

SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.  
 SHELDRIK, G. M. (1986). *SHELX86*. Program for crystal structure solution, Univ. of Göttingen, Federal Republic of Germany.

TOPPING, H. (1960). *Errors of Observation and their Treatment*. London: Chapman & Hall.  
 TRUEBLOOD, K. N. (1984). *THMV*. Univ. of California, Los Angeles, USA.  
 ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

*Acta Cryst.* (1989). **C45**, 1541–1543

## Structure of All-*trans*-1,6-diphenyl- (*A*) and All-*trans*-1,6-bis(*o*-methoxyphenyl)-1,3,5-hexatriene (*B*)

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**Abstract.** *A*: C<sub>18</sub>H<sub>16</sub>, *M<sub>r</sub>* = 232.32, orthorhombic, *Pbca*, *a* = 7.730 (2), *b* = 9.881 (2), *c* = 18.096 (3) Å, *V* = 1382 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.12 g cm<sup>-3</sup>, λ(Mo *Kα*) = 0.71073 Å, μ = 0.31 cm<sup>-1</sup>, *F*(000) = 496, *T* = 293 K, final *R* = 0.039 for 600 observed [*F<sub>o</sub>* ≥ 5σ(*F<sub>o</sub>*)] reflections. *B*: C<sub>20</sub>H<sub>20</sub>O<sub>2</sub>, *M<sub>r</sub>* = 292.38, monoclinic, *P2<sub>1</sub>/c*, *a* = 11.089 (6), *b* = 5.4886 (8), *c* = 14.351 (2) Å, β = 110.34 (3)°, *V* = 818.98 Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.19 g cm<sup>-3</sup>, μ = 0.82 cm<sup>-1</sup>, *F*(000) = 312, *T* = 293 K, final *R* = 0.041 for 877 observed reflections. Both compounds are centrosymmetric residing on crystallographic centers of inversion, and exhibit bilayer stacking. The hexatriene chains are similar with distinct bond alternation. *A* is nearly planar. In *B* the angle between the plane of the phenyl ring and that of the hexatriene chain is 15.6° with the methoxy O and C atoms lying 0.022 and 0.114 Å out of the phenyl ring plane, respectively.

**Introduction.** The crystal structures of two oligomeric conjugated diphenylpolyenes, all-*trans*-1,6-diphenyl-1,3,5-hexatriene (*A*) and all-*trans*-1,6-bis(*o*-methoxyphenyl)-1,3,5-hexatriene (*B*), are reported here. In addition to the general crystallographic interest in these structures (they can be compared to 1,8-diphenyl-1,3,5,7-octatetraene and 1,10-diphenyl-1,3,5,7,9-decapentaene) there is special interest in them since they have extended π-electron conjugated systems which may serve for basic investigation in the field of third-order non-linear optical materials (Agrawal & Flytzanis, 1976).

