ARTICLE IN PRESS

Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Chemical Physics 299 (2004) 139–145

Chemical Physics

www.elsevier.com/locate/chemphys

Quantum interference in polycyclic hydrocarbon molecular wires

Derek Walter [a], Daniel Neuhauser [a], Roi Baer [b,*]

[a] *Department of Chemistry and Biochemistry, University of California, P.O. Box 951569, Los Angeles, CA 90095-1569, USA*
[b] *Institute of Chemistry and the Lise Meitner Center for Quantum Chemistry, The Hebrew University of Jerusalem, Givat Ram, Jerusalem 91904, Israel*

Received 7 October 2003; accepted 30 December 2003

Abstract

The construction of devices based on molecular components depends upon the development of molecular wires with adaptable current–voltage characteristics. Here, we report that quantum interference effects could lead to substantial differences in conductance in molecular wires which include some simple polycyclic aromatic hydrocarbons (PAHs). For molecular wires containing a single benzene, anthracene or tetracene molecule a large peak appears in the electron transmission probability spectrum at an energy just above the lowest unoccupied orbital (LUMO). For a molecular wire containing a single naphthalene molecule, however, this same peak essentially vanishes. Furthermore, the peak can be re-established by altering the attachment points of the molecular leads to the naphthalene molecule. A breakdown of the individual terms contributing the relevant peak confirms that these results are in fact due to quantum interference effects.

1. Introduction

A great deal of progress has recently been made towards realization of miniature electronic devices constructed from molecular components [1,2]. The technological potential of these devices is obvious: such components could be orders of magnitude more powerful than their silicon counterparts [3]. Scientifically, the fundamental issues are of great interest, some are well understood [4,5], while others – remain to be explored [6–12]. We know, that unlike macroscopic conventional wires, the conductance properties of the molecular counterparts are intricate functions of the underlying electronic structure [13]. Rather than the conductance being simply proportional to the applied voltage, it generally exhibits step-like features corresponding to resonances with the molecular eigenstates. As a consequence of this, organic molecules that are slightly dissimilar can exhibit substantial differences in conductance as the various resonances shift in position and change in size. These changes have been attributed to reductions in electronic delocalization [14–16], wire–electrode interactions [17], and quantum interference effects [14,18].

There is a substantial body of experimental and theoretical work on the properties of polyacetylene molecular wires and their conduction behavior has been well understood for some time now [19–23]. More recently, experimental work on the conductance of molecular wires containing a single benzene molecule or benzene derivative has appeared [24,25]. This was followed by sophisticated theoretical research on the conductance of benzene-based molecular wires [26,27] that produced results in good agreement with the experiment. Researchers have since gone on to study both experimentally and theoretically the conductance of molecular wires based on even larger organic molecules. Work has appeared on the conductance of more complicated single organic molecules [28,29]. Hush and coworkers [30] have done extensive theoretical research on the possibility of using linked porphyrin molecules as molecular wires. The possibility of exploiting quantum interference in molecular wires based on the C_{60} molecule has also been noted [31]. Furthermore, the success in previous experimental studies on benzene-based molecular wires and the development of new synthetic techniques [32] strongly suggest that newly proposed systems will in fact be realizable.

One of the more striking differences between molecular and macroscopic wires is the possibility that quantum interference may be dominant. Such concepts

---

* Corresponding author. Tel.: +972-2-658-6114; fax: +972-2-651-3742.
E-mail address: roi.baer@huji.ac.il (R. Baer).

0301-0104/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemphys.2003.12.015

were considered by Paddon-Row and Jordan [33] in discussing bridge-assisted electron transfer. In the context of transport, Joachim and co-workers [34,35] studied theoretically a single benzene or benzene-based molecule embedded in a polyacetylene chain. The electron transmission probability was studied by Joachim and co-workers as a function of the attachment points of the polyacetylene chains to the ring structure. It was shown that the transmission changes quite significantly through such modifications and that interferences lead to dips in the transmission probability spectrum. Furthermore, a simple qualitative rule was given by Joachim and co-workers for determining whether or not two molecular eigenstates interfere with one another.

Recently, Baer and Neuhauser [36,37] studied a series of molecular wires containing different polyacetylene loop structures. Unlike the previous work these loop structures contained branches having lengths greater than the de Broglie wavelength of the conducting electrons. Their study was carried out with the prime objective of fleshing out possible interference effects in molecular wires. The results showed a striking variation of the conductance depending on the contact points of the interference loop structure.

