On the packing properties of poly(acetylene) chains

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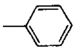
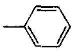
Packing calculations relevant to the crystal structure of *trans*-poly(acetylene) are described. Three classes of chain arrangements have been studied: pseudomonoclinic structures with one chain per unit cell and orthorhombic and monoclinic structures containing two symmetry related chains. The results are compared with experimental data on *trans*-poly(acetylene) reported in the literature and structure analyses of octatriene(2,4,6)-acid and 1,10-dicyanooctatetraene(1,3,5,7) which are reported as well. The same packing program has been used to recalculate the structure of *cis*-poly(acetylene). The results indicate the possibility for polymorphism in poly(acetylene) because several packing modes can be derived which differ very little with regard to their packing energy. However, literature data on the assignment of lattice parameters from poorly resolved X-ray, electron and neutron diffraction data can now be critically discussed.

Keywords Polyacetylene; packing calculations; crystal structure; polymorphism; model compounds

INTRODUCTION

Until now little was known about the crystalline state of *trans*-poly(acetylene) (PA). The *cis* material obtained by the usual methods of synthesis[1-5] consists of a random network (typical mesh dimension ~0.2 μm) the crystalline domains of which have dimensions of ~10 nm. On thermal isomerization at temperatures between 150° and 200°C the average size of the crystallites is decreased. Because PA is insoluble and cannot be melted there is no means to improve the morphology by subsequent treatment. The X-ray diffraction data show a powder pattern of very broad rings which, with only one exception, are so weak that they are almost lost in the background, thus providing limited information on the crystal structure of PA. More information can be gained by selected area electron diffraction[6]. Several attempts to determine the unit cell of PA have been reported but show large differences in the assumed structures[6,7].

Packing calculations were performed on PA chains in order to analyse which structures are favoured with respect to the lattice energy and to compare these with the packing found in model compounds of the type R_1–$(CH{=}CH)_n-R_2$:

	R_1	R_2	*n*
1	$-CH_3$	$-COOH$	3
2	$-CN$	$-CN$	4
3a			3
3b			4
3c			5

METHOD

The $(CH)_x$ chains are assumed to be in a rigid, planar zigzag conformation. The bond lengths of the two models used are given in *Table 1*. These starting points were chosen according to the *c* parameters found in PA and several oligoene model compounds[6,7,11-13]. The C–C bond angle is determined by the chain axis repeat *c* and the H atoms are potitioned so that they have the same projection on the chain axis as the C atoms to which they are attached. The interaction of different chains is modelled by the sum of the pairwise interaction of the individual atoms. As for the atom–atom potentials we chose a six-exponential potential:

$$V_{ij}(r) = -A_{ij}r^{-6} + B_{ij}\exp(-\alpha_{ij}r) \qquad (1)$$

This form is widely used for the description of the intermolecular interaction of hydrocarbons and suitable parameter sets can be found in the literature[8-10]. The sets with which the results quoted below were obtained are given in *Table 2*. The packing energy *F* which is minimized during the analysis is calculated by:

$$F = \sum_{\nu}\left[\sum_{\mu} V_{i\nu i\mu}(|\vec{r}_\nu - \vec{r}_\mu|)\right] + P_{i\nu} \qquad (2)$$

$$\varepsilon^{\text{unit with}}_{\text{cell}\ \vec{r}_\nu - \vec{r}_\mu} \leqslant R \text{ and chain } (\nu)^{\ddagger} \text{ chain } (\mu)$$

where *iν* indicates the sort of atom *ν* the position of which is $\vec{r}$. *R* defines a sphere around each atom of the unit cell which contains all other atoms whose potentials are explicitly taken into account.

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$$P_{iv} = 4\pi/3R^2\left[\sum_j(-A_{ij})N_j\right]/V_z \qquad (3)$$

P_{iv} is continuum approximation for the r^{-6} terms which have been neglected by restricting the direct summation to distances less than R. N_j denotes the number of atoms of sort j in the unit cell with the volume V_z. P_{iv} establishes the independence of F from the summation limit R at reasonable small values of R and is important in minimization runs where the unit cell parameters are allowed to change.

F is twice the lattice energy per unit cell due to interchain interaction at $T = 0$ K neglecting the zero point vibrational energy.

