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Structure of α, ω-Diphenyl-Polyenes. IV.* Crystal and Molecular Structure of 1,8-Diphenyl-1,3,5,7-Octatetraene

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The crystal and molecular structure of the orthorhombic modification of 1,8-diphenyl-1,3,5,7-octatetraene at −100° C. has been determined by three-dimensional Fourier and differential syntheses. The intensities of 1179 independent reflexions, representing 69% of the total possible with copper radiation, were recorded on ordinary and integrated Weissenberg photographs; most of them were measured photometrically.

The centrosymmetrical molecules have the all-*trans* configuration; they are not perfectly planar. The carbon atoms of the polyene chain are located in a plane, making an angle of 5·4° with the planes of the benzene rings. The hydrogen atoms are clearly visible in the three-dimensional Fourier synthesis. The experimental bond lengths are: average C–C bond in the benzene rings 1·396 Å, single bonds of the polyene chain 1·468, 1·438 and 1·441 Å, double bonds 1·350 Å, average C–H 1·08 Å. The standard deviations of the co-ordinates of the carbon atoms are 0·003 Å. The experimental C–C bond lengths are compared with values, predicted by the molecular orbital method.

Introduction

In a conjugated chain like $H-(CH=CH-)_nH$, the molecular orbital (MO) theory predicts a considerable decrease of the C–C single bonds and some increase in the lengths of the C–C double bonds as compared with the values for a pure single and double bond respectively (Coulson, 1939). To verify these conclusions an X-ray investigation of α,ω-diphenylpolyenes, $Ph-(CH=CH-)_nPh$, was undertaken. These compounds are crystalline and stable at room temperature, and therefore they are better suited to X-ray analysis than the unsubstituted polyenes. In connexion with the X-ray investigation, the C–C bond lengths in the first six members of the series of diphenylpolyenes with $n = 0, 1, 2, 3, 4$ and 5 were calculated (Drenth, 1954), following the LCAO–MO method.

Biphenyl ($n = 0$) has been the subject of various X-ray investigations, which indicate a plane configuration in the crystalline state (see, for example, Cagle, 1948; Dhar, 1949). The structure of stilbene ($n = 1$) was determined by Robertson & Woodward (1937) from Fourier projections. Crystal data of the compounds $n = 2$, 3 and 4 have recently been published (Drenth & Wiebenga, 1953) as well as the structure determinations of the monoclinic and of the orthorhombic modifications of 1,10-diphenyl-decapentaene ($n = 5$) from Fourier projections (Drenth & Wiebenga, 1954). It was not possible, however, to grow from the compound $n = 5$ crystals large enough to obtain a number of reflexions sufficient for an accurate X-ray analysis. Therefore the orthorhombic modification of 1,8-diphenyl-octatetraene ($n = 4$), of which larger crystals were available, was chosen for an accurate determination of the bond lengths. The diffraction data were recorded at a temperature of −100° C. in order to reduce the co-ordinate errors (Burbank, 1953).

Crystal data

Diphenyl-octatetraene, $C_{20}H_{18}$, is a yellow compound, m.p. 234° C.; it was prepared by the method of Kuhn & Winterstein (1928). Orthorhombic crystals were obtained from ethyl acetate (Krishnan, Corghade & Ananthapadmanabhan, 1940); they are described in a previous paper (Drenth & Wiebenga, 1953). The space group is *Pcab* with 4 centrosymmetrical molecules per unit cell. For the present work accurate values for the lattice constants were required. These were obtained by covering the small crystals with a thin layer of NaCl and measuring the Bragg angles of a number of reflexions relative to those of the NaCl powder lines. The spacing $d_{200} = 2{\cdot}8199$ Å for NaCl at 18° C. was taken from the literature (Batuecas, 1954); at −100° C. it was measured to be 2·8089 ±0·0006 Å. The results are listed in Table 1.

It is seen from Table 1, that the *a* axis of diphenyloctatetraene shows a remarkable increase with decreasing temperature.

Table 1. *Lattice constants*

	At 18±1° C.	At −100±5° C.
a (Å)	10·062±0·010	10·196±0·010
b (Å)	7·625±0·010	7·504±0·010
c (Å)	19·925±0·010	19·579±0·005

λ (Cu $K\alpha$) = 1·5418 Å.

