

π -Complexes incorporating tetrakis(phenylethynyl)ethene

Douglas Philp,^{*a} Volker Gramlich,^b Paul Seiler^c and François Diederich^{*c}

^a School of Chemistry, University of Birmingham, Edgbaston, Birmingham, UK B15 2TT

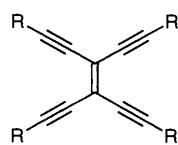
^b Institut für Kristallographie und Petrographie, ETH Zentrum, Sonneggstrasse 5, CH-8092 Zürich, Switzerland

^c Laboratorium für Organische Chemie, ETH Zentrum, Universitätstrasse 16, CH-8092 Zürich, Switzerland

Tetrakis(phenylethynyl)ethene and the π -acceptors 2,4,7-trinitrofluoren-9-one and (2,4,7-trinitrofluoren-9-ylidene)malononitrile form highly ordered donor-acceptor π -complexes having 1:2 stoichiometry in the solid state. In solution, relatively weak 1:1 complexes are formed whose stabilities are related to the spatial disposition of the donor phenyl rings rather than the HOMO-LUMO interactions of the donor-acceptor pair. The orientation of the donor with respect to the acceptor in the solid state shows a good correlation with the atom-centred point charges on each component of the complex. However, there is a very poor correlation between the orbital coefficients of the donor HOMO and the acceptor LUMO suggesting that the solid state structure is dominated by electrostatic interactions.

Introduction

The chemistry of compounds containing highly unsaturated, conjugated π -systems has undergone a remarkable renaissance¹ in recent times. The development of simple, efficient synthetic methods for the C(sp²)-C(sp) cross-coupling between aryl and alkyne units has resulted in the rapid development of a range of novel nanoscale architectures^{2,3} based on acetylenic frameworks. Highly unsaturated, conjugated π -systems, and, in particular, conjugated enediynes, are also receiving much attention currently in terms of their biological activity,⁴ electronic structure and unusual reactivity⁵ and material properties.⁶ Tetraethynylethene **1a** (3,4-diethynylhex-3-ene-1,5-diyne) and its derivatives are an interesting class of readily synthesised,^{7,8} cross-conjugated π -systems which can be elaborated to give a range of interesting macrocyclic and polymeric structures. The parent compound **1a** is isoelectronic with tetracyanoethylene **2**, but calculations by us[†] and others⁹ suggest that, although the frontier orbitals of **1a** and **2** have similar patterns of coefficients (Fig. 1), the ionisation potentials (IPs) of **1a** and **2** differ by around 2 eV, with the HOMO of **1a** being higher in energy. In this context, we suspected that the tetraethynylethene π -system might function as a π -electron donor and hence be amenable to incorporation into donor-acceptor type π -complexes. These complexes exhibit interesting electronic properties,¹⁰ especially when the donor-acceptor ratio is non-stoichiometric, and may also have potential application¹¹ in the field of non-linear optics as a result of their high third-order susceptibilities. We therefore sought to explore the behaviour of systems containing the tetraethynylethene molecular frame in two contexts. Firstly, their incorporation into donor-acceptor π -complexes might lead to potentially useful new materials. Secondly, a detailed analysis of the mechanism of association between tetraethynylethenes and

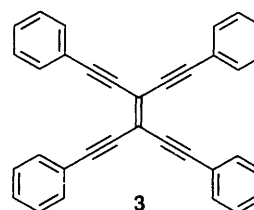


1a R = H

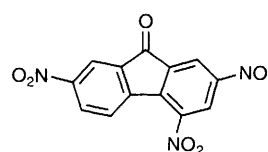
1b R = Me₃Si



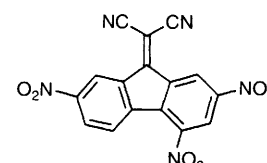
2



3



4

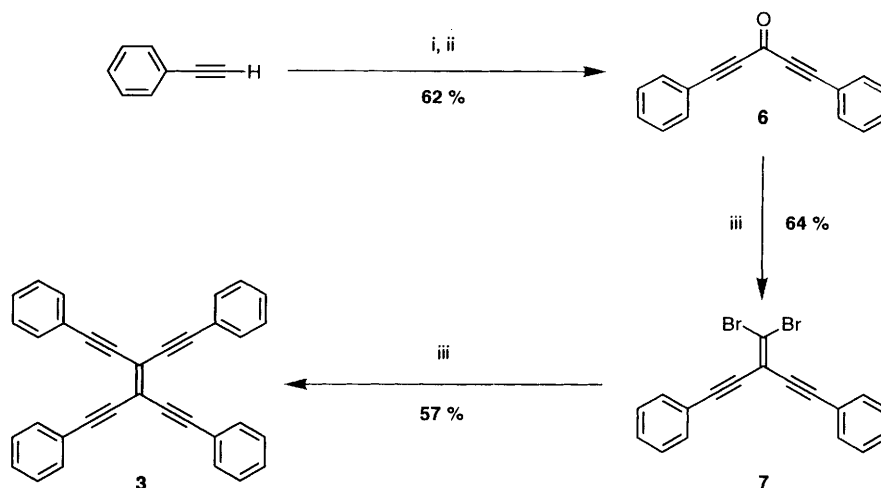


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π -acceptor molecules might advance the understanding of the nature of the non-covalent interactions which drive the association of π -systems. Here, we report[‡] (i) the formation and characterisation of π -complexes between tetrakis(phenylethynyl)ethene **3** and the π -acceptors 2,4,7-trinitrofluoren-9-one **4** and (2,4,7-trinitrofluoren-9-ylidene)malononitrile **5** in solution by UV-VIS, fluorescence, and ¹H NMR spectroscopies and in the solid state by X-ray crystallography, and (ii) a rationalisation of the interactions found in the solid state structures of these complexes.

[†] The calculated ionisation potential (IP) (B. Ma, Y. Xie and H. F. Schaefer III, *Chem. Phys. Lett.*, 1992, **191**, 521) of tetraethynylethene **1a**, using *ab initio* methods and the DZP basis set, is 8.73 eV. We have found that smaller basis sets, e.g., 3-21G, and the semiempirical methods AM1 and PM3, reproduce the IP, and the filled electronic energy levels, reasonably accurately, although calculated molecular geometries are slightly worse. Calculated IPs (AM1) for tetrakis(trimethylsilyl)ethynylethene **1b** of 8.63 eV and for tetrakis(phenylethynyl)ethene **3** of 8.41 eV suggest that these tetraethynylethene derivatives could function as π -electron donors.

[‡] Some of the work presented here has appeared in preliminary communication form, see F. Diederich, D. Philp and P. Seiler *J. Chem. Soc., Chem. Commun.*, 1994, 205.



Scheme 1 Reagents and conditions: i, BuLi, THF, -78°C , HCOOEt (0.4 equiv.); ii, HPyrClCrO₃, 20°C , CH₂Cl₂; iii, CBr₄ (2 equiv.), PPh₃ (5 equiv.), CH₂Cl₂; iv, PhCCH, [PdCl₂(PPh₃)₂], CuI, BuNH₂, C₆H₆

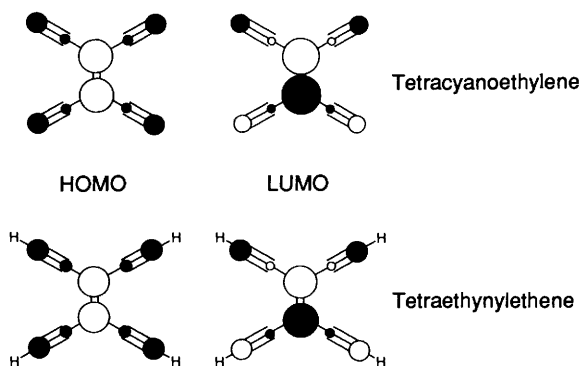


Fig. 1 Schematic representation of the HOMO and LUMO of tetraethynylethene **1a** and tetracyanoethylene **2**. The size of the circles is proportional to the size of the orbital coefficient at a particular atom and filled or open circles represent the sign of the orbital coefficient.

Results and discussion

Tetrakis(trimethylsilyl)ethyne **1b** and tetracyanoethylene **2** form a purple-coloured complex on mixing the two components in CHCl₃ solution ([**1b**] $\sim 10^{-1}$ mol dm⁻³; [**2**] $\sim 10^{-4}$ mol dm⁻³). The formation of a charge transfer complex is indicated by the appearance of a Gaussian shaped absorption band, centred on 535 nm, in the visible region of the spectrum. However, the lack of ¹H NMR probes in **2** and its poor solubility in CHCl₃, coupled with the lack of fluorescence emission from **1b**, hampered full characterisation of the [**1b**·**2**] complex. Further, the inaccessibility of the π -system in **1b** to π -acceptors larger than **2**, attributed to the presence of the bulky trimethylsilyl protecting groups in **1b**, indicated that an alternative tetraethynylethene system should be investigated. Tetrakis(phenylethynyl)ethene **3** was deemed to be an appro-

priate candidate, offering both unhindered access to the tetraethynylethene skeleton and an extended π -system by virtue of the phenyl rings. Compound **3** was first unequivocally§ synthesised^{7a} by Hori *et al.* in 1969 by reaction of 3-bromo-1,5-diphenylpenta-1,4-diyne with potassium *tert*-butoxide and dimerisation of the intermediately formed carbene. Subsequently, it was also obtained by Hauptmann,^{7b} by dehydrogenation of the corresponding tetrakis(phenylethynyl)ethane which, in turn, was formed in the reaction of 1,5-diphenyl-3-bromopenta-1,4-diyne with KI under Finkelstein conditions in acetone. Hopf *et al.*^{7c} improved the method of Hori and obtained **3** in 73% yield from 3-bromo-1,5-diphenylpenta-1,4-diyne. They also showed that McMurry coupling of 1,5-diphenylpenta-1,4-diyne-3-one **6** was unsuitable for the preparation of **3**—the desired product being obtained in only 2% yield. We achieved the synthesis of **3** in three steps from phenylacetylene following the route initially developed by Rubin *et al.*^{8b} for the preparation of the parent compound **1a** (Scheme 1). Reaction of lithium phenylacetylide with ethyl formate followed by oxidation of the 1,5-diphenyl-1,4-diyne-3-ol generated afforded ketone **6** which was converted by dibromomethylation, according to the method of Corey and Fuchs,¹² into the dibromomethylene derivative **7**. Palladium-catalysed ethynylation afforded **3** in an overall yield of 23%.

