

Tris(2,4-pentanedionato)vanadium-catalysed cyclotrimerization and polymerization of 4-(*N,N*-dimethylamino)phenylethyne: X-ray structure of 1,2,4-tris[4-(*N,N*-dimethylamino)phenyl]benzene

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Tris(pentane-2,4-dionato)vanadium-catalysed polymerization of 4-(*N,N*-dimethylamino)phenylethyne gave a polyene with π -conjugated donor substituents. Similarly, cyclotrimerization of the acetylene derivative gave a mixture of 1,2,4- and 1,3,5-tris[4-(*N,N*-dimethylamino)phenyl]benzene in variable yield, depending on the reaction conditions employed. The molecular structure of the main 1,2,4- isomer was determined by X-ray diffraction methods.

Introduction

The use of organic materials as conductors and in non-linear optics is of considerable interest since such materials have inherent synthetic flexibility which permits the design of specific molecular properties.¹ In this connection, the relationship between electronic structure and microscopic second-order non-linear polarizability for donor-acceptor phenylacetylene compounds linked by acetylenic bonds has been analysed.² Conjugate polyene chains can be obtained by catalytic polymerization of the appropriate acetylene and aromatic substituted acetylenic polymers, which can incorporate donor or acceptor functional groups, represent an important group of such macromolecules. The presence of alternate double bonds along the backbone in the polyene chain influence characteristics such as the colour, electrical conductivity and paramagnetism.³

Of the techniques used to polymerize substituted acetylenes,⁴ that most widely used to prepare thin films is by interfacial polymerization of the monomer on the surface of a concentrated homogeneous Ziegler-Natta catalyst solution.⁵ In such a way, polyphenylacetylene with a stereospecific *cis-transoidal* microstructure was obtained with both homogeneous⁶ and zwitterionic rhodium complexes,⁷ the morphology of the polyphenylacetylenes⁸ however, seems to be independent of the chemical structure of the rhodium(i) catalyst used. The influence of bulky pendent groups in the acetylene on the properties and reaction products with a rhodium(i) catalyst and comparison with substituted acetylenes have been reported.⁹

Here we report a catalysed reaction of 4-(*N,N*-dimethylamino)phenylethyne which gives both a polyene and oligo-phenyl derivatives with π -conjugated donor substituents which allows charge-transfer complex formation with acceptors.

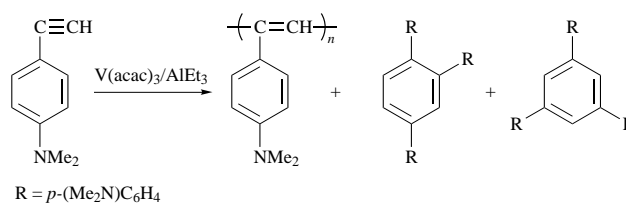
Results and discussion

4-(*N,N*-Dimethylamino)phenylethyne has been satisfactorily prepared by a Wittig reaction between chloromethylene-(triphenyl)phosphine ylide and 4-(*N,N*-dimethylamino)-benzaldehyde, followed by hydrochloric acid elimination.¹⁰

Attempted catalytic polymerization of 4-(*N,N*-dimethylamino)phenylethyne with triethylaluminium and titanium tetrabutoxide under a variety of conditions (different temperature and monomer:catalyst ratios), failed, giving only low yields of the cyclotrimers, 1,2,4- and 1,3,5-tris[4-(*N,N*-dimethylamino)phenyl]benzene (4%).

A parallel study with triethylaluminium and tris(pentane-

2,4-dionato)vanadium as the catalyst gave three main products, the poly[4-(*N,N*-dimethylamino)phenylethyne] and a mixture of cyclotrimers, 1,2,4- and 1,3,5-tris[4-(*N,N*-dimethylamino)phenyl]benzene derivatives (see Scheme 1). The ratio of



Scheme 1

cyclotrimers to polymer was variable, depending on the catalyst and reaction conditions (see Table 1). The optimum conversion was observed for a monomer:catalyst ratio of 10:1, in hexane-toluene (7:1) and a reaction temperature of 50 °C and a reaction time of 6 h. This gave a 20% yield of 1,2,4- and 1,3,5-tris[4-(*N,N*-dimethylamino)phenyl]benzene (ratio 63:37; determined by NMR and GPC), and poly[4-(*N,N*-dimethylamino)phenylethyne] (30%), after elimination of the residual catalyst salts (see Table 1).

