

**$\pi$ -Complexes incorporating Tetraphenyltetraethynylethene**

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Tetraphenyltetraethynylethene and the  $\pi$ -acceptors 2,4,7-trinitrofluoren-9-one and (2,4,7-trinitro-9-fluorenylidene)malononitrile form highly ordered donor-acceptor  $\pi$ -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.

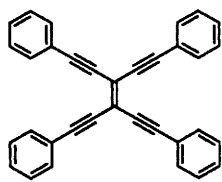
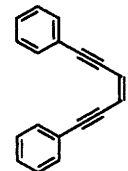
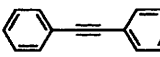
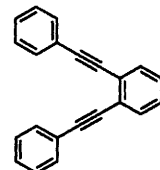
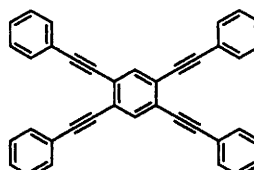
Recently, much attention has focused<sup>1,2</sup> on systems containing *cis*-enediynes units as a result of their potential pharmaceutical applications. Enediynes also represent an important class of conjugated  $\pi$ -systems with potentially interesting electronic properties. The tetraethynylethenes<sup>3-6</sup> **1** delineate a class of molecules containing two *cis*-enediynes units within a cross-conjugated  $\pi$ -electron framework. We have identified such systems as possessing potentially useful optical and electronic properties. Calculations<sup>†,7</sup> suggest that the tetraethynylethene  $\pi$ -system should act as a  $\pi$ -electron donor, and so could be incorporated into donor-acceptor  $\pi$ -complexes. Such complexes exhibit interesting electronic properties,<sup>8</sup> especially when the donor : acceptor stoichiometry is not 1 : 1, and also have potential application in non-linear optics<sup>9</sup> as a result of their often large third-order coefficients. Hence, we were

interested to explore the behaviour of systems containing the tetraethynylethene backbone in the presence of powerful  $\pi$ -electron acceptors.

Tetraphenyltetraethynylethene **2** has been previously synthesised by several methods.<sup>10-12</sup> We synthesised **2** in three steps from phenylacetylene, *via* the bis(phenylethynyl)-dibromoolefin **4**,<sup>†,13</sup> (Scheme 1) in 20% overall yield.

The addition of the  $\pi$ -electron acceptors 2,4,7-trinitrofluoren-9-one **5** or (2,4,7-trinitro-9-fluorenylidene)malononitrile **6** to a chloroform solution of tetraphenyltetraethynylethene **2** produced an instantaneous change, the yellow solution of **2** turning orange-red on addition of **5** and green on addition of **6**. This change is a result of the appearance (Fig. 1) of a charge transfer (CT) absorption band in the visible region of the spectrum, and is indicative of the formation of a  $\pi$ -complex

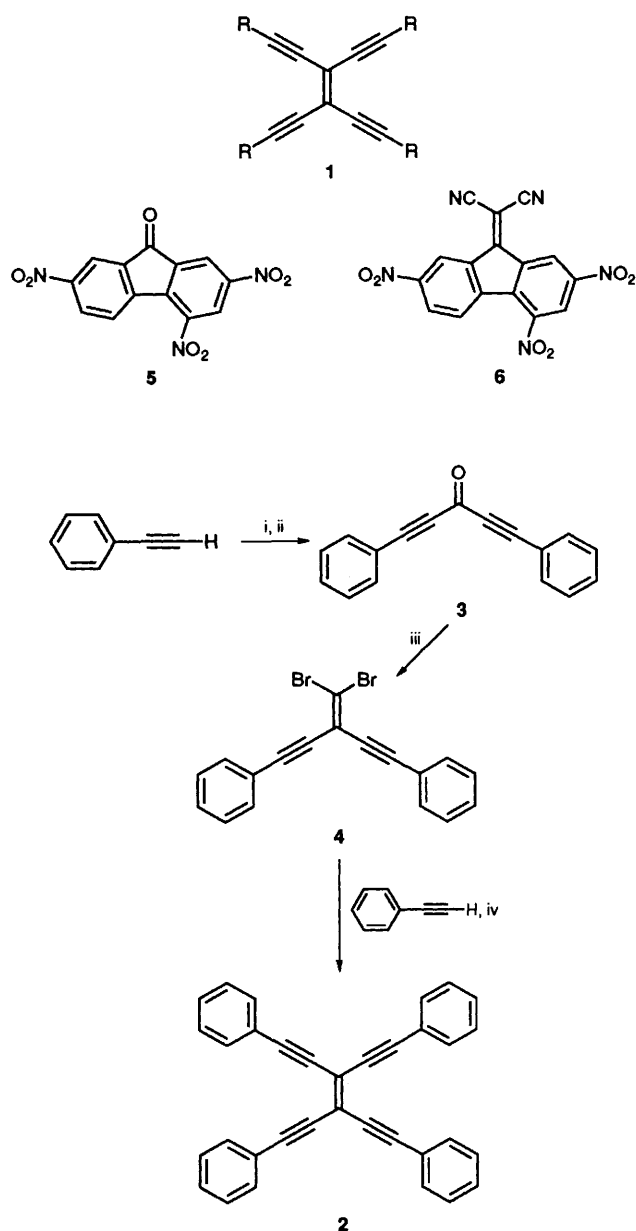
**Table 1** Association of 2,4,7-trinitrofluoren-9-one **5** with various molecules containing phenylethynyl units