The minimum search is performed in two steps. First the contacts (cell pairs, v, μ with $|\vec{r}_v - \vec{r}_\mu| < R$) which change in case of larger changes in the packing geometry are continuously updated. Second the last contacts are fixed and the ultimate refinement done thus avoiding convergence problems which arise from changing numbers of contacts. The required gradients are always calculated with the same contact table for the whole set of F values needed for one gradient evaluation.

RESULTS

For *trans*-poly(acetylene) three classes of chain arrangements have been studied in detail, pseudomonoclinic structures with one chain per unit cell, orthorhombic cells and oligoene analogue monoclinic cells containing two symmetry related chains in the unit cell. Experimental evidence for a pseudomonoclinic (triclinic) primitive unit cell was found by Lieser *et al.*[6]. A similar packing arrangement is observed in the crystal structures of the oligoenes 1 and 2. In both cases the chain repeat distance c was given as $c = 244$ pm. Assuming this value and the bond lengths given in *Table 1* a rigid, planar chain (model 2 in *Table 1*) was constructed and used for the packing analysis of the triclinic structure. The cutoff radius was chosen as $R = 500$ pm. By using different starting configurations, five different minimal packing energy configurations were obtained which are described as models I to V in *Table 3* and shown in *Figure 1*.

Table 1 Parameters of the $(CH)_x$ chain

		Model 1	Model 2
Bond length	C–C	145 pm	145 pm
	C=C	135 pm	130 pm
	C–H	109 pm	109 pm
Bond angle	C–C–C	135°	125°
Repeat unit c		259.2 pm	244 pm

Table 2 Potential parameters for 5-exp. pairpotentials from Taddei *et al.*[9]. Values given in parentheses are the values given by Kitaigorodskii[8]

ij	A_{ij} (eV)	B_{ij} (Å^{-1})	C_{ij} (eV Å)^6
C . . . C	3431	3.610	24.6
	(1822)	(3.58)	(15.52)
C . . . H	382	3.699	5.54
	(1822)	(4.12)	(6.68)
H . . . H	98	3.738	1.15
	(1822)	(4.86)	(2.47)

The minimum I compares well with the experimental values from Lieser *et al.*[6] and is analoguous to the packing in the oligoene 1. The angles α and β which according to Lieser are 90° retain this value to an accuracy better than 1° in the packing analysis. The setting angle was determined as $\theta = 47°$ (θ = angle between the projection of the chain and the a axis onto the a^*b^*-plane). Structure V is in approximate agreement with the packing found in **2**. Here the end-groups may cause differences in the packing properties with respect to infinite $(CH)_x$ chains. II is a mirror image of I as can be seen in *Figure 1*. Similarly V corresponds to IV. Slight deviations from perfect symmetry are due to numerical effects, e.g. not totally equivalent contact tables.

The orthorhombic unit cell we used in our calculation contains two symmetry related $(CH)_x$-chains. The axis of the first plane intersects the a–b plane at the origin, the other at the fractional coordinates $t = (1/2, 1/2, 0)$. The setting angles θ_i of the two chains are symmetry related. Either $\theta_2 = -\theta_1$ (a glide plane normal to the b axis), or $\theta_2 = (-\theta_1 - 180°)$ (b glide plane perpendicular to a). The cell parameter in chain direction used in the analysis of the orthorhombic structures was $c = 259$ mm and was taken from Lieser *et al.*[6] (model 1 in *Table 1*). As in the previous analysis, the cutoff radius was $R = 500$ pm. Starting from the two different symmetry relations and different starting

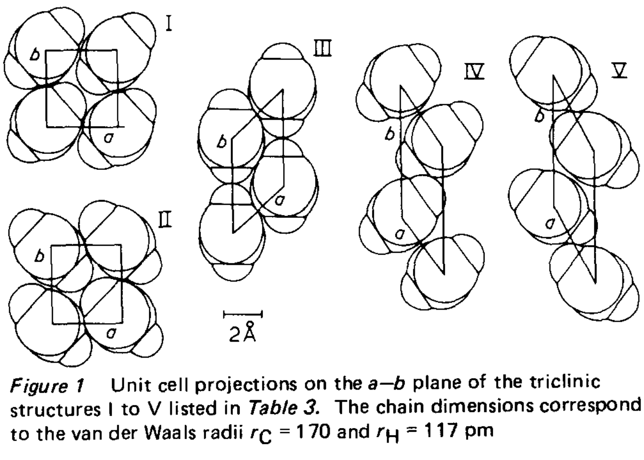

Figure 1 Unit cell projections on the a–b plane of the triclinic structures I to V listed in *Table 3*. The chain dimensions correspond to the van der Waals radii $r_C = 170$ and $r_H = 117$ pm

