

*Original Investigations***The Effect of Ring Opening on the MOs of a Cyclic Polymer**

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The usual Born–Kármán boundary conditions applied in a tight-binding calculation of a cyclic polymer are relaxed by mixing the Bloch MOs of a particular band under a perturbation which creates certain states associated with the newly-formed ends of the polymer and which have energies outside the range of the particular band.

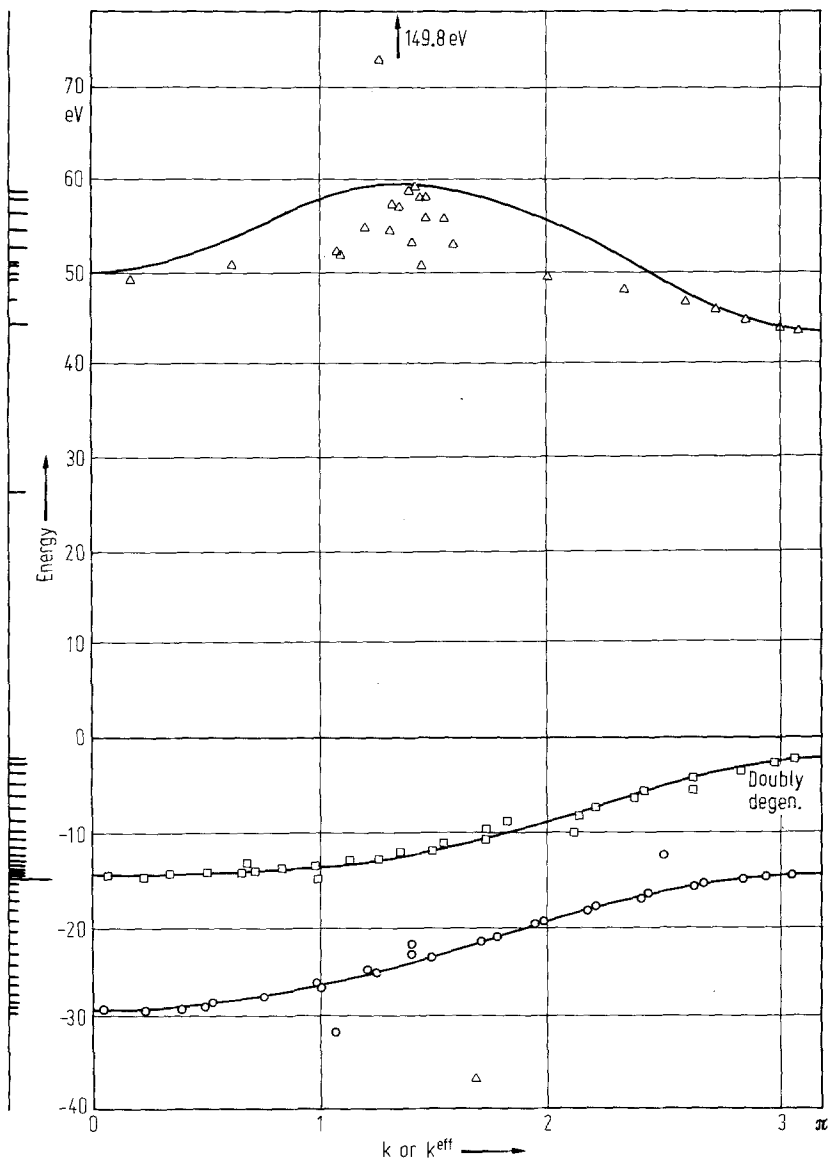
**Key words:** Bloch MOs – Ring-opening of a cyclic polymer

**1. Introduction**

Methods of calculating band structures in polymers are now well-developed on both *ab initio* [1] and semi-empirical levels [2, 3]. However, in these methods either a polymer is treated as an infinite cyclic molecule whose orbitals are obtained by applying the Born–Kármán boundary conditions [4], or else conclusions are drawn from the extrapolation of the results obtained from calculations on long but finite chain molecules.

The question relating to the contribution of the chain ends of a real polymer in determining the electronic energy levels may be an important one, just as the termination of a crystal in a surface may result in a superposition of discrete “surface states” on to the energy bands of an infinite crystal [5]. This possibility is necessarily neglected in methods using the usual crystal orbital functions derived from the Born–Kármán “cyclic lattice” conditions, but the surface problem has been treated by methods based on the nearly-free-electron approximation [6], the Mathieu approach [7], the Kronig–Penney model [8, 9] etc. (See Ref. [9] for useful references to such methods and to a discussion of Tamm and Shockley states).