| Compound  | Centroid-centroid distance / Å <sup>a</sup> | $K_a$ / dm <sup>3</sup> mol <sup>-1</sup> | $-\Delta G$ / kcal mol <sup>-1c</sup> |
|---|---|---|---------------------------------------|
|  | <b>2</b> 7.47                               | 7.9                                       | 1.23 ± 0.05                           |
|  | <b>7</b> 7.79                               | 1.6                                       | 0.24 ± 0.05                           |
|  | <b>8</b> 6.85                               | 1.6                                       | 0.24 ± 0.05                           |
|  | <b>9</b> 7.26                               | 9.9                                       | 1.36 ± 0.05                           |
|  | <b>10</b> 7.25                              | 10.3                                      | 1.38 ± 0.05                           |

<sup>a</sup> Distance in Å between the centroids of the two *cis* phenyl rings in **2**, **7**, **9** and **10**, and the centroids of the two phenyl rings in **8**. The centroid-centroid distances for **7**, **9** and **10** were derived from molecular modelling using the CVFF forcefield and the INSIGHT II/ DISCOVER package (Version 2.2.0, Biosym Technologies, San Diego, 1993), the distances in **2** and **8** were derived from X-ray crystal structures.

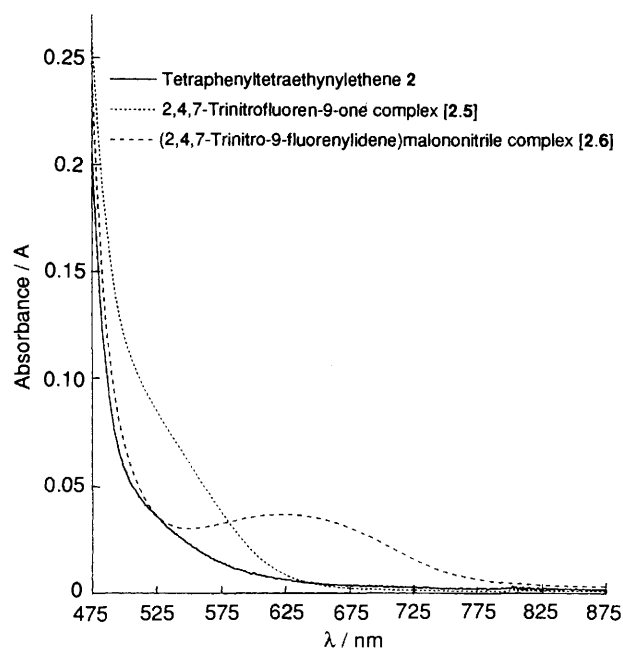
<sup>b</sup> In CDCl<sub>3</sub> at 300 K. The concentration of **5** was held constant. The chemical shift changes induced in the five probe protons in **5** by addition of increasing amounts of **2**, **7**, **8**, **9** or **10** were followed, and fitted by a non-linear curve fitting method to the 1 : 1 binding isotherm. The probe protons displayed upfield shifts at saturation in the range 0.35–0.60 ppm. The quoted values of  $K_a$  are the average of two determinations. <sup>c</sup> Errors in  $-\Delta G$  calculated from the values of  $K_a$  are ±0.05 kcal mol<sup>-1</sup> (1 cal = 4.184 J).

