

The Structure of 1:1:6:6 Tetraphenylhexapentaene

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1:1:6:6-Tetraphenylhexapentaene ($C_{30}H_{20}$) forms red monoclinic crystals of space group $P2_1/c$ with $a = 14.4$, $b = 7.8$, $c = 18.1$ Å and $\beta = 108\frac{1}{2}^\circ$. A trial structure was found directly from a study of the weighted reciprocal-lattice section of the $h0l$ zone. The final analysis showed that the molecules are non-planar, each of the benzene rings having a tilt of 32° relative to the general plane of the molecule. The only other departure from an idealized molecule is that the pairs of benzene rings on the same side of the central carbon chain are forced apart by steric hindrance.

1. Physical properties and X-ray data

Crystals of 1:1:6:6-tetraphenylhexapentaene (subsequently referred to as t.p.h.p.) were prepared by Dr M. Whitehead of the Chemistry Department, University of Manchester. The substance is a deep orange-red colour and forms extremely small monoclinic crystals, plate-like parallel to (010). The largest crystals found were approximately 0.1 mm. in their greatest dimension.

The unit-cell data, determined from oscillation and Weissenberg photographs, were

$$a = 14.4, b = 7.8, c = 18.1 \text{ \AA}, \beta = 108\frac{1}{2}^\circ.$$

This cell contains 4 molecules of $C_{30}H_{20}$ (Fig. 3). The calculated and measured densities were 1.22 and 1.20 g.cm.⁻³ respectively. From the systematic absences the space group was found to be $P2_1/c$.

Weissenberg photographs were taken for $h0l$ and $hk0$ zones. Despite long exposures (35 hr.), only 70 reflexions were observed for the $h0l$ zone and 22 (11 independent) for the $hk0$ zone.

2. Information from the weighted reciprocal lattice

In certain cases valuable information can be derived from the study of a weighted reciprocal-lattice section (Lipson & Taylor, 1951). An untilted benzene ring, for example, registers its presence by the existence of six strong transform peaks at a characteristic distance from the origin of the reciprocal lattice. These benzene peaks are fairly extensive so that if there are two or more rings in the same, or nearly the same, orientation within the unit cell some parts of these peaks will still be retained, even allowing for phase differences. The weighted reciprocal lattice for the $h0l$ section of t.p.h.p. is shown in Fig. 1, with the characteristic benzene radius and the positions of the benzene peaks indicated.

One side of the hexagon produced by these peaks is parallel to the a^* axis, which shows that, in the unit cell, one side of each benzene ring will be parallel to the c direction. The orientation of the molecule is thus

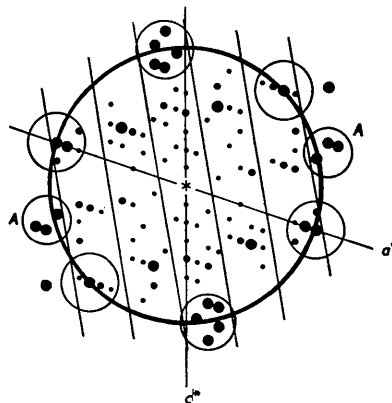


Fig. 1. Weighted reciprocal-lattice section for the $h0l$ zone of 1:1:6:6-tetraphenylhexapentaene.

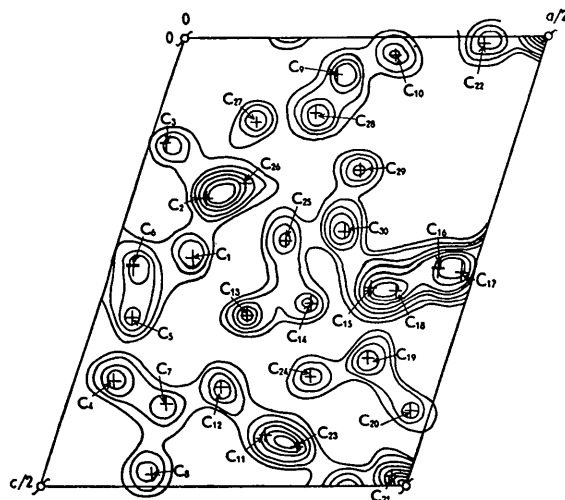


Fig. 2. The projection of 1:1:6:6-tetraphenylhexapentaene on (010) showing the final atomic positions. Contours at 1 e.Å⁻² intervals. Lowest contour 2 e.Å⁻².

