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CRYSTAL STRUCTURES OF ODD AND EVEN
TRANS POLYALKENAMERS

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Abstract—The odd *trans* polyalkenamers $(-CH=CH-(CH_2)-_{2n+1})_p$ crystallize in orthorhombic unit cells, the equatorial dimensions of which are very similar to those found for orthorhombic polyethylene. The space group is the same (*Pnam*) for odd *trans* polyalkenamers or for orthorhombic polyethylene and the packing of the macromolecules is nearly identical for all these polymers. A three dimensional least squares refinement was carried out for *trans* polypentenamer and for *trans* polyheptenamer. The "full matrix" methods and the weighing scheme by Cruickshank were employed. An overall temperature factor was used in the refinement. The standard deviations of the final atomic co-ordinates of the C atoms range between 0·01 and 0·02 Å for both polymers. The even *trans* polyalkenamers $(-CH=CH-(CH_2)-_{2n})_p$ can crystallize either in a monoclinic unit cell or in a triclinic unit cell. The *a* and *b* axes of the monoclinic unit cells have the same value for all the *trans* polyalkenamers examined; the same is verified also for the triclinic unit cells. A three dimensional least squares refinement was carried out for the monoclinic forms of *trans* polydecenamer and of *trans* polydodecenamer. The standard deviations of the final atomic co-ordinates of the C atoms range between 0·02 and 0·03 Å for both polymers. The triclinic form of even *trans* polyalkenamers may be in some way connected to the triclinic form shown by cold-worked polyethylene. The triclinic structure of *trans* polyoctenamer and of *trans* polydecenamer have been checked by a three-dimensional Fourier analysis. The standard deviations of the atomic co-ordinates range from 0·02 to 0·04 Å for the C atoms of both polymers.

As REPORTED in previous papers[1-5] crystalline stereoregular linear polymers have been prepared via ring cleavage of many cyclo-olefines, according to the scheme:

$$\text{p HC= CH} \longrightarrow (-CH=CH-(CH_2)_n-)_p.$$
$$(\quad)$$
$$(CH_2)_n$$

Thus cyclobutene could be converted into polymers having the structure of *trans* 1,4 polybutadiene (polybutenamer), cyclopentene to *trans* polypentenamer, cycloheptene to *trans* polyheptenamer and so on, *trans* polyhexenamer, cannot be obtained by this method.† The *trans/cis* ratio in polyalkenamers depends on the catalyst employed and on the polymerization conditions. When the configuration of the double bond in polyalkenamers is mainly *trans* (~ 80 per cent of the total amount of the double bonds present in the polymer) the polymers are highly crystalline at room temperature. The linearity of *trans* polyalkenamers is proved by the absence of pendant vinyl double bonds. The same conclusion is reached by examining the values of the fibre axes and the chain conformations of the crystalline polymers.

The stereoregular linear *trans* polyalkenamers constitute a homologous series, the first member of which is polyacetylene and the last is polyethylene. The homology of this polymer series derives from the different length of the methylene sequence

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†According to NATTA *et al.*,[6] *trans* polyhexenamer may be obtained by stereospecific alternating copolymerization of butadiene with ethylene.

separating two consecutive *trans* double bonds along the polymer chain. In the general formula of *trans* polyalkenamers, the length of the methylene sequence n of each repeating unit, i.e. the number of methylene groups between two subsequent HC=CH *trans* double bonds, directly derives from the size of the starting cyclo-olefine.

When considering the physical properties and the crystal structures of the homologous series of *trans* polyalkenamers, we must bear in mind that all differences observed among the properties of each member of the series in practice depend, when the type of the crystal structure is the same, only on the number n of methylene groups between two subsequent double bonds. The molecular weights of the *trans* polyalkenamers obtained fall in the range in which there is no significant variation in the physical and structural properties in the solid state with the molecular weight.

As shown,[3] starting from *trans* polypentenamer, the melting points of polyalkenamers, when the crystal structure is similar, increase almost linearly with the reciprocal of the number, N, of carbon atoms contained in the chemical repeating unit. The melting points of *trans* polyalkenamers tend to the melting point of orthorhombic polyethylene ($N = \infty$). The patterns for the melting points of *trans* polyalkenamers, of n-alkanes, fatty acids, polyethers $(-O-(CH)_n-)_p$ etc. are similar. As in the case of n-alkanes, a first systematic difference lies in a distinction between the *trans* polyalkenamers having respectively an even or an odd number (N) of carbon atoms in the starting cyclo-olefine.

This difference is apparent by comparing the identity periods along the chains. The members with even N always contain only one chemical repeating unit in the fibre axis, whereas the members with odd N always contain two of them.[3] This is valid independent of the modification in which *trans* polyalkenamers crystallize. Consequently, the chain conformations of the odd and of the even members of the homologous series of *trans* polyalkenamers are different. This difference directly affects the packing of the macromolecules in the crystal lattice; it follows that the crystal structures of the odd and even members differ markedly.

Owing to the structural differences between the odd and the even members of the homologous series of *trans* polyalkenamers, they are considered separately in the subsequent discussion.

ODD MEMBERS OF THE HOMOLOGOUS SERIES OF TRANS POLYALKENAMERS

The odd members studied by us are *trans* polypentenamer $(-CH=CH-(CH_2)_3-)_p$ and *trans* polyheptenamer $(-CH=CH-(CH_2)_5-)_p$. The former is an elastomer (dilatometric melting point $+ 23°$) and is practically amorphous at room temperature in the absence of unidirectional stretch;[7] the latter is a plastomer (melting point 51°) and is crystalline at room temperature also without stretch.[3, 8]

The fibre spectra of both polymers can be interpreted on the basis of orthorhombic unit cells, the equatorial axes of which are very similar to those of orthorhombic polyethylene[9] (see Table 1).

The measured values of the fibre axes of *trans* polypentenamer $(11 \cdot 90 \text{ Å})$ and of *trans* polyheptenamer $(17 \cdot 10 \text{ Å})$ clearly indicate that two repeating units must be contained in the identity periods and that the main chain conformation is close to a planar zig-zag chain. When all the carbon atoms of the main chain lie on the same

TABLE 1. COMPARISON BETWEEN THE UNIT CELL PARAMETERS OF ODD *trans* POLYALKENAMERS
AND OF ORTHORHOMBIC POLYETHYLENE

Trans polypentenamer	*Trans* polyheptenamer	Orthorhombic polyethylene
$a = 7 \cdot 28 \pm 0 \cdot 10$ Å	$a = 7 \cdot 40 \pm 0 \cdot 10$ Å	$a = 7 \cdot 40 \pm 0 \cdot 10$ Å
$b = 4 \cdot 97 \pm 0 \cdot 05$ Å	$b = 5 \cdot 00 \pm 0 \cdot 05$ Å	$b = 4 \cdot 93 \pm 0 \cdot 05$ Å
$c = 11 \cdot 90 \pm 0 \cdot 10$ Å	$c = 17 \cdot 10 \pm 0 \cdot 15$ Å	$c = 2 \cdot 53 \pm 0 \cdot 02$ Å
(chain axis)	(chain axis)	(chain axis)
$Z = 4$ (C_5H_8)	$Z = 4$ (C_7H_{12})	$Z = 4$ (CH_2)
$d_x = 1 \cdot 05$ g/cm^3	$d_x = 1 \cdot 01$ g/cm^3	$d_x = 1 \cdot 01$ g/cm^3
space groups D_{2h}^{16} or C_{2v}^9	space groups D_{2h}^{16} or C_{2v}^9	space groups D_{2h}^{16} or C_{2v}^9

plane, the identity period of an odd *trans* polyalkenamer may be calculated according to relation 1:

$$c = 2\,l_1 \sin\left(\frac{\phi_1}{2}\right) \cdot (N\text{–}1) + 2\,l_2 \sin\left(\phi_2 - \frac{\phi_1}{2}\right) \tag{1}$$

where:

ϕ_1 = bond angle $\overset{\frown}{\text{C-C-C}}$;

ϕ_2 = bond angle $\overset{\frown}{\text{C=C-C}}$;

l_1 = bond length C–C;

l_2 = bond length C=C:

N = number of carbon atoms contained in the cyclo-olefine.

By assuming the angles $\overset{\frown}{\text{C-C-C}} = 110°$, $\overset{\frown}{\text{C=C-C}} = 120°$ and the bond lengths C–C $= 1 \cdot 54$ Å and C=C $= 1 \cdot 34$ Å, the identity period of a zig-zag chain conformation for *trans* polypentenamer is $12 \cdot 5$ Å and that for *trans* polyheptenamer is $17 \cdot 5$ Å. The measured identity periods $11 \cdot 90$ Å and $17 \cdot 10$ Å respectively are shorter than those calculated for a planar zig-zag conformation. The shortening of the chain axis indicates that the chain conformations of these *trans* polyalkenamers is not fully planar zig-zag. These shortenings may be fully justified on the basis of the principle of staggered bonds[10-12] extended to the double bonds.[13, 14]

According to this principle, the internal rotation angles on the single bonds adjacent to each double bond assume the values of $180° \pm 60°$ and $180° \mp 60°$ respectively, whereas those about all the remaining bonds are $180°$.

Two possibilities now arise:

(a) The two chemical units contained in the fibre axes may be brought in repetition by a two fold screw axis. The succession of the internal rotation angles around the single bonds adjacent to the double bonds is in this case: $120°–240°$ and $120°–240°$. Owing to the symmetry centre placed in the middle of the double bonds the intrinsic chain symmetry is S $(2/1)m$[15] (see Fig. 1). The mirror m is perpendicular to the two fold screw axis and is placed in the middle of the methylene group which divides the repeating units in two mirrored parts ($C_4 = 1/4\ c$ and $C_{11} = 3/4\ c$ in the case of *trans* polyheptenamer).

