed by hydrochloric acid elimination. 1,4-Bis[4-(*N,N*-dimethylamino)phenyl]-buta-1,3-diyne was obtained by oxidative dimerization in good yield. The dimer forms a 1 : 1 charge-transfer complex with TCNE, an X-ray structure analysis of which is reported.

## Introduction

The use of 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.<sup>1</sup>

Solid-state polymerization of 1,3-diyne to form crystalline conjugated polydiynes has attracted much attention,<sup>1,2</sup> often a result of the large and fast nonlinear optical response of the latter, which suggests that they have potential in ultra-fast optical applications.<sup>3</sup> Although the electronic and optical properties of poly-1,3-diyne 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-diyne. This is because many of them are unreactive in the solid state,<sup>4-6</sup> although they do undergo liquid crystal polymerization to form polymers distinct from the solid-state polymers. However, preliminary studies show that 4-aminophenyl-4-nitrophenylbuta-1,3-diyne is solid-state reactive.<sup>6</sup>

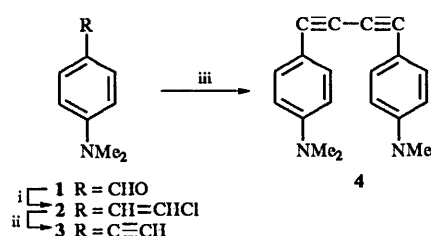
The discovery of a one-dimensional metallic state in the ion-radical solid formed from the  $\pi$ -donor tetrathiofulvalene and the acceptor tetracyanoquinodimethane has stimulated an interest in the structure-properties relationship of novel donors and acceptors.<sup>7</sup> Although the metallic conductivity 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.

Here we report the synthesis of the 1,4-bis[4-(*N,N*-dimethylamino)phenyl]buta-1,3-diyne **4**, as a molecule with  $\pi$ -conjugated donor substituents which can form charge-transfer complexes with acceptors.

## Results and discussion

### Synthesis of 1,4-bis[4-(*N,N*-dimethylamino)phenyl]buta-1,3-diyne **4**

The title compound was synthesized in good yield by oxidative dimerization<sup>8</sup> of 4-(*N,N*-dimethylamino)phenylethyne **3** with oxygen in pyridine in the presence of cuprous chloride at 40 °C as a yellow solid which is stable to sunlight.



Scheme 1 Reagents: i,  $\text{Ph}_3\text{P}=\text{CHCl}$ ; ii,  $\text{K}^+ \text{Bu}'\text{O}^-$ ; iii,  $\text{Cu}_2\text{Cl}_2$ , py,  $\text{O}_2$

The starting acetylene derivative **3**<sup>9</sup> was also prepared in good yield from a mixture of (*E*)- and (*Z*)-2-chloro-1-[4-(*N,N*-dimethylamino)phenyl]ethene **2** by dehydrochlorination with butyllithium in THF at room temperature.

The chlorovinyl derivative **2** was prepared by a Wittig reaction between chloromethylene(triphenyl)phosphine ylide<sup>10</sup> and 4-(*N,N*-dimethylamino)benzaldehyde **1** in THF in practically quantitative yield as a mixture of *E*:*Z* isomers (40 : 60) (Scheme 1).

A single crystal of the diyne derivative was used for X-ray crystallographic analysis. The crystal was stable to the radiation and no topopolymerization to the poly-1,3-diyne was observed.

### Crystal structure analysis

Final coordinates and bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.† A view of the molecule with the numbering scheme is shown in Fig. 1.<sup>11</sup> Since the molecule shows a symmetry centre in C(1)–C(1A) that coincides with the crystallographic one, and as *Z* = 4, there are four half molecules per unit cell. Bond distances of the ring are in the range 1.38–1.41 Å, the shortest being C(4)–C(5) = 1.377(4) and C(7)–C(8) = 1.377(4) Å. Thus, the aromatic ring shows some contribution of the quinoid structure to the resonance hybrid, which includes the triple bond C(2)–C(1) and C(1)–C(1A) in charge delocalization, along N(9) to C(1) which are in a plane. The angles in the ring are lower in the substituted carbon atoms (about 117°) compared with the rest of the ring (about 121°).

The herringbone packing of the molecules (Fig. 2)<sup>12</sup> is governed by interaction between the rings; the molecules form

† For details, see 'Instructions for Authors (1996)', *J. Chem. Soc., Perkin Trans 1*, 1996, Issue 1.

