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Dipole moments of polyenic oligomeric systems. Part II—molecular organic wire resistivities: polyacetylenes, allenes and polyynes

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ABSTRACT: Polyacetylenic, allenic and polyynic molecular wire series, containing electron-donor (D) and electron-acceptor (A) groups as two terminal units of the oligomeric bridge (D–wire–A), can be well described by means of a one-dimensional conduction model, which considers a scattering process of electrons through the charge-transfer conduction bridge. The conduction constants (γ_i) of the oligomeric structures of the three molecular series under study were determined from the functional dependence between the dipole moment of the oligomers (μ_n) and the π-molecular orbital bridge length (L). According to our one-dimensional molecular organic wire model:

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

where μ_o is the dipolar moment of the first compound of the oligomeric series without a bridge unit ($n = 0$) and μ_∞ is a limit value for $L \to \infty$. By means of the Landauer theoretical expression for the conductance of a metallic one-dimensional conductor and our molecular wire conduction constants (γ_i), we determined the intrinsic resistivities associated with the molecular resistances of these oligomeric wires. Using this approach we determined, for the first time, the linear and non-linear contributions to the net molecular resistivity. The order of magnitudes of the linear resistivities determined in these oligomeric systems agrees very well with the expected results of experimental measurements for macroscopic wires. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: oligomers; dipole moments; conduction constants; molecular resisitivities

INTRODUCTION

Molecular electronic devices in nanostructured materials are a new area of current interest. The synthesis of potential molecular wires based on oligomeric structures of conjugated molecules is proceeding at a rapid pace and the electronic conduction properties through different new materials have been the subject of novel studies at a molecular scale.[1–4]

Previous studies in our laboratory,[5–8] based on the electronic charge-transfer process between electron-donor (D) and electron-acceptor (A) groups, bound through a conjugated oligomeric molecular wire bridge (D–wire–A), led to useful prototypes in order to understand the conduction properties associated with new molecular electronic devices, such as molecular organic wires.

Recently, we determined conduction properties of the organic molecular wires involving D and A groups in a D–wire–A type system, based on dipole moments and the electronic properties of the π-molecular orbital channel of the molecular wire.[5–7] This simple approach permitted us to generate a new theoretical model capable of explaining the main aspect governing the electronic interaction between donor and acceptor sites linked by a conductor molecular bridge.

In the present work, we extended this 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 wire bridge. The π-conduction channel of the molecular wires can be seen as a one-dimensional channel of charge migration between the donor and acceptor groups.[5] In addition to the above, we considered the dipole moments as the physical parameter involved in the history of the charge-transfer migrations through the molecular wire.

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Thus, the inner conductance of this molecular wire associated with the charge flow between the D and A groups determines the final charge distribution in the compound, i.e. the dipole moment and the molecular resistances.[6]

Three molecular wire series, based on polyacetylenic, allenic and polyynic oligomers, containing two terminal units at the end of the conduction bridge (D–wire–A), $(CH_3)_2N$—as electron-donor (D) and—CHO as electron-acceptor (A) groups, were defined as prototype systems in the present work. These molecular wires can be well described by means of a one-dimensional conduction model, which considers a scattering process of electrons through the charge-transfer conduction bridge (Figs 1–3). Dipole moments, molecular resistances and linear and non-linear contributions to the molecular resistivity were determined and analyzed according to our approach.

THE MODEL

Some years ago, we developed a simple one-dimensional conduction model based on the scattering process of electrons through the π-conduction channel.[8] This model can be applied to any oligomeric molecular system that preserves the orientation of the dipole moment through the main axis of the molecular wire.

The observed molecular wire length, between the D and A terminal units, and the ground-state charge-transfer process from D to A, are two fundamental parameters which characterize the ground dipolar moment (μ_n) for every oligomer of these series, where n represents the number of oligomeric units.

Further, we proposed a novel description of the dipole moments in the oligomer series[5] based on a new consideration of the charge flow behavior through the polyenic conduction bridge, constituted by a π-molecular orbital channel, assuming a typical scattering process of electrons as can be found in the Landauer one-dimensional metal wire model.[9] Thus, in these polyenic series of n oligomeric units, where the molecular conductor wire length (L) of the oligomers under study can be determined by $L = nd$, d being the oligomeric unit length, the dipole moment can be represented as

$$\mu_n = \mu_o + \mu_\infty(1 - e^{-\gamma L}) \tag{1}$$

This fundamental equation defines new molecular parameters such as μ_o, the dipole moment of the first compound of the oligomeric series, i.e. the dipole moment of the first compound of the series without a bridge unit ($n = 0$); μ_∞, a molecular constant of the oligomeric series at the limit value for $L \to \infty$; and γ, the conduction constant of the oligomeric molecular wire. Obviously, this approach considers a scattering process of the electronic flow through the polyenic wire given by the transmission factor probability (T) and the reflection probability factor (R), where $T + R = 1$ and $T = T_0\, e^{-\gamma L}$.

