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THE MONOCLINIC STRUCTURE OF EVEN *TRANS*-POLYALKENAMERS

G. NATTA

Istituto di Chimica Industriale del Politecnico di Milano, Italy

and

I. W. BASSI and G. FAGHERAZZI

Istituto Ricerche "G. Donegani", Società Montecatini-Edison, Milano, Italy

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Abstract—The crystal structures of *trans*-polydecenamer [—CH═CH—$(CH_2)_8$—]$_p$ and *trans*-polyoctenamer [—CH═CH—$(CH_2)_6$—]$_p$ crystallized in the monoclinic modification of even *trans*-polyalkenamers are described. The structure of *trans*-polydecenamer has been determined from X-ray diffraction spectra of drawn fibres, while the structure of *trans*-polyoctenamer has been determined from X-ray powder diffraction spectra.

The unit cells parameters are:

$$\textit{trans}\text{-polydecenamer}\begin{cases} a=7{\cdot}42\text{ Å};\ b=5{\cdot}00\text{ Å};\ c=12{\cdot}41\text{ Å (fibre axis)}\\ \beta=85°\,50';\ \text{space group } P2_1/a\\ Z=2\ (C_{10}H_{18});\ d_x=1{\cdot}005\text{ g/cm}^3\end{cases}$$

$$\textit{trans}\text{-polyoctenamer}\begin{cases} a=7{\cdot}43\text{ Å};\ b=5{\cdot}00\text{ Å};\ c=9{\cdot}91\text{ Å (fibre axis)}\\ \beta=84°\,50';\ \text{space group } P2_1/a\\ Z=2\ (C_8H_{14});\ d_x=1{\cdot}001\text{ g/cm}^3\end{cases}$$

The internal rotation angles around the single bonds adjacent to each double bond assume, in the crystal state, the figures of 130° and 230° respectively. Due to symmetry centres, the repetition along the macromolecule axis occurs after one chemical unit. The macromolecular packing is regulated by the hydrogen atoms of the CH_2 groups which are arranged in such a way that each of them is interlocked among three H atoms on an adjacent molecule.

The β angles of the unit cells of *trans*-polydecenamer and *trans*-polyoctenamer are strictly related to the inclination, toward the *c* axis, of the plane on which the C atoms of the methylene groups lie.

The monoclinic structure of even *trans*-polyalkenamers is similar to the orthorhombic structure of odd *trans*-polyalkenamers and of polyethylene.

INTRODUCTION

HIGH molecular weight, linear, unsaturated *trans*-polyalkenamers [—CH═CH—$(CH_2)_{n-2}$—]$_p$ can be obtained by stereospecific polymerization via ring cleavage of several unsubstituted cyclo-olefins. They form a homologous series, the first member of which is polyacetylene ($n-2=0$) and the last can be considered polyethylene ($n \rightarrow \infty$).(1,2)

In the crystalline state, these polymers are polymorphous. The odd members of the homologous series can crystallize in two forms corresponding to structure I and structure II of *trans*-polyalkenamers. Also the even members can crystallize in two forms corresponding to structure III and structure IV of *trans*-polyalkenamers.(2,3)

Structure I of *trans*-polyalkenamers, having an orthorhombic symmetry(3,4) and structure IV of *trans*-polyalkenamers having a monoclinic symmetry(5) are similar to the structure of orthorhombic polyethylene.(6) As will be shown in subsequent papers, structure III of *trans*-polyalkenamers has a triclinic symmetry, and is comparable to that of cold-worked polymethylenes and polyethylenes.(7) Structure II of *trans*-polyalkenamers, on the contrary, could not be studied in detail: its presence may be indicated by the appearance of some i.r. absorption bands in the spectra of *trans*-polyheptenamers subjected to particular physical treatments.(2)

In the present paper, we describe structure IV (monoclinic) of *trans*-polydecenamer and of *trans*-polyoctenamer. We also report some general structure relations among the homologous even *trans*-polyalkenamers crystallized in the monoclinic structure.

The facility of even *trans*-polyalkenamers to crystallize in the form with structure IV seems to be a function of the number of carbon atoms of the starting cyclo-olefin. In fact, in the case of *trans*-polydodecenamer: $[\text{—CH=CH—(CH}_2)_{10}\text{—}]_p$ and of *trans*-polydecenamer $[\text{—CH=CH—(CH}_2)_8\text{—}]_p$, the monoclinic form is directly obtained by cooling from the melt, while in the case of *trans*-polyoctenamer: $[\text{—CH=CH—(CH}_2)_6\text{—}]_p$ a mixture of forms with crystal structures III and IV is obtained under the same conditions. Moreover, by hot stretching (below the melting point) moulded sheets of *trans*-polydecenamer and *trans*-polydodecenamer, we obtained fibres crystallized in structure IV, in the pure state; in the case of *trans*-polyoctenamer, under the same conditions, we obtained fibres crystallized in structure III, in the pure state. *Trans*-polyoctenamer may be crystallized in structure IV, in the pure state, only in unoriented films deposited from a benzene solution. When narrow ribbons of these films are drawn, both structures III and IV are produced.

Structure IV of even *trans*-polyalkenamers is characterized by X-ray diffraction spectra, the $(hk0)$ reflections of which are in agreement with the equatorial reflections of orthorhombic polyethylene, both in angular positions and in intensity.

The monoclinic structure of *trans*-polydodecenamer was described in a previous paper.(5) Here we report the monoclinic structure of *trans*-polydecenamer determined by interpretation of X-ray fibre spectra, and the monoclinic structure of *trans*-polyoctenamer determined by examination of powder spectra.

THE MONOCLINIC STRUCTURE OF *TRANS*-POLYDECENAMER

The fibre spectra of *trans*-polydecenamer are very rich in reflections including those for high angles.

The identity period along the macromolecule axis is 12·41 ± 0·10 Å and corresponds to one chemical repeating unit of the chain $(C_{10}H_{18})$.

All the reflections fit a monoclinic unit cell having the following constants: $a\sin\beta = 7{\cdot}40 \pm 0{\cdot}05$ Å; $a = 7{\cdot}42 \pm 0{\cdot}05$ Å; $b = 5{\cdot}00 \pm 0{\cdot}05$ Å; $c = 12{\cdot}41 \pm 0{\cdot}10$ Å (fibre axis); $\beta = 85°50' \pm 15'$; $Z = 2$; $d_x = 1{\cdot}005$ g/cm³.

The systematic absences of $(0k0)$ and $(h0l)$ reflections, when $k \neq 2n$ and $h \neq 2n$ respectively, indicate as probable space group C^5_{2h} in its $P2_1/a$ orientation.

The calculated identity period along the polymer chain, based on a planar zig-zag chain and on the generally accepted bond lengths and valence angles, is 12·65 Å ($\text{C—C} = 1{\cdot}54$ Å; $\text{C=C} = 1{\cdot}34$ Å; $\text{C—}\widehat{\text{C}}\text{—C} = 110°$; $\text{C=}\widehat{\text{C}}\text{—C} = 120°$). The difference between experimental and calculated repeats shows that the macromolecules, in the crystal state, cannot assume a planar zig-zag conformation.

