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THE CRYSTAL STRUCTURE OF *TRANS* POLYDODECENAMER

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Abstract—The structure of crystalline *trans* polydodecenamer $[\text{—CH=CH—(CH}_2)_{10}\text{—}]_n$ has been determined from the X-ray diffraction spectra given by hot drawn fibres. The unit cell is monoclinic with one chemical unit per fibre repeat and two chains per unit cell. The unit cell dimensions are: $a = 7{\cdot}43$ Å; $b = 5{\cdot}00$ Å; $c = 14{\cdot}85$ Å (fibre axis); $\beta = 86°30'$; space group $P2_1/a$.

The *c* projection of the cell has dimensions similar to those found in odd *trans* polyalkenamers and in orthorhombic polyethylene. Due to the *trans* double bonds, the chain conformation deviates from the planar zig-zag conformation of polyethylene. The value of the β angle of the monoclinic unit cell is correlated to the chain conformation. The chain packing is of the same type of those found for odd *trans* polyalkenamers and of orthorhombic polyethylene. The even members of the homologous series of *trans* polyalkenamers have crystal structures very similar to that found for *trans* polydodecenamer. A different crystalline modification of even *trans* polyalkenamers has been observed.

Trans POLYDODECENAMER $[\text{—CH=CH—(CH}_2)_{10}\text{—}]_n$, like the other even members of the homologous series of *trans* polyalkenamers, shows two different crystalline structures according to the physical treatment to which the polymer is subjected.(1)

The X-ray diffraction photograph of one of the crystalline forms of even *trans* polyalkenamers corresponds to that furnished by certain cold-worked polymethylenes.(2) This crystalline structure of *trans* polyalkenamers has been called by us structure III.

The other polymorphic form of even *trans* polyalkenamers gives a X-ray photograph very similar to that of orthorhombic polyethylene.(3) This crystalline structure of *trans* polyalkenamers has been called by us structure IV.

The relative stability of the two polymorphic forms of even *trans* polyalkenamers seems to be greatly influenced by the number of methylene groups between two successive double bonds.

Well oriented fibres of *trans* polydodecenamer, showing the crystal structure III of *trans* polyalkenamers, may be obtained by stretching at about 15°, in the presence of some residual solvent, a film obtained from a benzene solution of the polymer. The two innermost $(h\,k\,0)$ and most intense reflections of the spectrum correspond to Bragg distances of 4·48 Å and 3·83 Å; the fibre repeat is $14{\cdot}85 \pm 0{\cdot}10$ Å and comprises only one chemical repeating unit.

Oriented fibres of *trans* polydodecenamer showing the other polymorphic form, namely structure IV of *trans* polyalkenamers, may be obtained by hot stretching moulded sheets of the polymer below the melting temperature. The two innermost $(h\,k\,0)$ and most intense reflections of the fibre photograph correspond to Bragg distances of 4·13 Å and 3·78 Å, the fibre repeat is 14·85 ± 0·10 Å and still comprises only one chemical unit.

The repeat distance along the chain being the same for both crystal structures, it is reasonable to expect that the two crystalline forms of *trans* polydodecenamer differ one from another only in respect of packing of the macromolecules.

Oriented fibres of *trans* polyoctenamer $[-CH{=}CH-(CH_2)_6-]_n$, showing the structure III of *trans* polyalkenamers, may be easily obtained by hot stretching, below the melting temperature, moulded sheets of the polymer. The $(h\,k\,0)$ reflections of the fibre spectra correspond to those seen above for *trans* polydodecenamer possessing structure III. The fibre repeat is 9·78 ± 0·10 Å and comprises one chemical repeating unit.

Films obtained by solvent evaporation of benzene solutions of *trans* polyoctenamer give powder spectra very similar to those of the *trans* polydodecenamer form corresponding to structure IV. By cold drawing narrow ribbons of these films, both the previously reported crystalline modifications of *trans* polyoctenamer are obtained. The fibre repeat of the *trans* polyoctenamer form corresponding to structure IV has the same value as the fibre repeat of the other polymorphic form of *trans* polyoctenamer.

The X-ray powder spectra of *trans* polyhexenamer (alternating ethylene–butadiene copolymer⁽⁴⁾) exhibit the reflections corresponding to both III and IV crystalline structures of *trans* polyalkenamers.

The analogy we have seen between the X-ray diffraction spectra of even *trans* polyalkenamers derives from the analogies among the chain conformations and chain packing of these polymers.

In this paper a description will be given of the crystal structure of the form of *trans* polydodecenamer corresponding to structure IV.

The crystal structure determinations of the forms of *trans* polydodecenamer and of *trans* polyoctenamer corresponding to structure III are in progress and we shall refer to them in a subsequent paper.

Unit cell and space group of trans *polydodecenamer (modification with Structure IV)*

The fibre spectra of *trans* polydodecenamer is very rich in reflections also for high angular values. The unit cell dimensions have been established by the reciprocal lattice methods. The *d* spacings and the relative intensities of the $(h\,k\,0)$ reflections of this form of *trans* polydodecenamer agree with the Bragg distances and the relative intensities of the equatorial reflections of orthorhombic polyethylene⁽³⁾ and of odd *trans* polyalkenamers.⁽⁵⁾ This observation reasonably leads to their interpretation on the basis of an equatorial lattice having the same constants as those found for these last polymers. Thus:

$$a \sin\beta = 7{\cdot}40\ \text{Å} \qquad b \sin\alpha = 5{\cdot}00\ \text{Å}$$

$$180^\circ - \gamma^* = 90^\circ$$

The $(h\,0\,0)$ and $(0\,k\,0)$ reflections are absent when $h \neq 2n$ and $k \neq 2n$. The $(h\,k\,l)$ reflections with high l values, although excluding an orthorhombic unit cell, indicate that the c axis is nearly perpendicular to the a–b plane.

As we have seen previously, the fibre axis length is 14·85 ± 0·10 Å and comprises one chemical repeating unit of the chain $(C_{12}H_{22})$.

