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Symmetry classification of stereoregular polymers

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The symmetry of stereoregular polymers enables classification of elementary polymers according to the line groups. Their schemes are presented and the notation, extracting the data relevant for the symmetry considerations of the polymer, is proposed. The advantages of the concept (efficient and precise description of the structure, easy prediction of properties of the polymer, reductions of numerical calculations) are discussed and illustrated by several examples. © 1997 Elsevier Science Ltd.

INTRODUCTION

Line groups[1] describe the symmetries of systems with translational periodicity in one direction (e.g. stereoregular polymers or quasi-one-dimensional subsystems). These systems consist of an infinite number of atoms, and application of the symmetry is unavoidable in the calculations. The translational symmetry which is commonly used[2] enables reduction of the effective calculation to the translational cell. Nevertheless, since there is no crystallographic restriction† on the order of the principal axis ($n = 1, 2, 3, 4$ and 6), the high order screw axis can appear, and the translational cell can be much greater than the basic structural motive, the monomer. Also, other symmetries may be present, and this emphasizes the advantages of the full line group treatment.

Rigorously, the line group symmetry refers to the system infinitely long in the direction of the translational periodicity (z-axis, by default), while in the transversal direction the system may be finite, or even infinite. Therefore, the study of the boundary effects of the real system is beyond the scope of the methods applying this symmetry. Further, the polymer should not be bent. However, unless the bending causes some additional bonding between the distant monomers, the topology of the polymer is not changed, and the results obtained will be valid, but the quantum number related to quasi-linear momentum in the case of a stereoregular polymer should be interpreted as the generalized quasi momentum conjugated to the (bent) axis of the polymer[5].

The starting point of the application of symmetry in the various physical or chemical considerations of polymers is the classification of these systems according to the line groups, and the description of the monomer within such an approach. To this end the notion of elementary polymers, or orbits of line groups, is introduced[7]. The first aim of this paper is to elucidate this approach, by giving the schemes for all orbit types, together with the typical coordinates of the corresponding orbit representatives. Concise symmetry related data, sufficient for a number of applications, are contained in the proposed notation based on the introduced concept. The schemes simplify the use of the line group symmetry in polymer research, enabling easy recognition of the symmetry structure of the system (in this context, the minimal sets – i.e. the symmetry fixing sets – of orbits, determining the symmetry, are also supplied) and straightforward application of the symmetry oriented techniques.

ORBITS OF LINE GROUPS

The symmetry L of the stereoregular polymer consists of[8] the symmetry of the single monomer, described by the point group P, and the symmetry of the arrangement of the monomers in the three-dimensional space, given by the group of generalized translations, Z. (This implies that each line group can be factorized as the product, $L = PZ$, of the point group P and the infinite cyclic group Z.) While P is one of the axial point groups, Z can be (*Figure 1*) either the screw axis group, generated by $(C_q^r | \frac{n}{q})$ (with the standard translational group as a special case), or the glide plane group, with the generator $(\sigma_v | \frac{1}{2})$. The translational part is given in the units of the translational period.

Such a group of symmetry enables definition of the configuration of an infinite polymer through the coordinates of several representative atoms. This minimal set is found within the following steps: (1) determine the symmetry group, L, of the system; (2) single out an atom, A, and act on it by all the elements of the group L:
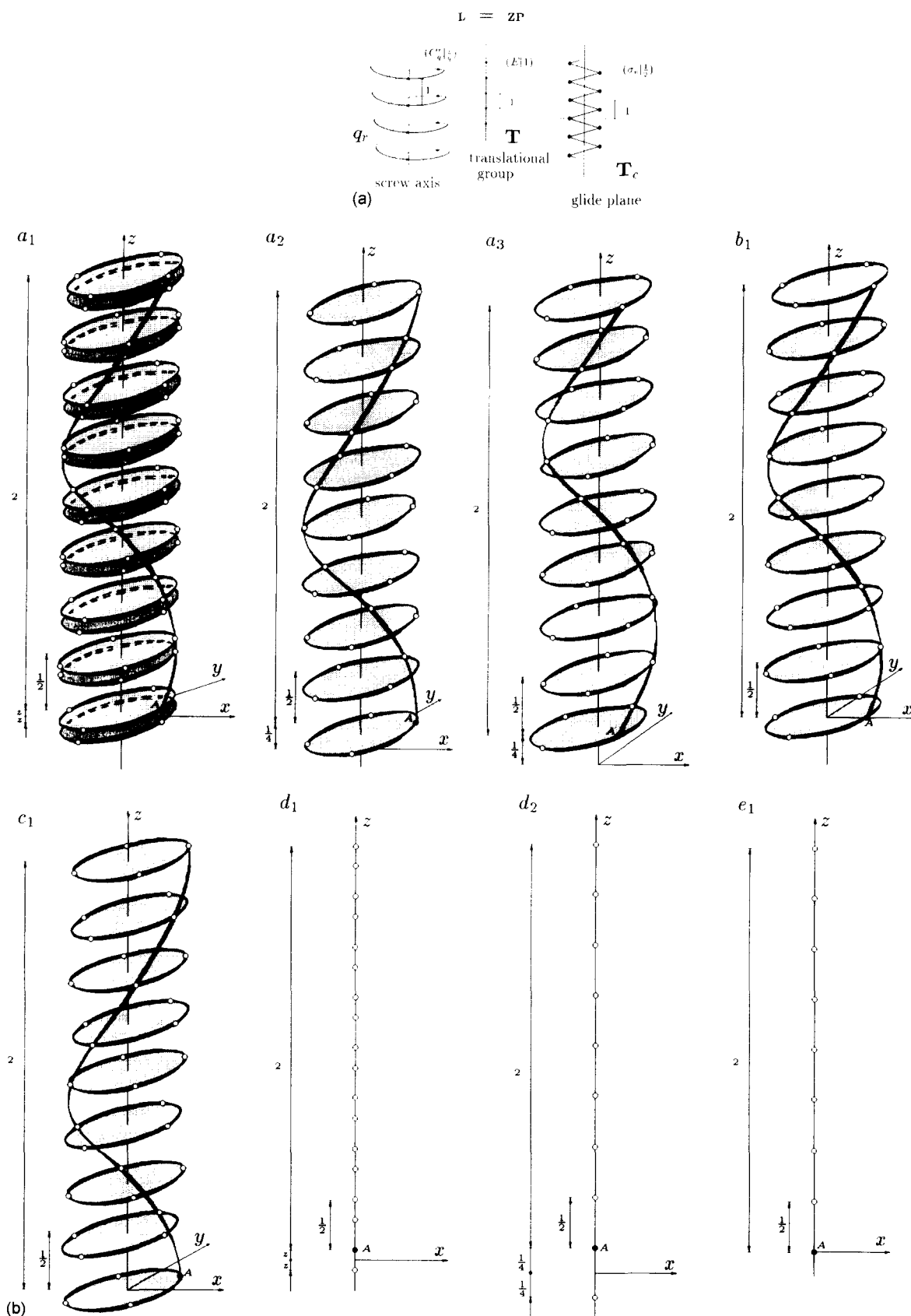
Figure 1 (a) Generalized translational groups. (b) Orbits of the line group Lq_p22, $Lq_p2 = q_rD_n = gp \{C_n, U, (C_q^r | \frac{n}{q})\}$ for $q = 8$, $r = 1$, $n = 4$. Symmetry fixing sets: a_1, a_2 and a_3 for $Ln2$, $Ln22$ and $L(2n)_n22$ and a_1, a_2, a_3, b_1, c_1 for other cases. The translational period is $\frac{q}{n}$