In order to assess the ability of **3** to associate with powerful π -acceptors, 2,4,7-trinitrofluorene-9-one **4** or (2,4,7-trinitrofluorene-9-ylidene)malonitrile **5** were added to CHCl₃ solutions of **3**. The addition of both **4** and **5** to solutions of **3** resulted in instantaneous colour changes—the yellow solution of **3** turning orange-red on addition of **4** and green on addition of **5**. The observed colour change is a result of the appearance (Fig. 2) of charge transfer (CT) absorption bands in the visible region of the spectrum, and is indicative of the formation of π -complexes between **3** and either **4** or **5**. Fluorescence spectroscopy confirms the presence of the CT interaction. In general, molecular fluorescence is quenched¹³ in charge-transfer complexes by radiationless decay of the excited state through the lower energy charge transfer state. Tetrakis(phenylethynyl)ethene **3** exhibits an intense blue fluorescence [λ_{max} (emission) 445 and 470 nm, λ_{exc} (excitation) 410 nm], however, the addition of increasing amounts of **4** to a CHCl₃ solution of **3** results (Fig. 3) in fluorescence quenching, indicating that the colour of the complexes arises from a charge transfer absorption.

Dark-red single crystals of the complex between **3** and **4**

§ The synthesis of tetrakis(phenylethynyl)ethene **3** by coupling of phenylethynylcopper(i) to tetraiodoethylene was reported in 1967 by Coe and co-workers (J. Burdon, P. L. Coe, C. R. Marsh and J. C. Tatlow, *J. Chem. Soc., Chem. Commun.*, 1967, 1259). Both Hori (Y. Hori, K. Noda, S. Kobayashi and H. Taniguchi, *Tetrahedron Lett.*, 1969, 3563) and Hopf (H. Hopf, M. Kreuzer and P. G. Jones, *Chem. Ber.*, 1991, **124**, 1471) have identified the product obtained in 40% yield in this reaction as diphenylbutadiyne.

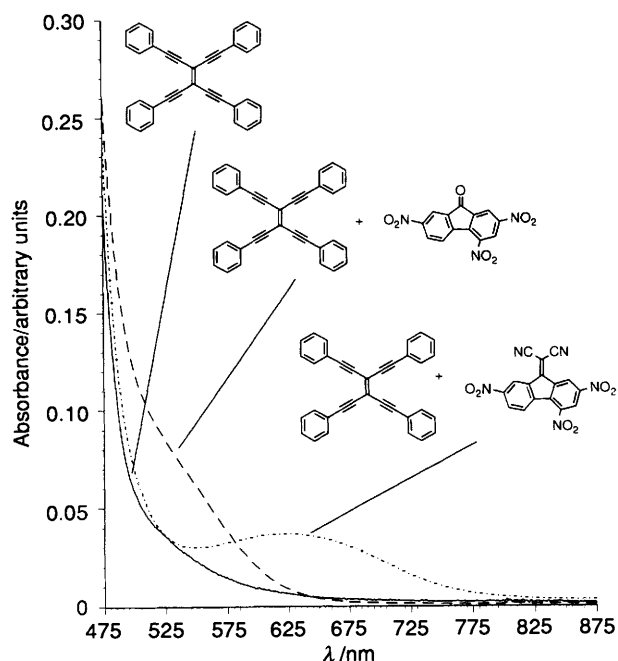


Fig. 2 Absorption spectra of pure tetrakis(phenylethynyl)ethene 3 (10^{-3} mol dm^{-3} in CHCl_3) (solid curve) and after additions of 4 (10^{-1} mol dm^{-3}) (dashed curve) and 5 (10^{-1} mol dm^{-3}) (dotted curve) at 298 K

suitable for X-ray diffraction[¶] were grown by vapour diffusion of pentane into a dichloromethane solution containing equimolar amounts of the two components. Surprisingly, the crystals have a stoichiometry of $[\mathbf{3}\cdot\mathbf{4}_2]$, i.e., a 1:2 complex is formed between donor 3 and acceptor 4 in the solid state. The tetrakis(phenylethynyl)ethene molecule within the complex $[\mathbf{3}\cdot\mathbf{4}_2]$, including the four phenyl groups, is planar to within ± 0.04 Å (Fig. 4). The structure of the tetraethynylethene backbone of 3 within $[\mathbf{3}\cdot\mathbf{4}_2]$ displays almost perfect D_{2h} symmetry and is almost identical with that of free 3.^{7c} The opportunity for extended π -delocalisation provided by the phenyl substituents within 3 is evident in the significant lengthening of the central double bond (1.378 Å) (Fig. 4) when compared with that (1.324 Å) found^{8a} in tetrakis(trimethylsilyl)ethynylethene 1b, where such delocalisation is not possible. Two independent molecules of 3 are located at inversion centres (000 and 0.5 0.5 0.5, respectively). The two molecules of 4 within the complex (Fig. 5) span two *cis*-enediynes units present in 3 and are disposed about the inversion centres. The nitro groups in the 2 and 7 positions lie essentially in the plane of the aromatic skeleton, whereas the nitro groups in the 4 position show some orientational disorder. There are continuous donor-acceptor stacks (Fig. 6) along the *a* axis of the unit cell, with two independent stacks per unit cell—one in the centre and one at

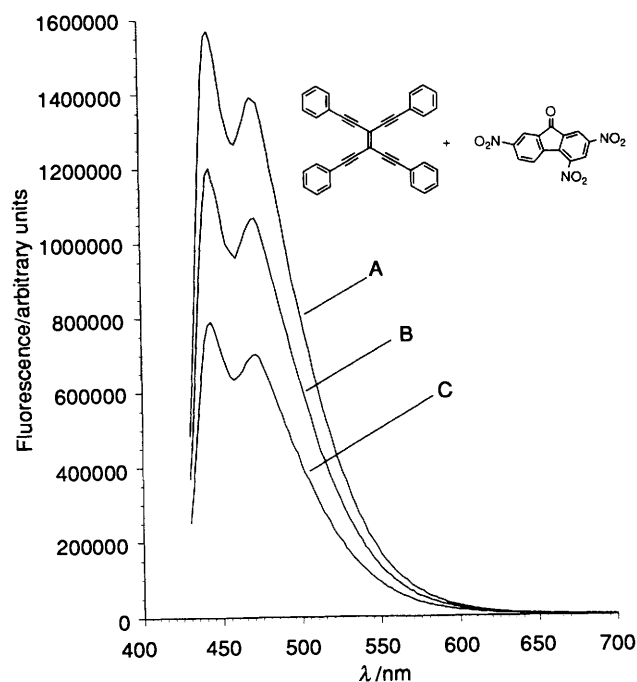


Fig. 3 Emission spectrum ($\lambda_{\text{exc}} = 410$ nm) of pure tetrakis(phenylethynyl)ethene 3 (10^{-8} mol dm^{-3} in CHCl_3) (curve A) and after addition of 4. Curve B was obtained after the addition of a 150-fold excess of 4 and curve C after the addition of a 400-fold excess of 4 to the solution of 3 at 298 K.

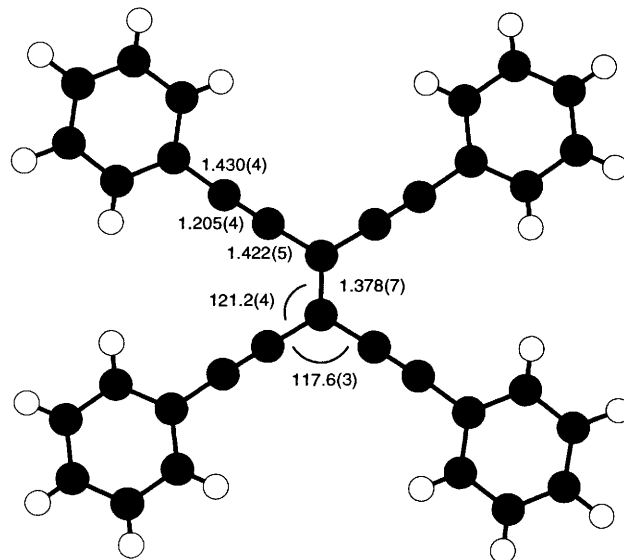


Fig. 4 Ball-and-stick representation of a molecule of 3 within the solid-state structure of the complex $[\mathbf{3}\cdot\mathbf{4}_2]$. Bond lengths are in Å, angles are in degrees.

[¶] Crystal data for $[\mathbf{3}\cdot\mathbf{4}_2]$ at 85 K: $[(\text{C}_{34}\text{H}_{20})\cdot(\text{C}_{13}\text{H}_5\text{N}_3\text{O}_7)_2]$. $M = 1058.6$, triclinic space group $P\bar{1}$ (No. 2), $Z = 2$, $D_c = 1.44$ g cm^{-3} , $a = 8.177(6)$ Å, $b = 15.146(5)$ Å, $c = 21.397(6)$ Å, $\alpha = 107.95(4)^\circ$, $\beta = 91.84(5)^\circ$, $\gamma = 103.84(5)^\circ$, $V = 2431.7(2.8)$ Å³. Data were measured on an Enraf-Nonius CAD4 diffractometer with Mo-K α radiation using ω/θ scans. The structure was solved by direct methods and refined anisotropically to give $R = 0.047$, $R_w = 0.054$ for 5016 independent observed reflections [$I \geq 3.0\sigma(I)$, $\theta \leq 23^\circ$].

Crystal data for $[\mathbf{3}\cdot\mathbf{5}_2]$ at 100 K: $[\frac{1}{2}(\text{C}_{34}\text{H}_{20})\cdot(\text{C}_{16}\text{H}_5\text{N}_5\text{O}_6)\cdot\text{CH}_2\text{Cl}_2]$. $M = 662.5$, triclinic space group $P\bar{1}$ (No. 2), $Z = 2$, $D_c = 1.48$ g cm^{-3} , $a = 8.640(3)$ Å, $b = 13.363(2)$ Å, $c = 14.101(8)$ Å, $\alpha = 82.47(3)^\circ$, $\beta = 72.20(4)^\circ$, $\gamma = 74.15(2)^\circ$, $V = 1489.2(1.1)$ Å³, $\mu = 2.45$ mm⁻¹. Data were measured on an Enraf-Nonius CAD4 diffractometer with Cu-K α radiation using ω/θ scans. The structure was solved by direct methods and refined anisotropically to give $R = 0.054$, $R_w = 0.066$ for 3642 independent observed reflections [$I \geq 3.0\sigma(I)$, $\theta \leq 65^\circ$].

each of the corners of the unit cell. The interplanar separation between the molecules of 3 and 4 within both stack types is 3.39 Å. The two independent stacks within the unit cell are inclined by 25° with respect to each other.