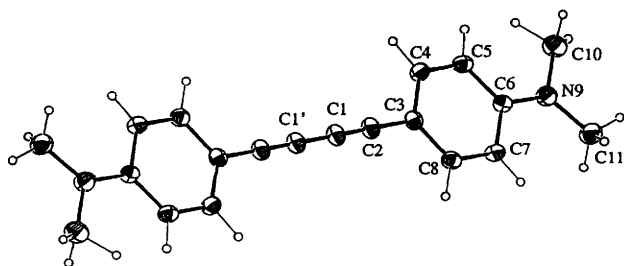


Fig. 1 View of the molecule showing the atom numbering<sup>7</sup>

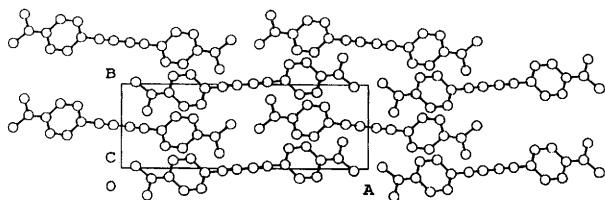


Fig. 2 Packing of the molecules viewed down the *c*-axis

layers in the plane *ab*, along the *c* axis. The shortest intermolecular contacts C(5)–C(6) = 3.830(4), C(5)–C(7) = 4.047(4) and C(5)–C(5) = 4.248(4) Å are greater than the sum of the carbon Van der Waals radii.

#### Charge-transfer complexation of the 1,4-bis[4-(*N,N*-dimethylamino)phenyl]buta-1,3-diyne **4**

The  $\pi$ -electronic excess of the ring with the *N,N*-dimethyl donor group and the  $\pi$ -extended conjugation to the diyne chain in compound **4** allowed it to take part in charge-transfer complexation with tetracyanoethene (TCNE) as acceptor. Thus, slow evaporation of an equimolar mixture of the two components dissolved in hot acetonitrile gave a metallic bright, black solid which is a conductor ( $\sigma = 2.0 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ ).

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

The molecular complex was examined spectroscopically. In solution, <sup>1</sup>H NMR spectroscopy showed a general deshielding of the phenyl rings. Two signals for the methyl groups at 3.19 and 3.12 ppm (*vs.* 2.98 ppm in the free diyne) seem to indicate  $\pi$ -bonding association of the TCNE molecule to only one of the aromatic rings in the diyne, which implies a resonance contribution of the *N,N*-dimethyl group to the complexation. This effect is more evident when the aromatic protons are considered; thus, 2'-H and 3'-H are deshielded at 7.80 and 6.75 ppm (*ortho* to *N,N*-dimethyl group), both as doublets, in the complexed ring, while the free aromatic ring in the molecular complex shows less conjugation, 2'-H at 7.51 and 3'-H at 6.68 ppm, both as doublets (7.40 and 6.63 ppm, as doublets, in the free diyne).

IR (KBr) spectroscopy showed absorption at 1600, 1535, 1505 and 1480  $\text{cm}^{-1}$  for the C=C conjugated bonds of the molecular complex (1600 and 1505  $\text{cm}^{-1}$  in free diyne) arising from resonance of the dimethylamino groups; because of the greater double-bond character of the C–N bond (1350  $\text{cm}^{-1}$  in free diyne) there was an absorption at 1380  $\text{cm}^{-1}$ . New absorptions at 825  $\text{cm}^{-1}$  together with those at 815 and 810  $\text{cm}^{-1}$  were assigned to *para*-substitution in the complex (810 and 800 in the free diyne). However, there was no evidence of  $\pi$ -extended conjugation to the chain since the absorption at 2120  $\text{cm}^{-1}$  (C≡C) underwent no modification in the complex. Moreover, absorption for C≡N at 2210  $\text{cm}^{-1}$  suggests the occurrence of an important shift compared with that for the parent compound (2260 and 2220  $\text{cm}^{-1}$  in free TCNE). UV-visible spectroscopy of the molecular complex shows a charge-transfer band at

524 nm ( $\epsilon$  749). A graphical representation of the absorbance *vs.* concentration exhibits a slight deviation from Beer's law.

## Experimental

Mps were determined using a Reichert hot-stage microscope and are uncorrected. IR spectra were recorded using a Perkin-Elmer 681 spectrophotometer. NMR spectra were recorded at 200 MHz using a Bruker WM-200-SY spectrometer, chemical shifts are given in  $\delta$ , using TMS as internal reference; *J* values given in Hz. Mass spectra were recorded using a Hewlett-Packard SP85 spectrometer. Elemental analyses were performed with a LECO CHN-900.