As in the case of several polymers containing *trans* double bonds in the main chain,(3–5,8) the internal conformational energy of an isolated macromolecule of *trans*-polyalkenamers, in the crystal state, reaches a minimum, when the internal rotation angles σ_1 and σ_2 around the single bonds adjacent to each double bond assume the values of 180° ± 60° respectively, while the remaining internal rotation angles retain the value of 180°. Structural investigations accomplished by us on some *trans*-polyalkenamers, viz. *trans*-polypentenamer(4) and *trans*-polyheptenamer(3) crystallized in structure I and *trans*-polydodecenamer(5) crystallized in structure IV, indicated 130° and 230° as preferred values of the internal rotation angles σ_1 and σ_2. The macromolecules of *trans*-polydecenamer, like those of all even *trans*-polyalkenamers, are intrinsically centrosymmetrical. The symmetry centres lie at the middle of the double bonds and at the middle of the single bond between the C_5 and C_6 atoms, as shown from the chain model drawn in Fig. 1 ($\mathrm{C{-}H} = 1{\cdot}08$ Å; $\mathrm{C{-}\widehat{C}{-}H} = 109°28'$, $\mathrm{H{-}\widehat{C}{-}H} = 190°28'$, $\mathrm{C{=}\widehat{C}{-}H} = 120°$). According to the nomenclature proposed by Corradini,(9) the symmetry of the macromolecule is *t i*.

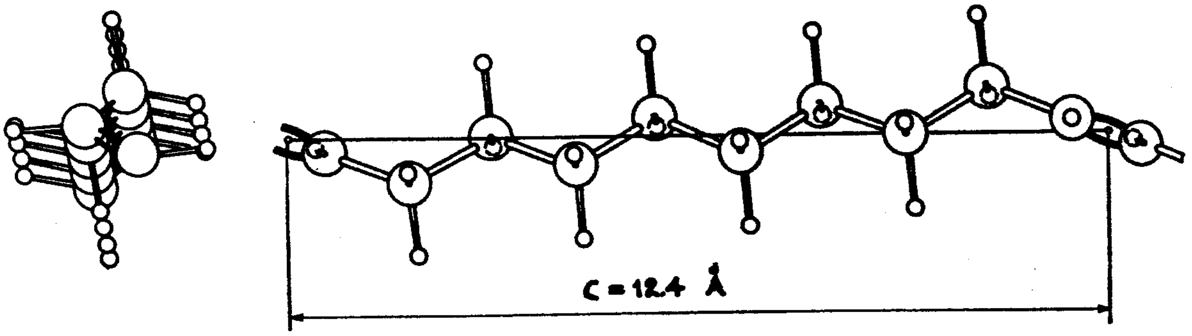

FIG. 1. Chain model of the macromolecule of *trans*-polydecenamer in the crystal state (side and end views).

The identity period, *c*, for any even *trans*-polyalkenamer can be calculated from the already defined intrinsic symmetry, bond lengths and valence angles on the basis of the relation (see Fig. 2 for *trans*-polydecenamer):

$$c = [d^2 + (1{\cdot}16 \sin \sigma_1)^2]^{\frac{1}{2}} \tag{1}$$

where *d*, projection of the chain axis on the plane on which the C atoms of the methylene groups lie, is given by the expression:

$$d = [(1{\cdot}26n - 0{\cdot}67 \cos\sigma_1 - 0{\cdot}71)^2 + (0{\cdot}95 \cos \sigma_1 - 0{\cdot}53)^2]^{\frac{1}{2}} \tag{2}$$

where *n* is the number of carbon atoms of the chemical repeating unit along *c*. For *trans*-polydecenamer *n* is 10 and, assuming $\delta_1 = 130°$, from (1) and (2) we calculate for *c* the value of 12·40 Å. This figure is in very good agreement with the experimental fibre repeat (12·41 ± 0·10 Å).

All carbon atoms of the monomeric unit of any even *trans*-polyalkenamer lie on a plane, inclined toward the *c* axis at an angle δ defined by the relation:

$$\tan \delta = \frac{1{\cdot}16 \sin \sigma_1}{d} \tag{3}$$

In the case of *trans*-polydecenamer, δ is 4° 7′.

As shown by us later, the calculated value of δ is governed by the value of the β angle of the monoclinic unit cell.

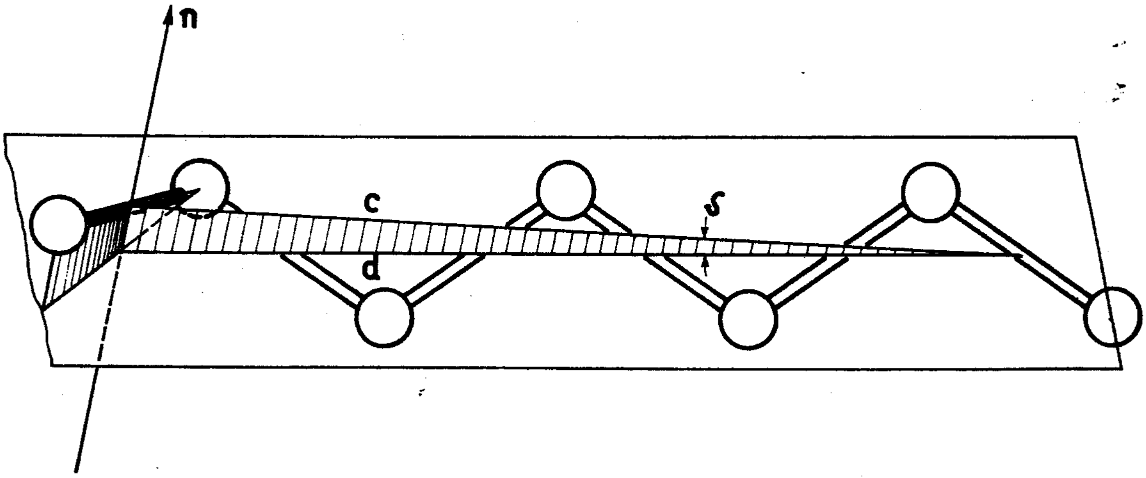

FIG. 2. Schematic representation of the macromolecule of *trans*-polydecenamer on the paraffinic zig-zag plane.

DETERMINATION OF THE CRYSTAL STRUCTURE OF MONOCLINIC *TRANS*-POLYDECENAMER

The $P2_1/a$ space group requires four asymmetric units in a general position, while the unit cell of *trans*-polydecenamer allows the presence of only two chemical units $C_{10}H_{18}$. Therefore, the independent asymmetric unit is half a chemical unit and the symmetry centres present in the macromolecule conformation are maintained as symmetry elements of the unit cell.

Considering the restrictions imposed by the macromolecule conformation and by the unit cell symmetry and size, the study of the intermolecular Van der Waals' contact distances reveals a good packing of the macromolecules when the ϕ angle, formed by the *b* axis of the unit cell and by the plane on which the 10 carbon atoms of the chemical repeating unit are arranged, reaches a value of about 40°.

We came to analogous conclusions with regard to the orientation in the unit cell of the macromolecules of *trans*-polydodecenamer having the crystal structure IV.