All X-ray photographs were taken using nickel-filtered copper radiation, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å. The

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* III: Drenth, 1954.

low-temperature photographs were obtained from crystals which were cooled to $-100°$ C. by a stream of vapour from boiling liquid air. The temperature was measured by a thermocouple and controlled by regulating the electric current of the heater in the boiling liquid air. To prevent condensation of water vapour, the whole Weissenberg goniometer was surrounded by a flexible plastic cover.

Reflexion intensities

The crystals used for the intensity determinations had the form of rhombs with edges of 0·035 cm. and a thickness of approximately 0·025 cm. Integrated equi-inclination Weissenberg photographs (Wiebenga & Smits, 1950) of the following layer lines were made:

Rotation axis	Layer lines
[100]	0, 1, 2, 3, 4, 5, 6
[010]	0, 1, 2, 3, 4, 5
[110]	0, 1, 2, 3

Most intensities were measured photometrically (Smits & Wiebenga, 1953). The intensities of the weaker reflexions were estimated visually on ordinary Weissenberg photographs. A graphical correction for absorption was applied to the reflexions of the four [110] layer lines only. After taking into account the Lorentz and polarization factors (Tunell, 1939; Buerger & Klein, 1946), the measurements on the various layer lines could be correlated. Almost 400 reflexions were recorded on even three or four different layer lines. In order to estimate the accuracy involved in the intensity measurements,

$$\Sigma|I_{\text{measured}}-I_{\text{average}}| \div \Sigma I_{\text{measured}}$$

was calculated for these 400 reflexions; the value obtained was 0·058.

Three 'forbidden' reflexions were observed, viz 009, 055 and 0,0,13, and three spots *hkl* had anomalously high intensities in comparison to equivalent spots on the same film. These anomalies may be explained by double reflexion (Renninger, 1937). Of the 1709 possible reflexions within the reflexion sphere for copper radiation, 1179 or 69% were actually observed.

Determination of the approximate co-ordinates

Neglecting the hydrogen atoms, the co-ordinates of ten independent carbon atoms had to be determined. The carbon atoms could be located approximately by trial and error, making use of the comparison with the known analogous structure of diphenyl-decapentaene (Drenth & Wiebenga, 1954).

The x and z co-ordinates of the carbon atoms were then refined by two-dimensional Fourier syntheses of the [010] projection. They were corrected for the termination of the series (Booth, 1946*a*). This correction resulted in an expansion of the benzene ring and an expansion of the double bonds in the polyene chain. The average backshift was 0·014 Å per co-ordinate. Using McWeeny's (1951) scattering curve for carbon atoms and a temperature factor $\exp[-1\cdot81 \sin^2\theta/\lambda^2]$, the discrepancy index R of the $h0l$ reflexions was 0·13. In the projection the peak densities of the carbon atoms were approximately 8·7 e.Å^{-2}, and the curvature -80 e.Å^{-4}. The standard deviations, estimated by Cruickshank's (1949) method, were $\sigma(x) = \sigma(z) = 0\cdot009$ Å.

The x and z co-ordinates, as derived from this two-dimensional synthesis, may be compared with the final co-ordinates which were obtained from the three-dimensional synthesis described in the following sections. It appears that the r.m.s. deviation between the two sets of parameters is 0·008 Å. This discrepancy is satisfactorily explained by the estimated standard deviations, which amount to 0·009 Å and 0·003 Å for the two-dimensional and three-dimensional syntheses respectively.

The approximate y co-ordinates were not refined by two-dimensional Fourier synthesis, because of overlapping in the [100] and [001] projections. Applying the temperature and scaling factors, as derived from the $h0l$ reflexions, the discrepancy index of the $0kl$ reflexions was 0·17; neglecting the strong reflexion 020, a value of 0·14 was obtained. Compared with the final co-ordinates, the r.m.s. discrepancy of the approximate y co-ordinates appeared to be 0·013 Å.

