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Ab initio Studies on Polymers

II. All-*trans* Polyene

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Ab initio crystal orbital calculations have been performed on the infinite all-*trans* polyene. A structure with $r_{C=C} = 1.346$ Å, $r_{C-C} = 1.446$ Å, $r_{C-H} = 1.08$ Å, and $\sphericalangle CCC = 125.3°$ was found to be most stable. The most important force constants, the band structure and the density of states were determined as well.

Key words: Polyene, all-*trans* ~

1. Introduction

Polyenes have been the subject of experimental and theoretical investigations for several decades. The question whether infinite polyene adopts an equidistant structure or an alternant one has attracted much interest and was treated extensively at all levels of approximations. It is impossible therefore to give a complete bibliography here. A few examples are chosen as typical representatives. Hückel-type and free electron methods [1–10], semiempirical methods of the PPP [11, 12], EHT [13, 14], CNDO [15, 16], and INDO [17]-type and *ab initio* calculations at a minimal basis set level [18–21] have been reported. UHF calculations [22] and LCAO calculations using the Slater exchange approximation [23, 24] have been performed as well.

An experimental elucidation of this problem has been attempted by an investigation of the lowest optical transition of small polyenes. The most noticeable result was that extrapolation to infinite chain length led to a finite value for the first optical excitation energy. Two recent review articles [25, 26] summarize the state of affairs although they arrive at different conclusions with respect to the origin of the finite

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optical gap. Whereas Ovchinnikov *et al.* [25] argue in favor of an equidistant structure, the finite optical gap being produced by correlation effects, the majority of other research workers in this field believe that the alternant structure is more stable, which as a consequence of symmetry has a finite optical gap as well.

Interest in the polyenes has been renewed due to the exciting experimental finding that polymer crystals or films of polyene [27–29] can be doped by electron acceptors and donors as well [30–33], resulting in a remarkable change in transport properties. Depending on the concentration of the doping agent, the conductivity varies over eleven orders of magnitude from semiconducting to metallic type behavior.

Unfortunately, due to the fibric nature of the polymer crystals, only interchain distances could be deduced from X-ray investigations [34, 35]. The geometrical parameters of the unit cell (bond distances and bond angles) are still unknown. Infrared and Raman spectra [27, 28] gave a hint that presumably two conformations are dominating: a) all-*trans* polyene and b) *cis-trans* polyene.

In two earlier *ab initio* crystal orbital studies [18, 19] two model geometries, an alternant one and an equidistant one, were discussed. The only previous *ab initio* crystal orbital study with inclusion of geometry optimization has been performed recently by the present authors [21]. Since at that time a minimal basis set (STO-3G [36]) has been used only, we extend these preliminary investigations by using a more flexible basis set of double zeta quality.

Although electron correlation effects are probably important for a quantitative evaluation of the ground state properties of infinite polyene, we felt it worthwhile to search in a first step for a reasonably accurate Hartree–Fock solution to that problem. The Hartree–Fock results will be a necessary prerequisite for a quantitative assessment of the influence of electron correlation on the computed ground state properties.

2. Method of Calculation

For the *ab initio* calculations on the infinite all-*trans* polyene chain the crystal orbital method [37–39] was used. This approach results from the usual Hartree–Fock LCAO MO method for finite molecules by including periodic boundary conditions to account for translational symmetry. Since the necessary formalism can be found in the literature we do not repeat it here. For a recent methodical discussion, however, we refer to a systematic study of some model polymers performed by one of us [40].

In the present application of the crystal orbital method no integral approximation was used, two-electron integrals smaller than 10^{-7}, however, have been neglected. For the elements of the density matrix and the total energy per unit cell we applied a convergence criterion of 10^{-6}. Nine k-points were used in half the Brillouin zone.

The size of the unit cell (C_2H_2) did not allow us to go beyond a $8s4p$ basis on carbon [41] and a $4s$ basis on hydrogen [42], which was contracted to $5s3p/3s$.[1] Our previous

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[1] One point on the hypersurface took approximately 4 h CPU time on a CDC-Cyber 73. Inclusion of polarization functions is prohibitive.