It is interesting to observe that the projections on the plane normal to the *c* axis of the *a* and *b* axes of the monoclinic unit cells of *trans*-polydecenamer and *trans*-polydodecenamer are practically equal to those of orthorhombic polyethylene and of odd *trans*-polyalkenamers. This fact is a direct consequence of the structural analogy among these crystalline polymers. In particular, the side-by-side arrangement of the macromolecules of all these polymers is governed by the same symmetry elements. Also the molecular orientation of all these polymers, with reference to the equatorial axes of the unit cell, is analogous.

On the basis of these considerations, we calculated the structure factors for *trans*-polydecenamerin some different orientations of the macromolecule around $\phi = 40°$. The best agreement between calculated a nd observed structure factors has been reached with the atomic co-ordinates of the asymmetric unit reported in Table 1.

TABLE 1. CO-ORDINATES OF THE ATOMS OF THE ASYMMETRIC UNIT OF MONOCLINIC *trans*-POLYDECENAMER

	x/a	y/b	z/c
C_1	0·029	0·080	0·041
C_2	0·095	0·955	0·143
C_3	0·997	0·075	0·246
C_4	0·064	0·945	0·347
C_5	0·968	0·068	0·449
H_1	0·024	0·293	0·033
H_2	0·236	0·983	0·145
H_2'	0·068	0·742	0·142
H_3	0·027	0·285	0·247
H_3'	0·855	0·043	0·244
H_4	0·209	0·978	0·348
H_4'	0·039	0·733	0·345
H_5	0·995	0·280	0·450
H_5'	0·823	0·035	0·447

A comparison between observed F_o and calculated F_c structure factors is given in Table 2. The isotropic temperature factor used in the final calculations is 6·9 Å^2. The F_o figures of Table 2 in parentheses correspond to unobserved reflections; their intensity was estimated as half the minimum intensity potentially observable in correspondence of each layer line of the fibre photographs. The intensities of the reflections were measured by the multiple film method, with a calibrated scale of blackenings. The observed intensities were corrected by Lorentz and polarization factors. The area of reflections was taken into account by visual estimation.

The reliability factor of the structure:

$$R = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|}.$$

calculated for 0, 1, 2, 3, 4 and 5 layer lines is 24 per cent. The calculation takes account of unobserved reflections.

Figure 3 shows the *c*-projection of the structure of *trans*-polydecenamer, and indicates the most significant intermolecular distances. Figure 4 shows the projection of the structure of *trans*-polydecenamer on the (010) plane. These two drawings clearly show that the crystal structure of *trans*-polydecenamer is regulated by the spatial juxtaposition of the hydrogen atoms of the CH_2 groups, which are arranged in such a way that each of them enters the cavity among three hydrogen atoms of an adjacent molecule. These packing conditions constitute the basis for the structures of many organic compounds, either polymers or low molecular weight compounds, the molecules of which contain long methylenic sequences. These conditions are achieved with orthorhombic unit cells in the case of polyethylene and of odd *trans*-polyalkenamers and with monoclinic unit cells in the case of even *trans*-polyalkenamers crystallized in the form with structure IV.

The same difference between the structures of the even and odd members of the homologous series is also observed in the case of *n*-alkanes. The difference between the symmetries of the unit cells (orthorhombic or monoclinic) of odd and even *trans*-polyalkenamers is due to the fact that the axis of the zig-zag paraffinic chain of the odd

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

h k l	d_c	d_o	nF_c		F_o
1 1 0	4·153	4·13	77·0		98·9
2 0 0	3·704	3·73	48·1		36·8
2 1 0	2·978	2·99	9·1		9·3
0 2 0	2·500	2·494	25·1		28·5
1 2 0	2·370	2·374	7·4		7·4
3 1 0	2·213	2·238	19·1		14·1
2 2 0	2·075	2·080	14·5		16·6
4 0 0	1·852	1·855	9·5		7·0
3 2 0	1·757	1·752	6·9	7·7	8·6
4 1 0	1·736		3·4		
1 3 0	1·627	1·629	9·4		12·5
2 3 0	1·520	1·519	6·3		7·7
4 2 0	1·487	—	2·5		(2·1)
5 1 0	1·420	1·435	2·5		4·0
3 3 0	1·381	1·388	1·7		vvw
5 2 0	1·274	1·283	1·9		vvw
0 4 0	1·250	1·242	0·5	4·5	6·7
4 3 0	1·239		3·4		
6 0 0	1·234		0·7		
1 4 0	1·233		2·8		
6 1 0	1·198	—	0·3	1·1	(2·4)
2 4 0	1·185		1·1		
3 4 0	1·115	1·115	3·9	4·0	5·4
5 3 0	1·107		0·7		
6 2 0	1·106		0·6		
4 4 0	1·036	—	1·4	1·4	(2·5)
7 1 0	1·035		0·2		
6 3 0	0·992	—	0·5	3·0	(2·5)
1 5 0	0·991		3·0		
0 0 1	12·380	—	0·3		(0·7)
0 1 1	4·645	—	3·9		(1·0)
1 1 1	3·978	3·95	13·9	18·1	17·6
$\bar{1}$ 1 1	3·891		11·6		
2 0 1	3·618	3·63	15·6		13·2
$\bar{2}$ 0 1	3·485	3·51	14·3		13·2
2 1 1	2·932	2·916	10·2		9·6
$\bar{2}$ 1 1	2·857	—	1·4		(2·1)
0 2 1	2·451	—	1·2		(2·3)
1 2 1	2·336	2·336	6·8	6·9	5·8
$\bar{1}$ 2 1	2·319		1·3		
3 1 1	2·204	2·190	11·4	14·3	12·2
$\bar{3}$ 1 1	2·155		8·7		
2 2 1	2·056	2·051	7·3	9·0	11·8
$\bar{2}$ 2 1	2·031		5·3		
4 0 1	1·852	1·845	8·2	9·5	9·0
$\bar{4}$ 0 1	1·812		4·9		
3 2 1	1·752	1·739	10·8	14·0	11·5
4 1 1	1·736		8·9		
$\bar{3}$ 2 1	1·727		1·2		
$\bar{4}$ 1 1	1·702	—	0·9		(3·1)
0 3 1	1·651	—	1·6		(3·2)
1 3 1	1·616	—	3·3	3·7	(3·2)
$\bar{1}$ 3 1	1·608		1·7		
2 3 1	1·514	1·509	6·5	8·0	7·4
$\bar{2}$ 3 1	1·505		0·7		
4 2 1	1·488		4·6		
$\bar{4}$ 2 1	1·466	—	2·0		(3·3)
5 1 1	1·422	—	4·3	4·6	(3·4)
$\bar{5}$ 1 1	1·400	—	1·6		
3 3 1	1·379	—	2·8	3·2	(3·5)
$\bar{3}$ 3 1	1·369		1·6		
5 2 1	1·277	1·276	8·6	8·6	8·3
$\bar{5}$ 2 1	1·259		0·5		
0 4 1	1·244	1·240	0·5	8·0	8·3
4 3 1	1·239		7·9		
6 0 1	1·238		1·0		
1 4 1	1·228	—	1·3	1·6	(3·8)
$\bar{4}$ 3 1	1·226		0·9		
$\bar{1}$ 4 1	1·226		0·2		
$\bar{6}$ 0 1	1·219	—	0·2	4·6	(3·8)
6 1 1	1·201		4·6		
$\bar{6}$ 1 1	1·185	—	0·1	1·7	(3·8)
2 4 1	1·182		1·6		
$\bar{2}$ 4 1	1·176		0·4		
3 4 1	1·116	—	4·1	4·4	(3·9)
6 2 1	1·109		0·2		
5 3 1	1·109		1·6		
$\bar{3}$ 4 1	1·109		0·5		
0 0 2	6·190	—	0·2		(1·2)
0 1 2	3·891	—	0·3		(1·5)
1 1 2	3·509	3·43d	6·5	9·4	9·3
$\bar{1}$ 1 2	3·388		6·8		
2 0 2	3·283	—	4·3		(1·8)
$\bar{2}$ 0 2	3·085	3·13	10·0		8·6
2 1 2	2·746	—	4·7		(1·9)
$\bar{2}$ 1 2	2·625	—	0·9		(2·0)
0 2 2	2·318	—	1·4		(2·2)
1 2 2	2·231	—	2·9	3·0	(2·3)
$\bar{1}$ 2 2	2·196		0·8		
3 1 2	2·128	—	2·0		(2·4)
$\bar{3}$ 1 2	2·043	2·061	7·1		5·8
2 2 2	1·989	—	2·7		(2·7)
$\bar{2}$ 2 2	1·942	—	3·9		(2·7)
4 0 2	1·811	—	0·4		(2·8)
$\bar{4}$ 0 2	1·739	—	4·2		(2·9)
3 2 2	1·712	—	4·3	5·2	(3·0)
4 1 2	1·701		2·9		
$\bar{3}$ 2 2	1·667	—	0·4	0·4	(3·1)
$\bar{4}$ 1 2	1·645		0·1		
0 3 2	1·610	—	0·3		(3·2)
1 3 2	1·582	—	1·9	2·0	(3·2)
$\bar{1}$ 3 2	1·567		0·5		