between **2** and either **5** or **6**. Fluorescence spectroscopy confirms the presence of the CT interaction. In general, molecular fluorescence is quenched<sup>14</sup> in CT complexes by radiationless decay of the excited state through the lower energy CT state. Tetraphenylethyne **2** exhibits an intense blue fluorescence [ $\lambda_{\text{max}}(\text{emission})$  445 and 470 nm], however, the addition of an excess of **5** to the solution of **2** results in almost complete (>99%) fluorescence quenching. Single crystals of the complex between **2** and **5** suitable for X-ray diffraction§ were grown by vapour diffusion of pentane into a dichloromethane solution of a 1:1 mixture of **2** and **5**. Surprisingly, the dark-red crystals have a stoichiometry of [2.5]<sub>2</sub>, i.e. a 1:2 donor-acceptor complex is formed in the solid state.¶ The tetraphenylethyne molecule within the complex [2.5]<sub>2</sub>, including the four phenyl groups, is planar within  $\pm 0.04$  Å, contrasting with free **2**<sup>11</sup> in which the phenyl rings show significant twists away from the mean plane of the tetraethynylethene skeleton. The structure of the

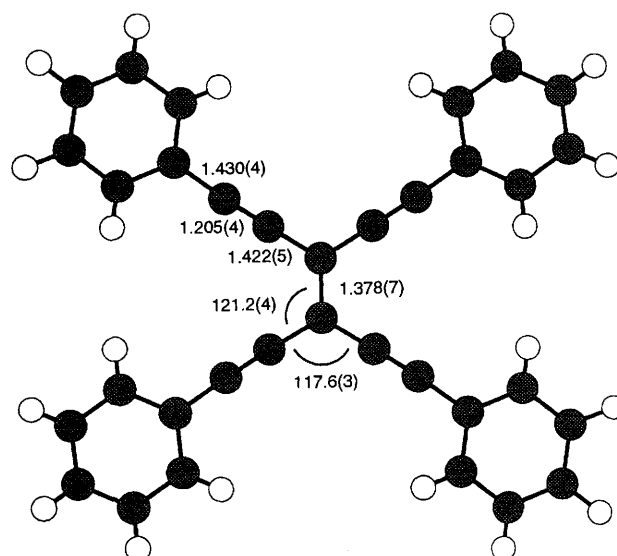


**Scheme 1** Reagents and conditions: i, Bu<sup>o</sup>Li/−78°C/HCO<sub>2</sub>Et (0.4 equiv.); ii, HPyrClCrO<sub>3</sub>/20°C/CH<sub>2</sub>Cl<sub>2</sub> (63%); iii, CBr<sub>4</sub> (2 equiv.), PPh<sub>3</sub> (5 equiv.), CH<sub>2</sub>Cl<sub>2</sub>; iv, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>/CuI, BuNH<sub>2</sub>/C<sub>6</sub>H<sub>6</sub> (41%)

tetraethynylethene backbone of **2** within [2.5]<sub>2</sub> displays almost perfect  $D_{2h}$  symmetry and is almost identical to that of free **2**. The opportunity for extended  $\pi$ -delocalisation afforded by the phenyl substituents within **2** is evident in the lengthening of the central double bond (1.378 Å) (Fig. 2) when compared to that (1.324 Å) found<sup>4</sup> in tetrakis(trimethylsilyl)tetraethynylethene **1** (R = Me<sub>3</sub>Si), where such delocalisation is not possible. The two molecules of **5** within the complex (Fig. 3) span the two *cis*-enediynes present in **2** and are disposed about a centre of symmetry. 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. 4) along the *a* axis of the unit cell, there being two independent stacks per unit cell. The interplanar separation between the molecules of **2** and **5** within the stacks is 3.39 Å. Single crystals of the complex between **2** and **6** suitable for



**Fig. 1** Absorption spectra of tetraphenylethyne **2** and its complexes with **5** ( $10^{-1}$  mol dm<sup>-3</sup>) and **6** ( $10^{-1}$  mol dm<sup>-3</sup>) in CHCl<sub>3</sub> solution ([**2**] =  $1 \times 10^{-3}$  mol dm<sup>-3</sup>) at 298 K



**Fig. 2** Ball-and-stick representation of a molecule of **2** within the complex [2.5]<sub>2</sub>, distances are in Å, angles are in degrees

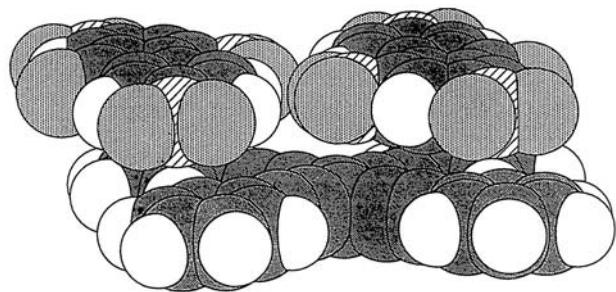


Fig. 3 CPK representation of the complex [2.5<sub>2</sub>]. Carbon atoms are shaded dark, oxygen atoms are shaded light and nitrogen atoms are striped