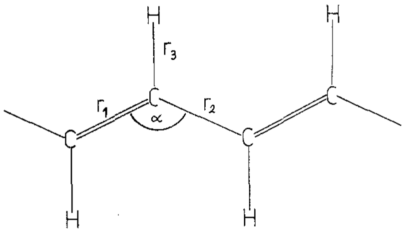

Fig. 1. Geometry of all-*trans* polyene

STO-3G calculations on polyene [21] showed that as a consequence of the unpolar nature of the polymer long-range electrostatic effects yield only vanishing contributions to the various computed ground state properties, with the exception of the band structure. Hence, calculations taking into account second neighbor's were performed only. The well-known numerical problems due to near linear dependencies in the k-dependent overlap matrix $S(k)$ [43, 44] were resolved by discarding those eigenvectors of $S(k)$ corresponding to eigenvalues smaller than 0.04. This procedure, which is well known from LCAO calculations on solids [45] and which corresponds effectively to a basis set truncation from an almost linearly dependent one to a linearly independent one, has recently been studied systematically in crystal orbital calculations on the linear chain of hydrogen atoms [46].

For the determination of the equilibrium geometry of the infinite all-*trans* polyene (see Fig. 1 for a definition of the geometrical parameters) the following potential curves have been calculated: A two-dimensional hypersurface as a function of r_1 and r_2 and two separate potential curves for r_3 and α. By applying this approximation we rely on our earlier minimal basis set results, where it was found that those coupling force constants which are neglected by this kind of treatment are rather small. Since we concentrated on all-*trans* polyene exclusively, we cannot answer the question whether this particular structure is the most stable conformation in the polyene crystals. This is, however, a general problem in the calculation of potential surfaces for crystals or polymers. Any prediction of equilibrium geometries in a periodic solid is necessarily constrained by the choice (size) of the unit cell. The manyfold of complicated structures as they are, for example, realized in polyoxymethylene [47] where a nine-fold screw axis occurs, or the various *cis-trans* conformations which are probably present in actual polyene samples hampers the prediction of absolute minima necessarily, even if periodic boundary conditions are applied.

3. Crystal Orbital Calculations

Table 1 shows the total energy per unit cell for 28 different geometries. The first 23 correspond to geometries with alternating distances, whereas the last five correspond to equidistant arrangements. The equilibrium geometries deduced from these points with the aid of polynomial fits are shown in Table 2 for the alternant and equidistant case and are compared with our earlier STO-3G results. In Table 3 the influence of the basis set extension on the force constants is demonstrated.

Table 1. Total energy per unit cell of all-*trans* polyene calculated with $8s4p/4s$ basis in second neighbors approximation as a function of the geometry[a]

r_1 (Å)	r_2 (Å)	r_3 (Å)	α (°)	Total energy per unit cell (hartree)
1.36	1.43	1.08	124.0	−76.863352
1.385	1.43	1.08	124.0	−76.862202
1.335	1.43	1.08	124.0	−76.863455
1.31	1.43	1.08	124.0	−76.862170
1.36	1.455	1.08	124.0	−76.863323
1.36	1.48	1.08	124.0	−76.862815
1.36	1.405	1.08	124.0	−76.862700
1.335	1.455	1.08	124.0	−76.863536
1.335	1.405	1.08	124.0	−76.862513
1.385	1.455	1.08	124.0	−76.862107
1.335	1.48	1.08	124.0	−76.862984
1.31	1.455	1.08	124.0	−76.862476
1.348	1.443	1.08	124.0	−76.863638
1.348	1.443	1.00	124.0	−76.854043
1.348	1.443	1.04	124.0	−76.861595
1.348	1.443	1.12	124.0	−76.861696
1.348	1.443	1.16	124.0	−76.855796
1.3434	1.4435	1.08	116.0	−76.853587
1.3434	1.4435	1.08	120.0	−76.860813
1.3434	1.4435	1.08	124.0	−76.863666
1.3434	1.4435	1.08	128.0	−76.863327
1.3434	1.4435	1.08	132.0	−76.858663
1.346	1.446	1.08	125.3	−76.863821[b]
1.29	1.29	1.08	125.3	−76.838130
1.34	1.34	1.08	125.3	−76.856291
1.39	1.39	1.08	125.3	−76.861146
1.44	1.44	1.08	125.3	−76.856090
1.49	1.49	1.08	125.3	−76.842712

[a] For a definition of the geometrical parameters see Fig. 1.