On the extreme left of Figs. 1 to 3 the electronic energy levels obtained from Extended Hückel (EH) calculations on finite-chain cumulene ( $C_{18}H_2$ ), polyene



**Fig. 1.** Electronic levels in  $C_{18}H_2$ , energy bands in cyclic cumulene polymer and the result ( $\odot$ ,  $\square$  and  $\triangle$ ) of ring-opening the latter

( $C_{14}H_{16}$ ) and alkane ( $C_9H_{20}$ ) molecules have been drawn. (States whose energy separations are less than the plotting resolution of the diagrams are shown at the same energy value but with an extended "intensity".) Also shown on the same diagrams as the  $E(k)$  curves are the energy bands of the corresponding infinite (cyclic) chain molecule obtained from an EH polymer calculation similar to that of Imamura [2], in which the usual boundary conditions were applied. It is seen that

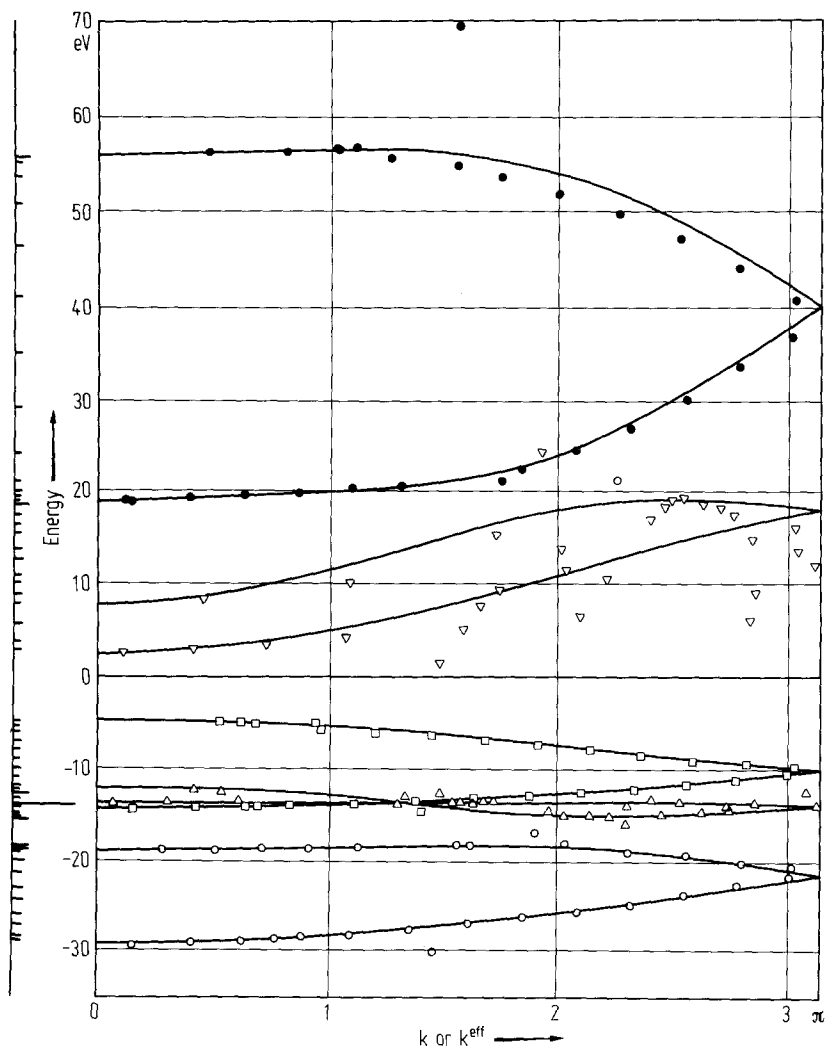


Fig. 2. Levels in  $C_{14}H_{16}$ , bands in polyacetylene and the result of ring opening

the energy level structures might extrapolate to the band structures in the limiting case of long polymers, with the possible exception of the two (unoccupied) almost degenerate MOs at 26.83 eV for  $C_{18}H_2$ .