Three-dimensional Fourier synthesis

The approximate co-ordinates were used to calculate the signs of the structure factors of all observed reflexions. Two reflexions had to be omitted, since their calculated F values were equal to zero. The signs of about eight reflexions were rather uncertain. Using the calculated signs and observed values of the structure factors, a three-dimensional Fourier synthesis was computed. The electron density was evaluated throughout one eighth of the unit cell. The x and the y axes were subdivided into intervals of 6°, the z axis into intervals of 3°. In the neighbourhood of the carbon peaks, the x axis was also subdivided into intervals of 3°.

The co-ordinates of each carbon atom, its peak density and the curvatures of the electron density in the peak were calculated from the equation

$$\ln\varrho = a+kx^2+ly^2+mz^2+px+qy+rz+sxy+txz+uyz$$

(Shoemaker, Donohue, Schomaker & Corey, 1950). For each carbon atom the constants in this equation were evaluated from the electron densities at the 27 points of a $3\times3\times3$ block. The co-ordinates and peak densities are given in Table 2. The average curvature is -105 e.Å^{-5} (r.m.s. deviation 5 e.Å^{-5}).

It appeared that the chain atoms C_6, C_7, C_8, C_9 and C_{10} (Fig. 3(*a*)) were approximately located in the plane

$$0\cdot2741x-0\cdot7672y-0\cdot5803z = 0;$$

Table 2. *Parameters and electron densities of the carbon peaks in the three-dimensional Fourier synthesis*

(For notation see Fig. 3(*a*))

Carbon atom	*x*/*a*	*y*/*b*	*z*/*c*	Peak density (e.Å^{-3})
1	0·6941	−0·0854	0·2232	10·2
2	0·5678	−0·1518	0·2326	10·3
3	0·4695	−0·1143	0·1855	10·3
4	0·7223	0·0146	0·1655	10·3
5	0·6232	0·0514	0·1185	10·6
6	0·4961	−0·0111	0·1281	10·8
7	0·3925	0·0357	0·0780	10·6
8	0·2696	−0·0216	0·0771	10·3
9	0·1722	0·0300	0·0271	10·5
10	0·0483	−0·0271	0·0249	10·3

the deviation from this plane was smaller than 0·01 Å. The benzene ring atoms C_1–C_6 lay closely to the plane

$$0{\cdot}2358x-0{\cdot}8298y-0{\cdot}5056z = 0;$$

the distance from this plane did not exceed 0·01 Å. The electron-density distributions in these planes were then evaluated by linear interpolation from the three-dimensional summation totals. They show, apart from the carbon peaks, distinct hydrogen maxima (Fig. 1). The co-ordinates of the hydrogen maxima in the molecular sections, the peak densities and the C–H bond lengths are given in Table 3. The average C–H distance amounts to 1·06 Å (r.m.s. deviation 0·04 Å). The displacement of a hydrogen maximum in the direction of the carbon atom as a result of the overlapping of the carbon and hydrogen electron densities was estimated to be about 0·02 Å, using Booth's (1946*a*) atomic electron-density equation. The corrected average C–H bond length, 1·08 Å, is in agreement with the results of spectroscopical work.

Table 3. *Parameters and electron densities of the hydrogen peaks in the three-dimensional Fourier synthesis*

H atom attached to C atom	*x*/*a*	*y*/*b*	*z*/*c*	Peak density (e.Å^{-3})	C–H bond length (Å)
1	0·766	−0·112	0·257	1·2	1·01
2	0·543	−0·233	0·279	1·1	1·11
3	0·382	−0·165	0·197	1·0	1·00
4	0·811	0·070	0·153	1·1	1·02
5	0·654	0·130	0·077	1·2	1·04
7	0·423	0·134	0·036	1·3	1·13
8	0·235	−0·112	0·115	1·0	1·06
9	0·210	0·122	−0·010	1·2	1·07
10	0·013	−0·119	0·064	1·1	1·08

The *hkl* structure factors were recalculated, using the positions of the carbon and hydrogen maxima as derived from the preceding three-dimensional Fourier synthesis (Table 4*). The contribution of the hydrogen atoms was included up to $\sin\theta = 0{\cdot}5$. Use was made of the atomic scattering factors, listed by McWeeny (1951) for carbon in the valence state and for hydrogen. One isotropic temperature coefficient was accepted for all carbon atoms, because their peak densities are practically the same and the peak curvatures in the three co-ordinate directions are approximately equal to each other. This temperature coefficient was also assigned to the hydrogen atoms. The temperature and