Type	a_1	a_2	a_3	b_1	c_1	d_1	d_2	e_1
Existence	$\forall_n$	$\forall_n$	n even	$\forall_n$	n even	$\forall_n$	$\forall_n$	$\forall_n$
Atom A	(x,y,z)	$(\rho\cos\frac{r\pi}{q}, \rho\sin\frac{r\pi}{q}, \frac{n}{2q})$	$(\rho\cos(\frac{r}{q}-\frac{1}{n}), \rho\sin(\frac{r}{q}-\frac{1}{n}), \frac{n}{2q})$	$(x,0,0)$	$(\rho\cos\frac{\pi}{n}, \rho\sin\frac{\pi}{n}, 0)$	$(0,0,z)$	$(0,0,\frac{n}{2q})$	$(0,0,0)$
Symmetry	D_n	$C_n + (C_q^r U | \frac{n}{q})C_n$	$C_n + (C_q^r U | \frac{n}{q})C_n$	D_n	D_n	D_n	$C_n + (C_q^r U | \frac{n}{q})C_n$	D_n
Stabilizer	C_1	$\{e, (C_q^r U | \frac{n}{q})\}$	$\{e, (C_q^r U C_n | \frac{n}{q})\}$	D_1	D_1	C_n	$C_n + (C_q^r U | \frac{n}{q})C_n$	D_n

the infinite subsystem, called the *orbit* of *A*, is obtained, with all the atoms of the same sort; (3) choose another atom, *B*, from the rest of the system, and repeat the procedure: another infinite subsystem is obtained, the orbit of the atom *B*, containing no common atoms with the previous one; (4) continue the procedure until the whole polymer has been partitioned into disjunctive orbits. Thus, the configuration of the polymer is completely defined by the symmetry group and the coordinates of the orbit representatives *A*, *B*, etc. The orbits can be thought of as the simplest, elementary, polymers.
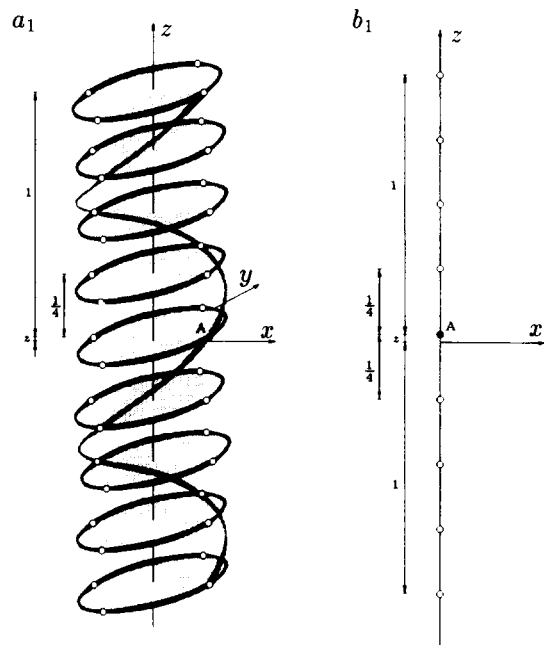
Note that some elements of **L** can leave the orbit representative, e.g. *A*, unmoved. All the transformations, *l*, with this property, $lA = A$, form the subgroup of **L**, called the *stabilizer* of the atom *A*. It is known[6] that the stabilizers of the atoms from the same orbit are conjugated, and that the orbits with the conjugated stabilizers are geometrically identical. This has been sufficient to find the algebraical classification of all of the orbits of the line groups[7].

For each of the 13 infinite families of the line groups, one group, defined by the order, *n*, of the principal rotational axis (conventionally directed along the *z* axis), is chosen, and the schemes of its orbits are presented (*Figures 2–13*). The orbits of the other groups from the same family are similar, and their geometries can be easily reconstructed by analogy. However, there are cases that for special values of *n* (for the groups of the same family), some orbits cannot be realized (as non-equivalent to other ones); therefore, in the table under the figure, it is indicated when the orbit exists. The atom chosen as the orbit representative is denoted on each scheme by the black circle, *A*. Its coordinates are in the table, presented in the most general form. The coordinates that are not fixed (i.e. *x*, *y* and/or *z* are found in the table) can take all the values except those which correspond to other orbits, with representatives in more specialized positions (e.g. $z = 0$, $1/2$, $1/4$, or the points on mirror planes or rotation axes). The monomer consists of the atoms (white circles) within a single ring (when the rings are equidistant), or within two closer rings (otherwise). Its symmetry group is isomorphic to the point factor **P** (given in the caption of the figure), but some of the elements can be combined with fractional translations. Therefore, the group of symmetry of the monomer is explicitly given in the third row of the table, while the stabilizer is in the fourth row. Some characteristic symmetry elements (reflection in the *xz*-plane, σ_v, rotation by the angle π around the horizontal axis *U*, and so on) are indicated, too.

The statement that the group of symmetry of the system is **L** generally means that **L** is the maximal symmetry group of the system, i.e. there is no other group $\mathbf{L}' > \mathbf{L}$, such that the system is invariant under its action. It can be easily seen from the schemes that some
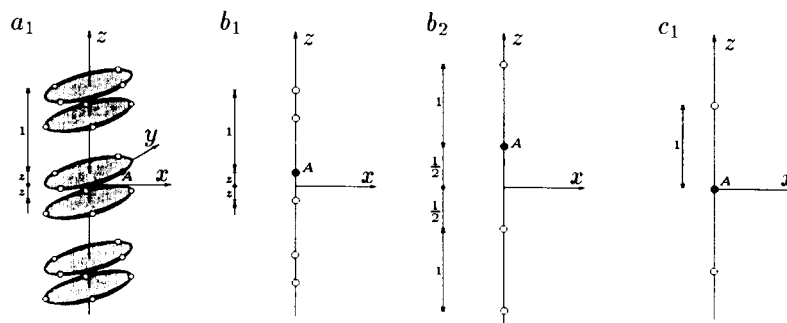

