# Molecular Scale Electronics: A Synthetic/Computational Approach to Digital Computing

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**Abstract:** This paper outlines a design paradigm for molecular scale electronic systems. The contrast between the present bulk devices and potential molecular systems is presented along with the limitations of using bulk design philosophies for molecular-sized components. For example, the overwhelming considerations of heat dissipation on molecular scale electronic architectures are shown which demonstrate the need for dramatically different information transfer methods if these ultradense molecular devices are to be used for computation. The use of changes in electrostatic potential for information coding is suggested. The issue of signal restoration is addressed using a periodic external potential through the underlying substrate. Several convergent synthetic routes are shown to conjugated molecules with various potential digital device applications including a two-terminal molecular wire with a tunnel barrier, a molecular wire with a quantum well to serve as a resonant-tunneling diode, three-terminal systems with switch-like possibilities, and four-terminal systems that could serve as logical gates without the use of multiple transistors. Ab initio computational methods are used to show that (i) molecules can be considered active electronic devices able to transfer the information from one molecule to another, (ii) the electrostatic potential can also be used as a tool to perform logical operations, and (iii) the molecules synthesized here could perform the functions for which they were designed.

## Introduction

The routine feature size of microchips has dramatically declined to ∼0.1 $\mu$m. Although a further decrease is likely, once the line size on integrated circuits becomes <0.01 $\mu$m, several quantum limitations will likely curtail the proper performance of solid-state devices which use electron currents as signal representations. New technological schemes will need to be developed for use at these small dimensions.[1−7] Molecular scale electronics is a field of study that proposes the use of single molecules to function as the key components in future computational devices.[8] Single molecules that have strategically placed charge barriers could serve as switches and logic devices. Typical molecular-sized systems would permit the use of $\sim 10^{13}$ logic gates/cm$^2$ compared to the present feature of a microchip, less than $10^8$ gates/cm$^2$, thereby offering a $10^5$ decrease in required size dimensions.[1] In addition, the response times of molecular devices can be in the range of femtoseconds while the fastest present devices operate in the nanosecond regime. Thus, a $10^6$ increase in speed may be attainable. Although numerous obstacles remain, a combined $10^{11}$ increase in computing performance offers an exciting impetus to consider molecular scale electronic architectures for future ultracomputing. A molecular-based paradigm using electrostatic potentials is outlined for new molecular systems that have been synthesized. Ab initio computational methods are used to substantiate the efficacy of the proposed architectural schemes.[1,9,10]

## The Present Devices

The present electronic digital devices are governed by considerations of size and speed. Optimizing the size of the basic units (usually the transistors) and their speed (limited by their natural temporal responses) are conflicting design goals.[11−13] Therefore, several tradeoffs have to be made. The most important compromise in computational technology is the hardware−software duality, which materializes in the requirements of a programmed logic (memory- or software-dominant) versus wired logic (CPU- or hardware-dominant). Components of programmed logic are smaller and able to handle larger problems than a wired logic system; however, a wired logic is faster than a programmed logic.[14] In one extreme there can be a bit adder (a minimum logic unit able to sum) with a small

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number of logical gates that will require a large memory to obtain the results, while in the other extreme, there could be a large CPU with all specific functions wired into the system that will be able to process the entire problem, having only a small memory for the input and output data. The present technology is heavily inclined toward programmed logic, for example, a computer with a large memory and a fast but simple CPU. This requires very large programs to solve the present problems.

