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The Crystal Structures of 1,6-Di-*p*- and 1,6-Di-*o*-chlorophenyl-3,4-dimethylhexatriene

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The crystals of 1,6-di-*p*- and 1,6-di-*o*-chlorophenyl-3,4-dimethylhexatriene (both $C_{20}H_{18}Cl_2$) are monoclinic with cell dimensions: $a=36{\cdot}40\pm0{\cdot}01$, $b=4{\cdot}184\pm0{\cdot}002$, $c=11{\cdot}454\pm0{\cdot}004$ Å; $\beta=107{\cdot}95\pm0{\cdot}02°$ and $a=17{\cdot}723\pm0{\cdot}003$, $b=6{\cdot}264\pm0{\cdot}001$, $c=7{\cdot}757\pm0{\cdot}004$ Å, $\beta=102{\cdot}97\pm0{\cdot}03°$ respectively. The space groups are $C2/c$ with $Z=4$ and $P2_1/a$ with $Z=2$. The structures were refined by least squares to final residuals R of 9·7 and 11·3 %. Both molecules are approximately planar. The C–Cl distances are 1·74 and 1·73. The effect of the methyl groups on the bond angles in the conjugated chain is to decrease the angle opposite the C–CH_3 bond in agreement with previous results on carotenoid compounds.

Introduction

The presence of methyl groups in a conjugated chain has been found to have an appreciable influence on the shape of the chain (Stam & MacGillavry, 1963; Sly, 1964; Sterling, 1964) which has been ascribed to the steric interaction of the methyl groups with the chain.

1,6-Di-*p*- and 1,6-di-*o*-chlorophenyl-3,4-dimethylhexatriene ($C_{20}H_{18}Cl_2$) both contain a hexatriene system with two methyl groups on adjacent atoms; it was expected that the crystal structures of these compounds would provide further information on the effect of methyl groups on the conjugated chain.

1,6-Di-*p*-chlorophenyl-3,4-dimethylhexatriene

Experimental

The crystals of the *para* compound were light-yellow monoclinic plates, parallel to (100) and elongated along [010]. The following cell constants were derived from zero layer Weissenberg diagrams about [010] and [001], calibrated with Al powder lines:

$$\begin{aligned} a&= 36{\cdot}40 \pm 0{\cdot}01 \text{ Å} \\ b&= 4{\cdot}184 \pm 0{\cdot}002 \\ c&= 11{\cdot}454 \pm 0{\cdot}004 \\ \beta&= 107{\cdot}95 \pm 0{\cdot}02° \end{aligned}$$

The density as found by flotation is 1·30 g.cm^{-3}; the calculated density for $Z=4$ is 1·32 g.cm^{-3}. The extinctions, hkl when $h+k$ odd, $h0l$ when l odd, are consistent with either of the space groups $C2/c$ and Cc.

Retigraph diagrams were collected for the layers $k=0,1\ldots4$ about [010] and $l=0,1\ldots3$ about [001], by means of a Nonius integrating Rimsky retigraph, using Cu $K\alpha$-radiation. The crystal cross sections were 0·18 × 0·18 and 0·20 × 0·06 mm respectively. 1075 independent reflexions were measured photometrically out of about 1600 within the reflexion sphere. No absorption corrections were applied ($\mu=34$ cm^{-1}).

