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Comparison of Soliton Geometry and Charge-Density Wave Structure, and Band Gaps, Between Odd Polyene and Symmetrical Polymethine Cyanine (Brooker) Ions and T - Polyacetylene : Scf and Model Hamiltonian Approaches with Implications For Molecular Wires and Switches

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COMPARISON OF SOLITON GEOMETRY AND CHARGE-DENSITY WAVE STRUCTURE, AND BAND GAPS, BETWEEN ODD POLYENE AND SYMMETRICAL POLYMETHINE CYANINE (BROOKER) IONS AND t - POLYACETYLENE : SCF AND MODEL HAMILTONIAN APPROACHES WITH IMPLICATIONS FOR MOLECULAR WIRES AND SWITCHES.

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Abstract The geometric and electronic structures of odd polyene anions and the isoelectronic Brooker ions are examined by SCF quantum chemical methods in both the small and large (infinite chain) limit. For both types of ion, a geometric and charge density wave soliton is established, with half widths 6.9-7.2 and 9.4 CH units respectively. The odd polyene anions retain C_{2v} symmetry, but the Brooker ions are predicted to break symmetry for chain lengths larger than about 15 CH units. Where the finite-length ions are used as bridges (molecular wires) linking donor and acceptor groups, rates of charge transfer will be considerably enhanced over those of even-membered polyenes in symmetrical structures; where symmetry is broken, the ion may function as a charged soliton molecular switch. Relations between properties of finite-length ions and those of t-polyacetylene are discussed.

INTRODUCTION

An underlying concept in the field of molecular electronics is the flow of electric current, i.e. the transfer of an electron or hole from one part of a molecule to another. A molecular wire is defined as a single molecule (or, at most, a group of molecules) which is able to carry electric current in a circuit, i.e. a molecule that can transfer charge from a donor to an acceptor over a long range (e.g. 50 Å). Even-membered polyenes have been considered both experimentally[1] and theoretically [2,3] as possible molecular wires. It has been pointed out by Reimers and Hush[4] that odd-membered trans-polyene cations or anions should have considerably higher conductivities than the even-membered ions. Reimers and Hush also noted that the symmetrical polymethinecyanine cations known as Brooker ions[5] are also expected to show a slow attenuation of conductance with increasing length. Such slow attenuation is a necessary condition for rapid long range electron or hole transfer. The basic idea behind the suggestion that conductance of these ions will attenuate unusually slowly with length is that the Peierls distortion which results in alternating single-double bond structure in the even-membered species should be much smaller in the odd - membered species [4,5] However, the extent to which this is so, and how far it persists as the chain length increases, are questions which remain to be addressed.

We shall confine attention here to odd t-polyene *anions* of general formula $H_2(CH)^-_{2n+1}$ and the formally isoelectronic Brooker cations, $H_4(CH)_{2n-1}N_2,^+$ referred to more briefly as PO_n^- and BR_n^+ respectively. In Fig.1, the C_{2v} structures (including the dominant valence-bond structures) are shown for typical ions.

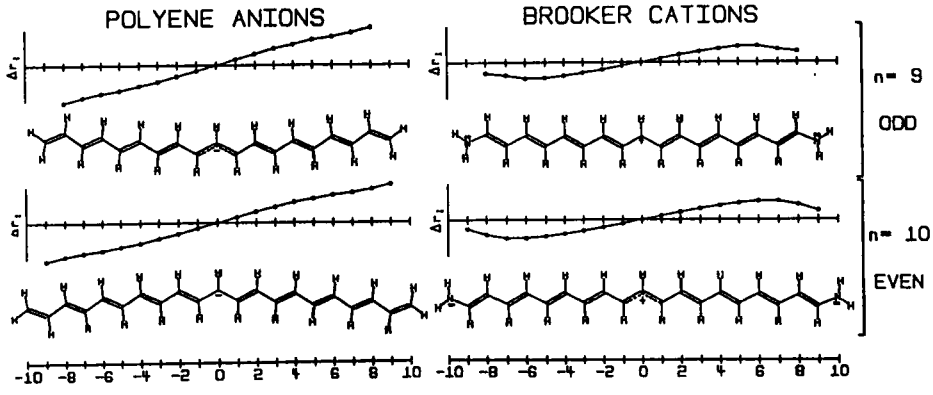

FIGURE 1 C_{2v} geometries (indicating the dominant valence-bond structures) and bond- length alternations for typical Brooker cations and polyene anions with odd and even n.