Figure 2 Orbits of the line group $\mathbf{L}q_p = \mathbf{q}_r\mathbf{C}_n = \mathrm{gp}\ \{C_n, (C_q^r|\frac{n}{q})\}$, for $n = 4$, $q = 8$, $r = 1$. Symmetry fixing set: $2a_1$. The translational period is $\frac{q}{n}$

Type	a_1	b_1
Existence	$\forall_n$	$\forall_n$
Atom A	(x, y, z)	$(0, 0, z)$
Symmetry	$\mathbf{C}_n$	$\mathbf{C}_n$
Stabilizer	$\mathbf{C}_1$	$\mathbf{C}_n$

Figure 3 Orbits of the line group $\mathbf{L}(2\bar{n})$, $\mathbf{L}\bar{n} = \mathbf{TS}_{2n} = \mathrm{gp}\ \{\sigma_h C_{2n}, (E|1)\}$ for $n = 4$. Symmetry fixing set: $2a_1$. The translational period is 1

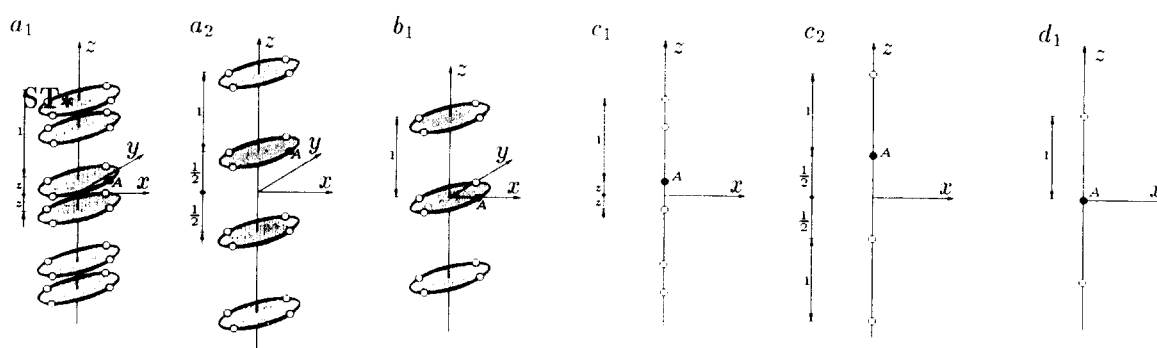| Type	a_1	b_1	b_2	c_1
Existence	$n > 1$	$\forall_n$	$\forall_n$	$\forall_n$
Atom A	(x, y, z)	$(0, 0, z)$	$(0, 0, \frac{1}{2})$	$(0, 0, 0)$
Symmetry	$\mathbf{S}_{2n}$	$\mathbf{S}_{2n}$	$\mathbf{C}_n + (C_{2n}\sigma_h|1)\mathbf{C}_n$	$\mathbf{S}_{2n}$
Stabilizer	$\mathbf{C}_1$	$\mathbf{C}_n$	$\mathbf{C}_n + (C_{2n}\sigma_h|1)\mathbf{C}_n$	$\mathbf{S}_{2n}$

Figure 4 Orbits of the line group Ln/m, L($\overline{2n}$) = $\mathbf{TC}_{nh}$ = gp $\{C_n, \sigma_h, (E|1)\}$ for $n = 4$. Symmetry fixing sets: $2a_1$, $2a_2$, $a_1 + a_2$, $2b_1$, $a_1 + b_1$, $a_2 + b_1$. The translational period is 1

Type	a_1	a_2	b_1	c_1	c_2	d_1
Existence	$n > 1$	$n > 1$	$n > 1$	$\forall_n$	$\forall_n$	$\forall_n$
Atom A	(x, y, z)	$(x, y, \frac{1}{2})$	$(x, y, 0)$	$(0, 0, z)$	$(0, 0, \frac{1}{2})$	$(0, 0, 0)$
Symmetry	$\mathbf{C}_{nh}$	$\mathbf{C}_n + (\sigma_h|1)\mathbf{C}_n$	$\mathbf{C}_{nh}$	$\mathbf{C}_{nh}$	$\mathbf{C}_n + (\sigma_h|1)\mathbf{C}_n$	$\mathbf{C}_{nh}$
Stabilizer	$\mathbf{C}_1$	$\{e, (\sigma_h|1)\}$	$\{e, \sigma_h\}$	$\mathbf{C}_n$	$\mathbf{C}_n + (\sigma_h|1)\mathbf{C}_n$	$\mathbf{C}_{nh}$
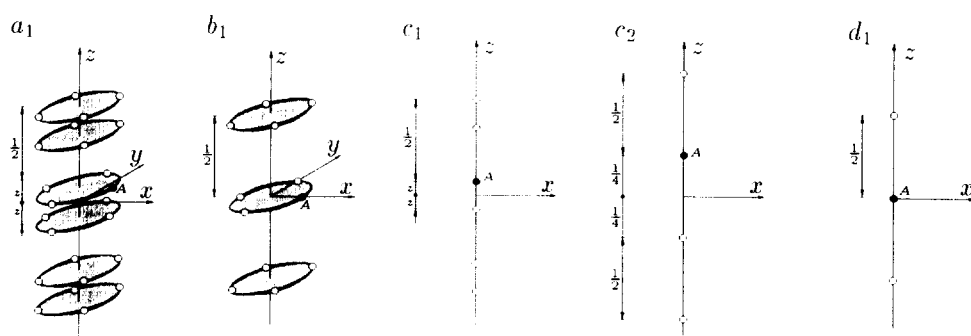
Figure 5 Orbits of the line group L$(2n)_n/m$ = $(\mathbf{2n})_1\mathbf{C}_{nh}$ = gp $\{C_n, \sigma_h, (C_{2n}|\frac{1}{2})\}$ for $n = 4$. Symmetry fixing sets: $2a_1$, $2b_1$, $a_1 + b_1$. The translational period is 1