In this paper, we examine the issue of interference in a more elaborate setup. We consider molecular resonators shown in Fig. 1 consisting of single or multiple ring systems: benzene (one ring), naphthalene (two rings), anthracene (three ring) and tetracene (4 rings). For naphthalene and anthracene, two configurations of the polyacetylene chains are considered. A *cis* configuration in which the chains are attached at the same side of the resonator and a *trans* configuration in which the chains are attached at opposite ends of the resonator.

Utilizing a simple Hückel model, Baer and Neuhauser [36] showed that *cis* configurations are under “destructive interference” situation. In order to explain this, consider Fig. 2 where the 3–3′ bond is ignored for simplicity. In the Hückel π-bond picture, all carbons are equivalent, all CC bonds are of the same length R_{CC}. The conduction electron mounts the molecular bridge at site 1 and leaves it at site 5. We show that the probability for this process is small. This conduction electron is within the Fermi level of the π system, having a de Broglie wavelength of $\lambda_F = 4R_{CC}$ (this is because of the half filled π band). There are two paths to consider: $P_1 = \{1, 2, 3, 4, 5\}$ and $P_2 = \{1, 1', 2', 3', 4', 5', 5\}$ with corresponding lengths of $L[P_1] = 4R_{CC}$ and $L[P_2] = 6R_{CC}$. The phase difference of the two paths is then $(2R_{CC}/\lambda_F) \times 2\pi = \pi$. Thus two paths the interfere *destructively*, yielding the process highly unfavorable.

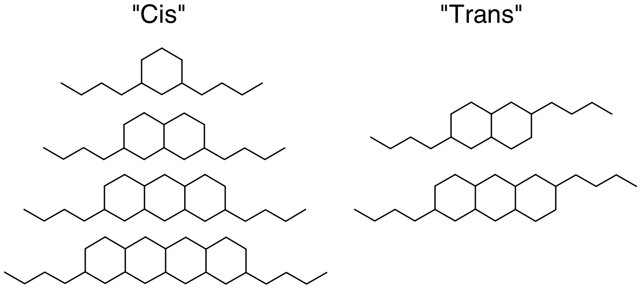

Fig. 1. Molecular wires considered. There are two classes of systems (denoted *cis*/*trans*) with respect to the polyacetylene chain connected to the polycyclic bridges.

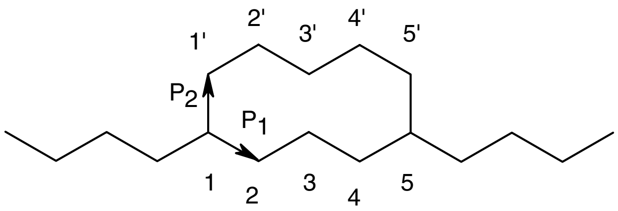

Fig. 2. Numbering of carbon atoms on the naphthalene bridge.

A similar reasoning, applied to the *trans* configuration, will involve the paths $P_1 = \{1, 2, 3, 4, 5, 5'\}$ and $P_2 = \{1, 1', 2', 3', 4', 5'\}$ both of the same length and therefore of the same phase. Thus, the conductance of *trans* molecules is expected to be high. This intuitive reasoning applies for all the systems and is borne out by exact Hückel calculations.

The arguments presented above contain many simplifying assumptions. For example, we have neglected the sigma system, assumed that all carbon atoms are identical, used unrelaxed nuclear configurations, did not account for realistic charge distributions and used an over simplified (one orbital per atom) basis set. In this paper, we endeavor to present more realistic computations that overcome some of these limitations employing a DFT-based approach. As we discuss in the next sections, there are still several effects we are not addressing here though and these will await further investigation. Within our model, we corroborate the previous conclusions that quantum interference can lead to significant differences in the conductance of these systems.

2. Method

The polyacetylene chains of Fig. 1 are connected through a sulfur atom on both sides to a pair of “electron reservoirs”, each consisting of a straight chain of 10 gold atoms. The length of the polyacetylene chains are determined such that the distance between the sulfur atoms remains relatively constant for all the systems studied here. In the case of benzene, polyacetylene chains having 5 carbon atoms are used. This leads to a total of 13 carbon atoms separating the sulfur atoms. For naphthalene, the use of 13 carbon atoms to separate the sulfur atoms leads to a slightly asymmetric molecule [38]. Prior to the electronic structure calculation, molecular geometries were optimized using the Universal Force Field molecular mechanics method [39] as implemented in the ArgusLab quantum chemistry package [40]. The Hamiltonian used for conductance computation (in Eq. (1)) was a DFT Fock operator as computed by the Jaguar quantum chemistry package [41] using pseudospectral DFT algorithms [42]. The LACVP [43] basis set and B3LYP exchange correlation functional, which consists of the correlation functional of Lee, Yang and Parr [44] in combination the exchange functional of Becke [45], were used in the calculations that were done to obtain the results shown here. A number of additional calculations were performed with different exchange-correlation functionals and a slightly larger basis set to check the convergence of the results with respect to these parameters. Calculations were performed with the B3LYP functional in combination with the LACV3P basis set, and a non-hybrid GGA functional [46,47] in combination with the LACVP basis set. Furthermore, Hartree–Fock calculations using the LACVP basis set were also carried out. Although the energetics changed slightly upon varying the basis set and exchange-correlation functional, the essential results did not differ from those shown here.

