

# Stereoselective *Z,E*-photoisomerization of formyl-substituted (*E,E,E*)-1,6-diphenylhexa-1,3,5-triene in solution

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Direct irradiation of (*E,E,E*)-1,6-bis(4-formylphenyl)hexa-1,3,5-triene in chloroform under argon atmosphere led to a fast equilibrium between *E,E,E* (62%) and *Z,E,E* (38%) isomers. Neither isomers nor photoproducts were detected by HPLC in the photostationary mixture. This is entirely different from the reaction of (*E,E,E*)-1,6-diphenylhexa-1,3,5-triene on irradiation under similar conditions, in which dimers and solvent adducts were formed *via* various kinds of *Z* isomers. The high stereoselectivity observed in the *Z,E*-photoisomerization of the formyl-substituted diphenylhexatriene can be explained by the assumption that a terminal twisted transient state has a zwitterionic character which is stabilized by the polarization of carbonyl groups.

## Introduction

$\alpha,\omega$ -Diphenylpolyenes have been extensively studied<sup>1–3</sup> because of their photochemical significance as model compounds for visual pigments.<sup>4</sup> Among these polyenes, 1,6-diphenylhexa-1,3,5-triene (DPH) is especially interesting because it is the shortest chromophore in this series that has the <sup>1</sup>A<sub>g</sub> state as its lowest excited singlet state.<sup>5,6</sup>

Since the pioneering work of Lunde and Zechmeister,<sup>7</sup> photochemical reactions of DPH have received little attention in comparison to numerous photophysical and spectroscopic studies. This is mainly due to the complex nature of the reactions of DPH. Irradiation of (*E,E,E*)-DPH in solution has been shown to give a cyclization product<sup>8</sup> and unidentified polymerized and/or decomposition products<sup>7,9</sup> in addition to various kinds of *Z* isomers.<sup>7,9,10</sup>

In the course of our study on the synthesis of a new conjugated polymer with 1,4-phenylenehexa-1,3,5-trienylene repeating units,<sup>11–13</sup> we found that (*E,E,E*)-1,6-bis(4-formylphenyl)hexa-1,3,5-triene [(*E,E,E*)-1], which was prepared as a model compound for the polymer, only underwent *Z,E* isomerization to give its *Z,E,E* isomer on irradiation in chloroform with  $\lambda > 330$  nm light in air.<sup>11</sup> The simplicity of this reaction of **1** seems to be quite different from the complex nature observed for unsubstituted DPH which has been reported up to now. Thus we decided to carry out further experiments in order to obtain a deeper insight into the stereoselective isomerization of **1**. This paper reports the photoreactions of **1** on irradiation in chloroform with  $397 \pm 7$  nm light under an argon atmosphere. Photoreaction of unsubstituted DPH under similar conditions was also studied for comparison.

## Results and discussion

### Photochemical reactions of (*E,E,E*)-1

Irradiation of (*E,E,E*)-1 ( $\lambda_{\max} = 397$  nm,  $\epsilon = 8.7 \times 10^4$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) in chloroform with  $397 \pm 7$  nm light under argon led rapidly to a photostationary state at room temperature. UV–VIS spectra showed a decrease in the absorption at 397 nm and the appearance of a new peak at 301 nm with an isobestic point at 368 nm (Fig. 1). The photostationary mixture was shown by GPC analysis to be an isomeric mixture of the triene. HPLC analysis showed the mixture to contain the *E,E,E* isomer and only one kind of *Z* isomer; no measurable amounts of other isomers and photoproducts were detected.

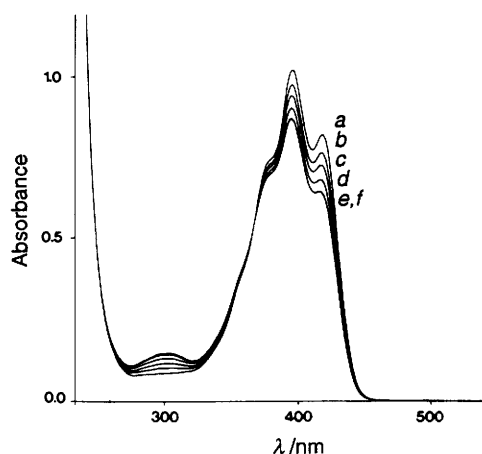


Fig. 1 Changes in UV–VIS spectra on irradiation of (*E,E,E*)-1 with  $397 \pm 7$  nm light in chloroform. Irradiation time: (a) 0, (b) 15, (c) 30, (d) 60, (e) 120 and (f) 240 s.