The identity period c can be calculated on the basis of relation (2).

$$c = 2\ \sqrt{[(1 \cdot 26\ N - 0 \cdot 67 \cos \sigma_1 - 0 \cdot 7)^2 + (0 \cdot 95 \cos \sigma_1 - 0 \cdot 53)^2]} \tag{2}$$
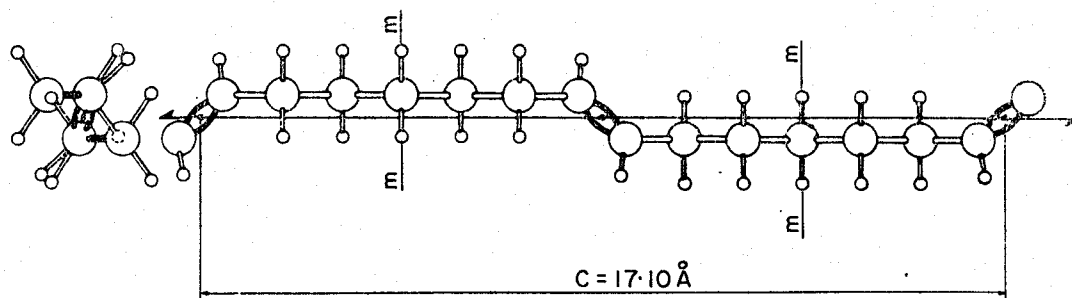
FIG. 1. *Trans* polyheptenamer, chain conformation in the crystal state (small circles H atoms, large circles C atoms).

where N = number or carbon atoms of the repeating unit and σ_1 is the torsional angle around the single bonds adjacent to a double bond ($120°$ or $130°$). The valence angles and the bond lengths assumed are the same as in relation 1.

The calculated identity periods are in this case, $11 \cdot 97$ and $17 \cdot 10$ Å respectively for *trans* polypentenamer and for *trans* polyheptenamer.

(b) The two units may be brought in repetition by a glide plane parallel to the fibre axis. The succession of the internal rotation angles about the above defined bonds is in this case $120°$, $240°$ and $240°$, $120°$.

The intrinsic symmetry of the resulting chain is $t\ i\ c$.[15] Besides the symmetry centres placed in the middle of the double bonds and the glide plane parallel to the chain axis, there are 2 two-fold axes, perpendicular to the glide plane and placed in the middle of the C atoms which divide the repeating units in two symmetrical parts ($C_3 = 1/4\ c$ and $C_8 = 3/4\ c$, in the case of *trans* polypentenamer). The calculated identity period is $12 \cdot 0$ Å for *trans* polypentenamer.

A choice between the two models is possible on the basis of the principle that all intrinsic symmetry elements of the macromolecule must be maintained in the crystal lattice.

As said before, the possible space groups are P*nam* (D_{2h}^{16})[16] or P*na*2_1 (C_{2v}^9); on the basis of the principle stated, the symmetry elements of the model labelled 2 (symmetry $t\ i\ c$) cannot find a respondence in any of the two space groups.

Now, we can say that the macromolecules of *trans* polypentenamer and of *trans* polyheptenamer in the crystals assume a two fold screw axis conformation. By assuming that all the intrinsic symmetry elements of the molecule are maintained in the unit cell, the space group is D_{2h}^{16} in its P*nam* orientation.

This crystalline form of odd *trans* polyalkenamers was designated by us Structure I. It is the only form observed so far with certainty in the odd series.[8-3]

The glide plane type conformation ($t\ i\ c$ symmetry), although never isolated with certainty, may be present, in special conditions, as shown by the presence of some i.r. absorption bands that cannot be attributed to Structure I. This modification will be called Structure II: probably it corresponds to the packing of chains with $t\ i\ c$ symmetry.[3]

From the study of packing according to model (1) and on the basis of the limitations imposed by the unit cell dimensions and symmetry (P*nam* space group), it follows that the macromolecules are oriented in the $a\ b$ plane in such a way that the two planes (see Fig. 2) containing the C atoms (five by five for polypentenamer and seven by seven for polyheptenamer) make an angle of $\sim 41°$ with the b axis. This leads to very good
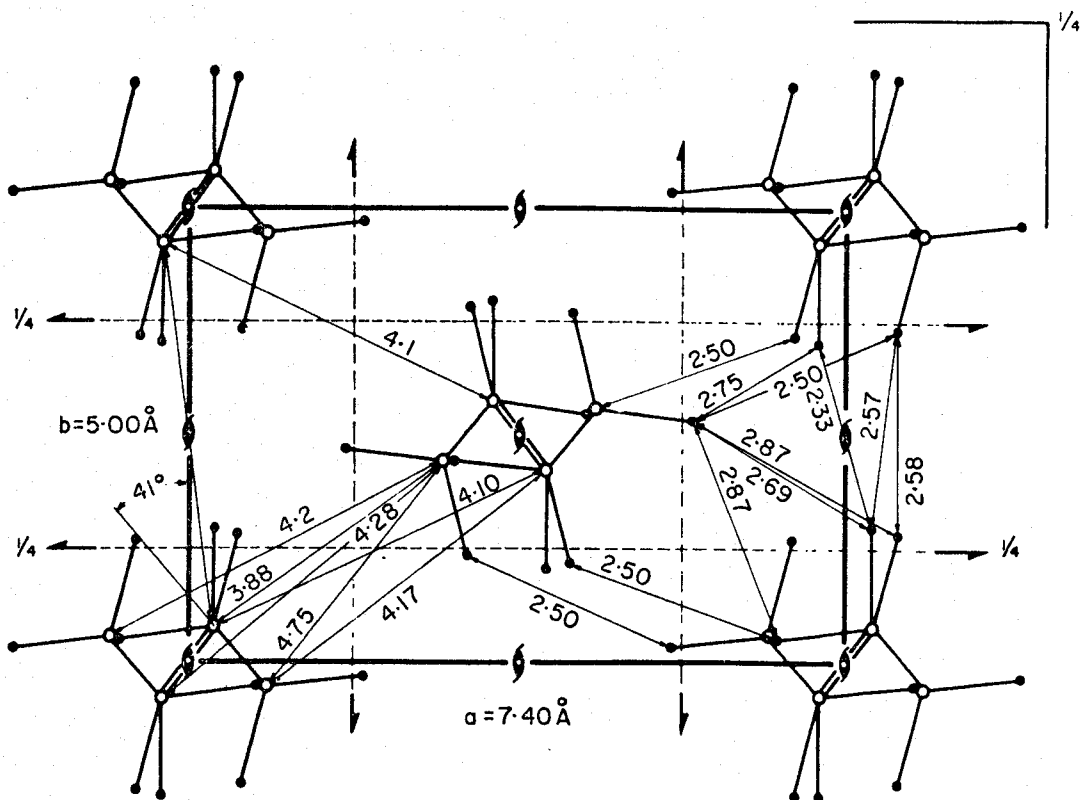
FIG. 2. Projection of the structure of *trans* polyheptenamer on (001). Open circles C atoms, full circles H atoms. Some of the most significant intermolecular distances are drawn.
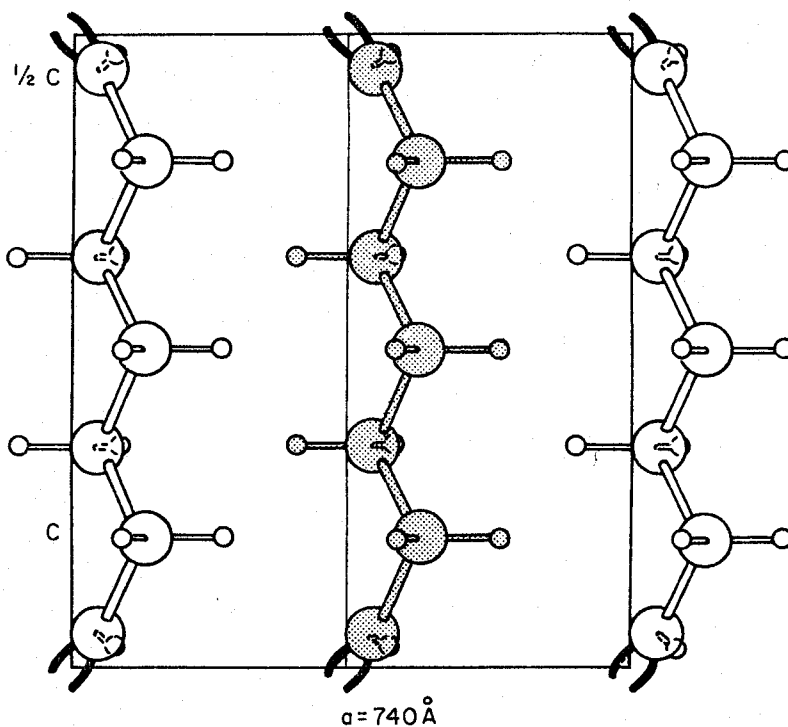
FIG. 3. Projection on (010) of the crystal structure of *trans* polyheptenamer. Large circles C atoms, small circles H atoms.

van der Waals interactions. Each H atom of the methylene groups is disposed in the depression among three H atoms of an adjacent molecule (Fig. 3); in other words, the macromolecules are close-packed at their best. Successive trial structure factors calculations were performed by rotating the molecule around its two fold screw axis.

Hydrogen atoms were also included in the calculations (C–H = 1·08 Å, $\overarc{\text{C–C–H}}$ = $\overarc{\text{H–C–H}}$ = 109°28', $\overarc{\text{C=C–H}}$ = 120°).

The best agreement between Fc and Fo was reached for a θ angle of 41°. The reliability index calculated on the basis of the relation 3

$$R = \frac{\Sigma \, \| \, Fo \, | \, - \, | \, Fc \, \|}{\Sigma \, | \, Fo \, |} \tag{3}$$

is 0·16 for *trans* polypentenamer and 0·20 for *trans* polyheptenamer. The absent reflections were not introduced in the calculations. The intensity of these reflections was estimated as being half the lowest intensity measured in correspondence of the layer of the reflection considered.

The macromolecular models used in the calculations had torsional angles around the single bonds adjacent to the double bonds of 130° and 230° owing to the indications of a two dimensional Fourier projection of the structure on (001).[17]

A three-dimensional least squares refinement was carried out using the general crystallographic programme by A. Immirzi.[18] The "full matrix" methods and the weighing scheme by Cruickshank[19] were employed. Sixty-seven observed reflections were employed for *trans* polypentenamer and 76 observed reflections were introduced in the three dimensional refinement for *trans* polyheptenamer.

An overall temperature factor was used in the refinement. The R index after four cycles dropped from 16 to 11 per cent for *trans* polypentenamer and from 20 to 16 per cent for *trans* polyheptenamer. The final co-ordinates of C atoms and their standard deviations (Å) are reported in Table 2. The $\overarc{\text{C–C–C}}$ and $\overarc{\text{C=C–C}}$ bond angles

TABLE 2. THREE-DIMENSIONALLY REFINED CO-ORDINATES AND THEIR STANDARD DEVIATIONS FOR *trans* POLYHEPTENAMER AND FOR *trans* POLYPENTENAMER

		x	y	z	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)	B
Trans poly	C1	0·0388	0·0777	0·0267	0·01	0·02	0·02	4·73
heptenamer	C2	0·1134	0·0543	0·1048	0·01	0·02	0·02	4·73
	C3	0·0347	0·0747	0·1753	0·01	0·02	0·02	4·73
	C4	0·1129	0·0582	0·2500	0·02	0·02	0·00	4·73
Trans poly	C1	0·0449	0·0690	0·0389	0·01	0·02	0·02	3·87
pentenamer	C2	0·1196	0·0540	0·1458	0·01	0·01	0·02	3·87
	C3	0·0385	0·0674	0·2500	0·01	0·02	0·00	3·87

tend to be 112° and 120° respectively, whereas the torsional angles around the single bonds adjacent to the double bonds tend to the values of 120° and 240° for both polymers. The torsional angles around all the remaining bonds tend to 180° and the bond lengths are 1·54 and 1·34 Å for C–C and C=C respectively. Figures 4(a) and (b) report the results of a three-dimensional Fourier synthesis for *trans* polypentenamer.

