Dipole moments of polyenic oligomeric systems. Part I. A One-dimensional molecular wire model

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ABSTRACT: Ground-state dipolar moments of oligomeric compounds, containing electron-donor (D) and electron-acceptor (A) groups as two terminal units of the polyenic bridge (D-wire-A), can well be described by means of a one-dimensional molecular wire model, which considers a scattering process of electrons through the charge-transfer conduction channel. The dipole moment of the oligomers ($\boldsymbol{\mu}_n$) follows a non-linear dependence of the polyenic bridge length (*L*) according to $\boldsymbol{\mu}_n = \boldsymbol{\mu}_0 + \boldsymbol{\mu}_\infty(1 - e^{-\gamma L})$ where $\boldsymbol{\mu}_0$ is the dipole moment of the first compound of the series, without a polyenic unit ($n = 0$), $\boldsymbol{\mu}_\infty$ is a limit value for $L \rightarrow \infty$ and γ is the one-dimensional conduction constant of the π-molecular orbital channel of the molecular wire. This model can be extended to all those conjugated oligomers of the D-wire-A type where the electronic charge of the donor group can induce a soliton wave as far as through the polyenic bridge towards the acceptor group. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: polyenic oligomerics; dipole moments; one-dimensional molecular wire model

INTRODUCTION

In the molecular architecture of new supra-structural electronic devices, the intramolecular electronic charge-transfer process between electron-donor (D) and electron-acceptor (A) groups, bound through a conjugated polyenic molecular wire (D-wire-A), is determined by the electronic properties of the π-molecular orbital channel present in the oligomeric compound.[1,2] Considerable implications concerning the nature of the conductor bridge can be deduced in the ground and excited states in order to determine optical linear properties of materials[1], and also new electrical properties, such as the resistivities or the conductances to a molecular scale.[2]

Recently, molecular structures involving D and A groups linked to olefinic molecular wires have been used by experimentalists and theorists as useful molecular probes in order to describe a unified view of linear and non-linear polarization.[3] So far, however, there is no general agreement on a theoretical model capable of explaining the main aspect governing the electronic interaction between donor and acceptor sites linked by a conductor molecular bridge.[1,4]

In the present work we have developed a new approach to the study of linear and non-linear electrical properties of these D-wire-A oligomeric systems, derived from a novel comprehension of the role of the polyenic bridge.[2] The π-conduction channel of the molecular wires can be seen as a one-dimensional channel of charge migration between the donor and the acceptor groups.[2,5] In addition to the above, we considered the dipole moment as a physical parameter involved in the history of the charge-transfer migrations through the molecular wire. Thus, the inner conductance or resistance of this molecular wire to the charge flow between the D and A groups determines the final charge distribution in the compound, i.e. the dipole moment. In the following we describe a simple one-dimensional conductor model based on the scattering process of electrons through the π-conduction channel for oligomeric molecular systems that preserve the orientation of the dipole moment with respect to the simplest compound of the series while increasing the length of the molecular wire in the remaining members of the oligomeric series.

In this work we applied our model to the analysis of two well known oligomeric series: olefinic and aromatic polyenic series involving an aldehyde group as an electron-acceptor group.

THE MODEL

According to the nature of the polyenic molecular wire (see Fig. 1), and from a thermodynamic point of view, it is expected to find the all-*trans*-configurations as the main stable conformer of these oligomeric systems.[2]

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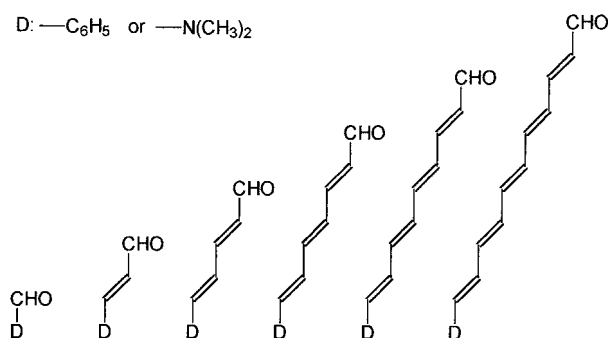
D: —C$_6$H$_5$ or —N(CH$_3$)$_2$

Figure 1. Polyenic oligomeric series of the D-wire-A type

Therefore, the molecular wire length between the D and A terminal units, and the ground-state charge-transfer (Δq) process from D to A involved in these oligomeric compounds must characterize the expected ground dipole moment (μ_n) of these series, where n represents the number of polyenic units. Thus, the molecular conductor wire length (L) of the oligomers under study can be determined as $L = nd$, where d is the polyenic unit mean length (2.81 Å for the series under study;[2] see Table 1).