The calculated identity period based on a planar zig-zag chain conformation and

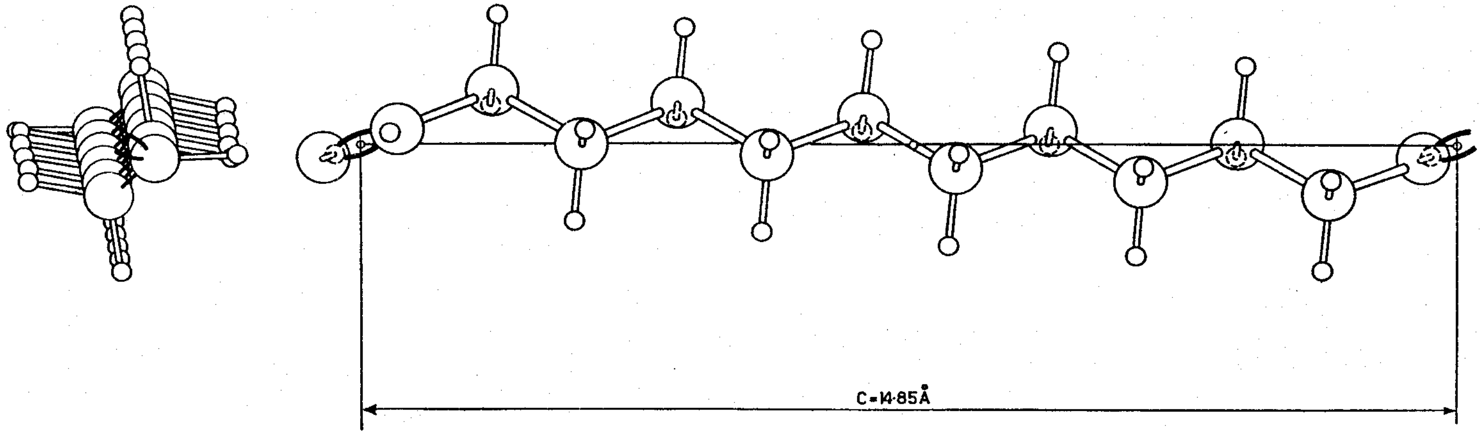

FIG. 1. Side and end views of the macromolecule of *trans* polydodecenamer in the crystalline state.

the generally accepted bond lengths and angles is 15·10 Å ($\mathrm{C{-}\hat{C}{-}C}=112^\circ$, $\mathrm{C{=}\hat{C}{-}C}=120^\circ$, $\mathrm{C{-}C}=1{\cdot}54$ Å, $\mathrm{C{=}C}=1{\cdot}34$ Å). As we have seen in the case of several hydrocarbon polymers containing *trans* double bonds along the main chain, the internal conformational energy of an isolated macromolecule in the crystal state reaches a minimum when the internal rotation angles around the single bonds adjacent to each double bond assume the value of $180^\circ \pm 60^\circ$ and $180^\circ \mp 60^\circ$ respectively, while the remaining internal rotation angles retain the value of 180°.(5, 6)

On the basis of this assumption, the calculated identity period is 14·95 Å; this value well agrees with the experimental fibre repeat ($14{\cdot}85 \pm 0{\cdot}10$ Å). Figure 1 shows the side and end views of the macromolecule of *trans* polydodecenamer.

The *trans* polydodecenamer molecular model, thus derived, according to the nomenclature proposed by Corradini(7) has *ti* symmetry. The symmetry centres are located on the double bonds and on the bond between the C_6 and C_7 carbon atoms.

Due to the quoted similarity between the intensities of the ($h\,k\,0$) reflections and between the equatorial dimensions of the unit cells of *trans* polydodecenamer and of odd members of *trans* polyalkenamers studied by us,(5) it seems reasonable that the arrangement side by side of the chains is very similar in all these structures. As we have seen in the previous paper, the odd *trans* polyalkenamer molecules are characterized in the crystal state by $S(2_1)m$ symmetry and are arranged side by side according to the *P n a m* space group (see Fig. 2 of the previous paper, p. 37). A similar arrangement side by side of the *trans* polydodecenamer molecules, characterized by *ti* symmetry, is evidently possible, since the space group symmetry must decrease.

In order to achieve for the *trans* polydodecenamer molecules a packing essentially similar to that found for the odd *trans* polyalkenamers, the symmetry elements of the P *n a m* space group that can be maintained are the symmetry centres, the 2_1 axis parallel to the *b* axis of the unit cell and the glide plane perpendicular to the 2_1 axis (glide components *a*/2).

TABLE 1. CO-ORDINATES OF THE ATOMS OF THE ASYMMETRIC UNIT OF *trans* POLYDODECENAMER (MODIFICATION HAVING STRUCTURE IV OF *trans* POLYALKENAMERS)

	$x/a.10^4$	$y/b.10^4$	$z/c.10^4$
C_1	304	750	328
C_2	963	9500	1178
C_3	0000	750	2020
C_4	726	9450	2870
C_5	9781	700	3720
C_6	473	9400	4554
H_1	220	2925	266
H_2	2382	9825	1187
H_2'	693	7350	1170
H_3	253	2875	2028
H_3'	8564	375	1995
H_4	2145	9800	2879
H_4'	439	7325	2862
H_5	34	2850	3721
H_5'	8345	375	3695
H_6	1926	9725	4579
H_6'	186	7275	4545

TABLE 2. COMPARISON BETWEEN THE OBSERVED AND CALCULATED STRUCTURE FACTORS OF *trans* POLYDODECENAMER. THE OBSERVED AND CALCULATED BRAGG DISTANCES ARE ALSO REPORTED