Dark-green single crystals of the complex between 3 and 5 suitable for X-ray diffraction[¶] were grown by slow evaporation of a dichloromethane solution containing an equimolar mixture of the two components. The solid state complex between 3 and 5 also has a stoichiometry of 1:2. The tetrakis(phenylethynyl)ethene molecule within $[\mathbf{3}\cdot\mathbf{5}_2]$, including the four phenyl groups, is planar to within ± 0.06 Å and, again, the structure of the tetraethynylethene backbone of 3 within $[\mathbf{3}\cdot\mathbf{5}_2]$ is almost identical with that of free 3^{7c} and that found in $[\mathbf{3}\cdot\mathbf{4}_2]$. Unlike

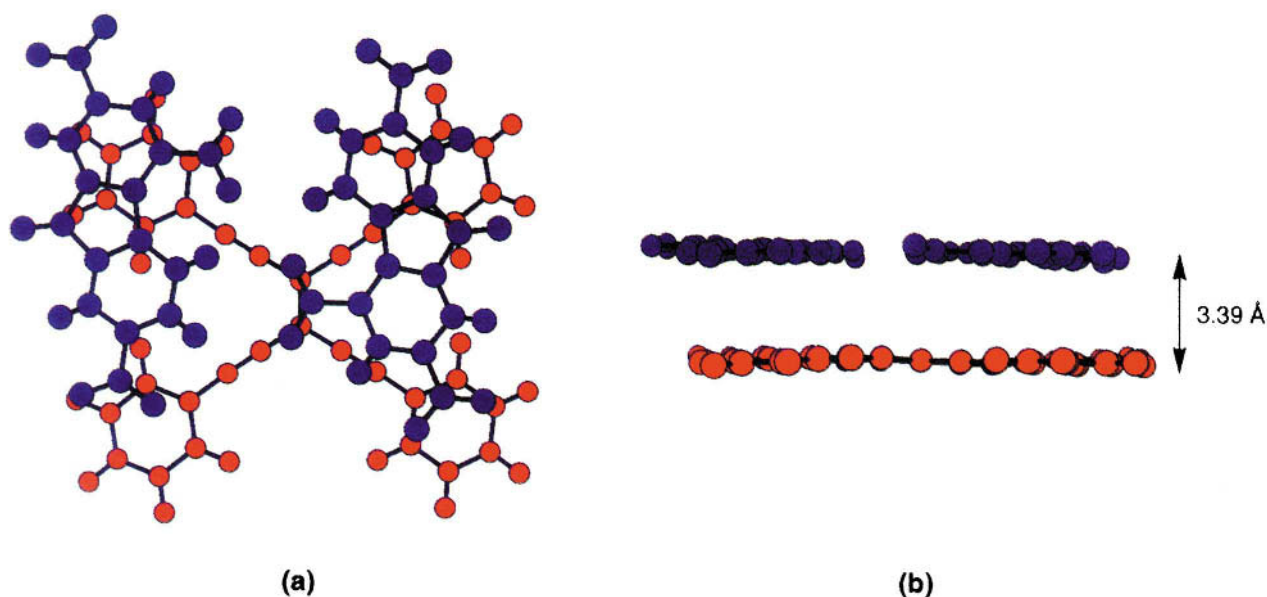


Fig. 5 Ball-and-stick representations of the solid-state structure of the complex $[3\cdot 4_2]$, (a) viewed perpendicular to the mean plane of 3 and (b) viewed parallel to the mean plane of 3. For clarity, 3 is coloured red and 4 is coloured blue.

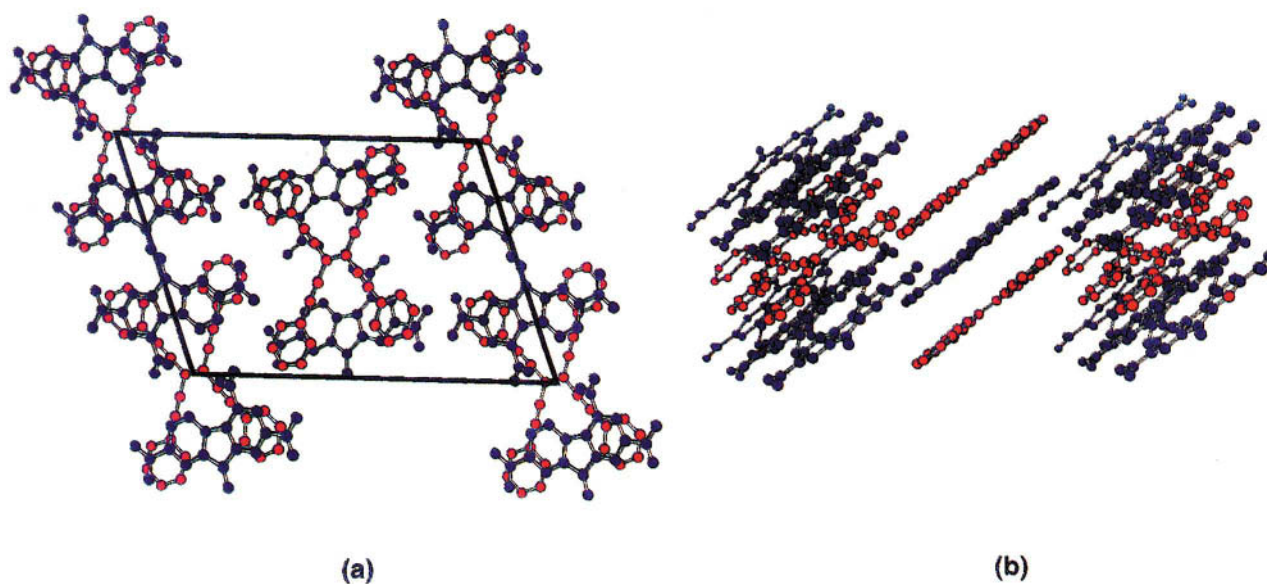


Fig. 6 (a) View along the crystallographic a direction of the unit cell of the solid-state structure of the complex $[3\cdot 4_2]$, showing the continuous donor-acceptor stacks; (b) view perpendicular to the crystallographic a direction in the solid-state structure of the complex $[3\cdot 4_2]$ showing the two independent donor-acceptor stacks tilted by 25° with respect to each other. For clarity, 3 is coloured red and 4 is coloured blue. The unit cell is marked as a bold green line.

$[3\cdot 4_2]$, the two molecules of 5 within the complex (Fig. 7) do not exactly span the two *cis*-enediynes present in 3, although they are disposed about a centre of symmetry. This may be attributed to the incorporation of solvent molecules (CH_2Cl_2) within the crystal lattice (*vide infra*). Once again, there are continuous donor-acceptor stacks (Fig. 8) roughly parallel to the a axis with one independent stack per unit cell. The interplanar separation between the molecules of 3 and 5 within the stacks is 3.33 Å. In contrast with $[3\cdot 4_2]$, $[3\cdot 5_2]$ has extended layer structure roughly parallel to the bc plane [Fig. 8(b)]. These layers consist of alternating molecules of 3 and 5 which form a checkerboard-type array (Fig. 9). The checkerboard pattern is stabilised by three sets of $\text{C-H}\cdots\text{X}$ interactions (Fig. 10) which form chains through the layers. The CH_2Cl_2 solvent molecules, incorporated in a stoichiometric amount,

play a pivotal role in the stabilisation of the layered structure. In addition to the 'in layer' contacts between the chlorine atoms of the CH_2Cl_2 molecules and hydrogen atoms on both 3 and 5, there are also short contacts between the H-atoms of the CH_2Cl_2 molecules and both the aromatic rings of 3 (centroid $\cdots\text{H}$ distance 2.98 Å) and the N-atoms of the nitrile groups of 5 (N $\cdots\text{H}$ distance 2.67 Å) in the adjacent layers.

The orientation of the acceptor molecules with respect to the tetrakis(phenylethynyl)ethene molecules in both $[3\cdot 4_2]$ and $[3\cdot 5_2]$ is somewhat surprising since, although there is clearly a charge transfer type interaction between 3 and either 4 or 5, the solid state structure does not maximise the HOMO-LUMO overlap between donor and acceptor. In order to investigate this observation further, we turned to alternative models of π - π interactions. Recent work from several laboratories¹⁴⁻¹⁶