The electron transmission probability across the molecular wire from reservoir ‘a’ to reservoir ‘b’ as a function of energy, $T_{\mathrm{ab}}(E)$, was computed using an expression given by Seideman and Miller [48]

$$T_{\mathrm{ab}}(E) = 4\,\mathrm{Re}\,\mathrm{Tr}\left[G^{\dagger}(E)W_{\mathrm{a}}G(E)W_{\mathrm{b}}\right]. \tag{1}$$

Here, W_{a} and W_{b} are absorbing potentials [49] which play a role analogous to the imaginary part of the self energies [50,51]. The quantity $G(E)$ is the total Green’s function for the system

$$G(E) = \frac{1}{E - H + iW_{\mathrm{a}} + iW_{\mathrm{b}}}. \tag{2}$$

We neglect in this work the effect of screening the bias potential. This may be taken into account within a non-equilibrium Green’s function SCF procedure [52–54] or a time-dependent density functional calculation [6,55]. While this effect will no doubt change the numerical value of the results, it is not expected to nullify the very strong signature of interference we are discussing.

The absorbing potentials required in Eqs. (1) and (2) were taken to be diagonal in the atomic orbital (AO) basis. The values of the absorbing potential were chosen to increase parabolically along the length of each reservoir from 0 eV at the initial gold atom, which is bound to the sulfur, to a maximum 5 eV at the terminal gold atom. It should be noted that the results are not sensitive to the exact form of the absorbing potential so long as it obeys a modest set of requirements outlined by Neuhauser and Baer [49]. Here, we observe that the results change by less than a few percent when the absorbing potential is doubled or even quadrupled in magnitude. The relation between the absorbing potentials and the Green’s function method for computing molecular conductance has been discussed in considerable detail by Galperin et al. [56].

We evaluate the conductance using Eq. (1) where the operators represented in the basis of eigenfunctions of the complex DFT Fock atomic-orbital- (AO-) matrix, which we shall denote as $\tilde{F}$

$$\tilde{F} = F - iW_{\mathrm{a}} - iW_{\mathrm{b}}. \tag{3}$$

Here, F is the usual DFT Fock AO-matrix obtained from Jaguar (assumed to contain N functions). In this basis, the Green’s function required (Eq. (2)) in Eq. (1) is a diagonal matrix. This facilitates the study the various contributions to the transmission probability. Note, however, that $\tilde{F}$ is not Hermitian and its eigenvectors are therefore no longer orthogonal. The transformation of the absorbing potentials, which are diagonal matrices in the AO basis, to the basis of eigenfunction of $\tilde{F}$ must then be handled carefully. Here, we first determine a matrix $\mathbf{X}$ which orthogonalizes the underlying AO basis

$$\mathbf{X}^{\mathrm{T}}\mathbf{S}\mathbf{X} = \mathbf{I}, \tag{4}$$

where $\mathbf{S}$ is the analytic overlap matrix. The complex Fock matrix is then formed in the AO basis and transformed to the orthogonal basis using the matrix $\mathbf{X}$

$$\tilde{\mathbf{F}}' = \mathbf{X}^{\mathrm{T}}\tilde{\mathbf{F}}\mathbf{X}. \tag{5}$$

The matrix $\tilde{\mathbf{F}}'$ is diagonalized and its resulting eigenvectors and eigenvalues are stored in the matrices $\mathbf{C}'$ and the diagonal matrix ε, respectively

$$\left(\tilde{\mathbf{C}}'\right)^{-1}\tilde{\mathbf{F}}'\tilde{\mathbf{C}}' = \mathrm{diag}[\varepsilon_1 \cdots \varepsilon_N]. \tag{6}$$