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Table 1. Observed and calculated structure factors

			h0l zone					
<i>h k l</i>	F_o	F_c	<i>h k l</i>	F_o	F_c	<i>h k l</i>	F_o	F_c
00 0	—	800	40 0	<i>a</i>	4	$\bar{7}$ 0 10	<i>a</i>	15
00 2	50	-59	40 2	16	-27	$\bar{7}$ 0 12	<i>a</i>	1
00 4	52	53	40 4	44	44	$\bar{7}$ 0 14	23	25
00 6	42	-46	40 6	17	-12	$\bar{7}$ 0 16	<i>a</i>	3
00 8	54	53	40 8	<i>a</i>	7	$\bar{7}$ 0 18	<i>a</i>	-1
00 10	16	10	40 10	<i>a</i>	9	$\bar{7}$ 0 20	<i>a</i>	6
00 12	<i>a</i>	1	40 12	<i>a</i>	-13	80 0	<i>a</i>	7
00 14	<i>a</i>	-3	40 14	<i>a</i>	-11	80 2	<i>a</i>	-10
00 16	<i>a</i>	-4	40 16	<i>a</i>	2	80 4	<i>a</i>	3
00 18	<i>a</i>	4	40 18	<i>a</i>	0	80 6	<i>a</i>	10
10 0	<i>a</i>	-9	$\bar{4}$ 0 2	<i>a</i>	11	80 8	<i>a</i>	0
10 2	<i>a</i>	-14	40 4	15	-12	80 10	<i>a</i>	0
10 4	62	-59	40 6	42	-44	80 12	<i>a</i>	2
10 6	<i>a</i>	2	40 8	<i>a</i>	1	80 2	13	8
10 8	42	-34	40 10	30	22	80 4	25	17
10 10	27	26	40 12	<i>a</i>	-10	80 6	19	-28
10 12	<i>a</i>	10	40 14	16	19	80 8	<i>a</i>	1
10 14	33	-37	40 16	<i>a</i>	2	80 10	<i>a</i>	8
10 16	<i>a</i>	4	40 18	<i>a</i>	0	80 12	37	34
10 18	<i>a</i>	-4	40 20	<i>a</i>	2	80 14	<i>a</i>	-10
$\bar{1}$ 0 2	42	-43	50 0	40	-34	80 16	<i>a</i>	-15
$\bar{1}$ 0 4	72	-84	50 2	<i>a</i>	5	80 18	<i>a</i>	7
$\bar{1}$ 0 6	<i>a</i>	-7	50 4	53	-40	80 20	<i>a</i>	1
$\bar{1}$ 0 8	<i>a</i>	0	50 6	<i>a</i>	-19	90 0	<i>a</i>	10
$\bar{1}$ 0 10	<i>a</i>	5	50 8	<i>a</i>	-7	90 2	<i>a</i>	0
$\bar{1}$ 0 12	<i>a</i>	-6	50 10	<i>a</i>	0	90 4	<i>a</i>	-4
$\bar{1}$ 0 14	<i>a</i>	3	50 12	<i>a</i>	-1	90 6	<i>a</i>	-9
$\bar{1}$ 0 16	<i>a</i>	-1	50 14	<i>a</i>	-3	90 8	<i>a</i>	-6
$\bar{1}$ 0 18	<i>a</i>	0	50 16	<i>a</i>	1	90 10	<i>a</i>	6
20 0	43	-44	$\bar{5}$ 0 2	25	-33	90 12	<i>a</i>	3
20 2	75	-77	50 4	40	34	90 2	<i>a</i>	-3
20 4	23	33	50 6	<i>a</i>	3	90 4	<i>a</i>	-3
20 6	28	-30	50 8	16	28	90 6	49	-32
20 8	49	54	50 10	33	18	90 8	0	-1
20 10	<i>a</i>	9	50 12	18	-9	90 10	<i>a</i>	-19
20 12	39	45	50 14	<i>a</i>	9	90 12	<i>a</i>	7
