

Preparation of all-*trans*-(1,4-Phenylenehexa-1,3,5-trienylene) Oligomers

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All-*trans*-(1,4-phenylenehexa-1,3,5-trienylene) oligomers, all-*trans*-1,4-bis(6-phenylhexa-1,3,5-trienyl)benzene (PHT2) and all-*trans*-1,6-bis[4-(6-phenylhexa-1,3,5-trienyl)phenyl]hexa-1,3,5-triene (PHT3), were prepared respectively by the Wittig reaction from 1,4-phenylenediacrylaldehyde or 1,6-bis[4-(2-formylvinyl)phenyl]hexa-1,3,5-triene. The ^1H NMR, IR and UV-VIS spectra of the crude oligomers indicated the presence of *cis* double bonds in the trienes. The *cis-trans* isomerization of these double bonds was carried out by heating the *cis*-containing crude product in an appropriate solvent with iodine catalysis. The structures of PHT2 and PHT3 were confirmed by comparison of their IR spectra with that of all-*trans*-1,6-diphenylhexa-1,3,5-triene.

Various α,ω -diphenylpolyenes and dithienylpolyenes have been prepared and their spectroscopic behaviour studied systematically.¹⁻³ The conjugated polyenes are considered to be very promising organic non-linear optic (NLO) materials, owing to their extended π -electron systems.⁴ Traditional electroconducting polymers, such as poly(1,4-phenylenevinylene) (PPV) and poly(2,5-thienylenevinylene), have been shown to exhibit significant third-order NLO activities.⁵⁻⁹

We previously reported the synthesis of poly(1,4-phenylenehexa-1,3,5-trienylene) (PPHT) by a Wittig reaction.¹⁰ PPHT has the structure **a**, in which the vinylene units in PPV are replaced with hexa-1,3,5-trienylene units. However, PPHT was hardly soluble in common organic solvents, thus leading to difficulties in the purification and identification of the polymer. *cis*-Bonds in the polymer appeared to cause increased photosensitivity.

For clarification of the electronic structures and other properties of the polymer, it is important to synthesize oligomers whose structures can be clearly identified. This paper reports the preparation of the dimer (PHT2) and trimer (PHT3), low molecular weight model compounds of PPHT. The structures of PHT2 and PHT3 are shown as **c** and **d**, respectively.

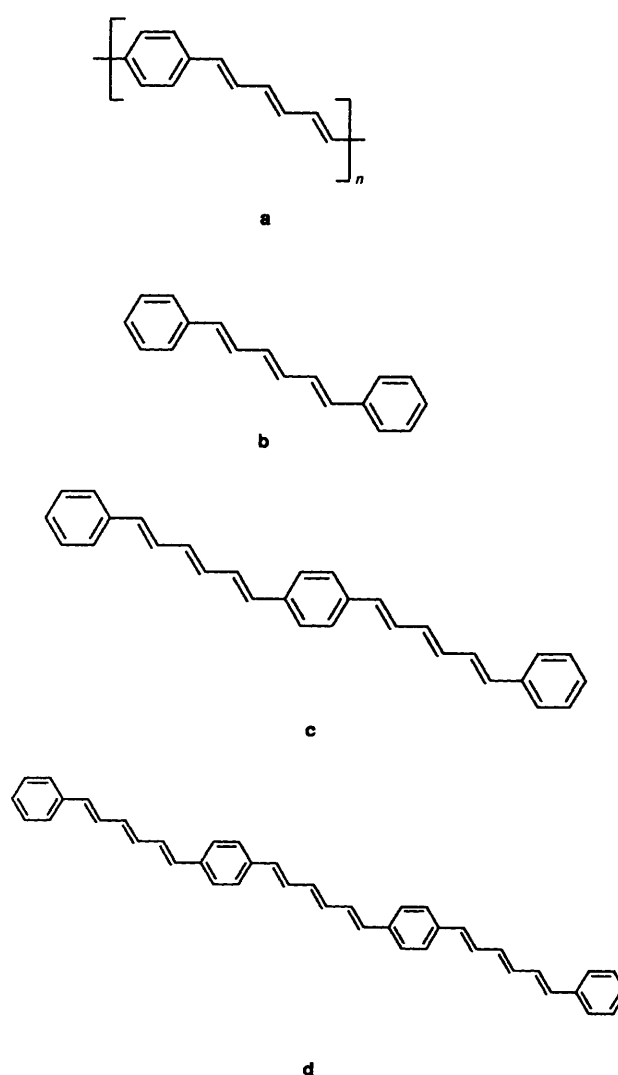
Although PHT2 has been synthesized previously by the Heck reaction,¹¹ the yield was rather low and spectral characteristics of the compound are not known. A comparison of the spectra of PHT2 and PHT3 with that of all-*trans*-1,6-diphenylhexa-1,3,5-triene (all-*trans*-DPH, **b**) should provide new insight into the structure-spectrum correlation for diphenylhexatriene derivatives.