Notice that in Eq. (6) the inverse of $\tilde{\mathbf{C}}'$ must be used rather than merely its transpose as the eigenvectors of $\tilde{\mathbf{F}}'$ are not necessarily orthogonal. This leads to the following expressions for the absorbing potentials in the basis of the eigenvectors of $\tilde{\mathbf{F}}$:

$$\begin{aligned} \tilde{\mathbf{W}}^{\mathrm{a}} &= \tilde{\mathbf{C}}'^{\mathrm{T}}\mathbf{X}^{\mathrm{T}}\mathbf{W}^{\mathrm{a}}\mathbf{X}\tilde{\mathbf{C}}', \\ \tilde{\mathbf{W}}^{\mathrm{a}} &= \left(\tilde{\mathbf{C}}'\right)^{-1}\mathbf{X}^{\mathrm{T}}\mathbf{W}^{\mathrm{b}}\mathbf{X}\left(\tilde{\mathbf{C}}'^{-1}\right)^{\mathrm{T}}, \end{aligned} \tag{7}$$

where $\mathbf{W}^{\mathrm{a}}$ and $\mathbf{W}^{\mathrm{b}}$ are the representations of the absorbing potentials on reservoirs ‘a’ and ‘b’, respectively, in the AO basis. The expression (Eq. (1)) for the transmission probability then becomes

$$T_{\mathrm{ab}}(E) = \sum_{i,j} T_{\mathrm{ab}}^{ij}(E) = 4\,\mathrm{Re}\sum\left(E - \varepsilon_i^{*}\right)^{-1}\tilde{W}_{ij}^{\mathrm{a}}\left(E - \varepsilon_j\right)^{-1}\tilde{W}_{ji}^{\mathrm{b}}. \tag{8}$$

3. Results

Fig. 3 shows the electron transmission probability as a function of energy for a series of polycyclic aromatic hydrocarbon (PAH)-based molecular wires having a *cis*

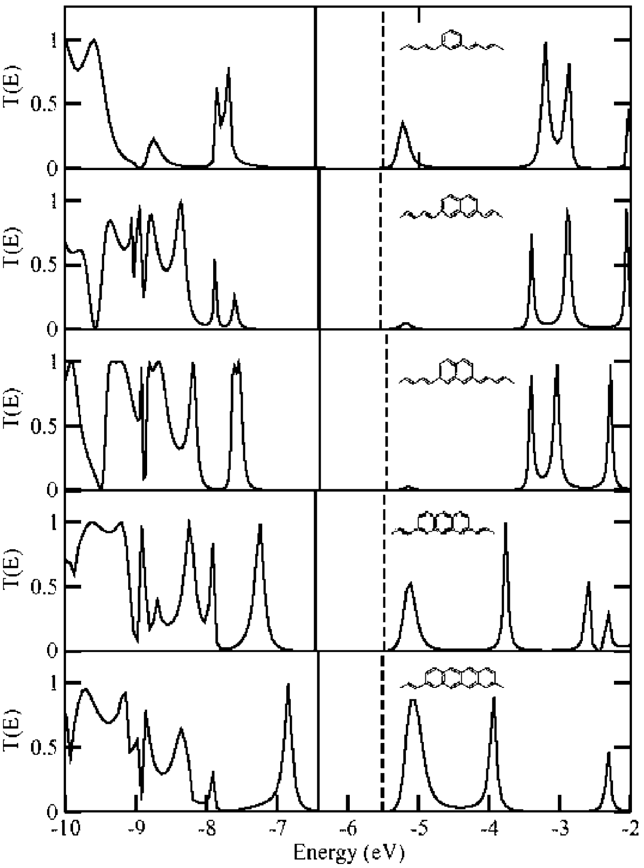

Fig. 3. Electron transmission probability across the molecular wire as a function of energy for systems with a *cis* configuration of polyacetylene chains. The energy of the HOMO is shown by the solid vertical line and the energy of the LUMO is shown by the dashed vertical line. For the naphthalene wire, we present results for two functonals (B3LYP and below GGA).

configuration of polyacetylene chains. For benzene, anthracene, and tetracene a broad and substantial resonance peak occurs at −5 eV. For naphthalene-based molecular wires, however, this resonance peak disappears almost completely. This striking behavior can be analyzed by evaluating the contributions of various states to the overall transmission probability Eq. (8) as follows.