Table 3 Minimum packing energy configurations of the triclinic (pseudomonoclinic) structures

Structure	I	II	III	IV	V	Ref. 6	1	2
a (pm)	376	372	366	359	431	373(5)	403	398
b (pm)	377	382	485	665	663	373(5)	407	634
c (pm)	244	244	259.2	244	244	244(5)	244	244
γ (°)	95	85	49	144	150	98(2)	99	147
θ (°)	48	129	41	90	25	–	50	43
F (eV)	–0.402	–0.400	–0.390	–0.397	–0.392	–	–	–
D_x (Mgm^{-3})	1.25	1.25	1.25	1.27	1.26	1.27	1.09	1.29

Table 4 Minimal packing energy configurations for the orthorhombic structures

Structure	VI	VII	VIII	IX	Experimental data Ref. 6	 Ref. 7
a (pm)	684	555	694	575	562	732
b (pm)	394	486	380	480	492	424
c (pm)	259.2	259.2	259.2	259.2	259.2	246
θ_2 (°)	$180-\theta_1$	$180-\theta_1$	$-\theta_1$	$-\theta_1$	–	$-\theta_1$
θ_1 (°)	56	90	90	85	–	24
F (eV)	−0.826	−0.798	−0.863	−0.772	–	–
D_x (Mgm^{-3})	1.24	1.23	1.26	1.21	1.20	1.13

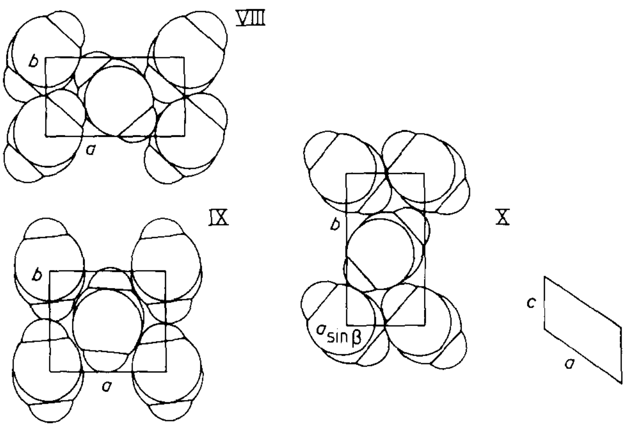

Figure 2 Unit cell projections of the orthorhombic structures VII and IX (*Table 4*) and the monoclinic structure X from *Table 5*

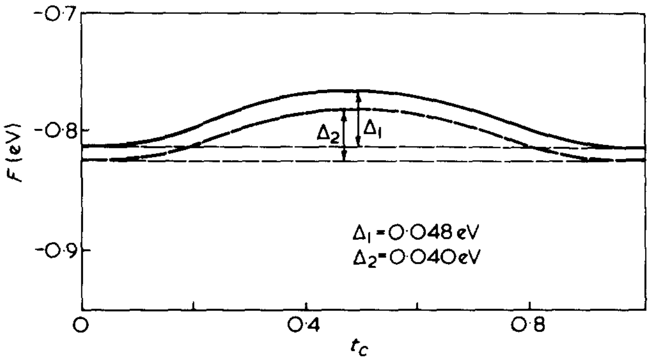

Figure 3 Dependence of the packing energy F on the translation t_c of the second chain in the c direction for structure VIII (solid line) and X (broken line). The small deviation of the absolute value of F compared to the values given in *Table 4* comes from the fact that the data in this Figure are calculated with a cutoff radius of 800 (900) instead of 500 pm

values for the parameters, a variety of distinct packing energy minima could be found (see *Table 4* and *Figure 2*). If the angles, α, β and γ were included in the set of variable parameters they virtually remained constant at 90° and the fractional coordinates t_a and t_b stayed at $t_a = 0.5$. In addition, the symmetry relations between the two chains were retained when the constraint by the symmetry was released. The dependence of the packing energy on the value of the fractional shift of the second chain in c direction t_c is shown in *Figure 3*. It can be seen that the value $t_c = 0$ corresponds to a very flat minimum. The 'barrier height' Δ_1 is only about 5% of the total packing energy.

