

A PPP-investigation of Structural Isomerism in Infinite Polyenes

Peter Karadakov

Faculty of Chemistry of the Sofia State University, Sofia, Bulgaria

Obis Castaño

Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

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It is shown on the grounds of a semiempirical PPP-treatment that for the equidistant *cis-trans* infinite polyene two types of Hartree-Fock solutions are possible—one yielding a *cis-transoid* and the other a *trans-cisoid* distribution of nearest-neighbour bond-orders. Relaxing the nuclear framework according to bond-order magnitudes for the bond-alternation wave (BAW) in the equidistant all-*trans* polyene, resp. for the two solutions for the equidistant *cis-trans* polyene mentioned above and using repeatedly the Coulson-Golebiewski formula, realistic self-consistent values of bond lengths have been obtained. The calculated energy differences between the investigated isomers are small, predicting almost equal probabilities. The expressions for the PPP-wavefunctions are presented in analytical form suitable for further applications. Long-range Coulomb interactions have been accounted for up to convergence of the groundstate energies.

Introduction

Long polyene chains have been for a long time the subject of numerous theoretical and experimental investigations. As a recent success in the theoretical field one should mention the performance of extensive Hartree-Fock ab-initio infinite polyene calculations [1–6]. Remarkable experimental events are the synthesis of comparatively pure polyene crystals [7] and the subsequent discovery of the drastic increase of polyene film specific conductivities (over twelve orders of magnitude) upon doping with electron donors or acceptors [8]. The exact X-ray determination of polyene chain structural parameters has yet been hindered by insufficient purity and low degree of orientation in available samples. The results from [9] show a predominant existence of all-*trans* and *cis-trans* isomers and propose also an estimate of unit cell dimensions and interchain distances.

Although the relative stability of equidistant and bond-length alternating all-*trans* and *cis-trans* infinite polyenes has been discussed more than once both at ab-initio level [2–6] and employing a semiempirical CNDO/2 technique [10], the agreement between the results of different authors is far from total. One should naturally expect that the performance of semiempirical PPP-calculations would

add to the confusion but we hope that the results of our investigation prove the contrary.

Several authors [11–13] have recently discussed the connection of the nearest-neighbour bond-order distribution in equidistant structures to possible distortions of the nuclear framework. As a consequence of their results, a good starting point for the discussion of the structure of all-*trans* and *cis-trans* infinite polyenes should be a study of the possible Hartree-Fock solutions for the equidistant conformations yielding different bond-order distributions. As is well-known, for the all-*trans* equidistant model one finds in addition to the metallic solution a bond-order-alternation-wave (BAW) solution with a non-zero gap. Whereas other authors [3, 5, 6, 10] report only one type of solution for the equidistant *cis-trans* conformer, we have found two types of solutions: one with a *cis-transoid* and another with a *trans-cisoid* nearest-neighbour bond-order distribution, differing significantly in energy. A relaxation of the nuclear framework according to the magnitudes of bond-orders between adjacent atoms using e.g. the Coulson-Golebiewski formula [14] leads immediately to alternating all-*trans*, resp. alternating *cis-transoid* and *trans-cisoid* geometries (Fig. 1). The relative simplicity of the PPP-equations leading to an efficient computer program has enabled us to find self-consistent values of the bond lengths applying repeatedly the Coulson-Golebiewski formula (see e.g. [15]) and

Reprint requests to Dr. P. Karadakov, Faculty of Chemistry of the Sofia State University, Sofia 1126, Bulgaria.