hkl	d_c	d_0	nF_c		F_0
110	4·13	4·13	94·8		119·8
200	3·70	3·68	58·1		49·8
210	2·98	2·98	12·7		12·5
020	2·50	2·50	31·9		37·7
120	2·37	2·37	10·0		8·7
310	2·21	2·21	23·4		21·5
220	2·08	2·07	18·5		21·5
400	1·85	1·85	11·9		11·0
320	1·75	1·74	10·1	11·4	10·8
410	1·74		5·2		
130	1·63	1·62	12·7		16·3
230	1·52	1·52	8·9		8·6
420	1·49	1·49	3·5		ddd
510	1·42	1·43	3·1		ddd
330	1·38	1·39	2·6		ddd
520	1·27	1·27	3·3		ddd
040	1·25	—	0·6		(3·2)
430	1·24	1·23	5·3	6·7	8·5
600	1·23		0·6		
140	1·23		4·0		
610	1·20	—	0·7	1·3	(3·3)
240	1·19	—	1·1		
340	1·12	1·12	5·4	5·5	7·2
530	1·11		0·5		
620	1·11		0·7		
710	1·04	—	0·4	1·4	(3·3)
440	1·04	—	1·3		
150	0·99	1·00	3·7	3·8	4·9
630	0·99		0·9		
720	0·99		0·1		
250	0·97	0·96	3·0	3·7	4·7
540	0·95		2·2		
350	0·93	—	2·5	2·5	(2·9)
800	0·93	—	0·0		
011	4·74	—	3·7		(1·9)
111	4·03	3·98	15·8	21·0	23·7
$\bar{1}11$	3·97		13·8		
201	3·65	3·60	18·6	24·7	21·9
$\bar{2}01$	3·55		16·2		
211	2·94	2·95	11·0		10·6
$\bar{2}11$	2·89	—	2·2		(2·5)
021	2·46	—	0·9		(2·8)
121	2·35	2·34	7·0	7·1	9·9
$\bar{1}21$	2·34		1·4		
311	2·20	2·20	14·2	17·3	15·3
$\bar{3}11$	2·17		9·9		
221	2·07	2·04	8·6	10·8	12·8
$\bar{2}21$	2·04		6·5		
401	1·85	1·85	11·2	12·7	11·5
$\bar{4}01$	1·83		6·1		
321	1·75	1·74	12·9	17·0	14·4
$\bar{3}21$	1·74		2·1		
411	1·74		10·9		
$\bar{4}11$	1·71	—	1·7		(3·5)
031	1·66	—	1·5		(3·6)
131	1·62	—	3·7	4·3	(3·7)
$\bar{1}31$	1·61		2·2		
231	1·52	1·50	7·4	9·7	6·1
$\bar{2}31$	1·51		1·2		
421	1·49		5·7		
$\bar{4}21$	1·48		2·5		
511	1·42	1·41	5·5	5·8	ddd
$\bar{5}11$	1·40		1·8		
331	1·38	—	4·2	4·6	(4·3)
$\bar{3}31$	1·37		2·0		
521	1·28	1·27	11·6	11·7	9·5
$\bar{5}21$	1·26		1·1		
041	1·25	1·24	0·5	11·2	11·9
431	1·24		10·7		
601	1·24		1·7		
141	1·23		1·5		
$\bar{1}41$	1·23		0·2		
$\bar{4}31$	1·23		1·5		
$\bar{6}01$	1·22		0·2		
611	1·20	1·19	6·6	6·8	ddd
$\bar{6}11$	1·19		0·3		
241	1·18		1·7		
$\bar{2}41$	1·18		0·4		
341	1·12	1·11	5·6	6·1	ddd
$\bar{3}41$	1·11		0·9		
531	1·11		2·1		
621	1·11		0·2		
$\bar{5}31$	1·10		0·3		
$\bar{6}21$	1·10		0·2		
012	4·15	—	0·5		(1·9)
112	3·68	3·61	7·0	10·5	11·0
$\bar{1}12$	3·57		7·9		
202	3·40	3·37	5·7		ddd
$\bar{2}02$	3·23	3·22	10·7		10·3
212	2·81	2·80	5·6		6·6
$\bar{2}12$	2·72	—	0·6		(2·5)
022	2·37	—	0·8		(2·8)
122	2·27	—	3·4		(2·9)
$\bar{1}22$	2·24	—	0·8		(2·9)
312	2·16	—	2·9		(3·1)
$\bar{3}12$	2·10	2·10	7·7		7·0
222	2·02	—	2·6		(3·2)
$\bar{2}22$	1·98	—	4·6		(3·2)
402	1·83	—	1·3		(3·5)
$\bar{4}02$	1·77	—	4·4		(3·5)
322	1·73	1·72	5·7	6·9	ddd
412	1·71		3·9		
$\bar{3}22$	1·70		0·1		
$\bar{4}12$	1·67	—	0·2		(3·6)
032	1·63	—	0·2		(3·7)
132	1·59	—	1·5	1·9	(3·8)
$\bar{1}32$	1·59		1·1		

TABLE 2—(*continued*)