An examination of the LCAO coefficients of these two MOs shows that they are unique in their degree of localization at the ends of the chain. Each is a MO composed almost entirely of  $(2s + 2p_z)$  on the end C atom, anti-bonding with the terminal H atom<sup>1</sup>. It must be stressed that whether or not such "discrete" energy

<sup>1</sup> The two LCAO wave functions for the 26.82 eV MOs (corrected so as to describe zero-overlap AOs) are of the form

$$\Psi = -0.03(2sC_3) + 0.04(2p_zC_3) + 0.06(2p_zC_2) - 0.21(2sC_1) + 0.23(2p_zC_1) + 0.33(1sH_1)$$

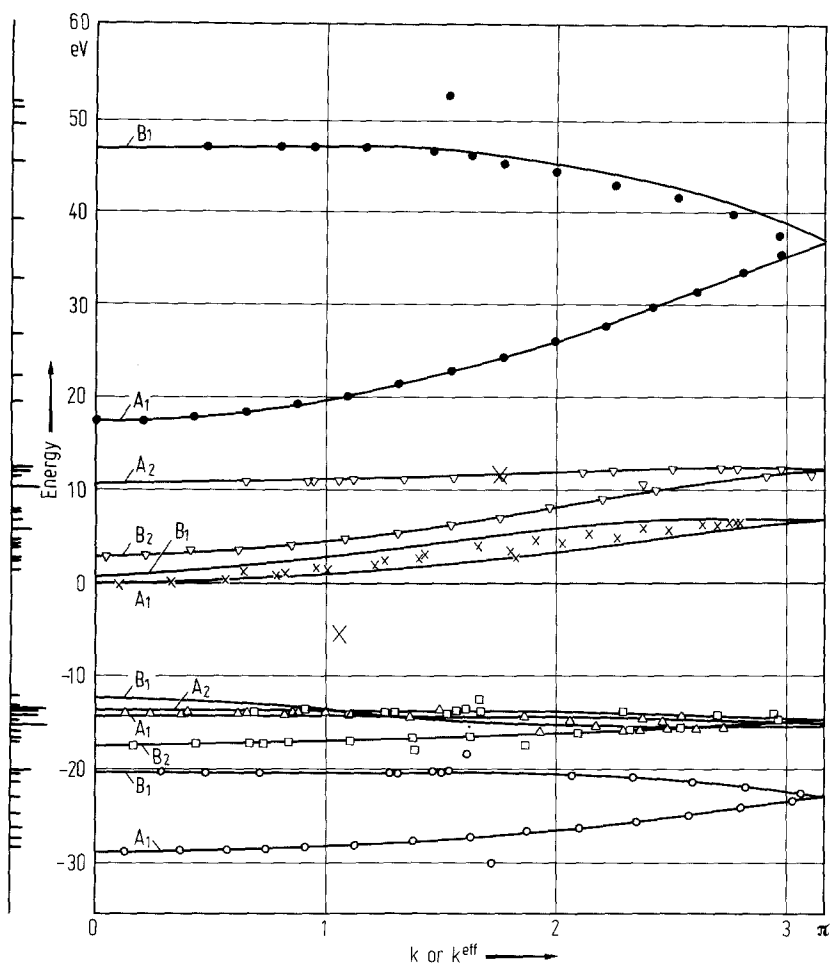


Fig. 3. Levels in  $C_9H_{20}$ , bands in all-trans polyethylene and the result of ring opening

levels are actually found in polymers it is important to examine the conditions in the model or theory which can give rise to them since such conditions might also occur in nature.

In these calculations and in the ones to be reported below the cumulene C—C and C—H bond lengths were taken as 1.29 and 1.0 Å respectively; the lengths in the polyenes were 1.4 and 1.1 and in the alkanes they were 1.53 and 1.1 Å [10]. Bond angles in the latter two polymers were the trigonal and tetrahedral values and the conformation of the alkane polymers were taken as all *trans*. Coulomb and overlap integrals were calculated by the same methods as those described by Hoffmann [11]

in which the C  $2p_z$  AOs are directed with their positive lobes in the chain direction. (The second MO associated with the 26.82 eV level is similar to the above but is localized at the opposite ( $C_{18}$ ) end of the molecule.)

and by Imamura [2]. The effects of bond length alternation was not investigated in this work.

### 2.1. Perturbation of Bloch MOs

The Born-Kármán boundary conditions imposed on a polymer, considered a cyclic  $N$ -fold one-dimensional system of repeating segments, lead to a Bloch LCAO-MO wave function  $\Psi_p^s$  given [4] by

$$\Psi_p^s = N^{-1/2} \sum_{j=1,2,\dots,N}^{\text{segments}} e^{2\pi i p j / N} \sum_{t=1,2,\dots,n}^{\text{seg. AOs}} c_{ip}^s \chi_t^j. \quad (1)$$

Here  $p$  labels the microstate within the  $s$ th band and takes integer values from 1 to  $N$ .  $c_{ip}^s$  is the LCAO coefficient of  $\chi_t^j$ , the  $t$ th AO in segment  $j$ , and may be determined by a variation procedure. As a result the  $\Psi_p^s$  will be eigen-functions of the molecular Hamiltonian  $H^0$  of the cyclic system.