The molecular mass of the poly[4-(*N,N*-dimethylamino)phenylethyne], determined by both the vapour pressure method and gel permeable chromatography (GPC) was *ca.* 2800.

From the results it is seen that for the catalyst system prepared in toluene at room temperature, transformation is only observed for a reaction temperature of *ca.* 120 °C, conditions which give poly[4-(*N,N*-dimethylamino)phenylethyne] (20% conversion) and the cyclotrimers in a ratio of 17:3 (ratio 1,2,4- to 1,3,5- of 1). For a catalyst system prepared at 90 °C the polymer (30% conversion) and cyclotrimers ratio was 2:1 (ratio 1,2,4- to 1,3,5- *ca.* 3:1).

For a catalyst system prepared in a hexane-toluene (7:1) mixture and used in a reaction carried out at room temperature, there was a 41% conversion with a cyclotrimers:polymer ratio of 1:3. For a reaction at 50 °C, the conversion was 50%, cyclotrimers:polymer ratio was 2:3. The use of hexane as solvent gives, in general, low conversion and an increasing proportion of cyclotrimers. Higher dilution of the reaction mixture (hexane, 5 times on run 6) gave a cyclotrimer:polymer ratio of 1:1.

Use of pyridine as a co-catalyst to modify the active centre configuration and diminish the number of monomer units

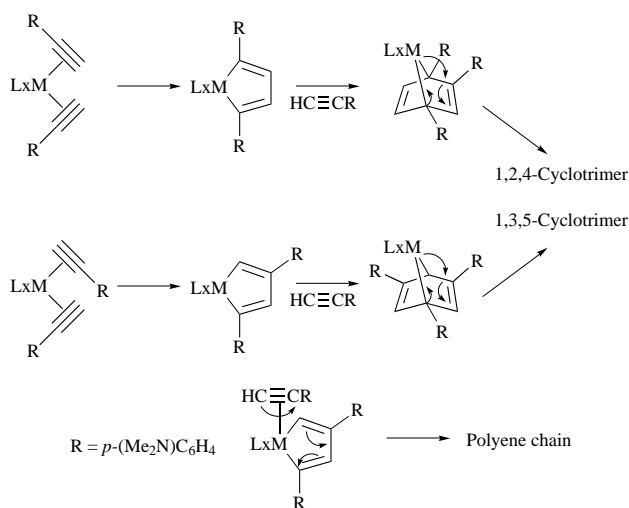
Table 1

Reaction run	r_m	$T_f/^\circ\text{C}$	t_p/h	$T_p/^\circ\text{C}$	Cyclotrimers (%)			$ \overline{M}_n $
					1,2,4-	1,3,5-	Polymer (%)	
1	10:1	25	48	120	1.5	1.5	17	
2	10:1	90	48	120	14.5	5.5	10	
3 ^a	10:1	25	6	25	5.5	4.5	31	2340
4 ^b	10:1	25	6	25	16.4	3.6	5	
5 ^c	20:1	25	6	25	4.5	1.5	14	2830
6 ^a	10:1	25	6	50	12.5	7.4	30	2860

V(acac)₃:Et₃Al (1:3), t_f , 1 h (formation time of the catalyst system) in toluene; r_m : monomer:catalyst ratio. ^aHexane-toluene. ^bHexane. ^cSonicated.

coordinated, thus avoiding cyclotrimerization resulted in complete inhibition of the reaction.