For the structure VIII it was also investigated how the assumed value of c influences the calculated values of a, b and the setting angle. By changing the bond angles until $c = 244$ pm, a and b change from 694 to 713 pm and 380 to 389 pm, respectively in a linear manner. The setting angle $\theta = 50°$ is virtually independent of changes of c within the range of reasonable values. Also changes of the C–H bond angle of up to 8% yield only slightly different values ($c = 244$ pm). Here a changed from 713 to 707, and b from 390 to 389 pm. The third starting point we used were monoclinic structures containing two symmetry related chains in the unit cell corresponding to the packing found in the diphenyloligoenes 3a–ec. The results are given in *Table 5*.

It can be seen that poly(acetylene) chains can be packed in structures similar to the subcell observed in 3c with very low packing energies. The structures X, XI and XII represent three such possibilities with slightly varying lattice energies. XIII shows the effect of a reduction of c and should be compared with X. Comparison of the structures XIV and XV with the packing in the monoclinic modifications of 3a–3c from which they were computed show larger differences. Especially the monoclinic angle β changes from 99° (oligoene) to 92°–93° (packing result).

To test the dependence of the results on the parameter set we recalculated the three structures (triclinic, $Z = 1$, orthorhombic and monoclinic with $Z = 2$) having the lowest packing energy using the values from Kitaigorodskii[8] for the potential parameters. These are listed in parentheses in *Table 2*. A comparison of the results obtained using the different parameter sets calculating structures I, VIII and X is given in *Table 6*.

As another test for the validity of the optimal parameters, the packing analysis for the *cis–trans*oid isomer, for which a structural model based on X-ray diffraction and packing calculations has been proposed[11], was repeated using the results reported by Baughman[11] as starting point, together with our parameter set. The assumed structure is orthorhombic, $Z = 2$, space group Pnma and a c value of 446.7 pm. Our choice of the unit cell is related to the cell given by Baughman[11] by exchange of b and c. The packing analysis yields the following values with the parameters deduced from X-ray data given in parentheses: $a = 739$ (760.6), $b = 419$ (439) pm $\theta = 50°$ (51°/59°) and $F = -1.55$ eV. The two values 51° and 59° for the setting angle are the values obtained from a packing calculation for θ only and from refinement of the scattering data, respectively. The orthorhombic cell as well as the symmetry relations $t_a = t_b = 0.5$ and $\theta_1 = -\theta_2$ remained unchanged in our analysis.

However, investigation of the dependence of F on the translation t_c of the second chain along the chain axis reveals that the minimal packing energy is achieved at $t_c = 0.25$ rather than at $t_c = 0$ as required by the assumption of space group Pnma. It should be noted, however, that the energy variation is only 0.03 eV corresponding to less than 2% of the total packing energy.

Table 5 Minimum packing energy configurations for the monoclinic structures containing two symmetry related $(CH)_x$ chains (compare *Figure 2*)

Structure	3c[12]†	X	XI	XII	XIII	3a–c[12,13]‡	XIV	XV
a (pm)	507	462	451	466	459	424	397	395
b (pm)	745	699	716	687	702	760	701	705
c (pm)*	248	248	248	248	244	245	245	245
β (°)	124	124	123	141	122	99	92	93
θ_1 (°)	150	130	44	35	130	140	126	37
θ_2 (°)	$-\theta_1$	$-\theta_1$	$-\theta_1$	$-180-\theta_1$	$-\theta_1$	$-\theta_1$	$-\theta_1$	$-\theta_1$
F (eV)	–	−0.876	−0.863	−0.837	−0.874	–	−0.822	−0.828
D_x (Mgm^{-3})	1.13	1.30	1.29	1.28	1.31	1.12	1.27	1.28

* *c* was kept fixed in the packing calculations

† Orthorhombic crystal modification

‡ Monoclinic crystal modifications

Table 6 Dependence of the calculated minimum energy structure on the parameter set. The first column gives the data obtained with the set we used throughout our calculations[9], the second the results obtained with Kitaigorodskii's parameters[8]

Structure	I		VIII		X	
a (pm)	376	378	694	728	462	442
b (pm)	377	376	380	374	699	772
γ (°)	95	95	90	90	90	90
F (eV)	−0.402	−0.400	−0.863	−0.784	−0.876	−0.838