Results and Discussion

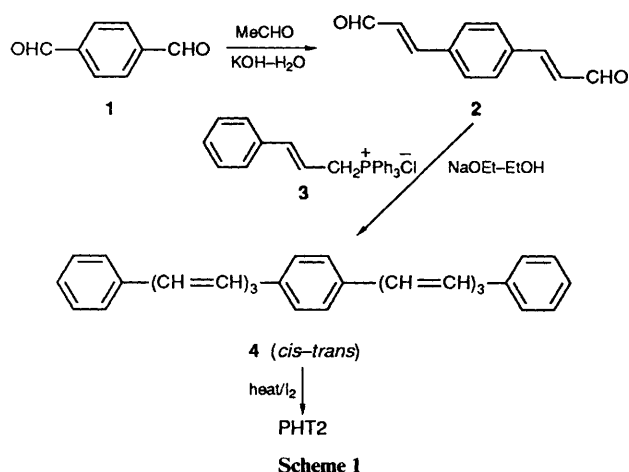
Preparation of PHT2.—PHT2 was prepared from 1,4-phenylenediacrylaldehyde **2** and triphenylcinnamylphosphonium chloride **3**. The synthetic route is shown in Scheme 1.

1,4-Phenylenediacrylaldehyde **2** was prepared by an aldol condensation between terephthalaldehyde **1** and acetaldehyde.¹² The Wittig reaction was also carried out, yielding 24% of compound **2** after refluxing in benzene for 24 h. The former reaction was found more suitable for the preparation of compound **2**, since the product was formed in higher yield under milder conditions.

cis-Containing crude dimer **4** was obtained by a Wittig reaction of compounds **2** and **3** in high yield at room temperature. The ^1H NMR, IR and UV-VIS spectra of dimer **4** clearly indicated the presence of *cis*-bonds in the trienes. Both *trans*- and *cis*-double bonds are thus formed by the reaction.



Preparation of PHT3.—The synthetic route to PHT3 is shown in Scheme 2. The Wittig aldehyde extension of compound **6** was carried out to give aldehyde **9a**. More than six different products were isolated by gel-permeation chromatography (GPC). NMR spectroscopic analysis of the compounds clarified the structures of **8**, **9a** and **9b**. Some polymeric materials