h k l	d_c	d_0	nF_c		F_0
232	1·50	—	3·8	3·8	(4·0)
$\bar{2}32$	1·48		0·5		
422	1·48		0·2		
$\bar{4}22$	1·45	—	2·1		(4·0)
512	1·41	—	0·2		(4·2)
$\bar{5}12$	1·38	—	1·6	2·2	(4·3)
332	1·37		0·4		
$\bar{3}32$	1·35		1·5		
522	1·27	—	2·8		(4·3)
$\bar{5}22$	1·24	—	0·0	3·8	(4·3)
042	1·23		0·4		
602	1·23		0·3		
432	1·23		3·6		
142	1·22		0·9		
$\bar{1}42$	1·21		0·6		
$\bar{4}32$	1·21		0·2		
$\bar{6}02$	1·21		0·1		
612	1·19		1·1	1·2	(4·4)
242	1·17		0·4		
$\bar{6}12$	1·17		0·1		
$\bar{2}42$	1·17		0·2		
342	1·11		2·6	2·8	(4·7)
622	1·10		0·7		
532	1·10		0·7		
$\bar{3}42$	1·10		0·0		
$\bar{5}32$	1·09		0·3		
$\bar{6}22$	1·09		0·2		
013	3·52	—	0·9		(1·9)
113	3·23	—	4·6		(2·1)
$\bar{1}13$	3·13	3·11	7·4		9·0
203	3·05	—	2·6		(2·3)
$\bar{2}03$	2·87	2·89	10·3		8·0
213	2·60	—	3·8		(2·5)
$\bar{2}13$	2·49	—	1·7		(2·5)
023	2·23	—	0·8		(2·8)
123	2·16	—	2·2		(2·9)
$\bar{1}23$	2·12	—	1·7		(2·9)
313	2·07	—	1·3		(3·1)
$\bar{3}13$	1·98	1·99	7·9		6·8
223	1·94	—	2·0		(3·2)
$\bar{2}23$	1·89	1·88	4·5		4·9
403	1·77	—	0·0		(3·5)
$\bar{4}03$	1·70	—	4·6		(3·5)
323	1·68		3·9	4·7	(3·6)
413	1·67		2·6		
$\bar{3}23$	1·63		0·9	0·9	(3·6)
$\bar{4}13$	1·61		0·3		
033	1·58	—	0·2		(3·7)
133	1·55	—	1·5	1·6	(3·7)
$\bar{1}33$	1·54		0·8		
233	1·46	—	2·7	2·9	(4·0)
423	1·45		0·1		
$\bar{2}33$	1·44		1·1		
$\bar{4}23$	1·40		2·5	2·5	(4·0)
513	1·39		0·3		
333	1·34		0·4	2·8	(4·2)
$\bar{5}13$	1·34		2·3		
$\bar{3}33$	1·32		1·6		
523	1·25	—	1·8		(4·5)
$\bar{5}23$	1·22	—	0·4	2·7	(4·5)
603	1·21		0·4		
433	1·21		2·5		
043	1·21		0·8		
143	1·20		0·6	1·5	(4·6)
$\bar{1}43$	1·19		1·0		
$\bar{4}33$	1·19		0·2		
613	1·18		0·6		
$\bar{6}03$	1·18		0·5		
243	1·16		0·6		
$\bar{2}43$	1·15		0·0		
$\bar{6}13$	1·15		0·2		
623	1·09		0·3	2·1	(4·7)
343	1·09		1·9		
533	1·09		0·4		
$\bar{3}43$	1·07		0·4		
$\bar{5}33$	1·07		0·5		
$\bar{6}23$	1·07		0·2		
014	2·98	2·90	1·6	4·1	4·0
114	2·81		3·7		
$\bar{1}14$	2·72	2·73	6·3	6·5	7·2
204	2·70		1·2		
$\bar{2}04$	2·54	2·54	9·7		10·6
214	2·38	2·37	3·6		ddd
$\bar{2}14$	2·26	2·26	3·6		ddd
024	2·08	—	1·0		(2·8)
124	2·02	—	1·7		(2·9)
$\bar{1}24$	1·98	1·97	3·0	3·0	ddd
314	1·95		0·1		
$\bar{3}14$	1·85	1·86	8·1	8·2	6·8
224	1·84		1·3		
$\bar{2}24$	1·79	1·80	4·3		ddd
404	1·70	—	1·1		(3·5)
324	1·61	1·62	3·5	6·6	ddd
414	1·61		2·5		
$\bar{4}04$	1·61		5·0		
$\bar{3}24$	1·56	—	2·1	2·4	(3·6)
$\bar{4}14$	1·54		1·1		
034	1·52	—	0·7	1·5	(3·8)
134	1·50		1·3		
$\bar{1}34$	1·48		0·5		
234	1·42	—	2·6	3·5	(4·0)
424	1·40		0·6		
$\bar{2}34$	1·40		2·2		
514	1·36		1·1	3·2	(4·2)
$\bar{4}24$	1·36		2·9		
334	1·31	—	0·1	3·1	(4·3)
$\bar{5}14$	1·30		2·6		
$\bar{3}34$	1·28		1·6		
524	1·23	—	1·6		(4·5)

TABLE 2—(*continued*)

hkl	d_c	d_0	nF_c		F_0
604	1·19	—	0·6	2·6	(4·5)
434	1·19		2·2		
044	1·18		0·9		
$\bar{5}24$	1·18		0·7		
144	1·17	—	0·7	1·9	(4·5)
$\bar{1}44$	1·17		1·4		
614	1·16		0·6		
$\bar{4}34$	1·16		0·8		
$\bar{6}04$	1·15		0·4		
244	1·13	—	0·5	0·7	(4·6)
$\bar{2}44$	1·12		0·1		
$\bar{6}14$	1·12		0·5		
624	1·08	—	0·5	2·1	(4·6)
344	1·08		1·9		
534	1·08		0·6		
$\bar{3}44$	1·06	—	1·0	1·2	(4·6)
$\bar{5}34$	1·05		0·6		
$\bar{6}24$	1·04		0·0		
015	2·55	2·55	4·5		6·1
115	2·45	—	2·3		(2·1)
205	2·38	2·38	1·7	9·6	9·8
$\bar{1}15$	2·37		9·5		
$\bar{2}05$	2·24	2·25	17·0		13·7
215	2·16	—	3·2		(2·3)
$\bar{2}15$	2·05	2·05	8·7		11·5
025	1·91	—	2·2		(2·9)
125	1·87	—	0·4		(2·9)
$\bar{1}25$	1·83	1·83	7·1	7·5	10·0
315	1·82		2·6		
225	1·72	1·73	0·7	17·9	14·3
$\bar{3}15$	1·72		17·9		
$\bar{2}25$	1·67	1·67	6·9		8·6
405	1·61	—	3·0		(3·5)
325	1·54	1·53	3·3	15·6	9·3
415	1·54		2·4		
$\bar{4}05$	1·53		15·0		
$\bar{3}25$	1·48	1·46	6·4	8·4	7·8
$\bar{4}15$	1·46		4·6		
035	1·45		2·8		
135	1·43	—	2·4	2·5	(3·8)
$\bar{1}35$	1·43		0·8		
235	1·37	1·36	2·4	6·9	ddd
425	1·36		1·4		
$\bar{2}35$	1·34		6·3		
515	1·31	1·32	2·5	9·2	8·7
$\bar{4}25$	1·31		8·9		
335	1·27	1·25	0·1	14·9	8·9
515	1·25		14·7		
$\bar{3}35$	1·24		2·2		
525	1·19		1·1	2·8	(4·4)
605	1·17		1·1		
435	1·16		2·0		
045	1·15		2·6	3·2	(4·4)
$\bar{5}25$	1·15		1·9		
145	1·14		0·3	3·2	(4·4)
615	1·13	1·12	0·3	11·2	6·6
$\bar{1}45$	1·13		3·9		
$\bar{4}35$	1·13		3·9		
$\bar{6}05$	1·12		9·7		
245	1·11		1·2		
$\bar{2}45$	1·09		1·7	1·8	(4·5)
$\bar{6}15$	1·09		0·5		
625	1·06	—	0·6	2·0	(4·5)
535	1·06		0·6		
345	1·06		1·8		
$\bar{3}45$	1·04	1·03	4·2	8·5	ddd
$\bar{5}35$	1·02		3·1		
$\bar{6}25$	1·02		6·7		
016	2·21	2·22	29·2		27·9
116	2·16	2·14	16·7		15·1
206	2·11	2·10	18·9	23·2	17·9
$\bar{1}16$	2·09		13·4		
$\bar{2}06$	2·00	2·00	12·4		11·4
216	1·95	1·93	20·2		22·2
$\bar{2}16$	1·85	1·85	14·8		14·5
026	1·76	—	0·2		(2·8)
126	1·72	1·72	24·9		24·4
316	1·70	1·70	18·3	28·3	24·1
$\bar{1}26$	1·70		21·6		
226	1·61	1·61	10·8	14·4	15·9
$\bar{3}16$	1·60		9·5		
$\bar{2}26$	1·56	1·54	8·5	12·9	10·7
406	1·52		9·8		
416	1·46	1·47	6·6	13·4	13·6
326	1·46		11·6		
$\bar{4}06$	1·44	—	4·2		(3·5)
$\bar{3}26$	1·40	1·38	7·5	21·4	22·3
036	1·38		19·5		
$\bar{4}16$	1·38		3·4		
136	1·37		3·1		
$\bar{1}36$	1·35	—	3·8		(3·7)
236	1·31	1·31	14·5	15·9	15·1
426	1·30		6·5		
$\bar{2}36$	1·28	1·29	11·1	13·3	12·4
516	1·27		7·3		
$\bar{4}26$	1·25	—	3·4		(3·9)
336	1·22	—	3·9	5·4	(4·1)
$\bar{5}16$	1·20		2·1		
$\bar{3}36$	1·19		3·1		
526	1·16	—	2·9		(4·1)
606	1·13	—	2·9	6·0	(4·1)
436	1·13		5·3		
046	1·12	1·10	0·7	16·6	13·4
616	1·11		1·1		
146	1·11		12·2		
$\bar{5}26$	1·11		1·1		
$\bar{1}46$	1·10		10·9		
$\bar{4}36$	1·09		2·6		