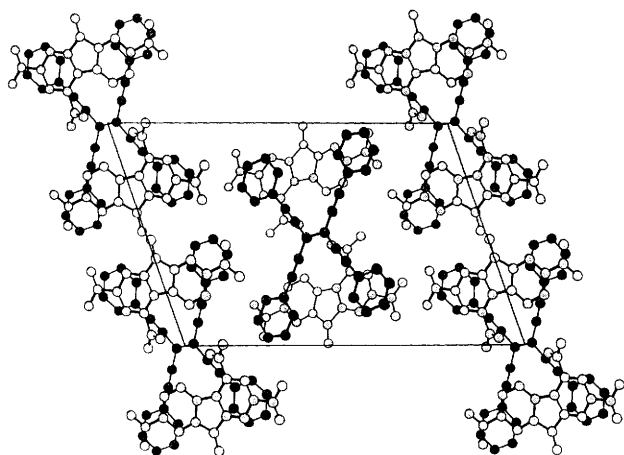


Fig. 4 A view down the *a* axis of the unit cell showing continuous donor-acceptor stacks in the crystals of the complex [2.5<sub>2</sub>]. Donors are shaded dark and acceptors are shaded light. The unit cell is marked as a black line.

X-ray diffraction§ were grown by slow evaporation of a dichloromethane solution containing **2** and **6** (1:1). The solid state complex between **2** and **6** has stoichiometry of 1:2, and the crystal structure shows essentially similar features to that of [2.5<sub>2</sub>], although there are solvent molecules included within the lattice with short contacts to the adjacent donor-acceptor stacks.

The stability of the solution state complex between **2** and **5** was assessed by <sup>1</sup>H NMR titration in CDCl<sub>3</sub> solution under conditions which favoured the formation of a 1:1 complex, *i.e.* **2** is in large excess. This experiment afforded a *K<sub>a</sub>* value (Table 1) of 7.9 dm<sup>3</sup> mol<sup>-1</sup> for a 1:1 complex [2.5] at 300 K, corresponding to a free energy of binding ( $-\Delta G$ ) of 1.23 ± 0.05 kcal mol<sup>-1</sup> (1 cal = 4.184 J). This is in the range expected for a normal molecular  $\pi$ -complex.<sup>15,16</sup> To probe the origin of the association between **2** and **5** further, we investigated the interaction between **5** and other structurally related compounds|| containing phenylethynyl units (Table 1). The association between acceptor **5** and **7** and **8** is very weak, whereas that between **5** and **2**, **9** and **10** is much stronger. These results suggest that the determining factor in the strength of complexation is the spatial displacement of the phenyl rings in the donor molecules rather than their electronic characteristics, since the conjugated  $\pi$ -systems in **2**, with a tetraethynylethene skeleton, and in **9** and **10**, with central benzene rings, are markedly different. Further evidence supporting this conclusion is derived from the fact that there is no measurable association between **5** and the dibromoolefin **4** containing two geminal phenylethynyl units. The phenyl rings presumably lie too far apart\*\* to permit **5** to interact simultaneously with both of the phenyl rings, even weakly.

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## Footnotes

† The calculated ionisation potential ( $E_i$ )<sup>7</sup> of tetraethynylethene (**1**, R = H), 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 semi-empirical methods AM1 and PM3, reproduce the  $E_i$ , and the filled electronic energy levels, reasonably accurately, although calculated molecular geometries are slightly worse. Calculated  $E_i$ s (AM1) for tetrakis-(trimethylsilyl)tetraethynylethene (**1**, R = SiMe<sub>3</sub>) of 8.63 eV and for tetraphenyltetraethynylethene (**1**, R = Ph) of 8.41 eV suggest that these tetraethynylethene derivatives could function as  $\pi$ -electron donors.

‡ Spectroscopic data for **4**: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  7.50–7.59 (4H, m), 7.30–7.41 (6H, m); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  132.0, 129.6, 128.8, 122.5, 114.6, 108.0, 96.0, 86.3.