The isomeric mixture was separated into (*E,E,E*)-1 and the *Z* isomer at room temperature by a recyclable GPC or a preparative TLC. Fig. 2 shows UV–VIS spectra of these two isomers in chloroform. From the combination of a small UV–VIS absorption at 301 nm [Fig. 2(b)] and two NMR peaks due to non-equivalent aldehyde protons, we had determined that the *Z* isomer had a *Z,E,E* geometry (Scheme 1).<sup>11</sup> This assignment was confirmed in this work by comparison of the <sup>1</sup>H NMR spectrum of the *Z* isomer with those of the authentic (*Z,E,E*)- and (*E,Z,E*)-DPH prepared according to the literature.<sup>14</sup> The molar content of the two isomers at the photostationary state was determined to be (*E,E,E*)-1: (*Z,E,E*)-1 = 62:38 from UV–VIS spectra.

The  $\lambda_{\max}$  of  $\pi$ – $\pi^*$  absorption for (*Z,E,E*)-1 was observed at 391 nm ( $\epsilon = 5.5 \times 10^4$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>), which was located at a shorter wavelength by 6 nm compared with that of the *E,E,E* isomer. It has been theoretically expected that (*Z,E,E*)-DPH has a non-planar structure in which the dihedral angle between the *Z* double bonds and aromatic rings is 55°, while *E,E,E* and *E,Z,E* isomers have planar structures.<sup>15</sup> Therefore, the blue shift of  $\lambda_{\max}$  with a decrease in  $\epsilon$  for (*Z,E,E*)-1 compared with its *E,E,E* isomer can be attributed to the steric hindrance between the terminal *Z* bonds and aromatic rings, which resulted in interrupting its conjugation system. Similar observations in UV–VIS spectra have been reported for sterically hindered *Z* isomers of DPH.<sup>7</sup> Moreover, the

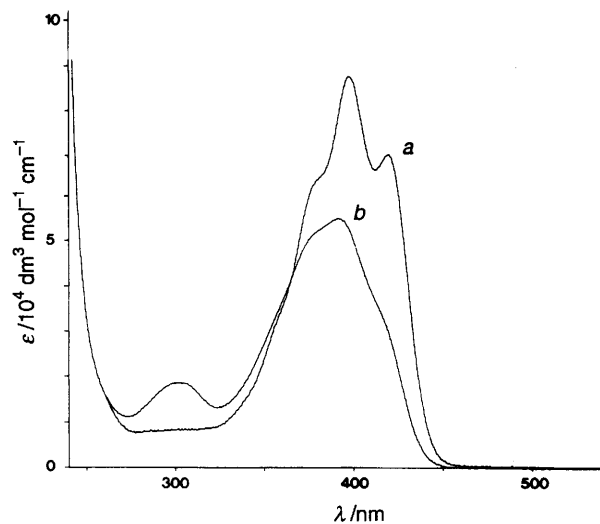
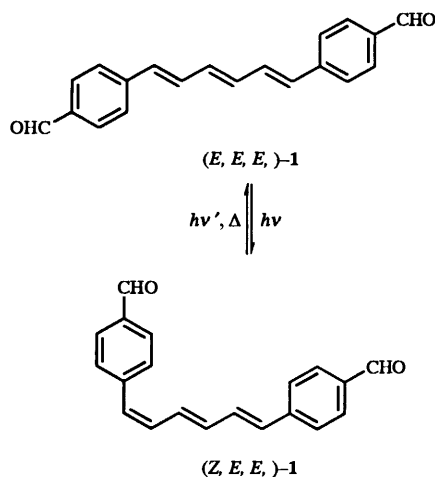


Fig. 2 UV-VIS spectra of (a) (*E,E,E*)- and (b) (*Z,E,E*)-1 in chloroform



Scheme 1 Stereoselective *Z,E*-isomerization of **1**

deviation from the planar structure of (*Z,E,E*)-**1** is also supported by its thermal instability; the *Z,E,E* isomer was shown to return slowly but completely to the *E,E,E* isomer in the dark at room temperature by  $^1\text{H}$  NMR and UV-VIS spectra.

The isosbestic point observed in the UV-VIS spectrum indicated that the reaction is completely reversible between these two isomers. There remained the possibility that other *Z* isomers are formed from (*E,E,E*)- and/or (*Z,E,E*)-**1**, when the irradiation was continued for a long time after the system reached the photostationary state. However, prolonged irradiation made little change to the UV-VIS spectrum. Although a trace amount of high molecular weight compounds (MW *ca.* 600–800, polystyrene standard) were detected by GPC analysis, the isomeric mixture was shown by HPLC to be composed of only the same two isomers that were produced after a short irradiation time.

