

# On the Band Structure of Möbius Polymers

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*Dedicated to Professor Günther O. Schenck on the occasion of his 70th birthday*

The  $\pi$ -band structure of Möbius polymers (M) is compared with that of the open strip (F) and the cylindrical form (R) of the polymer considered. Under certain conditions, the bands of all these forms coincide. This is to be expected also for the  $\sigma$ -bands within the framework of extended Hückel theory.

## Introduction

Nearly twenty years ago, the  $\pi$ -electronic properties of completely conjugated Möbius cycles were first reported [1]. A short time later, it was recognized [2] that some intermediates of certain photochemical reactions possess the structure of such Möbius cycles. In numerous papers, most of them cited in [3] and [4], the subject has been discussed in detail. Very recently, Möbius and Hückel cycles have been treated by means of the SCF-CI [4] and PPP method [5] and they have been compared with related twisted linear, cyclic, and helical systems [6]. In the course of this work [4], it was shown that the LCAO-MO's of the  $\pi$  electrons of an  $n$  membered Hückel or Möbius cycle belong to the appropriate irreducible representations of the double group constructed from the point group  $\mathbb{C}_n$ . Finally, a functional relation between these two types of cycles has been found [7].

Nearly all this work concerns fully conjugated monocyclic structures with zero or an even number of sign inversions between adjacent atomic orbitals (Hückel cycles) or an odd number of such inversions (Möbius cycles) respectively; in addition, the Hückel and the Möbius forms of alternant heteronuclear cycles [7], radilenes [8], and polyacenes [7] have been considered. Till now, however, no attempt has been made to compare polycyclic Hückel and Möbius systems in general. Interest in this subject may well increase due to the successful synthesis of such compounds: By a twofold ring closure of a bicyclic strip possessing four reactive centers nearly equals amounts of a cylindrical and a Möbius

isomer have been formed [9]. This result indicates some real chance for the formation of similar structures in the course of at least some polymerisations. In an earlier paper [10], we studied the electronic band structure of cylindrical polymers, termed "rota polymers" on that occasion. The aim of the present paper is to compare rota and Möbius polymers by means of simple Hückel theory.

## Rota and Möbius polymers

Let us imagine that by a simultaneous manifold ring closure of an intermediate strip (F), alternatively a rota (R) and a Möbius polymer (M) will be formed as shown schematically in Figure 1. The strip F is assumed to consist of  $N$  monomeric units linked pairwise by  $l$  bonds apiece,  $l \geq 1$ , in the regular manner shown in Figure 1. The monomeric units are labelled consecutively by  $J = 1, 2, \dots, N$ , and the linking bonds by  $(s_\lambda^J r_\lambda^{J+1})$ ,  $1 \leq \lambda \leq l$ . Each of the  $\pi$ -AO's, assumed to form an orthonormal basis set, is denoted by the label of its center and a superscript indicating the monomeric unit, e.g.  $|r_\lambda^J\rangle$ ; there are  $n$  such AO's in each monomeric unit.

Provided that there is an equal degree of polymerisation,  $N$ , the Hückel matrix,  $\mathcal{H}$ , of the three systems, F, R, and M, takes the same block form, namely:

$$\mathcal{H} = \begin{pmatrix} \mathcal{H} & \mathcal{Y} & \emptyset & \dots & \emptyset & \mathcal{Y}^T \\ \mathcal{Y}^T & \mathcal{H} & \mathcal{Y} & \dots & \emptyset & \emptyset \\ \emptyset & \mathcal{Y}^T & \mathcal{H} & \dots & \emptyset & \emptyset \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ \emptyset & \emptyset & \emptyset & \dots & \mathcal{H} & \mathcal{Y} \\ \mathcal{H} & \emptyset & \emptyset & \dots & \mathcal{Y}^T & \mathcal{H} \end{pmatrix}. \quad (1)$$