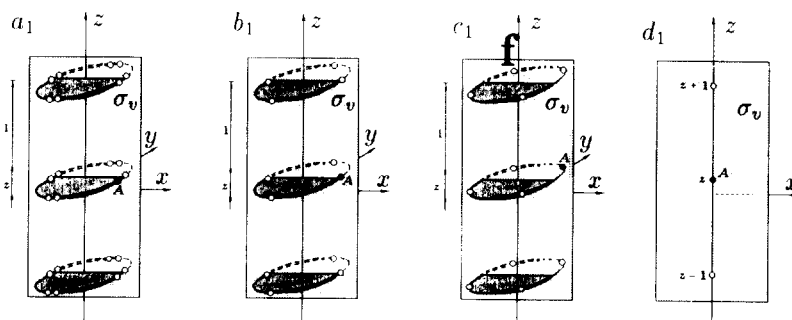| Type	a_1	b_1	c_1	c_2	d_1
Existence	$n > 1$	$n > 1$	$\forall_n$	$\forall_n$	$\forall_n$
Atom A	(x, y, z)	$(x, y, 0)$	$(0, 0, z)$	$(0, 0, \frac{1}{4})$	$(0, 0, 0)$
Symmetry	$\mathbf{C}_{nh}$	$\mathbf{C}_{nh}$	$\mathbf{C}_{nh}$	$\mathbf{C}_n + (C_2\sigma_h|\frac{1}{2})\mathbf{C}_n$	$\mathbf{C}_{nh}$
Stabilizer	$\mathbf{C}_1$	$\{e, \sigma_h\}$	$\mathbf{C}_n$	$\mathbf{C}_n + (C_2\sigma_h|\frac{1}{2})\mathbf{C}_n$	$\mathbf{C}_{nh}$

Figure 6 Orbits of the line group Lnmm, Lnm = $\mathbf{TC}_{nv}$ = gp $\{C_n, \sigma_v, (E|1)\}$ for $n = 4$. Symmetry fixing sets: $2a_1$, $2b_1$, $2c_1$, $a_1 + b_1$, $a_1 + c_1$, $a_1 + d_1$, $b_1 + c_1$, $b_1 + d_1$, $c_1 + d_1$. The translational period is 1

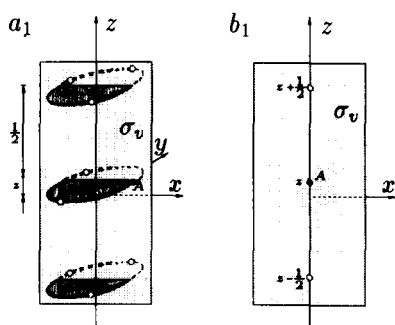| Type	a_1	b_1	c_1	d_1
Existence	$\forall_n$	$n > 1$	n even	$\forall_n$
Atom A	(x, y, z)	$(x, 0, z)$	$(\rho\cos\frac{\pi}{n}, \rho\sin\frac{\pi}{n}, z)$	$(0, 0, z)$
Symmetry	$\mathbf{C}_{nv}$	$\mathbf{C}_{nv}$	$\mathbf{C}_{nv}$	$\mathbf{C}_{nv}$
Stabilizer	$\mathbf{C}_1$	$\mathbf{C}_{1v}$	$\mathbf{C}_{1v}$	$\mathbf{C}_{nv}$

Figure 7 Orbits of the line group L*ncc*, L*nc* = T_cC_n = gp $\{C_n, (\sigma_v|\frac{1}{2})\}$ for $n = 3$. Symmetry fixing set: $2a_1$. The translational period is 1

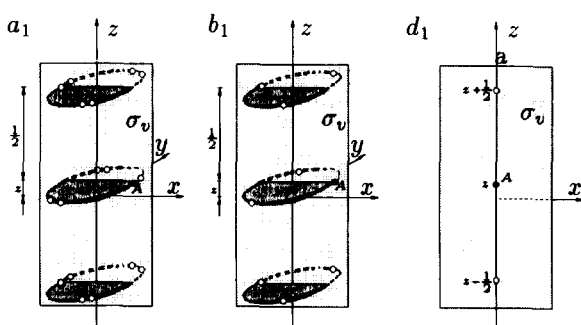| Type	a_1	b_1
Existence	$n > 1$	$\forall_n$
Atom A	(x, y, z)	$(0, 0, z)$
Symmetry	C_n	C_n
Stabilizer	C_1	C_n

Figure 8 Orbits of the line group $L(2n)_nmc$ = $(2n)_1C_{nv}$ = gp $\{C_n, \sigma_v, (C_{2n}|\frac{1}{2})\}$ for $n = 3$. Symmetry fixing sets: $2a_1$, $2b_1$, $a_1 + b_1$, $a_1 + d_1$, $b_1 + d_1$. The translational period is 1

Type	a_1	b_1	d_1
Existence	$\forall_n$	$n > 1$	$\forall_n$
Atom A	(x, y, z)	$(x, 0, z)$	$(0, 0, z)$
Symmetry	C_{nv}	C_{nv}	C_{nv}
Stabilizer	C_1	C_{1v}	C_{nv}

of the orbits have a symmetry greater than **L**. For example, the symmetry of all the one-dimensional orbits is $\mathbf{D}_{\infty h}T = L\infty/mmm$. Therefore, in general several orbits of **L** should be taken together to form the polymer, with the symmetry being exactly **L**. The minimal sets of orbit types, determining the line group symmetry, are listed under the figures. These symmetry fixing sets are the simplest systems with the exact symmetry of the given group. Hence, to verify that **L** is the symmetry group of the polymer, it must be shown that polymer can be built up from the orbits of **L** only, and that among them there is at least one of the symmetry fixing sets.

SYMMETRY NOTATION

Due to the large number of atoms in a polymer, it is impossible to define its conformation by explicit listing of the coordinates of all the atoms. Nevertheless, symmetry enables us to perform this, by giving only a few necessary data: line group; translational period; orbit composition (number of orbits of each type); coordinates of the atoms – orbit representatives (one for each appearing orbit). By extracting the pure symmetry data from these parameters of the structure of the polymer, the symmetry notation for the system (consisting of k different orbit types) emerges in the form $L[n_1O_1, \ldots, n_kO_k]$; here, **L** is the symbol of the relevant line group, while n_i, $i = 1, \ldots, k$, shows how many orbits of the type O_i the system contains. To illustrate this notation, some examples will be given here, while the discussion on the advantages of the concept is contained in the next section.

The symmetry formula for the *trans*-polyacetylene (*Figure 14*) is $L2_1/mcm[2e_1]$. The line group $L2_1/mcm$ belongs to the 13th line group family $L(2n)_n/mcm$, $n = 1, 2, \ldots$, with the order of the principal axis of pure rotations being $n = 1$. The generators are the reflection in the vertical mirror plane (xz, i.e. $y = 0$ plane), σ_v, the horizontal mirror plane (xy, i.e. $z = 0$ plane), σ_h, and the rotation by π around the z-axis followed by the translation for the half of the translational unit along the
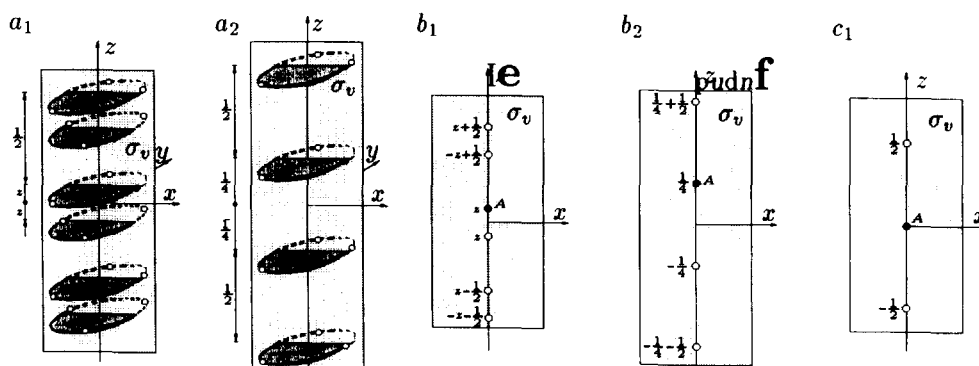