These results indicate that in this process, there are two different, competing reaction pathways as a result of coordination differences on the active centre. One of these arises from the known insertion-addition of the alkyne *via* a Ziegler-Natta catalyst,¹¹ to give the polyene chain and the 1,3,5-cyclotrimer through a 2,4-disubstituted metallocycle diene (see Scheme 2).



Scheme 2

From coordination of two molecules of the acetylene derivative on the active centre of the catalyst a 2,5-disubstituted metallocycle diene¹² can be formed which avoids polymerization; thus, the coordination and addition of a new molecule of the acetylene derivative produces only the 1,2,4-trisubstituted cyclotrimer (see Scheme 2). The 1,2,4-isomer is the major one in the mixture (minimum steric effect in the 2,5-disubstituted metallocycle diene) but when the polymer amount increases in the reaction, the ratio 1,2,4- to 1,3,5- is considerably decreased (see Table 1). Thus, the coordination to give the 2,4-disubstituted metallocycle diene pathway afforded the polyene chain and 1,3,5-cyclotrimer (see Scheme 1).

Structural analysis of 1,2,4- and 1,3,5-tris[4-(*N,N*-dimethylamino)phenyl]benzene

Spectroscopic analysis of 1,2,4- and 1,3,5-tris[4-(*N,N*-dimethylamino)phenyl]benzene. The cyclotrimer isomeric mixture was analysed by spectroscopic methods and the main 1,2,4-isomer was isolated by fractional crystallisation. An IR spectrum of the mixture showed absorptions at 1600, 1510 and 1480 cm^{-1} (conjugated C=C) which are observed also for the polymer; there was also absorption at 810 cm^{-1} (*para*-substitution) and 890, 880, 840 and 710 cm^{-1} (CH for trisubstitution).

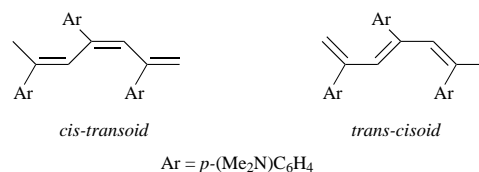
A ¹H NMR spectrum of the mixture allowed signals for each isomer to be distinguished. Thus, the 1,3,5- isomer gave rise to signals at 7.63 (s, trisubstituted benzene protons) and 3.0 ppm

(s, Me's as a result of molecular symmetry); other aromatic protons appeared as an unique AA'XX' system. The 1,2,4-isomer gave rise to signals at 7.6–7.4 ppm (m, the trisubstituted benzene protons) whilst the aromatic protons appeared as three AA'XX'; other signals for the methyl groups appeared at 2.99 (s, 6 H) and 2.92 ppm (s, 12 H).

The mass spectrum showed the molecular ion (m/z 435) as the base peak, and the M^{2+} (m/z 218) peak which corresponds to a second ionization of the molecule.

Spectroscopic analysis of poly[4-(*N,N*-dimethylamino)phenyl-ethyne]. Polymeric fractions obtained under different reaction conditions had almost identical IR and NMR spectroscopic features.

IR absorptions appeared at 1600, 1510 and 1480 cm^{-1} (conjugated C=C), 960 and 940 cm^{-1} (*trans* feature of the polymer chain) and 805 cm^{-1} (*para*-substitution). Broad ¹H NMR signals at 7.6, 7.15, 6.65, 6.28 and less intense at 5.8 ppm were assigned to aromatic and olefinic protons. These results suggest that the polymer structure is mainly *trans* although a signal at 5.8 ppm indicates the presence of a *cis* feature, possibly in the form of a *cis-transoid* structure (see Scheme 3).



Scheme 3

Differential scanning calorimetry (DSC) of these polymers showed relatively low melting temperatures with a t_g at 90 °C as a result of *cisoid-transoid* interchange of the polymer chain. Moreover, there was also an irreversible broad exothermic reactive transition around 136–189 °C. The kinetic study from the DSC diagram revealed the parameters of the Arrhenius equation which indicate that it is a first order reaction, and thus the reaction of the own polymer chain was produced.