TABLE 2—*continued.*

h k l	d_c	d_o	nF_c		F_o
2 3 2	1·484	—	3·0	3·1	(3·3)
$\bar{2}$ 3 2	1·466		0·6		
4 2 2	1·466		0·1		
$\bar{4}$ 2 2	1·429	—	1·9	2·0	(3·4)
5 1 2	1·404		0·6		
$\bar{5}$ 1 2	1·362	—	1·7	1·8	(3·5)
3 3 2	1·359		0·6		
0 0 3	4·127	—	1·1		(1·2)
0 1 3	3·189	—	0·6		(1·5)
1 1 3	2·989	—	3·7		(1·6)
$\bar{1}$ 1 3	2·870	2·871	6·5	6·6	8·6
2 0 3	2·870		1·2		
$\bar{2}$ 0 3	2·667	2·674	9·5		8·5
2 1 3	2·485	—	3·7		(2·0)
$\bar{2}$ 1 3	2·353	—	2·1		(2·2)
0 2 3	2·139	—	1·0		(2·4)
1 2 3	2·075	—	2·1		(2·5)
$\bar{1}$ 2 3	2·035	—	1·7		(2·6)
3 1 3	2·005	—	0·1		(2·7)
$\bar{3}$ 1 3	1·901	1·908	7·7		7·7
2 2 3	1·883	—	1·5		(2·7)
$\bar{2}$ 2 3	1·824	—	3·7		(2·8)
4 0 3	1·736	—	0·8		(2·8)
3 2 3	1·645	—	3·3	5·6	(3·1)
$\bar{4}$ 0 3	1·645		4·5		
4 1 3	1·639	—	2·4		(3·1)
$\bar{3}$ 2 3	1·587	—	1·1		(3·2)
$\bar{4}$ 1 3	1·563	—	0·6	0·6	(3·2)
0 3 3	1·546		0·1		
1 3 3	1·522	—	2·0	2·0	(3·3)
$\bar{1}$ 3 3	1·506		0·3		
2 3 3	1·441		2·4		(3·4)
4 2 3	1·425	—	0·4	1·2	(3·4)
$\bar{2}$ 3 3	1·412		1·1		
$\bar{4}$ 2 3	1·374	—	2·6	2·8	(3·5)
5 1 3	1·372		0·9		
0 0 4	3·095	—	0·9		(1·4)
0 1 4	2·632	2·604	2·8	3·8	5·0
1 1 4	2·532		2·5		
2 0 4	2·463	2·428	1·3	7·3	8·6
$\bar{1}$ 1 4	2·437		7·2		
$\bar{2}$ 0 4	2·297	2·306	13·8		11·2
2 1 4	2·212	—	3·6		(2·0)
$\bar{2}$ 1 4	2·088	2·106	6·4		9·3
0 2 4	1·946	—	2·7		(2·3)
1 2 4	1·901	—	1·1		(2·4)
$\bar{1}$ 2 4	1·860	1·876	4·9	5·3	9·0
3 1 4	1·859		2·0		
2 2 4	1·754	1·756	0·7	14·1	11·2
$\bar{3}$ 1 4	1·748		14·1		
$\bar{2}$ 2 4	1·690	1·702	4·9		7·0
4 0 4	1·642	—	2·3		(2·8)
3 2 4	1·563	1·557	3·2	13·0	10·2
4 1 4	1·560		2·5		
$\bar{4}$ 0 4	1·541		12·3		
$\bar{3}$ 2 4	1·497	—	4·5		(3·1)
$\bar{4}$ 1 4	1·473	—	3·4	3·8	(3·1)
0 3 4	1·466		1·7		
1 3 4	1·449	—	2·3	2·7	(3·1)
$\bar{1}$ 3 4	1·431		1·5		
2 3 4	1·380	—	2·2	2·5	(3·2)
4 2 4	1·374		1·3		
$\bar{2}$ 3 4	1·348	1·352	4·3		vvw
5 1 4	1·326	—	1·9		(3·2)
$\bar{4}$ 2 4	1·312	1·314	6·5		vvw
3 3 4	1·280	—	0·1		(3·3)
$\bar{5}$ 1 4	1·258	1·262	10·6		vw
$\bar{3}$ 3 4	1·244	—	1·3		(3·4)
5 2 4	1·205	—	1·2		(3·4)
6 0 4	1·176	—	0·8	1·9	(3·5)
4 3 4	1·170		1·7		
0 4 4	1·160	—	2·3	3·9	(3·6)
$\bar{5}$ 2 4	1·153		1·4		
1 4 4	1·149		0·4		
6 1 4	1·145		0·5		
$\bar{1}$ 4 4	1·142		2·7		
$\bar{4}$ 3 4	1·131	1·119	2·5	7·5	vvw
$\bar{6}$ 0 4	1·119		7·0		
2 4 4	1·110		0·9		
$\bar{2}$ 4 4	1·099	—	1·7	1·8	(3·7)
$\bar{6}$ 1 4	1·092		0·4		
0 0 5	2·476	—	0·8		(1·7)
0 1 5	2·220	2·223	23·7		22·1
1 1 5	2·165	2·144	13·2	19·6	15·0
2 0 5	2·129		14·5		
$\bar{1}$ 1 5	2·091	2·095	10·0		11·5
$\bar{2}$ 0 5	1·994	1·995	9·3		10·6
2 1 5	1·961	1·942	16·2		16·3
$\bar{2}$ 1 5	1·851	1·853	12·2		12·5
0 2 5	1·761	—	0·0		(3·1)
1 2 5	1·731	1·732	19·5		23·4
3 1 5	1·706	1·698	11·9	21·3	18·6
$\bar{1}$ 2 5	1·694		17·7		
2 2 5	1·622	1·608	8·3	11·1	13·4
$\bar{3}$ 1 5	1·601		7·3		
2 2 5	1·558	1·545	6·6	9·7	11·5
4 0 5	1·535		7·1		
3 2 5	1·469	1·475	9·3	10·7	12·2
4 1 5	1·469		5·3		
$\bar{4}$ 0 5	1·433	—	3·2		(3·9)
$\bar{3}$ 2 5	1·399	1·389	6·5	16·8	16·9
0 3 5	1·383		15·6		

