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THE CRYSTAL STRUCTURE OF *TRANS* POLYALKENAMERS

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Abstract—The structure of crystalline *trans* polyheptenamer $[-CH=CH-(CH_2)_5-]_n$ has been determined by the X-ray diffraction spectra given by cold drawn fibres. The fibre repeat is 17·10 Å and comprises two chemical units. The unit cell is orthorhombic, with two chains per cell. The cell dimensions are: $a = 7·40$ Å; $b = 5·00$ Å; $c = 17·10$ Å; space group D_{2h}^{16} (P $n a m$).

The a and b axes and the packing of the chains of *trans* polyheptenamer are very similar to those found for crystalline *trans* polypentenamer $[-CH=CH-(CH_2)_3-]_n$ and for orthorhombic polyethylene.

The carbon atoms of the polymeric chain lie on two separate planes, running parallel to the chain axis. A different crystalline modification of *trans* polyheptenamer has been observed in some i.r. spectra.

INTRODUCTION

Linear high polymers derived from a head-to-tail arrangement of $[-CH=CH-(CH_2)_n-]$ units, were synthesized in our laboratories, by ring cleavage of several cyclo-olefins.[1, 2] The linear polyalkenamers, obtained by stereospecific catalysts leading to polymers having a *trans* double bonds content higher than 80 per cent of the total amount of double bonds, are highly crystalline by X-ray examination. The *trans* polyalkenamers obtained in our laboratories differ between one another because of the different number of methylene groups between two successive double bonds; they constitute a homologous series, the first member of which is polyacetylene and the last is polyethylene.

From their fibre spectra, we may place the members of the homologous series of *trans* polyalkenamers into two classes depending on whether the number of carbon atoms of the starting cyclo-olefin is even or odd. While the fibre axis of the even *trans* polyalkenamers, examined hitherto, comprises only one chemical repeating unit, in the odd members the identity period along the chain axis is achieved with two chemical repeating units.

The behaviour of melting temperatures and the polymorphism phenomena shown by the odd and even members of the homologous series of *trans* polyalkenamers have been thoroughly described in a previous paper.[2]

The two crystalline forms shown by odd *trans* polyalkenamers have been previously denoted by us as modifications I and II while the two crystalline forms of even *trans* polyalkenamers have been denoted as modifications III and IV. In order to avoid the interpretation that any *trans* polyalkenamer could show four different crystalline

forms, it seems better to substitute the term "modification" for the term "structure". Odd *trans* polyalkenamers may be crystallized into two forms corresponding to structure I and structure II of *trans* polyalkenamers. Even *trans* polyalkenamers may be crystallized into two forms corresponding to structure III and structure IV of *trans* polyalkenamers.

We wish to point out here that the odd *trans* polyalkenamers show, at least under the conditions examined by us, only one crystalline form (structure I of *trans* poly-alkenamers). The X-ray diffraction spectra given by this crystalline form of odd *trans* polyalkenamers are very similar to the X-ray photographs given by orthorhombic polyethylene. Actually the $(h\,k\,0)$ reflections of these polymers have the same Bragg distances as the $(h\,k\,0)$ reflections of orthorhombic polyethylene and a great similarity in the X-ray spectra is shown also in a comparison of their relative intensities.

There is some evidence of a different crystalline form of odd *trans* polyalkenamers (structure II of *trans* polyalkenamers) from the presence of some i.r. absorption bands in specially treated *trans* polyheptenamers.

The even members of the homologous series of *trans* polyalkenamers are clearly polymorphous by X-ray examination. The X-ray diffraction spectra of one of the crystalline forms (structure III of *trans* polyalkenamers) in which even *trans* poly-alkenamers crystallize, are similar to those given by polymethylene subjected to particular mechanical treatments[3] and to those given by even n-alkanes.[4]

The X-ray diffraction spectra of the other crystalline form (structure IV of *trans* polyalkenamers) shown by even *trans* polyalkenamers are in some way similar to that of orthorhombic polyethylene.

Crystallization from the melt of even *trans* polyalkenamers predominantly leads to structure III or to structure IV of *trans* polyalkenamers depending on the number of methylene groups between two successive double bonds.

This paper describes the crystal structure of *trans* polyheptenamer crystallized in structure I and in a subsequent paper we shall report the crystal structure of *trans* polydodecenamer crystallized in structure IV.