A classical two-terminal semiconductor device is characterized by the ability to conduct charges (electrons or holes) in one direction with low impedance, and high impedance in the reverse direction. The simplest of these two-terminal devices is the diode where a p-type semiconductor is joined to an n-type semiconductor (p−n junction). Therefore, a potential in one direction will deplete the junction and will not allow a current to pass while a potential in the opposite direction will allow the crossing of charged carriers. A more advanced device is the transistor where an additional collector, p- or n-type semiconductor, is joined to the n- or p-side of the diode, or base, respectively. The main feature of this device is that a small current in the base is able to control a large current in the collector or emitter. This notable amplification can also be viewed as a device having a low input impedance and a high output impedance.[15] A parallel device which can be made even smaller than the bipolar transistor is the field effect transistor (FET). It is similar to the transistor, but the output current is controlled by an input voltage rather than an input current. It has the three-terminal arrangement: gate, source, and drain corresponding to the base, emitter, and collector of the bipolar transistor. These three-terminal electronic devices can be classified as amplifiers and switches. Normally good amplifiers are also good switches, but the opposite is not necessarily true. When the transistor is used as an amplifier, the goal is to increase the power (energy per unit of time) of an input signal. If the device has a small input resistance, it will have a small input power, and if it has a large output resistance, it will have a large output power. The power of the signal is amplified at the expense of a power supply; thus, an amplifier shapes the energy of a power supply according to the shape of a small input signal. Since the output must sustain a large amount of energy under amplification conditions, the use of single molecules as amplifiers is discouraged and is therefore not being considered within the paradigm described here. However, the other application of transistors is their use as digital systems for processing of information, such as in digital computers. This is the area where single molecules can be used with possibilities of making computers orders of magnitude more efficient.[2−6,16−18]

In bulk electronics, it is a simple task to convert a good amplifier to a switch in which a small signal controls the passage of current; therefore, the logic is based on whether the current passed. A large output current provides the circuit with a capable fan out, namely, the ability to drive subsequent circuits in a cascade with high reliability. Logical circuits, in addition to performing the logical operations, also need to have a good driving capability. The output of a gate needs to be powerful enough to excite the input of one or more gates. At the same time, this high output should not couple to the input of the same device. This implies that there must be a very high impedance between the input and output. These are problems that would limit the use of molecular devices if we use bulk device architectural philosophies. We probably will not be able to shape the energy of a power supply using a single molecule. Alternatively, triggering gates by neighboring electrostatic potentials is proposed (vide infra).

What is the difficulty in simply downsizing the present silicon-based devices so that the CPU's wired logic components could become smaller? The eventual limitation to downscaling of conventional devices will be brought about by a combination of difficulties in fabrication, reliability, yield, interconnects, economics of production, and ultimately fundamental limits. In this size regime, several fundamental properties of quantum systems have to be considered such as superposition, interference, entanglement, nonclonability, and uncertainty. Therefore, extension of microelectronics beyond current size regimes requires exploration of nonconventional electronic structures which scale far beyond these limits.[5,6,16−18]

Since conventional devices would be difficult to downsize, novel approaches to logic circuit design have to be devised wherein transistors and integrated circuits are substituted by using simple molecular structures. Of course, this implies the consideration of nonstandard architectures and design philosophies. Entirely new logic architectures would be required from molecular-based electronic components which will be complementary yet nonidentical to their bulk counterparts. Hence, molecules that work like the basic electronic devices (transistor, diodes, etc.) may not be desired, except for purely testing purposes. However, as we consider novel designs, we should not discard some basic principles that underpin CPU construction. For example, proposals in molecular scale electronics must regard the need for input/output signal homogeneity within devices. An electronic input and a photonic output (or vice versa) within a device would be difficult to consider since the second device in the series would then require photonic operation. We must maintain a homogeneity of input and output signal types (e.g., voltage in and voltage out) and magnitudes within a device so that the second device can be driven with the same signal type and signal size that operated the first device. Therefore, new architectural strategies must be proposed while fundamental needs of overall CPU operation are considered.

