

**(*E,E,E*)-1,6-Bis(4-nitrophenyl)hexa-1,3,5-triene**Yoriko Sonoda,<sup>a\*</sup> Yuji  
Kawanishi<sup>a</sup> and Midori Goto<sup>b</sup><sup>a</sup>Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan, and <sup>b</sup>Technical Centre, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

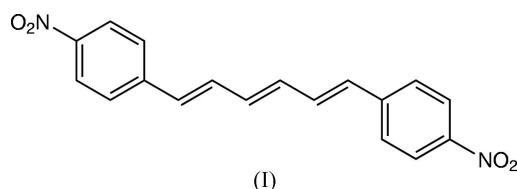
Correspondence e-mail: y.sonoda@aist.go.jp

**Key indicators**Single-crystal X-ray study  
 $T = 183\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$   
 $R$  factor = 0.040  
 $wR$  factor = 0.126  
Data-to-parameter ratio = 16.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

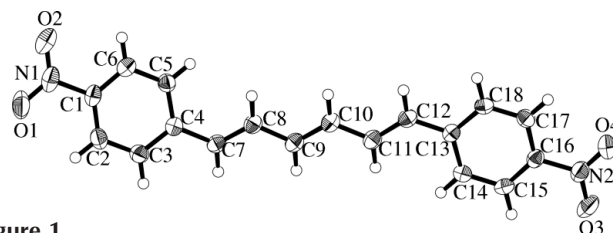
In the title compound,  $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_4$ , the torsion angles of the single bonds between the hexatriene chain and 4-nitrophenyl rings are  $18.0(2)$  and  $-0.7(2)^\circ$ . The molecules are linked weakly via intermolecular  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds to form sheets. These sheets are linked further by  $\text{N}\cdots\text{O}$  dipole interactions between the nitro groups and aromatic  $\pi-\pi$  stacking interactions, to form a three-dimensional framework.

**Comment**

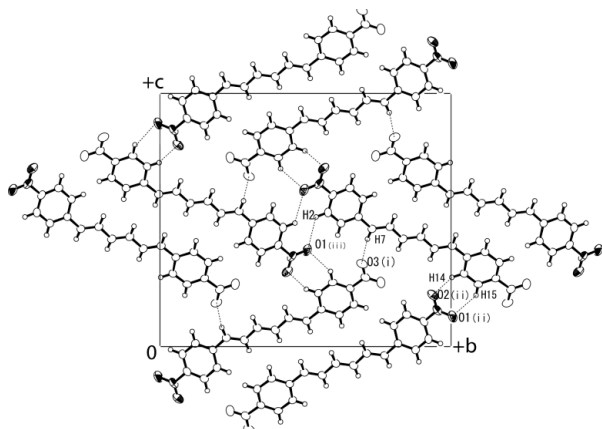
(*E,E,E*)-1,6-Diphenylhexa-1,3,5-triene [(*E,E,E*)-DPH] has been widely used as a fluorescence probe in photochemical and biological studies. Due to the extended  $\pi$ -conjugation systems, DPH and its ring-substituted derivatives are also attractive in the field of applied physics, because of their potential use as materials for third-order nonlinear optics and optical power limiting, and as two-photon absorbing chromophores (Rodenberger *et al.*, 1995; Spangler, 1999; Rumi *et al.*, 2000; Geskin *et al.*, 2003). We have previously reported the crystal structure of 1,6-bis(2,4-dichlorophenyl)hexa-1,3,5-triene (Sonoda, Kawanishi & Goto, 2003). In this paper, we report the structure of the title compound, (I), which is a symmetrically substituted DPH having nitro groups on the benzene rings.



During our study of the solid-state fluorescence properties and photochemical behaviours of a series of ring-substituted DPHs, we found that (I) showed strongly red-shifted fluorescence relative to that in solution (Sonoda, Kawanishi *et al.*, 2003), and that it showed no photoreactivity in the solid state (Sonoda, Miyazawa *et al.*, 2001). We undertook the crystal structure analysis of (I) in order to find an explanation for its red-shifted emission and photostability in the solid state. Our