**Experimental.** Compounds *A* and *B* were synthesized as reported by Spangler & Sapochak (1989) and

provided for this study. Compound *A* is colorless, compound *B* is yellow orange. *D<sub>m</sub>* not determined. Crystal *A*: 0.15 × 0.25 × 0.35 mm; *B*: 0.25 × 0.25 × 0.25 mm. Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Mo *Kα* radiation. Cell parameters refined by least squares from setting angle of 25 reflections (θ > 20°). Corrections for Lorentz-polarization effect, absorption ignored. No intensity variation for three standard reflections. Space groups established from systematic absences and successful refinement. With *A*, 1441 reflections collected (*h* 0 to 9, *k* 0 to 11, *l* 0 to 21, 2θ<sub>max</sub> = 50°), 600 independent observed reflections [*F<sub>o</sub>* ≥ 5σ(*F<sub>o</sub>*)]; with *B*, 1684 reflections collected (*h* 0 to 13, *k* 0 to 6, *l* -17 to 17, 2θ<sub>max</sub> = 50°), 877 independent observed reflections [*F<sub>o</sub>* ≥ 5σ(*F<sub>o</sub>*)]. Structures solved by direct methods (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); full-matrix least-squares refinement with *SHELX76* (Sheldrick, 1976). Σw(|*F<sub>o</sub>*| - |*F<sub>c</sub>*|)<sup>2</sup> minimized, weights = [σ(*F<sub>o</sub>*)<sup>2</sup> + *gF<sub>o</sub>*<sup>2</sup>]<sup>-1</sup> (*g* = 0.00012 for *A* and 0.00017 for *B*). Anisotropic thermal parameters for non-H atoms; isotropic refinement of H atoms. Scattering factors from *International Tables for X-ray Crystallography* (1974). *A*: 114 parameters varied, *R* = 0.039, *wR* = 0.039, *S* = 0.97, Δ/σ in final least-squares refinement cycle < 0.01, Δρ < 0.3 e Å<sup>-3</sup> in final difference map. *B*: 140 parameters varied, *R* = 0.041, *wR* = 0.041, *S* = 0.36, Δ/σ in final least-squares refinement cycle < 0.01, Δρ < 0.3 e Å<sup>-3</sup>.

**Discussion.** A previous attempt to determine the crystal structure of *A* reported crystal data for both monoclinic and orthorhombic lattices (Drenth & Wiebenga, 1953). We have solved the structure in the orthorhombic space group, *Pbca*. Fractional coordi-

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Table 1. Final fractional coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>)

$B_{eq} = \frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$ . The H atoms were assigned fixed isotropic thermal parameters of  $B = 5.5 \text{ \AA}^2$ .

	x	y	z	$B_{eq}$
<b>Compound A</b>				
C(1)	0.4732 (4)	0.0638 (3)	0.5011 (2)	4.32
C(2)	0.5200 (4)	0.1613 (3)	0.5562 (2)	4.19
C(3)	0.4618 (4)	0.2877 (3)	0.5586 (1)	4.10
C(4)	0.5049 (3)	0.3923 (3)	0.6130 (1)	3.63
C(5)	0.4366 (4)	0.5218 (3)	0.6059 (2)	4.43
C(6)	0.4752 (4)	0.6211 (3)	0.6578 (2)	5.01
C(7)	0.5802 (4)	0.5936 (4)	0.7167 (2)	4.84
C(8)	0.6499 (4)	0.4670 (4)	0.7240 (2)	4.95
C(9)	0.6139 (4)	0.3678 (3)	0.6729 (1)	4.31
H(1)[C(1)]	0.392 (3)	0.094 (2)	0.463 (1)	
H(1)[C(2)]	0.597 (3)	0.131 (3)	0.591 (1)	
H(1)[C(3)]	0.381 (4)	0.319 (2)	0.520 (1)	
H(1)[C(5)]	0.360 (4)	0.537 (2)	0.564 (1)	
H(1)[C(6)]	0.420 (3)	0.704 (3)	0.653 (1)	
H(1)[C(7)]	0.615 (4)	0.671 (3)	0.755 (2)	
H(1)[C(8)]	0.720 (4)	0.442 (3)	0.768 (2)	
H(1)[C(9)]	0.668 (3)	0.277 (3)	0.680 (1)	
<b>Compound B</b>				
O	0.3398 (2)	0.2823 (3)	0.6132 (1)	3.72
C(1)	0.0358 (2)	-0.3992 (4)	0.5054 (2)	2.56
C(2)	0.0906 (2)	-0.2648 (4)	0.5965 (2)	2.51
C(3)	0.1597 (2)	-0.0615 (4)	0.6041 (2)	2.52
C(4)	0.2127 (2)	0.0920 (4)	0.6921 (2)	2.38
C(5)	0.1739 (3)	0.0738 (5)	0.7745 (2)	3.37
C(6)	0.2226 (3)	0.2258 (5)	0.8555 (2)	4.07
C(7)	0.3107 (3)	0.4019 (5)	0.8558 (2)	3.89
C(8)	0.3517 (3)	0.4265 (5)	0.7760 (2)	3.34
C(9)	0.3030 (3)	0.2725 (4)	0.6949 (2)	2.65
C(10)	0.4210 (3)	0.4765 (7)	0.6062 (3)	4.58
H(1)[C(1)]	0.057 (2)	-0.330 (4)	0.446 (2)	
H(1)[C(2)]	0.072 (2)	-0.329 (4)	0.656 (2)	
H(1)[C(3)]	0.180 (2)	-0.006 (4)	0.547 (2)	
H(1)[C(6)]	0.107 (2)	-0.047 (4)	0.773 (2)	
H(1)[C(7)]	0.192 (3)	0.212 (5)	0.910 (2)	
H(1)[C(8)]	0.344 (2)	0.509 (5)	0.915 (2)	
H(1)[C(9)]	0.415 (2)	0.546 (5)	0.776 (2)	
H(1)[C(10)]	0.433 (3)	0.451 (6)	0.540 (2)	
H(2)[C(10)]	0.390 (3)	0.640 (5)	0.616 (2)	
H(3)[C(10)]	0.508 (3)	0.458 (5)	0.661 (2)	