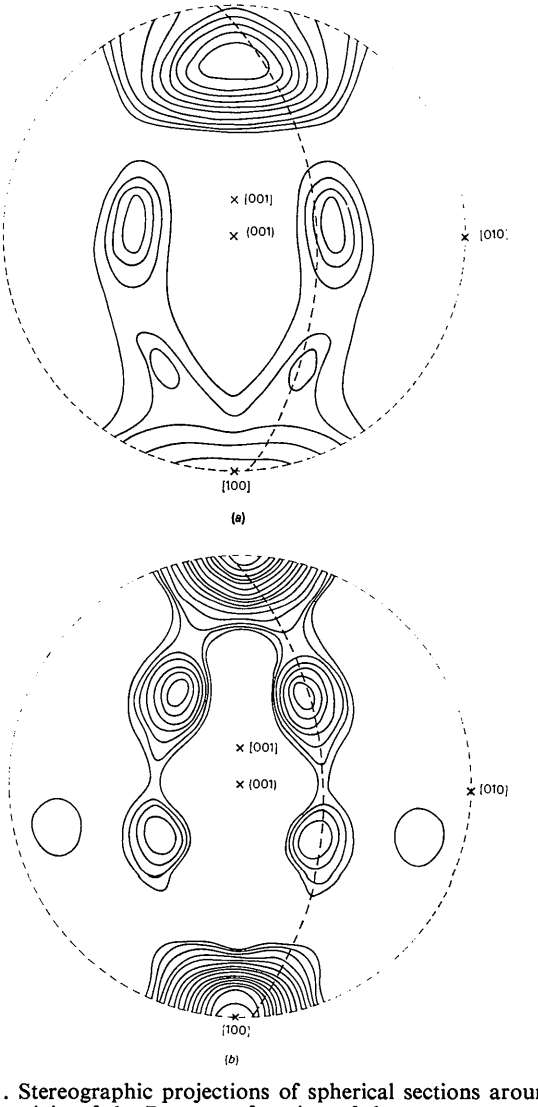

Fig. 1. Stereographic projections of spherical sections around the origin of the Patterson function of the *para* compound with radii (*a*) 1·4 Å and (*b*) 2·4 Å. The dashed lines indicate the probable plane of two of the four molecules in the unit cell.

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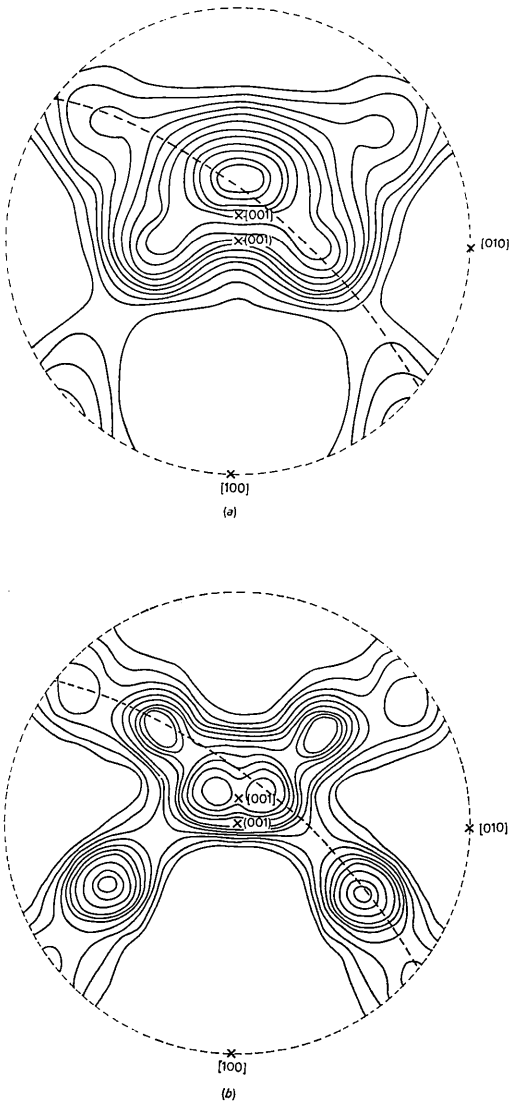

Fig. 2. Stereographic projections of spherical sections around the origin of the Patterson function of the *ortho* compound with radii (*a*) 1·4 Å and (*b*) 2·4 Å. The dashed lines indicate the probable plane of one of the two molecules in the unit cell.

Determination of the structure

The structure was solved from a three-dimensional Patterson synthesis. The molecule of the *para* compound could be expected to be planar. From examination under the polarizing microscope the crystals were found to be optically positive with n_γ very large ($n_\gamma > 2{\cdot}0$, $n_\alpha = 1{\cdot}5$, $n_\beta = 1{\cdot}6$) and in the direction of the *a* axis. This direction might very well correspond to that of the projection of the conjugated chain on (010).

Stereographic projections of spherical sections around the origin of the Patterson function with radii 1·4 and 2·4 Å (Fig. 1) gave the approximate position of the molecular plane. From the weights of the peaks in these sections the direction of the conjugated chain was derived, in accordance with the above optical result. With this information it was possible to interpret the complete three-dimensional Patterson function satisfactorily in terms of the space group $C2/c$ and to obtain approximate coordinates for all the atoms.