One of them (a) corresponds to the electron density at the heights 15/60 c and 8/60 c respectively, the other (b) corresponds to the electron density in the plane of the zig-zag part of the chain (plane 4x + 3y — 3/10 = 0).

EVEN MEMBERS OF THE HOMOLOGOUS SERIES OF
TRANS POLYALKENAMERS

The even members examined by us were *trans* polyoctenamer $(-CH=CH-(CH_2)_6)_p$, *trans* polydecenamer $(-CH=CH-(CH_2)_8-)_p$ and *trans* polydodecenamer $(-CH=CH-(CH_2)_{10}-)_p$. They are all plastomers at room temperature and can crystallize in at least two different modifications, one triclinic and the other monoclinic. We have labelled the triclinic modification as Structure III and the monoclinic as Structure IV.[3, 20, 21]

Trans polyoctenamer crystallizes in Structure III directly from the melt, and can be crystallized in Structure IV by evaporating a toluene solution of the polymer at low temperature ($\sim$ 0°).

Trans polydecenamer and *trans* polydodecenamer, on the contrary, crystallize in Structure IV directly from the melt and can be crystallized in Structure III by evaporating at low temperature ($\sim$ 0°) a toluene solution of the polymers.

The fibre axes of both modifications are practically identical and contain only one chemical repeating unit, i.e. the chain conformation is the same in the monoclinic and in the triclinic forms.

Owing to the very different packing of the molecules in the two crystalline modifications, they should be treated separately.

EVEN *TRANS* POLYALKENAMERS CRYSTALLIZED IN THE
MONOCLINIC FORM (STRUCTURE IV)

The fibre spectra of even *trans* polyalkenamers crystallized in Structure IV can be interpreted on the basis of monoclinic unit cells, the parameters of which are reported in Table 3.[20, 21]

The structure of monoclinic *trans* polyoctenamer was derived from the powder spectra. It is worth noticing that the $a \sin \beta$ and b axes of the unit cell of monoclinic *trans* polyalkenamers have values very similar to those of the orthorhombic unit cells of odd *trans* polyalkenamers and polyethylene (see Table 1).

When all the carbon atoms of the main chain lie on the same plane, the identity period of an even *trans* polyalkenamer may be calculated according to relation 4:

$$c = l_1 \sin \left(\frac{\phi_1}{2}\right) (N-1) + l_2 \sin \left(\phi_2 - \frac{\phi_1}{2}\right) \tag{4}$$

where c, l_1, ϕ_1 etc. have the same meaning as in relation 1. Also in this case, the measured identity periods are shorter than those calculated for a fully planar zig-zag chain and this shortening may be explained, as in the case of the odd members, on the basis of the principle of the staggered bonds extended to double bonds.

By assuming that the internal rotation angles are all 180°, except for the torsional angles around the single bond adjacent to each double bond which are 180° $\pm$ 60°

TABLE 3. COMPARISON BETWEEN THE UNIT CELL PARAMETERS OF MONOCLINIC EVEN
trans POLYALKENAMERS

Trans polyoctenamer	*Trans* polydecenamer	*Trans* polydodecenamer
a sin β = 7·40 ± 0·05 Å	a sin β = 7·40 ± 0·05 Å	a sin β = 7·40 ± 0·05 Å
b = 5·00 ± 0·05 Å	b = 5·00 ± 0·05 Å	b = 5·00 ± 0·05 Å
a = 7·43 ± 0·05 Å	a = 7·42 ± 0·05 Å	a = 7·43 ± 0·10 Å
c = 9·90 ± 0·10 Å	c = 12·40 ± 0·10 Å	c = 14·85 ± 0·15 Å
(chain axis)	(chain axis)	(chain axis)
β = 95°10′ ± 15′	β = 94°10′ ± 15′	β = 93°30′ ± 15′
Z = 2 (C_8H_{14})	Z = 2 ($C_{10}H_{18}$)	Z = 2 ($C_{12}H_{22}$)
d_x = 1·00 g/cm³	d_x = 1·00 g/cm³	d_x = 1·00 g/cm³
space group $P2_1/a$	space group $P2_1/a$	space group $P2_1/a$

and 180° ∓ 60° respectively, we can calculate identity periods along the chain in good agreement with the measured values.

According to relations 5 and 6 we have:

$$c = \sqrt{[d^2 + (1·16 \sin \sigma_1)^2]} \tag{5}$$

$$d = \sqrt{[(1·26 N - 0·67 \cos \sigma_1 - 0·71)^2 + (0·95 \cos \sigma_1 - 0·53)^2]} \tag{6}$$

where N is the number of carbon atoms in the chemical repeating unit, σ_1 is the torsional angle around the single bond adjacent to a double bond and d is the projection of the fibre axis on the plane on which the carbon atoms lie.

Relations 5 and 6 hold when the angle C–C–C is 110°, the angle C=C–C is 120° and the bond length C–C and C=C are 1·54 and 1·34 Å respectively.

By assuming for the torsional angle σ_1 the value of 130°, we can calculate the identity period of all *trans* polyalkenamers.

The chain conformation of the first member of the homologous series, polyacetylene {n = (number of CH_2 groups) = 0} because of the conjugated double bonds, is a fully extended planar zig-zag and its identity period may be calculated on the basis of relation 4. The chains of polyacetylene and of polyethylene have the same symmetry (S(2/1)d m).

In the case of monoclinic *trans* polyalkenamers, the torsional angles σ_1 seem to have the values of 130° and 230° instead of 120° and 240°.[22]

According to the nomenclature proposed by Corradini,[15] the intrinsic symmetry of the macromolecule is *ti*. The symmetry centres are placed in the middle of the double bonds and in the middle of the bond at half identity period (C_4C_5 in the case of *trans* polyoctenamer (see Fig. 5).

All carbon atoms of the repeating units lie on a plane inclined toward the c axes at an angle δ defined by relation 7:

$$\tan \delta = \frac{1·16 \sin \sigma_1}{d} \tag{7}$$

Relationships (5) and (6) and (7) hold for the macromolecules of even *trans* polyalkenamers having *ti* symmetry for the various values of the parameter N ($N > 2$), number of carbon atoms of the chemical repeating unit. Table 4 reports the calculated
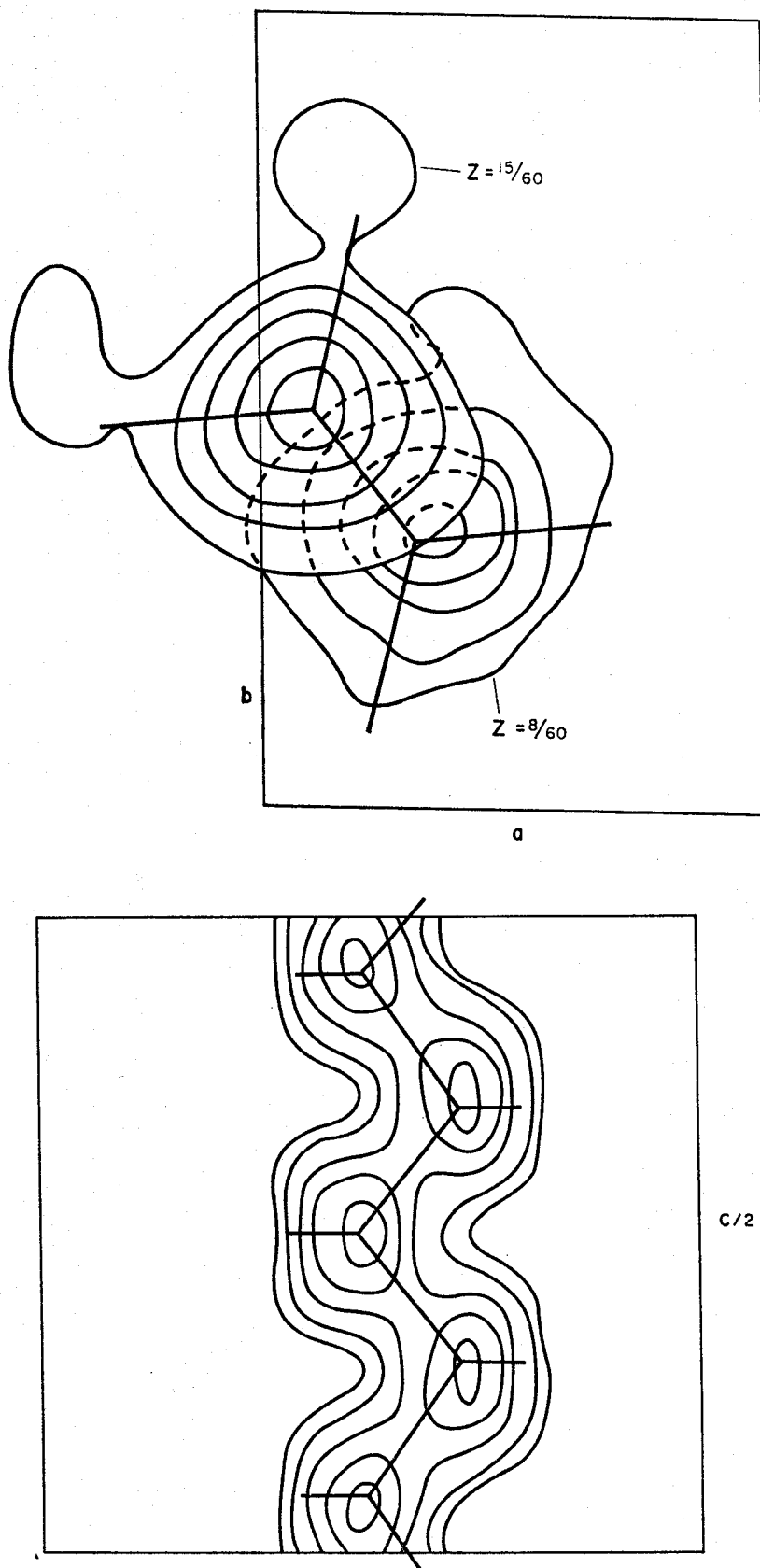
Fig. 4. (a) Three-dimensional Fourier summation, sections at 15/60 c and 8/60 c for *trans* polypentenamer. Contours are drawn at 0·5, 1, 2, 3, 4 e/Å². The C and H atoms of the molecule are indicated.