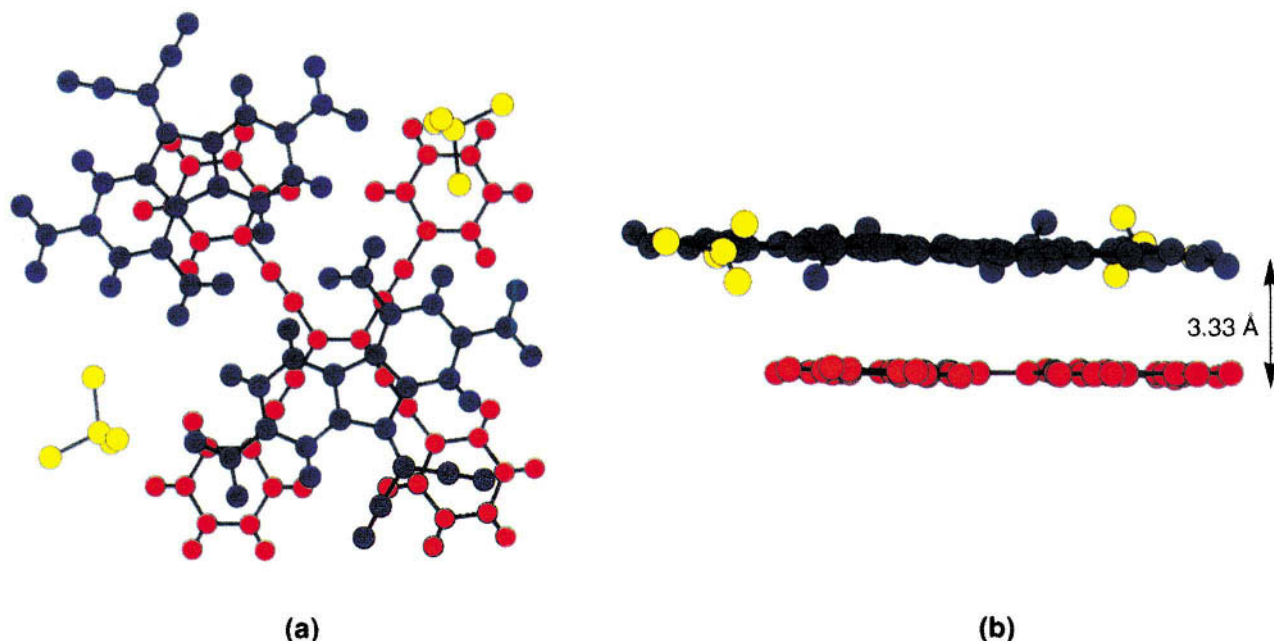


Fig. 7 Ball-and-stick representations of the solid-state structure of the complex $[3\cdot 5_2]$, (a) viewed perpendicular to the mean plane of **3** and (b) viewed parallel to the mean plane of **3**. For clarity, **3** is coloured red and **5** is coloured blue, and CH_2Cl_2 solvent molecules are coloured yellow.

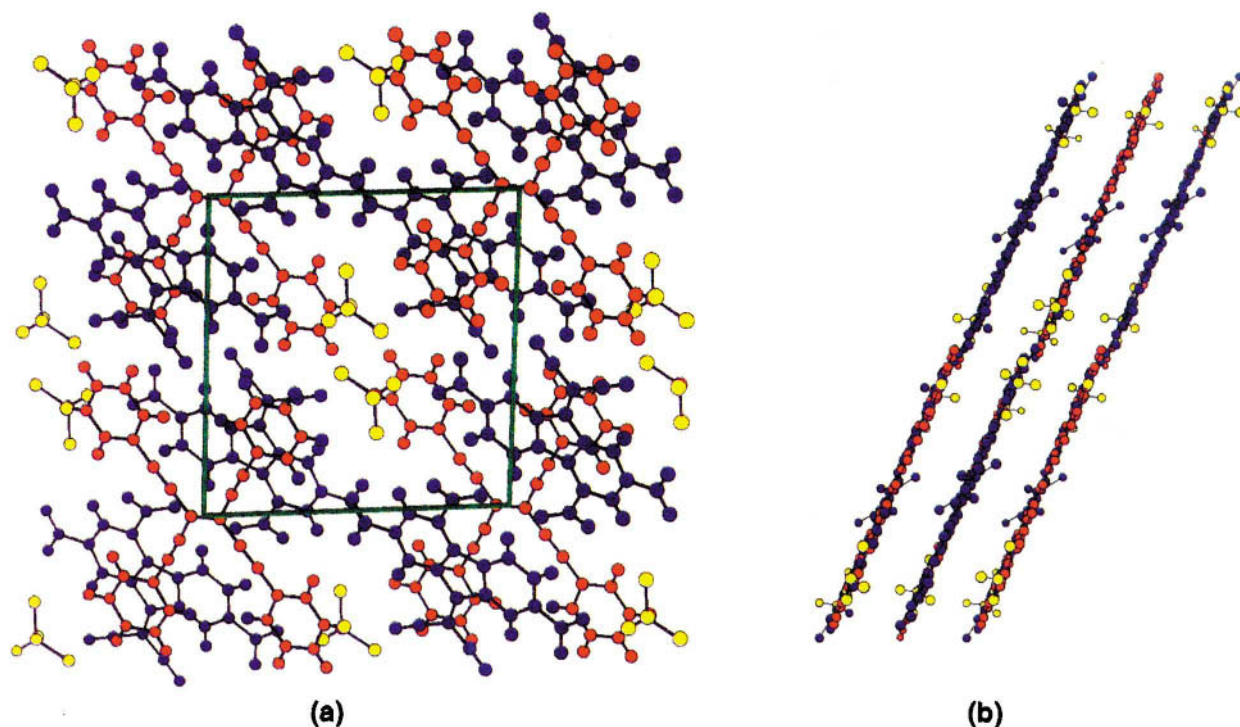


Fig. 8 (a) View along the crystallographic a direction of the unit cell of the solid-state structure of the complex $[3\cdot 5_2]$, showing the continuous donor-acceptor stacks; (b) view parallel to the bc plane in the solid-state structure of the complex showing the layered structure. For clarity, **3** is coloured red and **5** is coloured blue, and CH_2Cl_2 solvent molecules are coloured yellow. The unit cell is marked as a bold green line.

has asserted that electrostatic interactions are much more important in determining the orientations of π -surfaces with respect to each other than orbital interactions. We therefore calculated** the point charges present on each component of the two complexes $[3\cdot 4_2]$ and $[3\cdot 5_2]$. The calculated atom-centred partial charges were then projected on to the X-ray

crystal structures of $[3\cdot 4_2]$ and $[3\cdot 5_2]$ (Fig. 11). There is a good correlation between positive and negative charges in either **4** or

|| For an alternative view, see S. B. Ferguson, E. M. Sanford, E. M. Seward and F. Diederich, *J. Am. Chem. Soc.*, 1991, **113**, 5410.

** Atom-centred electrostatic potential charges were calculated using the MNDO Hamiltonian and then scaled by a uniform factor of 1.42. This scaling factor has been shown to give a good correlation with charges derived from 6-31G* *ab initio* calculations (B. H. Besler, K. M. Merz and P. A. Kollman, *J. Comput. Chem.*, 1990, **11**, 431). For the complexes $[3\cdot 4_2]$ and $[3\cdot 5_2]$, only centres with a charge of $> 0.1e$ were considered significant.

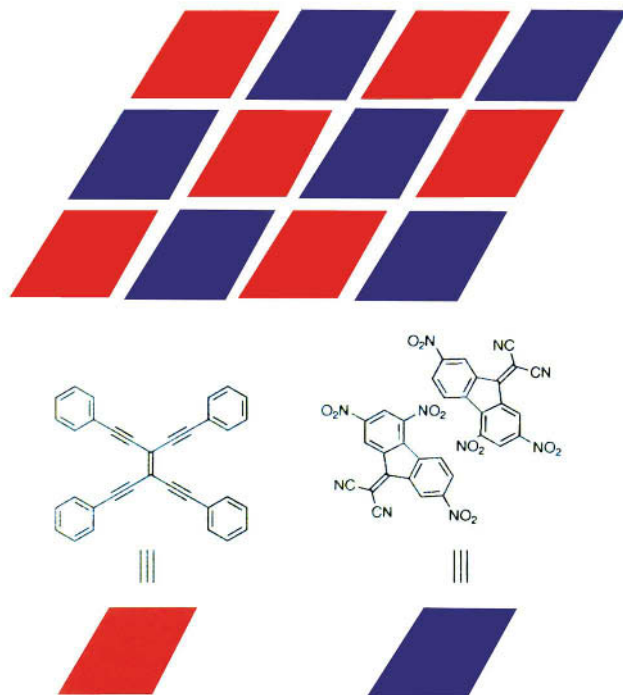


Fig. 9 Schematic representation of the checkerboard-type layers found in the solid state structure of the complex [3·5₂].

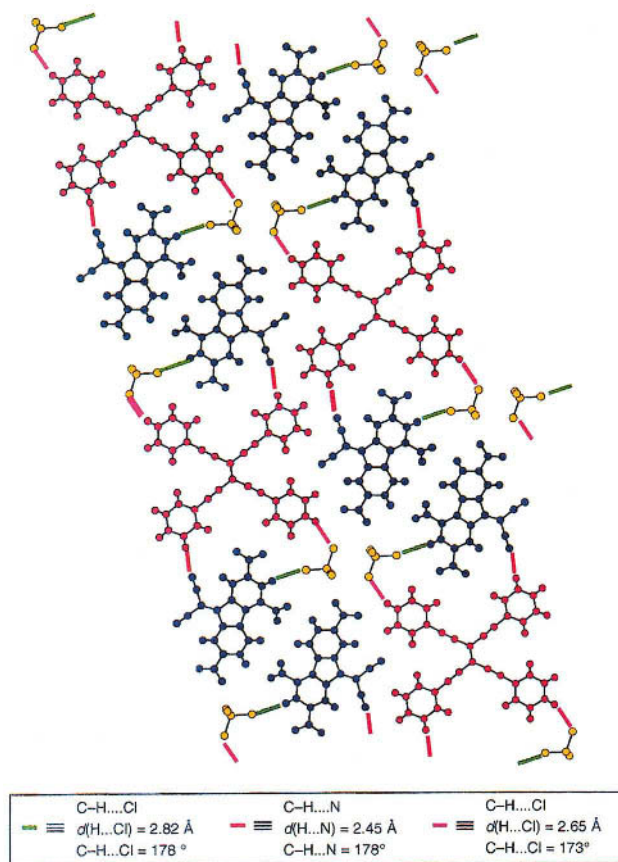


Fig. 10 A small section of the infinite layers found in the solid-state structure of the complex [3·5₂] illustrating the stabilising C-H...X interactions within the layer. For clarity, 3 is coloured red and 5 is coloured blue, and CH₂Cl₂ solvent molecules are coloured yellow.

5 with corresponding oppositely charged regions of 3. Interestingly, on both [3·4₂] and [3·5₂] there is one acceptor molecule which has a large number of charge correlations,

whereas the other acceptor molecule in the complex has only a few correlations, or even none as in the case of 5, suggesting that crystal packing effects, *i.e.*, the filling of voids in the crystal lattice may also have an important role in these examples.