CRYSTAL STRUCTURE OF TRANS POLYHEPTENAMER

Modification with the structure I of trans polyalkenamers

Fibres of *trans* polyheptenamer [—CH=CH—$(CH_2)_5$—]$_n$ having a good degree of crystallinity and a good orientation of crystallites can be obtained by annealing, under tension at $\sim 40°$, cold drawn fibres of the polymer. The X-ray fibre photographs were taken with a cylindrical camera and Cu(Kα) or Fe(Kα) radiations.

The measured chain repeat is $17\cdot10 \pm 0\cdot15$ Å and the diffraction data fit an ortho-rhombic unit cell. The dimensions of the unit cell in Ångström units are: $a = 7\cdot40 \pm 0\cdot10$; $b = 5\cdot00 \pm 0\cdot05$; $c = 17\cdot10 \pm 0\cdot15$ (chain axis) $Z = 4(C_7H_{12})$; $d = 1\cdot049$ g/cm^3.

The diffraction photographs show the absence of $(h\,0\,l)$ reflections when $h \neq 2n$ and of the $(0\,k\,l)$ reflections when $k + l \neq 2n$. The most probable space groups are C_{2v}^9 (P n a 2$_1$) or its centrosymmetrical D_{2h}^{16} (P n a m) (5).

We wish to point out that the unit cells of *trans* polypentenamer[6] and of ortho-rhombic polyethylene[7] are characterized by analogous figures for the a and b axes and by the same space groups (polyethylene $a = 7\cdot40$, $b = 4\cdot93$ Å; *trans* polypentenamer $a = 7\cdot28$, $b = 4\cdot97$ Å).

Conformation of the macromolecule of trans *polyheptenamer*

The fibre axis of *trans* polyheptenamer comprises two chemical repeating units and is $17\cdot10\pm0\cdot15$ Å. The calculated identity period based on a planar zig-zag chain conformation and the generally accepted bond lengths and angles is $17\cdot50$ Å. The difference between the observed and calculated identity periods can be fully explained by the fact that the internal rotation angles about the single bonds adjacent to a *trans* double bond tend to assume the values of $180° \pm 60°$ and $180° \mp 60°$ respectively. This occurrence has been seen in the case of several polymers containing *trans* double bonds in the main chain.[6, 8]

The shortenings of the chain axes of *trans* polypentenamer [—CH=CH—$(CH_2)_3$—]$_n$[6] and of *trans* polyheptenamer in respect of the repeats based on planar zig-zag conformations are practically the same ($0\cdot5$ Å); this suggests that the part of the chain involved in the shortening is the same for both polymers. This hypothesis is also supported by the great similarity between the X-ray diffraction spectra given by *trans* polypentenamer and *trans* polyheptenamer. The difference ($5\cdot1$ Å) between the experimental fibre repeats of these two polymers ($12\cdot00\pm0\cdot10$ Å for *trans* polypentenamer and $17\cdot10\pm0\cdot15$ Å for *trans* polyheptenamer) is also consistent with the hypothesis of a planar zig-zag part of the chain running parallel to the fibre axis.

On the basis of the remarks above, the chain conformation of crystalline *trans* polyheptenamer is quite similar to the chain conformation, already known, of crystalline *trans* polypentenamer.[6] As in the case of this last polymer, in accordance with the P *n a m* space group,[5] the macromolecule of *trans* polyheptenamer assumes in the crystal state $S(2_1)m$ symmetry.[9] Repetition is achieved after two chemical repeating units connected by a twofold screw axis running parallel to the chain axis. There are also symmetry centres on each double bond and two mirror planes (0, 0, 1/4) and (0, 0, 3/4) (Fig. 1).

As can be seen from Fig. 1, the carbon atoms of the *trans* polyheptenamer macromolecule, in the crystal state, lie on two parallel planes. These two planes run parallel to the fibre axis and are conjuncted by the *trans* double bonds.

The agreement between the calculated identity period and the fibre axis can be achieved in two different ways. The calculated repeat is $17\cdot00$ Å when the C—$\hat{C}$—C and C=$\hat{C}$—C bond angles are $112°$ and $123°$ respectively and the internal rotation angles around the single bonds adjacent to a double bond are $120°$ and $240°$ respectively (C—C = $1\cdot54$ Å, C=C = $1\cdot34$ Å).

The same result may be achieved also by assuming the bond angles C—$\hat{C}$—C and C=$\hat{C}$—C $110°$ and $120°$ respectively, while the internal rotation angles above mentioned are brought to $130°$ and $230°$.

A choice between the two models does not seem possible, therefore we have carried out the structure determination taking into account both possibilities.

