Structure of Infinite Polyenes: *Ab Initio* Quantum Chemical Study

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Summary Using a minimal basis Hartree–Fock crystal orbital formalism for five structurally different infinite polyene (polyacetylene) models it is concluded that, besides the all-*trans* configuration, other structures may be energetically equal or even more probable.

THE presence or absence of bond length alternation in infinite polyenes [or polyacetylenes, $(CH)_x$] and the stability of different forms of these polymers are still of current interest;[1] high-conductivity samples of halogenated polyenes (polyene films doped by Cl_2, Br_2, I_2, and AsF_5) have been prepared recently.[2]

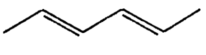
In support of the hypothesis of the alternation of short ('double') and long ('single') bonds one usually refers to the finite (non-zero) value of the first electronic transition energy, E_t, extrapolated from E_t values of finite polyenes.[3] For vibrational assignments of ring polyenes[4] and polyene polymers[5] also alternating models are preferred. Further support for bond length alternation arises from the concept of the Peierls-type instability of the equidistant metallic model with respect to introduction of bond length alternation.[6] On the other hand, the observed bond lengths of finite polyenes (and of somewhat similar carotenes) show some tendency towards equalization when going from the ends towards the middle of the molecules;[7] in our opinion, however, this is not a definite argument owing to the finiteness of these molecules. The E_t values can also be interpreted using non-alternating models involving electronic correlation.[1]

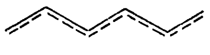
Recently we showed[8] that, at least within the framework of the Hartree–Fock theory, the alternating all-*trans* model is necessarily more stable than the non-alternating all-*trans* one. We now report on the question whether or not the forms C, D, and E, as suggested by Shirakawa and Ikeda,[5] are also energetically possible structures of long polyenes besides the all-*trans* A and B forms. In Table 1 we have collected the total energy values per CH unit for models A—E using the same *ab initio* minimal basis set and calculation method as previously[8] used for models A and B. Forbidden energy gap values and net hydrogen atomic populations are also given. For the geometry of the chains we have used idealised geometrical arrangements with $r_{C-C} = 1{\cdot}43$, $r_{C=C} = 1{\cdot}36$, and $r_{C-H} = 1{\cdot}08$ Å, and all bond angles of 120°.

TABLE 1. *Ab initio* Hartree–Fock crystal orbital results for different conformers of infinite polyene [polyacetylene, $(CH)_x$].

Form	Total energy per CH unit/ kcal mol^{-1}[a]	Forbidden energy gap/ a.u.	Atomic charges on H/Mulliken
A	−3·4	0·266	0·064
B (metallic[b])	0	0	0·064
B (charge density wave[c])	−0·7	0·152	0·095 and 0·032
C	−11·2	0·145	0·106
D	−19·3	0·321	0·054
E	−23·2	0·382	0·157

[a] Relative values with respect to the B form (metallic) for which it is −37·97035 a.u. per CH unit (1 a.u. = 27·21 eV = 4·359 × 10^{-18} J; 1 cal = 4·184 J). [b] Highest energy band half-filled. [c] Within the Hartree-Fock theory the presence of a charge density wave (CDW) solution having lower total energy than the metallic form indicates that the form A is necessarily more stable than form B (metallic). The two atomic charge values correspond to the CDW.


(A)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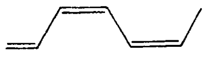
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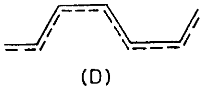
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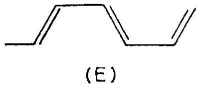
(E)

In order to assess the reliability of the approximations involved we have performed additional calculations as follows. Since basis set effects are of primary importance,