Figure 9 Orbits of the line group $L(\overline{2n})2c$, L*ñc* = T_cS_{2n} = gp $\{\sigma_hC_{2n}, (\sigma_v|\frac{1}{2})\}$ for $n = 3$. Symmetry fixing sets: $2a_1$, $2a_2$, $a_1 + a_2$, for n even and a_1, a_2 for n odd. The translational period is 1

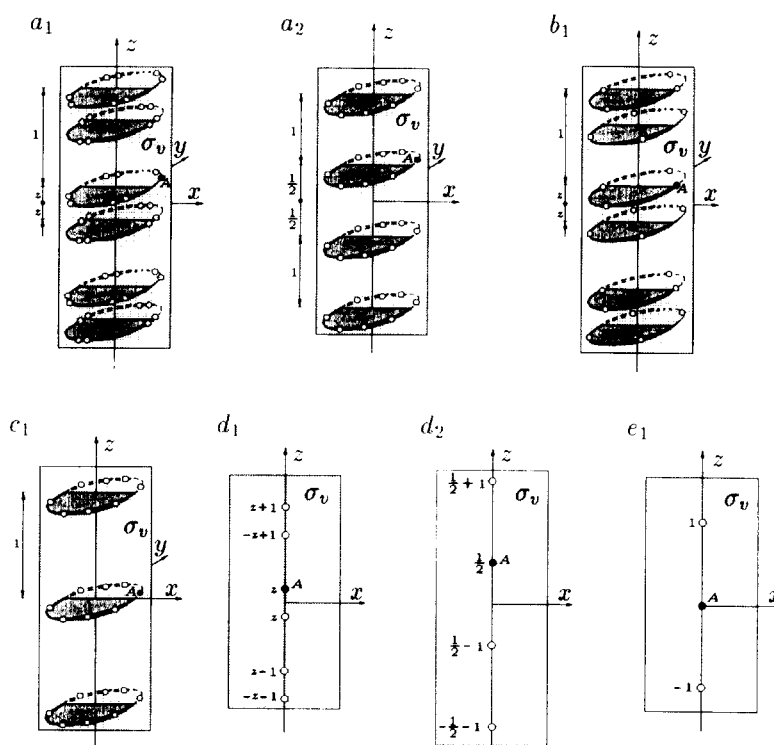| Type	a_1	a_2	b_1	b_2	c_1
Existence	$n > 1$	n odd	$\forall_n$	$\forall_n$	$\forall_n$
Atom A	(x, y, z)	$(0, y, \frac{1}{4})$	$(0, 0, z)$	$(0, 0, \frac{1}{4})$	$(0, 0, 0)$
Symmetry	S_{2n}	$C_n + (\sigma_v\sigma_hC_2|\frac{1}{2})C_n$	S_{2n}	$C_n + (\sigma_v\sigma_hC_2|\frac{1}{2})C_n$	S_{2n}
Stabilizer	C_1	$\{e, (\sigma_v\sigma_hC_2|\frac{1}{2})\}$	C_n	$C_n + (\sigma_v\sigma_hC_2|\frac{1}{2})C_n$	S_{2n}

Figure 10 Orbits of the line group $L(\bar{2n})2m$, $L\bar{n}m = TD_{nd} = gp\ \{C_n, \sigma_v, U'.(E|1)\}$ for $n = 4$. Symmetry fixing sets: a_1, a_2, b_1, c_1. The translational period is 1

Type	a_1	a_2	b_1	c_1	d_1	d_2	e_1
Existence	$\forall_n$	$\forall_n$	$\forall_n$	$\forall_n$	$\forall_n$	$\forall_n$	$\forall_n$
Atom A	(x,y,z)	$(\rho\cos\frac{\pi}{2n}, \rho\sin\frac{\pi}{2n}, \frac{1}{2})$	$(x,0,z)$	$(\rho\cos\frac{\pi}{2n}, \rho\sin\frac{\pi}{2n}, 0)$	$(0,0,z)$	$(0,0,\frac{1}{2})$	$(0,0,0)$
Symmetry	$\mathbf{D}_{nd}$	$\mathbf{C}_{nv} + (U'|1)\mathbf{C}_{nv}$	$\mathbf{D}_{nd}$	$\mathbf{D}_{nd}$	$\mathbf{D}_{nd}$	$\mathbf{C}_{nv} + (U'|1)\mathbf{C}_{nv}$	$\mathbf{D}_{nd}$
Stabilizer	$\mathbf{C}_1$	$\{e,(U'|1)\}$	$\mathbf{C}_{1v}$	$\mathbf{D}_1$	$\mathbf{C}_{nv}$	$\mathbf{C}_{nv} + (U'|1)\mathbf{C}_{nv}$	$\mathbf{D}_{nd}$

z axis, $(C_2|\frac{1}{2})$. Thus, the point group factor is $\mathbf{D}_{1h}$, while $\mathbf{2}_1$ is the group of generalized translations. *Trans*-polyacetylene consists of two orbits of the type e_1. The coordinates of the representative of e_1 are $(x \neq 0,0,0)$ (in the intersection of the horizontal and vertical mirror planes). The first orbit is formed by the carbon atoms, with the representative in $(0.6\,\text{Å}, 0, 0)$, and the other one is generated by the hydrogen at $(1.6\,\text{Å}, 0, 0)^9$. The configurations of the other polyacetylene isomers can be represented by the formula $L2_1/mcm[2b_1]$ for *cis-transoid*, *trans-cisoid* and *cis* polyacetylene: the line group symmetry is the same as for *trans*-polyacetylene, the number of orbits is also two, but the orbit types are different. Namely, the orbit representatives lie in the plane σ_v (with the coordinates $(x \neq 0, 0, z \neq 0)$). The structure of dimerized *trans-transoid* polyacetylene isomer is given by the symmetry formula $L\bar{1}m[2b_1]$ – ninth line group family for $n = 1$, two b_1 type orbits.