On the direct irradiation of (*E,E,E*)-**1**, the *Z,E,E* isomer was thus shown to be formed exclusively. No sizable amount of another mono-*Z* isomer, (*E,Z,E*)-**1**, or di-*Z* isomers, (*Z,Z,E*)- and (*Z,E,Z*)-**1**, were detected by HPLC. This high stereoselectivity is rather surprising, considering that **1** formally has five *Z* isomers: *Z,E,E*, *E,Z,E*, *Z,Z,E*, *Z,E,Z* and *Z,Z,Z*. Furthermore, in spite of having carbonyl groups, **1** underwent no photoreaction characteristic of carbonyl compounds<sup>16</sup> including  $\alpha$ -cleavage, hydrogen abstraction or oxetane formation on radiation in chloroform. This can be attributed to the low reactivities of C=O groups in the compound, probably due to the conjugation of C=O with the aromatic rings and trienes.

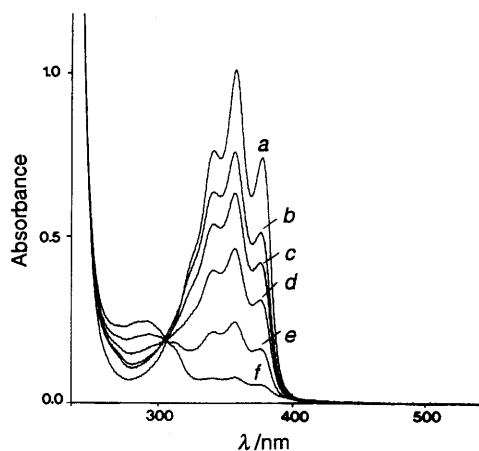
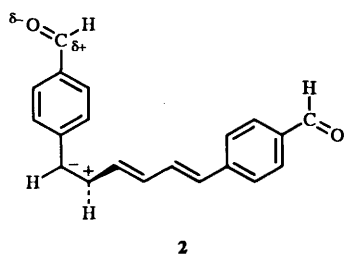


Fig. 3 Changes in UV-VIS spectra on irradiation of (*E,E,E*)-DPH with  $358 \pm 7$  nm light in chloroform. Irradiation time: (a) 0, (b) 15, (c) 30, (d) 60, (e) 120 and (f) 240 s.

#### Photochemical reactions of (*E,E,E*)-DPH

On irradiation of (*E,E,E*)-DPH ( $\lambda_{\text{max}} = 358$  nm) in chloroform with  $358 \pm 7$  nm light under argon atmosphere, the UV-VIS absorption of DPH disappeared rapidly within a few minutes; no photostationary state was observed in this case even with a short irradiation time (Fig. 3). The photoproduct at early stages of the reaction was shown by GPC analysis to be a mixture of *Z* isomers and high molecular weight compounds. HPLC analysis showed the isomeric mixture to contain (*E,Z,E*)- and (*Z,Z,E*)-DPH. *Z,E* geometries of these isomers were determined by comparison of their UV-VIS spectra with those of the authentic DPH isomers reported by Lunde and Zechmeister.<sup>7</sup> The presence of (*Z,E,E*)-DPH could not be clarified by HPLC analysis; although the peak of the isomer was not observed as a single peak, we could not exclude the possibility that the peak was overlapped by those of *E,Z,E* and/or *Z,Z,E* isomers in the chromatogram. However, it can clearly be seen in  $^1\text{H}$  NMR spectra that at least the *main* photoproduct of the short irradiation time is not the *Z,E,E* isomer, but the *E,Z,E* isomer of DPH. This finding is similar to the case of 1-(4-cyanophenyl)-5-methyl-6-phenylhexa-1,3,5-triene,<sup>17</sup> but quite different from the exclusive formation of the *Z,E,E* isomer from (*E,E,E*)-**1**.