TABLE 2—(*continued*)

hkl	d_c	d_0	nF_c		F_0
246	1·08	—	0·8	1·8	(4·1)
$\bar{6}06$	1·08		0·1		
$\bar{2}46$	1·06		1·6		
$\bar{6}16$	1·06		0·3		
626	1·03	1·02	1·9	7·9	ddd
536	1·03		1·9		
346	1·03		6·3		
$\bar{3}46$	1·02		3·9		
$\bar{5}36$	0·99	—	0·9	0·9	(4·1)
$\bar{6}26$	0·99		0·1		
0·0·11	1·34	1·34	5·0		dd
0·0·12	1·24	1·24	12·2		md
2·0·12	1·19	1·19	10·1	17·2	m
0·1·12	1·20		0·6		
1·1·12	1·19		13·9		
$\bar{1}$·1·12	1·17	1·16	10·2	11·8	md
2·1·12	1·16		2·7		
$\bar{2}$·0·12	1·15		5·4		
3·1·12	1·10	1·10	7·6	11·1	md
0·2·12	1·10		7·7		
1·2·12	1·10		2·5		

The space group becomes the C_{2h}^{5} space group in its $P2_1/a$ orientation. The $P2_1/a$ space group is consistent with the systematic absence, in the *trans* polydodecenamer spectra, of $(h\,0\,l)$ reflections when $h \neq 2n$ and of $(0\,k\,0)$ reflections when $k \neq 2n$.

For this purpose, it seems very interesting to observe that analogous unit cell dimensions and analogous packing conditions have been theoretically foreseen and widely justified by Kitaigorodskii for the centrosymmetrical molecules of even *n*-paraffins.(8)

The β angle of the monoclinic unit cell of *trans* polydodecenamer, measured by the reciprocal lattice methods, is 86° 30′ or its supplement. As we shall see later, a β angle of 86° 30′ finds its own justification in the macromolecule conformation and in the packing conditions.

The dimensions of the unit cell of *trans* polydodecenamer in Ångström units are: $a \sin \beta = 7{\cdot}40 \pm 0{\cdot}10$; $a = 7{\cdot}43 \pm 0{\cdot}10$; $b = 5{\cdot}00 \pm 0{\cdot}05$; $c = 14{\cdot}85 \pm 0{\cdot}15$ (chain axis); $\beta = 86°\ 30'$; $Z = 2(C_{12}H_{22})$; $d_x = 1{\cdot}001$ g/cm^3; space group $P2_1/a$.

Table 2 reports the observed Bragg distances and the d spacings calculated on the basis of the unit cell proposed.

Determination of the structure of trans *polydodecenamer (modification with Structure IV)*

The general position of the $P2_1/a$ space group requires four asymmetric units; two molecules being contained in the unit cell, the symmetry centre of the molecule is retained in the unit cell and the asymmetric unit corresponds to half the chemical repeating unit along the chain.

The arrangement of the molecules side by side has been defined on the basis of the Van der Waals' contact distances occurring by rotation of the molecule around its chain axis.

When the ϕ angle, formed by the b axis of the unit cell and the plane on which the twelve carbon atoms of the chemical repeating unit are disposed, reaches a value of about 40°, all the intermolecular Van der Waals' contacts are at their optimum ($\sim$4·2 Å between carbon atoms and $\sim$2·5 Å between hydrogen atoms).

Such an orientation of the methylenic zig-zag chains in respect of the a and b axes of the orthorhombic unit cell has been found also for polyethylene and for odd *trans* polyalkenamers (ϕ angles about 41°).

Figure 2 shows the projection on the (001) plane of the crystal structure of *trans* polydodecenamer.