The stability of the solution state complexes between 3, and 4 and 5 was assessed by ¹H NMR titrations in CDCl₃ solution under conditions which favoured the formation of only 1:1 complexes, *i.e.*, 3 is in large excess. This experiment afforded *K_a* values (Table 1) of 7.9 dm³ mol⁻¹ at 300 K for a 1:1 complex [3·4], corresponding to a free energy of binding ($-\Delta G$) of 1.23 ± 0.05 kcal mol⁻¹, and 31.5 dm³ mol⁻¹ at 300 K for a 1:1 complex [3·5], corresponding to a free energy of binding ($-\Delta G$) of 2.05 ± 0.05 kcal mol⁻¹. These values are in the range expected for normal molecular π -complexes.^{17,18} In order to probe the origin of the association between 3 and the π -acceptors 4 and 5 further, we investigated the interaction between 3 and a number of structurally related compounds containing phenylethynyl units. The results are summarised in Table 1. There is very weak association between both of the acceptors 4 and 5 and 8 and 11, whereas that between 4 and 5, and 3, 9 and 10 is much stronger. If the stability of the complex is determined purely by the degree of the orbital overlap between the HOMO of the donor and the LUMO of the acceptor¹⁹ (the degree of charge transfer) then there should be a direct correlation between the relative energies of these orbitals (the HOMO-LUMO gap) and the observed binding constants. The results in Table 1 demonstrate that there is no such correlation in the results obtained here—3 and 9 have almost identical binding constants with 4, however their IPs differ by around 1.5 eV (−8.47 eV for 3 and −9.96 eV for 9 from AM1 calculations). Thus, some other factor must be determining the strength of the association in these complexes. Interestingly, a plot (Fig. 12) of the spatial displacement of the phenyl rings in the donor molecules, as judged by the centroid-centroid separation of the phenyl rings, against *K_a* or ΔG reveals a Gaussian-type distribution. This suggests that the binding is mediated by the positioning of the phenyl rings in space, rather than their electronic characteristic, and that both phenyl rings are involved in binding. Further evidence supporting this conclusion was derived from the fact that there is no measurable association between 4 or 5 and the dibromoolefin 7 which contains two *geminal* phenylethynyl units. The X-ray crystal structure †† (Fig. 13) of 7 reveals that the phenyl rings are separated by 9.34 Å and hence they lie too far apart to permit 5 to interact simultaneously with both of the phenyl rings, even weakly.

In order to determine whether the tetraethynylethene skeleton itself was capable of interacting directly with π -acceptors, we synthesised a derivative of 3 in which the phenyl rings could not participate in the binding of the π -acceptor. Thus, dibromoolefination¹² (Scheme 2) of 3,5-bis(*tert*-butyl)benzaldehyde 12 followed by treatment of the resulting dibromoethene 13 with *n*-butyllithium afforded 3,5-bis(*tert*-butyl)phenylacetylene 14. Elaboration of 14 using methodology identical with that employed in the synthesis of 3 afforded tetrakis[3,5-bis(*tert*-butyl)phenylethynyl]ethene 17, *via* 15 and

†† Crystal data for 7 at 293 K: C₁₈H₁₀Br₂. *M* = 386.1, monoclinic space group *P*2₁/*c* (No. 14), *Z* = 4, *D_c* = 1.685 g cm⁻³, *a* = 4.206(2) Å, *b* = 10.325(2) Å, *c* = 35.072(7) Å, β = 91.93(3)°, *V* = 1522.2(8) Å³, μ = 5.312 mm⁻¹. Data were measured on a Picker Stoe diffractometer with Mo-K α radiation using 2 θ - θ scans. The structure was solved by direct methods and refined anisotropically to give *R* = 0.054, *R_w* = 0.065 for 1392 independent observed reflections [*F* ≥ 6.0 σ (*F*), 3° ≤ 2 θ ≤ 45°]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. For details of the CCDC deposition scheme see 'Instructions for Authors (1995)', *J. Chem. Soc., Perkin Trans. 2*, 1995, Issue 1.

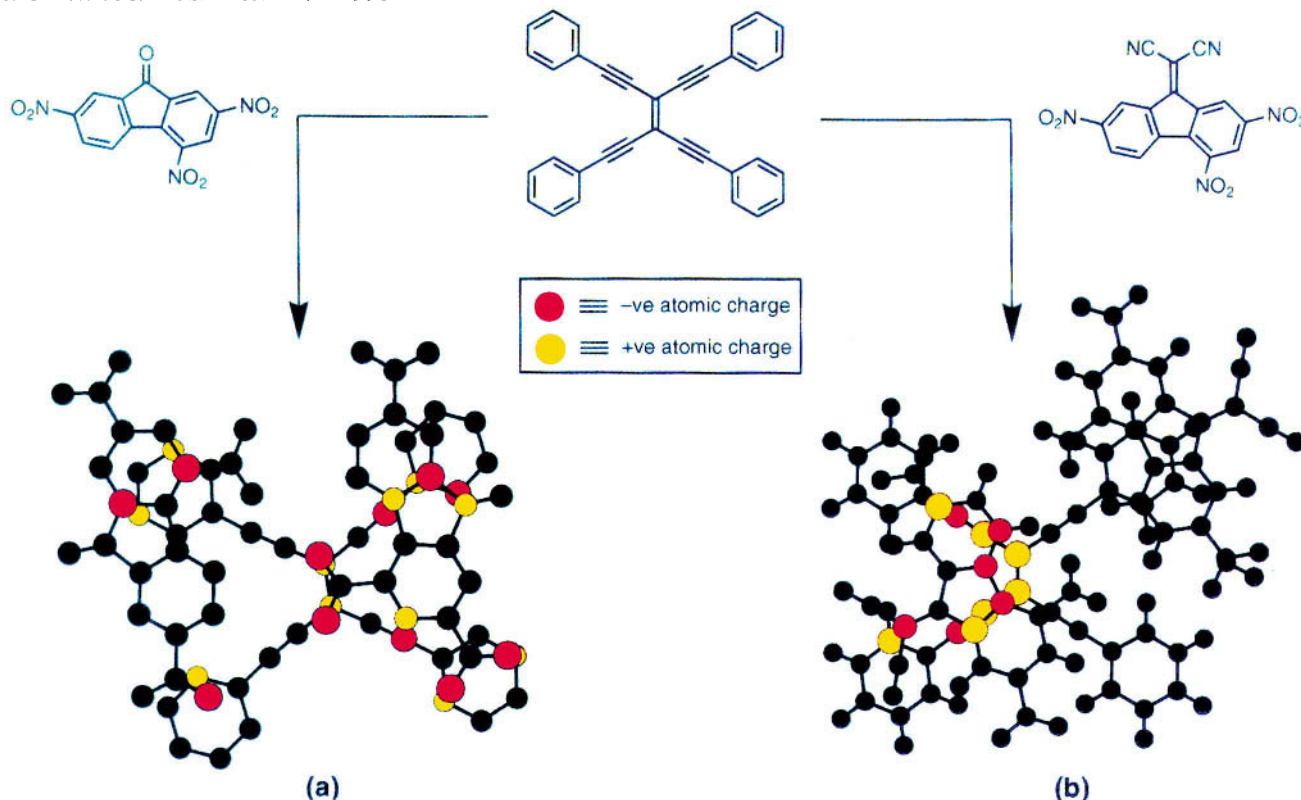


Fig. 11 Correlation of calculated atom-centred molecular electrostatic potential charges in the solid-state structures of (a) [3·4₂] and (b) [3·5₂]

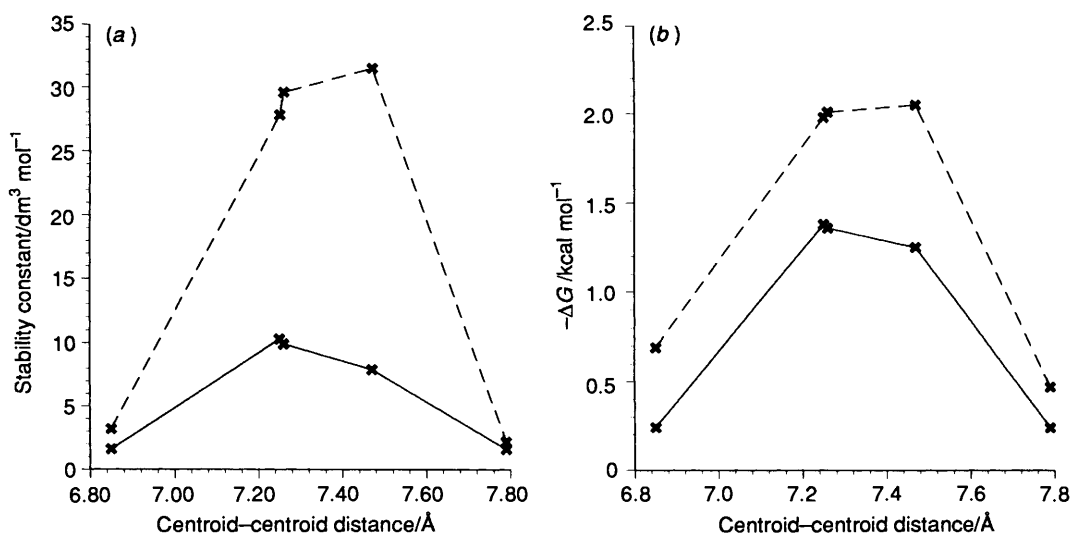


Fig. 12 Graph of (a) stability constant (K_a) in $\text{dm}^3 \text{mol}^{-1}$ and (b) free energy of association ($-\Delta G$) in kcal mol^{-1} against phenyl centroid-phenyl centroid distance for the association of the molecules containing phenylethynyl groups in Table 1 with 4 and 5. Data for 4 is the solid line, data for 5 is the dashed.

