(*E,E,E*)-1,6-Bis(2,4-dichlorophenyl)-hexa-1,3,5-triene

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The title molecule, $C_{18}H_{12}Cl_4$, lies about an inversion centre and the hexatriene chain is planar. The torsion angle of the single bond between the planes of the chain and the benzene ring is -8.6 (3)°. The dihedral angle between the planes defined by the chains of adjacent molecules is 50.0 (2)°. The shortest intermolecular distance between the Cl atoms is 3.514 (1) Å. The molecules are joined through π–π-stacking and strong attractive Cl···Cl interactions.

Comment

The structure and properties of (*E,E,E*)-1,6-diphenylhexa-1,3,5-triene (DPH) and its ring-substituted derivatives have been extensively studied. In the field of photophysics and photochemistry, their highly fluorescent properties and *Z–E* geometrical isomerization in solution have attracted much attention. Due to the extended π-conjugation systems, solid-state DPHs are also attractive in the field of materials science because of their potential use as materials for third-order non-linear optics and optical power limiting, and two-photon


(I)
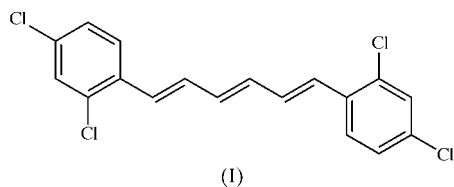
absorbing chromophores (Rodenberger *et al.*, 1992; Spangler, 1999; Rumi *et al.*, 2000). We report here the synthesis and structure of the title compound, (I), a symmetrically substituted DPH having Cl atoms on the benzene rings. Our data can be compared with those for the *E,E,E*-isomers of DPH, 1,6-bis(2-methoxyphenyl)hexa-1,3,5-triene (Hall *et al.*, 1989), and 1,6-bis(4-chlorophenyl)-3,4-dimethylhexa-1,3,5-triene and the 2-chlorophenyl analogue(Stam & Riva di Sanseverino, 1966), and the all-*E*-isomers of longer diphenylpolyenes (Drenth & Wiebenga, 1954, 1955). It is well known that 2,4-dichloro substitution on a benzene ring is very effective at inducing solid-state [2+2]-photocycloadditions of aromatic

olefins (Ramamurthy & Venkatesan, 1987). However, as we reported previously (Sonoda *et al.*, 2001), compound (I) is photochemically stable. In this study, the crystal structure analysis of (I) has been performed in order to find an explanation for its photostability in the solid state.

The molecular structure of (I) is shown in Fig. 1. In the hexatriene chain, the torsion angles [C1—C2—C3—C4 = 177.4 (2)°, C2—C1—C1^i—C2^i = 180° and C1—C1^i—C2^i—C3^i = 179.1 (2)°; symmetry code: (i) $1 - x$, $1 - y$, $1 - z$; Table 1] are almost 180°, indicating that the triene chain is planar. Distinct bond alternation is observed; although C—C single bonds [C1—C2 = 1.439 (2) Å and C3—C4 = 1.461 (2) Å] are shorter than the standard value of 1.54 Å, they are significantly longer than C=C double bonds [C1—C1^i = 1.340 (3) Å and C2—C3 = 1.335 (2) Å]. For conjugated olefins, the C=C double bonds are expected to be longer than the standard value of 1.34 Å for isolated olefins. In the present case, however, the C=C bond lengths are all similar to the standard value for mono-olefins. The C=C bond lengths of 1.328 (4) and 1.328 (5) Å for DPH are even shorter than the values for (I) (Hall *et al.*, 1989). It is known that X-ray structures of (*E*)-stilbene derivatives show unusually short C=C bond lengths. These are considered to be artifacts caused by dynamic averaging originating from the torsional vibrations of the C—Ph single bonds (Ogawa *et al.*, 1992; Harada & Ogawa, 2001). It is possible that similar thermal vibrations also exist in the crystals of longer polyenes. The relatively short C=C bonds observed for (I) (and DPH) may therefore be due to the vibrational motions around the C—Ph and/or C—C bonds. C—C—C bond angles in the chain are all somewhat wider than 120°, which minimizes the steric interaction between H atoms of the chain and the benzene ring. The C2—C3—C4 angle, for example, is 127.3 (2)°.