The x and z parameters were used to refine the [010] projection. After three Fourier cycles R had dropped from 41 to 17%. With the x and z coordinates thus obtained and y coordinates from the Patterson function a three-dimensional refinement was started. The initial R value was 22·5%. A three-dimensional Fourier synthesis was calculated which showed elongation of the Cl peak along [010]; this, together with bad agreement between observed and calculated structure factors for reflexions with higher k values, indicated rather strong anisotropy for Cl, with largest motion roughly along [010]. To check this, *h*4*l* structure factors were calculated after splitting the Cl atom after Kartha & Ahmed (1960) into two equal parts along the y axis, 0·35 Å apart. This made R_{h4l} drop from 41 to 26%. Four least-squares cycles with anisotropic temperature parameters for Cl and individual isotropic ones for the C atoms made R decrease to 12·7%. No weighting scheme was used at first. As a difference Fourier synthesis did not give clear indications for anisotropy of the C atoms, isotropic temperature parameters were maintained for them. Four additional cycles were calculated, this time with a weighting scheme as suggested by Cruickshank *et al.* (1961). The final R value was 9·7%. Four strong reflexions, 002, 202, 402 and 111,

Table 1. *Final positional and thermal parameters of the para compound*

	x	y	z	B	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
Cl	0·0305	0·3823	0·1650		0·0456	0·1037	0·0709	0·0118	−0·0079	0·0547
C(1)	0·1315	0·2092	0·0219	3·78						
C(2)	0·0951	0·0877	−0·0399	3·78						
C(3)	0·0633	0·1406	0·0025	4·30						
C(4)	0·0693	0·3128	0·1096	3·67						
C(5)	0·1050	0·4388	0·1746	4·24						
C(6)	0·1359	0·3830	0·1295	3·75						
C(7)	0·1636	0·1443	−0·0280	3·39						
C(8)	0·1997	0·2544	0·0189	3·23						
C(9)	0·2318	0·1946	−0·0289	3·07						
C(10)	0·2220	0·0101	−0·1508	3·85						

which apparently were badly affected by extinction, were omitted throughout*. The final positional and thermal parameters are listed in Table 1.

1,6-di-*o*-chlorophenyl-3,4-dimethylhexatriene
(in collaboration with R.E. Kisman)

Experimental

The crystals of the *ortho* compound were yellow monoclinic needles, elongated along [001]. The cell constants as derived from zero layer Weissenberg diagrams about [010] and [001], calibrated with Al powder lines, are:

$a = 17{\cdot}723 \pm 0{\cdot}003$ Å
$b = 6{\cdot}264 \pm 0{\cdot}001$
$c = 7{\cdot}757 \pm 0{\cdot}004$
$\beta = 102{\cdot}97 \pm 0{\cdot}03°$

* A table of observed and final calculated structure factors may be obtained from the first author on request.

The density as determined by flotation is 1·27 g.cm^{-3}; the calculated density with $Z=2$ is 1·30 g.cm^{-3}.

From the extinctions, $h0l$ for h odd and $0k0$ for k odd, the space group was found to be $P2_1/a$. Thus there is half a centrosymmetric molecule in the asymmetric unit.

The following equi-inclination Weissenberg films were made, with Cu $K\alpha$ radiation:

c axis: zero–6th layers
b axis: zero and 1st layers.

The dimensions of the crystal used were 0·15, 0·20 and 0·30 mm along a, b and c axes. 956 independent reflexions were measured photometrically, out of about 1600 within the reflexion sphere. No absorption correction was applied ($\mu = 34$ cm^{-1}).

Determination of the structure

The structure was solved from a three-dimensional Patterson synthesis.

Table 2. *Final positional and thermal parameters of the ortho compound*

	x	y	z	B	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
Cl	0·2022	0·7657	0·0971		0·0369	0·0527	0·0515	0·0096	−0·0256	0·0307
C(1)	0·1251	0·5337	0·3009	2·66						
C(2)	0·1702	0·7161	0·2892	2·47						
C(3)	0·1900	0·8586	0·4257	3·31						
C(4)	0·1699	0·8235	0·5841	3·72						
C(5)	0·1247	0·6448	0·6038	3·74						
C(6)	0·1032	0·5033	0·4662	3·63						
C(7)	0·0995	0·3898	0·1486	3·12						
C(8)	0·0512	0·2226	0·1466	2·89						
C(9)	0·0238	0·0860	−0·0042	2·54						
C(10)	0·0499	0·1435	−0·1721	3·67						