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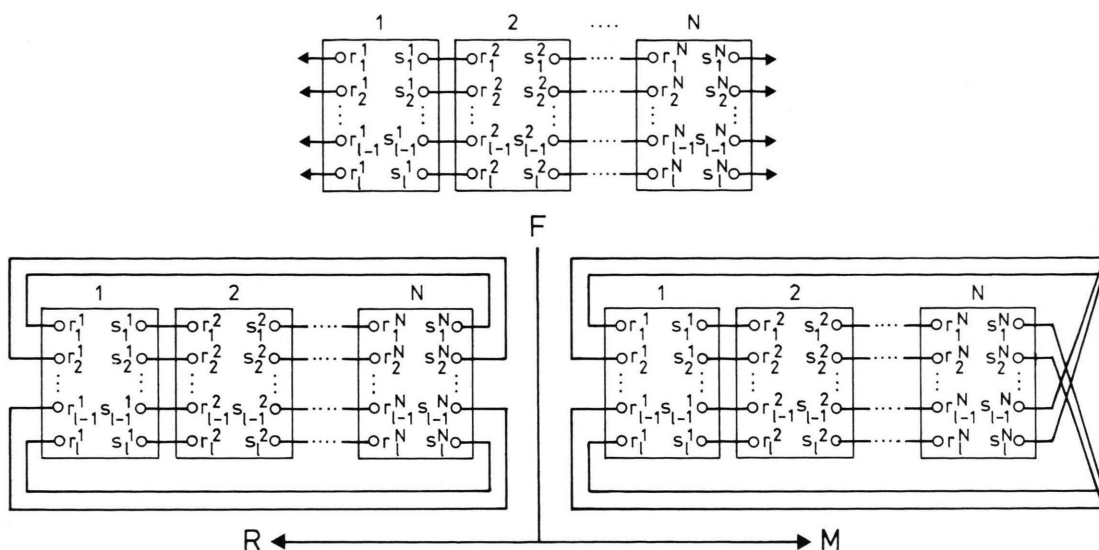


Fig. 1. Schematic picture of a polymer strip  $F$  consisting of  $N$  monomeric units.  $F$  closes alternatively to the rota polymer  $R$  or the Möbius polymer  $M$ . The centers where the ring closures take place are marked by arrows.

All the blocks of  $\mathcal{H}$  are of order  $n$ . Here,  $\mathcal{C}$  denotes a zero matrix,  $\mathcal{G}$  the Hückel matrix of an (isolated) monomeric unit, while  $\mathcal{V}$  has non-zero entries only in correspondence to the linking bonds between the monomeric units  $J$  and  $J+1$ ,  $1 \leq J \leq M-1$ . The non-zero entries of  $\mathcal{H}$  correspond to the bonds between the  $M$ -th and the first monomeric unit; hence we have  $\mathcal{H} = \mathcal{C}$  in the case of  $F$ , but  $\mathcal{H} = \mathcal{V}$  in the case of  $R$ ; in the case of  $M$ , it is evident that in general  $\mathcal{H}$  equals neither  $\mathcal{C}$  nor  $\mathcal{V}$ .

Before commencing the discussion of Möbius polymers  $M$ , the results obtained for rota polymers  $R$  will be reviewed [10]: Due to  $\mathcal{H} = \mathcal{V}$ , the matrix  $\mathcal{H}$  has the form of a circulant. The eigenvector  $\mathbf{C}_k$  of  $\mathcal{H}$  may be partitioned into  $N$  components  $\mathbf{c}_{kJ}$  of dimension  $n$  corresponding to the  $J$ -th monomeric unit

$$\mathbf{C}_k = \begin{pmatrix} \mathbf{c}_{k1} \\ \mathbf{c}_{k2} \\ \vdots \\ \mathbf{c}_{kN} \end{pmatrix}. \quad (2)$$

From the circulant property of  $\mathcal{H}$  the following additional equality is deduced:

$$\mathbf{c}_{kJ} = \omega_j^{J-1} \cdot \mathbf{c}_{k1}, \quad (3)$$

where  $\omega_j$  denotes a complex number. Via (3) the eigenvalue problem of  $\mathcal{H}$  is reduced to that of the

following secular determinant of order  $n$  [10]:

$$E(x, \Theta_j) = \det[\omega_j^* \cdot \mathcal{V}^T + (\mathcal{G} - x \cdot \mathcal{I}) + \omega_j \cdot \mathcal{V}] = 0. \quad (4)$$

From the first (last) row of  $\mathcal{H}$  there follows

$$\begin{aligned} \omega_j^N &= 1; & \omega_j &= \exp\{2ij\pi/N\}, \\ \Theta_j &= 2j\pi/N, & 0 &\leq j \leq N-1. \end{aligned} \quad (5)$$