[b] Energy minimum.

The calculations on the equidistant structures need further discussion. As a consequence of symmetry (screw axis) a metallic type band structure with exact degeneracy between the occupied and unoccupied π-bands, should occur. However in such a situation Hartree–Fock instabilities arise, leading to so-called "symmetry broken" solutions (see Refs. [19] and [56–58]) which have lower total energies per unit cell. These symmetry-broken solutions can be classified by an inspection of the density matrix. Two cases may occur: charge density waves and bond order bond alternation solutions. The first ones are characterized by periodic changes in the diagonal of the density matrix whereas the latter show periodic oscillations in the off-diagonal elements. For any arbitrarily small distortion from the equidistant arrangement the screw axis symmetry is lost and the distinction between symmetry adapted (metallic) and "symmetry broken" is meaningless since

Table 2. Equilibrium geometry and total energy of alternant and equidistant all-*trans* polyene

Basis set	Number of neighbors	alternant Total energy per unit cell (hartree)	r_1 (Å)[b]	r_2 (Å)	r_3 (Å)	α (°)	equidistant[c] Total energy per unit cell (hartree)	r (Å)
8*s*4*p*/4*s*	2	−76.86382	1.346	1.446	1.080	125.3	−76.86131	1.388
STO-3G[a]	2	−75.95144	1.328	1.475	1.085	124.2	−75.94384	1.392
STO-3G[a]	4	−75.94906	1.327	1.477	1.085	124.2	−75.94097	1.392

[a] See Ref. [21].

[b] For a definition of the geometrical parameters see Fig. 1.

[c] For the equidistant case r_3 and α have been kept at the values of the alternant equilibrium geometry.

only one solution exists. This solution, however, shows the same structure in the density matrix as a bond order bond alternation solution would show for the equidistant case since the two distances are now unequal. For a proper comparison with the alternating geometries we therefore calculated the bond order bond alternation solution for the equidistant arrangements. The symmetry adapted, metallic solutions have a higher total energy (~1.4 kcal/mole [19]) and consequently do not lie on the same energy surface.

The most important result which can be obtained from a comparison of the first three tables is that all-*trans* polyene is most stable at an alternating geometry within the framework of the Hartree–Fock model. From previous experience gained by *ab initio* calculations on the infinite linear chain of carbon atoms (polyyne) [48], which is an equally covalent and unpolar system like polyene, we believe that polarization functions will not change the picture essentially besides a small reduction in the C=C double bond length. This, however, would lead then again to an increase in the double bond force constant and equally to an increase in the energetic difference between alternant and equidistant structure. The small difference in the total energy per unit cell between these two structures is not surprising at all. Suppose, for example, a one-dimensional potential curve which is constructed in the following way: Starting out from an alternant geometry we keep the position

Table 3. Force constants of all-*trans* polyene. All values in mdyne/Å

Basis set	Number of neighbors	alternant $f_{r_1r_1}$[a]	$f_{r_1r_2}$	$f_{r_2r_2}$	$f_{r_3r_3}$	$f_{\alpha\alpha/r_1r_2}$	equidistant f_{rr}
8*s*4*p*/4*s*	2	8.2	0.9	4.6	6.0	0.9	9.2
STO-3G	2	12.1	0.7	6.7	8.1	1.0	10.8
STO-3G	4	12.2	0.7	6.3	7.7	0.9	10.7

[a] For a definition of the geometrical parameters see Fig. 1.

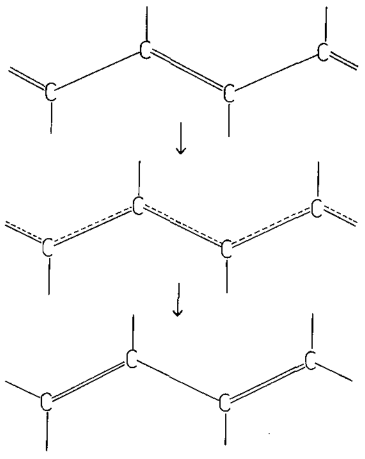

Fig. 2. Structures of all-*trans* polyene occurring along the double minimum potential: a) equilibrium structure of all-*trans* polyene; b) equidistant structure corresponding to the top of the barrier of the double minimum potential; c) equivalent equilibrium structure, single and double bonds interchanged