We now consider these MO functions  $\Psi_p^s$  as zeroth-order functions and, omitting the band index numbers for convenience, write them as  $\Psi_p^0$ . The corresponding energies  $E_p^0$  are the solutions of the Schrödinger equation

$$H^0 \Psi_p^0 = E_p^0 \Psi_p^0.$$

Let us introduce a perturbation term  $V$  into the Hamiltonian by writing

$$H = H^0 + V. \quad (2)$$

The eigenfunctions  $\Psi_q$  of  $H$  can be expressed as linear combinations of the zeroth-order Bloch orbital functions (LCBO)  $\Psi_p^0$

$$\Psi_q = \sum_{p=1}^N g_{pq} \Psi_p^0 \quad (3)$$

where however we neglect the possible contributions from the  $\Psi_p^0$  of other bands. The mixing coefficients  $g_{pq}$  and the energies  $E_q$  satisfying the Schrödinger equation

$$H \Psi_q = E_q \Psi_q$$

may again be determined by a variation procedure. The elements of the  $H$  matrix are given by

$$H_{p_1 p_2} = E_{p_1}^0 \delta_{p_1 p_2} + \int \Psi_{p_1}^{0*} V \Psi_{p_2}^0 d\tau = E_{p_1}^0 \delta_{p_1 p_2} + V_{p_1 p_2}. \quad (4)$$

In (4) the perturbation element  $V_{p_1 p_2}$ , expressed in terms of AO quantities is

$$V_{p_1 p_2} = N^{-1} \sum_j^N \sum_{j'}^N e^{-2\pi i p_1 j / N} e^{2\pi i p_2 j' / N} \sum_t \sum_u c_{ip_1}^* c_{up_2} \int \chi_t^j V \chi_u^{j'} d\tau \quad (5)$$

where  $j$  and  $j'$  label the segments and  $t$  and  $u$  the AOs.

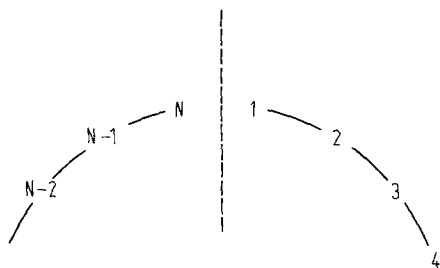


Fig. 4. The perturbation  $V$ , consisting of the elimination of interactions across a plane through segments 1 and  $N$

## 2.2 Ring Opening

We shall consider the effect of opening the  $N$ -fold cyclic polymer by breaking the link between the 1st and  $N$ th segments, which of course are adjacent. This is done explicitly by defining the perturbation term  $V$  in (5) as that which *eliminates* from  $H^0$  all interactions across a "boundary" between segments  $j=1$  and  $j=N$  (Fig. 4).  $V_{p_2 p_2}$  will therefore consist of terms containing

$$\beta_{iu}^{jj'} = \int \chi_i^j H^0 \chi_u^{j'} d\tau$$

in which the segments  $j$  and  $j'$  are those separated by the  $N/1$  boundary in the cyclic polymer.

Defined thus, the perturbation matrix element can be obtained from (5):

$$V_{p_1 p_2} = -\frac{1}{N} \sum_{j, j'} \left[ e^{2\pi i(j' p_2 - j p_1)/N} \sum_{i, u} \beta_{iu}^{jj'} c_{i p_1}^* c_{u p_2} + e^{2\pi i(j p_2 - j' p_1)/N} \sum_{i, u} \beta_{iu}^{jj'} c_{u p_1}^* c_{i p_2} \right]. \quad (6)$$

In order to express  $V_{p_1 p_2}$  as the summation of a convergent series in the segment terms  $j$  we replace the labels  $j$  and  $j'$  by the pair  $j_1 (=j)$  and  $j_2 (=N+1-j')$  which respectively count the segments starting at 1 and at  $N$  (i.e. from the right and from the left of the boundary as shown in Fig. 4). Transformed thus (6) now becomes

$$V_{p_1 p_2} = -\frac{1}{N} \sum_{j_1, j_2} \left[ e^{2\pi i((1-j_2)p_2 - j_2 p_1)/N} \sum_{i, u} \beta_{iu}^{j_1, N-j_2+1} c_{i p_1}^* c_{u p_2} + e^{2\pi i(j_1 p_2 - (1-j_2)p_1)/N} \sum_{i, u} \beta_{iu}^{j_1, N-j_2+1} c_{u p_1}^* c_{i p_2} \right]. \quad (7)$$

The elements  $H_{p_1 p_2}$  of the energy matrix may now be constructed using (4), and  $H$  diagonalized.