## Molecular Devices in the New Design Paradigm

Molecular-based systems can offer distinct advantages in uniformity and potential fabrication costs.[19] If devices were to be based upon single molecules, using routine chemical syntheses, one could prepare $6 \times 10^{23}$ (Avogadro's number) devices in a single reaction flask, hence, more devices than are presently in use by all the computational systems combined, worldwide.[5,6,19] Thus, molecular scale electronics would likely shift the software−hardware equilibrium in the direction of hardware, namely, massively wired logic or CPU dominant. Molecular circuits offer the possibility of constructing large and fast CPUs with complicated functions. Using large molecular arrays, problems could be calculated within the CPU with minimal need for main or auxiliary memories. Wired logic would supplant much of the programmed logic, thereby affording several additional orders of magnitude increase in performance.[1,9,10,20−32]

A major consideration in molecular devices is the energy consumption/dissipation needs. Transfer of large numbers of electrons or electron currents would lead to excessive heat problems with molecular scale devices, and such a strategy may only be useful for testing purposes. Considering $10^8$ gates/cm$^2$ (as in presently sized silicon-based systems) at the rate of $10^{-9}$

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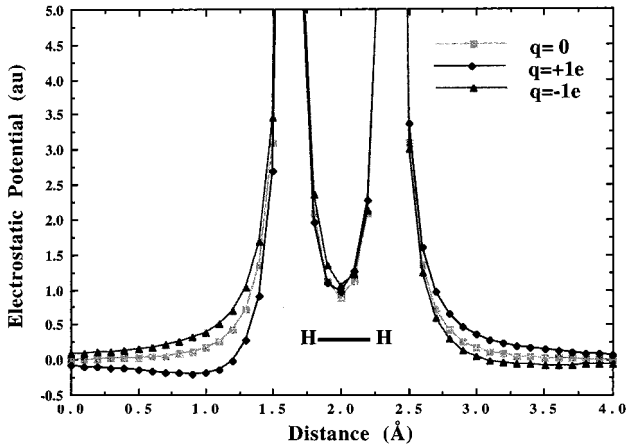


**Figure 1.** A charge (positive and negative) is placed 2 Å from the center of an $H_2$ molecule along the bond axis. The electrostatic potential is calculated along the bond axis at varying distances. Notice that the electrostatic potential in the molecule is slightly perturbed due to the presence of the charge. The small variations of the electrostatic potential at the 3.5−4.0 Å distances would be used to transfer the information to the next molecule. The computational method used is described in the Theoretical Calculations.

s (present speeds) yields $10^{17}$ electrons/s (∼0.02 A/cm$^2$) if only one electron per gate is used to transport, indicate, fetch, or represent a binary digit. At this point heat considerations are already extreme: if the average resistance of the circuit is 30 Ω, this represents 20 W/cm$^2$. If an increase of several orders of magnitude in performance is expected with molecular circuits, this would imply a proportional increase in power dissipation. Such levels of power dissipation rule out most conventional current or electron transfer methods for practical molecular devices wherein large numbers of devices are densely configured.

As part of the new design scenarios, molecular devices could function by electrostatic interactions produced by small reshapes of the electron density due to the input signals. In turn, electrostatic potential interactions between molecules would transport the information throughout the CPU. Using this approach, there is no need for electron currents or electron transfers as in the present devices; a small change in the electrostatic potential of one molecule could be enough to send the information to another molecule. These perturbations of the electrostatic potential imply a very small amount of charge transfer, far less than one electron. External fields or excitations are able to change the boundary conditions of the molecule, producing a change in the electrostatic potential generated by these sources. An example of this can be seen in Figure 1. A charge or field on the left side of the molecule would reshape the electron density, providing a different potential at the output which can be detected. This is an efficient way to transmit a signal. There is no need for electron transfer, just a charge reshape. If the excitation ceases, the shape comes back to its original form. Is this method of information transfer really detectable since, as seen in Figure 1, the change in the electrostatic potential is minimal (∼10 kcal/mol/electron where the formal units of electrostatic potential are energy per unit of charge)? The change observed in the electrostatic potentials is in the range of values of nonbonded interactions, such as van der Waals interactions, which are easily detected by neighboring molecules. In fact, these are precisely the range of signal energies needed if we will ultimately utilize large-scale integration in very small areas of materials. If the signals are large, problems of energy consumption and dissipation, as discussed above, rule out the use of molecular-based electronics. Thus, the use of electrostatics directly addresses energy concerns in downsizing.