Determination of the crystal structure of trans *polyheptenamer*

As in the case of *trans* polypentenamer the space group, the unit cell dimensions and the chain conformation suggest that the *trans* polyheptenamer macromolecules are packed side by side in much the same way as in orthorhombic polyethylene.

Actually, also in the case of *trans* polyheptenamer, the shortest Van der Waals' intermolecular distances have the usual values ($\sim4\cdot2$ Å between carbon atoms and $\sim2\cdot5$ Å between hydrogen atoms) when the ϕ angle between the *c* axis and the two
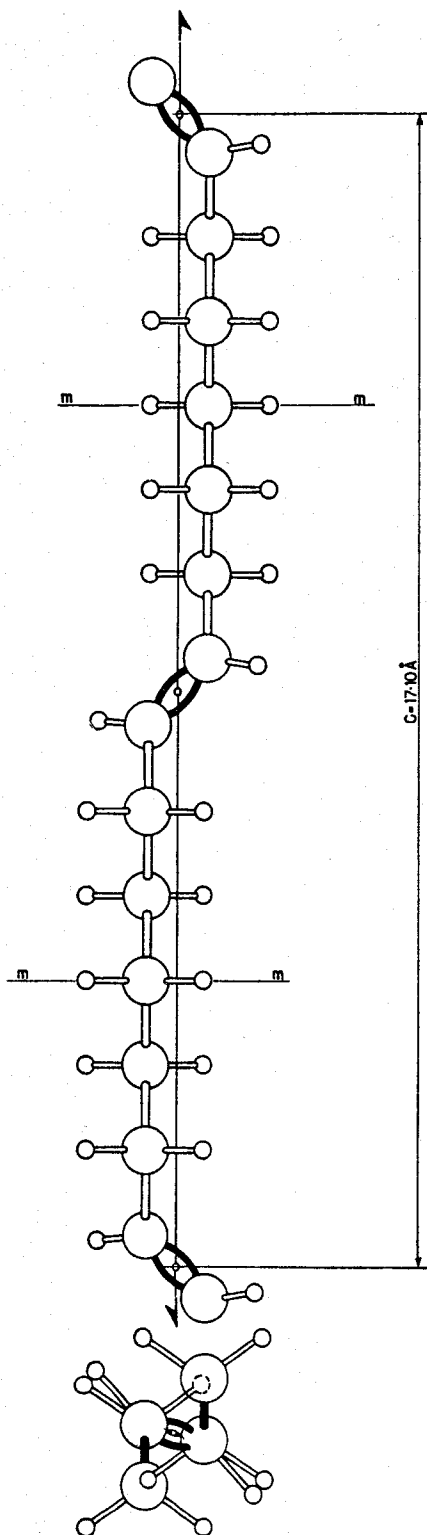
Fig. 1. Side and end views of the macromolecules of *trans* polyheptenamer in the crystalline state (symmetry S (2/1)m; the internal rotation angles on the single bonds adjacent to the double bonds are 130° and 230°).
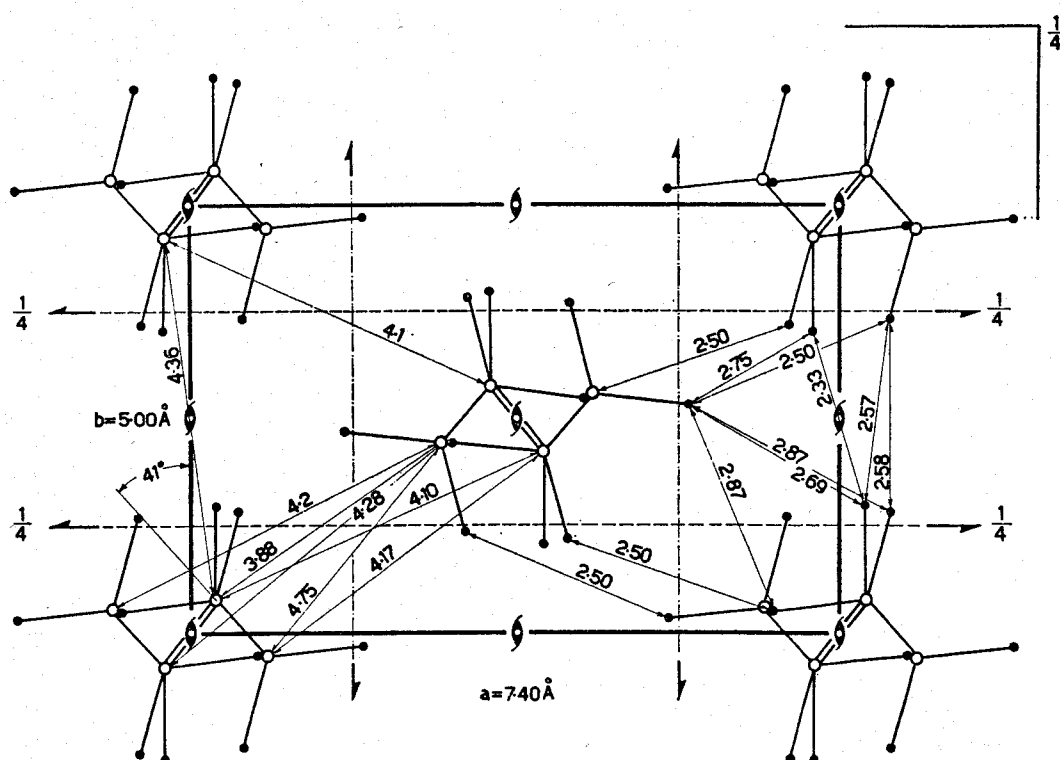
FIG. 2. Projection on the (001) plane of the structure of *trans* polyheptenamer. Some of the most significant Van der Waals' distances are indicated (open circles, C atoms, full circles H atoms).