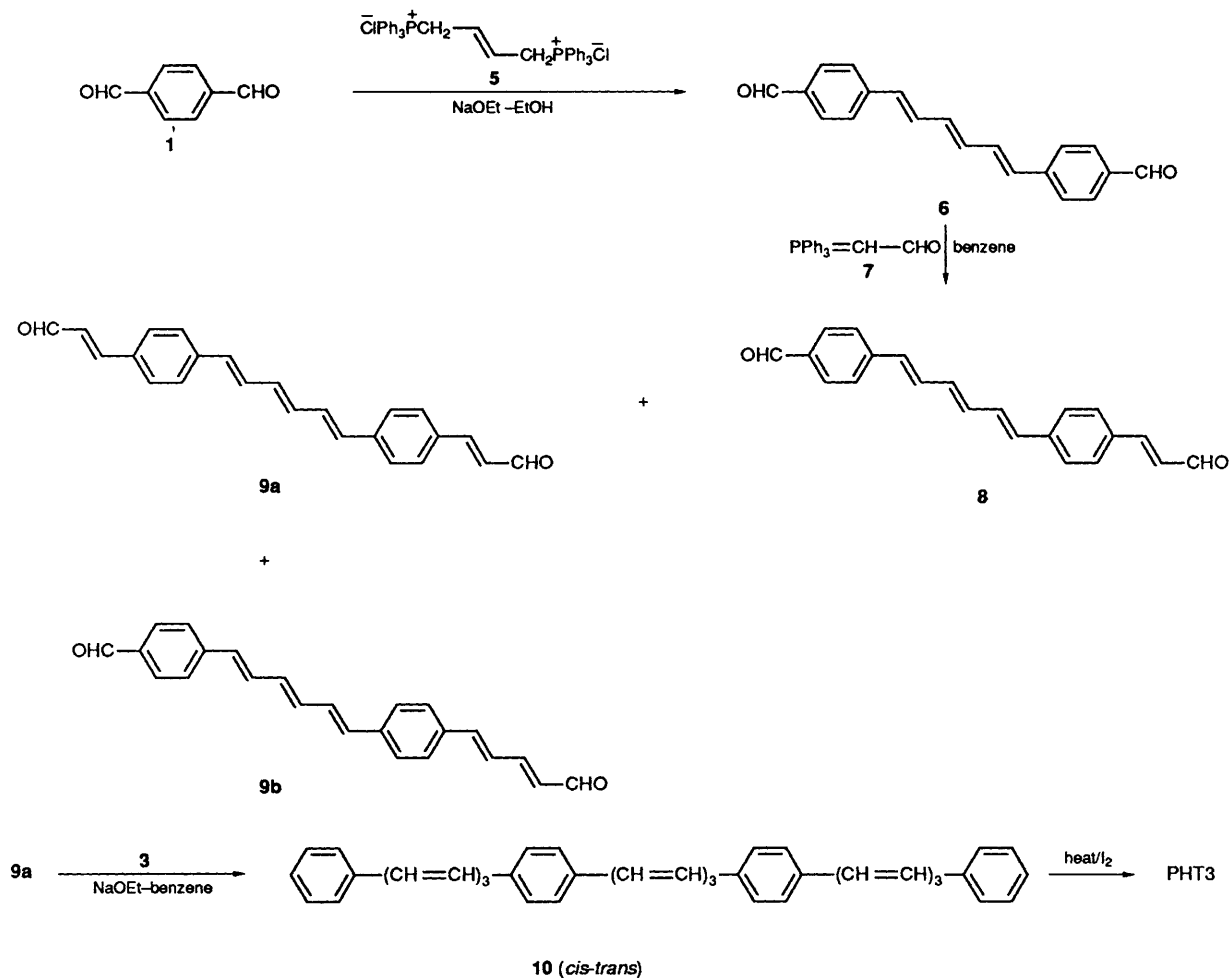
were also separated, whose NMR spectra indicated the presence of a $-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CHO}$ group formed by secondary reaction. A mixture of **9a** and **9b** was obtained after GPC separation, which could be further separated into each isomer by preparative TLC. The structures of **9a** and **9b** were established from their NMR and IR spectra. The UV-VIS spectra of the two isomers were virtually identical, indicating that they had essentially the same conjugation lengths. The starting material **6** was recovered after reaction for 16 h. However, prolonged heating caused undesirable polymerization and decreased yield of **9a**. Although the aldol reaction of **6** and acetaldehyde was

attempted, **9a** could not be obtained, possibly due to the low affinity of **6** for water.