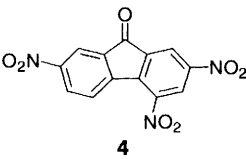
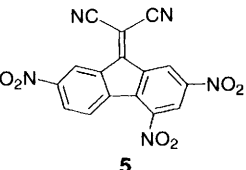
16, in 15% overall yield starting from 12. X-ray crystallography^{‡‡} reveals (Fig. 14) that, as expected, the bis(*tert*-butyl)phenyl rings in 17 are tilted out of the plane of the tetraethynylethene skeleton—one pair of *trans* 3,5-bis(*tert*-butyl)phenyl

rings is inclined by 89° relative to the mean plane of the tetraethynylethene system, whereas the other pair is inclined by 17° relative to the mean plane of the tetraethynylethene system. This arrangement is preserved in solution^{§§} and ensures that if the association of 17 with π -acceptors occurs, it has to be

^{‡‡} Crystal data for 17 at 295 K: $\text{C}_{66}\text{H}_{84}$. $M = 876$, monoclinic space group $P2_1/c$ (No. 14), $Z = 2$, $D_c = 1.00 \text{ g cm}^{-3}$, $a = 12.302(3) \text{ \AA}$, $b = 15.747(1) \text{ \AA}$, $c = 17.927(4) \text{ \AA}$, $\beta = 123.03(2)^\circ$, $V = 2911(1) \text{ \AA}^3$, $\mu = 0.41 \text{ mm}^{-1}$. Data were measured on an Enraf-Nonius CAD4 diffractometer with Cu-K α radiation using ω/θ scans. The structure was solved by direct methods and refined anisotropically to give $R = 0.089$, $R_w = 0.100$ for 3486 independent observed reflections [$I \geq 3.0\sigma(I)$, $\theta \leq 65^\circ$]. There is significant orientational disorder associated with the *tert*-butyl groups attached to the phenyl rings. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

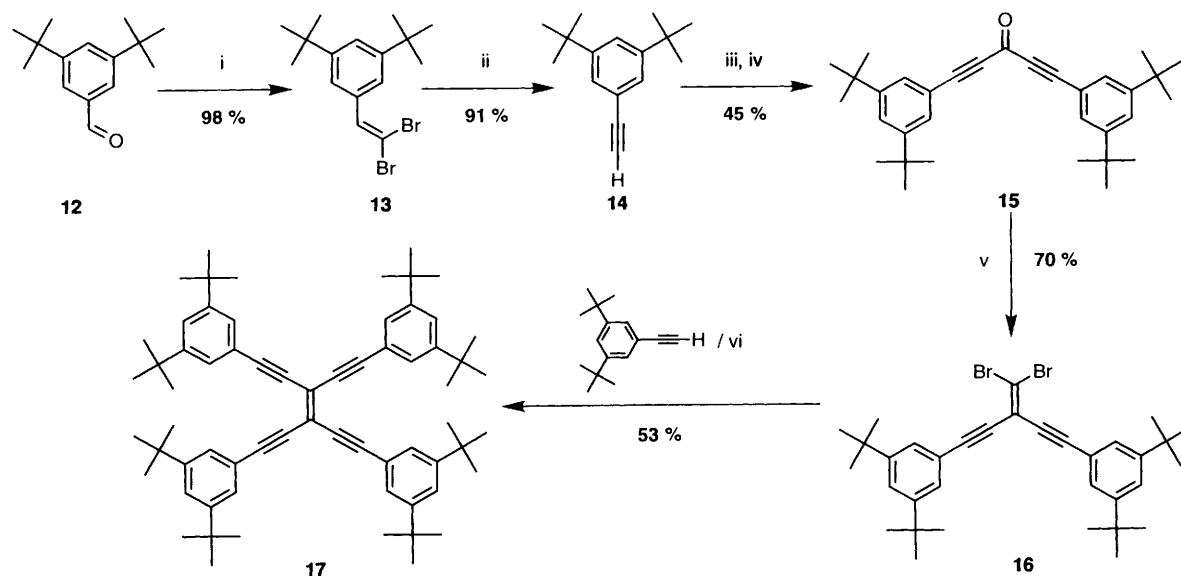
^{§§} Electrochemical measurements (C. Boudon, J.-P. Gisselbrecht, M. Gross, J. Anthony, A. M. Boldi, R. Faust, T. Lange, D. Philp, J. D. van Loon and F. Diederich, manuscript in preparation) reveal that the first reduction potential of 17 is -1.90 V (THF, $0.1 \text{ mol dm}^{-3} \text{ Bu}_4\text{NPF}_6$, ferrocene reference). This is much closer to the value for 1b (-1.96 V) than to the value for 3 (-1.76 V), suggesting that the conjugation between the 3,5-bis(*tert*-butyl)phenyl rings in 17 and the tetraethynylethene skeleton is weak, *i.e.*, the 3,5-bis(*tert*-butyl)phenyl rings are also twisted out of the plane of the tetraethynylethene skeleton in solution.

Table 1 Association of **4** and **5** with various molecules containing phenylethynyl units

	8	9	10	3	11
Phenyl centroid-centroid distance/Å ^a	6.85	7.25	7.26	7.47	7.79
	1.6	10.3	9.9	7.9	1.6
4	0.24	1.38	1.36	1.25	0.24
	3.2	27.8	29.6	31.5	2.2
5	0.69	1.98	2.01	2.05	0.47

^a Distance in Å between the centroids of the two *cis* phenyl rings in **3**, **9**, **10** and **11**, and the centroids of the two phenyl rings in **8**. The centroid-centroid distances for **10** and **11** were derived from molecular modelling using the CVFF forcefield and the INSIGHT II program (Version 2.2.0, Biosym Technologies, San Diego, 1993), the distances in **3**, **8** (A. A. Espiritu and J. G. White, *Z. Kristallogr.*, 1978, **147**, 177) and **9** (D. Philp, V. Gramlich, F. Diederich, unpublished results) were derived from X-ray crystal structures.

Top numbers for each complex are K_a values ($\text{dm}^3 \text{mol}^{-1}$), determined in CDCl_3 at 300 K by ^1H NMR titration. The concentration of **4** or **5** was held constant. The chemical shift changes induced in the five probe protons in **4** or **5** by addition of increasing amounts of **3**, **8**, **9**, **10** or **11** were followed, and fitted by a non-linear curve-fitting method²³ to the 1:1 binding isotherm. The probe protons displayed upfield shifts at saturation binding in the range 0.35–0.60 ppm. The quoted values of K_a are the average of two determinations. Errors in $-\Delta G$ (bottom numbers in kcal mol^{-1}) calculated from the values of K_a are $\pm 0.05 \text{ kcal mol}^{-1}$.



Scheme 2 Reagents and conditions: i, CBr_4 (2 equiv.), Zn (2 equiv.), PPh_3 (2 equiv.), CH_2Cl_2 ; ii, BuLi , THF , -78°C ; iii, BuLi , -78°C , HCOOEt (0.4 equiv.); iv, HPyrcrO_3 , 20°C , CH_2Cl_2 ; v, CBr_4 (2 equiv.), PPh_3 (5 equiv.), CH_2Cl_2 ; vi, $[\text{PdCl}_2(\text{PPh}_3)_2]$, CuI , BuNH_2 , C_6H_6

mediated by the tetraethynylethene π -system. The association of **3** and **17** with a variety of π -acceptors was assessed by a series of fluorescence quenching experiments (Table 2). The results indicate that the phenyl rings of **3** are essential for association to occur. The presence of the fluorene skeleton also appears to be essential—there is no association between **18** and either **3** or **17**. Thus, we can conclude that there is no significant association

between the tetraethynylethene π -system and any of the π -acceptors in Table 2.

Conclusions

The design of solid state structures²⁰ based on non-covalent interactions is a rapidly expanding area. Although we were not

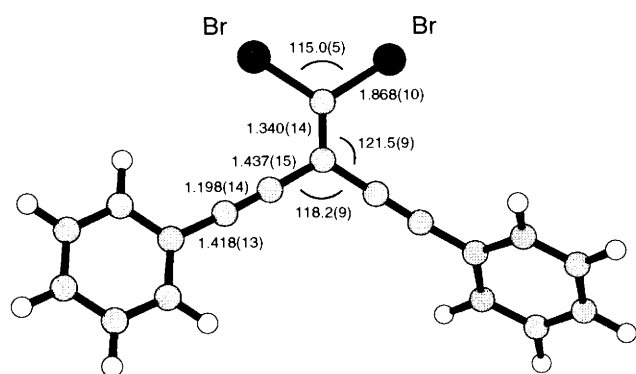


Fig. 13 Ball-and-stick representation of the X-ray crystal structure of **7**; distances are in Å, angles are in degrees

able to utilise the π -system of the unsubstituted tetraethynyl-ethene skeleton directly in the construction of π -complexes, the work presented here demonstrates that acetylene-based systems are useful rigid scaffolds for the construction of highly ordered molecular arrays.²¹ The lack of correlation between orbital energies in the donor and acceptor components of the complexes and the observed association constants emphasises that the role of orbital interactions in molecular complexation may be overplayed. In addition, if the excellent correlation between electrostatic point charges in the two components of the solid-state π -complexes is carried over into solution, further investigations may lead to new design criteria for donor-acceptor π -complexes, for both orientation and association, based on an electrostatic charge model.¹⁴ The results presented here illustrate that rigid frameworks based on tetraethynyl-ethene, coupled with relatively weak π - π interactions, have great potential for achieving the challenging goal of 'designer solids'.

Experimental

General procedures

Solvents and reagents were purified where necessary using literature methods.²² Tetrahydrofuran (THF) was heated under reflux over Na-benzophenone ketyl and distilled under nitrogen. Thin-layer chromatography (TLC) was performed on plastic or glass plates (10 × 5 cm) coated with Merck 5735 Kieselgel 60F. Developed plates were air-dried, scrutinised under a UV lamp, and then dipped in KMnO₄ solution and heated to *ca.* 100 °C. Column chromatography was performed using Kieselgel 60 (0.040–0.063 mm mesh, Merck 9385). Melting points were determined with a Büchi melting point apparatus and are uncorrected. UV-VIS spectra were recorded on a Varian Cary 5 spectrophotometer fitted with a thermostatted cell holder operated under microcomputer control. Fluorescence spectra were recorded in the emission mode using a SPEX 212 Fluorolog spectrometer. ¹H NMR spectra were recorded on Varian Gemini 200 (200 MHz) or 300 (300 MHz) spectrometers, using the deuterated solvent as lock and residual solvent or tetramethylsilane as an internal reference. ¹³C NMR spectra were recorded on Varian Gemini 200 (50 MHz) or 300 (75 MHz) spectrometers. Elemental analyses were carried out by the Microanalysis Services of the *Laboratorium für Organische Chemie* at the ETH or the University of Birmingham.