(b) Three-dimensional Fourier summation, section on the plane $4x + 3y - 3/10 = 0$, for *trans* polypentenamer. Contours are drawn at 0·5, 1, 2, 3, 4 e/Å². The C and H atoms of the molecule are indicated.

TABLE 4. CALCULATED IDENTITY PERIODS AND CALCULATED β ANGLES OF MONOCLINIC EVEN
trans POLYALKENAMERS

Trans polyalkenamer	$(-CH=CH-(CH_2)_{N-2}-)_p$	$c_{calc.}$ (Å)	$c_{obs.}$ (Å)	$\sigma_{calc.}$	$(\beta-90)_{obs.}$
Trans polybutadiene	$(-CH=CH-(CH_2)_2-)_p$	4·97	4·85 ± 0·05	10°18′	—
Trans polyhexenamer	$(-CH=CH-(CH_2)_4-)_p$	7·42	—	6°53′	—
Trans polyoctenamer	$(-CH=CH-(CH_2)_6-)_p$	9·9i	9·90 ± 0·10	5°8′	5°10′ ± 15′
Trans polydecenamer	$(-CH=CH-(CH_2)_8-)_p$	12·40	12·40 ± 0·10	4°7′	4°10′ ± 15′
Trans polydodecenamer	$(-CH=CH-(CH_2)_{10}-)_p$	14·91	14·85 ± 0·10	3°25′	3°30′ ± 15′
Trans polytetradecenamer	$(-CH=CH-(CH_2)_{12}-)_p$	17·41	—	2°55′	—

and experimental values of c and δ for many even *trans* polyalkenamers ($\sigma_1 = 130°$, $\sigma_2 = 230°$, $4 \leqslant N \leqslant 14$).

It is worth noticing that the angle δ tends to 0° with the increase of N so that the unit cell tends to become orthorhombic.

The arrangement of the molecules side by side was defined on the basis of the van der Waals interactions occurring by rotation of the molecule around its chain axis, and by taking into account the unit cell dimensions and symmetry (P2₁/a). When the angle, formed by the b axis of the unit cell and by the plane containing the carbon atoms of the chemical repeating unit, reaches a value of about 40°, all the intermolecular van der Waals contacts are at their best ($\sim 4·2$ Å between carbon atoms and $\sim 2·5$ Å between hydrogen atoms; C–H=1·08 Å, $\widehat{C-C-H}=\widehat{H-C-H} = 109°28'$, $\widehat{C=C-H}=120°$) (see Fig. 6).

A very similar orientation of the zig-zag chain in respect to the a and b axes of the unit cell was found for odd *trans* polyalkenamers ($\theta = 41°$) and for orthorhombic polyethylene ($\theta = 42°$).

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

The macromolecules of even *trans* polyalkenamers have intrinsically ti symmetry and the fibre axes are no longer parallel to the zig-zag paraffinic chain (see Fig. 5).

Due to the orientation (see Figs. 6 and 7) assumed by the molecules of even *trans* polyalkenamers in the monoclinic unit cells, a packing quite similar to that of orthorhombic
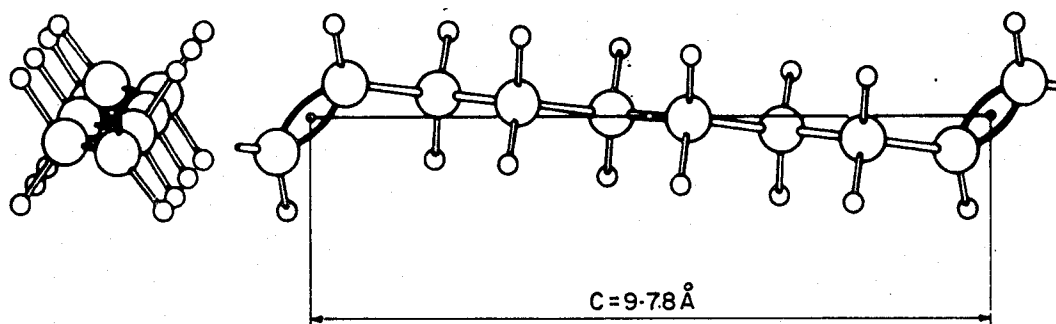

FIG. 5. Conformation of the chain of *trans* polyoctenamer in the crystal state. Large circles C atoms, small circles H atoms.
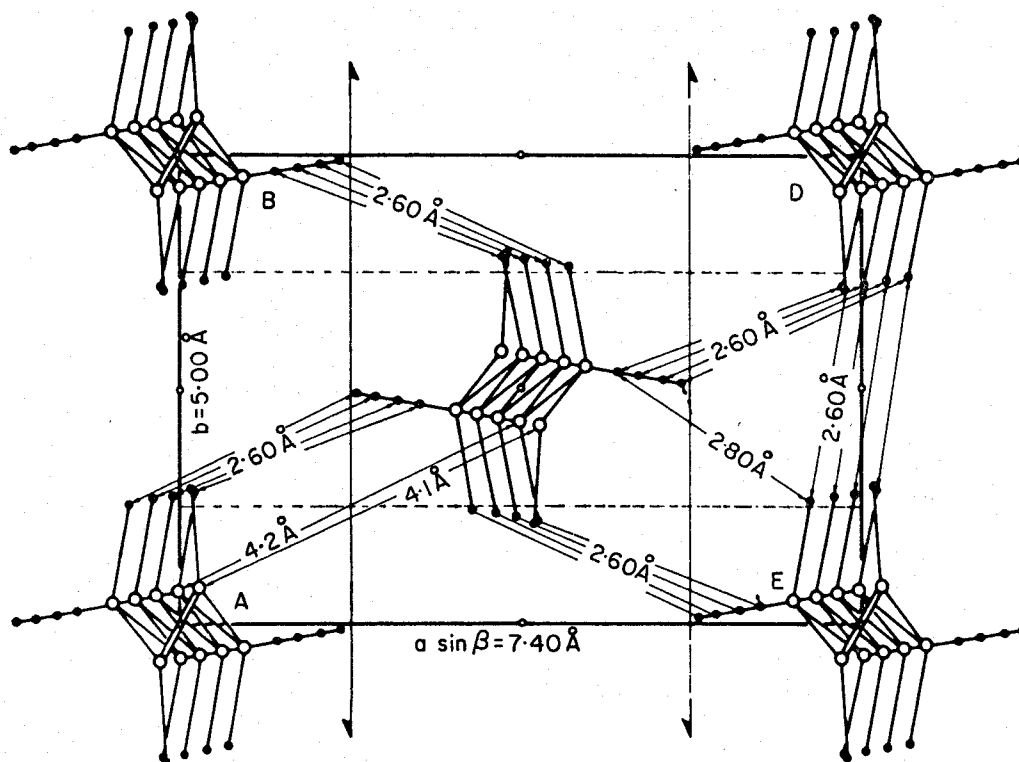
FIG. 6. Projection on (001) of the crystal structure of monoclinic *trans* polydecenamer. Open circles C atoms, full circles H atoms.
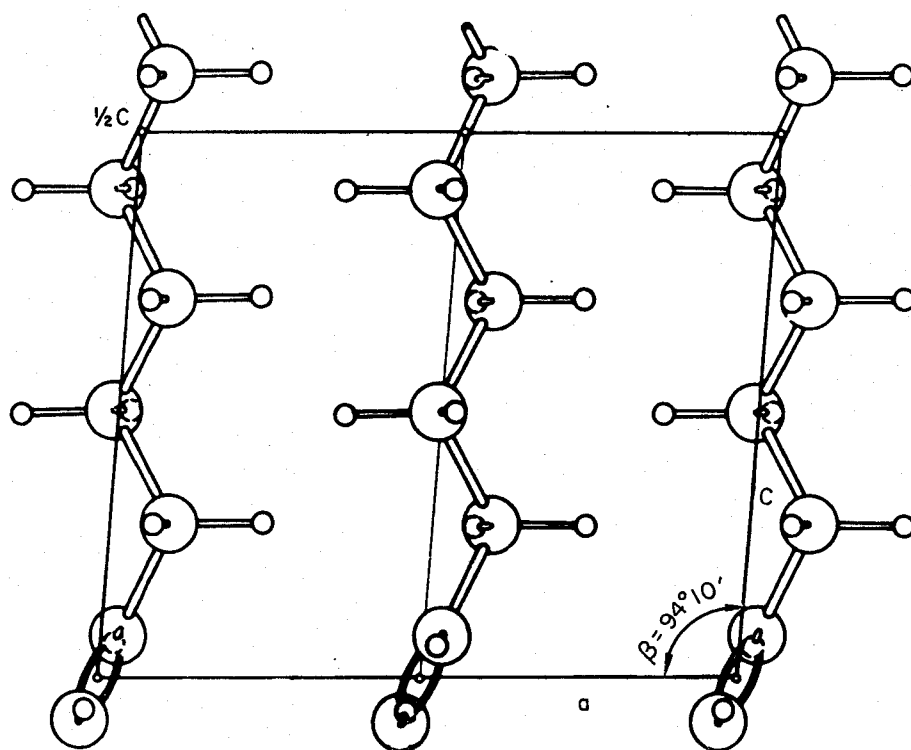

FIG. 7. Projection on (010) of the crystal structure of monoclinic *trans* polydecenamer. Large circles C atoms, small circles H atoms.

odd *trans* polyalkenamers may be reached only if the β angles deviate from 90°. Furthermore, if the (90° — β) angles are equal to the angles between the c axes and the plane of the zig-zag paraffinic chain, the H–H van der Waals' interactions between the macromolecules are exactly the same as in odd *trans* polyalkenamers and in orthorhombic polyethylene (see Fig. 7 c.f. with Fig. 3).

Furthermore the $P2_1/a$ space group can be simply derived from the P*nam* space group by changing the macromolecule intrinsic symmetry from $S(2_1)m$ (odd *trans* polyalkenamer) to *ti* (even *trans* polyalkenamers).