FIG. 3. Projection on the (010) plane of the structure of *trans* polyheptenamer.

parallel planes containing the zig-zag C atoms, reaches a value of about 40° (Fig. 2); the ϕ angle in the case of orthorhombic polyethylene is 41·2°, and in the case of *trans* polypentenamer $\phi = 40·8°$.

Similar orientations, in respect to the a and b axes of the unit cell, of the paraffinic planar part of the chain of molecules containing rather long methylene sequences have been found for many substances.

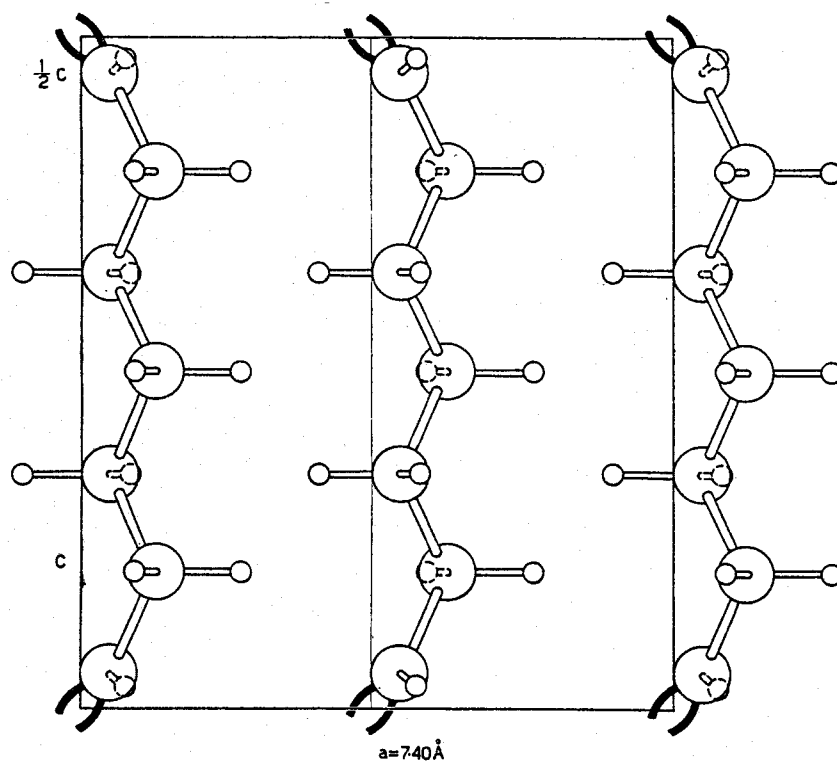The closest packing between molecules containing planar methylene sequences is achieved when the H atoms of the CH_2 groups from one molecule enter the depressions between three H atoms in an adjacent molecule. As shown by the studies of A. I. Kitaigorodskii on the close packing of long aliphatic chains,[4] the fulfilment of the previous condition fully explains the values of unit cell axes, the symmetry of the packing and the orientation of the molecules of orthorhombic polyethylene and of odd paraffins. Also in the case of *trans* polyheptenamer this condition is fulfilled; in fact, as we can see from Figs. 2 and 3, each hydrogen atom is located in the depression between three hydrogen atoms of an adjacent molecule.

