Revista Brasileira de Física, Volume 13, n? 2, 1983

Electronic Properties of Linear Polyenes

C. A. R. S. DE MELO , C. P. DE MELO

Departamento de Física, Universidade Federal de Pernambuco, 50.000, Recife, PE, Brasil

Recebido em 28 de julho de 1983

Abstract We have used the NDO approximation to study the convergence of electrcnic properties of linear polyenes, $C_{2n}H_{2n+2}$, with increasing n. We have found that, in terms of the delocalization of the π-system, convergence occurs remarkably fast: systems of $n \geq 4$ have bond-lengths resembling the infinite polymer. For properties depending on orbital energies, convergence is less pronounced. However extrapolated values agree with results, at the same level of approximation, for the band structure of polyacetylene.

1. INTRODUCTION

In recent years, there is growing interest in the study of the electronic structure of organic polymers especially after the discovery of unusual properties in the electrical conductivity of a certain class of these materials[1]. As an example, the fact that the conductivity of trans-polyacetylene, $(C_2H_2)_x$, can be varied over thirteen orders of magnitude, by effect of doping, has led to radical proposal concerning the nature of the mechanism involved[2]. However continuous, theoretical progress in the area has been hampered by the need oftaking into account the periodical structure of those systems, while describing the electronic interactions at a satisfactory, from a quantum chemistry point of view, level. Several semlempirical band structure schemes have been proposed in the literature[3-5]; there is, however, still a need for a comprehensive and critical evaluation of the scope and applicability of those methods. At the ab-initio level, on the other hand, the few calculatioris presented[6] indicate that electronic correlations can be important to the point of affect the interpretation of results. As a consequence, it seems desirable to examine the possibility of infer the electronic properties of polymers based on calculations performed on the corresponding finite chain molecules - the oligomers.

In this work, we study the rate of convergence of the degree of alternation of single and double bonds between carbon atorns in the

family of trans-isomers of linear polyenes ($C_{2n}H_{2n+2}$), with the progressive increase on the length of the chain. In the corresponding infinite polymer, polyacetylene, this alternation responds for the semiconductive properties of the material. As a matter of fact, the very question of the existence of this alternative on polyacetylene is of historical interest. Early quantum chemistry models, based on the concept of π-electron delocalization, predicted identical bond lengths - and consequent mettalic character - for the material[7]. Peierl's theorem for one-dimensional solids[8], on the other hand, would lead to an instability of the system with regard to dimerization - in termsofthe electronic bands, a gap would appear between valence and conduction states.

The question was settled after the synthesis of the material in the 60's and its semiconductor character - with a gapof 1.4 eV[9]- have been established. However, it is a well known fact in organic chemistry that conjugated π-electrons systems are delocalized in small molecules, and that the degree of delocalization increases with the length of the π-electrons backbone. Therefore, it still remains to be examined the question of how fast the bond lengths in the family of linear polyenes would converge to the values predicted for polyacetylene[10] (1.35 Å and 1.44 Å, for double and single bonds, respectively).

2. METHODOLOGY AND RESULTS

Recentiy, Duke[11] has obtained good agreement between the photoemission spectra of linear conjugated polymers and results for the density of valence states extrapolated from energy level calculations for the 16 carbon atoms corresponding oligomers. However, the semi-empirical scheme employed (CNDO/S3) is parametrized to reproduce spectroscopic data and, therefore, was not suitable for conformational studies. On the other hand, use of ab-initio methods was not recommended due to the size of the systems to be examined.

We have used then the semiempirical approximation NDO, inthe versions CNDO/2 and INDO (hereafter, referred as CNINDO) of Pople[12]. These schemes lead to good results for the equilibrium geometry of simple organic rnolecules. In order to reduce the number of variables to be optimized, at this stage we kept constant the total length of two consecutive single and double bonds.