A three-dimensional (l values from 0 to 10 or 12) four cycles least squares refinement based on Immirzi's formula (18) dropped the R index, based on the observed reflections only, from $0 \cdot 25$ to $0 \cdot 22$ for *trans* polydecenamer (IV) and from $0 \cdot 24$ to $0 \cdot 22$ for *trans* polydecenamer (IV). Fifty-nine observed reflections were introduced in the calculations for *trans* polydecenamer while in the case of *trans* polydodecenamer there were 81. The atomic co-ordinates, their standard deviations, and the B value are reported in Table 5. The torsional angles around the single bonds adjacent to the

TABLE 5. THREE-DIMENSIONAL REFINED CO-ORDINATES AND THEIR STANDARD DEVIATIONS FOR MONOCLINIC *trans* POLYDECENAMER AND *trans* POLYDODECENAMER

		x	y	z	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)	B
Trans poly-decenamer	C1	$0 \cdot 0262$	$0 \cdot 0720$	$0 \cdot 0427$	$0 \cdot 02$	$0 \cdot 02$	$0 \cdot 03$	$4 \cdot 81$
	C2	$0 \cdot 0953$	$\overline{0} \cdot 0425$	$0 \cdot 1423$	$0 \cdot 02$	$0 \cdot 02$	$0 \cdot 03$	$4 \cdot 81$
	C3	$\overline{0} \cdot 0030$	$0 \cdot 0725$	$0 \cdot 2495$	$0 \cdot 02$	$0 \cdot 02$	$0 \cdot 03$	$4 \cdot 81$
	C4	$0 \cdot 0685$	$\overline{0} \cdot 0564$	$0 \cdot 3444$	$0 \cdot 02$	$0 \cdot 02$	$0 \cdot 03$	$4 \cdot 81$
	C5	$\overline{0} \cdot 0295$	$0 \cdot 0737$	$0 \cdot 4474$	$0 \cdot 02$	$0 \cdot 02$	$0 \cdot 03$	$4 \cdot 81$
Trans poly-dodecenamer	C1	$0 \cdot 0351$	$0 \cdot 0720$	$0 \cdot 0310$	$0 \cdot 02$	$0 \cdot 02$	$0 \cdot 03$	$5 \cdot 49$
	C2	$0 \cdot 0886$	$\overline{0} \cdot 0463$	$0 \cdot 1211$	$0 \cdot 02$	$0 \cdot 02$	$0 \cdot 03$	$5 \cdot 49$
	C3	$\overline{0} \cdot 0022$	$0 \cdot 0776$	$0 \cdot 2052$	$0 \cdot 02$	$0 \cdot 02$	$0 \cdot 03$	$5 \cdot 49$
	C4	$0 \cdot 0747$	$\overline{0} \cdot 0553$	$0 \cdot 2886$	$0 \cdot 02$	$0 \cdot 02$	$0 \cdot 03$	$5 \cdot 49$
	C5	$\overline{0} \cdot 0220$	$0 \cdot 0705$	$0 \cdot 3695$	$0 \cdot 02$	$0 \cdot 02$	$0 \cdot 03$	$5 \cdot 49$
	C6	$0 \cdot 0437$	$\overline{0} \cdot 0607$	$0 \cdot 4548$	$0 \cdot 02$	$0 \cdot 02$	$0 \cdot 03$	$5 \cdot 49$

double bonds tend to 130° for *trans* polydecenamer and to 120° for *trans* polydecenamer. The bond lengths and the bond angles tend to the usual values ($1 \cdot 54$ C–C, $1 \cdot 34$ C=C, $\overbrace{C-C-C}$ = 109°28', $\overbrace{C=C-C}$ = 120°). Figure 8 reports two sections of a three-dimensional Fourier summation.

The monoclinic structure found for even *trans* polyalkenamers is very similar to the monoclinic structure foreseen by Kitaigorodskii for even *n*-alkanes on the basis of close packing considerations.[23]

The molecules of monoclinic even *trans* polyalkenamers are arranged in layers by means of a simple translation (b axis) and the adjacent layers are turned by 180° around the 2_1 axes parallel to the b axes. Each molecule is surrounded by six nearest neighbours in a nearly-hexagonal array (Fig. 6). 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
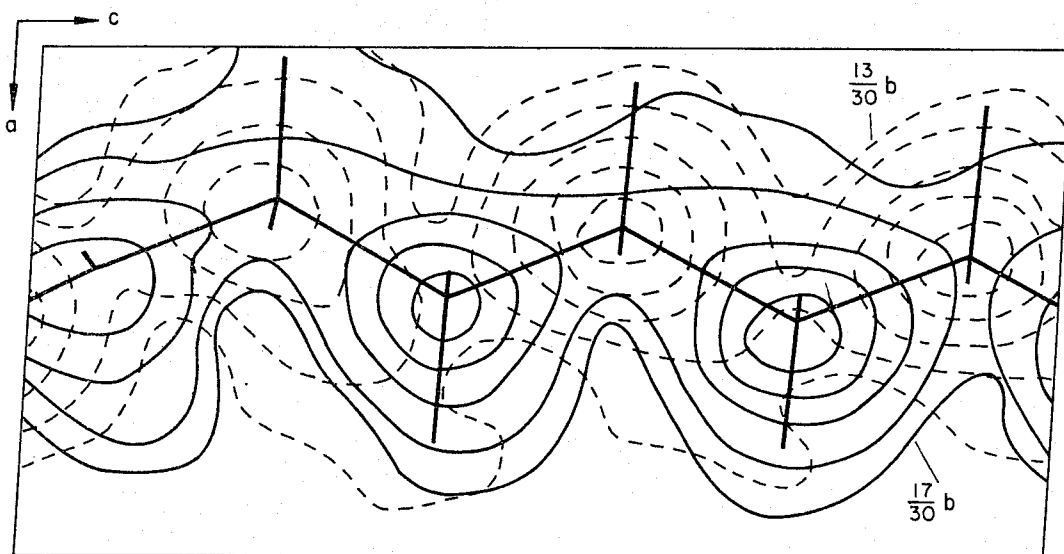
FIG. 8. Three-dimensional Fourier summation, sections at 13/30 b and 17/30 b. Contours are drawn at 0·5, 1, 2, 3 and 4 el/Å². The C and H atoms of the molecule of monoclinic *trans* polydodecenamer are indicated.

requirements of minimization of the lattice binding energy, whereas the latter by the minimization of the intramolecular conformational energy; obviously, the minimum lattice energy (β angle) largely depends on the shape of the molecules (torsional angles). As a result, the packing of the macromolecules of monoclinic even *trans* polyalkenamers are essentially conditioned by the paraffinic planar sequences as in the case of odd *trans* polyalkenamers.

EVEN *TRANS* POLYALKENAMERS CRYSTALLIZED IN THE TRICLINIC FORM (STRUCTURE III)

The fibre spectra of even *trans* polyalkenamers crystallized in Structure III can be interpreted on the basis of triclinic unit cells, the parameters of which are reported in Table 6.[24, 25]

The unit cells of odd *trans* polyalkenamers and of the monoclinic even *trans* polyalkenamers are similar to that of orthorhombic polyethylene; on the other hand,

TABLE 6. COMPARISON BETWEEN THE UNIT CELL PARAMETERS OF TRICLINIC EVEN *trans* POLYALKENAMERS

Trans polyoctenamer	*Trans* polydecenamer	*Trans* polydodecenamer
a sin β = 4·20 ± 0·05 Å	a sin β = 4·26 ± 0·05 Å	a sin β = 4·26 ± 0·05 Å
b sin α = 4·88 ± 0·05 Å	b sin α = 4·91 ± 0·05 Å	b sin α 4·91 ± 0·05 Å
a = 4·34 ± 0·05 Å	a = 4·40 ± 0·05 Å	a = 4·40 ± 0·05 Å
b = 5·41 ± 0·05 Å	b = 5·39 ± 0·05 Å	b = 5·39 ± 0·05 Å
c = 9·78 ± 0·10 Å	c = 12·30 ± 0·10 Å	c = 14·78 ± 0·10 Å
α = 64°25′ ± 25′	α = 65°30′ ± 25′	α = 65°30′ ± 25′
β = 104°50′ ± 25′	β = 104°30′ ± 25′	β = 104°30′ ± 25′
γ = 118°35′ ± 25′	γ = 118°25′ ± 25′	γ = 118°25′ ± 25′
180° − γ = 115° ± 25′	180° − γ = 115° ± 25′	180° − γ = 115° ± 25′
Z = 1(C_8H_{14})	Z = 1($C_{10}H_{18}$)	Z = 1($C_{12}H_{22}$)
d_x = 1·00 g/cm³	d_x = 0·98 g/cm³	d_x = 0·99 g/cm³
space group P$\bar{1}$	space group P$\bar{1}$	space group P$\bar{1}$

the unit cells of triclinic even *trans* polyalkenamers are equally similar to the triclinic unit cell proposed by Turner-Jones for the unstable modification of polyethylene.[26] By comparing Tables 3 and 6, the conformations of the macromolecule are clearly the same for even *trans* polyalkenamers crystallized either in the monoclinic or in the triclinic form. A little difference exists in the length of the fibre axis; the measured fibre axes of the triclinic form are a little shorter than those of the monoclinic form. We explained this difference by assuming that the torsional angles about the single bonds adjacent to each double bond tend, in the triclinic form, to the values of 120° and 240°, whereas in the monoclinic form they tend to 130° and 230°.

On the basis of relationships 5 and 6, it is possible to calculate the identity periods along the chain axes. The calculated identity periods are in agreement with those measured. The intrinsic symmetry of the chains is *ti* and the symmetry centres of the macromolecules are maintained as symmetry elements of the unit cell, so that the space group is P$\bar{1}$ for all the triclinic *trans* polyalkenamers examined.