Note that as  $N \rightarrow \infty$ ,  $\Theta_j$  becomes quasi-continuous. One may easily recognize  $\omega_j$  as the character of the rotation  $C_N$  mapping subsequent monomeric units onto each other in the  $j$ -th irreducible representation,  $\Gamma_j$ , of the point group  $\mathbb{C}_N$ , which is either itself the point group of the rota polymer  $R$  or a proper subgroup of it. The  $N$ -fold axis of rotation coincides with the axis of the cylinder formed by the rota polymer.

As shown by means of perturbation theory [10] in case of  $N \rightarrow \infty$ , the bands of the open strip form,  $F$ , and the rota form,  $R$ , of a given polymer coincide.

The expansion of the secular determinant (4) leads to the characteristic polynomial for the irreducible representation  $\Gamma_j$ , which may be written in two alternative general forms [10]:

$$\begin{aligned} E(x, \Theta_j) &= \sum_{\lambda=0}^l F_{\lambda}(x) \cos^{\lambda} \Theta_j \\ &= \sum_{v=0}^n A_v(\Theta_j) x^v = 0. \end{aligned} \quad (6)$$

Solving (6) one obtains  $n$  eigenvalues which correspond to  $n$  functions belonging to  $\Gamma_j$ ; in the case of the quasi-continuous argument  $\theta$ , each eigenvalue forms a band corresponding to  $0 \leq \theta < 2\pi$ . In the case of finite  $N$ , those eigenvalues of each band are realized [10] which correspond to multiples of  $2\pi/N$  as indicated by (5).

The rota polymers R exhibit the symmetry of one of the following point groups:  $\mathcal{C}_N$ ,  $\mathcal{C}_{Nv}$ ,  $\mathcal{C}_{Nh}$ ,  $\mathcal{S}_{2N}$ ,  $\mathcal{D}_N$ ,  $\mathcal{D}_{Nd}$ , and  $\mathcal{D}_{Nh}$ . Since the Abelian subgroups of these groups, namely  $\mathcal{C}_N$ ,  $\mathcal{C}_{Nh}$ , and  $\mathcal{S}_{2N}$ , are most effective for the construction of symmetry adapted basis functions [11], the rota polymers will be classified by them, i.e.,  $\mathcal{C}_N$  in case of  $\mathcal{C}_N$ ,  $\mathcal{C}_{Nv}$ , and  $\mathcal{D}_N$ ;  $\mathcal{C}_{Nh}$  in case of  $\mathcal{C}_{Nh}$  and  $\mathcal{D}_{Nh}$ ;  $\mathcal{S}_{2N}$  in case of  $\mathcal{S}_{2N}$  and  $\mathcal{D}_{Nd}$ . This classification will be also used in the discussion of Möbius polymers M. Although Möbius polymers do not exhibit higher point symmetries than  $\mathcal{C}_1$  or  $\mathcal{C}_2$ , the equivalence relationships among the centers of the polymer (leading to the relatively high symmetry expected for rota polymers R) remain and they are reflected by the permutations forming the automorphism group of the corresponding Möbius polymer M.

The main difference between the rota and the Möbius polymer formed from one and the same strip F involves the resonance integrals of the bonds linking the  $N$ -th and the first monomeric unit. While for R these integrals are given by

$$\langle r_{\lambda'}^1 | \hat{H} | s_{\lambda}^N \rangle = \beta \delta_{\lambda, \lambda'}, \quad (7)$$

in M they are as follows:

$$\langle r_{\lambda'}^1 | \hat{H} | s_{\lambda}^N \rangle = -\beta \delta_{\lambda, l+1-\lambda'}. \quad (8)$$

These two equations determine the non-zero entries of  $\mathcal{H}$ ; as (7) shows,  $\mathcal{H} = \mathcal{V}$  in the case of R without regard to the actual symmetry of R.

In the following comparison of Möbius and rota polymers, the classification mentioned above is used.