Table 2. Bond distances (Å) and angles (°)

<b>Compound A</b>			
C(1)—C(2)	1.433 (4)	C(1)—C(1 <sup>1</sup> )	1.328 (5)
C(2)—C(3)	1.328 (4)	C(3)—C(4)	1.466 (3)
C(4)—C(5)	1.390 (4)	C(4)—C(9)	1.393 (3)
C(5)—C(6)	1.392 (4)	C(6)—C(7)	1.366 (4)
C(7)—C(8)	1.369 (4)	C(8)—C(9)	1.376 (4)
C(1 <sup>1</sup> )—C(1)—C(2)	125.4 (4)	C(1)—C(2)—C(3)	124.7 (3)
C(2)—C(3)—C(4)	127.4 (3)	C(3)—C(4)—C(5)	120.0 (3)
C(3)—C(4)—C(9)	122.5 (3)	C(5)—C(4)—C(9)	117.5 (3)
C(4)—C(5)—C(6)	120.3 (3)	C(5)—C(6)—C(7)	120.9 (3)
C(6)—C(7)—C(8)	119.4 (3)	C(7)—C(8)—C(9)	120.4 (3)
C(4)—C(9)—C(8)	121.4 (3)		
<b>Compound B</b>			
O—C(9)	1.369 (2)	O—C(10)	1.421 (3)
C(1)—C(2)	1.439 (3)	C(1)—C(1 <sup>11</sup> )	1.339 (4)
C(2)—C(3)	1.337 (3)	C(3)—C(4)	1.460 (3)
C(4)—C(5)	1.395 (3)	C(4)—C(9)	1.400 (3)
C(5)—C(6)	1.380 (3)	C(6)—C(7)	1.373 (4)
C(7)—C(8)	1.377 (4)	C(8)—C(9)	1.388 (3)
C(9)—O—C(10)	118.3 (2)	C(1 <sup>11</sup> )—C(1)—C(2)	125.1 (3)
C(1)—C(2)—C(3)	123.5 (2)	C(2)—C(3)—C(4)	126.8 (2)
C(3)—C(4)—C(5)	122.8 (2)	C(3)—C(4)—C(9)	120.1 (2)
C(5)—C(4)—C(9)	117.0 (2)	C(4)—C(5)—C(6)	121.7 (3)
C(5)—C(6)—C(7)	119.8 (3)	C(6)—C(7)—C(8)	120.4 (3)
C(7)—C(8)—C(9)	119.6 (3)	O—C(9)—C(4)	115.3 (2)
O—C(9)—C(8)	123.4 (2)	C(4)—C(9)—C(8)	121.4 (2)