Consider first a system having only one single-particle state. Only the term T_{ab}^{11} will then arise in Eq. (8). This term must be positive since the product $(E-\varepsilon_1^*)^{-1}(E-\varepsilon_1)^{-1}$ is positive and the absorbing potentials $\mathbf{W}^{\mathrm{a}}$ and $\mathbf{W}^{\mathrm{b}}$ are represented by positive definite matrices. Furthermore, due to these inverse terms, the transmission probability will have appreciable amplitude only for energies near ε_2. Now, consider a system having two single particle states. In this case, Eq. (8) will admit two positive direct terms: T_{ab}^{11} and T_{ab}^{22}. If the energies ε_1 and ε_2 are well separated, these two terms will give rise to two distinct peaks in the transmission probability spectrum centered about ε_1 and ε_2. On the other hand, if ε_1 and ε_2 are close, the two peaks will overlap. One must then also consider the effect of the interference terms T_{ab}^{12} and T_{ab}^{21}. Unlike the direct terms, the interference terms can be either positive or negative and can therefore either reinforce the direct terms or partially cancel them out. This situation is analogous to that occurring in interfering electromagnetic waves. In principle, the interference terms could be large enough to completely cancel the effects of the direct terms. Whether or not this happens depends on the details of the individual system under consideration.

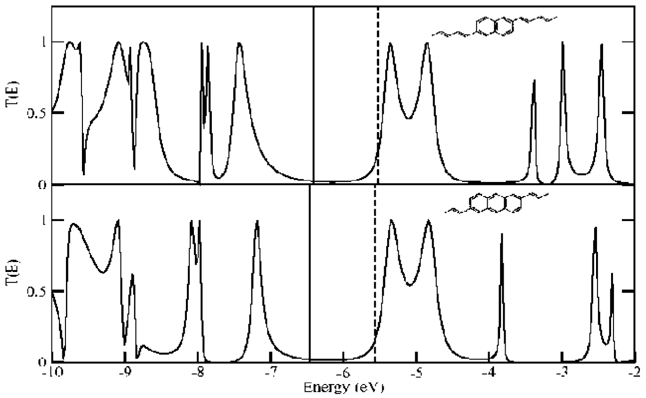

Fig. 4. Electron transmission probability across the molecular wire as a function of energy for systems with a *trans* configuration of polyacetylene chains. The energy of the HOMO is shown by the solid vertical line and the energy of the LUMO is shown by the dashed vertical line.

As an example of the interference effect, consider the peaks in Fig. 4 centered about −5 eV. These peaks are located energetically just above the lowest unoccupied orbital (LUMO) of these systems and is therefore expected to be quite important for conduction. A listing of the eigenvalues of $\tilde{\mathbf{F}}'$ reveals that there are four states contributing to this resonance peak. For two of them, denoted 1 and 2, the complex part of their eigenvalue is close to 0.1 eV. The other two states, denoted 3 and 4, the complex part of their eigenvalue is close to 0.4 eV and therefore contribute more to broadening the peak than states 1 and 2. A Mulliken analysis of the four orbitals further reveals that each of them have a similar form in their respective molecules.

The contributions that all possible pairs of these four states make to Eq. (8) are displayed in Table 1. The individual terms listed in the table are computed at the energy where the peaks centered at about −5 eV have their maximum heights. For the naphthalene-based molecular wire, one can see that the contributions of the first two states cancel each other almost completely (i.e. twice the value of the $i=1$, $j=2$ term approximately equals in magnitude the sum of the $i=1$, $j=1$ and $i=2$, $j=2$ terms) indicating that quantum interference is indeed at work here. For all other systems, there is only partial cancellation of states 1 and 2.

Table 1
Terms from Eq. (8) contributing to resonances near −5 eV in Fig. 3

State *i*	State *j*	1	2	3	4
1	1	1.30	1.09	1.26	0.93
1	2	−1.49	−1.90	−1.48	−1.08
2	2	2.08	1.92	2.25	2.16
1	3	−0.22	0.07	0.38	0.05
2	3	−0.91	−0.07	−1.28	−0.38
3	3	6.52	0.01	2.49	0.19
1	4	0.33	−0.08	−0.26	0.13
2	4	0.78	0.07	1.15	0.14
3	4	−6.50	−0.01	−2.47	−0.18
4	4	6.49	0.01	2.46	0.21

The terms were evaluated at an energy where the peaks centered about −5 eV have their maximum values. Data shown for the molecular wire having two fused rings (center panel in Fig. 3).

In terms of absolute magnitude, states 3 and 4 make only a small contribution to the peak in naphthalene and tetracene. On the other hand, for the benzene and anthracene-based wires the contributions of states 3 and 4 are large in magnitude but cancel one another almost completely. The additional cross terms involving either state 1 or 2 and either state 3 or 4 cancel almost completely in all systems. Based on this, it is evident that quantum interference plays a large role in determining the magnitudes of the resonance peaks in the molecular wires examined here.