(1)  $\mathcal{C}_N$  is the Abelian subgroup of highest order: If the monomeric units are linked pairwise by only one bond, i.e.,  $l=1$ , both blocks  $\mathcal{V}$  and  $\mathcal{H}$  contain a single non-zero element and from (7) and (8) it follows that

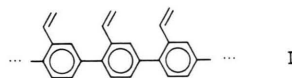
$$\mathcal{H} = -\mathcal{V}. \quad (9)$$

Comparing the secular determinants (4) derived from the first (last) and any other row of  $\mathcal{H}$ , one

obtains

$$\begin{aligned} \omega_j^N &= -1, & \omega_j &= \exp \{j i \pi / N\}, \\ j &= 2z + 1, & z &= 0, 1, \dots, N-1. \end{aligned} \quad (10)$$

This is the typical condition for the characters of the second set of double valued irreducible representations of a double group [12]. Hence, the results found in the comparison of Hückel and Möbius cycles [4] may be generalized: The bands of corresponding rota and Möbius polymers, in which subsequent monomeric units are linked by only one bond, coincide and the eigenvalues of these polymers belong to different sets of the irreducible representations of a double group isomorphic to that one which may be constructed from the point group  $\mathcal{C}_N$ . As an illustrative example, in Fig. 2 the half ( $0 \leq \theta \leq \pi$ ) of the deepest  $\pi$  band of  $(C_8H_6)_{N \rightarrow \infty}$ , poly-(2,5-styrylyden) (I), and the eigenvalues of the R and the M form of  $(C_8H_6)_{18}$  belonging to this band are shown. The complete eigenvalue spectrum of R and M consists of a eight-fold repetition of the pattern shown since all the eight bands of  $(C_8H_6)_{N \rightarrow \infty}$  are well separated by finite energy gaps. Due to the general symmetry of the band, i.e.,  $x(\theta) = x(2\pi - \theta)$ , doubly degenerate eigenvalues arise. It seems worthwhile to note that the eigenvalues of R and M obey an interlacing rule different from a similar rule recently observed in another context [13].



If the monomeric units are linked pairwise by more than one bond, i.e.,  $l \geq 2$ , then  $\mathcal{H}$  and  $\mathcal{V}$  are not simply related: The entries corresponding to  $(s_{\lambda}^J r_{\lambda'}^{J'})$  are non-zero in  $\mathcal{V}$  but zero in  $\mathcal{H}$ , whilst the entries corresponding to  $(s_{\lambda}^J r_{l+1-\lambda'}^{J'})$  are zero in  $\mathcal{V}$  but non-zero in  $\mathcal{H}$  where in the case of  $\mathcal{V}$ ,  $J' = J + 1$ ,  $1 \leq J \leq N - 1$ , but in the case of  $\mathcal{H}$ ,  $J = N$  and  $J' = 1$ . The conjecture that also in the case of  $l \geq 2$  the bands of R and M do coincide must remain unproved. As shown below, partial proofs may be given if the Abelian subgroup of highest order is either  $\mathcal{C}_{Nh}$  or  $\mathcal{S}_{2N}$ .

(2)  $\mathcal{C}_{Nh}$  is the Abelian subgroup of highest order: In this case, a symmetry operation,  $\hat{\sigma}_h$ , is presupposed which maps automorphically the centers of the monomeric units and the bonds between them