Similarly, for the chain conformation of the stereoregular butadiene[10] polymers in the crystal state (*Figure 15*), the symmetry formulas are: $L1c[10a_1]$ for *cis*-1,4 (seventh line group family, $n = 1$; ten orbits with representatives in general positions (x_i, y_i, z_i), $i = 1, \ldots, 10)$; $L\bar{1}[5a_1]$ for *trans*-1,4 (second line group family, $n = 1$, five orbits of the type a_1 with coordinates of the representatives (x_i, y_i, z_i) where $x_i, y_i, z_i \neq 0$); $L2_1/mcm[3a_2 3e_1 4d_1]$ for *syndiotactic* 1,2 (symmetry of the most of the polyacetylene isomers, with three orbits

of the representatives at $(0, y, \frac{1}{4})$, where $\frac{1}{4}$ stands for the quarter of the translational unit, three '*trans*-polyacetylene' orbits and four orbits generated by the atoms in the horizontal mirror plane). Finally, $L3_1[10a_1]$ describes the *isotactic* 1,2 form (screw axis group, ten general orbit types).

The backbone of the Watson–Crick B-form of DNA[11] can be approximately considered as a stereoregular polymer: it contains a large number of monomers and can be straightened well enough, while the observed local deviation of the helix parameters is small. The symmetry notation for this double helix is $L10_122[18a_1]$ (the fifth family, for $n = 1$, generated by $(C_{10}|\frac{1}{10})$, i.e. rotation for $\frac{\pi}{5}$ around the z axis followed by translation for the tenth of the translational unit along the z axis, and U, i.e. the rotation for π about the horizontal x axes).

DISCUSSION

There are many properties of the polymer which can be directly determined only by its symmetry formula $L[n_1 O_1, \ldots, n_k O_k]$. Among them there are some thermal and optical characteristics, normal modes of ionic vibrations, vibronic properties – stability of the given geometrical structure, classification and topology of the electronic zones, selection rules for various processes of absorption or emission of photons. Therefore, some
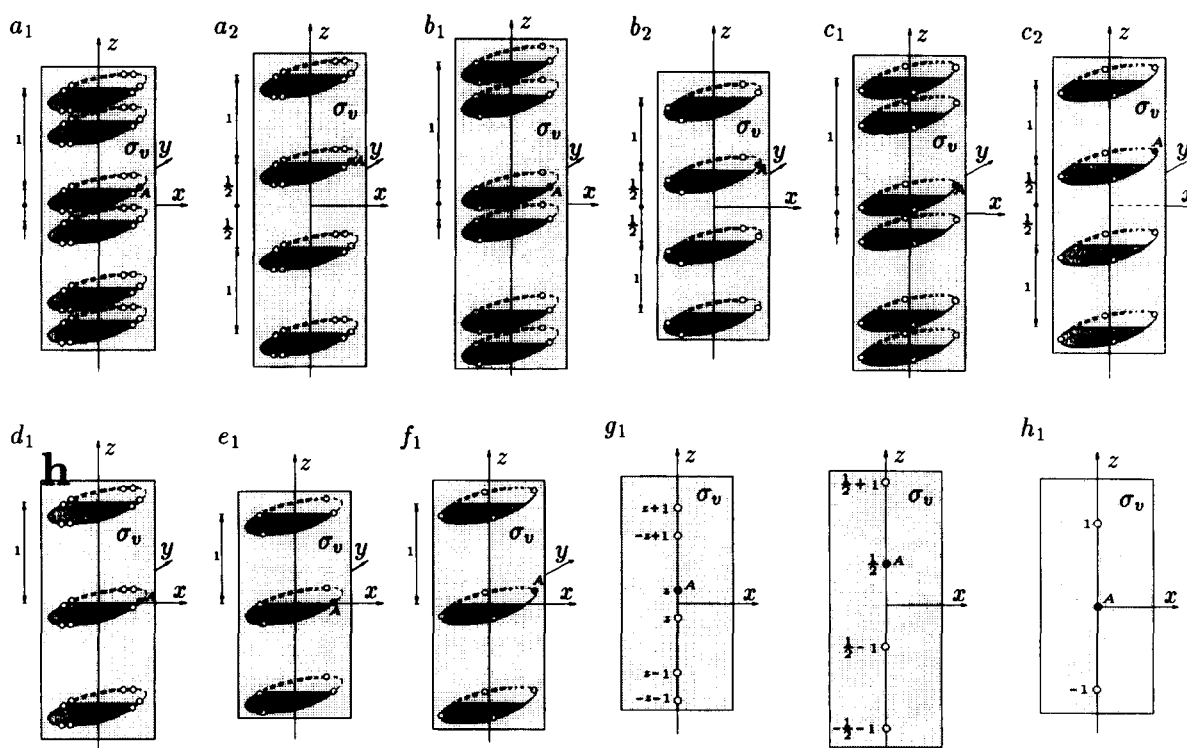
Figure 11 Orbits of the line group Ln/mmm, L$(\overline{2n})2m$ = TD$_{nh}$ = gp $\{C_n, \sigma_v, \sigma_h, (E|1)\}$ for $n = 4$. Symmetry fixing sets: a_1, a_2, b_1, b_2, c_1, c_2, d_1, e_1, f_1. The translational period is 1

Type	a_1	a_2	b_1	b_2	c_1	c_2	d_1	e_1	f_1	g_1	g_2	h_1
Existence	$\forall_n$	$\forall_n$	$n > 1$	$n > 1$	n even	n even	$\forall_n$	$n > 1$	n even	$\forall_n$	$\forall_n$	$\forall_n$
Atom A	(x,y,z)	$(x,y,\frac{1}{2})$	$(x,0,z)$	$(x,0,\frac{1}{2})$	$(\rho\cos\frac{\pi}{n}, \rho\sin\frac{\pi}{n}, z)$	$(\rho\cos\frac{\pi}{n}, \rho\sin\frac{\pi}{n}, \frac{1}{2})$	$(x,y,0)$	$(x,0,0)$	$(\rho\cos\frac{\pi}{n}, \rho\sin\frac{\pi}{n}, 0)$	$(0,0,z)$	$(0,0,\frac{1}{2})$	$(0,0,0)$
Symmetry	D_{nh}	$C_{nv} + (\sigma_h|1)C_{nv}$	D_{nh}	$C_{nv} + (\sigma_h|1)C_{nv}$	D_{nh}	$C_{nv} + (\sigma_h|1)C_{nv}$	D_{nh}	D_{nh}	D_{nh}	D_{nh}	$C_{nv} + (\sigma_h|1)C_{nv}$	D_{nh}
Stabilizer	C_1	$\{e, (\sigma_h|1)\}$	C_{1v}	$\{e, \sigma_v, (\sigma_h|1), (\sigma_v\sigma_h|1)\}$	C_{1v}	$\{e, \sigma_v, (\sigma_h|1), (\sigma_v\sigma_h|1)\}$	C_{1h}	D_{1h}	D_{1h}	C_{nv}	$C_{nv} + (\sigma_h|1)C_{nv}$	D_{nh}

precise conclusions about the similarities and distinctions between various polymers can be made, only on the grounds of the symmetry notations.