The unit cells defined by the reciprocal lattice methods may be fully justified by packing considerations. Also the hydrogen atoms were considered (C–H=1·08 Å, $\overparen{\text{C–C–H}}$=$\overparen{\text{H–C–H}}$=109°28′ $\overparen{\text{C=C–H}}$ = 120°). Starting from the *c* projections of the unit cells and on the basis of the macromolecule models defined according to the principles exposed above, the orientation of the macromolecules in respect of the *a* sin β and *b* sin α axes was fixed by trial and error methods. The sets of x and y co-ordinates which brought to the best agreement between the calculated and observed structure factors of (*hk*0) reflections were assumed as starting points.
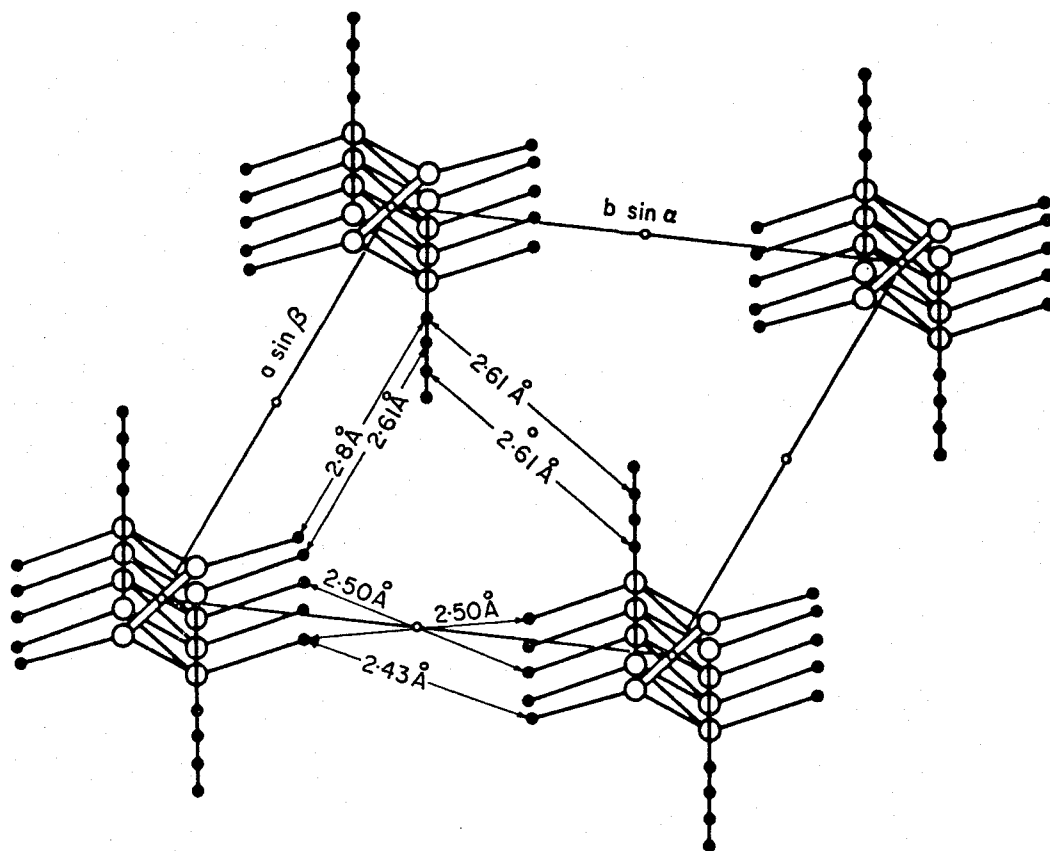

FIG. 9. Projection on (001) of the crystal structure of triclinic *trans* polydecenamer. Open circles C atoms, full circles H atoms.

The molecular orientation on the c projections being defined in this manner (see Fig. 9), we tested the β angle of the triclinic unit cells on the basis of the intermolecular van der Waals interactions. A β angle of $\sim 105°$, as shown in Figs. 10 and 11, is fully justified in order to have good distances between the C_1 carbon atoms of the molecules, whose chain axes are [0, 0, Z] and the C_8, C_{10}, C_{12}, carbon atoms of the molecules, whose chain axes are [1, 0, Z]. For these β values, the H atoms of the CH_2 groups of a molecule are interlocked in the hole among three H atoms of an adjacent molecule.
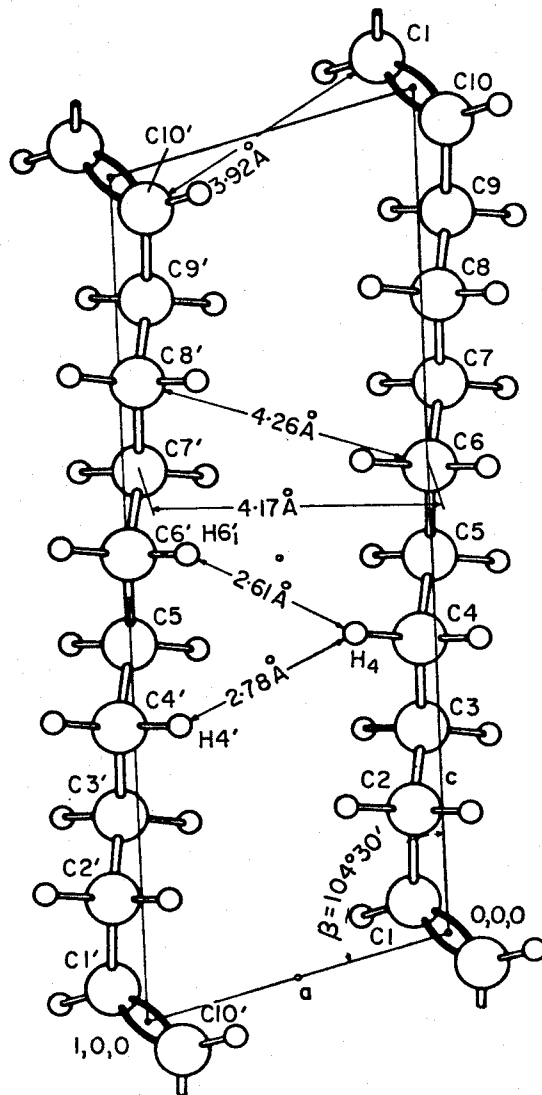
FIG. 10. Projection on (010) of the structure of *trans* polydecenamer. Large circles C atoms, small circles H atoms.

The molecules in [1, 0, Z] are lowered by $\sim 1 \cdot 10$ Å ($\sim -1/8\,c$, $\sim -1/10\,c$, $\sim -1/12\,c$ for *trans* polyoctenamer, *trans* polydecenamer, and *trans* polydodecenamer respectively) in respect of the molecules whose chain axes are [0, 0, Z].

The α figures of $\sim 64°$ are justified by the achievement of "optimum" conditions for the intermolecular distances between the molecules whose chain axes are [1, 1, Z] and the molecules in 0, 0, Z (Figs. 12 and 13). The molecules in [1, 1, Z] are raised by $\sim 1 \cdot 2$ Å ($\sim + 1/8\,c$, $\sim + 1/10\,c$, $\sim + 1/12\,c$) in respect of the molecule in [0, 0, Z]. The van der Waals distances between the pairs of the nearest C atoms placed at the
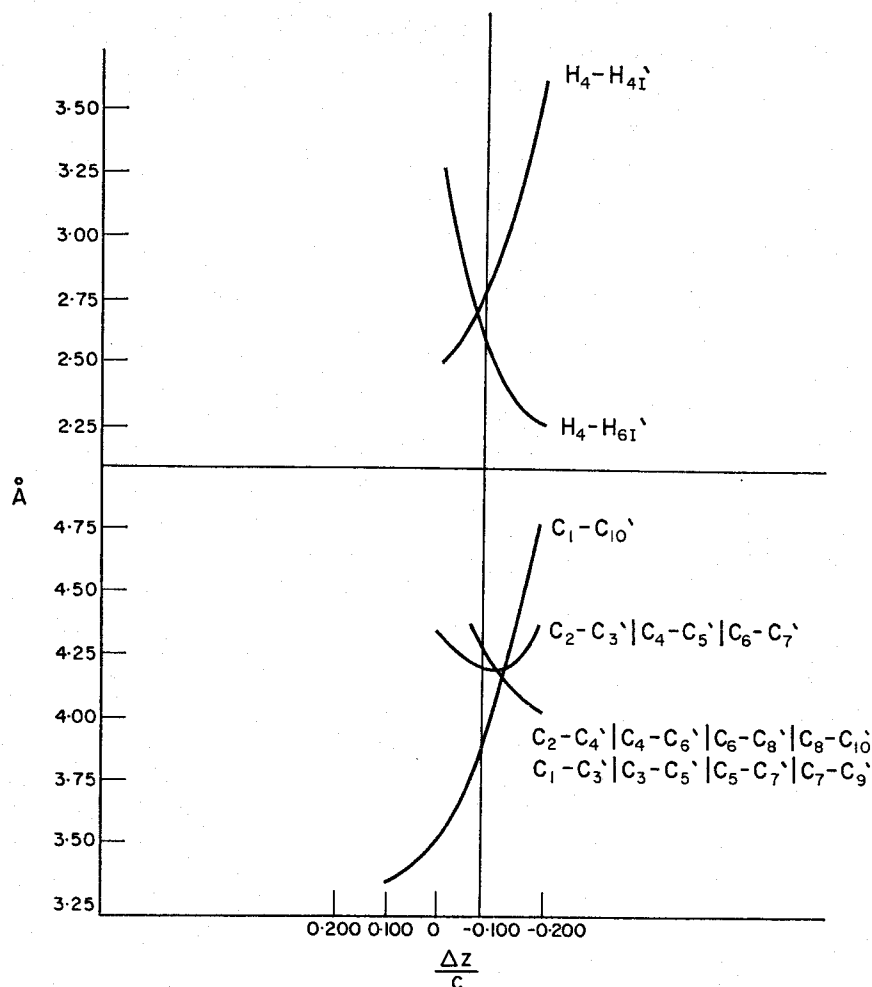
Fig. 11. Course of the C–C and H–H intermolecular interactions in the a, c plane of the structure of crystalline *trans* polydecenamer, as a function of the molecular displacements along the c axis.

same height along the c axes are all $4 \cdot 25$ Å and the shortest H–H interactions are $2 \cdot 50$ Å. All the C–C intermolecular interactions for these values of the α angles reach their maximum value ($4 \cdot 25$ Å).

The values found for the α angles are significant also with regard to the packing in the $b\ c$ planes. The molecules whose chain axis are $[0, 1, Z]$ are raised by $2 \cdot 30$ Å ($\sim + 2/8\ c$, $\sim + 2/10\ c$, $\sim + 2/12\ c$) in respect of the molecules in $[0, 0, Z]$; this disposition of the molecules is good for the close packing of the H atoms of the adjacent molecules (Fig. 14).

Table 7 reports the effective displacements along the c axes of the molecules of triclinic *trans* polyalkenamers adjacent to the molecules placed at the origin.

The packing of triclinic *trans* polyalkenamers is therefore such that each molecule is surrounded by six nearest neighbours displaced along the c axes by $\sim \pm 2/N\ c$ through the b axes, by $\sim \mp 1/N\ c$ through the a axes. The disposition of the macromolecules of triclinic even *trans* polyalkenamers obey the close packing conditions of molecules containing long paraffinic sequences. It is interesting to note that Kitaigorodskii, on the basis of close packing considerations, suggested for even n-alkanes a unit cell very similar to those found by us for even *trans* polyalkenamers.