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

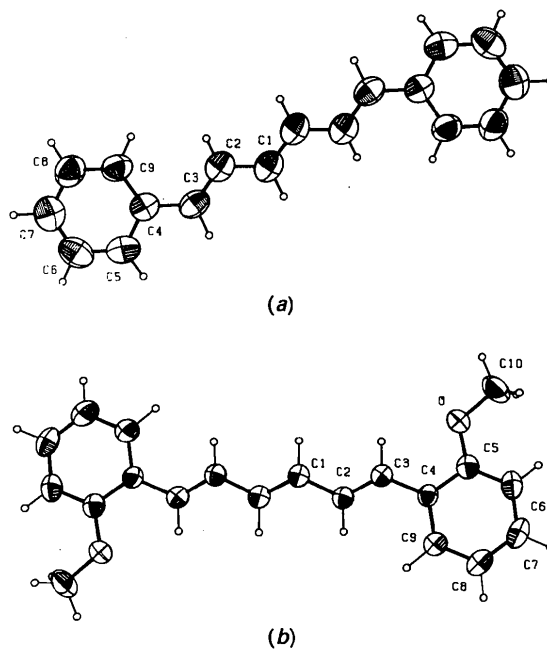


Fig. 1. ORTEP (Johnson, 1976) illustration of the molecular structure and atom-labeling schemes for (a) *A* and (b) *B*. The atoms are represented by their 50% probability ellipsoids for thermal motion. H atoms have been arbitrarily reduced.

nates and  $U_{eq}$  for *A* and *B*\* are given in Table 1, with pertinent bond distances and angles listed in Table 2. ORTEP illustrations of the formula units and representations of the packing schemes are given in Figs. 1 and 2, respectively.

The structure of the hexatriene chain is similar in *A* and *B*, and both are similar to conjugated chains previously reported (Drenth & Wiebenga, 1954, 1955; Buschmann & Rubin, 1978). Distinct bond alternation occurs along the chain, with C—C single bonds [C(1)—C(2) = 1.433 (4), C(3)—C(4) = 1.466 (3) Å in *A*; C(1)—C(2) = 1.439 (3), C(3)—C(4) = 1.460 (3) Å in *B*] being significantly shorter than typical C—C single-bond lengths (1.54 Å). This was also observed in 1,8-diphenyl-1,3,5,7-octatetraene (Drenth & Wiebenga, 1955), 1,10-diphenyl-1,3,5,7,8-decapentaene (Drenth & Wiebenga, 1954), and

\* Lists of structure factors, anisotropic thermal parameters, and least-squares-planes results for both compounds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51935 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1,6-di-2-thienyl-1,3,5-hexatriene (Buschmann & Rubin, 1978). C—C—C bond angles in the chain are all slightly larger than 120°, particularly the C(2)—C(3)—C(4) angle [127.4 (3)° in *A* and 126.8 (2)° in *B*]. These angles are large in order to minimize the interaction between H atoms on the

ring and the H atoms on the chain. This is also observed in the aforementioned compounds.

The phenyl rings in both compounds are planar; maximum displacement from the best-plane fit for the ring is 0.007 Å in *A* and 0.003 Å in *B*. Bond distances and angles in the rings are similar to those previously reported (Drenth & Wiebenga, 1954, 1955). The internal angle at C(4) is small in both compounds to accommodate the large exterior angle described above.

The major difference in the structures of *A* and *B* is in the orientation of the ring with the hexatriene

chain. In *A*, the least-squares plane defined by the phenyl ring makes an angle of only 1.9° with the least-squares plane defined by the hexatriene chain. The largest deviation from the plane defined for all 18 atoms in *A* is only 0.018 Å, confirming that *A* is nearly planar, as can be seen in the cell packing diagram shown in Fig. 2. The angles between the phenyl ring and the polyene chain in 1,8-diphenyl-1,3,5,7-octatetraene (Drenth & Wiebenga, 1955) and 1,10-diphenyl-1,3,5,7,8-decapentaene (Drenth & Wiebenga, 1954) are 5.4 and 7.5°, respectively. The correlation between increasing chain length and increasing ring-chain angle indicates that conjugation between the ring and the chain decreases with increasing chain length.