Distinguishing between two types of gates in molecular circuits is also in order. There are those gates at the interface of the logical circuits or CPU. The gates at the input interface would have to be able to take signals from standard electronic circuits, lasers, scanning probe microscopy (SPM) tips, or, in general, well-localized electrical fields. Molecular gates at the output would have to drive or inject a current onto a minuscule tip or metal cluster, or be able to excite the input of standard bulk devices. The vast majority of molecular gates, however, would be within the molecular CPU and would thus perform the information processing by controllably affecting the electrostatic potential of neighboring molecules. The compounds described here belong to the large group of gates that would allow the processing of information and the interconnection between them. The bulk/molecular interfacing structures are not being considered here since they are already the subject of several publications and they are the focus of most molecular scale electronics research.[2−6,33]

The present technologies are also beset with problems from working at very high frequencies.[2] The use of electrostatics also addresses this difficulty. Small spurious capacitances ($C$) usually appear between portions of devices and circuits that otherwise should be totally electrically disconnected, or at infinite impedance ($Z$). If the operational frequency of the device increases, the impedance would decrease proportionally with the frequency ($f$) of operation ($Z = 1/2\pi fC$), rendering the device useless after a characteristic cutoff frequency. This cutoff frequency constitutes an upper limit to the operational frequency which, in the present technology, approaches 1 GHz (which corresponds to a 1 ns operation time). Since the capacitance is also inversely dependent on the distance, making smaller circuits yields larger spurious capacitances, and therefore smaller impedances, exacerbating the move toward smaller devices. Since electrostatic potentials are only limited by the time in which the electron density rearranges in a molecule (<1 fs) and they do not imply a net transfer of current, they can lead to the high interdevice impedance levels required.

Therefore, any molecular system can be represented, following the philosophy of the theory of circuits, by a pseudoactive

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device $E$ (1) corresponding to the total energy of the molecule which keeps the molecule at its ground state, i.e., at its point of operation or quiescent point, and (2) connected to another pseudopassive device. The wave function ($\Psi$) of the molecular device is given by the shape of the electron density whose relation to the $\varphi_i$ (one-electron orbitals) and $\epsilon_i$ (the energy of the one-electron orbitals) is given by the rules of quantum mechanics and not attainable in the straightforward manner as in the theory of electronic circuits. However, since the partition in molecular orbitals is a valid one, an equivalent molecular circuit picture can be adopted while the rules of quantum mechanics are maintained. Therefore, we can speculate that, in the limit, for instance, in long-range interactions and beyond, both quantum mechanics and electronic circuit theories will merge as is widely demonstrated by classical mechanics simulations of quantum mechanical molecules. Therefore, a quantity $P$ is assigned and is indicative of a molecular system's opposition to change the electrostatic potential in a defined region. This quantity $P$ will be a better descriptor if the molecular circuit is designed to interact with others only through long-range interactions. $P$ is connected or directly related to the electron affinity and the chemical potential as well as polarizability and chemical hardness.[34,35] $P$ is also reminiscent of the impedance in electronic circuits and control theory, and practically represents the transfer function of the device. This quantity would depend on the wave function in a molecule, a much more complicated entity than in control theory. Therefore, $P$ is a measure of the reluctance of the electron density at the boundaries of the molecule to reshape the form of the electrostatic potential when an excitation on another spatial part of the molecule is applied. However, a direct relation to power, as in the standard impedance, is accepted. Thus, hereafter we refer to this molecular impedance as, simply, impedance $P$.