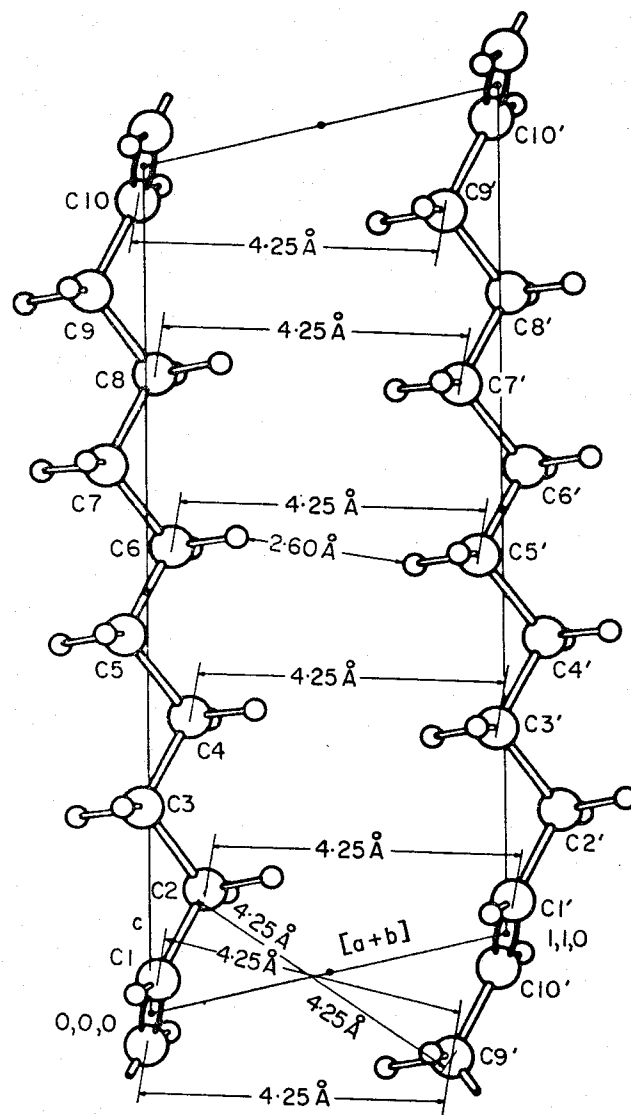For comparison purposes, we report here the unit cell parameters suggested by

Fig. 12. Projection on [a + b] c plane of the structure of *trans* polydecenamer. Large circles C atoms, small circles H atoms.

TABLE 7. DISPLACEMENTS ALONG THE c AXES OF THE MACROMOLECULES OF TRICLINIC *trans* POLYOCTENAMER, *trans* POLYDECENAMER AND *trans* POLYDODECENAMER

Trans polyalkenamer	Through the a axes	Displacements Through the b axes	Through the [a + b] axis	$c_{obs.}$ (Å)	c/n
Trans polyoctenamer	$- 0.90\ c/8$	$+ 0.96\ \dfrac{2c}{8}$	$+ 1.01\ c/8$	9.78	1.222
Trans polydecenamer	$- 0.89\ c/10$	$+ 0.91\ \dfrac{2c}{10}$	$+ 0.92\ c/10$	12.30	1.230
Trans polydodecenamer	$- 0.89\ c/12$	$+ 0.91\ \dfrac{2c}{12}$	$+ 0.92\ c/12$	14.78	1.231
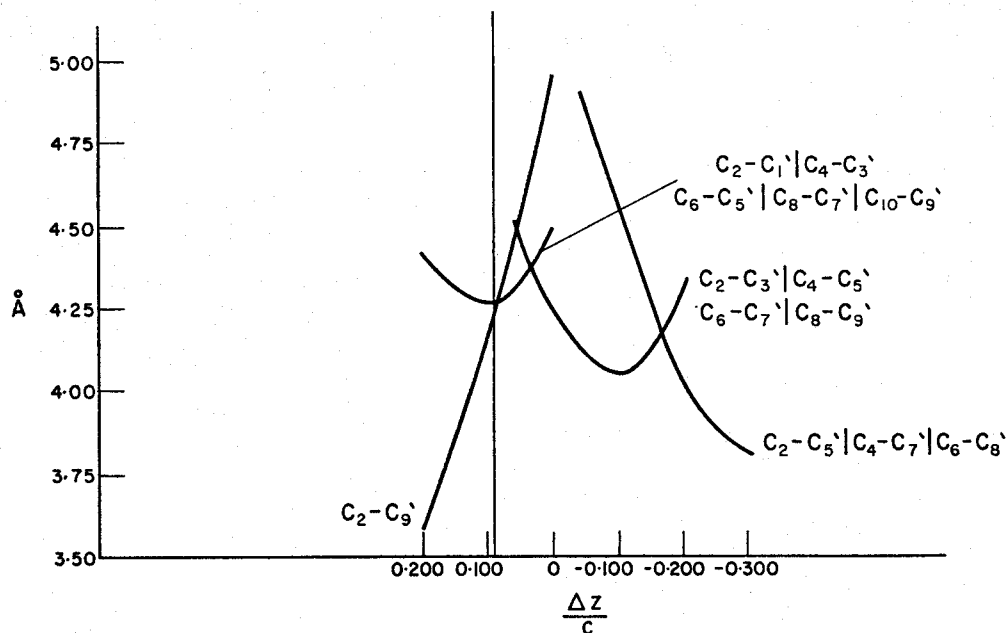
FIG. 13. Course of the C–C intermolecular interactions vs. the displacement of the molecules of *trans* polydecenamer along the c axis, in the $[a + b]$ c plane.

TABLE 8. COMPARISON BETWEEN THE UNIT CELL PARAMETERS OF TRICLINIC *trans* POLY-ALKENAMERS AND THOSE OF TRICLINIC n ALKANES SUGGESTED BY KITAIGORODSKII

	a	b	c	ϕ_a	ϕ_b	ϕ_c
Trans polyoctenamer III	4·34	5·41	9·78	111°	65°	27°
Trans polydecenamer III	4·40	5·39	12·30	109°30′	66°	26°
Trans polydodecenamer III	4·40	5·39	14·78	109°30′	66°	26°
Theoretical cell after Kitaigorodskii for even n-alkanes [T, $\bar{1}$, 1]	4·3	5·2	$C_0 = 2·54$	107°	60°	36°

TABLE 9. CO-ORDINATES AND THEIR STANDARD DEVIATIONS FOR *trans* POLYOCTENAMER AND FOR *trans* POLYDECENAMER (TRICLINIC)

		x	y	z	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)	B
Trans poly-octenamer	C1	0·0962	0·0151	0·0656	0·02	0·02	0·03	7·27
	C2	0·1445	0·1463	0·1694	0·02	0·02	0·03	7·27
	C3	0·0155	0·0546	0·3185	0·02	0·02	0·03	7·27
	C4	0·0757	0·1109	0·4197	0·02	0·02	0·03	7·27
Trans poly-decenamer	C1	0·0970	0·0254	0·0555	0·03	0·04	0·04	11·12
	C2	0·1708	0·1469	0·1332	0·03	0·04	0·04	11·12
	C3	0·0206	0·0627	0·2621	0·03	0·04	0·04	11·12
	C4	0·0961	0·1047	0·3410	0·03	0·04	0·04	11·12
	C5	0·0307	0·0832	0·4603	0·03	0·04	0·04	11·12

Kitaigorodskii for even *n*-alkanes and the parameters found for triclinic *trans* polyalkenamers (Table 8).

The angles ϕ_a, ϕ_b, ϕ_c are the angles formed by the paraffinic zig-zag chain with the *a* axes, with the *b* axes and with the normals to the [*a b*] planes (c^*) respectively.

The reliability index is R = 16°, R = 19 per cent for *trans* polyoctenamer and for *trans* polydecenamer respectively.
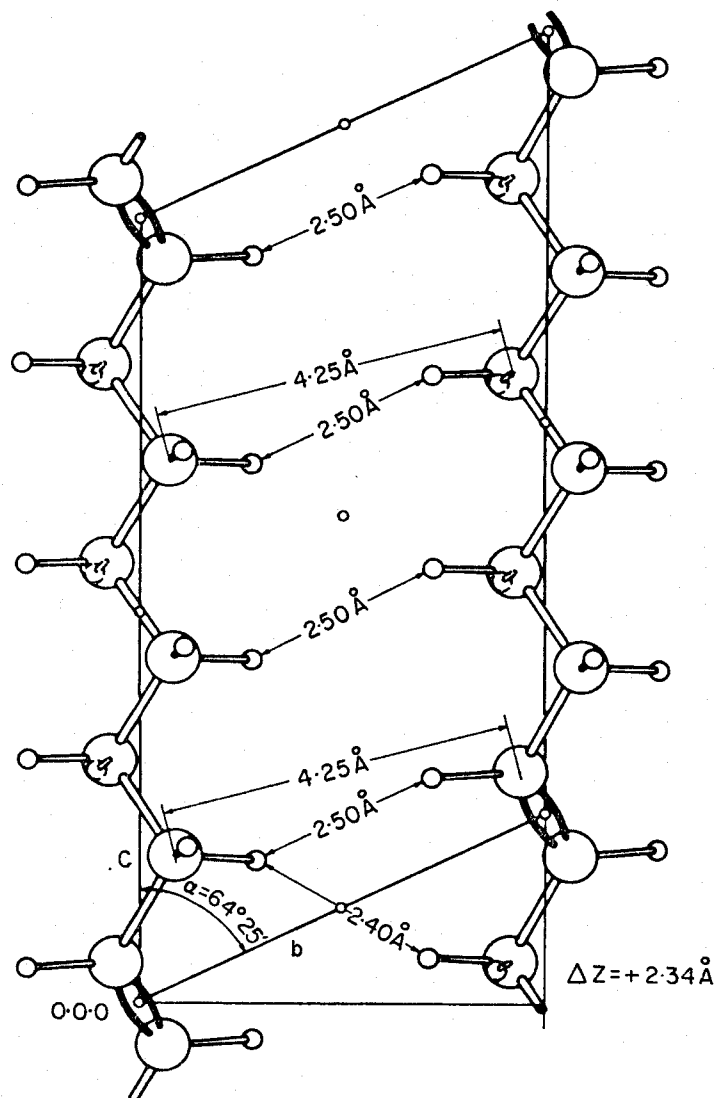

FIG. 14. Projection on (100) of the crystal structure of *trans* polydecenamer. Large circles C atoms, small circles H atoms.