By adjusting the connection points of the polyacetylene chains to the polycyclic bridge, we expect that the relative phases of the outgoing portions of the molecular states meeting at the terminal lead will differ. As discussed in Section 1, this is expected to dramatically alter the conductance properties due to the interference pattern along the bridge.

Fig. 3 shows the electron transmission probability for the naphthalene and anthracene-based molecular wires with a *trans* configuration of polyacetylene chains. As one can see by again analyzing the resonance peaks centered at −5 eV, the transmission of this same bridge has increased dramatically. Although four states still contribute to this peak, the states span a wider energy range and this leads to a bimodal peak.

The exceptional result is the large resonance peak which appears in Fig. 4 at −5 eV for the naphthalene-based molecular wire. This should be compared to the nearly non-existent peak in the *cis* configuration of the same bridge shown in Fig. 3. Certainly, the wider energy range spanned by the four states reduced the level of quantum interference. The relatively large size of the peaks in Fig. 4, also indicates that little quantum interference is occurring between states which are nearby in energy.

Once $T(E)$ is determined, the conductance of the molecular wires can be estimated by taking the derivative with respect to voltage of the Landauer formula

$$I(V) = \frac{2e}{\hbar} \int_{-\infty}^{\infty} \Delta F(E) T(E) \, \mathrm{d}E.$$

Here, $\Delta F(E, V) = F_\mathrm{L} - F_\mathrm{R}$ is the difference between left and right Fermi–Dirac distributions, at temperature room temperature of one-electron states in the left and right leads

$$F_{\mathrm{L/R}} = \left\{1 + \exp\left[\beta\left(E - \varepsilon_\mathrm{F} - eV_{\mathrm{L/R}}\right)\right]\right\}^{-1}.$$

We assumed that the voltage difference V is evenly distributed on both sides, i.e. $V_\mathrm{L} = -V_\mathrm{R} = V/2$ and that it is constant through the wire. This last assumption is in fact justified for the conducting systems [57] much less so for the non-conducting ones. Yet, the effect we are observing is quite striking, so it will not depend on delicate details.

The conductance of the two- and three-ringed systems is strongly affected by interference. This is clearly shown in Fig. 5, where the conductance as a function of bias is depicted. Even at zero bias there is a strong effect. This is especially visible when the ratio of *trans* to *cis* conductance is examined, as in Fig. 6, exhibiting some two or more orders of magnitude increase in conductance for the two-ring system. The interference effects are much reduced in the longer systems, most likely

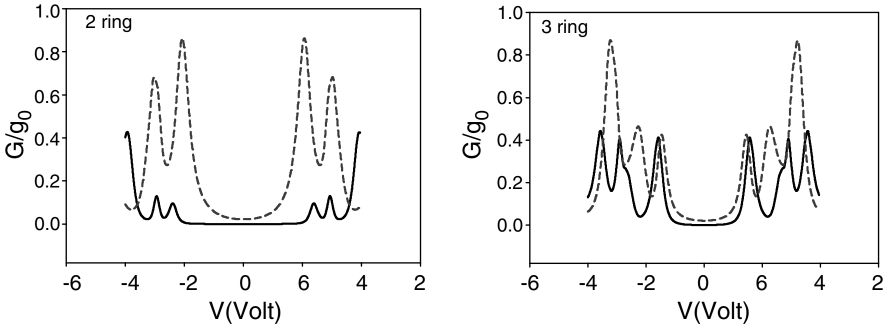

Fig. 5. The conductance (in units $g_0 = 2e^2/\hbar$) as a function of voltage for the *cis* (solid) and *trans* (dashed) conformations of the two- and three-ring systems.

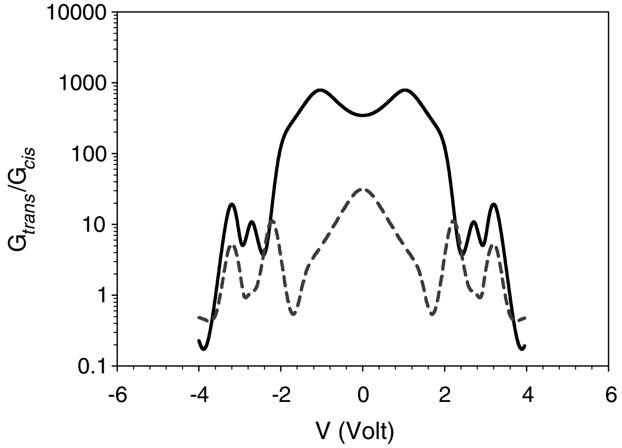

Fig. 6. The ratio of conductance in the *trans* conformation to that in the *cis* conformation for the two- and three-ring system.

because of tunneling and disorder that precludes complete destructive/constructive interference.