## Specific Molecular Structures

We present here several convergent synthetic routes to conjugated molecules with various potential digital device applications including a two-terminal molecular wire with a tunnel barrier, a molecular wire with a quantum well to serve as a resonant-tunneling diode (RTD), three-terminal systems with switch-like possibilities, and four-terminal systems that could serve as logical gates without the use of multiple transistors (Figures 2−5). In each case, the low $P$ segments are based on $\pi$-conjugated oligo(phenylene ethynylene)s. The synthesis of the oligo(phenylene ethynylene) branching arms was described previously, and we attached them to the cores of the device structures here using Pd/Cu-catalyzed cross-coupling reactions.[36] The high $P$ segments are based on methylene units since SPM studies showed us that alkyl units pose larger electronic transport barriers (higher resistance for currents, which intuitively implies higher $P$ for electrostatic potentials) than the $\pi$-conjugated moieties in single molecular systems.[37] The methylene units were either derived from readily available starting materials or made by aryllithium additions to aldehydes followed by the vigorous borohydride/trifluoroacetic acid (TFA)-induced reduction of the resulting bis(benzylic) alcohols.[38] The

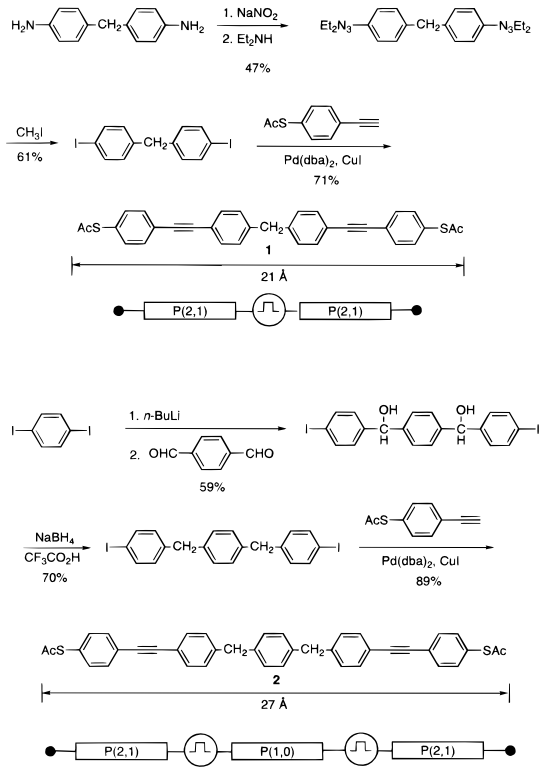


**Figure 2.** Chemical syntheses of **1** and **2** and their corresponding molecular circuit symbols as described in Table 1. **1** is a molecular wire with a tunnel barrier, and **2** is a wire with two barriers and is analogous to a RTD.

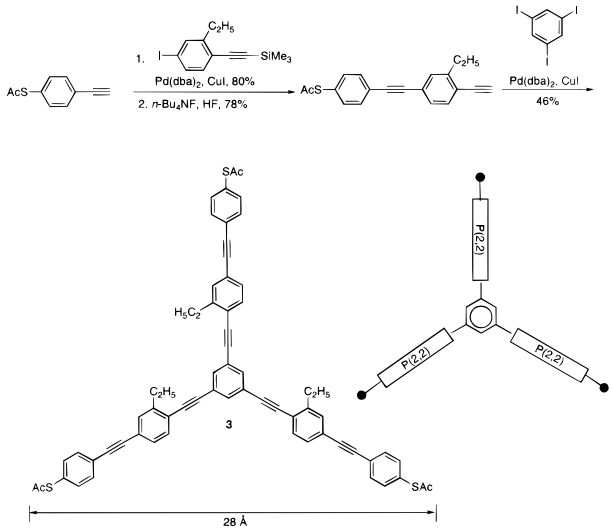


**Figure 3.** Chemical synthesis of **3**, a three-terminal molecular junction, and its corresponding molecular circuit symbol as described in Table 1.