Table 7 Crystallographic data

	1	2
a (pm)	2466(1)	975(2)
b (pm)	403(1)	1465(3)
c (pm)	1570(1)	674(5)
β (°)	99.6(5)	109.5(5)
D_x (Mgm^{-3})	1.18	1.14
Space group	$P2_1/c$	$P2_1/n$

DISCUSSION

The calculated minima may differ from the true experimental values for several reasons. Firstly, all our results are derived for zero temperature, so one has to take into account thermal expansion and the possibility that, due to entropy differences, a structure with a slightly higher packing energy at $T=0$ K may be favoured at elevated temperatures. The thermal expansion at 300 K for typical molecular crystals ranges from about 0.5 to 5% depending on the direction. However, as the potential parameters used are determined by fitting crystal properties at finite temperature, an average thermal expansion may already be taken into account. It should also be kept in mind that modelling the molecular interaction by the sum of atomic pair potentials with a fixed analytic form (here: 6-exp) is also valid only to a certain degree of approximation. However, due to the empirical determination of the parameters by fitting observed physical quantities of real organic solids, the effects of more complicated force contributions are to some degree taken into account.

As described above (*Table 6*) a test with quite different parameter sets for the pair of potentials yields essentially identical structures. The largest differences observed for structure X are about 10% in the lattice parameters. This gives some information on the sensitivity of our packing program to the details of the potentials. The triclinic structure I (*Table 3*) coincides almost perfectly with an experimentally observed modification of *trans*-$(CH)_x$. Structure II is a mirror image of I and the third minimum III can be considered as an orthorhombic structure with $a=549$, $b=484$ pm, $t_a=t_b=0.5$ and a setting angle of 90°. This corresponds to structure VII in *Table 4*. To compare the packing energies of the triclinic and orthorhombic structures, *F* must be divided by the number of chains in the unit cell. The additional freedom connected with the second chain in the unit cell (*Table 4*) yields a further improvement of the packing energy of ~8% (structure VIII) with respect to the triclinic lattices. Structure VI is structure VIII with the second chain rotated by 180°. Second minima with smaller a/b ratios (VII and IX) have significantly higher energies. Nevertheless, all four cells have energies differing to within 10% of the average packing energy. The comparison of the orthorhombic unit cell parameters with experimental values is far less satisfactory than in the case of the triclinic structures. Whereas the parameters from ref. 6 seem to match structure IX reasonably well, the corresponding scattering data show a strong reflection which cannot be produced by IX.

The unit cell given by Shimamura *et al.*[7] has a remarkably low density. Taken at starting point all parameters changed considerably to the final values of $a=700$ pm ($\Delta a/a=4.5\%$), $b=390$ pm ($\Delta b/b=12\%$) and $\theta=50°$. The structure obtained in this way is virtually identical to VIII neglecting small differences due to different *c* parameters.

The test calculations for *cis-trans*oid poly(acetylene) shows a similar but smaller discrepancy ($\Delta a/a=2.8\%$ and $\Delta b/b=4.5\%$). The lowest energy has been obtained for the oligoene analogue structure X (resp. XIII) which is 1.5% better than the energy of VIII. The results indicate that there is a good chance of finding a crystal structure which is closely related to the packing found in the diphenyloligoenes **3a**–**3c**. It should be emphasized, however, that depending on the parameter set used, the lattice parameters found for X may differ from the real values by up to 10%.

Table 8 Final atomic parameters for 1. Values given are fractional coordinates $\times 10^4$ for C and O and anisotropic temperature factors $U_{ij} \times 10^4$. E.s.d.'s are given in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4304(5)	1693(51)	1984(7)	470(71)	701(94)	602(84)	−153(99)	111(66)	−81(90)
C(2)	3738(5)	831(51)	1497(8)	516(85)	414(78)	589(85)	−5(97)	96(73)	165(95)
C(3)	3260(4)	2105(42)	1662(7)	436(74)	542(69)	460(77)	−62(63)	59(65)	91(63)
C(4)	2727(5)	1146(45)	1188(7)	528(83)	603(75)	454(83)	−109(61)	5(66)	65(65)
C(5)	2244(5)	2263(42)	1366(7)	468(76)	676(84)	412(76)	0(62)	18(62)	21(70)
C(6)	1722(5)	1316(41)	898(7)	507(82)	623(63)	352(72)	64(71)	40(64)	64(64)
C(7)	1240(5)	2295(42)	1083(7)	575(86)	576(68)	260(64)	−9(69)	27(63)	7(60)
C(8)	717(5)	1320(47)	598(8)	454(77)	599(88)	344(71)	−26(73)	−100(65)	41(67)
O(1)	289(3)	2500(34)	885(5)	420(51)	702(80)	715(64)	45(70)	194(47)	−113(81)
O(2)	666(3)	−657(32)	−34(5)	522(52)	892(89)	462(48)	−37(62)	27(40)	−139(67)