Computational studies

Molecular mechanics calculations were carried out on a Silicon Graphics Crimson workstation using the INSIGHT II/DISCOVER package (Version 2.2.0, Biosym Technologies Inc., San Diego, 1993) and the CVFF forcefield. Semiempirical self-consistent field molecular orbital (SCF-MO) calculations

were carried out on a Silicon Graphics Crimson workstation using the MOPAC 6 program (QCPE 455). The program was compiled to permit calculations on molecules containing up to 200 heavy atoms from FORTRAN source code provided by Biosym Technologies Inc. SCF-MO geometry optimisations were carried out using either the Broydon-Fletcher-Goldfarb-Shanno (BFGS) or the Eigenvector Following (EF) minimisation methods. All internal coordinates were optimised, and gradients of less than 0.20 were achieved in all cases. The structures obtained were characterised as local minima by means of a vibrational analysis (FORCE calculation). Single point SCF-MO molecular electrostatic potential calculations were performed on a Silicon Graphics Crimson workstation using the MOPAC 93 program (QCPE 455).

Determination of stability constants

Stability constants (K_a) were determined by ¹H NMR spectroscopic titrations. In a typical experiment, one of the components of the π -complexes was dissolved in CDCl₃ (*ca.* 10⁻³ mol dm⁻³) and the ¹H NMR spectrum of the resulting solution recorded. Successive amounts of the other component of the π -complex were then added, and the ¹H NMR spectra of these mixtures were recorded. The addition of the second component was adjusted, by means of an estimated stability constant of 15 dm³ mol⁻¹, such as to provide at least seven experimental points in the 20% to 80% binding region of the saturation curve for the complex. The data from the ¹H NMR titration were then treated by means of a non-linear curve fitting program²³ to extract values of K_a for the π -complex under investigation from the chemical shift changes observed in probe protons. All values quotes are the average of two determinations.

1,5-Diphenylpenta-1,4-diyne-3-one (6)

Phenylacetylene (25.14 g, 246 mmol) was dissolved in dry THF (200 cm³) and cooled under an atmosphere of N₂ to -78 °C. *n*-Butyllithium (154 cm³, 246 mmol, 1.6 mol dm⁻³ in hexanes) was added using a syringe. The reaction mixture was warmed to -50 °C and allowed to stir for 15 min. Ethyl formate (7.84 g, 105 mmol) was added dropwise over 30 min and the reaction mixture allowed to warm slowly to -10 °C over 4 h. Saturated aqueous NH₄Cl (15 cm³) was added, and the organic layer was washed successively with saturated aqueous NaCl, saturated aqueous NaHCO₃, and water. The residual dark brown oil obtained by removal of the solvent was redissolved in CH₂Cl₂ (200 cm³) and added to a vigorously stirred suspension of pyridinium chlorochromate (50 g, 234 mmol) and molecular sieves 4 Å (40 g) in CH₂Cl₂ (400 cm³). The resulting mixture was stirred at room temperature for 3 h and then filtered through a pad of silica gel. The resulting orange solution was evaporated to dryness and the residue purified by flash chromatography (SiO₂; hexane-CH₂Cl₂ 3:1). The fractions containing the product were combined and evaporated to dryness. Recrystallisation of the residue from pentane afforded **6** as a pale yellow solid (15.16 g, 62%). Mp 100–101 °C; *m/z* (EIMS) 230 (M⁺); δ_H (200 MHz; CDCl₃) 7.51–7.59 (4 H, m) and 7.33–7.41 (6 H, m); δ_C (50 MHz; CDCl₃) 161.7, 132.3, 129.3, 128.5, 122.6, 98.7 and 88.7 [Found: C, 88.6; H, 4.4. Calc. for C₁₇H₁₀O (*M*, 230.27): C, 88.67; H, 4.38%].

3-Dibromomethylene-1,5-diphenylpenta-1,4-diyne (7)

Method A. Triphenylphosphine (47.2 g, 180 mmol) was slurred with Zn powder (11.9 g, 180 mmol) in CH₂Cl₂ (650 cm³) and cooled to 0 °C. CBr₄ (59.19 g, 178 mmol) was added, and the resulting dark-coloured suspension was stirred rapidly at room temperature for 24 h. Ketone **6** (12.6 g, 55 mmol) was dissolved in CH₂Cl₂ (50 cm³) and added to the reaction mixture and the resulting tan-coloured suspension

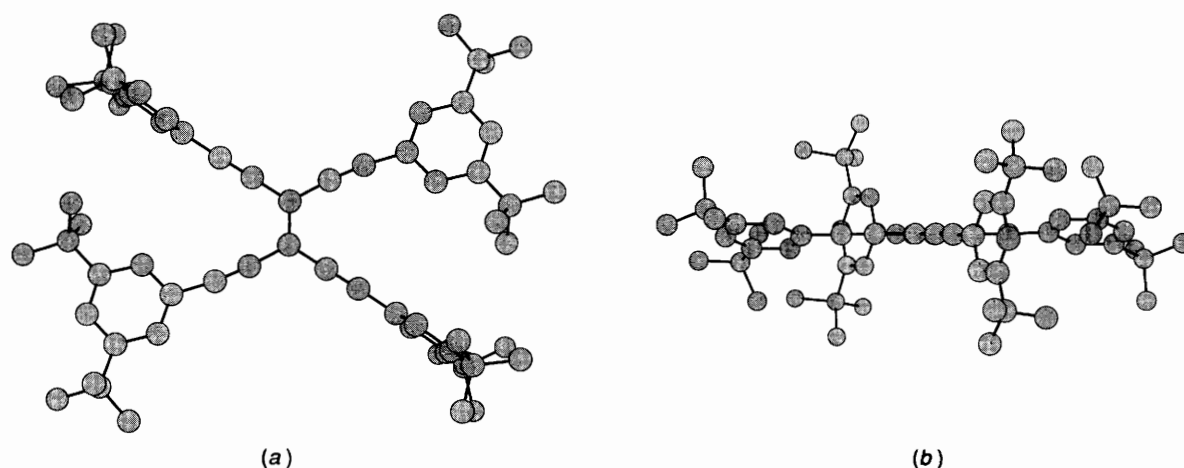
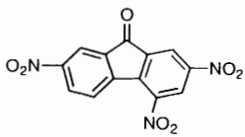
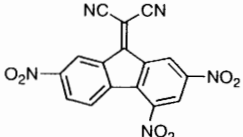
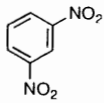

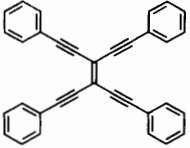

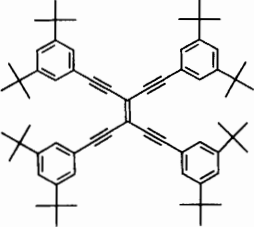
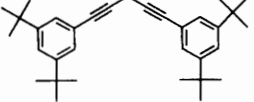


Fig. 14 Ball-and-stick representation of the X-ray crystal structure of **17**, viewed (a) from directly above the plane of the tetraethynylethene skeleton and (b) from in the plane of the tetraethynylethene skeleton. The *tert*-butyl groups are highly disordered and only one idealised geometry is shown for these groups. Hydrogen atoms have been omitted for clarity.

Table 2 Quenching of tetraethynylethene fluorescence by π -acceptors. Top numbers indicate % quenching at [acceptor]:[fluorophore] = 150:1; bottom numbers indicate % quenching at [acceptor]:[fluorophore] = 400:1

Fluorophore	Acceptor			
				
	4	5	18	2
	23	34	< 2	< 2
	50	67	< 2	< 2
	< 2	< 2	< 2	< 2
	< 2	8	< 2	< 2

stirred at room temperature for 12 h. Hexane (200 cm³) was added and the resulting slurry filtered rapidly through a pad of silica gel. The filtrate was evaporated to dryness and the residue purified by flash chromatography (SiO₂; hexane-CH₂Cl₂ 5:1) which afforded **7** as a colourless solid (17.1 g, 81%). Mp 97–98 °C; *m/z* (EIMS) 384/386/388 (M⁺); δ_{H} (200 MHz; CDCl₃) 7.50–7.59 (4 H, m) and 7.30–7.41 (6 H, m); δ_{C} (50 MHz; CDCl₃) 132.1, 129.6, 128.8, 122.5, 114.6, 108.0, 96.0 and 86.3 [Found: C, 56.1; H, 2.5. Calc. for C₁₈H₁₀Br₂ (*M*, 386.09): C, 56.00; H, 2.61%]. The product from this procedure gave highly variable results when utilised in Pd-catalysed alkynylations, producing, in general, poor yields of alkynylated products.

Method B. Triphenylphosphine (94.3 g, 360 mmol) was dissolved in CH₂Cl₂ (650 cm³) and cooled to 0 °C. CBr₄ (23.1 g, 72 mmol) was added and the resulting dark-coloured solution stirred at 0 °C for 45 min. Ketone **6** (8.28 g, 36 mmol) was dissolved in CH₂Cl₂ (50 cm³) and was added to the reaction mixture. The resulting solution was allowed to warm

slowly to room temperature and was stirred at room temperature for 12 h. Hexane (200 cm³) was added and the resulting slurry filtered rapidly through a pad of silica gel. The filtrate was evaporated to dryness and the residue purified by flash chromatography (SiO₂; hexane-CH₂Cl₂ 5:1) which afforded **7** as a colourless solid (8.89 g, 64%) which gave analytical data identical with those reported above. The product from this procedure gave consistently good results when employed in Pd-catalysed alkynylation reactions.

1,6-Diphenyl-3,4-bis(phenylethynyl)hex-3-ene-1,5-diyne (**3**)

Dibromoolefin **7** (1.83 g, 4.7 mmol) was dissolved in benzene (45 cm³) and the solution degassed by bubbling Ar gas through for 30 min. *n*-BuNH₂ (3.0 cm³, 30.4 mmol) was added and the degassing of the solution continued for a further 15 min. [PdCl₂(PPh₃)₂] (280 mg, 0.4 mmol) was added, followed by CuI (77 mg, 0.4 mmol) and the degassing procedure continued for a further 5 min. Phenylacetylene (1.02 g, 10 mmol) was

added and the resulting solution stirred under Ar at room temperature for 90 min. The reaction mixture was diluted with hexane (150 cm³) and filtered through a pad of silica gel to remove metal residues. Evaporation of the filtrate, flash chromatography (SiO₂; hexane–CH₂Cl₂ 9:1), and recrystallisation from pentane afforded **3** as a bright yellow solid (1.16 g, 57%). Mp 146–147 °C; *m/z* (EIMS) 428 (M⁺); δ_H(200 MHz; CDCl₃) 7.53–7.61 (8 H, m) and 7.31–7.40 (12 H, m); δ_C(50 MHz; CDCl₃) 131.8, 129.2, 128.5, 122.6, 117.2, 99.1 and 87.6 [Found: C 95.4; H 4.6. Calc. for C₃₄H₂₀ (M, 428.54): C, 95.32; H, 4.68%].