These are shown for both odd and even n: the qualitative difference is that the charge is always calculated to be zero on the central atom for odd n. If a symmetrical (C_{2v}) structure were to be maintained for all n, the Brooker ion could be thought of as a polyacetylene (PA) fragment with modified end groups, isoconjugate with an odd membered t-polyene anion. The latter becomes, in the infinite limit, negative-defect PA. The first analytical theory for the geometric properties of defect t-PA was put forward by Su, Schrieffer and Heeger (SSH)[6a] (see also[6b]). The SSH tight-binding Hamiltonian considers explicitly only the π electrons of the system[6b]. The most important feature of this theory is the prediction that long polyenes retain a symmetrical C_{2v} structure in which there is a geometric kink or *soliton* in the centre, flanked by regions of alternating single and double bonds. In the central soliton region, the bond lengths even out to values intermediate between those of single and double bonds. Thus, while the Peierls distortion is lessened in the central region, as the chain length increases the proportion showing bond alternation is predicted to increase.

THE GEOMETRIC SOLITON

For a polyene anion with $2n + 1$ π orbitals extending over the $2n + 1$ heavy atoms numbered from -n to n, the bond-length alternation Δr_i can be defined by

$$\Delta r_i = \text{sign}(i) \mid r_{i,i+1} - r_{i,i-1} \mid , \quad (1)$$

and according to the SSH theory this change in adjacent CC bond lengths is given as

$$\Delta r_i = \Delta r_\infty \tanh \frac{i}{\ell} \quad (2)$$

where Δr_∞ is the alternation for an infinite chain, and ℓ is the half width of the soliton kink. Calculations at the *ab initio* self-consistent field (SCF) level for t-PA have yielded values in the range 0.103-0.109 Å [7] for Δr_∞. For finite-length polyene ions, Villar, Dupuis and Clementi [8] assumed Δr_i = 0.112 Å, and for n up to 10 obtained a value of ℓ = 7 for the soliton half width of ions of this size. In order to investigate in more detail the development of geometric and electronic structure as the chain length increases, we[9] have studied both the polyene and Brooker ions , and have developed methods which enable very large ions to be examined.

COMPUTATIONAL METHOD AND RESULTS FOR GEOMETRIC SOLITON

For the smaller ions, for n up to 10, Restricted Hartree-Fock (RHF) SCF calculations were carried out[9] for both polyene and Brooker ions, using the double-zeta basis set of Dunning[10]. Both retained C_{2v} symmetry, and the results for polyene ions agreed well with those of Villar et al[8]. For larger systems it is necessary to use an approximate method. We repeated the calculations for n up to 20, using the semi-empirical AM1 method; very good agreement for geometries was found, agreement to within 0.003 Å being generally obtained. Finally, a model π electron Hamiltonian was developed[11] which was parametrized to reproduce AM1 results up to n = 21. The agreement is very close, and calculations on very large systems, up to n =160 were made using this AM1 model method.

For symmetrical (C_{2v}) polyene ions, the estimated values of Δr_∞ and half width ℓ are 0.095± 0.002Å and 6.9 ± 0.2 respectively.[9a] The former value is quite close to the most reliable experimental value for t-PA, 0.09 Å[12], which provides independent support for the accuracy of the AM1 model Hamiltonian. For Brooker ions with C_{2v} structure, the soliton calculated by the AM1 model approaches its infinite-chain limit near n = 29. The soliton is somewhat broader in the Brooker ion (7.2); this is because the charge contained within the soliton core is -1 e for the polyene anions and +1 e for the Brooker ions. Values of Δr_i calculated for ions with n = 9 and 10 are also shown in Fig.1; except for end effects (discussed in detail in[9]), the *tanh* relationship predicted by Eqn. 2 is closely obeyed.