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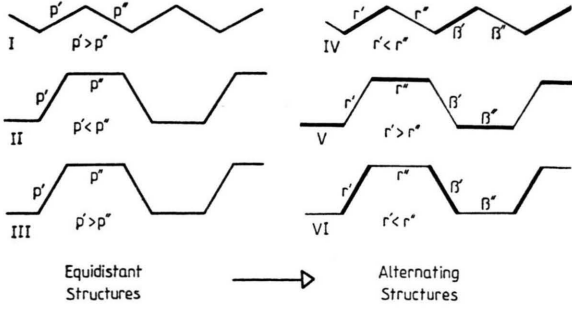


Fig. 1. Polyene structures investigated in the present paper. p' and p'' are the nearest-neighbour bond-orders. I is the BAW solution for the equidistant all-*trans* polyene, II is the solution with *cis-transoid* bond-order distribution for the *cis-trans* equidistant polyene and III is the solution with *trans-cisoid* bond-order distribution for the same geometry. Relaxation of the nuclear framework according to the magnitudes of nearest-neighbour bond-lengths leads to the structures with alternating bond-lengths: all-*trans* (IV), *cis-transoid* (V) and *trans-cisoid* (VI).

including long-range Coulomb forces till convergence of the ground state energy. Fairly converged values have been obtained also for the energy gap.

Method

The two-fold screw axis (\equiv glide-plane) in all *cis-trans* structures of Fig. 1 allows to express the wavefunctions of all-*trans* and *cis-trans* isomers with imposed Born-Kármán boundary conditions in identical form:

$$\psi(k) = 2^{-1/2} \{ \exp[i\phi(k)] \chi'(k) + \chi''(k) \}, \quad (1a)$$

$$\bar{\psi}(k) = 2^{-1/2} \{ \exp[i\phi(k)] \chi'(k) - \chi''(k) \}, \quad (1b)$$

$$k \in [-\pi/a, \pi/a],$$

where

$$\chi'(k) = N^{-1/2} \sum_{m=1}^N \exp(imka) \varphi'_m, \quad (2a)$$

$$\chi''(k) = N^{-1/2} \sum_{m=1}^N \exp(imka) \varphi''_m. \quad (2b)$$

k is the wavenumber, a in case of all-*trans* structures is the translational period and in case of *cis-trans* structures-its half. $N \gg 1$ is the number of unit cells (N should be even in case of *cis-trans* isomers). φ'_m and φ''_m are the $2p_z$ AO's for the m -th unit cell.

The energies of the orbitals (1) can readily be shown to be

$$E(k) = \alpha + \gamma/2 - |v(k)|, \quad (3a)$$

$$\bar{E}(k) = \alpha + \gamma/2 + |v(k)|. \quad (3b)$$

(1a), (3a) refer to occupied and (1b), (3b) to empty states. We have introduced the notation

$$v(k) = \langle \chi'(k) | \hat{F} | \chi''(k) \rangle, \quad (4)$$

where \hat{F} is the PPP-hamiltonian.

For the "phase" $\phi(k)$ one finds

$$\text{tg } \phi(k) = \text{Im } v(k) / \text{Re } v(k). \quad (5)$$

Using the well-known expressions for the matrix elements of the PPP-hamiltonian [16], $v(k)$ can be expanded as

$$v(k) = \beta' + \beta'' \exp(-ika) - \sum_{n=-L}^{L-1} p_n \gamma_n \exp(inka). \quad (6)$$

In (6) γ_n are the two-center Coulomb integrals between the AO's φ'_m and φ''_{m+n} , and p_n stand for the corresponding bond-orders. L restricts the interactions taken into account to $(2L-1)$ -th neighbours.

Using (1a) and passing to integration for $N \rightarrow \infty$ one obtains for p_n

$$p_n = a \pi^{-1} \int_0^{\pi/a} dk \cos[nka - \phi(k)], \\ -L \leq n \leq L-1. \quad (7)$$

The combination of (6) and (7) yields a system of $2L$ nonlinear self-consistency equations for p_n .