Starting from these considerations we have made the calculations of the structure factors on the basis of the P $n\,a\,m$ space group for both the macromolecule models above described and for some different values of the ϕ angle about the mean value of $40°$. In the calculations of the structure factors, we have taken into account also hydrogen atoms (C—$H = 1·08$ Å, C—$\hat{C}$—$H = 109°28'$, H—$\hat{C}$—$H = 109°28'$).

The comparison between calculated and observed structure factors is satisfactory when $\phi = 41°$ for both models. The choice between the two postulated models can be done with difficulty also on the basis of the agreement between F_c and F_0. However, we wish to point out that the reliability factor being the same for both the tested models,

$$R = \frac{\sum ||F_c| - |F_0||}{\sum |F_0|}$$

the model characterized by internal rotation angles of $130°$ and $230°$ around the single bonds adjacent to the double bonds, leads to an agreement between the calculated and observed structure factors that is slightly better than that achievable by the other model.

The figures of $230°$ and $130°$ of the internal rotation angles around the single bonds adjacent to a trans double bond have been accepted by us, on the basis of analogous reasonings, in the case of *trans* polypentenamer;[6] analogous figures have been found also in the case of crystalline dihydromuconic acid.[10]

TABLE 1. ATOMIC CO-ORDINATES OF THE ASYMMETRIC UNIT
OF CRYSTALLINE *trans* POLYHEPTENAMER

	$x/a.10^4$	$y/b.10^4$	$z/c.10^4$
C_1	372	775	278
C_2	1166	9430	1016
C_3	372	775	1762
1/2 C_4	1166	9430	2500
H_1	372	2950	251
H_2	2635	9700	1016
H_2'	811	7325	1016
H_3	736	2850	1762
H_3'	8953	490	1762
1/2 H_4	2635	9700	2500
1/2 H_4'	811	7325	2500

TABLE 2. COMPARISON BETWEEN THE OBSERVED AND CALCULATED STRUCTURE FACTORS FOR *trans* POLYHEPTENAMER. CALCULATED AND OBSERVED BRAGG DISTANCES ARE ALSO REPORTED. $B = 4.6$ Å^2

hkl	d_c	d_0	F_c	F_0
110	4·15	4·18	101·4	123·7
200	3·70	3·70	72·4	63·7
210	2·98	2·95	4·1	7·0
020	2·50	2·51	51·6	49·4
120	2·37	2·36	9·3	7·6
310	2·22	2·19	10·3	14·6
220	2·07	2·07	14·0	18·4
400	1·85	1·83	4·1	ddd
410	1·74	1·74	3·2 } 9·8	10·8
320	1·75		9·3	
130	1·63	1·63	11·9	14·6
230	1·52	1·52	4·9	5·3
420	1·49	—	3·8	(3·4)
510	1·42	1·40	6·3	5·7
330	1·38	—	1·8	(3·6)
520	1·28	1·26	15·4 } 15·5	9·6
040	1·25		2·1	
600	1·24		4·8	
430	1·24	1·22	9·5 }11·1	9·9
140	1·23		3·1	
610	1·20	1·19	4·1 }11·4	ddd
240	1·19		10·6	
340	1·12	—	0·2	
530	1·11	—	3·5 } 3·6	(4·0)
620	1·11	—	0·9	
440	1·03	—	3·1	
710	1·03	—	2·4 } 3·9	(3·9)
150	0·99		7·8	
630	0·99	0·99	13·9 }19·1	ddd
720	0·98		10·6	
250	0·97	0·96	3·7 }10·1	ddd
540	0·96		9·4	
350	0·93	—	3·6 } 4·6	(4·0)
800	0·93	—	2·8	
810	0·91	—	4·0	(3·5)

hkl	d_c	d_0	F_c	F_0
011	4·81	—	4·6	(2·5)
111	4·03	4·06	35·5	38·1
201	3·62	3·62	57·2	52·1
211	2·93	2·95	13·0	9·5
121	2·35	2·34	7·9	9·5
311	2·20	2·20	24·2	19·1
221	2·06	2·07	14·9	15·9
401	1·84	1·84	20·4	14·3
321	1·75	1·74	15·2 }17·9	12·1
411	1·73		9·4	
031	1·66	—	1·7	(3·9)
131	1·62	1·63	6·0	8·9
231	1·52	1·51	10·1	7·6
421	1·48	—	5·4	(3·9)
511	1·42	—	4·2	(4·0)
331	1·38	—	4·3	(4·1)
521	1·27	1·26	7·5	ddd
141	1·23		1·7 }11·3	ddd
431	1·23	1·22	11·1	