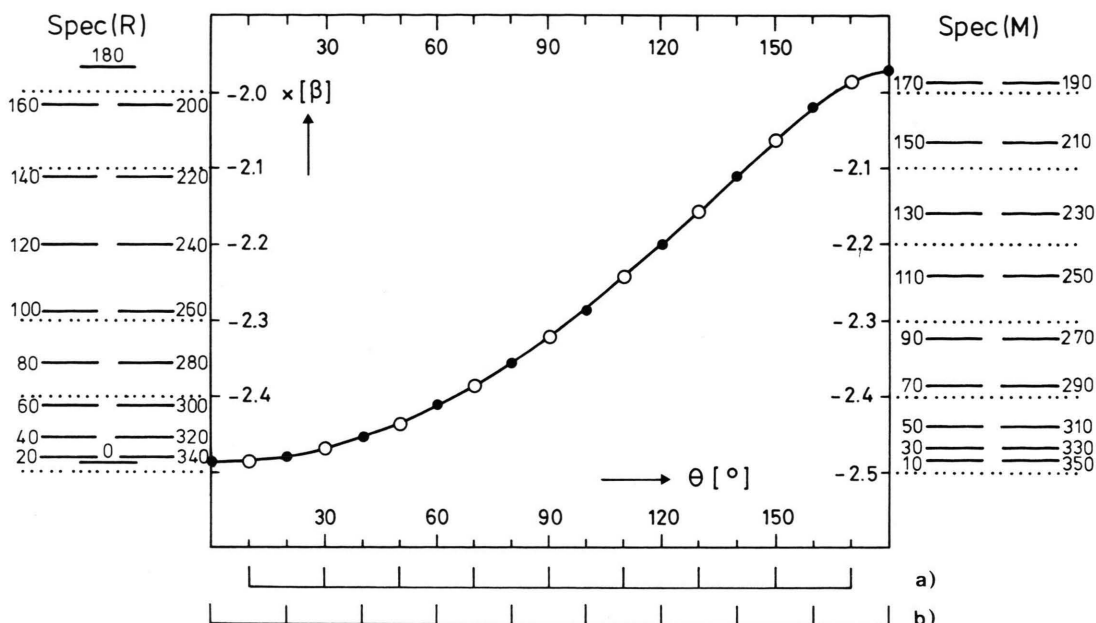


Fig. 2. Deepest  $\pi$ -band of polymer I. The eigenvalues of  $(C_8H_6)_{18}$  belonging to that band of the R and the M form are indicated by full and open circles, respectively. They are collected in the partial spectra spec(R) and spec(M), respectively. The representations to which the eigenvalues of M (a) and R (b) belong are shown at the bottom; their arguments are indicated in the partial spectra.

onto each other. Of especial interest are the following mappings,

$$|r_{\lambda'}^J\rangle \leftrightarrow |r_{l+1-\lambda'}^J\rangle, \quad |s_{\lambda'}^J\rangle \leftrightarrow |s_{l+1-\lambda'}^J\rangle$$

which may be used for the construction of locally symmetry-adapted basis functions, namely:

$$\begin{aligned} |r_{\lambda'}^J(\sigma)\rangle &= 2^{-1/2} \{ |r_{\lambda'}^J\rangle + \sigma |r_{l+1-\lambda'}^J\rangle \}, \\ |s_{\lambda'}^J(\sigma)\rangle &= 2^{-1/2} \{ |s_{\lambda'}^J\rangle + \sigma |s_{l+1-\lambda'}^J\rangle \}; \end{aligned} \quad (11)$$

$$\lambda' = l + 1 - \lambda, \quad \sigma \in \{+1, -1\}.$$

Here,  $\sigma$  denotes the character,  $\chi(\sigma_h)$ , of the symmetry operation  $\sigma_h$  in the irreducible representation considered. Note that there are  $N$  such representations with  $\chi(\sigma_h) = +1$  and  $N$  others with  $\chi(\sigma_h) = -1$ ; they are denoted by  $\Gamma_j^+$  and  $\Gamma_j^-$ , respectively. The cardinalities of the sets of locally symmetry-adapted basis functions are  $n^+$  and  $n^-$ , respectively; obviously,  $n^+ \geq n^-$  and  $n^+ + n^- = n$ .

Using the functions defined in (11) instead of the original AO's, one again obtains the Hückel matrix  $\mathcal{H}$  in the form given in (1); of course, the blocks now depend on the actual value of  $\sigma$  and, hence, they should be replaced by  $\mathcal{H}(\sigma)$ ,  $\mathcal{V}(\sigma)$ , and  $\mathcal{W}(\sigma)$ , which are now matrices of the order  $n^+$  and  $n^-$ , respectively.

The entries of  $\mathcal{W}(\sigma)$  are no longer given by (7) and (8), although the basic validity of these equations remains. The entries of  $\mathcal{V}(\sigma)$  are easily found to be

$$\langle s_{\lambda'}^J(\sigma) | \hat{\mathbf{S}} | r_{\lambda'}^{J+1}(\sigma) \rangle = \beta, \quad 1 \leq \lambda' \leq l(\sigma), \quad 1 \leq J \leq N-1, \quad (12)$$