For the ground-state energy per electron one obtains

$$\epsilon_0 = \alpha + \gamma/4 + 2^{-1} \cdot \left[\beta' p_0 + \beta'' p_{-1} - a \pi^{-1} \int_0^{\pi/a} dk |v(k)| \right]. \quad (8)$$

The gap energy is

$$\Delta E = \bar{E}(\pi/a) - E(\pi/a) = 2|v(\pi/a)|. \quad (9)$$

The metallic solution for the equidistant all-*trans* structure is characterized by

$$\phi(k) = -ka/2, \\ p_n = 2\pi^{-1} (-1)^n (2n+1)^{-1}, \\ \epsilon_0 = \alpha + \gamma/4 + 4\beta/\pi \\ - 2\pi^{-2} \sum_{l=0}^{L-1} \gamma_l (2l+1)^{-2}.$$

Parametrization and Numerical Results

The resonance integrals have been calculated using Mulliken's relation:

$$\beta(r) = \beta(r_0) S(r) / S(r_0)$$

with $r_0 = 1.40 \text{ \AA}$ and $\beta(1.40) = -2.388 \text{ eV}$ ($Z_C = 3.18$).

For the two-center Coulomb integrals we have used two parametrizations:

(i) the Mataga-Nishimoto parametrization [17]: $\gamma = 10.84 \text{ eV}$ and

$$\gamma(r) = e^2 / [(e^2/\gamma) + r]. \quad (10)$$

(ii) the Ohno parametrization [18]: $\gamma = 10.84 \text{ eV}$ and

$$\gamma(r) = e^2 / [(e^2/\gamma)^2 + r^2]^{1/2}. \quad (11)$$

For small r (10) yields lower values for the two-center Coulomb integrals than (11) and can be considered to include more correlation and σ -electron screening. α has everywhere been chosen equal to zero.

The system of Eqs. (7) can be solved readily through a simple iterative procedure. The self-consistency criterion was chosen equal to 1.10^{-4} . The integrals have been calculated through a Simpson quadrature with an error bound 1.10^{-5} . In order to produce solutions differing in bond-order distribution for equidistant structures we have used correspondingly modified starting approximations for p_n . The number of interacting neighbours has been gradually increased till convergence of the ground state energy per electron within 1.10^{-4} eV , which is achieved usually for 23–25 neighbours ($L = 12$ –13). All results reported correspond to converged energy values.

The bond-orders of the BAW-solution of the all-*trans* equidistant structure and of the two solutions for the *cis-trans* equidistant structure have been used to calculate a first approximation to alternating bond-lengths through the relation [14]

$$r = 1.517 - 0.18p.$$

From the bond-orders of the solutions for the new geometry new bond-lengths have been calculated and the procedure has been repeated till the bond-lengths calculated in two successive iterations differed by less than 5.10^{-4} \AA (usually achieved after 5–6 iterations). All CCC angles have been kept constant and equal to 120° .

Table 1 shows the nearest-neighbour bond-orders together with the values for the gaps and for the π -electron ground-state energies obtained using (10), resp. (11) for the equidistant structures (all bond-lengths equal to 1.40 \AA).

Table 1. Results from the calculations for equidistant structures. p' and p'' stand for the nearest-neighbour bond-orders from Figure 1. Gap-widths in eV and energies in eV per electron.

Structure	Parametrization	p'	p''	ΔE	ϵ_0
Im ¹	MN ²	0.6366	0.6366	0.00	-1.5067
I	MN	0.7809	0.4821	2.76	-1.5113
II	MN	0.4924	0.7721	2.58	-1.5151
III	MN	0.7778	0.4853	3.08	-1.5293
Im	Ohno	0.6366	0.6366	0.00	-1.9288
I	Ohno	0.8305	0.4208	4.47	-2.0004
II	Ohno	0.4291	0.8242	4.30	-2.0038
III	Ohno	0.8201	0.4336	4.80	-2.0268

¹ All-*trans* equidistant metallic solution.

² Mataga-Nishimoto parametrization.

Table 2. Results from the calculations for structures with alternating bond-lengths. r' and r'' are the optimized bond-lengths (see Figure 1). Bond-lengths in \AA , gap-widths in eV and energies in eV per electron.

Structure	Parametrization	r'	r''	ΔE	ϵ_0
IV	MN	1.363	1.448	4.32	-1.5641
V	MN	1.447	1.363	4.24	-1.5647
VI	MN	1.364	1.446	4.48	-1.5761
IV	Ohno	1.356	1.458	6.38	-2.0908
V	Ohno	1.457	1.356	6.30	-2.0912
VI	Ohno	1.358	1.455	6.53	-2.1054

Table 2 contains the results for the self-consistent bond-lengths and the corresponding gaps and π -electron ground state energies for the alternating structures.