**Figure 1**  
A view of the molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

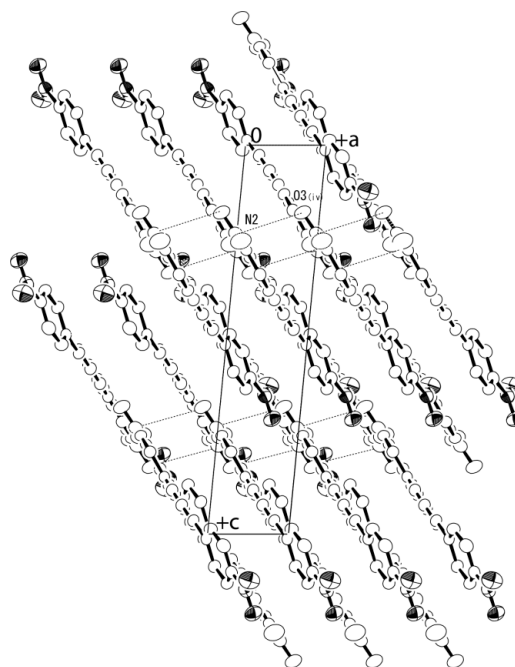
**Figure 2**

A packing diagram of (I), viewed along the  $a$  axis. Intermolecular C—H $\cdots$ O hydrogen bonds are represented by dashed lines. The shortest intermolecular distances between the H and O atoms and between the C and O atoms are H7 $\cdots$ O3<sup>i</sup> = 2.44 Å and C7 $\cdots$ O3<sup>i</sup> = 3.371 (2) Å, respectively, and the corresponding intermolecular angle is C7—H7 $\cdots$ O3<sup>i</sup> = 166°. [Symmetry codes: (i)  $-x, y - \frac{1}{2}, \frac{1}{2} - z$ , (ii)  $x - 2, \frac{3}{2} - y, z - \frac{1}{2}$ , (iii)  $3 - x, 1 - y, 1 - z$ .]

data can be compared with those for the (*E,E,E*)-isomers of DPH and 1,6-bis(2-methoxyphenyl)hexa-1,3,5-triene (Hall *et al.*, 1989), 1,6-bis(4- and 1,6-bis(2-chlorophenyl)-3,4-dimethylhexa-1,3,5-triene (Stam & Riva di Sanseverino, 1966), and all-(*E*)-isomers of other diphenylpolyenes (Drenth & Wiebenga, 1954, 1955; Glaser *et al.*, 2003).

The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1. In the hexatriene chain of (I), the torsion angles are almost 180°, indicating that the triene chain is planar. Distinct bond alternation is observed. Although the C—C single bonds [1.437 (2)–1.459 (2) Å] are shorter than the standard value of 1.54 Å, they are significantly longer than the C=C double bonds [1.340 (2)–1.342 (2) Å]. Although C=C bonds in conjugated olefins are expected to be longer than the standard value of 1.34 Å for isolated olefins, the C=C bond lengths in (I) are all similar to the standard value for mono-olefins. This may be due to the thermal vibrations around the C—Ph and/or C—C bonds, as discussed previously for the structure of a 2,4-dichloro-derivative of DPH (Sonoda, Kawanishi & Goto, 2003). The C—C—C bond angles in the chain are all somewhat larger than 120°. In particular, the C4—C7—C8 and C11—C12—C13 angles are 126.0 (1) and 127.4 (1)°, respectively, in order to minimize the steric interaction between the H atoms of the chain and the benzene ring. The benzene rings are planar, and the nitro groups are coplanar with the rings.

The C5—C4—C7—C8 and C11—C12—C13—C14 torsion angles are 18.0 (2) and  $-0.7$  (2)°, respectively. The corresponding dihedral angles for the least-squares planes of the ring and the chain are 18.9 (1) and 2.4 (1)°, respectively. The twist around the C4—C7 bond axis is probably due to intermolecular interactions. The dihedral angles between the planes of the ring and the chain are 1.9° for unsubstituted DPH, 15.6° for its 2-methoxy-derivative (Hall *et al.*, 1989) and 9.9 (1)° for the 2,4-dichloro-derivative (Sonoda, Kawanishi & Goto, 2003). It is interesting that the dihedral angle of

**Figure 3**

A packing diagram of (I), viewed along the  $b$  axis. For clarity, H atoms have been omitted. Intermolecular N $\cdots$ O dipole interactions are represented by dashed lines. The shortest intermolecular distance between the N and O atoms is N2 $\cdots$ O3<sup>iv</sup> = 3.366 (2) Å. [Symmetry code: (iv)  $1 + x, y, z$ .]