4. Conclusions

In this paper, we have examined the possibility that quantum interference can substantially affect conductance in molecular wires constructed from PAHs. Simple Hückel models predict that all PAHs will exhibit the same destructive interference effect. Yet the more realistic density functional-based calculations show that while interference effects do exist in all species, their intensity or total effect on conductance depends strongly on the PAH considered. One striking result we find is that quantum interference occurs more readily in naphthalene-based molecular wires compared to wires containing benzene, anthracene, or tetracene. The reasons for this are not fully understood.

Previous experimental work on benzene-based molecular wires portends the possibility of constructing molecular wires similar to the systems presented here in which the theoretical predictions could be tested. Additionally, previous theoretical work has suggested that the addition of various organic sidegroups [26] can alter the conductance. This fact, taken in conjunction with the differing quantum interference behavior seen here when the lead attachment points are varied, suggest new possibilities using multilead-based molecular switches.

Acknowledgements

Professors Emily A. Carter (UCLA), Mark Ratner (Northwestern) and Eran Rabani (Tel Aviv University) are acknowledged for helpful comments. This research was supported by the Israel Science Foundation founded by the Israel Academy of Sciences and Humanities.

References

[1] J. Jortner, M. Ratner, Molecular Electronics, Blackwell Science Publications, Oxford, 1997.
[2] A. Aviram, M.A. Ratner, Molecular Electronics: Science and Technology, New York Academy of Sciences, New York, 1998.
[3] J.M. Tour, M. Kozaki, J.M. Seminario, J. Am. Chem. Soc. 120 (9) (1998) 8486.
[4] M. Ratner, Nature 404 (6774) (2000) 137.
[5] A. Nitzan, Ann. Rev. Phys. Chem. 52 (2001) 681.
[6] R. Baer, D. Neuhauser, Int. J. Quantum Chem. 91 (3) (2003) 524.
[7] S. Alavi, B. Larade, J. Taylor, H. Guo, T. Seideman, Chem. Phys. 281 (2–3) (2002) 293.
[8] J. Taylor, M. Brandbyge, K. Stokbro, Phys. Rev. Lett. 89 (13) (2002) 138301.
[9] S.N. Yaliraki, M.A. Ratner, in: Molecular Electronics II, vol. 960, 2002, p. 153.
[10] E.G. Emberly, G. Kirczenow, Phys. Rev. B 60 (8) (1999) 6028.
[11] H. Ness, S.A. Shevlin, A.J. Fisher, Phys. Rev. B 63 (12) (2001) 125422.
[12] I.V. Krive, E.N. Bogachek, A.G. Scherbakov, U. Landman, Phys. Rev. B 64 (23) (2001) 233304.
[13] C. Joachim, C. Roth, Atomic and Molecular Wires, Dordrecht, The Netherlands, 1997.
[14] J.-P. Launay, C.D. Coudret, in: A. Aviram, M.A. Ratner (Eds.), Molecular Electronics, New York Academy of Sciences, New York, 1998.
[15] J.L. Breda, V.M. Geskin, D.A. dos Santos, D. Beljonne, J. Cornil, in: C. Joachim, S. Roth (Eds.), Atomic and Molecular Wires, Kluwer Academic Publishers, The Netherlands, 1997, p. 47.
[16] N.A. Hush, J.R. Reimers, L.E. Hall, L.A. Johnston, M.J. Crossley, in: A. Aviram, M.A. Ratner (Eds.), Molecular Electronics Science and Technology, New York Academy of Sciences, New York, 1998, p. 1.
[17] N.D. Lang, P. Avouris, Phys. Rev. Lett. 81 (16) (1998) 3515.
[18] M. Magoga, C. Joachim, Phys. Rev. B 59 (24) (1999) 16011.
[19] J.M. Andre, in: R. Carbo (Ed.), Studies in Physical and Theoretical Chemistry, Studies in Physical and Theoretical Chemistry, The Netherlands, 1982, p. 273.
[20] J.M. Andre, J.L. Bredas, B. Themans, L. Piela, Int. J. Quantum Chem. 23 (1983) 1065.
[21] E.G. Emberly, G. Kirczenow, Phys. Rev. B 6412 (12) (2001) 125318.
[22] S. Suhai, Phys. Rev. B 27 (1983) 3506.
[23] C.K. Chiang, C.R. Fincher Jr., Y.W. Park, A.J. Heeger, H. Shirakawa, E.J. Louis, S.C. Gau, A.G. MacDiarmid, Phys. Rev. Lett. 39 (1977) 1098.
[24] M.A. Reed, C. Zhou, C.J. Muller, T.P. Burgin, J.M. Tour, Science 278 (5336) (1997) 252.
[25] J. Chen, M.A. Reed, A.M. Rawlett, J.M. Tour, Science 286 (5444) (1999) 1550.
[26] S.T. Pantelides, M. Di Ventra, N.D. Lang, Physica B 296 (1–3) (2001) 72.
[27] S.N. Yaliraki, M. Kemp, M.A. Ratner, J. Am. Chem. Soc. 121 (14) (1999) 3428.
[28] V.J. Langlais, R.R. Schlittler, H. Tang, A. Gourdon, C. Joachim, J.K. Gimzewski, Phys. Rev. Lett. 83 (14) (1999) 2809.
[29] M. Magoga, C. Joachim, Phys. Rev. B 56 (8) (1997) 4722.
[30] J.R. Reimers, L.E. Hall, M.J. Crossley, N.S. Hush, J. Phys. Chem. A 103 (22) (1999) 4385.
[31] C. Chavy, C. Joachim, A. Altibelli, Chem. Phys. Lett. 214 (6) (1993) 569.
[32] K. Mullen, S. Valiyaveettil, V. Franke, V.S. Iyer, in: C. Joachim (Ed.), Atomic and Molecular Wires, Kluwer Academic Publishers, The Netherlands, 1997, p. 61.