hkl	d_c	d_0	F_c	F_0
601	1·23		0·4 11·3	ddd
611	1·19	—	1·4 } 1·4	(4·4)
241	1·18	—	0·2	
341	1·11		8·1 }	
531	1·11	1·10	0·4 } 8·2	ddd
621	1·11		1·2 }	

hkl	d_c	d_0	F_c	F_0
112	3·74	—	1·7	(1·5)
202	3·40	3·36	10·8	6·2
212	2·81	2·83	5·0	6·3
022	2·40	—	1·7	(1·9)
122	2·28	2·27	4·1	7·0
312	2·16	2·14	6·8	5·7
222	2·02	—	2·3	(2·3)
402	1·81	1·81	8·3	9·9
322	1·72	—	4·3 }4·9	(2·6)
412	1·70	—	2·5	
132	1·56	—	0·5	(2·9)
232	1·50	—	4·0	(2·9)
422	1·47	—	2·5	(3·0)
512	1·40	—	3·2	(3·1)
332	1·36	—	1·2	(3·2)
522	1·26	—	1·3 } 1·9	(3·4)
042	1·24	—	1·4	
432	1·23	—	1·8 }	
142	1·22	—	2·2 } 3·2	(3·4)
602	1·22	—	1·5 }	
242	1·17	—	0·7	(3·4)

hkl	d_c	d_0	F_c	F_0
013	3·76	—	1·6	(1·8)
113	3·36	3·37	13·1	12·7
203	3·11	3·11	19·6	17·9
213	2·64	—	3·4	(1·9)
123	2·19	—	0·6	(2·1)
313	2·06	2·06	8·9	8·2
223	1·95	1·96	6·4	ddd
403	1·76	1·74	6·3	ddd
323	1·68	—	4·8 } 6·0	(2·7)
413	1·66	—	3·7	
033	1·60	—	0·8	(2·5)
133	1·56	—	2·3	(2·7)
233	1·47	—	2·8	(3·0)
423	1·44	—	1·9	(3·0)
513	1·38	—	0·7	(3·1)
333	1·34	—	1·7	(3·2)
523	1·24	—	2·7	(3·4)
143	1·21	—	0·2 }	
433	1·21	—	3·9 } 3·9	(3·4)
603	1·21	—	0·6 }	
613	1·17	—	0·1 }	
243	1·16	—	0·7 } 0·7	(3·4)
343	1·10	—	2·7 }	
533	1·09	—	0·2 } 2·9	(3·4)
623	1·09	—	0·9 }	

TABLE 2—(continued)

hkl	d_c	d_0	F_c	F_0
114	2·98	2·99	3·9	ddd
204	2·80	2·78	13·1	9·9
214	2·44	2·44	6·7	5·7
024	2·16	—	1·2	(1·9)
124	2·07	2·05	4·8	7·0
314	1·97	1·96	8·8	5·7
224	1·87	—	3·5	(2·3)
404	1·70	1·70	9·3	ddd
324	1·62	—	5·3 ⎫ 6·3	(2·7)
414	1·61	—	3·4 ⎭	
134	1·52	—	0·5	(2·8)
234	1·43	—	5·2	(2·9)
424	1·41	—	3·5	(3·0)
514	1·35	—	4·1	(3·1)
334	1·32	—	1·3	(3·2)
524	1·22	—	1·7	(3·2)
044	1·20	—	1·8	(3·2)
434	1·19	—	2·4 ⎫	
604	1·19	—	2·9 ⎬ 4·1	(3·4)
144	1·19	—	1·7 ⎭	
614	1·15	—	0·9 ⎫ 1·3	(3·4)
244	1·14	—	0·9 ⎭	
624	1·07	—	3·2 ⎫	
534	1·07	—	1·0 ⎬ 3·4	(3·4)
344	1·07	—	0·6 ⎭	
015	2·83	2·81	5·6	6·2
115	2·64	2·64	9·9	8·2
205	2·51	2·51	13·4	10·8
215	2·24	—	0·6	(1·9)
125	1·95	—	2·6	(2·2)
315	1·86	1·84	6·2	3·8
225	1·77	1·76	5·5	ddd
405	1·63	—	3·1	(2·7)
325	1·56	—	2·5 ⎫ 3·7	(2·7)
415	1·55	—	2·8 ⎭	
035	1·50	—	3·1	(2·8)
135	1·47	—	1·9	(2·9)
235	1·39	—	0·6	(3·0)
425	1·37	—	1·1	(3·0)
515	1·31	—	0·8	(3·0)
335	1·28	—	1·4	(3·1)
525	1·20	—	1·9	(3·2)
435	1·17	—	1·5 ⎫	
145	1·16	—	2·7 ⎬ 3·7	(3·2)
605	1·16	—	2·0 ⎭	
245	1·12	—	0·3 ⎫ 0·8	(3·2)
615	1·13	—	0·7 ⎭	
345	1·06	—	1·8 ⎫	
535	1·06	—	0·3 ⎬ 2·4	(3·2)
625	1·06	—	1·5 ⎭	
116	2·35	2·34	9·3	8·6
206	2·26	2·25	28·8	25·5
216	2·06	2·05	17·5	17·1
026	1·88	—	3·3	(2·3)