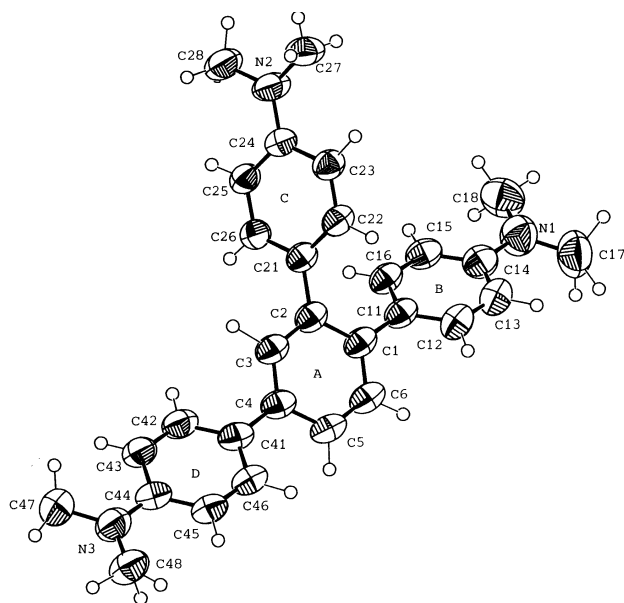
Crystal structure analysis of 1,2,4-tris[4-(*N,N*-dimethylamino)phenyl]benzene. A crystal of 1,2,4-tris[4-(*N,N*-dimethylamino)phenyl]benzene was isolated by careful fractional crystallisation from methanol of the mixture of the cyclotrimer isomers.

The molecular structure of 1,2,4-tris[4-(*N,N*-dimethylamino)phenyl]benzene showing the crystallographic numbering scheme is shown in Fig. 1. Table 2 lists; (a) some bond distances, (b) some bond angles and (c) some torsion angles.

The molecular structure confirms the structure of the 1,2,4-trisubstituted compound which was the major isomer from the cyclotrimerization of the 4-(*N,N*-dimethylamino)phenylethyne. The orientation between the different rings is given by the values of the dihedral angles between the benzene and the 4-(*N,N*-dimethylamino)phenyl rings B, C and D which are 42.4(1), 58.5(1) and 32.3(1)° respectively, while the relative

Table 2 (a) Bond distances

C(1)–C(11)	1.485(4)	C(24)–N(2)	1.379(5)
C(2)–C(21)	1.478(5)	N(2)–C(27)	1.431(7)
C(4)–C(41)	1.476(4)	N(2)–C(28)	1.431(8)
C(14)–N(1)	1.388(5)	C(44)–N(3)	1.389(4)
N(1)–C(17)	1.428(9)	N(3)–C(47)	1.434(8)
N(1)–C(18)	1.414(10)	N(3)–C(48)	1.430(8)
(b) bond angles			
C(17)–N(1)–C(18)	116.7(6)	(c) Torsion angles for methyl groups	
C(17)–N(1)–C(14)	120.6(4)	C(13)–C(14)–N(1)–C(17)	16.0(8)
C(18)–N(1)–C(14)	121.5(4)	C(13)–C(14)–N(1)–C(18)	–176.4(5)
C(13)–C(14)–C(15)	116.8(5)	C(15)–C(14)–N(1)–C(17)	–163.8(5)
C(13)–C(12)–C(11)	121.4(4)	C(15)–C(14)–N(1)–C(18)	3.8(8)
C(12)–C(11)–C(16)	116.7(4)	C(23)–C(24)–N(2)–C(27)	–8.8(6)
C(11)–C(16)–C(15)	122.4(3)	C(23)–C(24)–N(2)–C(28)	179.0(4)
C(16)–C(15)–C(14)	121.0(3)	C(25)–C(24)–N(2)–C(27)	171.4(4)
C(12)–C(13)–C(14)	121.5(4)	C(25)–C(24)–N(2)–C(28)	–0.9(7)
C(11)–C(1)–C(6)	120.0(2)	C(43)–C(44)–N(3)–C(47)	–6.8(7)
C(11)–C(1)–C(2)	122.3(2)	C(43)–C(44)–N(3)–C(48)	–177.1(4)
C(2)–C(1)–C(6)	117.5(2)	C(45)–C(44)–N(3)–C(47)	173.4(5)
C(1)–C(2)–C(3)	118.5(3)	C(45)–C(44)–N(3)–C(48)	3.0(7)
C(2)–C(3)–C(4)	124.1(3)		
C(3)–C(4)–C(5)	116.9(3)		
C(4)–C(5)–C(6)	120.2(3)		
C(5)–C(6)–C(1)	122.9(3)		