#### 2-Chloro-1-[4-(*N,N*-dimethylamino)phenyl]ethene **2**

To a suspension of chloromethyl(triphenyl)phosphonium chloride (38 g, 109 mmol) in dry THF (210  $\text{cm}^3$ ) under argon at 0 °C was slowly added a solution of butyllithium (1.6 mol  $\text{dm}^{-3}$  in hexane; 90  $\text{cm}^3$ , 144 mmol). The solution became red and after being stirred for 30 min, was treated with 4-(*N,N*-dimethylamino)benzaldehyde **1** (11 g, 73 mmol). The mixture was stirred at room temperature overnight after which it was evaporated to leave a brown oil. Chromatography of this on silica gel with hexane–toluene (1:1) as eluent yielded the chlorovinyl derivative **2** as a yellow solid mixture of *E*:*Z* isomers (40:60) (13.16 g, 99%);  $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  3078 (C=CH), 2810 (CH<sub>3</sub>), 1600 (C=C, conj.), 1360 (NMe<sub>2</sub>), 960 (*E*), 830 (*p*-subst.) and 700 (*Z*);  $\delta_{\text{H}}(200 \text{ MHz}; \text{CDCl}_3)$  2.94 (6 H, s, N-Me, *Z*), 2.98 (6 H, s, N-Me, *E*), 6.04 (1 H, d, *J* 8.0, 1-H, *Z*), 6.41 (1 H, d, *J* 13.5, 1-H, *E*), 6.50 (1 H, d, *J* 8.0, 2-H, *Z*), 6.66 (1 H, d, *J* 13.5, 2-H, *E*) and 7.63–6.70 (8 H, m, 2'-H and 3'-H, *E* and *Z*); *m/z* 183 (29), 181 (*M*<sup>+</sup>, 95), 180 (100) and 165 (91).

#### 4-(*N,N*-Dimethylamino)phenylethyne **3**

To a solution of the (*E,Z*)-chlorovinyl derivative **2** (13.16 g, 72 mmol) in dry THF (200  $\text{cm}^3$ ) under argon at 0 °C was slowly added a solution of butyllithium (1.6 mol  $\text{dm}^{-3}$  in hexane; 90  $\text{cm}^3$ , 144 mmol). The mixture was stirred for 4 h at room temperature after which it was treated with saturated aqueous ammonium chloride and extracted with dichloromethane. The extract was dried (MgSO<sub>4</sub>), filtered and evaporated to give a brown oil. Chromatography of this on silica gel with hexane–toluene (1:1) as eluent yielded the acetylene derivative **3** (6.3 g, 60%), as a yellow solid, mp 51–52 °C (lit.,<sup>9</sup> 52–53 °C) (Found: C, 82.5; H, 7.45; N, 9.3. Calc. for C<sub>10</sub>H<sub>11</sub>N: C, 82.72; H, 7.64; N, 9.65%);  $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  3300 (CH), 2100 (C≡C), 1615 and 1520 (C=C, conj.), 1360 (NMe<sub>2</sub>) and 820 (*p*-subst.);  $\delta_{\text{H}}(200 \text{ MHz}; \text{CDCl}_3)$  2.99 (6 H, s, NMe), 3.00 (1 H, s, 1-H), 6.62 (2 H, d, *J* 8.6, 3'-H) and 7.37 (2 H, d, *J* 8.6, 2'-H); *m/z* 145 (*M*<sup>+</sup>, 100), 144 (99), 129 (25) and 101 (18).