The angle between the plane of the phenyl ring and the plane of the hexatriene chain in *B* is 15.6°. This is due to the interaction between O and the C(3) H atom and between the C(2) and C(9) H atoms. These interactions outweigh the advantage of planar conjugation. The methoxy O and C atoms lie 0.022 and 0.114 Å out of the phenyl ring plane, respectively. Moreover, displacement of C(4) and C(7) out of the plane of the hexatriene suggests that the phenyl ring is bent rather than rotated away from the chain. Phenyl atoms C(4) and C(7) deviate 0.080 and 0.298 Å, respectively, from the hexatriene plane.

The two compounds pack in alternating directions. The angles formed between the planes for adjacent molecules are 75.4° in *A* and 80.7° in *B*.

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#### References

- AGRAWAL, G. P. & FLYTZANIS, CHR. (1976). *Chem. Phys. Lett.* **44**, 366–370.
- BUSCHMANN, J. F. & RUBIN, G. (1978). *Acta Cryst.* **B34**, 1923–1927.
- DRENTH, W. & WIEBENGA, E. H. (1953). *Recl Trav. Chim. Pays-Bas*, **72**, 39–43.
- 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.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 72, 99, 149. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination, as locally modified. Univ. of Cambridge, England.
- SPANGLER, C. W. & SAPOCHAK, L. S. (1989). In preparation.

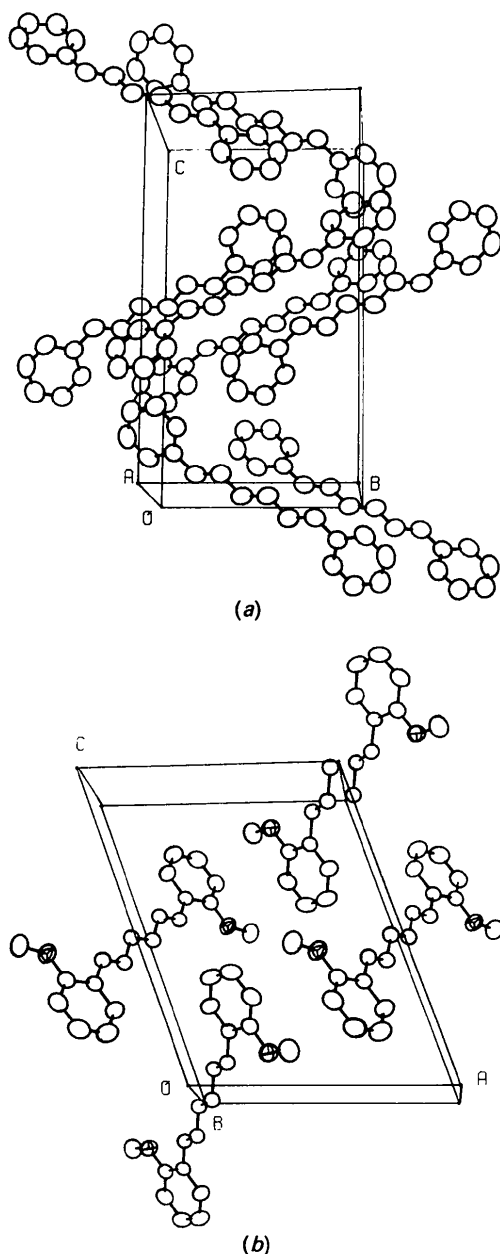


Fig. 2. Cell packing diagrams for (a) *A* and (b) *B*.