TABLE 2—*continued*

$h\ k\ l$	d_c	d_o	nF_c		F_o
$\bar{4}$ 1 5	1·379	—	3·1	4·0	(4·0)
1 3 5	1·370		2·5		
$\bar{1}$ 3 5	1·350	—		3·0	(4·0)
2 3 5	1·312	1·312	10·5	11·5	14·4
4 2 5	1·309		4·8		
$\bar{2}$ 3 5	1·280	1·269	8·4	9·6	6·7
5 1 5	1·269		4·7		
$\bar{4}$ 2 5	1·244	—	2·6	4·0	(4·4)
3 3 5	1·229		3·0		
$\bar{5}$ 1 5	1·196	—	1·5	2·9	(4·4)
$\bar{3}$ 3 5	1·188		2·5		
5 2 5	1·163	—		2·4	(4·4)
6 0 5	1·138	—	1·6	4·3	(4·6)
4 3 5	1·131		4·0		
0 4 5	1·119	1·100	0·5	11·9	9·9
1 4 5	1·111		8·9		
6 1 5	1·111		0·9		
$\bar{5}$ 2 5	1·106		1·3		
$\bar{1}$ 4 5	1·099		7·8		
$\bar{4}$ 3 5	1·089	—	2·3	2·5	(4·6)
2 4 5	1·080		0·9		
$\bar{6}$ 0 5	1·075		0·1		
$\bar{2}$ 4 5	1·059	—	1·4	1·4	(4·7)
$\bar{6}$ 1 5	1·050		0·4		
6 2 5	1·035	—	1·2	5·0	(4·8)
5 3 5	1·033		1·5		
3 4 5	1·031		4·6		
*0 0 9	1·376	1·379		2·1	vw
0 0 10	1·238	1·239		7·6	ms
2 0 10	1·202	1·200	7·3	10·3	ms
1 1 10	1·202		7·3		

* These reflections are observable on the tilted spectra.

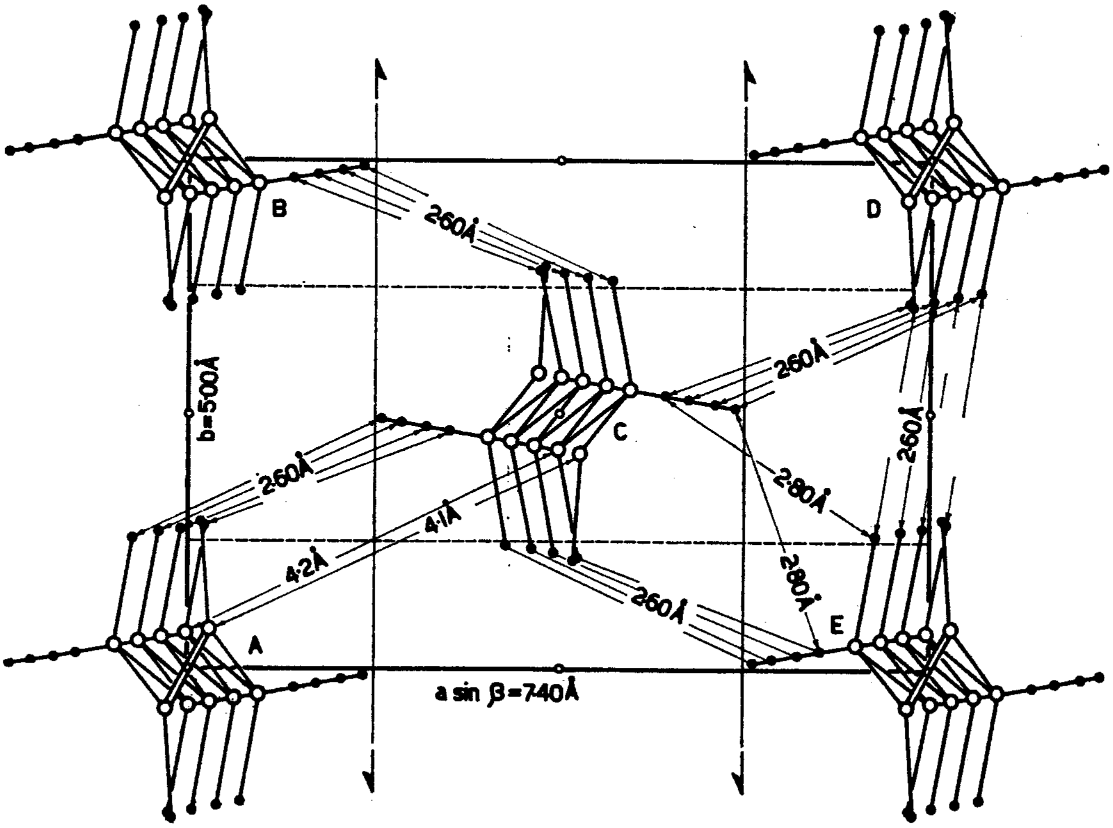

FIG. 3. *c*-Projection of the molecules of monoclinic *trans*-polydecenamer. Some of the most significant H—H intermolecular Van der Waals' distances are indicated. The solid circles represent hydrogen atoms and the open circles carbon atoms.