#### 1,4-Bis[4-(*N,N*-dimethylamino)phenyl]buta-1,3-diyne **4**

Oxygen was bubbled into a solution of cuprous chloride (0.17 g, 0.86 mmol) in pyridine (10  $\text{cm}^3$ ) warmed at 40 °C after which the acetylene derivative **3** (0.5 g, 3.44 mmol) was added. The mixture was stirred for 4 h after which it was cooled and concentrated by removal of the pyridine by distillation. The crude mixture was washed with ammonium hydroxide, until the blue colour disappeared after which it was extracted with dichloromethane. The extract was dried (MgSO<sub>4</sub>), filtered and evaporated to give a brown solid, chromatography of which on silica gel with toluene as eluent yielded the diyne derivative **4** (0.3 g, 60%) as a yellow solid, mp 233 °C (Found: C, 82.9; H, 7.15; N, 9.5. C<sub>20</sub>H<sub>20</sub>N<sub>2</sub> requires C, 83.29; H, 6.99; N, 9.71%);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2930 (CH, Me), 2120 (C≡C), 1600 and 1505 (C=C, conj.), 1430 (Me), 1350 (NMe<sub>2</sub>), 1220 (Me, gem.), 810 and 800 (*p*-subst.);  $\delta_{\text{H}}(200 \text{ MHz}; \text{CDCl}_3)$  2.98 (12 H, s, N-Me), 6.63 (4 H, d, *J* 8.2, 3'-H) and 7.40 (4 H, d, *J* 8.2, 2'-H);  $\delta_{\text{C}}(200 \text{ MHz}, \text{CDCl}_3)$  150.2 (2 C, 4'-C), 133.5 (4 C, 2'-C), 111.6 (4 C, 3'-C), 108.4 (2 C, 1'-C), 82.2 (2 C, 1-C and 4-C), 72.5 (2 C, 2-C and

3-C) and 39.9 (4 C, N-Me);  $m/z$  288 ( $M^+$ , 100), 272 (16) and 144 (13);  $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$  228 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  28 000), 351 ( $\epsilon$  64 000) and 377 ( $\epsilon$  55 000).

#### X-Ray crystallographic analysis of 1,4-bis[4-(*N,N*-dimethylamino)phenyl]buta-1,3-diyne 4

Slow evaporation of a dilute ethyl acetate solution of the diyne derivative gave light yellow crystals suitable for X-ray analysis. A crystal of  $0.38 \times 0.32 \times 0.21$  mm dimensions was used for the crystallographic study. Accurate cell dimensions were determined by least-squares analysis of setting angles of 53 reflections ( $2 < \theta < 35^\circ$ ) using graphite monochromated  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), automatically located and centred on a four-circle, Seifert XRD 3000S diffractometer. The crystal was monoclinic, space group  $P2_1/a$ , with  $a = 17.259(2)$ ,  $b = 5.968(1)$ ,  $c = 8.205(1) \text{ \AA}$ ,  $\beta = 98.83(1)^\circ$ ,  $V = 835.1(1) \text{ \AA}^3$ . The molecular formula was  $\text{C}_{20}\text{H}_{20}\text{N}_2$ , molecular weight 288.33,  $D_c = 1.147(2) \text{ g cm}^{-3}$ ,  $Z = 4$ ,  $F(000) = 308.0$ . Correction by absorption was neglected,  $\mu = 4.857(4) \text{ cm}^{-1}$ . Data collection: two reflections were measured every 90 min to ascertain 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  $2 < 2\theta < 135^\circ$ , from 1448 independent reflections measured, 1042 were considered as observed, satisfying the criterion  $I > 3\sigma(I)$  in the range  $h \pm 20$ ,  $k$  0/7, 0/10, and were used in the subsequent calculations.

The crystal structure was partially elucidated by direct methods.<sup>13</sup> After preliminary adjustment of the heavy atoms, H-atoms were positioned from difference Fourier maps and then, the coordinates refined. Thereafter, several cycles of full-matrix least-squares calculations were carried out with anisotropic thermal parameters for heavy atoms and with the H-atoms included as fixed contributors;<sup>14</sup> convergence was reached at  $R = 0.085$  and  $R_w = 0.086$  with a weighting scheme<sup>15</sup> to prevent trends in  $w\Delta^2 F$  vs.  $\langle F_o \rangle$  and vs.  $\langle \sin\theta/\lambda \rangle$ . The final difference synthesis showed no peaks exceeding  $0.27 \text{ e \AA}^{-3}$ .

The atomic scattering factors and the anomalous dispersion correction were taken from the literature.<sup>16</sup>

#### Charge-transfer complex of the 1,4-bis[4-(*N,N*-dimethylamino)phenyl]buta-1,3-diyne 4 with TCNE (1 : 1)

A hot solution of TCNE (32 mg, 0.25 mmol) in acetonitrile was added to a nearly boiling solution of the buta-1,3-diyne derivative 4 (72 mg, 0.25 mmol) in acetonitrile. The resulting dark-red solution was allowed to cool and then to evaporate slowly to provide a metallic bright, black solid.