On the other hand, if the charge flow behavior through the polyenic conduction bridge, constituted by a π-molecular orbital channel,[2] follows a typical scattering process of electrons as we see in one-dimensional metal wire models,[6,7] we are able to propose a new description of the dipole moments in these oligomeric compounds. In this case, we have two main factors determining the scattering process of the electronic flow through the polyenic wire:[7] the transmission probability factor (T) and the reflection probability factor (R), where

$$T + R = 1 \qquad (1)$$

In the following, the ground-state charge transfer involved in these molecular systems (see Fig. 1) will define μ_n through the transmission factor T, if the orientation of the first molecule of the series (μ_0), according to the D–A vector, is maintained constant in all the compounds. Based on this one-dimensional conduction model, if we introduce a polyenic bridge between the D and A groups, the dipolar moments will be constrained to a maximum value (μ_{max}) when $n \to \infty$ and a minimum

value (μ_0) when $n = 0$. The value of μ_n will be determined by the product of the molecular wire length (L) and the charge transferred from D to A. In this process we can expect that the flow of the charge transfer will decrease as the molecular wire length increase, because the molecular resistance of the polyenic wire depends on the molecular wire length.[2] Hence,

$$\lim_{n \to \infty} (\mu_{max} - \mu_0) = \mu_\infty \qquad (2)$$

Thus, and according to the charge transfers associated with the dipolar moments, we have defined the reflection probability factor as

$$R = (\mu_n - \mu_0)/\mu_\infty \qquad (3)$$

where μ_∞ determines the normalization factor.

Now, it is well known[8] that physical quantities such as resistance or conductance vary exponentially with L. Therefore, in order to determine in our one-dimensional conduction channel the functional dependence between the transmission probability factor and the molecular wire length, we have assumed an electronic scattering transmission of the type

$$T = T_0\, e^{-\gamma L} \qquad (4)$$

where T_0 is the transmission probability factor at $L = 0$, i.e. $T_0 = 1$, and γ is the one-dimensional conduction constant of the molecular wire. Thus, if we substitute Eqn (3) in Eqn (1), we will have

$$T + (\mu_n - \mu_0)/\mu_\infty = 1 \qquad (5)$$

and after resubstitution of Eqn (4) in Eqn (5):

$$e^{-\gamma L} + (\mu_n - \mu_0)/\mu_\infty = 1 \qquad (6)$$

From Eqn (6), we can obtain a simple, final relationship between μ_n and L

$$\mu_n = \mu_0 + \mu_\infty(1 - e^{-\gamma L}) \qquad (7)$$

RESULTS AND DISCUSSION

In the present work, we analyzed our model with two polyenic oligomeric series of the D—[CH=CH]$_n$—CHO type, where D correspond to N(CH$_3$)$_2$ and C$_6$H$_5$ groups. These oligomers follow well the previous model backgrounds. Unfortunately, other molecular systems are not available, since systematic experimental studies of dipole moments in oligomeric series are scarce and the values are difficult to determine, mainly owing to solubility problems.