where  $l(\sigma)$  stands for  $l(\sigma = +1) = \lceil l/2 \rceil$ , the smallest integer equal or greater than  $l/2$ , and for  $l(\sigma = -1) = \lfloor l/2 \rfloor$ , the greatest integer equal or smaller than  $l/2$ . In the same manner, one obtains the following intermediate results for the entries of  $\mathcal{W}(\sigma)$ :

$$\begin{aligned} \langle r_{\lambda'}^l(\sigma) | \hat{\mathbf{S}} | s_{\lambda'}^N(\sigma) \rangle &= (1/2) \{ \langle r_{\lambda'}^l | \hat{\mathbf{S}} | s_{\lambda'}^N \rangle + \sigma \langle r_{\lambda'}^l | \hat{\mathbf{S}} | s_{\lambda'}^N \rangle \\ &\quad + \sigma \langle r_{\lambda'}^l | \hat{\mathbf{S}} | s_{\lambda'}^N \rangle + \sigma^2 \langle r_{\lambda'}^l | \hat{\mathbf{S}} | s_{\lambda'}^N \rangle \}; \\ \lambda' &= l + 1 - \lambda, \quad 1 \leq \lambda' \leq l(\sigma). \end{aligned}$$

From this and (7) and (8), it follows that

$$\langle r_{\lambda'}^l(\sigma) | \hat{\mathbf{S}} | s_{\lambda'}^N(\sigma) \rangle = \begin{cases} \beta & \dots \text{ in case of R,} \\ -\sigma \beta & \dots \text{ in case of M.} \end{cases} \quad (13)$$

Finally, comparison of (12) and (13) shows that required relationships between  $\mathcal{W}(\sigma)$  and  $\mathcal{V}(\sigma)$  are

as follows:

in the case of R:

$$\mathcal{H}(\sigma) = \mathcal{V}(\sigma);$$

in these case of M:

$$\mathcal{H}(\sigma = +1) = -\mathcal{V}(\sigma = +1),$$

$$\mathcal{H}(\sigma = -1) = +\mathcal{V}(\sigma = -1).$$

(14)

It follows from the last line of (14) that, in the case of the antimetric MO's ( $\sigma = -1$ ), the  $\mathcal{H}$  matrices of R and M do not differ; this means that the antimetric eigenvalues of R and M equal each other in pairs provided that R and M have the same number,  $N$ , of monomeric units. In the case of the symmetric MO's ( $\sigma = +1$ ), a similar situation arises as discussed above and characterized by (9) and (10), i.e., the symmetric MO's of M belong to the second set of irreducible representations of the double group constructed from  $\mathfrak{C}_{N_h}$ . Both results

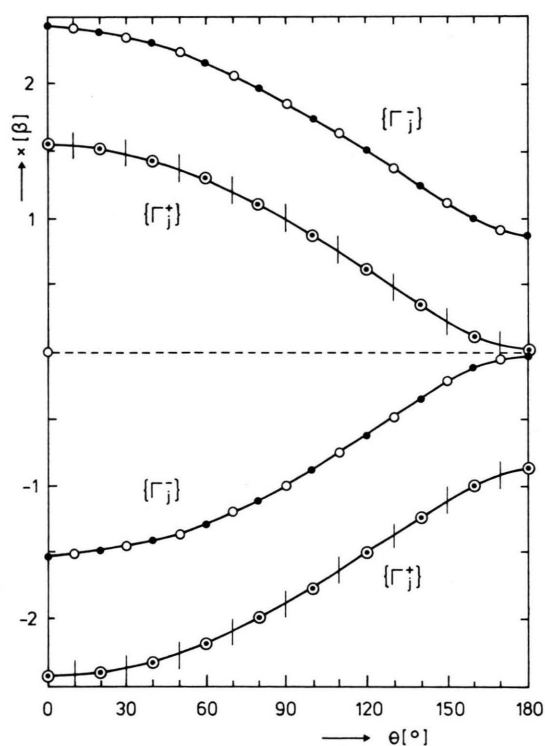


Fig. 3. The  $\pi$ -bands of polymer II using a geometrical parametrisation according to bond lengths of 1.40, 1.42, and 1.44 Å for the double, the peripheric, and the inner single bonds, respectively. The  $\pi^*$ -bands are symmetric in respect to  $x = 0$ . The eigenvalues of the R and the M form of  $(C_4H_2)_{18}$  are indicated by full and open circles, respectively.