18.9 (1)° for (I) is even larger than the values for the 2-methoxy- and 2,4-dichloro-derivatives, having a large steric hindrance between the olefinic H atoms and the 2-substituents of the rings.

Figs. 2 and 3 show the crystal structure of (I). Atoms O1, O2 and O3 of the nitro groups are in close contact with either a neighbouring aromatic H atom or with the olefinic H atom of a neighbouring molecule, to form weak C—H $\cdots$ O hydrogen bonds (Table 2) of the type described by Desiraju & Steiner (1999). The molecules are linked weakly by these intermolecular hydrogen bonds into sheets (Fig. 2). The shortest intermolecular distances between the H and O atoms and between the C and O atoms are H7 $\cdots$ O3<sup>i</sup> = 2.44 Å and C7 $\cdots$ O3<sup>i</sup> = 3.371 (2) Å, respectively, and the corresponding intermolecular angle is C7—H7 $\cdots$ O3<sup>i</sup> = 166° [symmetry code: (i)  $-x, y - \frac{1}{2}, \frac{1}{2} - z$ ].

The molecules are assembled along the  $a$  axis to form parallel plane-to-plane stacks. Attractive intermolecular interactions between the nitro O atoms and nitro N atoms of neighbouring molecules are observed. The sheets formed by the C—H $\cdots$ O hydrogen bonds are linked by the intermolecular N $\cdots$ O dipole interactions and the aromatic  $\pi$ — $\pi$  stacking interactions into a three-dimensional framework (Fig. 3). The shortest intermolecular distance between the N and O atoms is N2 $\cdots$ O3<sup>iv</sup> = 3.366 (2) Å [symmetry code: (iv)  $1 + x, y, z$ ], which is comparable with the shortest C $\cdots$ O distance of 3.371 (2) Å in the C—H $\cdots$ O hydrogen bonds. The line of N2 $\cdots$ O3<sup>iv</sup> makes an angle of *ca* 76° with the least-squares plane defined by the nitrophenyl ring including atoms C13 and N2.

Experimental

Compound (I) was prepared according to the literature method of Spangler *et al.* (1989). Crystals of (I) were grown from an acetonitrile solution by slow evaporation (m.p. 513–514 K).

Crystal data

$C_{18}H_{14}N_2O_4$	$D_x = 1.385 \text{ Mg m}^{-3}$
$M_r = 322.31$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3502 reflections
$a = 3.8710 (4) \text{ \AA}$	$\theta = 2.2\text{--}28.1^\circ$
$b = 21.440 (2) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$c = 18.7091 (19) \text{ \AA}$	$T = 183 (2) \text{ K}$
$\beta = 95.555 (2)^\circ$	Needle, yellow
$V = 1545.4 (3) \text{ \AA}^3$	$0.30 \times 0.25 \times 0.02 \text{ mm}$
$Z = 4$	

Data collection

Bruker SMART CCD area-detector diffractometer	3490 independent reflections
$\varphi$ and $\omega$ scans	2640 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.026$
$T_{\text{min}} = 0.909, T_{\text{max}} = 0.998$	$\theta_{\text{max}} = 28.2^\circ$
9325 measured reflections	$h = -5 \rightarrow 5$
	$k = -28 \rightarrow 20$
	$l = -22 \rightarrow 23$

Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0743P)^2 + 0.088P]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.126$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$
3490 reflections	$\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
218 parameters	Extinction correction: SHELXTL (Sheldrick, 2000)
H-atom parameters constrained	Extinction coefficient: 0.0075 (15)

Table 1

Selected geometric parameters ( $\text{\AA}, ^\circ$ ).