In Fig. 2 we present the dipole moments of these two series versus their molecular wire lengths. In Table 2 we give the published experimental dipole moments used in this work. By using the functional dependence defined by Eqn (7), we fitted the best curve to the experimental data for both the N(CH$_3$)$_2$ and C$_6$H$_5$ oligomeric series. It is amazing to observe the goodness of the fitted curve in
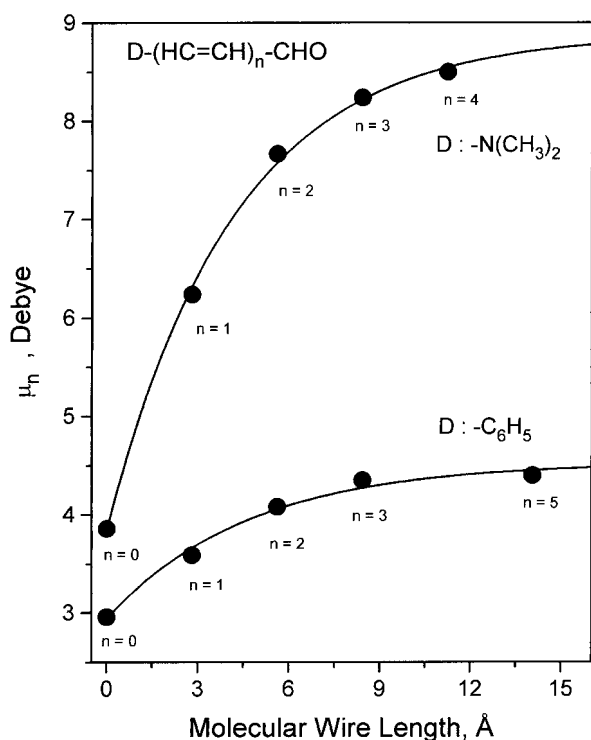
Table 1. Standard and optimized polyenic lengths (Å) in two oligomeric series of the D—(HC=CH)$_n$—CHO type

n	Standard	INDO calc.	ZINDO1 calc.	AM1 calc.
1	2.80	2.77 ± 0.02	2.78 ± 0.02	2.80 ± 0.02
2	5.60	5.55 ± 0.03	5.58 ± 0.03	5.59 ± 0.03
3	8.40	8.33 ± 0.05	8.37 ± 0.05	8.38 ± 0.05
4	11.20	11.10 ± 0.06	11.16 ± 0.06	11.18 ± 0.06
5	14.00	13.88 ± 0.07	13.95 ± 0.07	13.97 ± 0.07

Figure 2. Experimental dipole moments versus molecular wire length of the polyenic oligomeric series depicted in Fig. 1
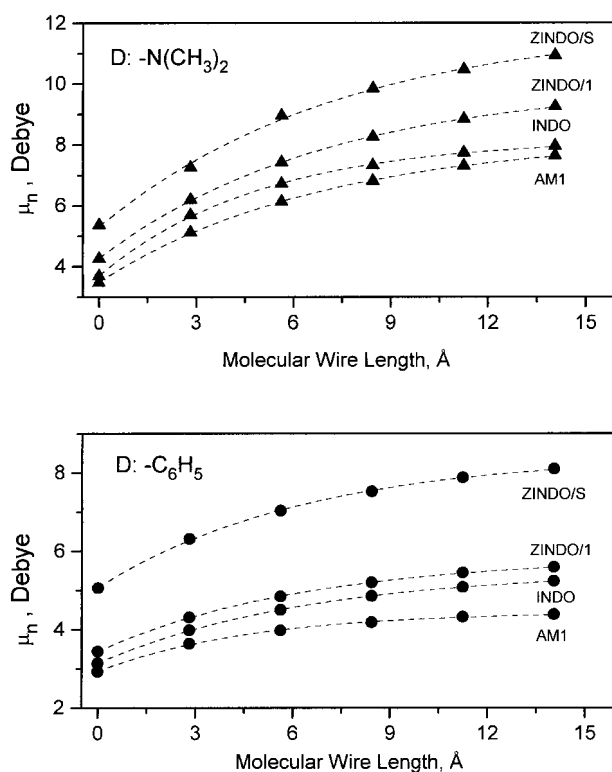

Figure 3. Theoretical dipole moments versus molecular wire length of the polyenic oligomeric series depicted in Fig. 1, calculated by means of the AM1, INDO, ZINDO1 and ZINDO/S-CI approaches

both cases, where we found a similar one-dimensional conduction constant (γ) of $0.24 \pm 0.02\,\text{Å}^{-1}$ and $0.22 \pm 0.05\,\text{Å}^{-1}$, respectively. In spite of the short distance effect expected between the substituent group and the terminal unit of the polyenic molecular wire, the experimental mean value of γ comes out as a representative parameter of the π-conduction channel of the molecular wire, regardless of the nature of the substituent, in agreement with the present model.