When the solution was further irradiated until only a very weak absorption of DPH was observed in the UV-VIS spectrum, a mixture of many kinds of high molecular weight compounds was obtained as a final product. These compounds are possibly formed *via* various kinds of *Z* isomers. The product was roughly separated into the following three GPC fractions: the first fraction (MW *ca.* 700, polystyrene standard) is considered to be a mixture of DPH trimers. However, we did not analyse it further, because it was obtained in very low yield and composed of so many kinds of compounds. The second fraction (MW *ca.* 450) is probably a mixture of DPH dimers. Its  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) and IR (KBr) spectra indicated the presence of mono-substituted benzene rings [ $\delta_{\text{H}}$  6.8–7.8 (m);  $\nu/\text{cm}^{-1}$  739 and 699], (*E*)-vinylene and/or (*E,E*)-buta-1,3-diene [ $\delta_{\text{H}}$  5.5–6.7 (m);  $\nu/\text{cm}^{-1}$  3027 and 967] and methylene and/or methine groups [ $\delta_{\text{H}}$  2.8–3.9 (m);  $\nu/\text{cm}^{-1}$  2976, 2927 and 2897]. Broad UV-VIS absorption (270–300 nm) and the absence of the IR peak characteristic of trienes (*ca.*  $1000\text{ cm}^{-1}$ )<sup>18</sup> suggest the shorter conjugation length of these compounds compared with DPH. The dimers would therefore be formed by intermolecular [4 + 2] and/or [2 + 2] cycloaddition reactions, although the presence of cyclohexene or cyclobutane rings cannot be confirmed by the NMR or IR spectral analysis. These reactions would proceed *via* excimers, similar to the case of many aromatic compounds.<sup>19</sup> Photoinduced intra- and inter-molecular [4 + 2] cycloadditions, Diels-Alder reactions, have



similarly been observed for aliphatic hexa-1,3,5-triene derivatives,<sup>20</sup> cyano-substituted DPH<sup>17</sup> and between DPH and tetracyanoethene.<sup>21</sup> The compounds contained in the last fraction are considered from their molecular weights (MW *ca.* 320) to be 1:1 adducts of DPH and dichlorocarbene derived from the solvent ( $C_{10}H_{16}Cl_2 = 315.24$ ). The calculated value of the chlorine content from the formula (22.5%) was in fairly good agreement with the experimental value from elemental analysis (21.5%). Similar to the case of the dimers, <sup>1</sup>H NMR ( $CDCl_3$ ) and IR (KBr) spectra showed the presence of mono-substituted benzene rings [ $\delta_H$  7.0–8.1 (m);  $\nu/cm^{-1}$  745 and 700], (*E*)-vinylene and/or (*E,E*)-buta-1,3-diene [ $\delta_H$  5.7–6.7 (m);  $\nu/cm^{-1}$  3030 and 971] and methylene and/or methine groups [ $\delta_H$  4.7–4.9 (m), 4.2–4.4 (m) and 3.2–3.8 (m);  $\nu/cm^{-1}$  2975, 2929 and 2895] in the compounds. These NMR and IR spectral data, together with a broad UV–VIS absorption at 270–300 nm supported the proposed structure. Since chloroform was expected to have no absorption in the wavelength range used in the irradiation experiment, the adducts would probably be formed *via* an exciplex derived from excited DPH and ground-state chloroform. An adduct of DPH and a polar solvent (1:1) was also obtained from irradiation in alcohol.<sup>9</sup>

The formation of these compounds, which was not observed for **1**, is possibly due to the higher energy of the excited states of DPH than that of **1**. The excited energy of DPH is expected to be high enough to allow the formation of excimers and exciplexes, the possible excited intermediates for the cycloaddition and solvent addition reactions, respectively. In contrast, **1** can undergo only *Z,E*-isomerization due to its low excited energy.

#### Stereoselectivity in the *Z,E*-isomerization of **1** and DPH

Recently, Saltiel *et al.* have reported that the molar content of (*Z,E,E*)-DPH at the photostationary state increased dramatically by changing the solvent from methylcyclohexane to acetonitrile.<sup>10</sup> They have interpreted these results by the assumption that terminal and central twisted transient states had zwitterionic and biradicaloid character, respectively.

If we assume that the partitioning of the ionic and biradicaloid transient states are also changed with the polarity of the molecule, then the high stereoselectivity observed in the isomerization of **1** can be explained as follows: in the isomerization of **1**, terminal twisted transient state **2** with zwitterionic character is expected to be more stable than a central twisted biradicaloid state by the polarization of carbonyl groups. Transient state **2** is deactivated to give (*E,E,E*)-**1** or (*Z,E,E*)-**1**, the exclusive photoproduct from (*E,E,E*)-**1**. In the irradiation of DPH, the partitioning of a central twisted biradicaloid transient state would be larger than in **1** because of the non-polarity of the molecule. This results in the formation of (*E,Z,E*)-DPH.