CHARGE DENSITY WAVE IN C_{2v} STRUCTURES

In contrast to predictions of geometry, no uniquely defined method exists for the calculation or observation of molecular atomic charges. The most commonly used atomic charges for π systems are Mulliken charges for each centre. These are shown in Fig. 2 for polyene ions and C_{2v} Brooker ions for n up to 80 (i.e. chain

lengths of up to 161 centres). Only results for positive index i are shown: the structure reflects symmetrically in the $-i$ direction. The gradual build-up of an isolated charge density wave essentially congruent with the geometric soliton is evident, the charge density wave being predicted to be broader [9]. These results were obtained from AM1 model calculations.

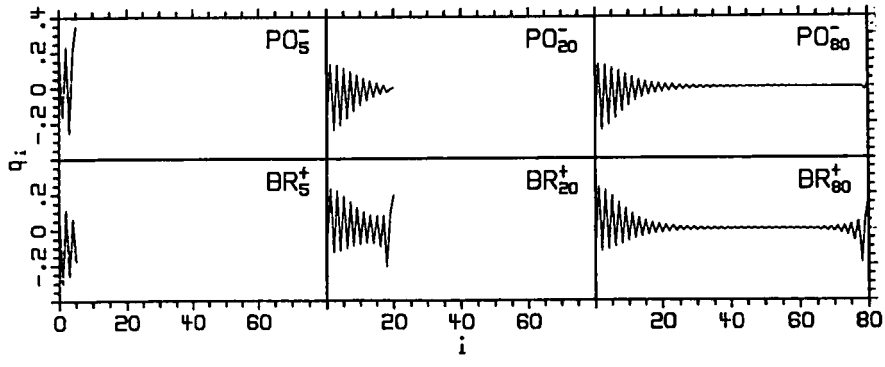

FIGURE 2 AM1 model atomic charges q_i versus displacement from the centre for the C_{2v} structures of ions BR_n^+ and PO_n^- with n = 5, 20 and 80.

The SSH theory[6] predicts the net charge on each atom for an infinite polyene to be given by

$$q_i = \frac{1}{\ell} \operatorname{sech}^2 \frac{i - i_c}{\ell} \cos^2 \frac{(i - i_c)\pi}{2}, \qquad (3)$$

with half width equal to that of the geometric soliton. If we consider the net accumulated charge Q_i between the centre of the soliton i_c and atom i, this follows from the SSH Eqn 3 as

$$Q_i = \int_{i_c}^{i} q_j \, dj = \frac{Q_\infty}{2} \tanh \frac{i - i_c}{\ell} \qquad (4)$$

yielding a *tanh* relationship of similar form to that predicted (Eqn 2) for bond -length displacements. Many of the problems arising from the non-uniqueness of the definition of atomic charges can be circumvented by considering not the charges themselves, but rather integral and differential properties of the charges along the chain. Thus the net

accumulated charge Q_i can be defined iteratively as

$$Q_i = Q_{i-1} + \frac{1}{2}(q_{i-1} - q_i). \qquad (5)$$

Calculated accumulated charges obey the predicted relationship (Eqn. 4) remarkably well. As shown in ref 9, the net accumulated charge is theoretically a "robust" quantity: it is much less sensitive to the method of calculation than individual atomic charges. This has been discussed in detail [13] in the context of correlation of measured ^{13}C NMR shifts [14] with calculated charge density wave in α,ω-diphenylpolyene anions. In the infinite limit, the charge density wave half width for both polyene and C_{2v} Brooker ions is calculated to be 9.4 CH units, significantly broader than the geometric soliton.

SYMMETRY BREAKING IN BROOKER IONS : MOLECULAR SWITCHES ?

Calculations mentioned so far for the Brooker ions refer to a C_{2v} structure. However, the very interesting result is obtained [9] fom AM1 calculations that as n increases above about 10 (21 unit chain length) a C_s structure has slightly lower energy. The energy difference increases linearly from 0.02 kcal/mole at n= 0 to 5.56 kcal /mole for n = 21. In the low-symmetry regime, the soliton is translated to a region close to one end of the chain. Since the barrier to translation to the other end is calculated to be small, the prediction is of rapid (> 10^{10} s^{-1}) dynamic motion of the charge density packet along the chain. This is illustrated for n = 10 in Fig.3.