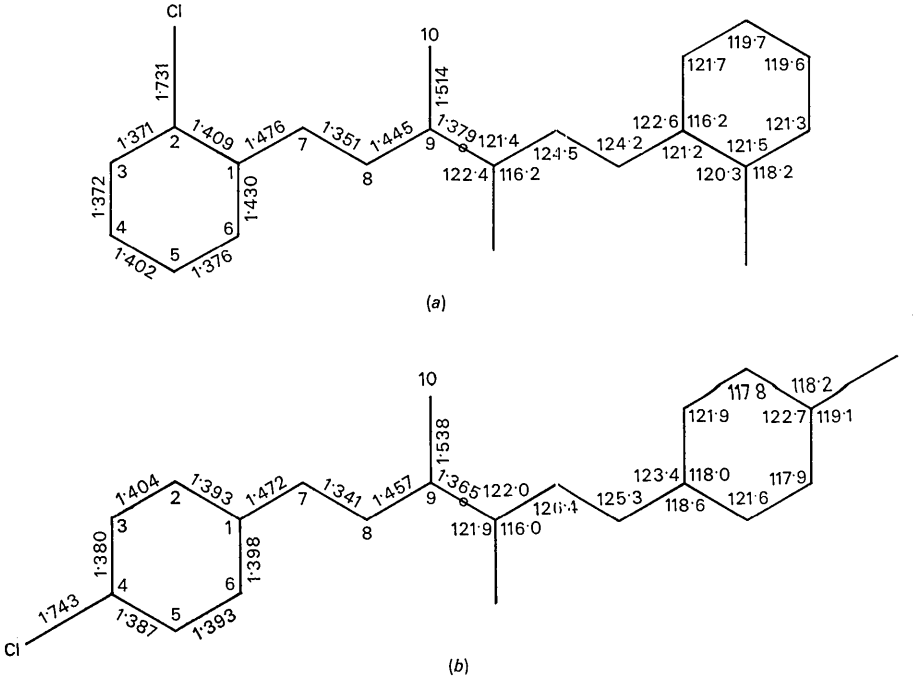

Fig. 3. Bond distances and interbond angles in (*a*) the *ortho* and (*b*) the *para* compound.

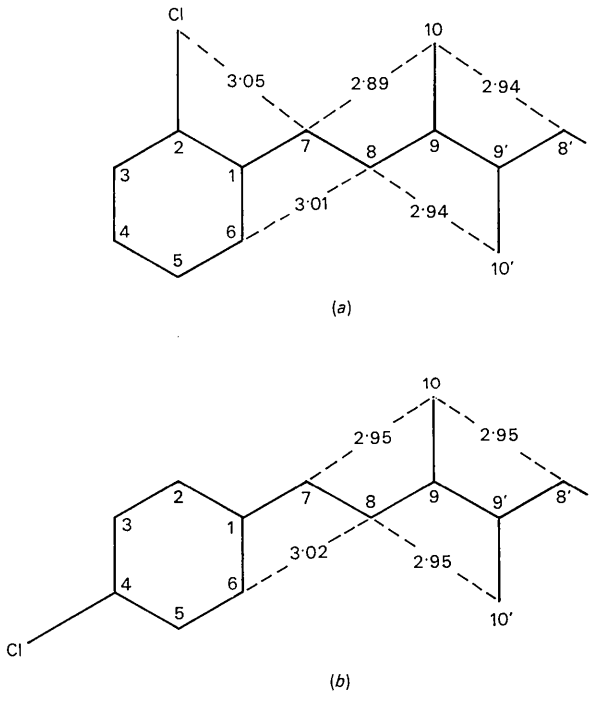

Fig. 4. Some intramolecular non-bond distances in (*a*) the *ortho* and (*b*) the *para* compound.

The ultraviolet spectrum of the *ortho* compound in solution seems to indicate non-planarity of the molecule, part of the fine structure of the spectrum of the *para* compound being absent from that of the *ortho* isomer (Heitman, 1964). Stereographic projections of spherical sections around the origin of the Patterson function of radii 1·4 and 2·4 Å were constructed in an attempt to determine the planes of the ring and the hexatriene part. They are reproduced in Fig. 2. From these sections it could be inferred that in all probability the molecule as a whole is approximately planar. The dashed lines in Fig. 2 indicate the probable plane of the molecule. The peaks on these lines are about 60° apart in both sections, while those on the 2·4 Å section are midway between those on the 1·4 Å one, as it should be for a planar centrosymmetric molecule.

A section through the Patterson function along the assumed molecular plane was now compounded and in this section the molecule as viewed from the Cl atom could clearly be seen. In this way approximate coordinates for all the atoms in the asymmetric unit were found.