of each second C—H group fixed. All other C—H groups are now shifted simultaneously in the same direction along the polymer axis until an equivalent structure occurs (see Fig. 2). For an infinite chain this rigid shift of the sublattice must by symmetry result in a double minimum potential which is shown in Fig. 3. Because the change in the carbon–carbon distance between one minimum and the barrier, that is between alternating and equidistant geometry, amounts only to 0.05 Å, the energetic difference between these two structures must be small, otherwise one would arrive at unrealistically large force constants. A similar discussion has recently been given for the case of the linear chain of hydrogen fluoride molecules [49]. It should, however, be stressed that this is only a static picture. The actual dynamics of this process is much more complicated since changes in a crystal- or "polymer"-lattice do not occur under conservation of translational symmetry for entropical reasons.

Systematic investigations on the basis set dependence of the equilibrium geometry of ethylene [50] yielded a C=C distance of 1.322 Å for a basis set of comparable size. Thus, the double bond is slightly elongated in the infinite chain in comparison with the isolated molecule. Whereas the equilibrium geometry obtained with the minimal basis set is in reasonable agreement with the double zeta calculations, force

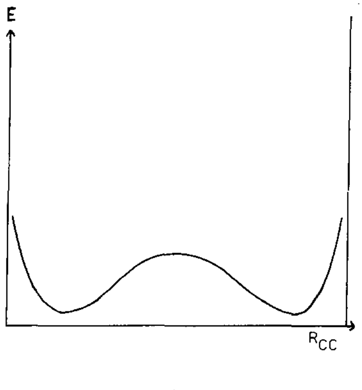

Fig. 3. Double minimum potential originating from an idealized change in the lattice of all-*trans* polyene. The minima correspond to equivalent alternant structures. The top of the barrier corresponds to the equidistant geometry

constants, especially the stretching force constants, show a marked basis set dependence. This sensitivity is well known from *ab initio* studies on molecules and has also been found in a similar study on infinite polyyne [48].

Originally, the first *ab initio* crystal orbital study on all-*trans* polyene has been published by André and Leroy [18]. These authors reported the equidistant structure to be stabilized by 115.8 kcal/mole and unit cell over the alternating structure. Kertesz, Koller and Azman [19] on the other hand obtained a lower energy for the alternating structure by 2.7 kcal/mole in fair agreement with our results. In these two previous works the same two geometries have been used for the alternating and equidistant structures. To elucidate this discrepancy between the results of André and Leroy on the one side and those of Kertesz *et al.* and our own on the other side we performed two calculations at the identical geometries and used a $7s3p/3s$ basis set [41, 42] contracted to $2s1p/1s$, a basis set which should be comparable to the one used by André and Leroy. Our computed total energies per unit cell are in marked contrast to the ones by André and Leroy. Whereas they report values of -76.9222 and -76.7377 hartrees for the equidistant and alternant case, respectively, we find -76.51961 and -76.52136, correspondingly. Thus, not only are our values substantially higher in energy, but more importantly the relative order of stabilities is now reversed, in qualitative agreement with our results obtained by the larger basis set. Presumably, the total energies per unit cell reported in Ref. [18] are erroneous.

Figure 4 shows the band structure (core bands omitted) of all-*trans* polyene with the $8s4p/4s$ basis at the computed equilibrium geometry together with the density of states. Although strictly only the occupied bands do have a physical meaning within the framework of the Hartree-Fock method, the first virtual, unoccupied band is shown as well. The energetic difference between the last occupied and first unoccupied bands cannot, however, be interpreted as an optical gap, without explicit consideration of electron correlation.

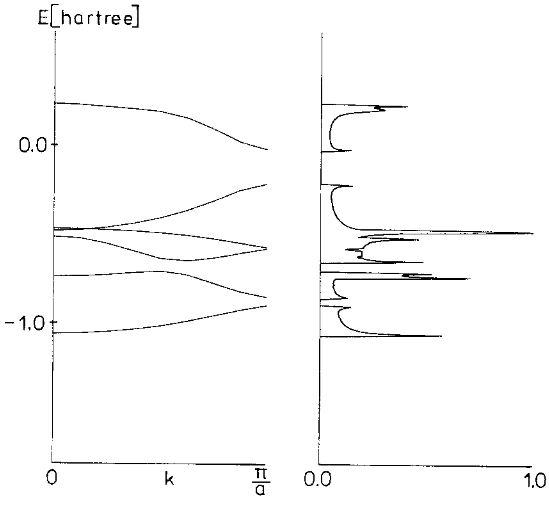

Fig. 4. a) Band structure of all-*trans* polyene. b) Density of states

Table 4. Comparison of the most important band structure data obtained with two different basis sets at the respective equilibrium geometries (all values in hartrees)