The reaction of **3** and **9a** was very slow. In ethanol, unchanged formyl groups were detected by IR and NMR spectroscopy even after refluxing for 3 days. In benzene, the solubility of **9a** was enhanced and the reaction was complete after refluxing for 2 days. *cis*-Double bonds were found in the crude trimer **10** as well as in **4**.

Thermal cis-trans Isomerization with Iodine Catalysis.—In the case of 1,4-distyrylbenzene and 1,4-bis(4-phenylbuta-1,3-dienyl)benzene, *cis-trans* isomerization occurred thermally with iodine catalysis.^{13,14} The present dimer **4** and trimer **10** isomerized to PHT2 and PHT3, respectively, under similar conditions. The isomerization of **4** was carried out more successfully in chloroform than in *p*-xylene. Compound **4** appeared to decompose in boiling *p*-xylene, while PHT2 could be recrystallized from the same solvent. The all-*trans* isomer may thus possibly be thermally more stable than the *cis*-containing product. Compound **10** also isomerized in boiling toluene or *p*-xylene. The IR spectrum of the resulting crystal indicated an all-*trans* structure shown as **d**. Although purification of PHT3 was attempted, no solvent was found to be adequate for recrystallization.

¹H NMR Spectra.—The NMR spectra of compounds **4** and **10** were obtained in deuteriochloroform at room temperature. To analyse these spectra, NMR spectra of a mixture of all-*trans*- and *trans-cis-trans*-DPH was measured. The two isomers were prepared from compound **3** and cinnamaldehyde.



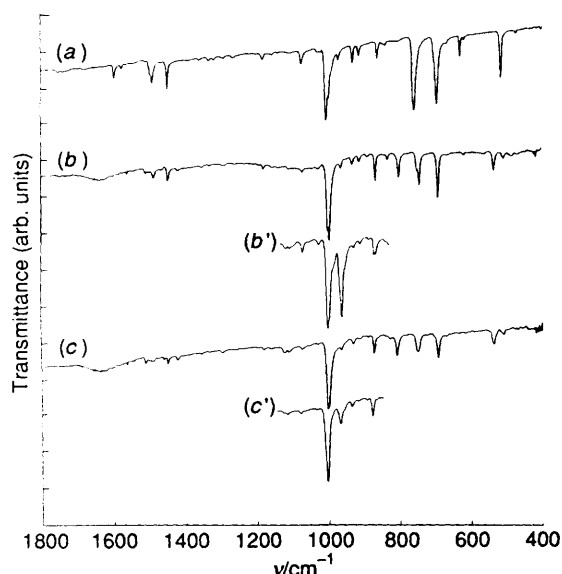


Fig. 1 IR spectra of (a) all-*trans*-DPH, (b) PHT2 and (c) PHT3 (KBr). The two characteristic peaks of *cis*-containing isomers **4** and **10** are shown in (b') and (c'), respectively

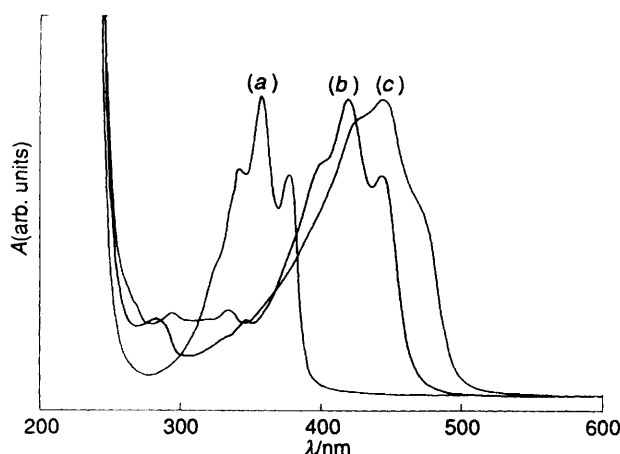


Fig. 2 UV-VIS spectra of (a) all-*trans*-DPH, (b) PHT2 and (c) PHT3 in chloroform