A three-dimensional structure factor calculation based on these coordinates, with an overall isotropic temperature parameter $B=2{\cdot}5$ Å^2, resulted in an R value of 33%. After two Fourier cycles R had dropped to 17%. A three-dimensional least-squares refinement

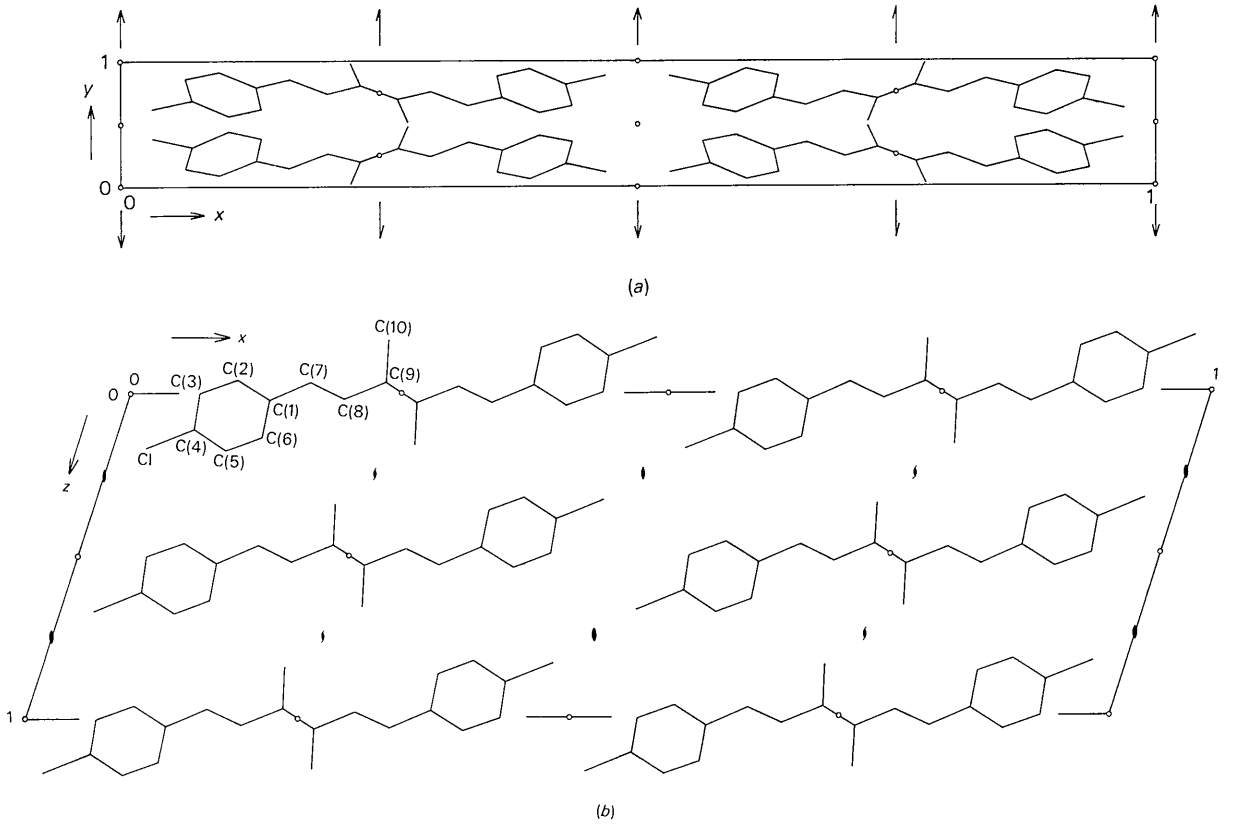

Fig. 5. Projections of the structure of the *para* compound along (*a*) [001] and (*b*) [010].

was now started. Two cycles with individual isotropic temperature parameters made R decrease to 13·3%. A difference Fourier synthesis at this stage showed clear anisotropy only for Cl, and after three more least-squares cycles with anisotropic temperature parameters for Cl only, the refinement was terminated. The final R value was 11·3%*). In the least-squares refinement a weighting scheme as suggested by Cruickshank *et al.* (1961) was used.

The final positional and thermal parameters are listed in Table 2.

The least-squares program, written by Mrs E. Rutten-Keulemans for the X1 Electrologica computer, is a block diagonal one, with a 3×3 matrix for the positional, and a 6×6 matrix for the thermal parameters of each atom. The scale factor is refined in a 2×2 matrix

* A table of observed and final calculated structure factors may be obtained from the first author on request.