## 3. Results of Extended Hückel Ring-Opening Calculations on Polymers

EH cyclic polymer calculations (in which the boundary conditions were applied) were first performed on the three polymers discussed in the Introduction. 30  $k$ -points or microstates were calculated for each polymer, the energy eigenvalues and eigenvectors being retained for each  $k$  point. (Complex) elements of the perturbation matrix  $H$  were then calculated using Eqs. (4) and (7). Now (7) was derived for

a finite,  $N$ -segment chain, and simply letting  $N$  go to infinity would obviously result in zero perturbation. Although zero perturbation is indeed the correct limiting case for a long polymer (since the chain ends are then insignificant in comparison with the chain bulk) we are interested in the effects of the chain ends themselves, which must be somehow exaggerated so as to be able to superpose them on those of the bulk polymer. We must therefore make  $N$  finite, and we choose to give it the same value as the number of  $k$  points taken in the EH cyclic-polymer calculation. As we shall see the broad results of the ring-opening calculations seem to be rather insensitive to the value of  $N$ .

The matrix  $H$  was constructed and diagonalized using a complex Hermitian eigenvalue subroutine [12]. Defining an "effective  $k$  value" according to

$$k_q^{\text{eff}} = \sum_p |g_{pq}|^2 k_p$$

the energy eigenvalues  $E_q$  are plotted against  $k_q^{\text{eff}}$  on the energy band curves in Figs. 1 to 3, in which the energy points calculated from different bands are distinguished from one another by different plotting symbols. Because of the symmetry of the  $E^0(k)$  and  $E(k^{\text{eff}})$  points about  $k = \pi$  (the energy of microstate  $k$  is equal to that of microstate  $2\pi - k$ ), the calculated  $k^{\text{eff}}$  values, which spanned the Brillouin zone  $0 \leq k < 2\pi$  have been "folded back" into the range  $0 \leq k \leq \pi$ .

The ring opening perturbation  $V$  mixes the  $N$  Bloch microstates  $\Psi_p^0$  producing 1st order states  $\Psi_q$  as described by Eq (3). An examination of Figs. 1 to 3 shows that of these  $N$  "new" energy states  $\Psi_q$ ,  $N - 2$  are almost always within the energy range  $E_{\text{max}}^0 - E_{\text{min}}^0$  of the band  $\Psi_p^0$  (we shall refer to these as "ordinary" states), while the remaining two comprise states which are outside this range ("special" states), sometimes markedly so.

The symbols used to plot the  $E_q$  values in Figs. 1 to 3 reveal the special states, e.g. the  $-31.36$  and  $-12.02$  eV pair from the lowest band in cumulene polymer. A prominent example of such a special state is the  $-5.28$  eV level in polyethylene, occurring between the Fermi band and the ( $A_1$ ) conduction band which generated the state. We also find fairly prominent special states generated by the highest and lowest bands in the polymers considered; the highest band in cumulene polymer is an extreme example—it generates one state with energy  $-36.4$  eV which is lower than that of the lowest band of the cyclic infinite polymer, and two high energy states, one of which (at 149.8 eV) is too high for inclusion on Fig. 1.

In an attempt to understand the nature and origin of the special states, those formed from the lowest-energy band of cumulene polymer were (rather arbitrarily) selected for closer scrutiny. However the same features to be described below obtain for similar states in other bands and in other polymers. Table 1 lists (horizontally) the weights  $|g_{pq}|^2$  of the various basis microstates  $\Psi_p^0$  contributing to the first order states  $\Psi_q$  as defined by Eq. (3). For reasons of readability large areas of the table in which the  $|g_{pq}|^2$  are zero or negligibly small have been left blank. Because of the symmetrical dependence of  $|g_{pq}|^2$  on  $p$  (i.e. the contribution of  $\Psi^0(k)$  is equal to that of  $\Psi^0(2\pi - k)$ ) only the values in the range  $0 \leq k < \pi$  have been introduced in Table 1.