20 14	<i>a</i>	-13	50 16	<i>a</i>	5	90 14	53	-45
20 16	31	31	50 18	<i>a</i>	0	90 16	<i>a</i>	-5
20 18	<i>a</i>	7	50 20	<i>a</i>	1	90 18	<i>a</i>	-6
$\bar{2}$ 0 2	22	11	60 0	19	-11	100 0	15	19
$\bar{2}$ 0 4	<i>a</i>	0	60 2	44	36	100 2	25	-21
$\bar{2}$ 0 6	<i>a</i>	3	60 4	68	-44	100 4	<i>a</i>	5
$\bar{2}$ 0 8	44	37	60 6	<i>a</i>	3	100 6	<i>a</i>	-4
$\bar{2}$ 0 10	<i>a</i>	-13	60 8	<i>a</i>	5	100 8	<i>a</i>	12
$\bar{2}$ 0 12	<i>a</i>	2	60 10	<i>a</i>	-2	100 10	<i>a</i>	-7
$\bar{2}$ 0 14	<i>a</i>	-1	60 12	<i>a</i>	11	$\bar{1}$ 0 2	<i>a</i>	16
$\bar{2}$ 0 16	<i>a</i>	-4	60 14	<i>a</i>	-4	$\bar{1}$ 0 4	<i>a</i>	-21
$\bar{2}$ 0 18	<i>a</i>	0	60 16	<i>a</i>	-3	$\bar{1}$ 0 6	42	22
$\bar{2}$ 0 20	<i>a</i>	3	60 18	60	49	$\bar{1}$ 0 8	19	-20
30 0	13	-9	60 20	<i>a</i>	2	$\bar{1}$ 0 10	23	31
30 2	16	27	70 0	<i>a</i>	14	$\bar{1}$ 0 12	<i>a</i>	-5
30 4	<i>a</i>	-14	70 2	30	25	$\bar{1}$ 0 14	34	23
30 6	25	18	70 4	24	-24	$\bar{1}$ 0 16	<i>a</i>	-10
30 8	<i>a</i>	-10	70 6	24	18	$\bar{1}$ 0 18	<i>a</i>	9
30 10	<i>a</i>	6	70 8	<i>a</i>	12	110 0	41	-32
30 12	41	-48	70 10	<i>a</i>	-8	110 2	<i>a</i>	-10
30 14	24	26	70 12	20	16	110 4	<i>a</i>	9
30 16	<i>a</i>	-10	70 14	<i>a</i>	-9	110 6	<i>a</i>	-5
30 18	<i>a</i>	8	70 16	<i>a</i>	11	110 8	<i>a</i>	-3
$\bar{3}$ 0 2	65	-81	70 18	<i>a</i>	-8	110 10	<i>a</i>	-5
$\bar{3}$ 0 4	<i>a</i>	2	70 20	<i>a</i>	-4	$\bar{1}$ 1 0 2	<i>a</i>	-16
$\bar{3}$ 0 6	<i>a</i>	-8	70 2	<i>a</i>	11	$\bar{1}$ 1 0 4	<i>a</i>	3
$\bar{3}$ 0 8	19	22	70 4	<i>a</i>	15	$\bar{1}$ 1 0 6	<i>a</i>	-4
$\bar{3}$ 0 10	62	-72	70 6	<i>a</i>	2	$\bar{1}$ 1 0 8	<i>a</i>	2
$\bar{3}$ 0 12	33	-17	70 8	<i>a</i>	-2	$\bar{1}$ 1 0 10	<i>a</i>	10
$\bar{3}$ 0 14	<i>a</i>	5	70 10	<i>a</i>	-2	$\bar{1}$ 1 0 12	<i>a</i>	4
$\bar{3}$ 0 16	<i>a</i>	-7	70 12	<i>a</i>	15	$\bar{1}$ 1 0 14	<i>a</i>	1
$\bar{3}$ 0 18	<i>a</i>	14	70 14	<i>a</i>	2	$\bar{1}$ 1 0 16	<i>a</i>	7
$\bar{3}$ 0 20	<i>a</i>	-1	70 16	<i>a</i>	-2	$\bar{1}$ 1 0 18	<i>a</i>	-1