The benzene rings are also planar. Distances from the best-plane fit for the ring are -0.042 (2), 0.016 (3) and 0.053 (3) Å for atoms Cl1, Cl2 and C3, respectively. The C5—C4—C9 internal angle of 115.8 (1)° is narrower than 120° to accommodate the large exterior angle described above. The structures of the hexatriene moiety and the benzene ring of (I) are very similar to those reported for the unsubstituted and 2-methoxy derivatives of DPH (Hall *et al.*, 1989).

The C2—C3—C4—C5 torsion angle of -8.6 (3)° displays the maximum deviation from values of 0 or 180° in this molecule. The least-squares plane defined by the ring makes an angle of 9.9 (1)° with the least-squares plane defined by the
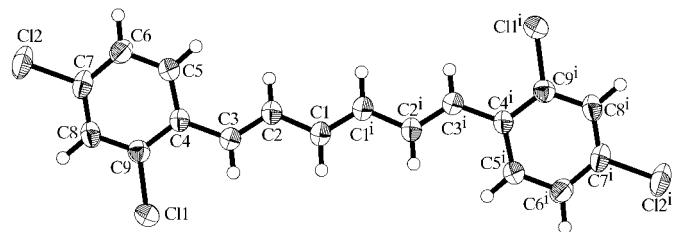
Figure 1
A view of the molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $1 - x$, $1 - y$, $1 - z$.]
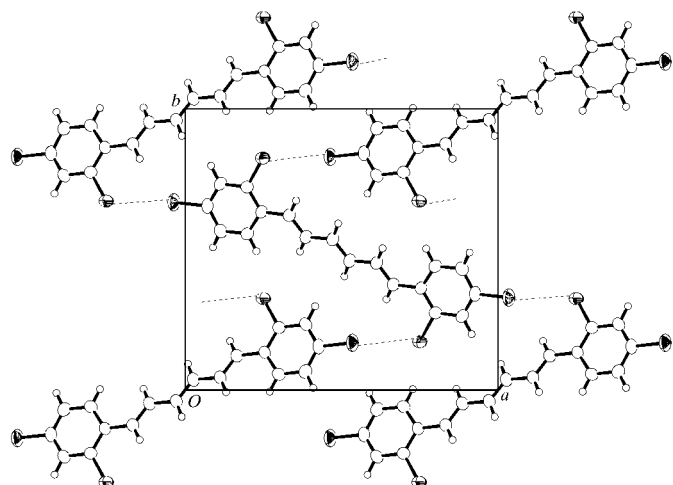
organic compounds

Figure 2
A packing diagram for (I). Dashed lines indicate the shortest Cl···Cl intermolecular distance of 3.514 (1) Å.

hexatriene chain. The twisting around the C3—C4 single bond is due to steric interactions between the Cl1 and C3-H atoms, and between the C2-H and C5-H atoms. These steric interactions are more important in this case than the complete planar conjugation. It is found that the C2—C3—C4—C5 torsion angle, or the dihedral angle between the planes of the ring and the chain, is most sensitive to the substituents introduced on the benzene ring for DPH derivatives; this angle is 1.9° for unsubstituted DPH and 15.6° for its 2-methoxy derivative (Hall *et al.*, 1989). The molecule of (I) is thus more planar than that of the 2-methoxy derivative.

Fig. 2 shows the crystal structure of (I). The molecules are piled up along the *c* axis to form parallel plane-to-plane stacks. The angle formed between the planes defined by the chains of adjacent molecules related by the *a* glide is 50.0 (2)°. The shortest intermolecular distance between the Cl atoms is Cl1···Cl2($x - \frac{1}{2}, -y + \frac{1}{2}, z - 1$) of 3.514 (1) Å, which is shorter than the van der Waals contact distance of 3.6 Å. Most of the C—Cl···Cl—C distances in aromatic chlorinated compounds lie in the range 3.5–4.2 Å (Ramamurthy & Venkatesan, 1987). The molecules are thus joined through strong attractive Cl···Cl interactions between adjacent molecules. In addition, it should be noted that the distances between the Cl atoms of the stacking molecules are Cl1···Cl1($x, y, z + 1$) of 3.950 (1) Å and Cl1···Cl2($-\frac{1}{2} + x, \frac{1}{2} - y, z$) of 4.218 (1) Å.