C1–N1	1.463 (2)	C12–C13	1.457 (2)
C4–C7	1.459 (2)	C16–N2	1.463 (2)
C7–C8	1.340 (2)	N1–O2	1.225 (2)
C8–C9	1.437 (2)	N1–O1	1.226 (2)
C9–C10	1.342 (2)	N2–O3	1.223 (2)
C10–C11	1.437 (2)	N2–O4	1.224 (2)
C11–C12	1.341 (2)		
C3–C4–C5	117.9 (1)	C14–C13–C12	123.0 (1)
C5–C4–C7	122.7 (1)	O2–N1–O1	123.3 (1)
C8–C7–C4	126.0 (1)	O1–N1–C1	118.2 (1)
C11–C12–C13	127.4 (1)	O3–N2–O4	123.4 (1)
C14–C13–C18	118.0 (1)	O4–N2–C16	118.3 (1)
C5–C4–C7–C8	18.0 (2)	C11–C12–C13–C14	−0.7 (2)
C4–C7–C8–C9	178.2 (1)	C6–C1–N1–O2	−1.4 (2)
C7–C8–C9–C10	−177.5 (1)	C2–C1–N1–O1	−1.0 (2)
C8–C9–C10–C11	179.0 (1)	C15–C16–N2–O3	2.7 (2)
C9–C10–C11–C12	−179.9 (1)	C17–C16–N2–O4	3.2 (2)
C10–C11–C12–C13	178.6 (1)		

Table 2

Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ ).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
C7–H7 $\cdots$ O3 <sup>i</sup>	0.95	2.44	3.371 (2)	166
C14–H14 $\cdots$ O2 <sup>ii</sup>	0.95	2.57	3.366 (2)	141
C15–H15 $\cdots$ O1 <sup>iii</sup>	0.95	2.61	3.454 (2)	148
C2–H2 $\cdots$ O1 <sup>iii</sup>	0.95	2.71	3.364 (2)	127

Symmetry codes: (i)  $-x, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (ii)  $x - 2, -y + \frac{3}{2}, z - \frac{1}{2}$ ; (iii)  $-x + 3, -y + 1, -z + 1$ .

H atoms were positioned geometrically and treated as riding atoms, with C–H distances of 0.95  $\text{\AA}$  and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: TEXSAN (Molecular Structure Corporation, 1999); software used to prepare material for publication: SHELXTL.

References

Bruker (2001). SMART (Version 5.625) and SAINT (Version 6.22). Bruker AXS Inc., Madison, Wisconsin, USA.

Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond in Structural Chemistry and Biology*. New York: Oxford University Press.

Drenth, W. & Wiebenga, E. H. (1954). *Recl Trav. Chim. Pays-Bas*, **73**, 218–228.

Drenth, W. & Wiebenga, E. H. (1955). *Acta Cryst.* **8**, 755–760.

Geskin, V. M., Lambert, C. & Brédas, J.-L. (2003). *J. Am. Chem. Soc.* **125**, 15651–15658.

Glaser, R., Dendi, L. R., Knotts, N. & Barnes, C. L. (2003). *Cryst. Growth Des.* **3**, 291–300.

Hall, T., Bachrach, S. M., Spangler, C. W., Sapochak, L. S., Lin, C. T., Guan, H. W. & Rogers, R. D. (1989). *Acta Cryst.* **C45**, 1541–1543.

Molecular Structure Corporation (1999). TEXSAN. Version 1.11. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.

Rodenberger, D. C., Heflin, J. R. & Garito, A. F. (1995). *Phys. Rev. A*, **51**, 3234–3245.

Rumi, M., Ehrlich, J. E., Heikal, A. A., Perry, J. W., Barlow, S., Hu, Z., McCord-Maughon, D., Parker, T. C., Röckel, H., Thayumanavan, S., Marder, S. R., Beljonne, D. & Brédas, J.-L. (2000). *J. Am. Chem. Soc.* **122**, 9500–9510.

Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.

Sheldrick, G. M. (2000). SHELXTL. Version 6.12. Bruker AXS, Madison, Wisconsin, USA.

Sonoda, Y., Kawanishi, Y. & Goto, M. (2003). *Acta Cryst.* **C59**, o311–o313.

Sonoda, Y., Kawanishi, Y., Ikeda, T., Goto, M., Hayashi, S., Yoshida, Y., Tanigaki, N. & Yase, K. (2003). *J. Phys. Chem. B*, **107**, 3376–3383.

Sonoda, Y., Miyazawa, A., Hayashi, S. & Sakuragi, M. (2001). *Chem. Lett.* pp. 410–411.

Spangler, C. W. (1999). *J. Mater. Chem.* **9**, 2013–2020.

Spangler, C. W., McCoy, R. K., Dembek, A. A., Sapochak, L. S. & Gates, B. D. (1989). *J. Chem. Soc. Perkin Trans. 1*, pp. 151–154.

Stam, C. H. & Riva di Sanseverino, L. (1966). *Acta Cryst.* **21**, 132–138.