Table 1 (cont.)

<i>h k l</i>	<i>F_o</i>	<i>F_c</i>	<i>h k l</i>	<i>F_o</i>	<i>F_c</i>	<i>h k l</i>	<i>F_o</i>	<i>F_c</i>
12 0 0	24	-28	13 0 6	<i>a</i>	-5	14 0 12	<i>a</i>	2
12 0 2	<i>a</i>	6	13 0 2	<i>a</i>	-1	14 0 14	<i>a</i>	0
12 0 4	<i>a</i>	-2	13 0 4	<i>a</i>	-3	15 0 0	<i>a</i>	5
12 0 6	<i>a</i>	15	13 0 6	<i>a</i>	-9	15 0 2	<i>a</i>	-1
12 0 8	<i>a</i>	-2	13 0 8	<i>a</i>	-1	15 0 2	<i>a</i>	1
12 0 2	17	28	13 0 10	<i>a</i>	-1	15 0 4	<i>a</i>	-9
12 0 4	<i>a</i>	1	13 0 12	<i>a</i>	3	15 0 6	<i>a</i>	-5
12 0 6	<i>a</i>	7	13 0 14	<i>a</i>	5	15 0 8	<i>a</i>	-2
12 0 8	<i>a</i>	-3	13 0 16	23	-14	15 0 10	<i>a</i>	9
12 0 10	<i>a</i>	1	14 0 0	<i>a</i>	2	15 0 12	<i>a</i>	0
12 0 12	<i>a</i>	-3	14 0 2	<i>a</i>	-1	15 0 14	<i>a</i>	5
12 0 14	<i>a</i>	2	14 0 4	<i>a</i>	2	16 0 2	<i>a</i>	-6
12 0 16	<i>a</i>	7	14 0 2	<i>a</i>	20	16 0 4	<i>a</i>	2
12 0 18	22	13	14 0 4	<i>a</i>	-6	16 0 6	<i>a</i>	-5
13 0 0	<i>a</i>	14	14 0 6	<i>a</i>	8	16 0 8	<i>a</i>	-4
13 0 2	<i>a</i>	-2	14 0 8	<i>a</i>	-11	16 0 10	<i>a</i>	-7
13 0 4	<i>a</i>	4	14 0 10	31	26			

<i>hk0</i> zone								
<i>h k l</i>	<i>F_o</i>	<i>F_c</i>	<i>h k l</i>	<i>F_o</i>	<i>F_c</i>	<i>h k l</i>	<i>F_o</i>	<i>F_c</i>
0 2 0	262	-293	2 3 0	<i>a</i>	-16	4 3 0	<i>a</i>	-21
0 4 0	44	57	3 0 0	<i>a</i>	-9	5 0 0	40	-34
1 1 0	<i>a</i>	-9	3 1 0	74	-79	5 1 0	<i>a</i>	-2
1 2 0	40	42	3 2 0	<i>a</i>	6	5 2 0	<i>a</i>	13
1 3 0	32	-25	3 3 0	77	47	6 0 0	<i>a</i>	-11
1 4 0	25	-32	4 0 0	<i>a</i>	4	6 1 0	<i>a</i>	-3
2 0 0	43	-44	4 1 0	<i>a</i>	10	6 2 0	<i>a</i>	5
2 1 0	75	91	4 2 0	<i>a</i>	-11	7 0 0	<i>a</i>	14
2 2 0	39	20						

restricted to one of three possibilities; the correct orientation may be found from areas *A* (Fig. 1), which are due to the recurring vector distance between atoms in the central carbon chain.

Another feature of the weighted reciprocal lattice which can be used in this case is the fringe system shown in Fig. 1 by the parallel equidistant lines. T.p.h.p. is an example of an hypercentric structure (Lipson & Woolfson, 1952) and the separation of the molecules causing the fringes is given by

$$\cos 2\pi\mathbf{s} \cdot \mathbf{r}' = 0 \text{ for a line of zero intensity,}$$

where

$$\mathbf{s} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$

and

$$\mathbf{r}' = x'\mathbf{a} + y'\mathbf{b} + z'\mathbf{c}.$$

The coordinates of the molecular centres of symmetry relative to the crystallographic centres are $\pm(x', y', z')$, and from Fig. 2 it was found that $x' = 0.100$ and $y' = 0.014$.

The weighted reciprocal-lattice section then led directly to the first trial structure for which structure-factors were calculated which gave a reliability index of 0.38.

3. Refinement of the *h0l* projection

The structure found from the considerations discussed in § 2 was refined by repeated Fourier syntheses and structure-factor calculations until the signs of the calculated structure factors ceased to change. It will be seen from Table 1 that the range of observed *h0l*

reflexions was not as great as could be desired. This is partly due to the small crystals available, and is exaggerated by the fact that the structure is of the hypercentric type for which there are a large number of reflexions in the lower intensity range.

The reliability index is 0.20 for the observed reflexions only. Wilson (1950) has shown that the maximum probable values of the reliability index for centrosymmetrical and non-centrosymmetrical structures are 0.828 and 0.586 respectively. The two figures are due to the difference in the statistical distribution of structure factors for the two types of symmetry. The more uniform distribution of a non-centrosymmetric structure means that, when a structure factor is calculated for a random structure of the same space group and component atoms, the value is more likely to be close to the correct value. By the same reasoning the maximum probable value for the reliability index of a hypercentric structure will be higher than 0.828, and a given value of the index represents higher accuracy for this type of structure.