| Zeroth<br>order<br>micro-<br>states | $k$              |                  | $\{F_0^s(k)$ |        |        |        |        |        |        |        |        |        |        |        |        |        |        |  |
|-------------------------------------|------------------|------------------|--------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--|
|                                     | $k$              | $k$              | 0.00         | 0.22   | 0.43   | 0.65   | 0.87   | 1.08   | 1.30   | 1.52   | 1.73   | 1.95   | 2.17   | 2.38   | 2.60   | 2.82   | 3.03   |  |
| $E_0(\text{eV})$                    | $k_{\text{eff}}$ | $k_{\text{eff}}$ | -29.41       | -29.27 | -28.85 | -28.11 | -27.05 | -25.71 | -24.17 | -22.53 | -20.86 | -19.24 | -17.73 | -16.38 | -15.27 | -14.45 | -14.02 |  |
| -31.36                              | 1.07             | 0.00             | 0.02         | 0.05   | 0.08   | 0.08   | 0.09   | 0.08   | 0.06   | 0.04   | 0.03   | 0.02   | 0.01   | 0.01   | 0.00   | 0.00   | 0.00   |  |
| -29.37                              | 0.05             | 0.79             | 0.10         | 0.00   |        |        |        |        |        |        |        |        |        |        |        |        |        |  |
| -29.24                              | 0.24             | 0.00             | 0.48         | 0.01   | 0.00   | 0.00   | 0.00   |        |        |        |        |        |        |        |        |        |        |  |
| -29.08                              | 0.29             | 0.09             | 0.26         | 0.19   | 0.01   | 0.00   | 0.00   |        |        |        |        |        |        |        |        |        |        |  |
| -28.71                              | 0.49             | 0.00             | 0.01         | 0.41   | 0.05   | 0.01   | 0.01   | 0.01   | 0.00   |        |        |        |        |        |        |        |        |  |
| -28.45                              | 0.52             | 0.03             | 0.05         | 0.19   | 0.24   | 0.01   | 0.01   | 0.00   | 0.00   |        |        |        |        |        |        |        |        |  |
| -27.79                              | 0.74             | 0.00             | 0.01         | 0.01   | 0.34   | 0.11   | 0.11   | 0.02   | 0.01   | 0.00   |        |        |        |        |        |        |        |  |
| -27.47                              | 0.74             | 0.02             | 0.02         | 0.03   | 0.15   | 0.28   | 0.01   | 0.01   | 0.00   | 0.00   |        |        |        |        |        |        |        |  |
| -26.50                              | 0.99             | 0.00             | 0.00         | 0.00   | 0.02   | 0.26   | 0.11   | 0.18   | 0.03   | 0.01   |        |        |        |        |        |        |        |  |
| -26.15                              | 0.97             | 0.01             | 0.01         | 0.02   | 0.03   | 0.11   | 0.02   | 0.32   | 0.01   | 0.00   |        |        |        |        |        |        |        |  |
| -29.93                              | 1.22             | 0.00             | 0.00         | 0.00   | 0.00   | 0.02   | 0.02   | 0.19   | 0.25   | 0.03   | 0.01   |        |        |        |        |        |        |  |
| -24.58                              | 1.19             | 0.01             | 0.01         | 0.01   | 0.02   | 0.03   | 0.03   | 0.08   | 0.34   | 0.00   | 0.00   |        |        |        |        |        |        |  |
| -23.19                              | 1.46             | 0.00             | 0.00         | 0.00   | 0.00   | 0.00   | 0.00   | 0.02   | 0.13   | 0.31   | 0.02   | 0.01   | 0.00   |        |        |        |        |  |
| -22.89                              | 1.37             | 0.01             | 0.01         | 0.01   | 0.02   | 0.02   | 0.02   | 0.03   | 0.08   | 0.31   | 0.00   | 0.00   | 0.00   | 0.01   |        |        |        |  |
| -21.71                              | 1.38             | 0.02             | 0.02         | 0.03   | 0.03   | 0.04   | 0.04   | 0.04   | 0.06   | 0.18   | 0.01   | 0.01   | 0.01   | 0.01   | 0.02   | 0.02   | 0.02   |  |
| -21.40                              | 1.69             | 0.00             | 0.00         | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.01   | 0.09   | 0.36   | 0.02   | 0.00   | 0.00   | 0.01   | 0.01   | 0.01   |  |
| -20.87                              | 1.74             |                  |              |        |        |        |        |        | 0.00   | 0.00   | 0.49   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   |  |
| -19.65                              | 1.91             |                  |              |        |        |        |        |        | 0.00   | 0.01   | 0.06   | 0.41   | 0.01   | 0.00   | 0.00   | 0.00   | 0.00   |  |
| -19.23                              | 1.94             |                  |              |        |        |        |        |        | 0.00   | 0.00   | 0.00   | 0.49   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   |  |
| -18.01                              | 2.14             |                  |              |        |        |        |        |        | 0.00   | 0.00   | 0.00   | 0.00   | 0.44   | 0.01   | 0.01   | 0.01   | 0.01   |  |
| -17.63                              | 2.16             |                  |              |        |        |        |        |        | 0.00   | 0.00   | 0.01   | 0.03   | 0.47   | 0.01   | 0.00   | 0.00   | 0.00   |  |
| -16.56                              | 2.37             |                  |              |        |        |        |        |        | 0.00   | 0.01   | 0.01   | 0.00   | 0.01   | 0.47   | 0.00   | 0.00   | 0.01   |  |
| -16.20                              | 2.39             |                  |              |        |        |        |        |        | 0.00   | 0.01   | 0.00   | 0.00   | 0.00   | 0.45   | 0.03   | 0.01   | 0.01   |  |
| -15.36                              | 2.59             |                  |              |        |        |        |        |        | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.01   | 0.48   | 0.00   | 0.00   |  |
| -15.04                              | 2.64             |                  |              |        |        |        |        |        | 0.00   | 0.00   | 0.00   | 0.49   | 0.00   | 0.01   | 0.39   | 0.07   | 0.03   |  |
| -14.49                              | 2.81             |                  |              |        |        |        |        |        | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.49   | 0.00   | 0.00   |  |
| -14.25                              | 2.90             |                  |              |        |        |        |        |        | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.26   | 0.01   | 0.23   |  |
| -14.05                              | 3.03             |                  |              |        |        |        |        |        | 0.00   | 0.00   | 0.01   | 0.00   | 0.00   | 0.00   | 0.01   | 0.00   | 0.50   |  |
| -12.02                              | 2.48             | 0.01             | 0.02         | 0.02   | 0.02   | 0.01   | 0.01   | 0.01   | 0.01   | 0.00   | 0.00   | 0.00   | 0.00   | 0.02   | 0.05   | 0.13   | 0.21   |  |