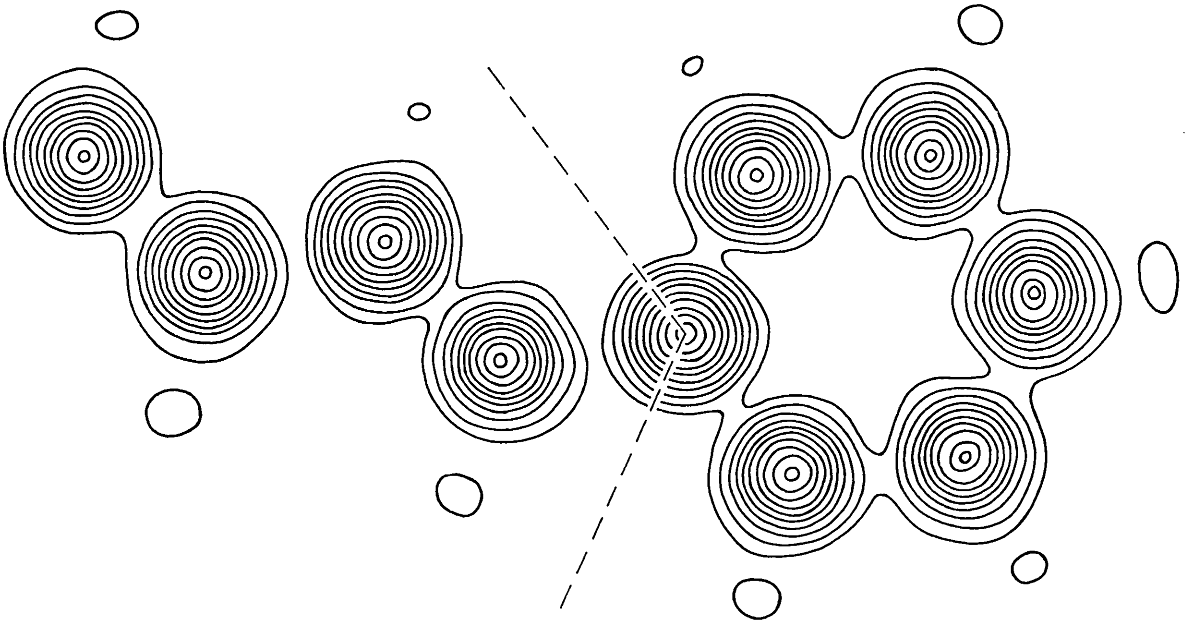

Fig. 1. Electron-density map of one half of a molecule. Contour lines are drawn at 1, 2, 3, ... e.Å^{-3}. The sections through the chain atoms and through the benzene ring atoms are separated by a broken line.

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* Table 4 has been deposited as Document No. 4666 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C., U.S.A. A copy may be secured by citing the Document number and by remitting $1·25 for photoprints, or $1·25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress. A copy may also be obtained from the authors.

scaling factors were adjusted from a plot of $\ln [F_c(B = 0)/F_o]$ against $\sin^2 \theta$. For the constant B in $F_c = F_c(B = 0) \exp [-B \sin^2 \theta/\lambda^2]$ a value of 1·93 Å^2 was obtained.

From the recalculation of the structure factors it appeared that three reflexions had changed their signs and that the signs of six weak reflexions, used in the Fourier synthesis, had remained uncertain. The discrepancy index R for all observed reflexions amounts to 0·11. The estimated standard deviations of the co-ordinates of the carbon atoms, calculated by Cruickshank's (1949) method, are $\sigma(x)=\sigma(y)=\sigma(z)=0{\cdot}003$ Å; the standard deviations of the co-ordinates of the hydrogen atoms are 0·03 Å.

Differential syntheses

A last refinement of the co-ordinates of the carbon atoms was obtained by computing two differential syntheses (Booth, 1946*b*). In one of these syntheses all observed structure factors with the signs as listed in Table 4 were used. The slopes of the electron-density distribution were evaluated at the atomic positions deduced from the three-dimensional Fourier synthesis (Table 2). The co-ordinate shifts could be calculated, using the curvatures as known from this Fourier synthesis.