It is well known that if the delocalization is complete, the bond lengths become equivalent (1.40 Å for benzene). In case of partial delocalization, the increase on the length d of double bonds is equal to the decrease on the length s of the single bonds.

Our procedure was then, for each n, to optimize the variable x, where d = 1.40 Å - x and $s+d$ = 2.80 Å. We have adopted the geometry of the trans isomers, with the angles of two consecutive CC bonds being kept constant and equal to 120° (Fig. 1). The results for the bond lengths were identical for the methods CNDO/2 and INDO, and are presented on Table 1. The rate of convergence is remarkably fast: in terms of electronic delocalization, and consequent relaxation of bond lengths, the n=4 oligomer has already the same properties of the polyacetylene.

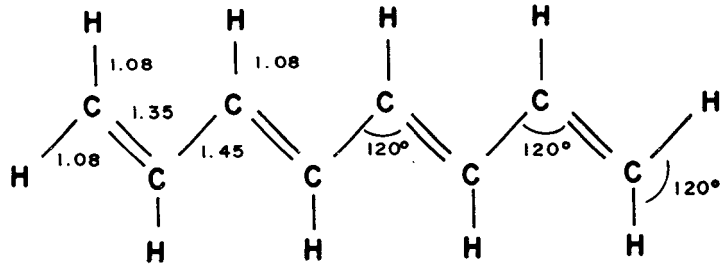

Fig.1 - Example of the adopted geommetry for the linear polyenes in the CNINDO calculations. In this case n=4.

Table 1 - Evolution of the lengths of double, d = 1.40-x, and single, s = 1.40+x, bonds with the increase of the chain for linear polyenes $C_{2n}H_{2n+2}$. Results are for the rnethod CNINDO. Bond Lengths in Å.

n	1	2	3	4	5	6	7
x	0.08	0.06	0.06	0.05	0.05	0.05	0.05
d	1.32	1.34	1.34	1.35	1.35	1.35	1.35
s	-	1.46	1.46	1.45	1.45	1.45	1.45

Notwithstanding the fact that the absolute values of total energies calculated by the CNINDO method are not meaningful, one should note that the increase in energy per addition of each C_2H_2 group in constant (15.16 Hartrees for INDO). The energy levels, however, do not evolve in order to form a compactness structure that could resemble bands. The separation $\Delta\epsilon$ between the highest occupied and lowest unoccupied levels also evolve slowly (Table 2). These values must be compared with the excitation energy of the order of 2.2 eV found experimentally as the limiting value for the series of linear polyenes[13-14].

In the method above, however, we have not included the relaxation due to the termination of the chain. To include those end effects, we have repeated the calculation using the MNDO[15] method, with geometry optimization. All geometric parameters — bond lengths, and bond and dihedral angles — were optimized for each case. The results (Fig.2) indicate that relaxation is confined to the terminal bonds. There is a rapid damping of those effects along the chain. Results of Fig. 2 reinforce the idea that, if one disregards the terminal bonds, the oligomer chains rapidly converge to the geometry of the infinite polymer.

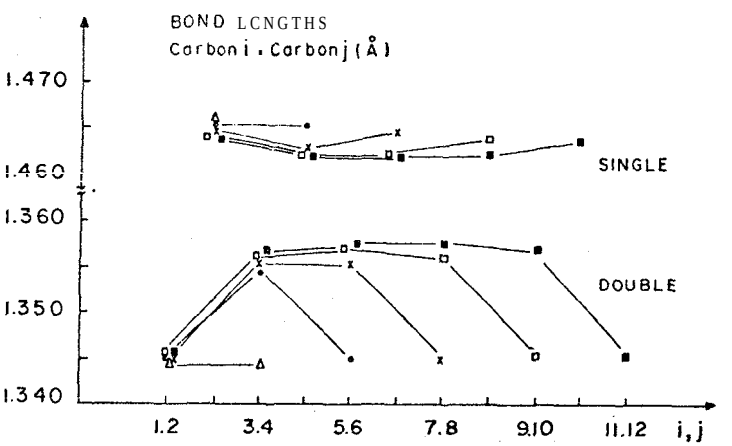

Fig.2 - MNDO optimized CC bond length results. Convention: $\Delta n = 2$, $\bullet n = 3$, $X n = 4$, $\square n = 5$, $\blacksquare n = 6$. Points were connected to help visualization.