The results of a three-dimensional Fourier analysis for triclinic *trans* polyoctenamer and triclinic *trans* polydecenamer are reported in Table 9. There were 47 observed reflections in the case of *trans* polyoctenamer while in the case of *trans* polydecenamer there were 48. The bond angles tend to 112° for *trans* polyoctenamer and for *trans* polydecenamer, and the bond lengths tend to the usual values. The torsional angles around the single bonds adjacent to the double bonds are 120° for both polymers. No three-dimensional refinement has been undertaken due to the diffuseness of the observed reflections and to the overlapping of many lattice planes.

For *trans* polydodecenamer the R value was not calculated it being difficult to define the experimental intensities of the reflections, due to the overlapping with some reflections of the monoclinic form.[3]

It is worth noticing that the packing of *trans* polybutadiene molecules ($N = 4$) does not follow the rules set out for monoclinic or triclinic even *trans* polyalkenamers.[27]

CONCLUSIONS

From a structural point of view, *trans* polyalkenamers constitute a homologous series, the first member of which is polyacetylene (-CH = CH-)$_p$ and the last is polyethylene (-CH$_2$-)$_p$. The internal rotation angles of *trans* polyalkenamers obey the principle of the staggered bonds. All torsional angles are 180°, except for the torsional angles on the single bonds adjacent to each double bond. The last torsional angles tend to assume the values of $180° \pm 60°$ and $180° \mp 60°$ respectively, so that in the middle of a double bond, a symmetry centre always occurs. Owing to the considerations above the chain does not assume a fully planar zig-zag conformation.

The odd members of the homologous series studied so far crystallize in orthorhombic units cells (Structure I of *trans* polyalkenamers) the equatorial axes of which are very similar to the a and b axes found in orthorhombic polyethylene. The space group is D$_{2h}^{16}$ (*Pnam*), the same as that of polyethylene, and the chain has S(2$_1$)m symmetry. The carbon atoms are disposed N by N (N = number of carbon atoms of the chemical repeating unit) on two parallel planes having the same orientation in respect of the a and b axes of the unit cell, as the planar zig-zag chain of polyethylene (angle between the zig-zag and the b axes $\sim 42°$). Each molecule is surrounded by six nearest neighbours in a nearly pseudo-hexagonal array. The chain packing is regulated by the juxtaposition of the H atoms of the CH$_2$ groups in such a way that each H atom is placed in the hole among three H atoms of an adjacent molecule.

The even members of the homologous series crystallize in two modifications, one monoclinic and the other triclinic. The second member of the series, i.e. *trans* polybutadiene, as in the case of the first members of other homologous series, does not obey this rule. The unit cell of the modification, stable at room temperature, of *trans* 1,4 polybutadiene is monoclinic, but the unit cell parameters[27] are very different from those of the even members with $N < 4$.

The monoclinic structure (Structure IV of *trans* polyalkenamers) may be derived directly from the orthorhombic structure of the odd members. The equatorial axes of the monoclinic modification ($a \sin \beta$ and b) have the same values as those found for the a and b axes of the odd members. The chain conformation is characterized by a *ti* symmetry and the C atoms are disposed on a plane inclined in respect of the chain axes by an angle δ, the value of which depends on the number of carbon atoms (N) of the starting cyclo-olefine.

The δ angle decreases as N increases and the angle δ is related to β by the relationship $\delta = \beta - 90°$. The molecules are packed in the same way as in the odd orthorhombic members. The δ angle is related to the β angle owing to the fact that each H atom of a molecule is exactly interlocked in the hole among three H atoms of an adjacent molecule.

The triclinic form of *trans* polyalkenamers (Structure III) may be somehow connected with the triclinic structure of polyethylene. The chain symmetry and the chain

conformation of triclinic *trans* polyalkenamers are the same as in the case of the monoclinic modification.

Each molecule is surrounded by six nearest neighbours in a nearly pseudo-hexagonal array.

The displacements of the molecules along the c axes in respect of that placed at the origin are $\sim \pm 2/N\, c$ through the b axes, $\sim \pm 1/N\, c$ through the $[a + b]$ axes and $\sim \mp 1/N\, c$ through the a axes.

The disposition of the molecules obey the close packing conditions of molecules containing long paraffinic sequences.

Packing conditions similar to those of the odd and even *trans* polyalkenamers were foreseen by Kitaigorodskii, on the basis of close packing considerations, for n alkanes.

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Résumé—Les polyalkénamères-*trans* à nombre de motifs impairs $(-CH = CH - (CH_2)-_{2n+1})_p$ forment des mailles cristallines orthorhombiques dont les dimensions équatoriales sont très proches de celles que l'on trouve pour le polyéthylène orthorhombique. Le groupe spatial (*Pnam*) est le même pour les polyalkénamères-*trans* impairs et pour le polyéthylène orthorhombique et l'empilement des

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macromolécules est presque identique pour tous ces polymères. On a effectué un traitement par écarts quadratiques moyens à trois dimensions pour le polypentenamer-*trans* et le polyheptenamer-*trans*. On a utilisé les méthodes de matrices pleines et le schéma pondéral de Cruickshank. Un facteur de tempéra-moyen a été utilisé dans le traitement Les écarts moyens des coordonnées atomiques des atomes de C sone de 0,01 à 0,02 Å pour les deux polymères.

Les polyalkénamères-*trans* pairs $(-CH=CH-(CH_2)-_{2n})_p$ forment des mailles cristallines monocliniques ou tricliniques. Les paramètres a et b de la maille élémentaire monoclinique ont la même valeur pour tous les polyalkénamères-*trans* examinés. On retrouve la même relation pour les mailles élémentaires tricliniques. Un traitement par écarts quadratiques moyens tridimensionnel a été effectué pour les formes monocliniques du polydécénamère-*trans* et le polydodécénamere-*trans*. Les écarts moyens des coordonnées des atomes de C ainsi obtenues sone de 0,02 à 0,03 Å pour les deux poly-mères. Les formes tricliniques des polyalkénamères-*trans* pairs semblent se rapprocher de la forme triclinique du polyéthylène déformé à froid. La structure triclinique du polyocténamère-*trans* et du polydécénamère-*trans* a été vérifiée par une analyse de Fourier à trois dimensions. Les écarts moyens des coordonnées des atomes de C ainsi obtenus sont de 0,02 à 0,04 Å pour les deux polymères.

Sommario—I trans polialchenameri dispari $(-CH=CH-(CH_2)-_{2n+1})_p$ cristallizzano in celle elementari rombiche i cui assi equatoriali sono molto simili a quelli del polietilene rombico. Il gruppo spaziale è uguale (*Pnam*) sia per il politene sia per i *trans* polialchenameri dispari e l'impacchettamento delle molecole è praticamente uguale per tutti questi polimeri. E' stato eseguito un ciclo di affinamento tridimensionale mediante i minimi quadrati delle strutture del *trans* polipentenamero e del *trans* polieptenamero. Sono stati impiegati i metodi "full matrix" e per i pesi ci siamo basati sullo schema fornito da Cruickshank. Le deviazioni standard delle coordinate atomiche finali degli atomi di carbonio sono comprese fra 0,01 e 0,02 Å per entrambi i polimeri. I *trans* polialchenameri della serie pari $(-CH=CH-(CH_2)-_{2n})_p$ possono cristallizzare in due forme cristalline una monoclina e l'altra triclina. Gli assi a e b delle celle elementari monocline sono uguali per tutti i *trans* polialchenameri pari esaminati; lo stesso si verifica nel caso delle modificazioni tricline. Si è eseguito un affinamento tridimensionale mediante i minimi quadrati delle strutture monocline del *trans* polidecenamero e del *trans* polidodecenamero. Le deviazioni standard delle coordinate atomiche finali degli atomi di carbonio sono comprese fra 0,02 e 0,03 Å per entrambi i polimeri. La struttura della forma triclina dei *trans* polialchenameri poi può essere ricondotta alla struttura triclina del politene lavorato a freddo. Le strutture tricline del *trans* poliottenamero e del *trans* polidecenamero sono state esaminate mediante una sintesi di Fourier tridimensionale. Le deviazioni standard delle coordinate degli atomi di carbonio sono comprese fra 0,02 e 0,04 Å. Non si è proceduto ad un affinamento di queste due strutture a causa delle numerose sovrapposizioni delle riflessioni.

Zusammenfassung—Die ungeraden *trans*-Polyalkenamere $(-CN=CH-(CH_2)-_{2n+1})_p$ kristallisieren in orthorhombischen Elementarzellen, deren äquatoriale Dimensionen denen für orthorhombisches Polyäthylen sehr nahe kommen. Die Raumgruppe (*Pnam*) ist die gleiche für ungerade *trans*-Poly-alkenamere und orthorhombisches Polyäthylen, auch ist die Packung der Makromoleküle nahezu identisch bei allen diesen Polymeren. Eine Anpassungsrechnung nach der Methode der kleinsten Quadrate wurde für *trans*-Polypentenamer und *trans*-Polyheptenamer durchgeführt.

Die "vollen Matrix" Methoden und das Bewertungsschema von Cruickshank wurden angewendet. Ein genereller Temperaturfaktor wurde bei dieser Anpassungsrechnung verwendet. Die Standardab-weichungen der sich ergebenden Atomkoordinaten der C-Atome lagen zwischen 0,01 Å und 0,02 Å bei beiden Polymeren.

Die geraden *trans*-Polyalkenamere $(-CH=CH-(CH_2)-_{2n})_p$ können entweder in einer mono-klinen oder einer triklinen Elementarzelle kristallisieren. Die a und b Achsen der monoklinen Zelle haben denselben Wert bei allen untersuchten *trans*-Polyalkenameren, das gleiche trifft zu für die trikline Zelle. Eine dreidimensionale Anpassungsrechnung nach der Methode der kleinsten Quadrate wurde bei den monoklinen Formen von *trans*-Polydecenamer und *trans*-Polydodecenamer ausgeführt. Die Standardabweichungen der sich ergebenden Atomkoordinaten für die C-Atome liegt zwischen 0,02 und 0,03 Å bei beiden Polymeren.

Die trikline Form der geraden *trans*-Polyalkenamere könnte in gewisser Beziehung zu der triklinen Foim des kalt bearbeiteten Polyäthylens stehen. Die trikline Struktur von *trans*-Polyoctenamer und von *trans*-Polydecenamer sind durch eine dreidimensionale Fourieranalyse nachgeprüft worden. Die Standardabweichungen der Atomkoordinaten für die C-Atome liegen zwischen 0,02 und 0,04 Å bei beiaen Polymeren.