	STO-3G[a]		$8s4p/4s$[a]		STO-3G[b]	
	$k = 0$	$k = \pi$	$k = 0$	$k = \pi$	$k = 0$	$k = \pi$
ε_1	−11.086	−11.086	−11.307	−11.306	−11.062	−11.062
ε_2	−11.085	−11.085	−11.304	−11.305	−11.061	−11.061
ε_3	−1.125	−0.945	−1.194	−1.010	−1.102	−0.918
ε_4	−0.782	−0.881	−0.836	−0.962	−0.759	−0.863
ε_5	−0.523	−0.610	−0.592	−0.664	−0.497	−0.587
ε_6	−0.467	−0.599	−0.542	−0.658	−0.450	−0.577
ε_7 (π-band)	−0.502	−0.226	−0.554	−0.262	−0.480	−0.195
ε_8 (first virtual π-band)	0.441	0.085	0.232	−0.051	−0.463	0.101

[a] Second neighbor's interaction.
[b] Fourth neighbor's interaction.

To demonstrate the effect of the basis set variation on the computed band structure we compare the band edges of the seven occupied bands and the first virtual one obtained with the $8s4p/4s$ basis and the STO-3G basis at the corresponding equilibrium geometries in Table 4. As is well known from MO calculations on molecules, STO-3G eigenvalues (Koopmans' energies) are consistently too high. The same is true for energy bands as well. Inspection of the STO-3G energy bands also shows that convergence of the band structure with respect to the number of neighbors taken into account is much slower than the convergence of the total energy per unit cell. This behavior is easily understood if one remembers that off-diagonal elements of the Fock matrix decay approximately like r^{-1} [37]. The total energy per unit cell on the other hand should fall off like the lowest multipole–multipole interaction between more distant unit cells. In the case of all-*trans* polyene this is a quadrupole–quadrupole interaction which falls off like r^{-5}. Actually the situation is slightly more complicated. An exclusively electrostatic reasoning is not fully correct since $S(k)$ has to be brought to convergence and exchange contributions must be vanishingly small before the above argument is strictly valid.

From our computed band structure we obtain an ionization potential of 7.1 eV for the infinite chain. For the above reasons this value has to be treated with caution, however.

Very recently the UPS-spectrum of polyene has been measured [51] and could in principle be compared with our computed density of states. A proper comparison with the experimental result is, however, hampered by the low resolution of the experimental spectrum. Much more structure is seen in our density of states, which is in good overall agreement with the results of Grant and Batra [24]. Since, moreover, cross sections are not included in our calculations the intensities of those bands which roughly correspond to C–H bonds have to be modified. For a discussion of this problem see also a recent work on polyethylene [52].

4. Conclusions

Ab initio crystal orbital calculations have been performed on the infinite all-*trans* polyene to evaluate its equilibrium geometry, force constants and band structure. The numerical results show that within the framework of the Hartree–Fock approximation all-*trans* polyene adopts an alternant configuration. This result is not unexpected, however, since the existence of Hartree–Fock instabilities for the equidistant structures already points to the fact that correlation effects are more important in this case. Whether the alternant structure remains the more stable one if one goes beyond the Hartree–Fock picture, can only be answered definitively if correlation effects are taken into account explicitly. For an understanding of the principal effect of electron correlation we refer again to Fig. 3. Force constants calculated within the Hartree–Fock model are almost always too large. Hence, the curvature around the minimum is too large also. One result of electron correlation consequently is that this curvature is reduced which clearly results in lowering the barrier of the double minimum potential. For a discussion of this problem we refer to recent works on $H_5O_2^+$ [53] and $H_3O_2^-$ [54, 55]. Whether this effect is strong enough to change the picture qualitatively from a double minimum potential to a single minimum potential can only be answered by more sophisticated techniques.

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