The analogies between the crystal structure of *trans* polydodecenamer and the crystal structures of odd *trans* polyalkenamers become more evident if the projections of their unit cells on the (010) plane are examined.

The arrangement side by side of the macromolecules of odd *trans* polyalkenamers and of orthorhombic polyethylene is such that each hydrogen atom enters the depression between three hydrogen atoms in an adjacent molecule (Fig. 3). This type of packing leads, for these last polymers, to α and β angles of 90° owing to the fact that the axis of the zig-zag paraffinic chain is parallel to the *c* axis.

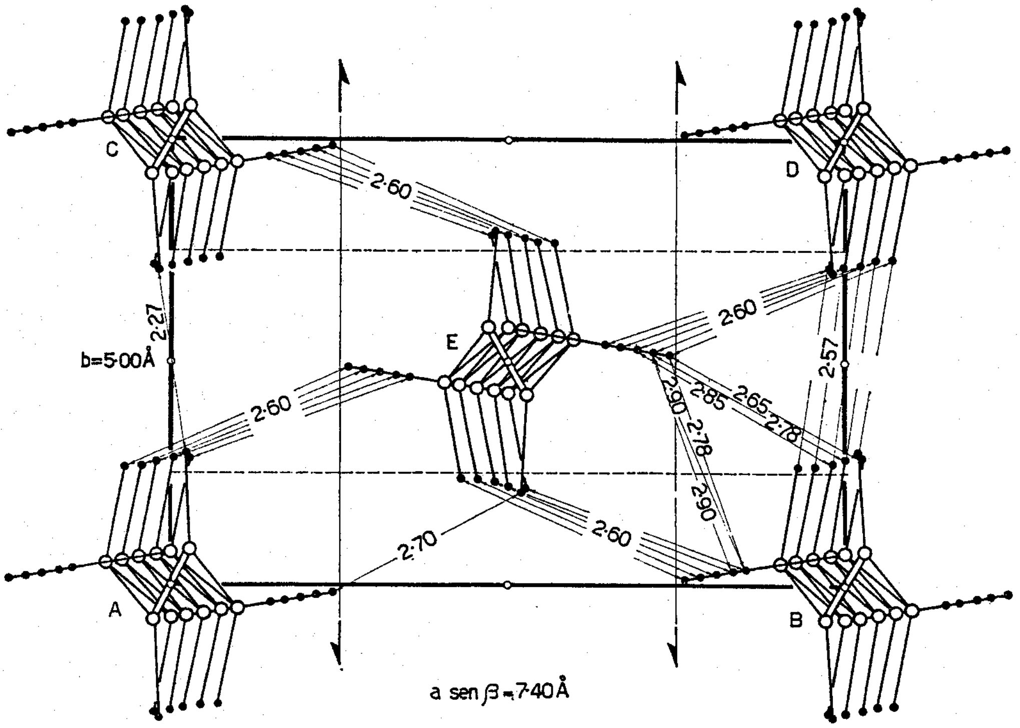

FIG. 2. Projection on the (001) plane of the crystal structure of *trans* polydodecenamer (mod. having Structure IV of trans polyalkenamers). Some of the most significant H–H intermolecular Van der Waals' distances are indicated. The full circles represent hydrogen atoms and the open circles carbon atoms.

The macromolecules of *trans* polydodecenamer and of even *trans* polyalkenamers show, in the crystal state, *ti* symmetry and the fibre axis is no longer parallel to the zig-zag planar paraffinic chain (see Fig. 1). Due to the orientation assumed by *trans* polydodecenamer molecules in the unit cell, a packing quite similar to that of orthorhombic odd *trans* polyalkenamers may be reached by *trans* polydodecenamer molecules only if the β angle deviates from 90°. Furthermore, if the angle between the *c* axis and the plane of the zig-zag paraffinic chain is the complement of the β angle of the monoclinic unit cell, the H–H Van der Waals' interactions between the macromolecules of *trans* polydodecenamer are exactly the same as in odd *trans* polyalkenamers and in orthorhombic polyethylene (Fig. 4).

The model of *trans* polydodecenamer molecule based on internal rotation angles about the single bonds adjacent to each double bond of 120° and 240° leads to an angle

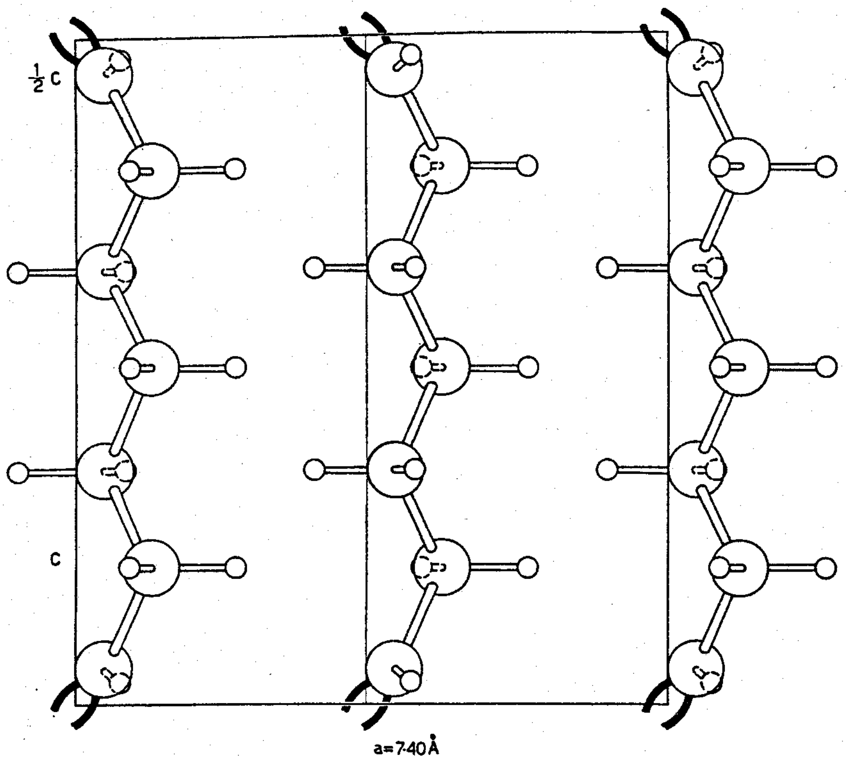

FIG. 3. Projection on the *a-c* plane of the structure of crystalline *trans* polyheptenamer (mod. having Structure I of *trans* polyalkenamers).