The optical activity of the system is determined by the line group symmetry only[11]. For example, from the symmetry notation it follows that the polyacetylene isomers are completely optically inactive and cannot be distinguished by this characteristic. Nevertheless, for symmetry reasons only, the thermal properties (expansion and conductivity) of *trans-transoid*-polyacetylene differ from the other polyacetylene isomers[9,12]. For *trans*, *cis-transoid*, *trans-cisoid* and *cis* isomers (with the same line group, symmetry predicts the same form of thermal conductivity tensor. Nevertheless, within this set of isomers the *trans*-polyacetylene is distinguished by a specific orbit structure, causing specific vibrational properties. Namely, the reduced forms of the vibrational representation (the modes corresponding to translations and allowed rotations of the system have been already subtracted) of the polyacetylene isomers are:

1. For *cis-transoid*, *trans-cisoid* and *cis* polyacetylene

$$4(_0A_0^+ + {}_0A_1^+ + {}_0A_1^- + {}_\pi E_B) + 3(_0A_1^+ + {}_0A_0^-)$$

$$+ 2(_0B_0^- + {}_0B_0^+ + {}_0B_1^-) + {}_0B_1^+ + 8_\pi E_{A_0}$$

$$+ 4\sum_k ({}_kE_{B_0} + {}_kE_{B_1} + 2_kE_{A_0} + 2_kE_{A_1}).$$

2. For *trans*-polyacetylene

$$_0A_0^+ + {}_0A_0^- + 2(_0A_1^+ + {}_0A_1^- + {}_\pi E_B + {}_0B_1^+)$$

$$+ 4_\pi E_{A_0} + 2\sum_k ({}_kE_{B_0} + {}_kE_{B_1} + 2_kE_{A_0} + 2_kE_{A_1}).$$

3. For *trans-transoid*-polyacetylene

$$4(_0A_0^+ + {}_\pi A_0^+ + {}_\pi A_0^-) +_0 B_0^+ + {}_0B_0^-$$

$$+ 2(_0A_0^- + {}_\pi B_0^+ + {}_\pi B_0^-) + 4\sum_k ({}_kE_{B_0} + 2_kE_{A_0}).$$

This classification of the normal vibrations, combined with the selection rules (i.e. Clebsch–Gordon decompositions for the irreducible representations), easily gives the active modes for the Jahn–Teller (or Peierls) instability (the *trans* isomer is frequently analysed in this context[6]). The differences between the *trans* and the other polyacetylene isomers with the same symmetry group can be predicted for the electron band structure, vibrational zones and the selection rules for various processes of absorption and emission. However, symmetry notation predicts no differences between the *cis-transoid*, *trans-cisoid* and *cis* isomers, concerning classification of electronic zones.

Data contained in the symmetry formula are of great importance in simplifying the numerical calculations in the various problems. Namely, since the orbits are invariant under the group action, the representation of
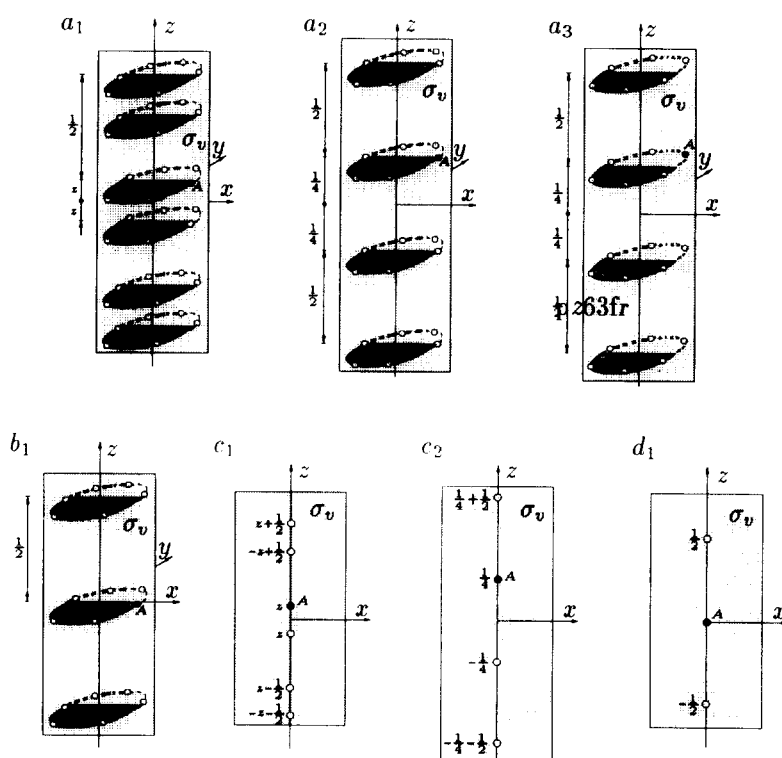
Figure 12 Orbits of the line group Ln/mcc, $L(\overline{2n})2c = T_cC_{nh} = gp\ \{C_n \cdot \sigma_h \cdot (\sigma_v | \frac{1}{2})\}$ for $n = 6$. Symmetry fixing sets: $2a_1$, $2a_2$, $2a_3$, $a_1 + a_2$, $a_1 + a_3$, $a_2 + a_3$, $2b_1$, $a_1 + b_1$, $a_2 + b_1$, $a_3 + b_1$. The translational period is 1

Type	a_1	a_2	a_3	b_1	c_1	c_2	d_1
Existence	$n > 1$	$n > 1$	$n = 2, 6, 10, \ldots$	$n > 1$	$\forall_n$	$\forall_n$	$\forall_n$
Atom A	(x, y, z)	$(x, 0, \frac{1}{4})$	$(0, y, \frac{1}{4})$	$(x, y, 0)$	$(0, 0, z)$	$(0, 0, \frac{1}{4})$	$(0, 0, 0)$
Symmetry	C_{nh}	$C_n + (\sigma_v \sigma_h | \frac{1}{2})C_n$	$C_n + (\sigma_v \sigma_h | \frac{1}{2})C_n$	C_{nh}	C_{nh}	$C_n + (\sigma_v \sigma_h | \frac{1}{2})C_n$	C_{nh}
Stabilizer	C_1	$\{e, (\sigma_v \sigma_h | \frac{1}{2})\}$	$\{e, (\sigma_v \sigma_h C_2 | \frac{1}{2})\}$	$\{e, \sigma_h\}$	C_n	$C_n + (\sigma_v \sigma_h | \frac{1}{2})C_n$	C_{nh}

the group in the state space of the system can be reduced to the orbit subspaces. Besides, the reduced representations are obtained by the induction[13] from the point factor **P** of the line group. This enables us to perform all the calculations at the level of the monomer, with finite dimensional matrices.