Photochemical *Z,E*-isomerization of polyenes in solution is generally considered to show little stereoselectivity, which is different from the selective isomerization observed in biological systems. In our present work, however, high stereoselectivity was observed in the photochemical *Z,E*-isomerization of **1** in solution. It is very interesting that the polarization of C=O possibly plays an important role in exhibiting the stereoselective isomerization of **1** because CHO groups that are conjugated with double bonds are also present in the well known visual

pigment of retinal. However, it is also possible that *n*- $\pi^*$  and/or triplet excited states of **1** are concerned with its isomerization. Further investigations are now in progress to clarify these points and the results will be published elsewhere in the near future.

## Experimental

### General

Mps were determined on a Laboratory Device Mel-Temp melting point apparatus and reported uncorrected. Mass spectra were obtained using a Hitachi M-80B instrument. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL GSX 270 spectrometer. <sup>1</sup>H and <sup>13</sup>C chemical shifts in ppm are respectively based on tetramethylsilane (internal reference) and the  $CDCl_3$  resonance (77.0 ppm). *J* values are given in Hz. IR and UV–VIS spectra were recorded on a Perkin-Elmer 1720 and a Hitachi U-3400 spectrometer, respectively. Measurements of molecular weight and purification of each product were carried out with an LC-908 gel-permeation chromatograph (Japan Analytical Industry Co. Ltd.). Product analysis was also performed with a CCPD/SD-8013/PX-8010 reverse-phase HPLC (Tosoh Co. Ltd.) with an MCPD-3600 multichannel photo-detector (Photal Co. Ltd.).

### Irradiation experiments

A CRM-FA 2KW spectroirradiator (Japan Spectroscopic Co. Ltd.) was used as a light source. Light wavelengths were set at  $397 \pm 7$  and  $358 \pm 7$  nm in the irradiation of **1** and DPH, respectively. A solution of (*E,E,E*)-**1** or (*E,E,E*)-DPH in chloroform (4 cm<sup>3</sup>) degassed with argon was irradiated in a quartz cell at room temperature. The reaction was followed by UV–VIS spectroscopy. After irradiation, the solvent was evaporated in the dark at or below room temperature under reduced pressure. The residue was dissolved in methanol or chloroform and the solution was subjected to reverse-phase HPLC (methanol eluent) or GPC (chloroform eluent). When the reaction was followed by <sup>1</sup>H NMR, a solution of each triene in  $CDCl_3$  (0.6 cm<sup>3</sup>) was irradiated in an NMR sample tube. Sample concentrations were  $1 \times 10^{-5}$  mol dm<sup>-3</sup> (UV–VIS spectral measurement and HPLC analysis),  $2 \times 10^{-4}$  mol dm<sup>-3</sup> (GPC analysis) and  $5 \times 10^{-3}$  mol dm<sup>-3</sup> (<sup>1</sup>H NMR spectral measurement).

### Chemicals

Chloroform (spectroscopic grade, containing 1% ethanol as a stabilizer) was purchased from Dojin Kagaku and used without further purification. The preparatory procedure for (*E,E,E*)-**1** has already been reported.<sup>11</sup> The triene was isolated from the crude product by GPC and further purified by multiple recrystallization from acetonitrile. (*E,E,E*)-DPH (scintillation grade) was purchased from Wako Pure Chemicals and recrystallized from 1,4-dioxane–ethanol (2:1 v/v) before use. Isomers of (*Z,E,E*)- and (*E,Z,E*)-DPH were prepared according to the literature.<sup>14</sup>

**(*E,E,E*)-1,6-Bis(4-formylphenyl)hexa-1,3,5-triene [(*E,E,E*)-**1**]**  
Mp 212–214 °C (Found:  $M^+$ , 288.1136. Calc. for  $C_{20}H_{16}O_2$ :  $M$ , 288.1149);  $\delta_H$ (270 MHz;  $CDCl_3$ ) 9.98 (2 H, s, CHO), 7.84 (4 H, d, *J* 8.4, arom.), 7.57 (4 H, d, *J* 8.2, arom.), 7.05 (2 H, ddd, *J* 15.4, 7.0 and 2.8, triene, 2-H and 5-H), 6.69 (2 H, d, *J* 15.6, triene, 1-H and 6-H) and 6.63 (2 H, dd, *J* 7.0 and 2.8, triene, 3-H and 4-H);  $\delta_C$ (68.5 MHz;  $CDCl_3$ ) 191.5 (2 C, CHO), 143.1 (2 C, arom., C-4), 135.3 (2 C, arom., C-1), 135.0 (2 C, triene, C-3 and C-4), 132.4 (2 C, triene, C-1 and C-6) and 132.1 (2 C, triene, C-2 and C-5);  $\lambda_{max}$ ( $CHCl_3$ )/nm 418 ( $\epsilon/dm^3 \text{ mol}^{-1} \text{ cm}^{-1}$   $7.0 \times 10^4$ ), 397 ( $8.7 \times 10^4$ ) and 376 ( $6.2 \times 10^4$ ).