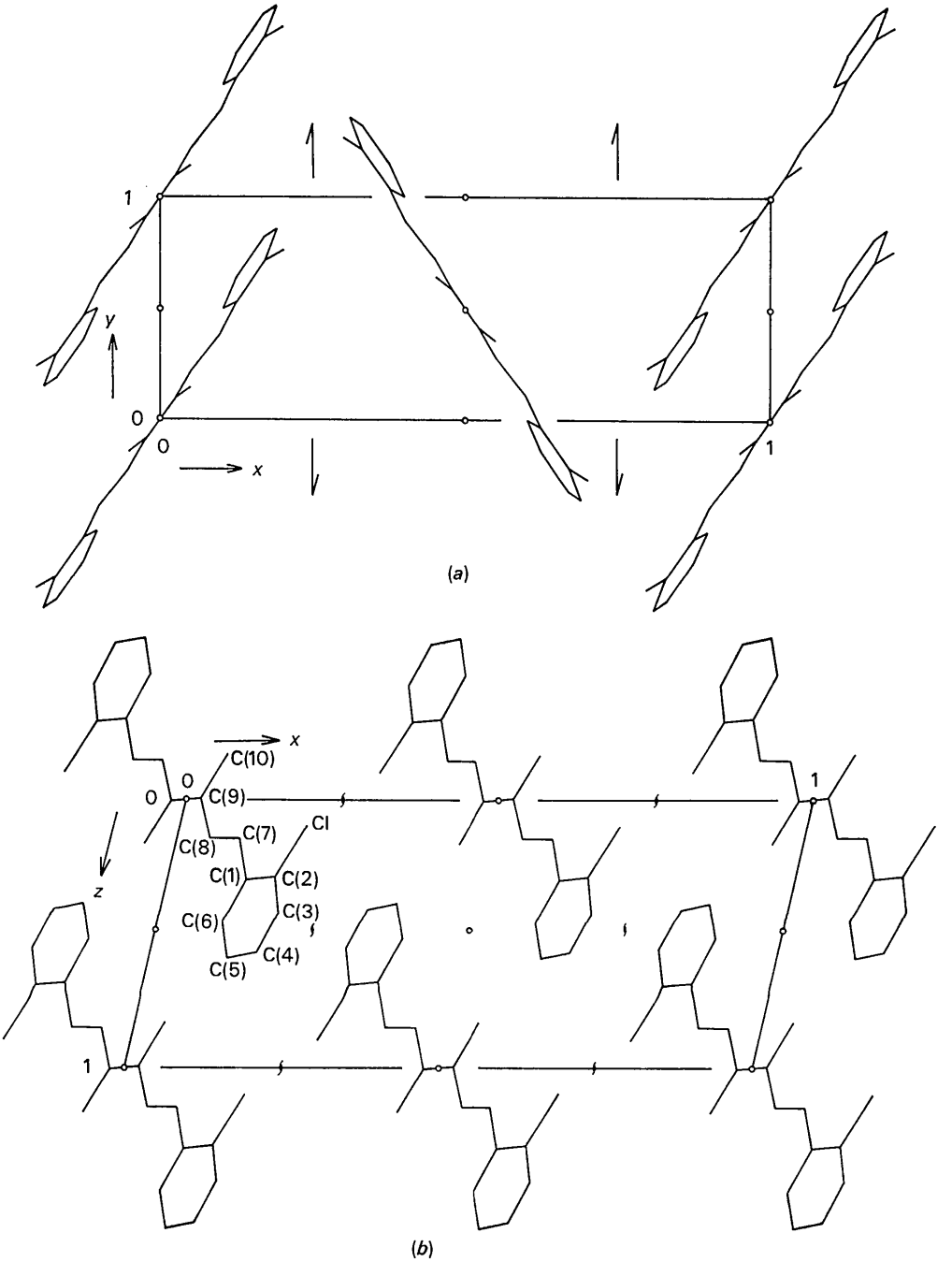

Fig. 6. Projections of the structure of the *ortho* compound along (*a*) [001] and (*b*) [010].

with the average isotropic temperature parameter (Cruickshank *et al.*, 1961).

Results and discussion

Bond lengths

The bond lengths for both isomers are shown in Fig. 3. The standard deviations are about 0·006 Å for C–Cl and 0·009 Å for C–C in the *para* compound and 0·009 Å for C–Cl and 0·013 Å for C–C in the *ortho* compound.