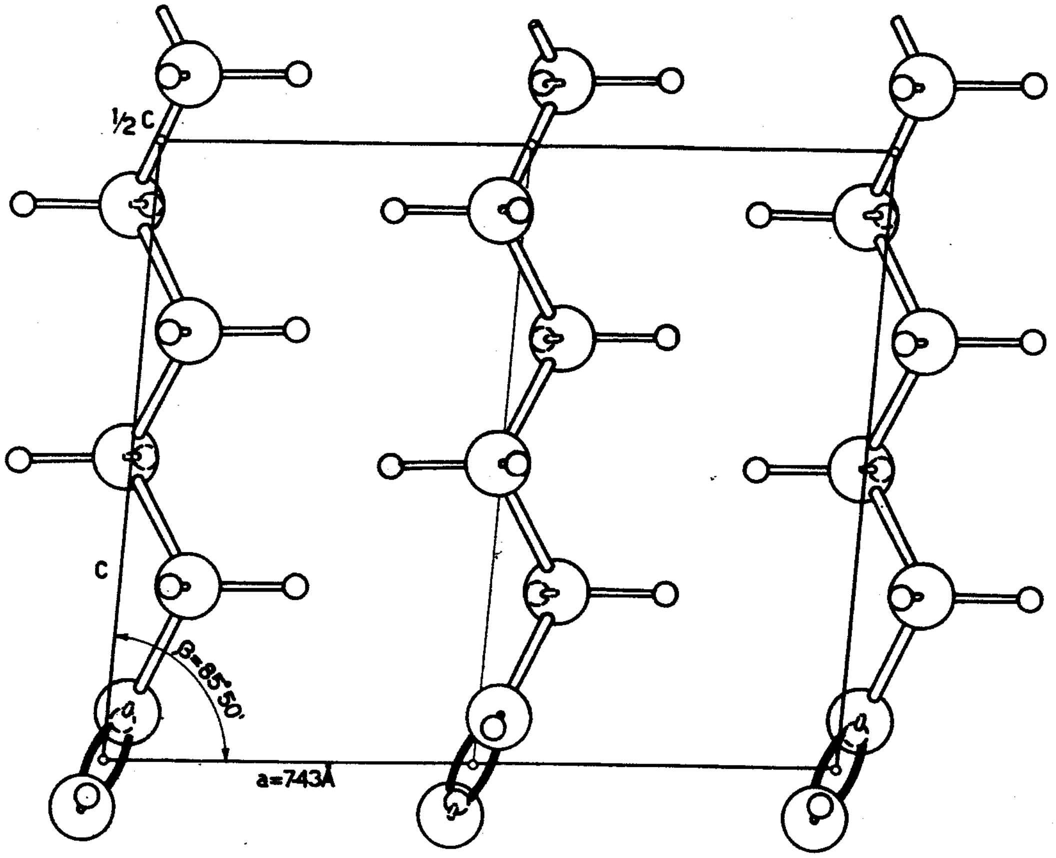

FIG. 4. Projection on the *a–c* plane of the structure of monoclinic *trans*-polydecenamer.

members of the homologous series is parallel to the *c* axis while, in the monoclinic structure, the axis of the zig-zag paraffinic chain of the even members is inclined by a δ angle toward the *c* axis. In the latter case, the same type of packing as that present in the orthorhombic structure is attained, because the *a* and *c* axes form a β angle which is just the complement of δ.

THE MONOCLINIC STRUCTURE OF *TRANS*-POLYOCTENAMER

The relationships (1)–(3) are valid for the macromolecules of even *trans*-polyalkenamers having *t i* symmetry, for various values of the parameter n ($n > 2$), number of carbon atoms of the chemical repeating unit along *c*.

Assuming the internal rotation angle σ to be 130° for all even *trans*-polyalkenamers, as already checked for *trans*-polydodecenamer and *trans*-polydecenamer, the values of Table 3 are obtained for *c* and δ ($4 \leqslant n \leqslant 14$). The experimental values of $(90° - \beta)$ found for *trans*-polydodecenamer and *trans*-polydecenamer are also shown in this Table. The agreement between calculated and experimental values of the *c* axis and $\delta = 90° - \beta$ is very good.

It seemed reasonable to extend these findings to the monoclinic unit cells of the other *trans*-polyalkenamers, crystallized in structure IV.

The calculated values of the *c* and δ parameters reported in Table 3 for *trans*-polyoctenamer were employed by us to determine the structure of this polymer, for which only powder spectra had been available. The *c*-projection of the unit cell of *trans*-

TABLE 3. COMPARISON BETWEEN THE OBSERVED AND CALCULATED c AND δ VALUES OF EVEN *trans*-POLYALKENAMERS (INTERNAL ROTATION ANGLE $\sigma_1 = 130°$)

trans-polyalkenamer	$[\text{—CH=CH—(CH}_2)_{n-2}\text{—]}_p$	$c_{calc.}$ (Å)	$c_{obs.}$ (Å)	$\delta_{calc.}$	$(90-\beta)_{obs.}$
trans-polybutadiene	$[\text{—CH=CH—(CH}_2)_2\text{—]}_p$	4·97	4·85 ± 0·05	10° 18′	—
trans-polyhexenamer	$[\text{—CH=CH—(CH}_2)_4\text{—]}_p$	7·42	—	6° 53′	—
trans-polyoctenamer	$[\text{—CH=CH—(CH}_2)_6\text{—]}_p$	9·91	9·91 ± 0·10	5° 8′	5° 10′ ± 15′
trans-polydecenamer	$[\text{—CH=CH—(CH}_2)_8\text{—]}_p$	12·40	12·41 ± 0·10	4° 7′	4° 10′ ± 15′
trans-polydodecenamer	$[\text{—CH=CH—(CH}_2)_{10}\text{—]}_p$	14·91	14·85 ± 0·10	3° 25′	3° 30′ ± 15′
trans-polytetradecamer	$[\text{—CH=CH—(CH}_2)_{12}\text{—]}_p$	17·41	—	2° 55′	—

polyoctenamer is assumed equal to those of *trans*-polydodecenamer and of *trans*-polydecenamer. Therefore, the assumed constants of the monoclinic unit cell of *trans*-polyoctenamer are: $a \sin \beta = 7{\cdot}40 \pm 0{\cdot}05$ Å; $a = 7{\cdot}43 \pm 0{\cdot}05$ Å; $b = 5{\cdot}00 \pm 0{\cdot}05$ Å; $c = 9{\cdot}91 \pm 0{\cdot}10$ Å (fibre axis); $\beta = 84°\ 50' \pm 15'$; $Z = 2$; $d_x = 1{\cdot}001$ g/cm^3. Space group $P2_1/a$.

The atomic co-ordinates of the asymmetric unit in the orientation analogous to that of *trans*-polydodecenamer and *trans*-polydecenamer ($\phi = 40°$) are reported in Table 4. Table 5 shows the values of observed and calculated interplanar distances d_{hkl} and the observed I_o and calculated I_c values of the intensities of powder diffraction lines of *trans*-polyoctenamer. The estimation of the observed intensities is only qualitative. The I_c figures, reported on a relative scale, were corrected by Lorentz, polarization and temperature factors ($B = 6{\cdot}0$ Å^2). The agreement between observed and calculated intensities is satisfactory. This result confirms the structural model proposed by us for even *trans*-polyalkenamers crystallized in the monoclinic structure.

TABLE 4. CO-ORDINATES OF THE ATOMS OF THE ASYMMETRIC UNIT OF MONOCLINIC *trans*-POLYOCTENAMER

	x/a	y/b	z/c
C_1	0·028	0·078	0·053
C_2	0·087	0·951	0·180
C_3	0·990	0·073	0·310
C_4	0·052	0·943	0·438
H_1	0·023	0·300	0·043
H_2	0·235	0·983	0·184
H_2'	0·059	0·740	0·178
H_3	0·019	0·288	0·294
H_3'	0·846	0·043	0·322
H_4	0·198	0·975	0·441
H_4'	0·022	0·728	0·435

Moreover the structure proposed by us has been theoretically foreseen and widely justified by Kitaigorodskii$^{(10)}$ for the centrosymmetrical molecules of even n-paraffins on the basis of close-packing considerations.