The final synthesis (Fig. 2) showed that, within the limits of experimental error, the central carbon chain appeared parallel to the plane of projection and that the benzene rings are tilted about 32° from this plane.

4. Treatment of the *hk0* projection

Only 11 independent reflexions were observed for the *hk0* zone, these extending in reciprocal space to $\sin \theta = 0.40$. The molecule was fitted by trial-and-error

Table 2. *Atomic coordinates*

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
1	0.112	0.205	0.247	11	0.286	0.285	0.443	21	0.520	0.285	0.010
2	0.104	0.285	0.177	12	0.207	0.205	0.385	22	0.590	0.205	0.991
3	0.019	0.285	0.112	13	0.209	0.205	0.304	23	0.665	0.125	0.046
4	0.940	0.205	0.121	14	0.288	0.205	0.288	24	0.674	0.125	0.123
5	0.948	0.125	0.193	15	0.366	0.205	0.272	25	0.771	0.125	0.271
6	0.032	0.125	0.255	16	0.445	0.205	0.256	26	0.854	0.125	0.334
7	0.138	0.125	0.406	17	0.522	0.205	0.239	27	0.863	0.205	0.406
8	0.148	0.125	0.488	18	0.600	0.205	0.223	28	0.785	0.285	0.411
9	0.223	0.205	0.542	19	0.605	0.205	0.146	29	0.698	0.285	0.348
10	0.294	0.285	0.521	20	0.528	0.285	0.089	30	0.693	0.205	0.280

methods to agree with the available data. The tilt of the benzene rings can be measured from the $h0l$ projection but it was not possible to differentiate between clockwise and anticlockwise rotations about the lines such as C_1C_4 (Fig. 3). By the consideration

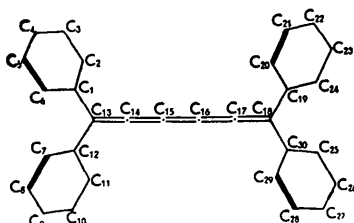


Fig. 3. View of a molecule projected on (010) showing the tilt of the benzene rings. Sides tilted upwards are shown by the heavy lines.

of a wire model, and from packing considerations, a few possible rotation combinations for the rings and corresponding positions for the centre of the molecule were found for each of which structure factors were calculated. Good agreement was found by tilting the rings as shown in Fig. 3, where the sides of the rings tilted towards the observer are indicated by the heavy lines. The central carbon chain is on the plane $y = 0.205$. The nearest approach of two molecules related by a centre of symmetry is 3.2 \AA ; for molecules separated by one unit cell in the a direction it is 3.15 \AA and for molecules related by a glide plane it is 3.1 \AA . The reliability index for the observed reflexions of the $hk0$ zone is 0.18, but this increases to 0.30 for all the reflexions of the range $\sin \theta \leq 0.40$.

The y coordinates are probably of limited accuracy. The atoms were found to lie on three planes parallel to (010). The effect of shifting these planes slightly has been tried, particularly to make the calculated values of F_{220} and F_{330} larger, but without success.

The molecules possibly have a small tilt relative to (010) but this cannot be very large and the data available were considered insufficient to find if this was so.

5. Molecular dimensions and atomic coordinates

The unobserved reflexions for the $h0l$ zone will cause the synthesis of Fig. 2 to be of limited accuracy. The benzene ring atoms are placed by assuming that the projection of each ring should be similar, and they represent the best fit on the synthesis which could be made. The distance between atoms of the central carbon chain has been made uniform; this gives a fit of atoms on the synthesis consistent with its accuracy. Any change of the distance between these atoms will have five times the effect on the total length of the chain, and the mean value of this bond length is subject to a smaller probable error than others. The molecular data are now given and may be followed by reference to Fig. 3.

Phenyl group bond C_1C_2	$1.37 \pm 0.05 \text{ \AA}$
Central carbon chain double bond $C_{13}C_{14}$	$1.31 \pm 0.03 \text{ \AA}$
Single bond C_1C_{13}	$1.51 \pm 0.05 \text{ \AA}$
$\angle C_1C_{13}C_{12}$	$112 \pm 3^\circ$
$\angle C_{13}C_1C_4$	$173 \pm 3^\circ$
Angle of tilt of benzene rings about C_1C_4	$32 \pm 5^\circ$

The coordinates found for the 30 atoms of a single molecule are listed in Table 2.

References

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