hyde.¹⁵ In the spectrum of the isomeric mixture, four multiplets were observed at δ 7.17–7.51, 6.82–6.95, 6.47–6.67 and 6.19–6.31. Commercial all-*trans*-DPH showed the following signals: δ 7.18–7.46 (10 H, m), 6.89 (2 H, ddd, J 15.39, 7.02, 2.90), 6.60 (2 H, d, J 15.58) and 6.53 (2 H, dd, J 7.02, 3.10). After subtracting the spectrum of the all-*trans*-DPH from that of the isomeric mixture, the following spectrum was obtained: δ 7.17–7.51 (12 H, m), 6.63 (2 H, d, J 15.56) and 6.19–6.31 (2 H, m). These signals must, therefore, be due to the *trans*-*cis*-*trans* isomer of DPH. The multiplet at δ 6.19–6.31 was found to be characteristic of *trans*-*cis*-*trans* trienes.

In the spectra of compounds **4** and **10**, four multiplets were observed at δ 7.10–7.52, 6.82–6.97, 6.50–6.67 and 6.21–6.28, and δ 7.01–7.54, 6.83–6.95, 6.46–6.65 and 6.18–6.27, respectively. Of these signals, multiplets at δ 6.2–6.3 showed the presence of *trans*-*cis*-*trans* trienes in compounds **4** and **10**.

PHT2 and PHT3 were much less soluble than the corresponding *cis*-containing isomers. The NMR spectrum of neither PHT2 nor PHT3 was obtained in deuteriochloroform at room temperature. The solubility of PHT2 in chloroform was 3–4 mg dm⁻³ at room temperature. PHT3 was less soluble than PHT2.

IR Spectra.—Fig. 1 shows the IR spectra of (a) all-*trans*-

DPH, (b) PHT2 and (c) PHT3. Compounds **4** and **10** showed peaks at 962, 1001, 963 and 999 cm⁻¹, respectively [Fig. 1 (b') and (c')]. These are assignable to the C-H out-of-plane vibration of *cis*-containing trienes.^{16,17} After isomerization, the peak at 960 cm⁻¹ completely disappeared and only a strong peak at 1000 cm⁻¹ was observed. This peak at 1000 cm⁻¹ is attributed to the C-H out-of-plane vibrations which are characteristic of all-*trans* trienes.^{16,17} The peaks at 690 and 745 cm⁻¹ are due to the C-H out-of-plane vibration of mono-substituted benzene rings. The spectra of PHT2 and PHT3 showed peaks of 1,4-disubstituted benzene rings at about 800 cm⁻¹. Broad absorptions due to the C=C stretching vibrations of polyenes were observed at around 1635 cm⁻¹ in the spectra of PHT2 and PHT3. All-*trans*-DPH, PHT2 and PHT3 showed peaks at 3013 cm⁻¹, which were assignable to the C-H stretching vibrations of =CH-. The origin of the peaks at 860–870 cm⁻¹ could not be determined.

UV-VIS Spectra.—Small absorptions were observed at around 340 nm in the UV-VIS spectra of **4** and **10** and attributed to *cis* double bonds in trienes. Similar absorptions, called '*cis*-peaks', were observed for DPH and 1,4-bis(4-phenylbuta-1,3-dienyl)benzene **11**.^{15,18} Following isomerization, the dimer and trimer showed no '*cis*-peak' in their UV-VIS spectra.

Fig. 2 shows the UV-VIS spectra of (a) all-*trans*-DPH, (b) PHT2 and (c) PHT3. Absorption maxima (λ_{\max}) red-shifted with an increase in the degree of polymerization (n). (1,4-Phenylenevinylene) oligomers show their λ_{\max} at 310 ($n = 1$, stilbene), 355 ($n = 2$) and 385 nm ($n = 3$) in chloroform.¹⁹ In the case of (1,4-phenylenebuta-1,3-dienylene) oligomers, λ_{\max} values are 334 and 389 nm for 1,4-diphenylbuta-1,3-diene ($n = 1$) and **11** ($n = 2$), respectively.^{1,15} These spectral data indicate that the shifts in the λ_{\max} of DPH, PHT2 and PHT3 can be attributed to the increase in conjugation length.