As one would expect, the molecules are essentially planar, in spite of the fact that the angles C = C – C are now of the order of 125^0. As a example, in Fig. 3 we present the optimized geometry and charge distribution for the n=4 oligomer, C_8H_{10}. As before, tne increase inenergy per addition of each C_2H_2 group is constant (now 10.43 Hartrees). The evolution of AE is again slow (Table 2).

3. CONCLUSIONS

Our calculations indicate that different properties converge to the resuilts of the infinite system in different ways. Although geometrical characteristics of the polyacetylene are already present inthe n=4 oligomer, orbital energies evolve at a much slower rate to structures which could resemble bands. This conclusion is in agreement with recent ab-initio results for oligomers with $n \leq 4$ [16].

We have used polynomial expansions in n^{-1} to extrapolate the values for the gap energy, Eg, and for the width of the conduction band, A. Corresponding experimental values are Eg $\sim$ 1.4 eV and A $\sim$ 4 eV[11-17] Since the semiempirical schemes we have used are parametrized to reproduce geometrical data, one should not expect to obtain good agreement for results which depend on the orbital energies. Accordingly, extrapolation with basis on a third-degree polynomial, for the CNINDO results, lead to Eg $\sim$ 6.7 eV and A a 14.4 eV. Similar extrapolation for the MNDO calculation gives Eg $\sim$ 6.4 eV. Even if these results show that those methods are not appropriate to describe excitation energies, it is important for the present study to note that these values are in reasonable agreement with CNDO/2 band structure results for polyacetylene[10,18] (7.4 eV and 15.1 eV, respectively).

The fact that the rate of convergence of geometrical parameters with the progressive increase of the length of the chain is remarkably fast has important implications for the studyofconformational defects on polyacetylene. Defects of this kind, which results from a break of the regular alternation of single and double bonds, have been associated to the charge carriers in dopped polyacetylene[2]. The simplicity of the calculations here presented open now the possibility for the study of those defects using finite chains.

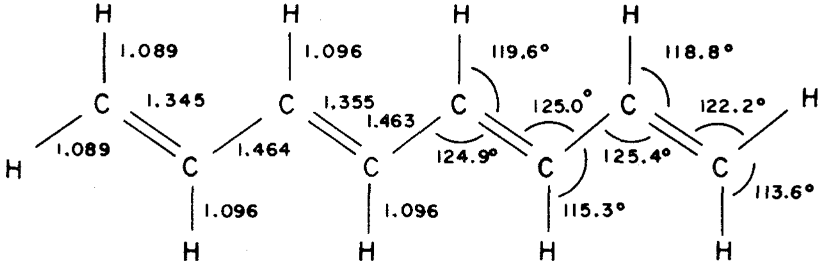

Fig.3a

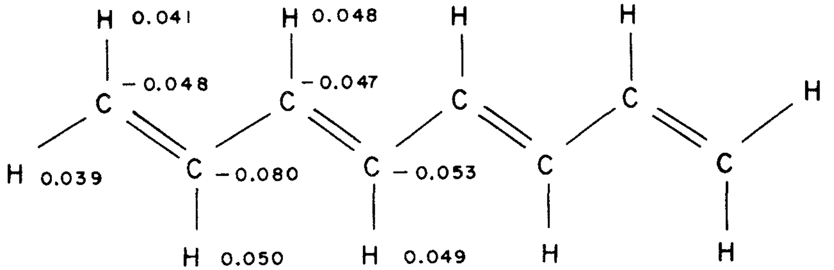

Fig.3b

Fig.3 - MNDO resultç for the $n=4$ oligomer. a) optimized geometry. b) net charge on different atoms.