TABLE 5. COMPARISON BETWEEN OBSERVED AND CALCULATED INTENSITIES OF THE REFLECTIONS OF MONOCLINIC *trans*-POLYOCTENAMER. THE OBSERVED AND CALCULATED BRAGG DISTANCES ARE ALSO REPORTED

h k l	d_c	d_o	nI_c		I_o
0 0 1	9·872	—	0		—
0 0 2	4·936	—	0		—
0 1 1	4·464	—	10		—
1 1 0	4·149	4·14	4297		ss
1 1 1	3·891	3·88	137		w
$\bar{1}$ 1 1	3·757	3·72	1452	77	s
2 0 0	3·704			1375	
2 0 1	3·579	3·59	113		w
0 1 2	3·521	—	0		—
$\bar{2}$ 0 1	3·372	3·36	119		w
0 0 3	3·291	—	13	0	—
1 1 2	3·262			13	
$\bar{1}$ 1 2	3·102	3·11	36	30	vw
2 0 2	3·102			6	
2 1 0	2·976	2·93d	63	25	vw
2 1 1	2·907			38	
$\bar{2}$ 0 2	2·841	2·84	42		vw
$\bar{2}$ 1 1	2·795	—	0		—
0 1 3	2·747	—	2		—
1 1 3	2·645	—	9	3	—
2 1 2	2·636			6	
2 0 3	2·577	—	0		—
$\bar{1}$ 1 3	2·513	2·505	180	14	mw
0 2 0	2·500			165	
$\bar{2}$ 1 2	2·473			1	
0 0 4	2·468			0	
0 2 1	2·425	—	1		—
1 2 0	2·370	2·344	56	11	w
2 0 3	2·358			45	
1 2 1	2·318	—	14	10	—
2 1 3	2·293			4	
$\bar{1}$ 2 1	2·290			0	
0 2 2	2·231	2·212	211	0	m
3 1 0	2·213			80	
0 1 4	2·212			109	
3 1 1	2·201			22	
1 1 4	2·169	2·164	66	28	w
1 2 2	2·162			1	
2 0 4	2·146			37	
$\bar{2}$ 1 3	2·128	—	28	7	—
$\bar{3}$ 1 1	2·125			20	
$\bar{1}$ 2 2	2·111			1	
3 1 2	2·083	2·080	56	1	w
$\bar{1}$ 1 4	2·075			15	
2 2 0	2·073			40	
2 2 1	2·049	—	9		—
$\bar{2}$ 2 1	2·008	1·973	58	6	w
0 2 3	1·992			1	
$\bar{2}$ 0 4	1·976			10	
2 1 4	1·976			41	
0 0 5	1·974			0	
$\bar{3}$ 1 2	1·961	—	13	11	—
1 2 3	1·953			1	
2 2 2	1·945			1	
3 1 3	1·908	—	0	0	—
$\bar{1}$ 2 3	1·901			0	
$\bar{2}$ 2 2	1·877	—	0		—
4 0 0	1·852	1·850	42	14	vw
4 0 1	1·850			8	
$\bar{2}$ 1 4	1·838			19	
0 1 5	1·838			1	
1 1 5	1·818	—	5	1	—
2 0 5	1·811			4	
2 2 3	1·792	—	5	0	—
$\bar{4}$ 0 1	1·789			5	
4 0 2	1·786			0	
$\bar{3}$ 1 3	1·773	1·760	31	26	vw
3 2 0	1·757			5	
0 2 4	1·754			0	
3 2 1	1·749	1·736	69	14	w
$\bar{1}$ 1 5	1·748			1	
1 2 4	1·736			45	
4 1 0	1·735			0	
4 1 1	1·734			9	
3 1 4	1·718	—	19	15	—
$\bar{2}$ 2 3	1·712			4	
$\bar{3}$ 2 1	1·711			0	
2 1 5	1·704	1·683	38	0	vw
3 2 2	1·689			2	
$\bar{4}$ 1 1	1·686			0	
$\bar{4}$ 0 2	1·684			3	
$\bar{1}$ 2 4	1·684			33	
4 1 2	1·683			1	
$\bar{2}$ 0 5	1·681			0	
4 0 3	1·678			0	
0 0 6	1·645	—	1	0	—
0 3 1	1·644			1	
2 2 4	1·629	1·625	16	6	vvw
1 3 0	1·627			10	
$\bar{3}$ 2 2	1·622			0	
1 3 1	1·610	—	1	1	—
$\bar{1}$ 3 1	1·600			0	
$\bar{4}$ 1 2	1·596			0	
3 2 3	1·592	—	8	2	—
4 1 3	1·592			1	
$\bar{2}$ 1 5	1·592			1	
$\bar{3}$ 1 4	1·587			4	
0 3 2	1·581			0	

TABLE 5—*continued*

$h\ k\ l$	d_c	d_o	nI_c		I_o
0 1 6	1·563	1·548	25	0	vw
1 1 6	1·555			0	
2 0 6	1·555			0	
1 3 2	1·554			0	
$\bar{4}$ 0 3	1·553			13	
0 2 5	1·548			0	
$\bar{2}$ 2 4	1·548			3	
4 0 4	1·548			4	
1 2 5	1·538			0	
3 1 5	1·536			5	
$\bar{1}$ 3 2	1·536			0	
2 3 0	1·520	—		3	—
$\bar{3}$ 2 3	1·511	—	8	2	—
2 3 1	1·511			4	
$\bar{1}$ 1 6	1·502			1	
$\bar{1}$ 2 5	1·497			1	
$\bar{2}$ 3 1	1·493	—	13	0	vvw
0 3 3	1·488			0	
4 2 0	1·487			1	
4 2 1	1·486			2	
2 1 6	1·484			0	
$\bar{4}$ 1 3	1·483			1	
3 2 4	1·479			7	
4 1 4	1·479			2	
1 3 3	1·470	—	2	1	—
2 3 2	1·468			1	
2 2 5	1·466			0	
$\bar{4}$ 2 1	1·456	—	0	0	—
$\bar{2}$ 0 6	1·456			0	
4 2 2	1·453			0	
$\bar{1}$ 3 3	1·445	—		0	—
$\bar{2}$ 3 2	1·436	—		0	—
5 1 1	1·422	—	8	1	—
5 1 0	1·420			1	
$\bar{4}$ 0 4	1·420			1	
$\bar{3}$ 1 5	1·416			0	
*4 0 5	1·414			5	
3 3 0	1·381	1·379	19	0	vvw
0 3 4	1·381			17	
3 3 1	1·377			1	
0 2 6	1·374			0	
3 1 6	1·374			1	
$\bar{4}$ 2 3	1·319	1·316	14	3	vvw
2 3 4	1·316			8	
4 2 4	1·316			1	
$\bar{1}$ 1 7	1·316			2	
$\bar{3}$ 3 2	1·312			0	
4 3 0	1·238	1·235	19	1	vvw
4 3 1	1·238			4	
6 0 1	1·238			0	
$\bar{4}$ 2 4	1·235			1	
3 1 7	1·235			0	
0 0 8	1·235			10	
6 0 0	1·233			0	
1 4 0	1·233			0	
3 3 4	1·232			1	
4 2 5	1·232			1	

* Starting from (4 0 5), reflections have been omitted if the calculated intensities are lower than 8.