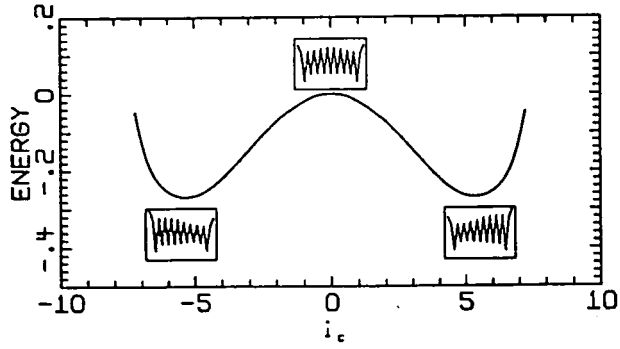

FIGURE 3 Energy (Kcal/mole-1) of the symmetry-broken C_s configuration relative to that of the C_{2v} configuration for Br^+_{10} versus distance from the soliton centre i_c (AM1 data).

Since a relatively small electric field could cause the soliton to switch and localise at one end, carrying a unit of charge, these materials are candidates for an unusual type of molecular switch. This possibility has also been considered by other workers.[16] Some caution must be exercised: the energy involved in symmetry-breaking is small, and environmental effects could conceivably modify it. However, it is also possible

to consider further stabilisation of the C_s state by appropriate substitution of the NH_2 groups- e.g. with electronegative groups.

BAND GAPS

In order to obtain reliable estimates of absolute band gaps in the infinite chain limit it is necessary to take account of electron correlation, i.e. to proceed beyond the SCF level. However, the relative band gaps for Brooker ions and polyene ions are probably reasonably well predicted at the SCF level. Results obtained using the AM1 model method are shown in Fig 4. The qualitative point of interest is that these calculations predict a finite band gap, about half that of an even polyene, owing to the presence of soliton levels in the occupied-virtual gap of the alternating structure, for both odd polyene and C_{2v} Brooker chains. In addition, a finite (rather, as often assumed(e.g, ref. 15) zero limit) is predicted for the lowest Brooker ion singlet absorption frequency: this should be the same as that of positive-defect PA[14].

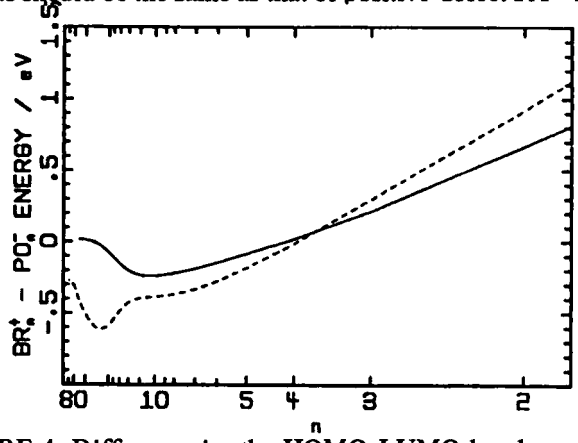

FIGURE 4 Difference in the HOMO-LUMO band gap ——— and the lowest singlet absorption frequency ----- between the C_{2v} and polyene ions (AM1 model data).

IMPLICATIONS FOR MOLECULAR ELECTRONICS

Our calculations connect the properties of finite chains with those of the infinite conducting polymer. The presence of the discrete soliton molecular orbitals within the nearly-continuous manifold of orbitals constituting the alternating single and double bond regions will result in a considerable enhancement of the rate of electron or hole exchange through a symmetric Brooker ion bridge; this would be amplified if the donor and acceptor groups contain levels resonant with those of the bridge[4]. The effect of symmetry-breaking, however, is profound: the two nitrogen atoms become non-equivalent, any resonances are lost, and conduction in the bridge occurs by soliton transport. In this regime, if the C_s or C_1 symmetry is stable, the ion will function as a fast molecular switch. Further investigation of the conditions for establishing symmetry-broken states is currently being undertaken.

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