In order to extend this study to other oligomeric series and considering the scarce experimental data in the

literature, we determined γ values from ground-state dipole moments calculated from molecular orbital theory. We developed a set of semi-empirical computational approaches[12,13] for both molecular series under study. We chose the AM1, INDO, ZINDO-1 and ZINDO/S-CI semi-empirical calculations of the HyperChem Software Package,[13] where the INDO calculation is similar to the INDO/2 method, ZINDO/1 is similar to the INDO/1 method and ZINDO/S-CI is modified INDO method parametrized to reproduce UV–visible spectroscopic transitions when used with the configuration interactions (CI) singles methods. These calculations were developed at the Departmento de Informática y Computación of the University of Chile.

In Fig. 3 we present the calculated dipole moments versus the molecular wire length for the four different molecular orbital approaches. As in Fig. 2 we found that the best fitting curve follows the exponential functional dependence given by Eqn (7); the γ values determined with this methodology are given in Table 3.

Although the μ_n values arising from these four approaches are different, all of them follow the same exponential dependence with L. This means that the different computational calculations give a good description of the variability of the molecular dipole moments of the series, in spite of the fact that they give different

Table 2. Experimental dipole moments of the two polyenic oligomeric series D—(HC=CH)$_n$—CHO

	L	μ_n (D)	
n	(Å)	D=C$_6$H$_5$	D=−N(CH$_3$)$_2$
0	0	2.96[b]	3.86[d]
1	2.81[a]	3.59[b]	6.24[d]
2	5.62	4.08[c]	7.67[d]
3	8.43	4.35[c]	8.24[d]
4	11.24	—	8.50[d]
5	14.05	4.40[b]	—

[a] Polyenic unit length = 2.81 Å.
[b] Ref. 99.
[c] Ref. 10.
[d] Ref. 11.

Table 3. One-dimensional molecular wire parameters

Donor	Parameter	INDO	ZINDO/1	ZINDO/S	AM1	Exp.
C_6H_5						
	$\boldsymbol{\mu}_0$ (D)	3.14 ± 0.01	3.44 ± 0.01	5.07 ± 0.03	2.94 ± 0.02	2.94 ± 0.09
	$\boldsymbol{\mu}_{\infty_o}$ (D)	2.37 ± 0.02	2.43 ± 0.02	3.38 ± 0.06	1.52 ± 0.03	1.60 ± 0.10
	γ (Å^{-1})	0.152 ± 0.003	0.154 ± 0.003	0.156 ± 0.007	0.21 ± 0.01	0.22 ± 0.05
$N(CH_3)_2$						
	$\boldsymbol{\mu}_0$ (D)	3.48 ± 0.03	4.27 ± 0.03	5.30 ± 0.11	3.70 ± 0.04	3.80 ± 0.09
	$\boldsymbol{\mu}_{\infty_o}$ (D)	4.76 ± 0.07	5.72 ± 0.06	6.70 ± 0.30	4.51 ± 0.07	5.00 ± 0.20
	γ (Å^{-1})	0.145 ± 0.005	0.143 ± 0.003	0.13 ± 0.01	0.20 ± 0.01	0.24 ± 0.02

absolute magnitudes. In general, the three INDO and ZINDO methods yield a mean γ value of 0.147 ± 0.005 Å^{-1} whereas the AM1 method gives a mean γ value of 0.205 ± 0.085 Å^{-1} for both oligomeric series. However, it is the last method which gives the best agreement with the experimental mean γ value of 0.23 ± 0.04 Å^{-1}.

Finally, we emphasize that this model of charge-transfer transmission through a polyenic molecular wire will permit one to initiate new research work by means of experimental and theoretical tools in order to characterize the π-conduction channel in future electronic molecular devices.

Acknowledgments

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