A second differential synthesis was computed, using the calculated instead of the observed structure factors. From this synthesis the correction for the effect of finite series could be obtained (Booth, 1946*a*).

The co-ordinate shifts, calculated from the F_o-differential synthesis, had a r.m.s. value of 0·003 Å. The back-shift corrections, from the F_c-differential synthesis, had a r.m.s. value of 0·005 Å, the maximum back-shift being 0·011 Å. This finite-series correction resulted in a decrease of about 0·01 Å in the lengths of the single bonds in the polyene chain, whereas the two independent double bonds increased by 0·01 and 0·02 Å respectively.

Molecular dimensions and orientation

The final atomic co-ordinates are given in Table 5. The origin of the co-ordinate axes is the centre of the molecule. The co-ordinates (in Å) of the chain atoms C_6–C_{10} can be fitted to the plane $Ax+By+Cz = 0$; using the method of least squares, $A = +0{\cdot}27008$, $B = -0{\cdot}77466$ and $C = -0{\cdot}57180$. The deviations from this plane do not exceed 0·007 Å (Table 6).

Table 5. *Final co-ordinates of the carbon atoms*

Carbon atom	x/a	y/b	z/c
1	0·6939	−0·0861	0·2232
2	0·5677	−0·1517	0·2329
3	0·4695	−0·1148	0·1859
4	0·7226	0·0145	0·1650
5	0·6237	0·0523	0·1181
6	0·4954	−0·0106	0·1279
7	0·3936	0·0358	0·0778
8	0·2683	−0·0221	0·0772
9	0·1731	0·0301	0·0269
10	0·0476	−0·0271	0·0251

Table 6. *Deviations from mean planes*

(Distances in Ångström units)

Carbon atom	Benzene ring plane	Plane of chain atoms
1	−0·009	—
2	+0·003	—
3	+0·005	—
4	+0·008	—
5	+0·002	—
6	−0·008	−0·006
7	—	+0·004
8	—	+0·003
9	—	+0·001
10	—	+0·007

This plane is inclined by 39·2° to (010); their intersecting line and the a-axis enclose an angle of 25·3°. The carbon atoms of the benzene ring lie closely to the plane $Ax+By+Cz+D = 0$. A, B, C and D, as determined by the method of least squares, are: $A = +0{\cdot}23268$, $B = -0{\cdot}83082$, $C = -0{\cdot}50557$, $D = +0{\cdot}01657$. The deviations from this plane do not exceed 0·009 Å (Table 6). This plane makes an angle of 33·8° with (010) and of 5·4° with the mean plane through the chain atoms.

The molecules are arranged in layers, parallel to (010). Some short intermolecular distances are given in Fig. 2.

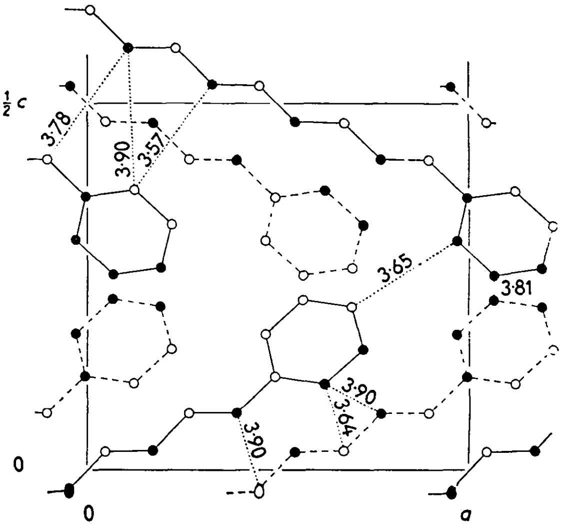

Fig. 2. Orientation and intermolecular carbon–carbon distances (Å).
———: molecules at $y = 0$; ●: atoms above (010); ○: atoms below (010).
- - -: molecules at $y = \frac{1}{2}b$; ●: atoms above the plane $y = \frac{1}{2}b$; ○: atoms below the plane $y = \frac{1}{2}b$.