The results obtained by means of (10), resp. (11), differ quantitatively, but qualitatively they are in fair agreement. The optimized bond-lengths obtained using the two parameter sets differ by less than 0.01 \AA ($\leq 0.7\%$).

Discussion

The comparison of the PPP-results to the results obtained using other methods (Table 3) shows that the differences between the ground-state energies of the equidistant structures are of the same order*, which is a good justification for attributing them to π -electronic effects. We cannot compare directly our results for the energies of equidistant and alternating structures because we do not use a σ -

* The large differences reported in [3] form an exception.

Table 3. Relative stabilities and gap-widths of equidistant polyene structures as reported by different authors. Energy differences in kcal mol⁻¹ per π -electron, gap-widths in eV.

Structure	ΔE				
	This work	[3]	[5]	[10a]	
Im	0.00 ¹	0.00 ²	0.00	0.00	0.00
I	2.76	4.47	4.14 ³	—	—
II	2.58	4.30	8.74 ⁴	5.21 ⁴	3.22
III	3.08	4.80			—

Structure	Relative energy					
	This work	[3]	[5]	[6]	[10a]	
Im	0.0 ¹	0.0 ²	0.0	0.0	0.0	0.0
I	-0.1	-1.6	-0.7 ³	—	-1.0	—
II	-0.2	-1.7	-19.3 ⁴	-0.8 ⁴	-0.14	1.0
III	-0.5	-2.3				—

¹ The column contains results obtained through the MN parametrization.

² The column contains results obtained through the Ohno parametrization.

³ These results are for a charge-density wave, CDW solution.

⁴ We cannot assign these values to II or III because the authors have not reported the π -electron bond-orders.

Table 4. Relative stabilities and gap-widths of polyene structures with alternating bond-lengths as reported by different authors. Energy differences in kcal mol⁻¹ per π -electron, gap-widths in eV.

Structure	ΔE				
	This work	[3]	[5]	[10a]	
IV	4.32 ¹	6.38 ²	7.24	9.74	7.46
V	4.24	6.30	3.95	8.19	8.54
VI	4.48	6.53	10.39	7.83	—

Structure	Relative energy						
	This work	[3]	[5]	[6]	[10a]	[19]	
IV	0.0 ¹	0.0 ²	0.0	0.0	0.0	0.0	0.0 ³
V	-0.01	-0.01	-7.8	-1.3	1.0	1.6	11.4
VI	-0.3	-0.3	-19.8	-0.02	1.0	- ⁴	10.0

¹ The column contains results obtained through the MN parametrization.

² The column contains results obtained through the Ohno parametrization.

³ The results from [19] have been obtained by the extended Hückel method (EHT).

⁴ In [10b] V lies ~ 1.2 kcal mol⁻¹ below VI. The results from [10a] and [10b] are for different bond-lengths and cannot be compared directly.

potential in explicit form; the magnitudes of the π -electron energies, however, show that the alternating structures should be lower in energy for any

realistic choice of the σ -potential. The calculated energy differences (Table 4) for the alternating structures (a comparison of their π -electron energies is possible because the self-consistent bond-lengths in the three cases practically coincide) are relatively smaller than those found by other investigators. This can be explained partially by the alternancy properties of the PPP-bond-order matrix implying zero interactions between even neighbours, which leads to a higher contribution to the ground-state energy of the first-neighbour-interactions (approximately equal for the three structures).

We find the solution with *trans*-cisoid bond-order distribution for the *cis-trans* geometry to be the most stable equidistant solution, next following the solution with *cis-transoid* bond-order distribution for the same geometry, and then come the BAW-all-*trans* solution and the metallic all-*trans* solution. This ordering is preserved also for the corresponding alternating solutions but the magnitudes of the energy differences substantially decrease, which leads to the conclusion that the three alternating conformations should be generally equally probable. Our energy ordering is in qualitative agreement with the results of Kertész et al. [3]. We would like to point at the small differences between the energies of (I) and (II), resp. of (IV) and (V). In the case of (I) and (II) one can find a similar *trans*-pattern of distribution of the bigger nearest-neighbour bond-orders; (IV) and (V) can be considered as constructed of similar *trans*-butadiene unit cells.