Over two decades ago, Landauer[9] developed a theoretical expression for the conductance of a metallic one-dimensional conductor (G) as

$$G = (2e^2/h)f(T, R) \tag{2}$$

where e is the electron charge, h is Planck's constant and $f(T,R)$ is a function of the transmission and reflection probability factors of the electrons. These last factors are defined according to the relationships $f(T,R) = T/R$ or $f(T,R) = T/(1 - T)$.

However, if we want to represent the molecular resistance (R_m) of the one-dimensional conductor ($R_m = 1/G$), we can make use of the same Eqn (2) according to

$$R_m = (h/2e^2)[T/(1 - T)] \tag{3}$$

Now, if we assume an electronic scattering transmission of the type[5]

$$T = T_0 e^{-\gamma L} \tag{4}$$

we substitute in Eqn (3) with $T_0 = 1$, and finally we obtain a general equation for the molecular resistance R_m:

$$R_m = (h/2e^2)[e^{\gamma L} - 1] \tag{5}$$

However, in order to determine the linear and non-linear contributions to the molecular resistance we can make use of the Maclaurin series[10] and R_m, according to Eqn (5), can finally be expressed as follows:

$$R_m = (h/2e^2)\left[\gamma L + \frac{1}{2}!\gamma^2 L^2 + \frac{1}{3}!\gamma^3 L^3 + \cdots + \frac{1}{n}!\gamma^n L^n\right] \tag{6}$$

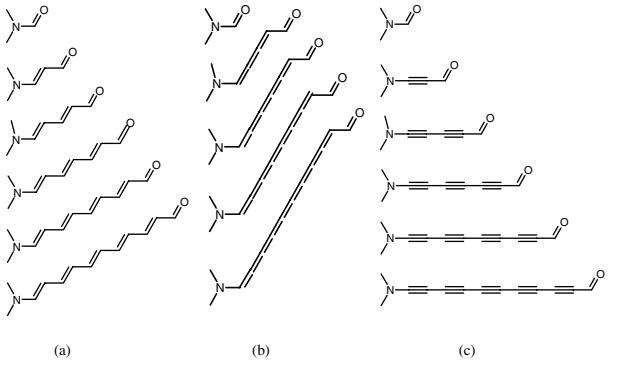

Figure 1. Polyacetylenic (a), allenic (b) and polyynic (c) oligomers, containing two terminal units at the end of the conduction bridge (D–wire–A). D = $(CH_3)_2N$—, as electron-donor and A = —CHO, as electron-acceptor groups. The allenic oligomers under study correspond to the uneven bridges ($n = 1, 3, 5, 7$, etc.)

Table 1. Dipole moments of polyenic and polyynic series from AM1 molecular orbital calculations (in debye)

	μ_0	μ_1	μ_2	μ_3	μ_4	μ_5	μ_6	μ_7	μ_8	μ_9	μ_{10}
Polyenic series											
L (Å)	0	2.81	5.62	8.43	11.2	14.0	16.8	19.7	22.5	25.1	27.9
$Me_2N(HC{=}CH)_nCHO$[a]	3.58	5.71	6.74	7.37	7.78	8.06	8.25	8.39	8.49	8.57	8.62
Polyynic series											
L (Å)	0	2.62	5.17	7.73	10.28	12.83	15.38	17.93	20.48	23.03	25.59
$Me_2N(C{\equiv}C)_nCHO$	3.58	4.95	5.75	6.38	6.77	7.10	7.40	7.60	7.70	7.81	7.94

[a] Ref. 5.

Table 2. Dipole moments of allenic series from AM1 molecular orbital calculations (in debye)

	μ_0	μ_3	μ_5	μ_7	μ_9	μ_{11}	μ_{13}	μ_{15}	μ_{17}
L (Å)	0	5.28	7.82	10.36	12.89	15.43	17.96	20.50	23.04
$Me_2NHC{=}(C{=}C)_n{=}CHCHO$	3.58	7.57	9.36	11.10	12.76	14.34	15.92	17.44	18.83

From this last equation, the linear contribution to the molecular resistance is given by the first term of the series:

$$R_m(L) = (h/2e^2)[\gamma L] \tag{7}$$

and the non-linear contribution to R_m is given by

$$R_m(L^n) = (h/2e^2)\left[\frac{1}{2}!\gamma^2 L^2 + \frac{1}{3}!\gamma^3 L^3 + \cdots + \frac{1}{n}!\gamma^n L^n\right] \tag{8}$$

Hence

$$R_m = R_m(L) + R_m(L^n) \tag{9}$$

Now, if we made use of the linear contribution to the molecular resistance R_m (L) [(Eqn (7)] and compare it with the classical resistance observed in macroscopic metal wires given by $R = \rho(L/S)$, where ρ is the molecular resistivity, L is the length of the molecular wire and S is the cross-section of the conduction channel of the molecular wire, we find the following relationship:

$$(h/2e^2)[\gamma L] = \rho(L/S) \tag{10}$$

From this last equation, we obtain the following expression for the linear molecular resistivity in the oligomeric wire:

$$\rho = (h/2e^2)\gamma S[\Omega\,\mathrm{cm}] \tag{11}$$

RESULTS AND DISCUSSION

Molecular geometry, electronic charge distribution and dipole moment calculations of the $(CH_3)_2N$–wire–CHO systems studied in this work were obtained by means of AM1 semiempirical molecular orbital theory calculations,[11] under complete relaxation of the bond lengths and bond angles reaching the lowest energy condition. Although AM1 is not parametrized for dipole moments, after comparing different molecular orbital calculations in *ab initio* and semiempirical approaches, we observed that AM1 follows very well the experimental dipole moment trends in similar molecular organic systems.[7] The computational work was done using the WinMOPAC 3.0 software package[12] on a PC network station in our laboratory.