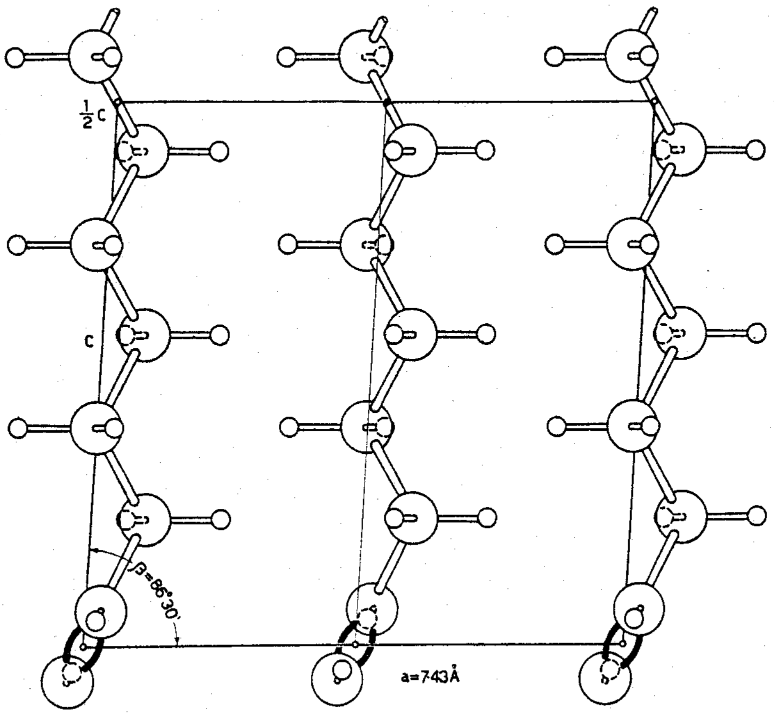

FIG. 4. Projection on the *a-c* plane of the structure of crystalline *trans* polydodecenamer (mod. having Structure IV of *trans* polyalkenamers).

between the chain axis and the plane of the zig-zag of the carbon atoms of 4°. A change of the internal rotation angles about the single bonds adjacent to each double bond from 120° and 240° to 130° and 230° leads to an angle between the chain axis and the zig-zag of the carbon atoms of 3° 25′. The latter model of the *trans* polydodecenamer molecule seems to be preferable over the former because analogous values of the internal rotation angles, about the single bonds adjacent to *trans* double bonds, have been found by us for odd *trans* polyalkenamers(5) and by Corradini and co-workers for di-hydromuconic acid.(9)

A model of the macromolecule based on internal rotation angles of 130° and 230°, around the single bonds adjacent to each double bond, has been derived. The bond lengths and bond angles used are: $C—\hat{C}—C = 110°$, $C{=}\hat{C}—C = 120°$, $C—\hat{C}—H = 109° 28'$, $H—\hat{C}—H = 109° 28'$, $C—C = 1{\cdot}54$ Å, $C{=}C = 1{\cdot}34$ Å, $C—H = 1{\cdot}08$ Å.

The structure factor calculations, based on the model described above, have been carried out for some different orientations of the molecule with respect to the *a* and *b* axes.

The best agreement between calculated and observed structure factors has been reached with the atomic co-ordinates of the asymmetric unit reported in Table 1.

In Table 2 a comparison of the observed, F_0, and calculated, F_c, structure factors is given. The temperature factor used in the final calculations is $B = 6{\cdot}3$ Å^2. The F_0 figures given in brackets in Table 2 correspond to half the minimum intensity potentially observable for all reflections which are absent from the fibre photographs. These figures increase with the number of the layer line 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 observed intensities have been corrected for Lorentz and polarization factors. The area of the reflections has been taken into account by visual estimation. The reliability factor of the structure

$$R = \frac{\Sigma\,||F_0| - |F_c||}{\Sigma\,|F_0|}$$

calculated for 0, 1, 2, 3, 4, 5 and 6 layer lines is 23 per cent. In the calculation of *R* also the F_0 figures of the not observed reflections (F_0 figures in brackets, Table 2) have been included.

CONCLUSION

The monoclinic structure of *trans* polydodecenamer crystallized in Structure IV of *trans* polyalkenamers, is similar to the orthorhombic structure of odd *trans* polyalkenamers, crystallized in Structure I. In spite of the fact that the chain conformations in the crystal state are markedly different [*ti* symmetry for the chains of *trans* polydodecenamer and $s(2_1)m$ symmetry for the chains of odd *trans* polyalkenamers] the arrangement of the chains side by side is the same for these polymers.

Also the equatorial dimensions of the unit cell and the orientation of the molecules with respect to the equatorial axes are practically the same for these *trans* polyalkenamers. The intermolecular Van der Waals' interactions occur by simple translation along the *b* axis and by means of a glide plane (0, 1/4, 0) with glide component 1/2 *a* along the *a* axis.

The molecules are arranged in layers by means of a simple translation (*b* axis) and the adjacent layers result turned of 180° around the 2_1 axes parallel to the *b* axis. Each molecule is surrounded by six closest neighbour molecules.

Each hydrogen atom of the paraffinic chain of a molecule enters the cavity between three hydrogen atoms of an adjacent molecule. These packing conditions are achieved through orthorhombic unit cells in the case of odd *trans* polyalkenamers and through a monoclinic unit cell for *trans* polydodecenamer, according to the conformations of the macromolecules. The value of the monoclinic angle, β, is connected with the values assumed by the internal rotation angles around the single bonds adjacent to each double bond. The former is essentially determined by the requirements of minimization of the lattice binding energy while the latter by the minimization of the intramolecular conformational energy; obviously, the minimum lattice energy (β angle) is closely dependent on the molecular shape (rotation angles).

As a result, the packing of the macromolecules of *trans* polydodecenamer is essentially conditioned by the paraffinic planar sequences as in the case of odd *trans* polyalkenamers.