The differences in bond lengths between corresponding bonds in both compounds are not significant. The bond distances in the hexatriene part are normal if compared with those in vitamin A acid (Stam & MacGillavry, 1963), 15,15′-dehydro-β-carotene (Sly, 1964) and diphenyloctatetraene (Drenth & Wiebenga, 1955), with a tendency for the double bonds to increase and for the single bonds to decrease towards the centre of the molecule. The C–Cl bond distances of 1·73 and 1·74 Å are in agreement with the values found in bis-(*m*-chlorobenzoyl)methane (Engebretson & Rundle, 1964), and in 1-(4-chlorobenzoyl)-1-nitroso-2-(4,5-dihydro-2-imidazolyl)hydrazine monohydrate (Palenik, 1965). The distances in the rings are normal, the deviations from the average of 1·39 Å are not significant.

Bond angles

The bond angles are also indicated in Fig. 3. The standard deviations are about 0·4° for C–C–C and 0·6° for C–C–Cl angles in the *para* compound and 0·6° for C–C–C and 1·0° for C–C–Cl angles in the *ortho* compound.

The most interesting angles are those around C(9). These angles are not significantly different for the two isomers. The angles C(8)C(9)C(9′) are 3 to 3·5° larger than the corresponding angles in the conjugated chains of vitamin A acid and 15,15′-dehydro-β-carotene. The other angles around C(9) are accordingly smaller. This difference can be explained by the presence of the methyl group C(10′) on the other side of the chain. Its steric interaction with the hydrogen on C(8) counteracts that of the methyl group C(10) with the hydrogen atoms on C(7) and C(8′), thus preventing the angle C(8)C(9)C(9′) from becoming as small as in the above mentioned compounds. This is illustrated by Fig. 4, where the relevant distances between C(10) and C(10′) and the chain are indicated. These results lend further support to the view that the bending of the conjugated chain as found in vitamin A acid, 15,15′-dehydro-β-carotene and 7,7′-dihydro-β-carotene, is due to steric repulsion between the methyl groups and the chain.

The angles around C(1) in the *para* compound are very similar to the corresponding ones in diphenyloctatetraene. In the *ortho* compound they are somewhat different, which may be explained by the repulsion between the chlorine atom and the hydrogen atom on C(7). This will cause the angle C(2)C(1)C(7) to increase. This increase is compensated by a decrease of the angle C(2)C(1)C(6), the third angle C(6)C(1)C(7) being fixed more or less by the repulsion of the hydrogen atoms on C(6) and C(7).

The angles around C(4) and C(2) are not significantly different for the *para* and *ortho* compounds. An angle larger than 120° opposite the C–Cl bond has also been found in bis-(*m*-chlorobenzoyl)methane.

The remaining ring angles adapt themselves to the angles already discussed.

Planarity

Both molecules are approximately planar but not completely so; this is apparent from Table 3, in which the deviations of the atoms from the overall best planes through the molecules are given.

Table 3. *Distances from the best planes through the molecules*

	para	*ortho*
Cl	−0·02 Å	−0·04 Å
C(1)	0·01	−0·07
C(2)	0·02	0·00
C(3)	0·00	0·10
C(4)	0·00	0·07
C(5)	−0·01	0·00
C(6)	0·00	−0·07
C(7)	0·03	−0·08
C(8)	−0·02	−0·04
C(9)	0·00	0·00
C(10)	−0·05	0·04

Better planarity is found for the parts ClC(1)–C(7), C(1)C(7)–C(9) and C(8)–C(10)C(8′)–C(10′) in the *para* compound, as is demonstrated by Table 4. The angles between the successive parts are 3·0 and 4·7°. From Table 5, where the corresponding data for the *ortho* compound are collected, it is seen that here the system ClC(1)–C(7) is considerably less planar, probably as a result of the steric interaction of Cl with the H atom on C(7). The ring itself however, is reasonably planar with Cl and C(7) on opposite sides at 0·06 and 0·07 Å respectively. (Table 6). The angles between the successive parts are 4·2 and 3·0°.

Packing

The packings are shown in Figs. 5 and 6. The intermolecular distances less than 4·0 Å are listed in Tables 7 and 8. There is one short Cl · · · Cl distance of 3·37 Å (sum of the accepted van der Waals radii: 3·6 Å).