**Fig. 1** View of the molecule showing the crystallographic numbering scheme

dihedral angles between the rings A/B, A/C and B/C are 64.6(1), 11.4(1) and 56.9(1)°.

The dimethylamino groups are not co-planar with their respective phenyl rings, the slightly prismatic N atoms deviating from the plane as can be seen by the torsion angles C–C–N–CH₃ (see Table 2c).

Experimental

Mps were determined using a Reichert stage microscope and are uncorrected. IR spectra were recorded using a Perkin-Elmer 681 spectrophotometer. NMR spectra were recorded at 200 MHz using a Bruker WM-200-SY spectrometer, chemical shifts are given in δ , using TMS as internal reference. J values in Hz. Mass spectra were recorded using a Hewlett-Packard SP85 spectrometer. Elemental analyses were performed with a LECO CHN-900. The molecular mass distribution by HPLC were performed in a liquid chromatography Perkin-Elmer INTEGRAL 4000, using a GPC column PL gel of Polymer Laboratories.

Molecular mass was determined in a vapour pressure osmometer Gonotec OSMOMAT 070

Reaction of 4-(*N,N*-dimethylamino)phenylethyne with tris(pentane-2,4-dionato)vanadium

A Schlenk tube previously flamed was charged with a suspension of V(acac)₃ (0.24 g, 0.689 mmol) in dry hexane (2 cm³) and a solution of AlEt₃ in toluene (1.9 ml, 1.1 cm³, 2.06 mmol) under argon at room temperature. After 1 h at room temperature the tube was immersed in a bath thermostatted at 50 °C. A solution of 4-(*N,N*-dimethylamino)phenylethyne (1 g, 6.89 mmol) in hexane–toluene (7:1; 5.5 cm³) was then added to the mixture after which it was at 50 °C for 6 h. After this time the mixture was allowed to cool and the catalytic complex was hydrolysed with ethanol (20 cm³) overnight; the solvent was then removed. The crude product was washed with hexane and the insoluble fraction was treated with aqueous sodium hydroxide (20%). The crude polymer was then extracted in a Soxhlet apparatus with hexane. After this the polymer was dried to give poly[4-(*N,N*-dimethylamino)phenylacetylene] as a brown powder (308 mg, 30%), mp 84–106 °C (DSC); ν_{\max} (KBr)/cm^{–1} 2910, 2840 and 2790 (CH), 1600 and 1510 (C=C, conj.), 1480 (C=C), 1440 (CH₃), 1340 (C–N), 1190, 1160, 1125 and 1060 (CH), 940 (CH, *trans*), 880 (*cis*) and 805 (*p*-subst.); δ_{H} (200 MHz, CDCl₃) 2.80 (s, CH₃), 2.92 (s, CH₃), 2.98 (s, CH₃), 7.6, 7.15, 6.65, 6.28 and 5.8 (br s, aromatic and olefinic H); λ_{\max} (CH₂Cl₂)/nm 228, 263 and 300.