Dipole moments of the polyacetylenic and polyynic molecular wire series are depicted in Table 1 and those of the allenic series in Table 2. This last oligomeric series was determined for the uneven oligomer units, because the pair units determine a change in the molecular orientation of the dipolar moments and do not follow the one-dimensional model basis.

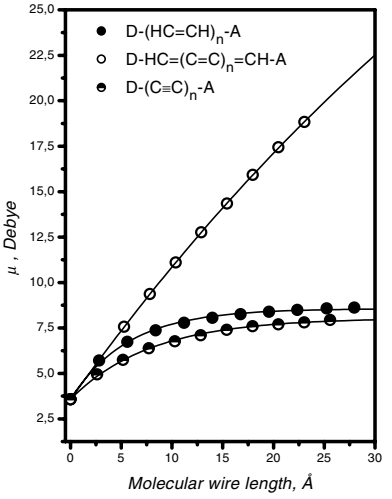

Figure 2. Dipole moments of the polyenic, polyynic and allenic oligomers from AM1 molecular orbital calculations, where D = $(CH_3)_2N$— and A = —CHO

Table 3. Conduction constants (γ) of the polyenic, polyynic and allenic molecular wire series

Molecular wire series	μ_0 (D)	μ_∞ (D)	γ (Å^{-1})
$Me_2N(HC{=}CH)_nCHO$	3.58	4.98 ± 0.05	0.180 ± 0.007
$Me_2N(C{\equiv}C)_nCHO$	3.58	4.47 ± 0.05	0.130 ± 0.004
$Me_2NHC{=}(C{=}C)_n{=}CHCHO$	3.58	52.0 ± 0.9	0.015 ± 0.001

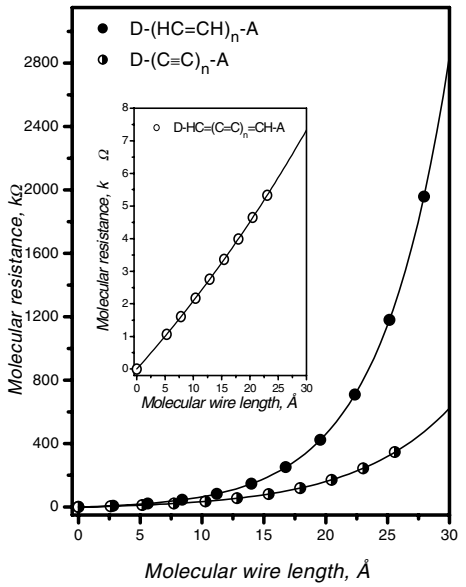

Figure 3. Molecular resistances of the oligomeric series as function of the molecular wire length

In order to determine the conduction constants γ_i of the molecular wires under study, we plotted the dipole moments (μ_n) versus the bridge length (L) following the functional dependence defined by Eqn (1). In Fig. 2 we present the best curves for the corresponding γ_i conduction constants of every oligomeric series. These constants are given in Table 3.

It is interesting to note from our results that all these molecular series follow Eqn (1) and, therefore, our model can be understood as a first approximation to the one-dimensional conduction description of the organic molecular wires. Hence, the allenic oligomer emerges as the best conduction wire, and the polyynic oligomer is slightly better than the polyenic oligomer wire.

Based on the conduction constants, we determined the molecular resistances for every oligomeric series, according to Eqn (4). The functional dependence of the molecular resistance versus the molecular wire length can be observed in Fig. 3. Allenic oligomers follow a quasi-linear functionality, whereas the other two oligomers show a strong non-linear behavior. Therefore, in order to compare the linear resistivity in every molecular wire, we used Eqn (11), with consideration of a molecular wire cross-section[8] of 4.5 Å^2. In Table 4, where the three systems are compared, it can be appreciated that the orders of magnitude are similar to macroscopic metal and non-metal wires. However, the allenic oligomers present the best conduction properties as one-dimensional organic wires.

Table 4. Molecular linear resistivity

Material	$\rho(\mu\Omega\,\text{cm})$
Molecular wires	
$Me_2N(HC{=}CH)_nCHO$	104 ± 4
$Me_2N(C{\equiv}C)_nCHO$	75 ± 2
$Me_2NHC{=}(C{=}C)_n{=}CHCHO$	9.0 ± 0.2
Macroscopic wires[a]	
Cu (electrolytic)	1.7
Constantan	49
Hastelloy C	125
Polyacetylene (doped)[b]	100.0

[a] Ref. 13.
[b] Ref. 14.

Acknowledgments

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