As Table 5 shows, our bond-lengths correspond to weaker bond-alternations than those calculated by Karpfen and Höller [6]. Better agreement is established with the results of the earlier paper by Karpfen and Petkov [4b] where an improved basis set has been used. Generally, our self-consistent bond-lengths agree well with the common concept for bond-lengths in long polyenes (see e.g. [2–5]) and with the results from X-ray diffraction analysis [9].

The calculated gaps are smaller than the ab-initio results but still higher than the experimental value. A correspondence is observed between gap-widths and relative energies, reversed only for the pairs (I), (II) and (IV), (V).

We have not considered the possibility of charge-density-waves (CDW) or spin-density-waves (SDW) formation because it may be shown that they are incompatible to bond-alternation, especially when

Table 5. Comparison of optimized polyene bond-lengths reported by different authors. All values in Å. X-ray diffraction analysis studies [9] propose 1.35 Å for the shorter bond-length and 1.46 Å for the longer bond-length.

Structure	This work		This work		[6]		[10a]	
	r'	r''	r'	r''	r'	r''	r'	r''
IV	1.363 ¹	1.448 ¹	1.356 ²	1.458 ²	1.327 ³	1.477 ³	1.350	1.435
V	1.447	1.363	1.457	1.356	1.480	1.329	1.445	1.350
VI	1.364	1.446	1.358	1.455	1.325	1.489	—	—

¹ MN parametrization. ² Ohno parametrization.

³ Ab-initio results using a STO-3G basis. The results for all-*trans* alternating polyene using an improved C(8s4p)/H(4s) basis are [4b]: 1.346, resp. 1.446 Å.

long-range Coulomb interactions are accounted for [20].

The comparison carried out in this section shows that the PPP-treatment describes the infinite polyenes nearly as reasonably as more rigorous methods. However, the existence of analytical

expressions for the PPP-wavefunctions and the possibility of quick calculations including sufficiently long-range Coulomb interactions makes it suitable for further investigations of more involved effects, e.g. optical properties [21] or periodic structure perturbations [22].