[33] M.N. Paddon-Row, K.D. Jordan, J. Am. Chem. Soc. 115 (7) (1993) 2952.
[34] P. Sautet, C. Joachim, Chem. Phys. Lett. 153 (6) (1988) 511.
[35] V. Marvaud, J.P. Launay, C. Joachim, Chem. Phys. 177 (1) (1993) 23.
[36] R. Baer, D. Neuhauser, J. Am. Chem. Soc. 124 (16) (2002) 4200.
[37] R. Baer, D. Neuhauser, Chem. Phys. 281 (2002) 353.
[38] We therefore also examined a symmetric naphthalene-based molecular wire with a 15 carbon long polyacetylene backbone to be certain that the asymmetry does not appreciably affect the results. As one might expect, the results were almost identical.
[39] A.K. Rappe, C.J. Casewit, K.S. Colwell, W.A. Goddard III, W.M. Skiff, J. Am. Chem. Soc. 114 (1992) 10024.
[40] ArgusLab 3.0, Planaria Software, Seattle, Washington, 2002.
[41] Jaguar 4.1, Schrodinger, Inc., Portland, Oregon, 2000.
[42] R.B. Murphy, Y. Cao, M.D. Beachy, M.N. Ringnalda, R.A. Friesner, J. Chem. Phys. 112 (23) (2000) 10131.
[43] P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 299.
[44] C.T. Lee, W.T. Yang, R.G. Parr, Phys. Rev. B 37 (2) (1988) 785.
[45] A.D. Becke, Phys. Rev. A 38 (6) (1988) 3098.
[46] J.C. Slater, Quantum Theory of Molecules and Solids, Vol. 4: The Self-Consistent Field, McGraw-Hill, New York, 1974.
[47] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B 46 (1992) 6671.
[48] T. Seideman, W.H. Miller, J. Chem. Phys. 97 (4) (1992) 2499.
[49] D. Neuhauser, M. Baer, J. Chem. Phys. 90 (8) (1989) 4351.
[50] S. Datta, Electronic Transport in Mesoscopic Systems, Cambridge University Press, Cambridge, 1995.
[51] S.N. Yaliraki, M.A. Ratner, J. Chem. Phys. 109 (12) (1998) 5036.
[52] M. Brandbyge, J.L. Mozos, P. Ordejon, J. Taylor, K. Stokbro, Phys. Rev. B 65 (16) (2002).
[53] Y.Q. Xue, S. Datta, M.A. Ratner, Chem. Phys. 281 (2–3) (2002) 151.
[54] M. Di Ventra, S.T. Pantelides, N.D. Lang, Phys. Rev. Lett. 84 (5) (2000) 979.
[55] R. Baer, T. Seideman, S. Ilani, D. Neuhauser, J. Chem. Phys. (2003) in press.
[56] M. Galperin, S. Toledo, A. Nitzan, J. Chem. Phys. 117 (23) (2002) 10817.
[57] H.B. Weber, J. Reichert, F. Weigend, R. Ochs, D. Beckmann, M. Mayor, R. Ahlrichs, H. von Lohneysen, Chem. Phys. 281 (2–3) (2002) 113.