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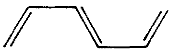
we have made comparative calculations for hexa-1,3,5-triene using the previous STO 3G basis as well as the more reliable[9,10] 4-31 G basis[9] which is of almost double zeta quality. As can be seen from Table 2, the two sets of results compare well. In concordance with these calculations for the hexatriene the form denoted by tTt is most probably more stable than the tCt form.[10] Furthermore, in order to gain some insight into the behaviour of the energy surface as a function of bond angles and bond lengths we have done some additional calculations on infinite polyenes on structure E which is probably the most stable. Increasing all C–C–C bond angles to 125° (provided all other parameters are fixed) leads to an energy decrease of *ca.* 0·6 kcal mol^{-1}. A simultaneous decrease in the length of the 'double' bonds to 1·34 Å and increase in that of the 'single' bonds to 1·46 Å (values closer to 'standard' lengths) lead to a further energy decrease of 0·7 kcal mol^{-1} (bond angles fixed at 125°). A further change in the same direction ($r_{\mathrm{C-C}}$ = 1·47, $r_{\mathrm{C=C}}$ = 1·33 Å) leads to about the same total energy per CH unit as that of model E in Table 1. Therefore the energy surface seems to be relatively flat around model E.

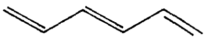
TABLE 2. *Ab initio* molecular orbital results for 3 conformers of hexa-1,3,5-triene using two different basis sets (total energy, *E* in atomic units)

	E	
Conformers[a]	STO 3G basis	4–31 G basis
tTt	−228·95147	−231·46838
tCt	−228·94249	−231·45915
cTc	−228·93154	−231·44058

[a] Geometrical parameters are not optimized: $r_{\mathrm{C-C}}$ = 1·43, $r_{\mathrm{C=C}}$ = 1·36, and $r_{\mathrm{C-H}}$ = 1·08 Å, and all bond angles 120°.


cTc


tCt


tTt

Among the results given in Table 1 the most remarkable is the relatively small stabilization energy of form A (−3·4 kcal mol^{-1}) with respect to form B in contrast to the much larger energy gain of other forms with *cis*-type configurations (in particular, E is −23 kcal mol^{-1} more stable). Despite limits of our crystal orbital calculations (small basis set, no electron correlation, no geometry optimization) we may conclude that, in the polyene polymers, the newly proposed forms C,D, and particularly E, are energetically at least as likely as the all-*trans* form A and B. We note that the insulating type energy band structure (non-zero gap) of model D is due to its lower symmetry as compared to that of B.

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[1] A. A. Ovchinnikov, I. I. Ukrainsky, and G. F. Kventsel, *Uspekhi Fiz. Nauk*, 1972, **108**, 81; see also ITP Preprint 28E (1972) of the Institute for Theoretical Physics, Kiev.

[2] H. Shirakawa, E. J. Luis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, *J.C.S. Chem. Comm.*, 1977, 578; C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Luis, S. C. Gau, and A. G. MacDiarmid, *Phys. Rev. Letters*, 1977, **39**, 1098.

[3] J. N. Murrell, 'The Theory of the Electronic Spectra of Organic Molecules,' Methuen, London, 1963; F. A. Van Catledge and N. L. Allinger, *J. Amer. Chem. Soc.*, 1969, **91**, 2582.

[4] C. Tric, *J. Chem. Phys.*, 1971, **55**, 827.

[5] H. Shirakawa and S. Ikeda, *Polymer J.*, 1971, **2**, 317.

[6] H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.*, 1959, **A251**, 172; see, *e.g.*, E. M. Shustorovich, 'Electronic Structure of Polymers with Short Bonds in the Main Chain' (in Russian), Nauka, Moscow, 1967.

[7] C. Sterling, *Acta Cryst.*, 1964, **17**, 1224.

[8] M. Kertész, J. Koller, and A. Ažman, *J. Chem. Phys.*, 1977, **67**, 1180.

[9] W. J. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 1970, **52**, 2769.

[10] C. J. Mains, P. George, M. Trachtman, A. M. Brett, and C. W. Bock, *J. Mol. Struct.*, 1977, **36**, 317.

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