- [1] J.-M. André and G. Leroy, *Int. J. Quantum Chem.* **5**, 557 (1971).
- [2] M. Kertész, J. Koller, and A. Ažman, *J. Chem. Phys.* **67**, 1180 (1977).
- [3] M. Kertész, J. Koller, and A. Ažman, *J. C. S. Chem. Commun.* **575** (1978).
- [4] (a) A. Karpfen and J. Petkov, *Solid State Commun.* **29**, 251 (1979); (b) A. Karpfen and J. Petkov, *Theor. Chim. Acta Berlin* **53**, 65 (1979).
- [5] S. Suhai, *J. Chem. Phys.* **73**, 3843 (1980).
- [6] A. Karpfen and R. Höller, *Solid State Commun.* **37**, 179 (1981).
- [7] (a) H. Shirakawa and S. Ikeda, *Polymer J.* **2**, 231 (1971); (b) H. Shirakawa, T. Ito, and S. Ikeda, *Polymer J.* **4**, 460 (1973); (c) H. Shirakawa, T. Ito, and S. Ikeda, *J. Polymer Sci. Polymer Chem. Ed.* **12**, 11 (1974); (d) T. Ito, H. Shirakawa, and S. Ikeda, *J. Polymer Sci. Polymer Chem. Ed.* **13**, 1943 (1975); (e) T. Ito, S. Shirakawa, and S. Ikeda, *Makromol. Chem.* **179**, 1565 (1978).
- [8] (a) H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, *J.C.S. Chem. Commun.* **578** (1977); (b) C. K. Chiang, C. R. Fincher Jr., Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, and A. G. MacDiarmid, *Phys. Rev. Lett.* **39**, 1098 (1977); (c) C. K. Chiang, M. A. Drury, S. C. Gau, A. J. Heeger, H. Shirakawa, E. J. Louis, A. G. MacDiarmid, and Y. W. Park, *J. Amer. Chem. Soc.* **100**, 1013 (1978); (d) T. C. Clarke, R. H. Geiss, J. F. Kwak, and G. B. Street, *J.C.S. Chem. Commun.* **489** (1978); (e) C. K. Chiang, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, and A. G. MacDiarmid, *J. Chem. Phys.* **69**, 5098 (1978); (f) S. C. Gau, J. Milliken, A. Pron, A. G. MacDiarmid, and A. J. Heeger, *J.C.S. Chem. Commun.* **662** (1979); (g) Y. W. Park, M. A. Drury, C. K. Chiang, A. J. Heeger, A. G. MacDiarmid, H. Shirakawa, and S. Ikeda, *J. Polymer Sci. Polymer Chem. Ed.* **17**, 195 (1979).
- [9] (a) R. H. Baughman, S. L. Hsu, and A. J. Signorelli, *J. Chem. Phys.* **68**, 5405 (1978); (b) S. L. Hsu, A. J. Signorelli, P. G. Pez, and R. H. Baughman, *J. Chem. Phys.* **69**, 106 (1978); (c) R. H. Baughman, S. L. Hsu, and A. J. Signorelli, *Mol. Cryst. Liq. Cryst.* **52**, 251 (1979).
- [10] (a) T. Yamabe, K. Tanaka, H. Terame-e, H. Fukui, A. Imamura, H. Shirakawa, and S. Ikeda, *J. Phys. C* **12**, L257 (1979); (b) T. Yamabe, K. Tanaka, H. Terame-e, H. Fukui, A. Imamura, H. Shirakawa, and S. Ikeda, *Solid State Commun.* **29**, 329 (1979).
- [11] J.-L. Calais, *Int. J. Quantum Chem. Symp.* **11**, 547 (1977).
- [12] (a) M. Kertész, J. Koller, and A. Ažman, *Int. J. Quantum Chem.* **18**, 645 (1980); (b) M. Kertész, J. Koller, and A. Ažman, *Int. J. Quantum Chem. Symp.* **14**, 463 (1980).
- [13] (a) A. Toyota, T. Tanaka, and T. Nakajima, *Int. J. Quantum Chem.* **10**, 917 (1976); (b) A. Toyota, M. Saito, and T. Nakajima, *Theor. Chim. Acta Berlin* **56**, 231 (1980).
- [14] C. A. Coulson and A. Golebiewski, *Proc. Phys. Soc. London* **78**, 1314 (1961).
- [15] M. J. S. Dewar, *The Molecular Orbital Theory of Organic Chemistry*, McGraw-Hill, New York 1969, p. 167.
- [16] J. A. Pople, *Trans. Faraday Soc.* **49**, 1375 (1953); R. Pariser and R. G. Parr, *J. Chem. Phys.* **21**, 466 (1953).
- [17] N. Mataga and K. Nishimoto, *Z. Phys. Chem. Frankfurt* **13**, 140 (1957).
- [18] K. Ohno, *Theor. Chim. Acta Berlin* **2**, 219 (1964).
- [19] M.-H. Whango, R. Hoffman, and R. B. Woodward, *Proc. Roy. Soc. London* **A366**, 23 (1979).
- [20] (a) M. Kertész, J. Koller, and A. Ažman, *Phys. Rev.* **B19**, 2034 (1979); (b) N. Tyutyulkov, I. Kanev, O. Castaño, O. E. Polansky, and H. Barentzen, *Theor. Chim. Acta Berlin* **55**, 207 (1980).
- [21] C. Cojan, G. P. Agrawal, and C. Flytzanis, *Phys. Rev.* **B15**, 909 (1977).
- [22] D. A. Morton-Blake, *Theor. Chim. Acta Berlin* **59**, 213 (1981).