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Résumé—On décrit les structures cristallines du *trans*-polydécénamère $[\text{—CH=CH—(CH}_2)_8\text{—}]_p$ et du *trans*-polyocténamère $[\text{—CH=CH—(CH}_2)_6\text{—})_p$ cristallisés dans la modification monoclinique des *trans*-polyalkénamères pairs. La structure du *trans*-polydécénamère a été déterminée par l'étude aux rayons X des spectres de fibre, tandis que celle du *trans*-polyocténamère a été déterminée à partir des spectres de poudre.

Les constantes des mailles élémentaires sont les suivantes:

$$\textit{trans}\text{-polydécénamère}\left\{\begin{array}{l} a=7{,}42\ \text{Å};\ b=5{,}00\ \text{Å};\ c=12{,}41\ \text{Å (axe de la fibre)}\\ \beta=85^\circ\, 50';\ \text{groupe spatial P}2_1/a\\ Z=1\ (C_{10}H_{18});\ d_x=1{\cdot}005\ \text{g/cm}^3\end{array}\right.$$

$$\textit{trans}\text{-polyocténamère}\left\{\begin{array}{l} a=7{,}43\ \text{Å};\ b=5{,}00\ \text{Å};\ c=9{,}91\ \text{Å (axe de la fibre)}\\ \beta=84^\circ\, 50';\ \text{groupe spatial P}2_1/a\\ Z=2\ (C_8H_{14});\ d_x=1{\cdot}001\ \text{g/cm}^3\end{array}\right.$$

Les angles de rotation interne sur les liaisons simples adjacentes à chaque double liaison ont respectivement, à l'état cristallin, les valeurs de 130° et 230°. La répétition le long de l'axe de la macromolécule a lieu après une unité chimique grâce à des centres de symétrie.

L'assemblage des macromolécules est réglé par la juxtaposition des atomes d'hydrogène des groupes CH_2 de sorte que chacun d'eux se place dans l'espace laissé libre par trois atomes d'hydrogène d'une molécule adjacente.

Les valeurs des angles β des mailles élémentaires du *trans*-polydécénamère et du *trans*-polyocténamère sont strictement liées à l'inclinaison, sur l'axe *c*, du plan sur lequel sont placés les atomes de carbone.

La structure monoclinique des *trans*-polyalkénamères pairs est semblable à la structure rhombique des *trans*-polyalkénamères impairs et du polyéthylène.

Sommario—Si descrivono le strutture cristalline del *trans*-polidecenamero $[\text{—CH=CH—(CH}_2)_8\text{—}]_p$ e del *trans*-poliottenamero $[\text{—CH=CH—(CH}_2)_6\text{—}]_p$ cristallizzati nella modificazione monoclina dei *trans*-polialchenameri pari. La struttura del *trans*-polidecenamero è stata determinata mediante lo studio ai raggi X di spettri di fibra, mentre quella del *trans*-poliottenamero è stata determinata mediante lo studio di spettri di polvere.

Le costanti delle celle elementari sono:

$$\textit{trans}\text{-polidecenamero}\left\{\begin{array}{l} a=7{,}42\ \text{Å};\ b=5{,}00\ \text{Å};\ c=12{,}41\ \text{Å (asse della fibra)}\\ \beta=85^\circ\, 50';\ \text{gruppo spaziale P}2_1/a\\ Z=2(C_{10}H_{18});\ d_x=1{,}005\ \text{g/cm}^3\end{array}\right.$$

$$\textit{trans}\text{-poliottenamero}\left\{\begin{array}{l} a=7{,}43\ \text{Å};\ b=5{,}00\ \text{Å};\ c=9{,}91\ \text{Å (asse della fibra)}\\ \beta=84^\circ\, 50';\ \text{gruppo spaziale P}2_1/a\\ Z=2(C_{10}H_{14});\ d_x=1{,}001\ \text{g/cm}^3\end{array}\right.$$

Gli angoli di rotazione interna sui legami semplici adiacenti a ciascun doppio legame assumono, allo stato cristallino, i valori di 130° e 230° rispettivamente. La ripetizione lungo l'asse della macromolecola si ha dopo una unità chimica ad opera di centri di simmetria. L'impacchettamento delle macromolecole è regolato dalla giustapposizione degli atomi di indrogeno dei gruppi CH_2 in modo tale che ognuno di essi si dispone nello spazio lasciato libero da tre atomi di idrogeno di una molecola adiacente.

I valori degli angoli β delle celle elementari del *trans*-polidecenamero e del *trans*-poliottenamero sono in stretta relazione con l'inclinazione, sull'asse *c*, del piano sul quale giacciono gli atomi di carbonio dei gruppi metilenici.

Le struttura monoclina dei *trans*-polialchenameri pari è simile alla struttura ortorombica dei *trans*-polialchenameri dispari e del politene.

Zusammenfassung—Man beschreibt die Kristallstrukturen des *trans*-Polydecenamers [—CH═CH—$(CH_2)_8$—$]_p$ und des *trans*-Polyoctenamers [—CH═CH—$(CH_2)_6$—$]_p$, die in der monoklinen Modifikation der geradzahligen Glieder der Serie der *trans*-Polyalkenameren kristallisieren. Die Struktur des *trans*-Polydecenamers wurde mit Hilfe der Röntgenbeugungsspektren von Fasern und die des *trans*-Polyoctenamers mit Hilfe der Pulverspektren bestimmt.

Die Parameter der Elementarzellen sind:

$$\textit{trans}\text{-Polydecenamer}\ \begin{cases} a = 7{\cdot}42\ \text{Å};\ b = 5{\cdot}00\ \text{Å};\ c = 12{\cdot}41\ \text{Å (Faserachse)} \\ \beta = 85^\circ\ 50';\ \text{Raumgruppe P}2_1/a \\ Z = 2(C_{10}H_{18});\ d_x = 1{\cdot}005\ \text{g/cm}^3 \end{cases}$$

$$\textit{trans}\text{-Polyoctenamer}\ \begin{cases} a = 7{\cdot}43\ \text{Å};\ b = 5{\cdot}00\ \text{Å};\ c = 9{\cdot}91\ \text{Å (Faserachse)} \\ \beta = 84^\circ\ 50';\ \text{Raumgruppe P}2_1/a \\ Z = 2(C_8H_{14});\ d_x = 1{\cdot}001\ \text{g/cm}^3 \end{cases}$$

Die inneren Rotationswinkel um die Einfachbindungen den Doppelbindungen benachbarten betragen 130° bzw. 230°.

Die Faseridentitätsperiode enthält eine chemische Struktureinheit, die sich durch Operation eines Symmetriezentrums wiederholt.

Die Raumpackung der Ketten ist durch die Anordnung der Wasserstoffatome der Methylengruppen so geregelt, dass jedes von ihnen in der durch drei Wasserstoffatome einer benachbarten Molekel gebildeten Lücke zu liegen kommt.

Die Werte der β-Winkel der Elementarzelle des *trans*-Polydecenamers und des *trans*-Polyoctenamers stehen in engem Zusammenhang mit dem Winkel, den die *c*-Achse mit der Ebene bildet, in der die Kohlenstoffatome der Methylengruppen liegen.

Die monokline Struktur der geradzahligen Glieder der Serie der *trans*-Polyalkenameren ist ähnlich der rhombischen Struktur der ungeradzahligen Glieder der Serie der *trans*-Polyalkenameren und des Polyäthylens.