Thermal analysis of this charge-transfer complex was followed by DSC. No melt peaks were observed, decomposition occurring at  $> 200^\circ\text{C}$  ( $200\text{--}250^\circ\text{C}$ );  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2210 ( $\text{C}\equiv\text{N}$ ), 2120 ( $\text{C}\equiv\text{C}$ ), 1600, 1535, 1505 and 1480 ( $\text{C}=\text{C}$ , conj.), 1380 ( $\text{NMe}_2$ ), 1215 ( $\text{Me}$ , gem.), 825, 815 and 810 (*para*-subst.);  $\delta_{\text{H}}(200 \text{ MHz}; \text{CDCl}_3)$  3.12 (6 H, s, N-Me), 3.19 (6 H, s, N-Me,

complexed ring), 6.68 (2 H, d,  $J$  8.4, 3'-H), 6.75 (2 H, d,  $J$  8.4, 3'-H, complexed ring), 7.51 (2 H, d,  $J$  8.4, 2'-H) and 7.80 (2 H, d,  $J$  8.4, 2'-H, complexed ring);  $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$  250 ( $\epsilon \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  300), 278 ( $\epsilon$  319), 428 ( $\epsilon$  480), 483 ( $\epsilon$  640) and 524 ( $\epsilon$  749).

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#### References

- 1 D. Bloor and R. R. Chance (eds.), *Polydiacetylenes*, NATO ASI series E, No. 102, Martinus Nijhoff Publishers, Boston 1985; A. E. Stigman, E. Graham, K. J. Perry, R. Khundkard, L. T. Cheng and J. W. Perry, *J. Am. Chem. Soc.*, 1991, **113**, 7658, and references cited herein.
- 2 G. Wegner, *Z. Naturforsch. B*, 1969, **24**, 824.
- 3 G. M. Carter, Y. J. Chen, M. F. Rubner, D. J. Sandman, M. K. Thakur and S. K. Tripathy, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, eds. D. S. Chemla and J. Zyss, Academic Press, New York, 1987, vol. 2, p. 85.
- 4 G. Wegner, *J. Polym. Sci., Part B*, 1971, **9**, 133.
- 5 Y. Ozcayir, J. Asrar and A. Blumstein, *Mol. Cryst. Liq. Cryst.*, 1984, **110**, 1424.
- 6 G. H. W. Milburn, A. R. Wernick, J. Tsibouklis, E. Bolton, G. Thomson and A. Shand, *Polymer*, 1989, **30**, 1004.
- 7 J. P. Ferraris, D. O. Cowan, V. Walatka and J. Perlstein, *J. Am. Chem. Soc.*, 1973, **95**, 948.
- 8 L. Bradma, *Studies in Organic Chemistry: Preparative Acetylenic Chemistry*, Elsevier Science Publishers B.V., Amsterdam, 1988, vol. 34, p. 220.
- 9 (a) E. J. Corey and P. L. Fuchs, *Tetrahedron Lett.*, 1972, **36**, 3769; (b) S. Akiyama, S. Nakatsuji, K. Yoshida, K. Nakashima, T. Hagiwara, H. Tsuruta and T. Yoshida, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 361; (c) Man Shing Wong and J. F. Nicoud, *Tetrahedron Lett.*, 1994, **35** (33), 6113.
- 10 G. Köbrig, H. Trapp, K. Flory and W. Drischel, *Chem. Ber.*, 1966, **99**, 689.
- 11 W. D. S. Motherwell and W. Clegg, 1978 PLUTO. A program for plotting crystal and molecular structures, University of Cambridge, England.
- 12 A. Albert and F. H. Cano, CONTACTOS. A Program for Systematic Study of Aromatic Rings Interactions, Instituto Rocasolano, CSIC, Madrid, 1990.
- 13 A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, Dip. Geomineralogico, Univ. of Bari; M. C. Burla, Dip. Science della Terra, Univ. of Perugia; M. Camalli, Ist. Strutt. Chimica, CNR, Monterotondo Stazione, Roma, SIR92, 1992.
- 14 S. R. Hall, Crystallography Centre, University of Western Australia; J. M. Stewart, Chemistry Department, University of Maryland, XTAL3.0, 1990.
- 15 M. Martínez-Ripoll and F. H. Cano, PESOS, Program for the Automatic Treatment of Weighting Schemes, Instituto Rocasolano, CSIC, Madrid, 1975.
- 16 International Tables for X-RAY Crystallography, vol. 4, Birmingham, Kynoch, 1974.

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