This recently developed technique[14] has been applied to *trans*-polyacetylene. The normal vibrational modes of the polyacetylene (*a priori*, this is an infinite-dimensional problem) are found at the monomeric level (finite-dimensional problem). The simplification appeared powerful enough to enable the analytical treatment of the problem (within four- and eight-dimensional matrices), without approximations concerning the number of the monomers included into the calculations. The same procedure can be applied to the electronic system.

Note that this concept has been already implemented in the programme *POLSym*, intended for use in polymer physics. It enables calculations on large macromolecules, polymers, or even subsystems of crystals using personal computers, without approximations regarding the length of the system (in fact, the proposed method assumes infinite length in one direction). Some results on the DNA vibrational spectra are available[5].

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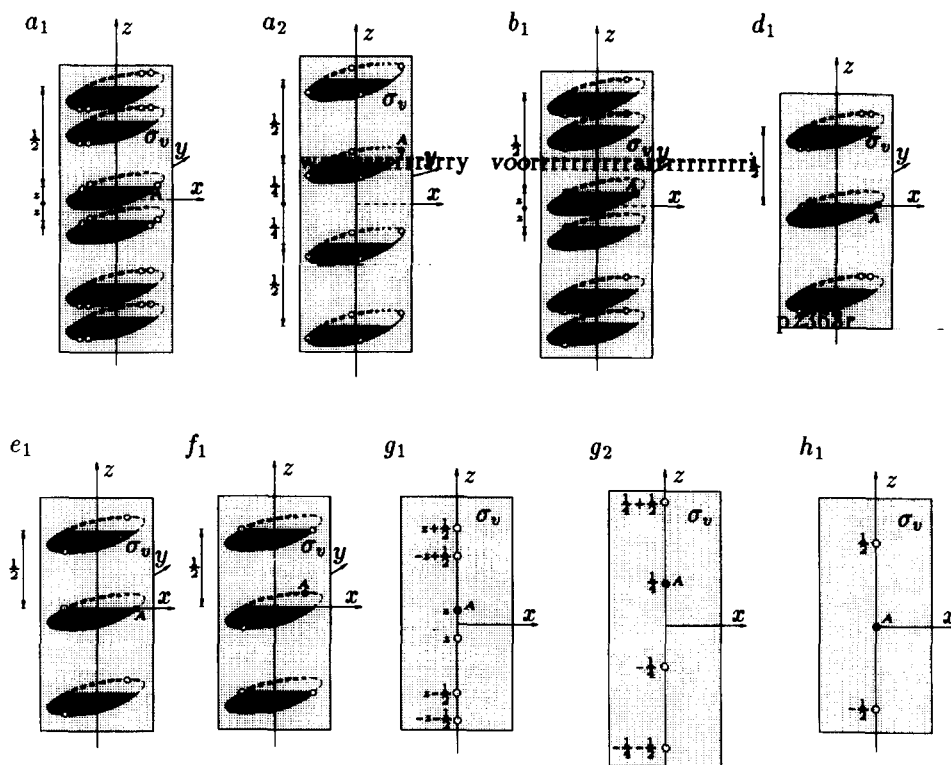14. Damjanović, M. and Milošević, I., *J. Phys., A*, 1995, **28**, 1669.

Figure 13 Orbits of the line group $\mathbf{L}(2n)_n/mcm = (2\mathbf{n})_1\mathbf{D}_{nh} = \mathrm{gp}\ \{C_n, \sigma_v, \sigma_h, (C_{2n}|\frac{1}{2})\}$ for $n = 2$. Symmetry fixing sets: a_1, a_2, b_1, d_1, e_1, f_1. The translational period is 1

Type	a_1	a_2	b_1	d_1	e_1	f_1	g_1	g_2	h_1
Existence	$\forall_n$	$\forall_n$	$n > 1$	$\forall_n$	$n > 1$	n even	$\forall_n$	$\forall_n$	$\forall_n$
Atom A	(x,y,z)	$(\rho\cos\frac{\pi}{2n}, \rho\sin\frac{\pi}{2n}, \frac{1}{4})$	$(x,0,z)$	$(x,y,0)$	$(x,0,0)$	$(\rho\cos\frac{\pi}{n}, \rho\sin\frac{\pi}{n}, 0)$	$(0,0,z)$	$(0,0,\frac{1}{4})$	$(0,0,0)$
Symmetry	$\mathbf{D}_{nh}$	$\mathbf{C}_{nv} + (C_{2n}\sigma_h|\frac{1}{2})\mathbf{C}_{nv}$	$\mathbf{D}_{nh}$	$\mathbf{D}_{nh}$	$\mathbf{D}_{nh}$	$\mathbf{D}_{nh}$	$\mathbf{D}_{nh}$	$\mathbf{C}_{nv} + (C_{2n}\sigma_h|\frac{1}{2})\mathbf{C}_{nv}$	$\mathbf{D}_{nh}$
Stabilizer	$\mathbf{C}_1$	$\{e, (C_{2n}\sigma_v\sigma_h|\frac{1}{2})\}$	$\mathbf{C}_{1v}$	$\mathbf{C}_{1h}$	$\mathbf{D}_{1h}$	$\mathbf{D}_{1h}$	$\mathbf{C}_{nv}$	$\mathbf{C}_{nv} + (C_{2n}\sigma_h|\frac{1}{2})\mathbf{C}_{nv}$	$\mathbf{D}_{nh}$
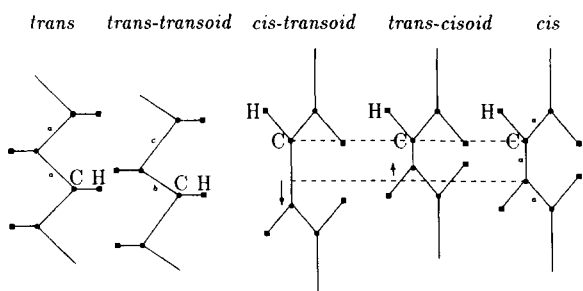
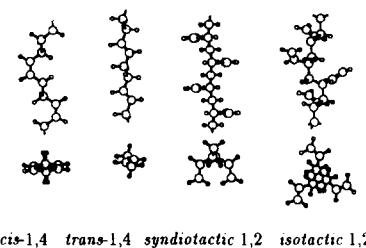**Figure 14** Isomers of the polyacetylene

cis-1,4 *trans*-1,4 *syndiotactic* 1,2 *isotactic* 1,2

Figure 15 Butadiene isomers[10]