The soluble fraction was purified by chromatography on silica gel with hexane–ethyl acetate (4:1), as eluent to give a mixture of cyclotrimers as a yellow solid (200 mg, 20%); GPC analysis gave the cyclotrimer ratio (63:37). Fractional crystallization of the mixture of cyclotrimers gave crystalline 1,2,4-tris[4-(*N,N*-dimethylamino)phenyl]benzene; the structure of which was confirmed by X-ray diffraction; ν_{\max} (KBr)/cm^{–1} 2780 (C–H), 1605, 1515 and 1480 (C=C, conj.), 1440 (CH₃), 1345 (CN), 1190, 1160, 1120 and 1060 (CH), 890, 880, 840 and 710 (CH, *trans*), 810 (*p*-subst.); δ_{H} (200 MHz, CDCl₃) 1.3, 5-tris[4-(*N,N*-dimethylamino)phenyl]benzene, 3.0 (s, 18 H, CH₃), 6.84 (6 H, d, *J* 8.9, Ph), 7.57 (6 H, d, *J* 8.9, Ph) and 7.63 (3 H, s, Ph *trans*); 1,2,4-tris[4-(*N,N*-dimethylamino)phenyl]benzene, 2.92 (12 H, s, CH₃), 2.99 (6 H, s, CH₃), 6.64 (4 H, m, Ph), 6.82 (2 H, d, *J* 8.9, Ph), 7.11 (4 H, m, Ph) and 7.6–7.4 (5 H, m, 3 H Ph *trans* and 2 H Ph); m/z 436 (M⁺ + 1, 43), 435 (M⁺, 100) and 218 (M²⁺, 16).

Monomer was also recovered (250 mg, 25%).

X-Ray crystallographic analysis of 1,2,4-tris[4-(*N,N*-dimethylamino)phenyl]benzene

Crystals of 1,2,4-tris[4-(*N,N*-dimethylamino)phenyl]benzene, C₃₀H₃₃N₃, molecular weight 435.611, were monoclinic with $a = 17.705(3)$, $b = 6.127(1)$, $c = 11.494(1)$ Å, $\beta = 95.41(1)^\circ$; $V = 1241.3(3)$ Å³. Accurate cell dimensions were determined by least-squares refinement on setting angles of 61 reflections ($19 < 2\theta < 75^\circ$) using graphite monochromated Cu- $K\alpha$ radiation ($\lambda = 1.5418$ Å) automatically located and centred on a four-circle Philips PW1100 diffractometer, space group $P2_1$, $Z = 2$, $D_c = 1.166(3)$ g cm^{–3}, $F(000) = 468.0$. Colourless prismatic crystals of 1,2,4-tris[4-(*N,N*-dimethylamino)phenyl]benzene were grown by slow evaporation from a methanol solution. A crystal of dimensions 0.60 × 0.52 × 0.33 mm³ was selected for X-ray diffraction analysis. The linear absorption coefficient (μ) was 5.216 cm^{–1}.

Data collection. Two standard reflections were measured every 90 min to ascertain the crystal stability; no significant variation was observed. The intensities were corrected for Lorentz and polarization effects; no corrections were made for absorption. For the intensity measurement, reflections were surveyed in the range $2 < \theta < 65^\circ$, from 2213 independent reflections measured, 2095 were considered as observed, satisfying the criterion $I > 2\sigma(I)$ in the range $h - 21/21$, $k 0/8$, $l 0/14$,

and were used in the subsequent calculations. The structure was solved by direct methods, SIR92.¹⁴ The H atoms were located on a difference map except those attached to C(47) which were introduced geometrically. All parameters were refined,¹⁵ excepting H(171), H(172) and H(173) which were fixed. After several cycles of least-squares refinement, convergence was reached at $R = 0.050$ and $R_w = 0.063$, with a weighting scheme¹⁶ to minimise trends in $w\Delta^2F$ vs. $\sin \theta/\lambda$.

The atomic scattering factors and the anomalous dispersion corrections were taken from the literature.¹⁷ Atomic coordinates, bond distances and angles were calculated using the PARST program.¹⁸ Full crystallographic details for this study have been deposited with the Cambridge Crystallographic Data Centre. Requests for this material should be accompanied by a full bibliographic citation together with the reference number CCDC 207/86.

Acknowledgements

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