In the spectrum of PHT2, λ_{\max} was found at 421 nm in benzene. Diphenyldodecahexaene, having the same number of double bonds as PHT2, showed λ_{\max} at the same wavelength (420 nm) in benzene.¹ It thus follows that middle phenylene rings do not interrupt the conjugation system in PHT2. Similar findings were observed for diphenyloctatetraene (λ_{\max} 384 nm)¹ and **11** (λ_{\max} 389 nm).¹⁵

The λ_{\max} of PPHT was 407 nm in chloroform, which was located at a shorter wavelength compared with that of PHT2.¹⁰ Since PPHT could not be purified because of its low solubility, it might contain *cis* and/or saturated bonds. Such structural disorders would lead to a torsion of the main chain of the polymer, thus interrupting its conjugation system. Consequently, λ_{\max} was shifted to a shorter wavelength than expected for pure all-*trans*-PPHT. These structural disorders should be detected by NMR spectroscopy. However, no peak due to saturated bonds was found and only a small peak corresponding to *cis*-bonds was observed. It is not clear why the λ_{\max} of PPHT was observed at a shorter wavelength than that of PHT2.

Vibrational fine structures were observed in the spectra of PHT2 and PHT3. The spacings were 1300–1400 cm⁻¹, which should correspond to the energy gaps of vibration in the excited states.

Experimental

M.p.s were determined on a Laboratory Device Mel-Temp melting point apparatus and uncorrected. High-resolution mass spectra were obtained with a VG Auto Spec Q spectrometer. Elemental analysis was performed with a Heraeus CHN-O-Rapid machine. ¹H NMR spectra were recorded on a JEOL GSX 270 spectrometer operating at 270 MHz; J values are given in Hz. IR and UV-VIS spectra were recorded on a Perkin-

Elmer 1720 and a Hitachi U-3210 spectrometer, respectively. Each product was isolated with an LC-908 gel-permeation liquid chromatograph (Japan Analytical Industry Co. Ltd.).

Terephthalaldehyde **1** was purchased from Aldrich and recrystallized from water before use.

Triphenylcinnamylphosphonium chloride **3** was prepared according to the literature.¹⁴ The preparatory procedure for 1,6-bis(4-formylphenyl)hexa-1,3,5-triene **6** has already been reported.¹⁰ (Triphenylphosphoranylidene)acetaldehyde **7** was obtained from Aldrich and used without further purification.

1,4-Phenylenediacrylaldehyde 2.—(a) *Aldol condensation.* Compound **2** was prepared according to the literature.¹² Yield 42% (lit. 12.49%), m.p. 159–162 °C (lit. 162.5–164 °C); δ (CDCl₃) 9.75 (2 H, d, *J* 7.67), 7.64 (4 H, s), 7.49 (2 H, d, *J* 16.07) and 6.77 (2 H, dd, *J* 16.07, 7.67); ν_{\max} (KBr)/cm⁻¹ 1666s, 1621m, 1421m, 1394w, 1298m, 1252w, 1129s, 1014w, 978s, 799s, 582w and 525w.

(b) *Wittig condensation.* A solution of compound **1** (1.00 g, 7.5 mmol) and **7** (4.56 g, 15.0 mmol) in benzene (95 cm³) was heated at reflux for 24 h under a nitrogen atmosphere. Water was added to the reaction mixture and the products were extracted with ether. Evaporation of the extract gave a brown oil, which crystallized from 60% ethanol in water (50 cm³) to afford 0.33 g (24%) of compound **2**. The NMR spectrum of the product was identical with that of **2** obtained by procedure (a).