The arrangement side by side of the *trans* polydodecenamer molecules is in fact very similar to that found in orthorhombic polyethylene and to that found in odd *trans* polyalkenamers.

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REFERENCES

(1) G. Natta, G. Dall'Asta, I. W. Bassi and G. Carella, *Makromolek. Chem.* **91**, 87 (1966).
(2) G. Natta, P. Corradini, *Ricerca scient.*, (Suppl.), **25**, 3 (1955);
R. H. Pierce, J. P. Tordella and W. M. D. Bryant, *J. Am. chem. Soc.* **74**, 282 (1952);
A. Turner Jones, *J. Polym. Sci.* **62**, 53 (1963).
(3) C. W. Bunn, *Trans. Faraday Soc.* **35**, 482 (1939).
(4) G. Natta, A. Zambelli, I. Pasquon and F. Ciampelli, *Makromolek. Chem.* **79**, 161 (1964).
(5) G. Natta, I. W. Bassi, *Accad. Naz. Lincei Rc.* **38**, 315 (1965); see also the preceding paper.
(6) G. Natta, P. Corradini, *Nuovo Cim.* (Suppl.), **15**, 29 (1960);
G. Natta, P. Corradini and L. Porri, *Atti Accad. Naz. Lincei Memorie* **20** (8), 128 (1955);
G. Natta, P. Corradini, L. Porri and D. Morero, *Chimica Ind.* **40**, 362 (1958);
G. Perego, I. W. Bassi, *Makromolek. Chem.* **61**, 198 (1963);
G. Natta, I. W. Bassi and G. Perego, *Accad. Naz. Lincei Rc.* **36**, 291 (1964).
(7) P. Corradini, *Accad. Naz. Lincei Rc.* **28**, 1 (1960).
(8) A. I. Kitaigorodskii, *Organic Chemical Crystallography*, pp. 177–215, Consultants Bureau, New York (1961).
(9) P. Ganis and E. Martuscelli, *Ricerca scient.* **36**, 439 (1966).

Resumé—La structure cristalline du *trans* polydodécénamère $[-CH{=}CH-(CH_2)_{10}-]_n$ a été définie en se basant sur les spectres aux rayons X obtenus à partir de fibres étirées à chaud. La maille élémentaire monoclinique comprend deux chaînes polymériques. La répétition au long de l'axe de la macromolécule a lieu après une unité $C_{12}H_{22}$. Les dimensions de la maille élémentaire sont les suivantes: $a = 7{\cdot}43$ Å; $b = 5{\cdot}00$ Å; $c = 14{\cdot}85$ Å (axe de la macromolécule); $\beta = 86°30'$; groupe spatial $P2_1/a$.

La projection de la maille élémentaire sur le plan (001) a les mêmes dimensions que celle des mailles rhombiques des *trans* polyalkénamères impairs et du polyéthylène. Les doubles liaisons *trans* aboutissent à une conformation non-planaire de la chaîne polymérique. La valeur de l'angle β de la chaîne élémentaire est en relation avec la conformation de la macromolécule. L'assemblage des macromolécules est du même type de ceux qu'on a trouvé pour les *trans* polyalkénamères impairs et pour le polyéthylène rhombique. Les termes pairs de la série homologue des *trans* polyalkénamères ont une structure cristalline très semblable à celle du polydodécénamère. On a remarqué, pour les polyalkénamères pairs, la présence d'une différente modification cristalline.

Sommario—Mediante spettri ai raggi X forniti da fibre stirate a caldo è stata definita la struttura cristallina del *trans* polidodecenamero [—CH═CH—$(CH_2)_{10}$—$]_n$. La cella elementare monoclina contiene due catene polimeriche. La ripetizione lungo l'asse della macromolecola si ha dopo una unità $C_{12}H_{22}$. Le dimensioni della cella elementare sono: $a = 7\cdot43$ Å; $b = 5\cdot00$ Å; $c = 14\cdot85$ Å (asse della macromolecola); $\beta = 86°30'$; gruppo spaziale $P2_1/a$.

La proiezione della cella sul piano (001) ha dimensioni uguali a quelle delle celle elementari rombiche dei *trans* polialchenameri dispari e del polietilene. I doppi legami *trans* portano ad una conformazione non planare della catena polimerica. Il valore dell'angolo β della cella elementare è in relazione con la conformazione assunta dalla macromolecola. L'impacchettamento delle macromolecole è dello stesso tipo di quelli trovati per i *trans* polialchenameri dispari e per il polietilene rombico. I termini pari della serie omologa dei *trans* polialchenameri hanno strutture cristalline molto simili a quella del *trans* polidodecenamero. È stata osservata la presenza di una diversa modificazione cristallina per i *trans* polialchenameri pari.

Zusammenfassung—Die Kristallstruktur des trans-Polydodecenamers [—CH═CH—$(CH_2)_{10}$—$]_n$ wurde mit Hilfe der Röntgenbeugungsspektren Heissverstreckter Fasern bestimmt. Die monokline Elementarzelle enthält zwei Ketten mit je einer chemischen Struktureinheit pro Faserperiode. Die Dimensionen der Elementarzelle sind: $a = 7\cdot43$ Å; $b = 5\cdot00$ Å; $c = 14\cdot85$ Å (Faserachse); $\beta = 86°30'$; Raumgruppe P_{21}/a (C^5_{2h}).

Die 001-Projektion der Zelle hat Dimensionen ähnlich denen der ungeraden Glieder der trans-Polyalkenameren und des rhombischen Polyäthylens. Das Vorliegen der trans-Doppelbindungen verursacht ein Abweichen von der planaren Zick-zack-Konformation des Polyäthylens. Der Wert des Winkels β der monoklinen Elementarzelle steht mit der Konformation der Kette im Zusammenhang.

Die Raumpackung der Ketten ist von der gleichen Art wie die der normalen Modifikation der ungeraden Glieder der trans-Polyalkenameren und des rhombischen Polyäthylens. Die geraden Glieder der homologen trans-Polyalkenameren in der hier beschriebenen Modifikation stellen eine Serie mit analogen Kristalleigenschaften dar.