1,1-Dibromo-2-[3,5-bis(*tert*-butyl)phenyl]ethene (**13**)

Triphenylphosphine (70.5 g, 270 mmol) was slurred with Zn powder (17.5 g, 180 mmol) in CH₂Cl₂ (650 cm³) and cooled to 0 °C under N₂. CBr₄ (89.3 g, 270 mmol) was added, and the resulting dark-coloured suspension was stirred rapidly at room temperature for 24 h. The reaction mixture was cooled to 0 °C, and 3,5-bis(*tert*-butyl)benzaldehyde²⁴ (29.3 g, 134 mmol) in CH₂Cl₂ (150 cm³) was added. The resulting tan-coloured suspension was allowed to warm to room temperature and stirred for a further 6 h. Hexane (200 cm³) was added and the resulting slurry filtered rapidly through a pad of silica gel. The filtrate was evaporated to dryness and the residue purified by flash chromatography (SiO₂; hexane) affording **13** as a clear oil (49.6 g, 98%). *m/z* (EIMS) 372/374/376 (M⁺); δ_H(200 MHz; CDCl₃) 7.45 (2 H, t, *J* = 1.8 Hz), 7.37 (4 H, d, *J* = 1.8 Hz), 7.14 (1 H, s) and 1.36 (36 H, s); δ_C(50 MHz; CDCl₃) 151.8, 128.9, 126.1, 119.8, 116.4, 95.9, 35.2 and 31.5 [Found: C 51.45; H 6.0. Calc. for C₁₆H₂₂Br₂ (M, 374.16): C, 51.36; H, 5.93%].

3,5-Bis(*tert*-butyl)phenylacetylene (**14**)

Dibromoolefin **13** (49.0 g, 130 mmol) was dissolved in dry THF (400 cm³) and cooled under N₂ to –78 °C. *n*-Butyllithium (250 cm³, 400 mmol, 1.6 mol dm^{–3} in hexanes) was added to the reaction mixture over a period of 5 min and the resulting dark orange solution stirred at –78 °C for 1 h. The reaction mixture was warmed to room temperature and stirred for a further 90 min. Saturated aqueous NH₄Cl (100 cm³) was added and the organic layer separated and dried (MgSO₄). The solvent was removed *in vacuo* and the residual oil purified by flash chromatography (SiO₂; hexane) to afford **14** as a colourless solid (25.6 g, 91%). Mp 88–89 °C; *m/z* (EIMS) 214 (M⁺); δ_H(200 MHz; CDCl₃) 7.56 (1 H, t, *J* = 1.7 Hz), 7.48 (2 H, d, *J* = 1.7 Hz), 3.01 (1 H, s) and 1.34 (18 H, s); δ_C(50 MHz; CDCl₃) 151.6, 128.3, 126.4, 119.5, 94.7, 78.8, 35.0 and 31.3 [Found: C, 89.85; H, 10.15. Calc. for C₁₆H₂₂ (M, 214.35): C, 89.65; H, 10.35%].

1,5-Bis[3,5-bis(*tert*-butyl)phenyl]penta-1,4-diyne-3-one (**15**)

Alkyne **14** (14.81 g, 69.2 mmol) was dissolved in dry THF (200 cm³) and cooled under an atmosphere of N₂ to –78 °C. *n*-Butyllithium (46 cm³, 73 mmol, 1.6 mol dm^{–3} in hexanes) was added using a syringe. The reaction mixture was warmed to –50 °C and allowed to stir for 15 min. Ethyl formate (2.43 g, 33 mmol) was added dropwise over 30 min and the reaction mixture allowed to warm slowly to –10 °C over 4 h. Saturated aqueous NH₄Cl (15 cm³) was added, and the organic layer was washed successively with saturated aqueous NaCl, saturated aqueous NaHCO₃, and then water. The residual dark brown oil obtained by removal of the solvent was redissolved in CH₂Cl₂ (200 cm³) and added to a vigorously stirred suspension of pyridinium chlorochromate (25 g, 117 mmol) and molecular sieves 4 Å (20 g) in CH₂Cl₂ (400 cm³). The resulting mixture was stirred at room temperature for 3 h and then filtered through a short silica plug. The red solution was evaporated to dryness and the residue purified by flash chromatography

(SiO₂; hexane–CH₂Cl₂ 4:1). The fractions containing the product were combined and evaporated to dryness. Recrystallisation of the residue from pentane afforded **15** as a highly viscous yellow oil (6.77 g, 45%). *m/z* (EIMS) 454 (M⁺); δ_H(200 MHz; CDCl₃) 7.56 (2 H, t, *J* = 1.9 Hz), 7.52 (4 H, d, *J* = 1.9 Hz) and 1.34 (36 H, s); δ_C(50 MHz; CDCl₃) 161.8, 151.8, 128.1, 126.2, 118.9, 93.5, 89.2, 35.2 and 31.5 [Found: C, 87.3; H, 9.25. Calc. for C₃₃H₄₂O (M, 454.70): C, 87.17; H, 9.31%].

3-Dibromomethylene-1,5-bis[3,5-bis(*tert*-butyl)phenyl]penta-1,4-diyne (**16**)

Triphenylphosphine (23.4 g, 89.5 mmol) was dissolved in CH₂Cl₂ (450 cm³) and cooled to 0 °C. CBr₄ (9.90 g, 29.8 mmol) was added and the resulting dark-coloured solution stirred at 0 °C for 45 min. Ketone **15** (6.50 g, 14.3 mmol) was dissolved in CH₂Cl₂ (50 cm³) and was added to the reaction mixture. The resulting solution was allowed to warm slowly to room temperature and was stirred at room temperature for 12 h. Hexane (200 cm³) was added and the resulting slurry filtered rapidly through a pad of silica gel. The filtrate was evaporated to dryness and the residue purified by flash chromatography (SiO₂; hexane–CH₂Cl₂ 5:1) which afforded **16** as a colourless solid (6.07 g, 70%). Mp 111–112 °C; *m/z* (EIMS) 608/610/612 (M⁺); δ_H(200 MHz; CDCl₃) 7.46 (2 H, t, *J* = 1.8 Hz), 7.40 (4 H, d, *J* = 1.8 Hz) and 1.33 (36 H, s); δ_C(50 MHz; CDCl₃) 151.4, 126.3, 124.1, 121.6, 114.9, 107.2, 97.3, 85.3, 35.1 and 31.5.

1,6-Bis[3,5-bis(*tert*-butyl)phenyl]-3,4-bis[3,5-bis(*tert*-butyl)phenylethynyl]hex-3-ene-1,5-diyne (**17**)

Dibromoolefin **16** (800 mg, 1.31 mmol) was dissolved in benzene (45 cm³) and the solution degassed by bubbling Ar gas for 30 min. *n*-BuNH₂ (1.0 ml, 9.8 mmol) was added and the degassing continued for 15 min. [PdCl₂(PPh₃)₂] (70 mg, 0.1 mmol) was added, followed by CuI (19 mg, 0.1 mmol). Degassing was continued for a further 5 min. Alkyne **14** (540 mg, 2.50 mmol) was added to the reaction mixture and the resulting solution stirred under Ar at room temperature for 90 min. The reaction mixture was diluted with hexane (150 cm³) and filtered through a pad of silica gel to remove the metal residues. Evaporation of the filtrate, flash chromatography (SiO₂; hexane–CH₂Cl₂ 9:1), and recrystallisation from pentane afforded **17** as a bright yellow solid (650 mg, 53%). Mp 167–169 °C; *m/z* (EIMS) 876 (M⁺); δ_H(300 MHz; CDCl₃) 7.39 (12 H, br s) and 1.27 (72 H, s); δ_C(75 MHz; CDCl₃) 150.8, 126.0, 123.4, 121.7, 117.2, 99.9, 86.3, 34.9, 31.3 [Found: C, 90.35; H, 9.5. Calc. for C₆₆H₈₄ (M, 877.41): C, 90.65; H, 9.35%].

(*Z*)-1,6-Diphenylhex-3-ene-1,5-diyne (**11**)

Dry argon was bubbled through a solution of (*Z*)-1,2-dichloroethene (3 g, 31 mmol) in dry benzene (40 cm³) at 0 °C for 15 min. While the bubbling of argon was continued, *n*-BuNH₂ (15.3 cm³, 155 mmol) was added and, after a further 15 min, [PdCl₂(PPh₃)₂] (80 mg, 1.1 mmol) was added, followed immediately by CuI (20 mg, 1 mmol). Phenylacetylene (7.14 g, 70 mmol) was added to the reaction mixture and the resulting solution stirred under argon at room temperature for 3 h. The reaction mixture was diluted with hexane (45 cm³) and filtered through a short plug of silica. The solvent was removed *in vacuo* and the residue purified using flash chromatography (SiO₂; hexane–CH₂Cl₂ 2:1). The fractions containing the product were combined and reduced to dryness affording **11** as a clear oil (4.41 g, 62%). *m/z* (EIMS) 228 (M⁺); δ_H(200 MHz; CDCl₃) 7.48–7.58 (4 H, m), 7.30–7.39 (6 H, m), 6.11 (2 H, s); δ_C(50 MHz; CDCl₃) 132.1, 129.0, 1228.7, 123.5, 119.8, 97.9 and 84.6 (Found: C, 94.6; H, 5.05. Calc. for C₁₈H₁₂ (M, 228.29): C, 94.70; H, 5.30%). The *Z*-enediyne **11** is sensitive to light, isomerising

slowly to the crystalline *E*-isomer and should be stored in the dark at $-18\text{ }^{\circ}\text{C}$.

1,2,4,5-Tetrakis(phenylethynyl)benzene **9** and 1,2-bis(phenylethynyl)benzene **10** were prepared using slightly modified literature procedures.²⁵

Acknowledgements

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