The ordinary states  $\Psi_q$ , i.e. those with energies within the band range  $-29.37$  to  $-14.03$  eV are observed to have large contributions from only a narrow range of  $\Psi_p^0(k)$  microstates. The figures in heavy type emphasize the leading  $\Psi_p^0(k)$  contributions to the  $\Psi_q$  state considered; the general location of these quantities along the diagonal of the table indicates a fairly small degree of interaction between the  $E_p^0$  levels to form these  $\Psi_q$  states. The special states at  $-31.36$  and  $-12.02$  eV, in contrast, each have contributions from a much wider  $\Psi_p^0(k)$  range. This may result in a greater degree of interaction between the basis states and hence in a greater shift in the calculated energies relative to those of the basis functions  $\Psi_p^0$ . The only other "broadly based" state in the table is the one with energy  $-21.71$  eV. However since the greatest contribution to this state comes from the middle of the band ( $\sim -23$  eV) we would not expect the first-order energy to be shifted appreciably beyond the band limits.

It remains for us to investigate the possible association of the special states with the perturbation-created *ends* of the polymer chain as we discussed for the EH MO calculations in the Introduction. The  $q$ th final state can be expressed as the LCAO

$$\Psi_q = \sum_t \sum_j a_{tjq} \chi_t^j$$

where, from Eqs. (1) and (3) the coefficient  $a_{tjq}$  of a particular AO  $\chi_t$  in segment  $j$  is given by

$$a_{tjq} = N^{-1/2} \sum_p^N g_{pq} c_{tp} e^{ijk}$$

In the limit of a sufficiently long polymer the above summation may be replaced by an integral:

$$a_{tjq} = N^{-1/2} \int_0^{2\pi} g_q(k) c_t(k) e^{ijk} dk$$

where the vectors  $g_q$  and  $c_t$  have been extended into functions of the continuous variable  $k$ .

From the properties of convoluted functions it can be understood that if the variations of  $g$  and  $c$  with  $k$  are slow in comparison with that of the periodic function  $e^{ijk}$  then the integral will have a small numerical value. But we have seen from Table 1 that the ordinary states are distinguished from the special ones by the "peaked" nature of their  $g(k)$  functions at a narrow range of  $k$  in comparison with the wider range associated with the latter states. For the special states, therefore, we would expect  $a_{tjq}$  to be small for  $j$  values which are not close to the range limits 0 or  $N$ , when  $e^{ijk}$  varies rapidly with  $k$ ; conversely the only appreciable coefficients should be those for values of  $j$  for which  $e^{ijk}$  varies rapidly with  $k$ —i.e. for segments near the ends of the chain.