hkl	d_c	d_0	F_c	F_0
126	1·82	1·80	12·5	10·5
316	1·75	1·74	22·4	18·1
226	1·68	1·66	9·5	13·3
406	1·55	1·54	22·6	17·5
326	1·49	1·49	13·8 ⎫ 16·3	14·3
416	1·48		8·7 ⎭	
136	1·41	—	2·0	(2·8)
236	1·34	1·33	13·6	11·4
426	1·32	1·31	10·3	ddd
516	1·27	1·27	11·7	ddd
336	1·24	—	3·5	(3·1)
526	1·16	—	4·3	(3·2)
046	1·15	—	4·7	(3·2)
146	1·14		7·3 ⎫	
436	1·14	1·14	7·7 ⎬ 11·4	ddd
606	1·13		4·2 ⎭	
246	1·10	—	2·5 ⎫ 3·0	(3·2)
616	1·10	—	1·6 ⎭	
346	1·04		9·0 ⎫	
536	1·03	1·04	2·8 ⎬ 9·6	ddd
626	1·03		2·1 ⎭	
017	2·20	2·19	38·6	30·5
117	2·11	2·09	15·1	12·7
207	2·04	2·02	12·5	14·5
217	1·89	1·88	17·6	17·8
127	1·70	1·70	30·7	25·4
317	1·64	—	0·3	(2·3)
227	1·58	—	7·7	(2·3)
407	1·48	1·49	12·7	ddd
327	1·43	—	6·3 ⎫ 6·3	(2·6)
417	1·42	—	0·6 ⎭	
037	1·38	1·38	29·0	23·3
137	1·36	—	4·8	(2·8)
237	1·29	1·29	14·0	13·4
427	1·27	—	4·6	(2·9)
517	1·23	1·22	16·2	15·2
337	1·20	—	2·5	(3·0)
527	1·13	—	1·4	(3·0)
147	1·10		17·2 ⎫	
437	1·10	1·10	0·6 ⎬ 26·3	19·1
607	1·10		19·9 ⎭	
617	1·08	—	0·7 ⎫ 2·9	(3·0)
247	1·07	—	2·8 ⎭	
347	1·02		2·5 ⎫	
537	1·01	1·01	2·5 ⎬ 10·3	ddd
627	1·01		9·7 ⎭	
0·0·12	1·43	1·43	11·1	d
0·0·14	1·22	1·22	24·5	m
1·1·14	1·17	1·17	15·8 ⎫ 19·1	md
2·0·14	1·16		10·8 ⎭	
2·1·14	1·13	—	0·8	—
0·2·14	1·11	1·11	11·2	d
1·2·14	1·08	—	1·6	—

Table 1 shows the atomic coordinates corresponding to this model of the macro-molecule and in Table 2 the comparison between F_c and F_0 is reported.

The isotropic temperature factor used in the final F_c calculations is $4 \cdot 6 \text{ Å}^2$. The reliability factor R, calculated for 0, 1, 2, 3, 4, 5, 6, 7 layer lines, is 21 per cent. The F_0 figures given in brackets in Table 2, correspond to half the minimum observable intensity for all reflections which are not detected on the photographs. These figures tend to increase with the number of the layer lines because of the increasing diffuseness of the reflections.

The intensities of the reflections were measured, using the multiple-film method, by visual comparison with calibration spots of known relative exposure. The area of the reflections has been taken into account by visual estimation. The observed intensities have been corrected for Lorentz and polarization factors and multiplicity.