The molecular dimensions are shown in Fig. 3(*a*). The standard deviations of the atomic distances are 0·004 Å; that of the distance between the atoms C_{10}

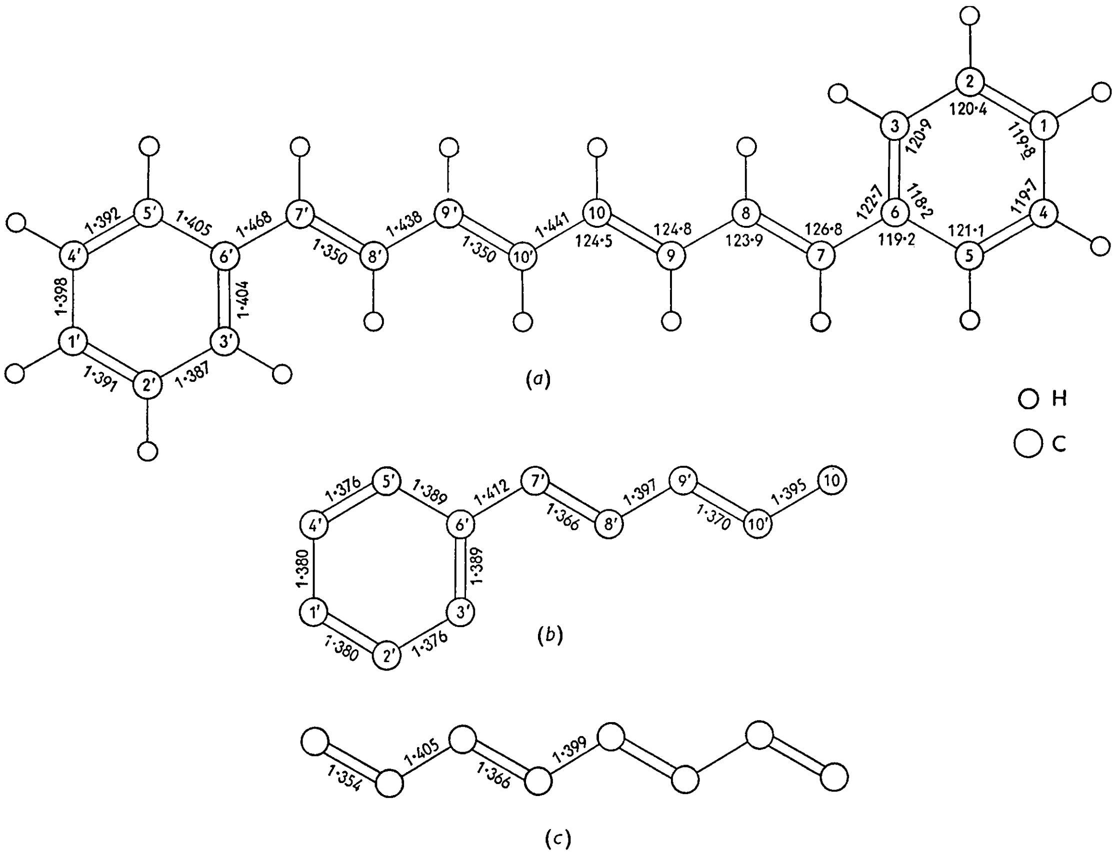

Fig. 3. (a) Experimental bond lengths (Å) and bond angles (degrees). (b) Bond lengths (Å), as calculated using the MO method. (c) Bond lengths (Å) in unsubstituted octatetraene, as calculated using the MO method.

and $C_{10'}$ is 0·006 Å. The standard deviation of the bond angles (Cruickshank & Robertson, 1953) amounts to 0·3°.

The effect of the use of a low temperature

The standard deviations of the co-ordinates were calculated using Cruickshank's (1949) equation $\sigma(x) = \sigma(A_h)/A_{hh}$, in which

$$\sigma(A_h) = 2\pi\{\sum_3 h^2(\Delta F)^2\}^{\frac{1}{2}}/aV \quad \text{and} \quad A_{hh} = -\partial^2\varrho/\partial x^2\,.$$