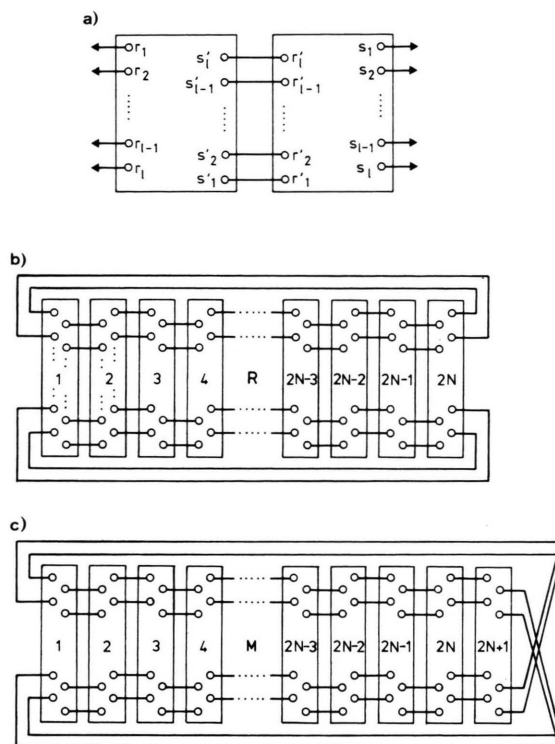
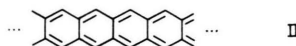


Fig. 4. Schematic pictures of the monomeric unit (a), the R form (b), and the M form (c) of polymers belonging to the type discussed in Section (3). The monomeric unit can be divided into two isomorphic half cells. R is constructed from an even, M from an odd number of such half cells.

indicate the coincidence of the bands of the R and M form of the polymers considered here. All this is illustrated by Fig. 3 showing the bands of  $(C_4H_2)_{N \rightarrow \infty}$ , poly-acene (II). The first and the third band from below correspond to the symmetric representations  $\{\Gamma_j^+\}$ , the two other bands to  $\{\Gamma_j^-\}$ .



(3)  $\mathfrak{S}_{2N}$  is the Abelian subgroup of highest order: One of the essentials of this class of polymers is a certain symmetry of the monomeric units which allows one to divide them into two moieties (half cells) in such a way that they may be mapped automorphically onto each other (see Fig. 4a) when the bonds between the moieties are deleted. To facilitate the discussion, let us distinguish these two moieties as the "left" and the "right" one. By the symmetry operation  $\hat{S}_{2N}$ , the left moieties of the



monomeric units of R are mapped onto the right moieties of the same unit but the right moieties onto the left moieties of the consecutive monomeric unit. Hence, it is very convenient to use only the AO's of one moiety (half cell) as basis functions. Certainly, the rota polymer R consists of an even number,  $2N$ , of such half cells.

In the matrix  $\mathcal{H}$  of (1), the blocks refer now to the half cells, hence  $\mathcal{H}$  has  $2N \times 2N$  blocks. As illustrated in Fig. 4, the entries of  $\mathcal{H}$  are given as follows:

$$\begin{aligned} \langle r_{\lambda'}^{J+1} | \hat{\mathbf{H}} | s_{\lambda}^J \rangle &= \beta \delta_{\lambda, \lambda'}; \\ 1 \leq \lambda \leq l, \quad 1 \leq J \leq 2N-1, \end{aligned} \quad (15)$$

and one also easily derives

$$\begin{aligned} \text{for R (2N half cells):} \\ \mathcal{H} = \mathcal{V}, \end{aligned} \quad (16)$$

On the other hand, in the case of Möbius polymers, M, consisting of  $2N$  half cells, the entries of  $\mathcal{H}$  are given by

$$\langle r_{\lambda'}^1 | \hat{\mathbf{H}} | s_{\lambda}^{2N} \rangle = -\beta \delta_{\lambda, l+1-\lambda'}$$

and the comparison with (15) clearly shows that  $\mathcal{H}$  equals neither  $+\mathcal{V}$  nor  $-\mathcal{V}$ . But considering a Möbius polymer consisting of an odd number,  $2N+1$ , of half cells, one obtains

$$\langle r_{\lambda'}^1 | \hat{\mathbf{H}} | s_{\lambda}^{2N+1} \rangle = -\beta \delta_{\lambda, \lambda'}, \quad (17)$$

leading immediately to

$$\begin{aligned} \text{for M (2N+1 half cells):} \\ \mathcal{H} = -\mathcal{V}. \end{aligned} \quad (18)$$