Our thanks are due to Dr H. Heitman for providing the crystals, to Professor C. H. MacGillavry for her constant advice, and to Mr A. Kreuger for his assistance in the experimental part of the investigation.

The calculations were carried out on the X1 Electrologica computer of the Mathematical Centre in Amsterdam. The various programs were written by Mrs E. Rutten-Keulemans, Mr W. Rutten, Mr B. Hesper

Table 4. *Distances from best planes through parts of the molecule of the para compound*

Distances from the best plane through ClC(1)–C(7)		Distances from the best plane through C(1)C(7)–C(9)		Distances from the best plane through C(8)–C(10)C(10′)–C(8′)	
Cl	−0·001 Å	C(1)	−0·001 Å	C(8)	−0·003 Å
C(1)	−0·005	C(7)	0·001	C(9)	0·011
C(2)	0·003	C(8)	0·001	C(10)	−0·002
C(3)	−0·004	C(9)	−0·001	C(10′)	0·002
C(4)	0·006			C(9′)	−0·011
C(5)	−0·001			C(8′)	0·003
C(6)	0·000				
C(7)	0·003				

Table 5. *Distances from best planes through parts of the molecule of the ortho compound*

Distances from the best plane through ClC(1)–C(7)		Distances from the best plane through C(1)C(7)–C(9)		Distances from the best plane through C(8)–C(10)C(10′)–C(8′)	
Cl	−0·032 Å	C(1)	−0·013 Å	C(8)	0·000 Å
C(1)	−0·014	C(7)	0·013	C(9)	−0·001
C(2)	−0·002	C(8)	0·013	C(10)	0·000
C(3)	0·041	C(9)	−0·013	C(10′)	0·000
C(4)	0·002			C(9′)	0·001
C(5)	−0·009			C(8′)	0·000
C(6)	−0·024				
C(7)	0·037				

Table 6. *Ortho compound: distances from the best plane through* C(1)–C(6)

Cl	−0·056 Å
C(1)	0·002
C(2)	−0·012
C(3)	0·017
C(4)	−0·012
C(5)	0·002
C(6)	0·002
C(7)	0·069

Table 7. *Intermolecular distances in the para compound smaller than* 4 Å

I	x	y	z
II	x	$y+1$	z
III	x	$\bar{y}$	$z+\frac{1}{2}$
IV	x	$\bar{y}+1$	$z+\frac{1}{2}$
V	$\bar{x}$	y	$\bar{z}+\frac{1}{2}$
VI	$\bar{x}$	$\bar{y}+1$	$\bar{z}$
VII	$\bar{x}+\frac{1}{2}$	$\bar{y}-\frac{1}{2}$	$\bar{z}$

I	II		I	III	
1	2	3·90 Å	Cl	2	3·99 Å
4	2	3·91	6	10	3·74
	3	3·66	8	10	3·79
5	1	3·93	I	IV	
	2	3·61	5	2	3·94
	3	3·60		7	3·84
	4	3·88	I	V	
6	1	3·66	Cl	Cl	3·37
	2	3·59	I	VI	
	7	3·94	Cl	Cl	3·87
8	7	3·93		3	3·91
	10	3·92	I	VII	
9	10	3·66	9	9	3·94
				10	3·69

Table 8. *Intermolecular distances in the ortho compound smaller than* 4 Å

I	x	y	z
II	x	$y+1$	z
III	x	y	$z+1$
IV	x	$y+1$	$z+1$
V	$\bar{x}$	$\bar{y}+1$	$\bar{z}$
VI	$\bar{x}$	$\bar{y}+1$	$\bar{z}+1$
VII	$\bar{x}+\frac{1}{2}$	$y-\frac{1}{2}$	$\bar{z}+1$

Table 8 (*cont.*)

I	II		I	V	
2	8	3·83 Å	1	9	3·90 Å
	9	3·82		10	3·65
3	8	3·68	2	9	3·85
Cl	9	3·68		10	3·90
	10	3·84	6	10	3·83
			7	8	3·94
I	III			9	3·96
4	Cl	3·91		10	3·98
5	10	3·96			
	Cl	3·84	I	VI	
6	10	3·88	6	6	3·81
I	IV		I	VII	
4	10	3·73	1	3	3·65
5	10	3·95		4	3·78
			2	3	3·69
				4	3·71
			3	3	3·82
			4	3	3·84
			5	3	3·79
			6	3	3·69

and Dr H. Geise, all of Leiden University, and Mr J. van Loenen of the Mathematical Centre, Amsterdam.

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