Table 2 - Evolution of the energy separation $\Delta\varepsilon$ between the highest occupied level and the lowest unoccupied level with the increase of n.

	n	1	2	3	4	5	6	7
$\Delta\varepsilon$	INDO	21.34	16.42	14.03	12.23	11.33	10.71	10.26
(eV)	MNDO	11.50	9.53	8.53	7.98	7.63	7.46	-

This work was favored by several suggestions and discussions with Prof. Bernard Kirtman. We thank especially for the access to the results for the ab-initio calculation on polyacetylene (Ref.16) prior to its publications. This project was partially supported by the Brazilian agencies CNPq and FINEP.

REFERENCES

1. J.Mort, Adv. Phys. 29, 367 (1980)

2. W.P.Su, J.R.Schrieffer and A.J.Heeger, Phys.Rev.Lett., 42, 1698 (1979); Phys. Rev. B22, 2099 (1980).

3. E.A.Cetina, V.Perkins, P.G.Perkins, Theor.Chim.Acta (Berlin) *58*, 257 (1981).

4. J.L.Brédas, R.R.Chance, R.Silbey, G.Nicolas and Ph.Durand, J.Chem. Phys. *75*, 255 (1981).

5. W. K. Ford, C.B.Duke and A.Paton, J.Chem.Phys. 77, 4564 (1982).

6. S.Suhai, J.Chem.Phys. 73, 3843 (1980).

7. C.A.Coulson, Proc. Roy. Soc. A 164, 383 (1938).

8. R.E.Peierls, *Quantum* **Theory of** *Solids*, Oxford University Press (London), 1955.

9. C.R.Fincher, Jr., M.Ozaki, M.Tanaka, D.Peebles, L.Lanchlan, A.J. Heeger and A.G.MacDiarmid, Phys. Rev. 820, 1589 (1979).

10. T.Yamabe, K.Tanaka, H.Terama-e, K. Fukui, A. Imamura, H. Shirakawa, and S. Ikeda, J.Phys. C*12*, L257 (1979).

11.C.Duke and A.Paton, in *Conducting Polymers*, ed. by. R.Seymour,Plenum (New York), 1981.

12. J.Pople and D.Beveridge, *Approximate Molecular Orbital* **Theory**, Mc Graw-Hill (New York), 1970.

13. B.Hudson and B.Kohler, Annual Review of Physical Chemistry *25*, 437 (1974).

14. S.Basu, Adv. Quantum Chemistry *11*, 33 (1978).

15. M.Dewar and W.Thiel, J.Am.Chem.Soc. 99, 4899 (1977).

16. B.Kirtman, W.Nilsson and W.Palke, Solid State Commun. 46, 791 (1983).

17. C.Duke, A.Paton, W.Salaneck, H.Thomas, E.Plummer, A.Heeger and A. MacDiarmid, Chem. Phys. Lett. *59*, 146 (1978).

18. M.C. dos Santos e C.P. de Melo, "Band-Structure of Polymers: A Semi

-Empirical Treatment" Rev.Bras.Física, special issue dedicated to the 1ª Escola Brasileira de Física de Semicondutores, Campinas, February 1983.

Resumo

A aproximação NDO foi usada para estudar a convergência de propriedades eletrônicas dos polienos lineares $C_{2n}H_{2n+2}$, com o aumento da cadeia. Em termos da deslocalização do sistema de elétrons π, a convergência é notavelmente rápida: polienos de $n \geq 4$ já apresentam geometria semelhante ao do polímero infinito. Convergência de propriedades que dependam das energias dos orbitais é menos pronunciada. Entretanto, a extrapolação dos valores encontrados leva à boa concordância com resultados obtidos por cálculos de banda, no mesmo nível de aproximação, para o poliacetileno.