In the same manner as for (10) one derives here  $\omega_j^* = -\omega_j^{2N}$  and consequently one obtains

$$\begin{aligned} \omega_j^{2N+1} &= -1, \quad \omega_j = \exp \{i j \pi / (2N+1)\}, \\ j &= 2\alpha + 1, \quad \alpha = 0, 1, \dots, 2N. \end{aligned} \quad (19)$$

Once again, the eigenvalues of the Möbius polymer belong to the second set of the irreducible representations of a double group, but it is hard to indicate its construction since no point group exists which might be identified as  $\mathfrak{S}_{2N+1}$ . On the other hand, from (19) one can conclude that the double group in question must be isomorphic with the one constructed from  $\mathfrak{C}_{2N+1}$ . In this connection, attention should be paid to the isomorphism between the point groups  $\mathfrak{S}_{2M}$  and  $\mathfrak{C}_{2M}$ .

Another consequence of (19) is the coincidence of the bands of the R and the M form of the polymers

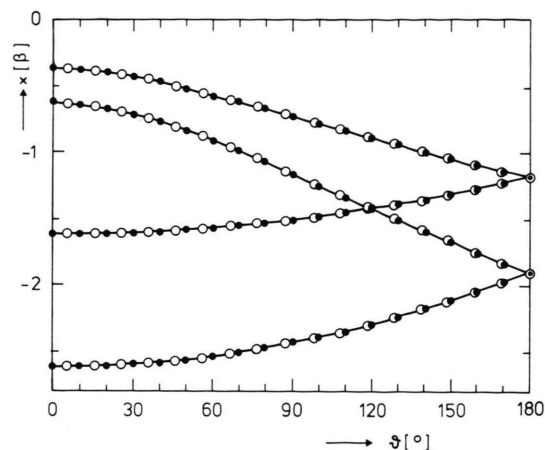
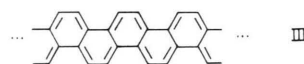


Fig. 5. The  $\pi$ -bands of polymer III, the  $\pi^*$ -bands are symmetrical in respect to  $x=0$ . The eigenvalues of the R form of  $(C_4H_2)_{36}$  and those of the M form of  $(C_4H_2)_{35}$  are indicated by full and open circles, respectively.

possessing the symmetry considered here, since for an infinite polymer, the differences in the parity of the number of half cells (assumed for R as even but for M as odd) becomes immaterial. This is not true, however, for polymers with finite  $N$ . As an illustration, Fig. 5 shows the  $\pi$ -bands of the polymer  $(C_4H_2)_{2N \rightarrow \infty}$ , polyphen (III), and the eigenvalues of a finite R form  $(C_4H_2)_{36}$ , and a finite M form,  $(C_4H_2)_{35}$ , of this polymer indicated by full and open circles respectively.



## Conclusions

The  $\pi$ -bands of corresponding rota and Möbius polymers coincide if either  $l=1$  or the polymers exhibit that symmetry presumed in subsections (2) and (3). As shown earlier [10], the bands of the open strip form, F, of a polymer coincide also with those of the corresponding R form and, hence, under the above conditions also with those of the corresponding M form.

This result is also valid for  $\sigma$ -bands in the framework of the extended Hückel method. Since the integrals corresponding to the  $\sigma$  bonds between the first and the last monomeric units (expressed in AO's) do not change their sign in the R and the M form, (9) and (18) must be replaced by  $\mathcal{H} = \mathcal{V}$ , and

in the last two lines of (14) the sign must be changed.

The effects of the different geometries of the F, R, and M form on the band structure might not be completely negligible but should be quite moderate provided that the degree of polymerisation,  $N$ , is not too small. This leads to the conclusion that the band pattern of these forms is not greatly altered, but the energies where the bands are located may differ significantly. Thus, some properties such as heat content, spectral behaviour, etc. might depend

more pronouncedly on the actual form of the polymer, especially in the case of small values of  $N$ .

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