§ Crystal data for [2.5<sub>2</sub>] at 85 K: [(C<sub>34</sub>H<sub>20</sub>).(C<sub>13</sub>H<sub>5</sub>N<sub>3</sub>O<sub>7</sub>)<sub>2</sub>], *M* = 1058.6, triclinic space group *P*1 (No. 2), *Z* = 2, *D<sub>c</sub>* = 1.44 g cm<sup>-3</sup>, *a* = 8.177(6) Å, *b* = 15.146(5) Å, *c* = 21.397(6) Å,  $\alpha$  = 107.95(4)°,  $\beta$  = 91.84(5)°,  $\delta$  = 103.84(5)°, *V* = 2431.7(2.8) Å<sup>3</sup>. Data were measured on an Enraf-Nonius CAD4 diffractometer with Mo-K $\alpha$  radiation using  $\omega/\theta$  scans. The structure was solved by direct methods and refined anisotropically to give *R* = 0.047, *R<sub>w</sub>* = 0.054 for 5016 independent observed reflections [*I* ≥ 3.0 $\sigma$ (*I*),  $\theta$  ≤ 23°].

For [2.6<sub>2</sub>] at 100 K: [ $\frac{1}{2}$ (C<sub>34</sub>H<sub>20</sub>).(C<sub>16</sub>H<sub>5</sub>N<sub>5</sub>O<sub>6</sub>).CH<sub>2</sub>Cl<sub>2</sub>], *M* = 662.5, triclinic space group *P*1 (No. 2), *Z* = 2, *D<sub>c</sub>* = 1.48 g cm<sup>-3</sup>, *a* = 8.640(3) Å, *b* = 13.363(2) Å, *c* = 14.101(8) Å,  $\alpha$  = 82.47(3)°,  $\beta$  = 72.20(4)°,  $\gamma$  = 74.15(2)°, *V* = 1489.2(1.1) Å<sup>3</sup>,  $\mu$  = 2.45 mm<sup>-1</sup>. Data were measured on an Enraf-Nonius CAD4 diffractometer with Cu-K $\alpha$  radiation using  $\omega/\theta$  scans. The structure was solved by direct methods and refined anisotropically to give *R* = 0.054, *R<sub>w</sub>* = 0.066 for 3642 independent observed reflections [*I* ≥ 3.0 $\sigma$ (*I*),  $\theta$  ≤ 65°].

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

¶ Hori and coworkers<sup>10</sup> reported a red-brown 1:2 complex between **2** and **5**, but no details beyond the stoichiometry, as determined by elemental analysis, were given.

|| *cis*-1,2-Bis(phenylethynyl)ethene **7** was prepared as a colourless oil by the Pd-catalysed coupling of phenylacetylene to *cis*-1,2-dichloroethene. This compound slowly isomerises to the corresponding crystalline *trans*-enediynes at room temp. and must, therefore, be stored in the dark at -18 °C. Spectroscopic data for **7**: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  7.48–7.58 (4H, m), 7.30–7.39 (6H, m), 6.11 (2H, s); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  132.1, 129.0, 128.7, 123.5, 119.8, 97.9, 87.6.

\*\* The centroid-centroid distance between the geminal phenyl rings in **4** is calculated to be 9.34 Å using the CVFF forcefield and the INSIGHT II/DISCOVER package (Version 2.2.0, Biosym Technologies, San Diego, 1993).

## References

- 1 K. C. Nicolaou and N.-M. Dai, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1387.
- 2 R. Gleiter and D. Kratz, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 842.
- 3 F. Diederich and Y. Rubin, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1101.
- 4 Y. Rubin, C. B. Knobler and F. Diederich, *Angew. Chem., Int. Ed. Engl.*, 1991, **31**, 698.
- 5 A. M. Boldi, J. Anthony, C. B. Knobler, F. Diederich and Y. Rubin, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1240.
- 6 J. Anthony, C. B. Knobler and F. Diederich, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 406.
- 7 B. Ma, Y. Xie and H. F. Schaefer III, *Chem. Phys. Lett.*, 1992, **191**, 521.
- 8 K. Pignak and H. Chojnacki, in *Molecular Interactions*, ed. H. Ratajczak and W. J. Orville-Thomas, Wiley, 1981, vol. 2, p. 451.
- 9 H. S. Nalwa, *Adv. Mater.*, 1993, **5**, 341.

- 10 Y. Hori, K. Noda, S. Kobayashi and H. Taniguchi, *Tetrahedron Lett.*, 1969, 3563.
- 11 H. Hauptmann, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 498.
- 12 H. Hopf, M. Kreutzer and P. G. Jones, *Chem. Ber.*, 1991, **124**, 1471.
- 13 E. J. Corey and P. L. Fuchs, *Tetrahedron Lett.*, 1972, **36**, 3769.
- 14 V. Balzani and F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood, London, 1991, Chapter 9.
- 15 M. J. S. Dewar and C. C. Thompson Jr., *Tetrahedron Suppl.*, 1966, **7**, 97.
- 16 K. A. Connors, *Binding Constants: The Measurement of Molecular Complex Stability*, Wiley, NY, 1987, ch. 5.