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Bond Length Alternation in Infinitely Long Conjugated Polyacenes

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This paper concludes that whereas linear polyacenes are stable to distortions that preserve mirror symmetry with respect to the plane which is the perpendicular bisector of their interior bonds, they are unlikely to be stable with respect to distortions that do not preserve this symmetry.

Some years ago, Longuett-Higgins and Salem investigated the problem of bond length alternation in linear polyenes [1] and linear polyacenes [2] using periodic boundary conditions. They were able to show that bond length alternation would occur in the linear polyenes independantly of any assumptions about the numerical values of the parameters used in their calculation. They also came to the conclusion that such external bond alternation would not occur in the case of the linear polyacenes.

We believe that this latter conclusion is a result of their considering only a particular type of bond alternation. Thus, in the undistorted molecule, there is symmetry not only about the molecular plane, but also about the plane bisecting the interior bonds perpendicularly.

In their paper, Longuett-Higgins and Salem consider only a bond alternation which preserves this latter element of symmetry. Such distortions would not be expected to occur in the ground state of the molecule. This is because, whilst the energy spectrum of the infinitely long polyacene is continuous, it may be broken up into four bands of energy: one full band and one empty band of orbitals, symmetrical and antisymmetrical with respect to the perpendicular bisector of the internal bonds, with an energy gap between bands of the same symmetry. Thus distortions which preserve the symmetry would tend to mix orbitals differing widely in energy and hence be energically unfavourable.

Whilst the symmetrical distortion investigated by Longuett-Higgins and Salem would tend to distort the bond angles in the hexagonal units of the polyacene this would not be true of the assymetrical distortion caused by merely lengthening one pair of parallel external bonds with respect to the other pair of parallel external bonds in each hexagonal unit of the polyacene. In this case the distortion would tend to mix orbitals of the different symmetry classes of each of which there is a high density at the Fermi level. This distortion appears to be energetically favourable, in contrast to the symmetrical distortion and hence should occur in the ground state. We note that the distorted polyacene should resemble a pair of long distorted polyenes linked at alternate carbon atoms.

We thus conclude that the paraquinoid system of double bonds should be favoured with respect to the orthoquinonoid system investigated by Longuett-Higgins and Salem. The energy gain on distortion (if any) appears to be reduced by electron withdrawing substituents either, in the ring (e.g. nitrogen), or, external to the ring.

It is at present uncertain to what extent the imposition of periodic boundary conditions has an effect on the apparent solution to this problem.

References

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