Discussion of the structure of trans *polyheptenamer* (*Structure I of* trans *polyalkenamers*)

Trans polyheptenamer, as well as *trans* polypentenamer, the first odd member of the homologous series of *trans* polyalkenamers studied by us, as far as structure properties are concerned, belongs to the class of compounds (low molecular weight substances and polymers) whose molecules possess rather long planar paraffinic sequences. The packing of the macromolecules of *trans* polyheptenamer is essentially conditioned by the paraffinic planar sequences; the *trans* double bonds, although imposing a non-planar conformation to the macromolecule, have a little influence on the packing itself. As we have seen, the unit cells of *trans* polyheptenamer and of *trans* polypentenamer have the same equatorial dimensions and the same symmetry as those of the stable modification of odd *n*-alkanes and of orthorhombic polyethylene. These analogies are the direct consequence of a strict similarity between the chain conformations and the packing of the molecules of these compounds.

As it will be later observed, these structural analogies in the crystal state, between *trans* polyalkenamers and *n*-alkanes, hold also in the case of the even members of the two homologous series.

It can be reasonably expected that the odd terms of the homologous series of crystalline *trans* polyalkenamers having more than five —CH_2— groups between two consecutive double bonds, crystallize in unit cells, whose a and b cell edges and space groups should be the same as those found for *trans* polypentenamer and for *trans* polyheptenamer. The crystal structure found for these two polymers correspond, in fact, to the crystal structure of polyethylene, the last member of the homologous series.

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Résumé—La structure cristalline du *trans* polyhepténamère [—CH=CH—$(CH_2)_5$—]$_n$ a été définie en se basant sur les spectres aux rayons X obtenus à partir de fibres étirées. La maille élémentaire rhombique a deux chaînes polymériques. La répétition le long de l'axe de la fibre a lieu après deux unités C_7H_{12}. La maille élémentaire a les suivantes dimensions: $a = 7 \cdot 40$ Å; $b = 5 \cdot 00$ Å; $c = 17 \cdot 10$ Å; (axe de la macromolécule) groupe spatial D_{2h}^{16} (P *n a m*).

Les axes *a* et *b* de la maille éléméntaire ainsi que l'assemblage des molécules du *trans* polyhepténamère sont semblables à ceux qu'on a trouvés pour le *trans* polypenténamère et pour le polyéthylène rhombique. Les atomes de carbon de la chaîne polymérique du *trans* polyhepténamère se trouvent sur deux plans distincts. On a remarqué, dans quelques spectres i.r., la présence d'une autre modification cristalline du *trans* polyhepténamère.

Sommario—Mediante spettri ai raggi X, ottenuti da fibre stirate, è stata definita la struttura cristallina del *trans* polieptenamero [—CH=CH—$(CH_2)_5$—]$_n$. La cella elementare rombica contiene due catene polimeriche. La ripetizione lungo l'asse della fibra si ha dopo due unità C_7H_{12}. Le dimensioni della cella elementare sono: $a = 7 \cdot 40$ Å; $b = 5 \cdot 00$ Å; $c = 17 \cdot 10$ Å (asse della macromolecola) gruppo spaziale D_{2h}^{16} (P *n a m*).

Gli assi *a* e *b* della cella elementare e l'impacchettamento delle molecole del *trans* polieptenamero sono simili a quelli trovati per il *trans* polipentenamero e per il polietilene rombico. Gli atomi di carbonio della catena polimerica del *trans* polieptenamero giacciono su due piani distinti. È stata osservata la presenza di un'altra modificazione cristallina del *trans* polieptenamero, in alcuni spettri i.r.

Zusammenfassung—Die Kristallstruktur des trans-Polyheptenamers [—CH=CH—$(CH_2)_5$]$_n$ wurde mit Hilfe der Röntgenbeugungspektren kaltverstreckter Fasern bestimmt.

Die rhombische Elementarzelle enthält zwei Ketten mit je zwei chemischen Struktureinheiten pro Faser-periode. Die Zelldimensionen sind: $a = 7 \cdot 40$ Å; $b = 5 \cdot 00$ Å; $c = 17 \cdot 10$ Å (Faserachse) Raumgruppe D_{2h}^{16} (P *n a m*).

Die *a*- und *b*-Achsen und die Raumpackung der Ketten sind sehr ähnlich denen, die für das rhombische Polyäthylen gefunden wurden.

Die Kohlenstoffatome der Polymerenkette liegen auf zwei verschiedenen Ebenen. Die ungeraden Glieder der homologen trans-Poyalkenameren in der hier beschriebenen Modifikation stellen eine Serie mit analogen Kristallstrukturen dar.