Table 9 Final atomic parameters for 2. Values given are fractional coordinates $\times 10^4$ and isotropic temperature factors for C and N. Parameters for H have not been refined. E.s.d.'s are given in parentheses

Atom	x	y	z	B (Å^2)
C (1)	9879(30)	2379(22)	1906(51)	6.20(77)
C (2)	8499(23)	2404(19)	2067(43)	4.85(62)
C (3)	7757(28)	1656(20)	2128(44)	5.71(73)
C (4)	6247(25)	1586(19)	2127(38)	4.54(63)
C (5)	5605(22)	815(19)	2294(34)	4.41(70)
C (6)	4101(25)	798(20)	2216(40)	5.27(78)
C (7)	3452(22)	7(19)	2396(38)	4.78(62)
C (8)	2010(24)	−53(20)	2547(43)	5.76(73)
C (9)	1320(26)	−789(20)	2723(44)	4.87(68)
C(10)	−140(34)	−775(24)	2746(57)	5.91(81)
N (1)	1 1022(20)	2394(17)	1804(36)	6.38(58)
N (2)	−1212(21)	−801(16)	3002(39)	6.37(62)
H (1)	7852	3043	2397	
H (2)	8347	1092	1789	
H (3)	5740	2425	1500	
H (4)	6389	219	2115	
H (5)	3311	1363	2119	
H (6)	3859	−676	1999	
H (7)	1521	645	2899	
H (8)	2044	−1419	2569	

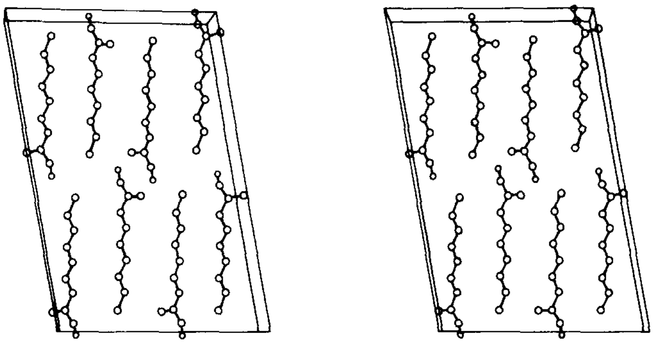

Figure 4 Stereoscopic view of the packing in 1. *c* is horizontal and *a* is vertical

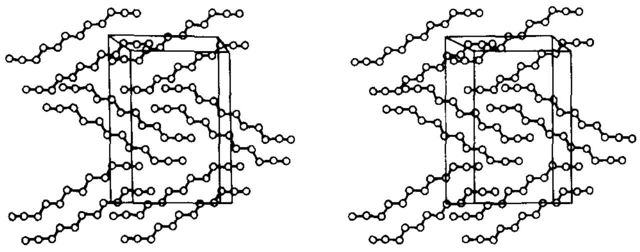

Figure 5 Stereoscopic view of the packing in 2. *a* is horizontal and *b* is vertical

Finally, the crystalline regions in the real material are very small, so one has to expect surface effects. Especially, stresses due to crosslinks outside the crystalline lamellae in the amorphous regions may drive parts of the crystallites, or all of them, in other structures as predicted. If strong crosslinking occurs in *cis*-PA before isomerization, there may even be a memory effect on the previous *cis*-structure. It is probable, therefore, that depending on the history of the sample, and with respect to the packing energy, several structures may degenerate to tabulated structures. As a consequence polymorphism could occur in poly(acetylene). The translation t_c along the chain direction may even be random giving rise to nematic structures.

CONCLUSION

We do not claim that the cell parameters found in our packing calculations are highly accurate, but we have shown that a number of different structure types should be considered possible and therefore should be expected to occur in *trans*-$(CH)_x$.