cis-Containing Dimer 4.—To a suspension of compound **2** (0.50 g, 2.7 mmol) and triphenylcinnamylphosphonium chloride **3** (2.46 g, 5.9 mmol) in absolute ethanol (30 cm³) was added a solution of sodium ethoxide (0.25 mol dm⁻³; 23.7 cm³) over 30 min, under a nitrogen atmosphere. After the suspension had been stirred in the dark for 3 days at room temperature, 60% ethanol in water (120 cm³) was added and the mixture was stirred for 10 min. The precipitate was filtered off and washed with water (50 cm³) and absolute ethanol (50 cm³). The crude 1,4-bis(6-phenylhexa-1,3,5-trienyl)benzene **4** (0.93 g, 90%) was obtained as yellow crystals; ν_{\max} (KBr)/cm⁻¹ 3014m, 1591w, 1508w, 1490m, 1447m, 1073w, 1001s, 962s, 873m, 803w, 783w, 748s, 691s, 537w and 517m.

All-trans-1,4-bis(6-phenylhexa-1,3,5-trienyl)benzene (PHT2).—A solution of dimer **4** (20 mg) in chloroform (100 cm³) was heated at reflux for 15 h in the dark with a trace of iodine. After evaporation of the solvent under reduced pressure, the residue was recrystallized from *p*-xylene (15 cm³) to give PHT2 as bright orange leaflets (8 mg); m.p. 257–262 °C (Found: C, 92.8; H, 6.8%; *M*, 386.2022. Calc. for C₃₀H₂₆: C, 93.22; H, 6.78%; *M*, 386.2035); ν_{\max} (KBr)/cm⁻¹ 3013w, 1636w, 1486w, 1446w, 996s, 933w, 913w, 868m, 833w, 802m, 745m, 691s, 537m and 509w; λ_{\max} (CHCl₃)/nm 419 (ϵ = 8.0 × 10⁴).

Reaction of 6 and 7.—A solution of 1,6-bis(4-formylphenyl)hexa-1,3,5-triene **6** (0.20 g, 0.69 mmol) and (triphenylphosphoranylidene)acetaldehyde **7** (0.43 g, 1.4 mmol) was heated at reflux for 16 h in benzene (10 cm³). After cooling to room temperature, water (100 cm³) was added to the reaction mixture. The products were extracted with dichloromethane (200 cm³) and the extract was evaporated under a reduced pressure. To the residue was added 60% ethanol in water (40 cm³) to precipitate a bright yellow solid (0.217 g).

The crude products were subjected to GPC analysis. Compound **8** (22 mg, 10%), the isomeric mixture of **9a** and **9b**, and some polymeric materials (85 mg, 39% w/w) were obtained. The starting material **6** was recovered (34 mg, 17%). The mixture of **9a** and **9b** was separated into each isomer [**9a** (53 mg, 22%), **9b** (23 mg, 10%)] by preparative TLC with dichloromethane eluent.

1-(4-Formylphenyl)-6-[4'-(2-formylvinyl)phenyl]hexa-1,3,5-triene **8**; m.p. 198.5–200 °C (Found: *M*⁺, 314.128 6. Calc. for

C₂₂H₁₈O₂: *M*, 314.130 7); δ _H(CDCl₃) 9.98 (1 H, s), 9.71 (1 H, d, *J* 7.67), 7.84 (2 H, d, *J* 8.15), 7.56 (2 H, d, *J* 8.15), 7.55 (2 H, d, *J* 8.15), 7.48 (2 H, d, *J* 8.40), 7.46 (1 H, d, *J* 16.07), 6.94–7.10 (2 H, m), 6.72 (1 H, dd, *J* 15.82, 7.91) and 6.57–6.71 (4 H, m); ν_{\max} (KBr)/cm⁻¹ 3016w, 1691s, 1685sh, 1666s, 1621w, 1597m, 1562m, 1420w, 1394w, 1295w, 1213m, 1160m, 1132s, 1106w, 998s, 975m, 926w, 872w, 806s, 797sh, 662w, 588w and 526m; λ_{\max} (CHCl₃)/nm 411 (ϵ = 7.9 × 10⁴).