With decreasing temperature A_{hh} increases, and also $\sigma(A_h)$ can be expected to increase. In order to estimate the effect of the use of a low temperature on the calculated standard deviations, the values of A_{hh} and $\sigma(A_h)$, as obtained for diphenyl-octatetraene at −100° C., may be compared with the values obtained for these quantities in a similar structure determination at room temperature. For this purpose the three-dimensional analysis of dibenzyl (Jeffrey, 1947; Cruickshank, 1949) was chosen. The comparison of A_{hh} and $\sigma(A_h)$ for the two compounds is somewhat complicated by the fact that different atomic scattering factors were used. It appeared from the two-dimensional $h0l$ data for diphenyl-octatetraene, that, if Hartree scattering factors were used instead of the scattering factors from McWeeny's paper, the 'absolute' scale, and therefore A_{hh}, was decreased by approximately 18%. The factor B in the temperature coefficient increased from 1·81 to 2·60 Å^2; the change in $\sigma(A_h)$ was negligible.

	Dibenzyl at room temperature	Diphenyl-octatetraene at −100° C. McWeeny's f curve
$\sigma(A_h)$ (e.Å^{-4})	0·26	0·32
A_{hh} (e.Å^{-5})	34	105
$\sigma(x)$ (Å)	0·008	0·003

It is seen that the expected increase of $\sigma(A_h)$ at low temperatures is small. Probably this increase is counterbalanced by the effect of somewhat more accurate intensity measurements in the case of diphenyl-octatetraene. The decrease of the standard deviation from 0·008 to 0·003 Å is predominantly caused by the large increase of the curvature.

A similar comparison can be made for the two-dimensional data:

	Dibenzyl at room temperature	Diphenyl-octatetraene at −100° C.	
		McWeeny's *f* curve	Hartree's *f* curve
$\sigma(A_h)$ (e.Å^{-3})	0·63	0·70	0·70
A_{hh} (e.Å^{-4})	37	80	66
$\sigma(x)$ (Å)	0·017	0·009	0·011

Discussion of the molecular dimensions

The accuracy of the experimental atomic distances is sufficient to justify a comparison with theoretical values. Differences larger than 0·01 Å may be considered to be significant. In Fig. 3(*b*) the atomic distances, as calculated (Drenth, 1954) using the simple LCAO molecular orbital method, are shown.

It follows from Fig. 3(*a*) and (*b*), that the lengths of the C–C single bonds of the polyene chain are significantly smaller than the pure single-bond length of 1·54 Å, but that the differences are not as large as predicted theoretically. The theoretically predicted increase of the lengths of the double bonds in the chain, as compared with the pure double-bond length of 1·34 or 1·35 Å, does hardly or not appear.

In the MO calculations the molecule was supposed to be planar, whereas actually an angle of 5·4° between the planes of the chain and of the benzene rings is observed. This deviation from planarity will decrease the interaction between the π orbitals of the chain and those of the benzene rings. A comparison with the theoretical results for unsubstituted octatetraene (Fig. 3(*c*)) shows, however, that the effect of a decreased interaction is not sufficient to account for the discrepancy between theoretical and observed bond lengths.

The theoretically predicted bond lengths in the benzene ring are shorter than the experimental ones. The averages of C_6–C_3 and C_6–C_5, of C_3–C_2 and C_5–C_4 and of C_2–C_1 and C_4–C_1 are 1·405 Å, 1·390 Å and 1·395 Å respectively. The differences with the theoretical values are +0·016 Å, +0·014 Å and +0·015 Å respectively. Though the absolute scale is different, the relative values are in close agreement with each other.

The bond angles in the polyene chain are significantly larger than 120°. The large increase of the angles $C_3C_6C_7$ and $C_6C_7C_8$ may be due to a repulsion between the hydrogen atoms attached to C_3 and C_8 (Robertson & Woodward, 1937; Drenth & Wiebenga, 1954). The angle $C_3C_6C_5$ of the benzene ring is significantly smaller than 120°; correspondingly, the angles $C_2C_3C_6$ and $C_4C_5C_6$ are larger than 120°.

The distance of the centre of the molecule from the plane of a benzene ring is only 0·017 Å. Accordingly, both benzene rings of one molecule are arranged approximately in one plane. Hence the distortion of the molecule, possibly caused by a repulsion between the hydrogen atoms attached to C_3 and C_8, is not simply a rotation of the benzene rings about the bonds C_6–C_7, but approximately a rotation about the molecular axis.

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