REFERENCES

1 Shirakawa, H. and Ikeda, S. *Polym. J.* 1971, **2**, 231
2 Ito, T., Shirakawa, H. and Ikeda, S. *J. Polym. Sci., Polym. Chem. Edn.* 1974, **12**, 11
3 Karasz, F. E., Chien, J. C. W., Galkiewicz, R., Wnek, G. E., Heeger, A. J. and McDiarmid, A. G. *Nature* 1979, **282**, 286
4 Luttinger, L. B. *Chem. Ind. (London)* 1960, **36**, 1135
5 Luttinger, L. B., *J. Org. Chem.* 1962, **27**, 1591
6 Lieser, G., Wegner, G., Müller, W., Enkelmann, V. and Meyer, W. *Makromol. Chem. Rapid Comm.* 1980, **1**, 627
7 Shimamura, K., Karasz, F. E., Hirsch, J. A. and Chien, J. C. W. *Makromol. Chem.* to be published
8 Kitaigorodskii, A. I. 'Molecular Crystals and Molecules', Academic Press, New York and London, 1973
9 Taddei, G., Bonadeo, H., Marzochi, M. P. and Califano, S. *J. Chem. Phys.* 1972, **58**, 966 (We adopted the parameter from Table X)
10 Williams, D. E. *J. Chem. Phys.* 1966, **45**, 3770
11 Baughman, R. H., Hsu, S. L., Pez, G. P. and Signorelli, A. J. *J. Chem. Phys.* 1978, **68**, 5405
12 Drenth, W. and Wibenga, E. H. *Rec. Trav. Chim.* 1954, **73**, 218
13 Drenth, W. and Wibenga, E. H. *Acta Crystallogr.* 1955, **8**, 755
14 Kuhn, R. and Hoffer, M. *Ber. dt. chem. Ges.* 1939, **63**, 2164
15 Moever, H. *Tetrahedron Letters* 1962, **6**, 255
16 Declercq, J. P., Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr.* 1973, **A29**, 231
17 Stewart, J. M., Machin, P. A., Dickinson, C., Ammon, H. L., Heck, H. and Flack, H. 'The XRAY system—version of March 1976', Techn. Rep. TR-446 Computer Science Center, Univ. of Maryland, College Park, ML 1976

18 'International Tables for X-ray Crystallography', Vol. III, 2nd Edn., Kynoch Press, Birmingham, 1968
19 Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 1965, **42**, 3175
20 Tables of observed and calculated structure factors are available upon request from V. Enkelmann

APPENDIX

Structure determination and refinement

Octatriene(2,4,6) acid (1) and 1,10-dicyanooctatetraene (1,3,5,7) (2) were prepared as described in the literature[14,15] and crystallized from ethanol and $CHCl_3$, respectively. Unit cell dimensions were determined from Straumanis-type double radius Weissenberg photographs ($R = 57.3$ mm). Intensities were recorded by multiple-film equi inclination Weissenberg photographs using Ni filtered CuKα radiation. The intensities were estimated visually by comparison with a series of timed exposures of a selected reflection. 710 and 297 unique reflections were measured for 1 and 2, respectively. Of these 217 for 1 and 8 for 2 were considered having intensities less than the threshold value of observable intensity. They were assigned half this value and were given zero weight in the refinement. Pertinent crystallographic data are given in *Table 7*. The structures were solved by direct methods using the program MULTAN[16]. Refinement was done by full matrix least-squares analyses with unit weights. No absorption corrections were applied. The hydrogen atoms were found in difference maps and their contributions were included in structure factor calculations but their parameters were not refined. The programs used were those of the XRAY76 system[17]. Scattering factors for C, N and O were taken from the International Tables for X-ray Crystallography[18] and for H from Stewart, Davidson and Simpson[19]. Final R indices were 0.11 for 1 and 0.09 for 2. The final atomic parameters are listed in *Tables 8* and *9*. Lists of observed and calculated structure factors are available[20]. Bond lengths and angles meet the expected values. Stereoscopic views of the packing in both crystal structures are shown in *Figures 4* and *5*. The packing configurations given in *Tables 3, 4* and *5* for the oligoenes 1, 2 and 3 are the averaged values of the appropriate inter- and intramolecular contacts.