**(*Z,E,E*)-1,6-Bis(4-formylphenyl)hexa-1,3,5-triene [(*Z,E,E*)-**1**]**  
A solution of (*E,E,E*)-**1** in chloroform ( $5 \times 10^{-3}$  mol dm<sup>-3</sup>,

4 cm<sup>3</sup>) was irradiated for 10 min in a quartz cell under argon or in air at room temperature. The reaction mixture was separated into *E,E,E* and *Z,E,E* isomers by GPC. Elution with chloroform gave 15 × 5 cm<sup>3</sup> fractions at the 30th cycle. The fractions 10–15 were collected and the solvent was evaporated under reduced pressure at or below room temperature to afford pure (*Z,E,E*)-1 as a yellow oil;  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 10.02 (1 H, s, CHO), 9.97 (1 H, s, CHO), 7.89 (2 H, d, *J* 8.7, arom.), 7.83 (2 H, d, *J* 8.4, arom.), 7.55 (2 H, d, *J* 8.4, arom.), 7.52 (2 H, d, *J* 7.9, arom.), 6.91–7.05 (2 H, m, triene, 3-H and 5-H), 6.69 (1 H, d, *J* 15.5, triene, 6-H), 6.59–6.69 (1 H, m, triene, 4-H), 6.56 (1 H, d, *J* 12.1, triene, 1-H) and 6.48 (1 H, dd, *J* 11.3 and 11.3, triene, 2-H);  $\lambda_{\text{max}}$ (CHCl<sub>3</sub>)/nm 391 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1}$  5.5 × 10<sup>4</sup>) and 301 (1.9 × 10<sup>4</sup>).

**(*E,E,E*)-1,6-Diphenylhexa-1,3,5-triene [(*E,E,E*)-DPH]**

Mp 196 °C (lit.,<sup>14</sup> 198–199 °C);  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 7.18–7.46 (10 H, m, arom.), 6.89 (2 H, ddd, *J* 15.4, 7.0 and 2.9, triene, 2-H and 5-H), 6.60 (2 H, d, *J* 15.6, triene, 1-H and 6-H) and 6.53 (2 H, dd, *J* 7.0 and 3.1, triene, 3-H and 4-H);  $\delta_{\text{C}}$ (68.5 MHz; CDCl<sub>3</sub>) 137.3 (2 C, arom., C-1), 133.5 (2 C, triene, C-3 and C-4), 132.6 (2 C, triene, C-1 and C-6) and 129.1 (2 C, triene, C-2 and C-5).

**(*Z,E,E*)-1,6-Diphenylhexa-1,3,5-triene [(*Z,E,E*)-DPH]**

Oil;  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 7.17–7.44 (10 H, m, arom.), 6.80–6.97 (2 H, m, triene, 3-H and 5-H), 6.59 (1 H, d, *J* 15.5, triene, 6-H), 6.54 (1 H, dd, *J* 14.5 and 10.9, triene, 4-H), 6.47 (1 H, d, *J* 11.6, triene, 1-H) and 6.34 (1 H, dd, *J* 11.4 and 11.4, triene, 2-H).

**(*E,Z,E*)-1,6-Diphenylhexa-1,3,5-triene [(*E,Z,E*)-DPH]**

Mp 104–106 °C (lit.,<sup>14</sup> 109–110 °C);  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 7.45–7.51 (4 H, m, arom.), 7.38–7.45 (2 H, m, triene 2-H and 5-H), 7.30–7.38 (4 H, m, arom.), 7.21–7.30 (2 H, m, arom.), 6.62 (2 H, d, *J* 15.9, triene, 1-H and 6-H) and 6.19–6.31 (2 H, m, triene, 3-H and 4-H).

### Acknowledgements

We thank Dr M. Sakuragi for her helpful discussions and technical advice on the irradiation experiments. We also thank Dr K. Hayamizu for her help in the <sup>1</sup>H NMR spectral assignments of DPH isomers.

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Paper 5/04412J

Received 6th July 1995

Accepted 21st September 1995