1,6-Bis[4-(2-formylvinyl)phenyl]hexa-1,3,5-triene **9a**, m.p. 218–219 °C (Found: *M*⁺, 340.1458. Calc. for C₂₄H₂₀O₂: *M*, 340.146 3); δ _H(CDCl₃) 9.71 (2 H, d, *J* 7.66), 7.54 (4 H, d, *J* 8.16), 7.48 (4 H, d, *J* 8.41), 7.45 (2 H, d, *J* 16.07), 6.99 (2 H, ddd, *J* 15.37, 6.86, 3.03), 6.72 (2 H, dd, *J* 16.07, 7.92), 6.64 (2 H, d, *J* 15.58) and 6.60 (2 H, dd, *J* 7.34, 2.97); ν_{\max} (KBr)/cm⁻¹ 3017w, 1692s, 1670sh, 1621s, 1594s, 1553w, 1507w, 1421m, 1296m, 1255w, 1127s, 1107m, 1009s, 1002sh, 967s, 879m, 804s, 585w and 536m; λ_{\max} (CHCl₃)/nm 424 (ϵ = 6.9 × 10⁴).

1-[4-(4-Formylbuta-1,3-dienyl)phenyl]-6-(4'-formylphenyl)hexa-1,3,5-triene **9b**; m.p. 214–216 °C (Found: *M*⁺, 340.1458. Calc. for C₂₄H₂₀O₂: *M*, 340.1463) δ _H(CD₂Cl₂) 9.89 (1 H, s), 9.54 (1 H, d, *J* 7.91), 7.76 (2 H, d, *J* 8.15), 7.52 (2 H, d, *J* 7.91), 7.43 (2 H, d, *J* 6.91), 7.39 (2 H, d, *J* 8.88), 7.23 (1 H, ddd, *J* 14.96, 7.55, 2.83), 6.85–7.10 (4 H, m), 6.51–6.70 (4 H, m) and 6.18 (1 H, dd, *J* 14.96, 8.29); ν_{\max} (KBr)/cm⁻¹ 3018w, 1691s, 1669s, 1618s, 1593s, 1561w, 1457w, 1396m, 1301w, 1261w, 1212m, 1162s, 1153s, 1116s, 998s, 987s, 871m, 822w, 806m, 585w and 531w; λ_{\max} (CHCl₃)/nm 423 (ϵ = 3.4 × 10⁴).

cis-Containing Trimer 10.—A solution of sodium ethoxide (0.30 mol dm⁻³; 1.1 cm³) was added to one of compound **9a** (50.0 mg, 0.15 mmol) and compound **3** (134.0 mg, 0.32 mmol) in benzene (14 cm³). This solution was heated at reflux in the dark for 2 days, and then 60% ethanol in water (15 cm³) was added to crystallize the crude trimer. The resulting red crystals were filtered and dried under a reduced pressure. Yield 22.1 mg (28%); ν_{\max} (KBr)/cm⁻¹ 3014w, 1636w, 1508w, 1490w, 1457w, 1447w, 1420w, 1110w, 1073w, 999s, 963m, 930w, 873m, 809m, 745s, 691s, 541m and 511w.

All-trans-1,6-bis[4-(6-phenylhexa-1,3,5-trienyl)phenyl]hexa-1,3,5-triene (PHT3).—A solution of trimer **10** in toluene or *p*-xylene was refluxed for 1.5 h with a trace of iodine. The red crystals were filtered off, washed with absolute ethanol, and dried under reduced pressure. M.p. > 250 °C (decomp.) (Found: *M*⁺, 540.2803. Calc. for C₄₂H₃₆: *M*, 540.2817); ν_{\max} (KBr)/cm⁻¹ 3013w, 1635w, 1508w, 1488w, 1457w, 1446w, 1121w, 1109w, 1072w, 1000s, 930w, 872m, 807m, 747m, 691m, 537m and 509w; λ_{\max} (CHCl₃)/nm 443. The molar extinction coefficient could not be determined due to the low solubility of PHT3.

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