The calculations for the three polymers were repeated using different values of  $N$ , the number of  $k$  points (microstates) used to calculate the energy band results. In each case any differences observed, using  $N = 10, 20$  and  $30$ , concerned only the

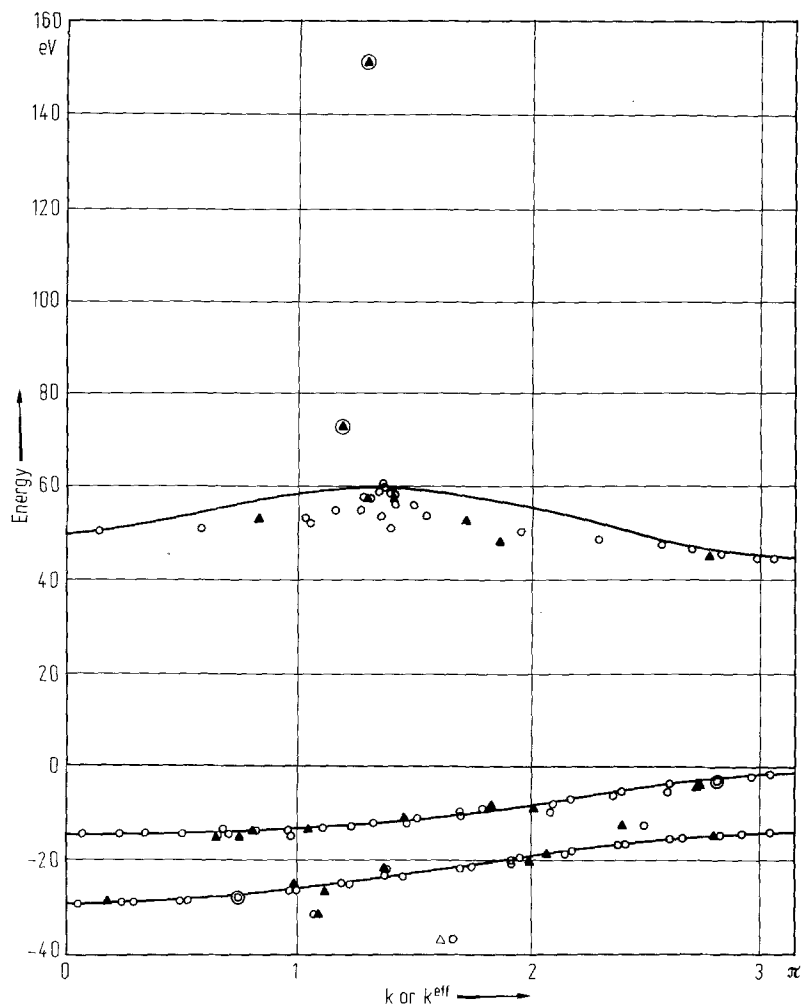


Fig. 5. Comparison of ring opening results on cumulene polymer using  $N = 10$  ( $\blacktriangle$ ) and  $N = 30$  ( $\odot$ )

positions of the ordinary states on the  $E(k^{\text{eff}})$  diagram – those of the special states were unchanged. The effect of  $V$  on the bands therefore seem to be independent of the value of  $N$  selected for the calculation. Fig. 5 shows the  $E(k^{\text{eff}})$  points calculated using  $N = 10$  and  $N = 30$ .

## 5. Conclusions

The Bloch MOs of a cyclic polymer can be combined, under the perturbing action of a ring opening, to create states which have features in common with either the basis Bloch orbitals or with orbitals largely localized near the free ends of the ruptured chain. The former produce energy bands practically indistinguishable from those of the basis MOs; the latter states are easily distinguished by their

energies which are outside the energy range of the band which generated them. Although demonstrated for orbitals derived using the Extended Hückel method, the procedure may be applied to any method in which the crystal orbitals may be conveniently derived.

Because of the paucity of chain ends in comparison with the units comprising the polymer chain, a direct experimental revelation of any chain-end states in a broken polymer chain might be difficult. But it would seem to be desirable to investigate at least the possibilities of their existence since they might be usefully invoked in a discussion of the reactivity of a polymer at the chain end.

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