For solid-state [2+2]-photocycloadditions, it is well known that the distance between the two potentially reactive double bonds should be less than 4.2 Å (Ramamurthy & Venkatesan, 1987). In the crystals of DPH, the distance between parallel double bonds is 7.730 (2) Å (= *a*) (Hall *et al.*, 1989), which is consistent with its photostability in the microcrystalline state (Sonoda *et al.*, 2001). In the crystal structure of (I), on the other hand, the distance between the double bonds of neighboring molecules in the stack is 3.950 (1) Å (= *c*). Thus, it is clear that the attractive Cl···Cl interactions between the stacking molecules strongly reduce the double-bond distance in (I) relative to the value for DPH. In spite of the short distance of 3.95 Å, however, the crystalline powder of (I) is

photostable (Sonoda *et al.*, 2001). There are several examples of similar exceptions to the 4.2 Å rule in the literature (Murthy *et al.*, 1987). Methyl 4-hydroxy-3-nitrocinnamate, for example, is photostable in the solid state, although the double-bond distance is 3.78 Å. It is likely that the extensive intermolecular hydrogen bonds and C—H···O interactions do not permit the easy spatial movement of the double bonds in the lattice for the reaction to proceed. Also in the case of (I), the photostability may possibly be due to the (too) strong attractive Cl···Cl interactions between the adjacent molecules, which prevent any motion of the reactive molecules.

Experimental

Crystal data

$C_{18}H_{12}Cl_4$	$D_x = 1.506$ Mg m^{-3}
$M_r = 370.10$	Mo *Kα* radiation
Monoclinic, $P2_1/a$	Cell parameters from 22
$a = 15.163$ (4) Å	reflections
$b = 13.639$ (3) Å	$\theta = 16.0–17.6°$
$c = 3.950$ (1) Å	$\mu = 0.72$ mm^{-1}
$\beta = 92.39$ (2)°	$T = 278.2$ K
$V = 816.2$ (4) Å^3	Prism, yellow
$Z = 2$	$0.50 \times 0.10 \times 0.10$ mm

Table 1
Selected geometric parameters (Å, °).

Cl1—C9	1.747 (2)	C1—C2	1.439 (2)
Cl2—C7	1.741 (2)	C2—C3	1.335 (2)
C1—C1^i	1.340 (3)	C3—C4	1.461 (2)
C1^i—C1—C2	125.3 (2)	C3—C4—C9	122.2 (1)
C1—C2—C3	123.8 (2)	C5—C4—C9	115.8 (1)
C2—C3—C4	127.3 (2)	Cl1—C9—C4	120.3 (1)
C3—C4—C5	121.9 (1)		
Cl1—C9—C4—C3	−2.9 (2)	C2—C1—C1^i—C2^i	180
C1—C1^i—C2^i—C3^i	179.1 (2)	C2—C3—C4—C5	−8.6 (3)
C1—C2—C3—C4	177.4 (2)	C2—C3—C4—C9	172.9 (2)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Data collection

Rigaku AFC-7R diffractometer	$h = -19 \rightarrow 0$
$\theta/2\theta$ scans	$k = -17 \rightarrow 1$
2083 measured reflections	$l = -5 \rightarrow 5$
1866 independent reflections	3 standard reflections
1584 reflections with $F^2 > 2\sigma(F^2)$	every 150 reflections
$R_{int} = 0.010$	intensity decay: 0.5%
$\theta_{max} = 27.5°$	

Refinement

Refinement on F^2	H-atom parameters not refined
$R(F) = 0.041$	$w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$
$wR(F^2) = 0.109$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.50$	$(\Delta/\sigma)_{max} < 0.001$
1866 reflections	$\Delta\rho_{max} = 0.23$ e Å^{-3}
100 parameters	$\Delta\rho_{min} = -0.49$ e Å^{-3}

H atoms were placed geometrically and refined as riding with C—H distances in the range 0.92–0.99 Å.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

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.

Hall, T., Bachrach, S. M., Spangler, C. W., Sapochak, L. S., Lin, C. T., Guan, H. W. & Rogers, R. D. (1989). *Acta Cryst.* C**45**, 1541–1543.

Harada, J. & Ogawa, K. (2001). *J. Am. Chem. Soc.* **123**, 10884–10888.

Molecular Structure Corporation (1993). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

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

Murthy, G. S., Arjunan, P., Venkatesan, K. & Ramamurthy, V. (1987). *Tetrahedron*, **43**, 1225–1240.

Ogawa, K., Sano, T., Yoshimura, S., Takeuchi, Y. & Toriumi, K. (1992). *J. Am. Chem. Soc.* **114**, 1041–1051.

Ramamurthy, V. & Venkatesan, K. (1987). *Chem. Rev.* **87**, 433–481.

Rodenberger, D. C., Heflin, J. R. & Garito, A. F. (1992). *Nature*, **359**, 309–310.

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.

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

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

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