ethyl groups impart solubility to the larger molecules so that synthetic manipulations and depositions can be freely executed in solution.[36] All of the final compounds described have termini bearing self-assembling moieties, namely, acetyl-protected thiols, to serve as protected "alligator clips", and we have previously described their preparation and utility.[39,40] The

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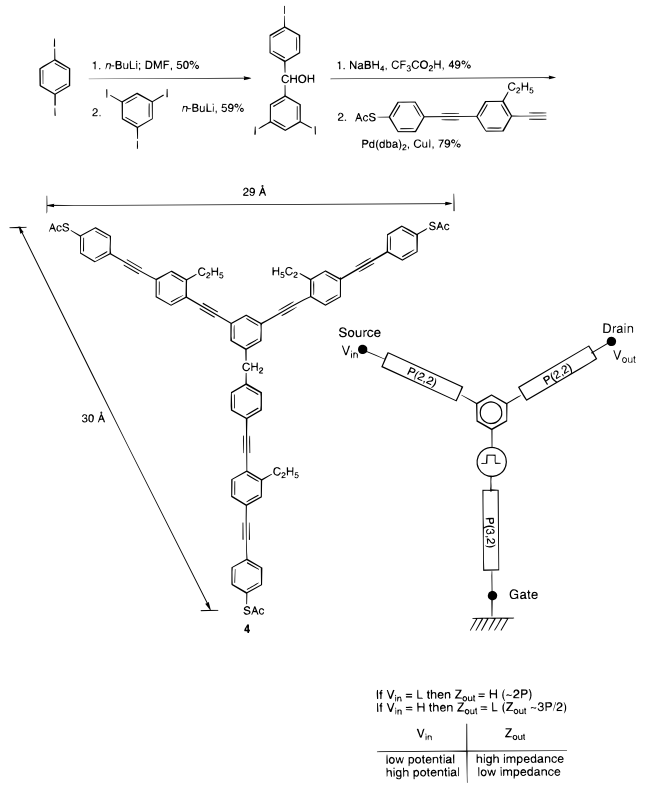



**Figure 4.** Chemical synthesis of **4**, which acts as a molecular switch, and its corresponding molecular circuit symbol as described in Table 1. The corresponding logic table is also shown.

precise termini needed for the ultimate arrangement in a molecular-based CPU is, or course, not known; however, the capability of modern synthetic methods to construct precise molecular frameworks is exemplified. For our specific molecules $P(m,n)$ refers to the molecular electrostatic potential impedance of a system with $m$ 1,4-phenylene moieties and $n$ ethynylene moieties. To have a preliminary idea of the qualitative form of the interactions using molecules designed and synthesized in our laboratory, the nomenclature in Table 1 has been adapted to aid in explaining the behavior of electronic circuits.

Compound **1** is a molecular wire with a tunnel barrier. The term molecular wire refers to the ability to make connections to other devices. Beyond that, no physical similarity to macroscopic wires is implied. An ideal wire has zero resistance, and practical wires normally have a resistance much smaller than 1 Ω; however, the resistance of molecular wires is likely considerably larger.[33,37] Thus, as discussed above, in molecular scale electronics we do not want to transport electrons through the molecules; simply a reshape of the electron density would be necessary to perform a logical function. Therefore, the applied potential between the sulfur terminals would determine the ability of the circuit embodied by **1** to reshape its electron density. Due to the methylene transport barrier in **1**, it is proposed that the reshape of the electron density will be practically unnoticeable on the output end if the potential on the input end is relatively small. However, if the applied potential is above a threshold imposed by the methylene barrier, the electron density will reshape the electrostatic potential at the output end. With this simple structure, we could assess the barrier height imparted by a single methylene, the simplest alkylidene unit.

Compound **2** is a more sophisticated device with two barriers which resembles a linear quantum dot or a RTD, while **3** is a

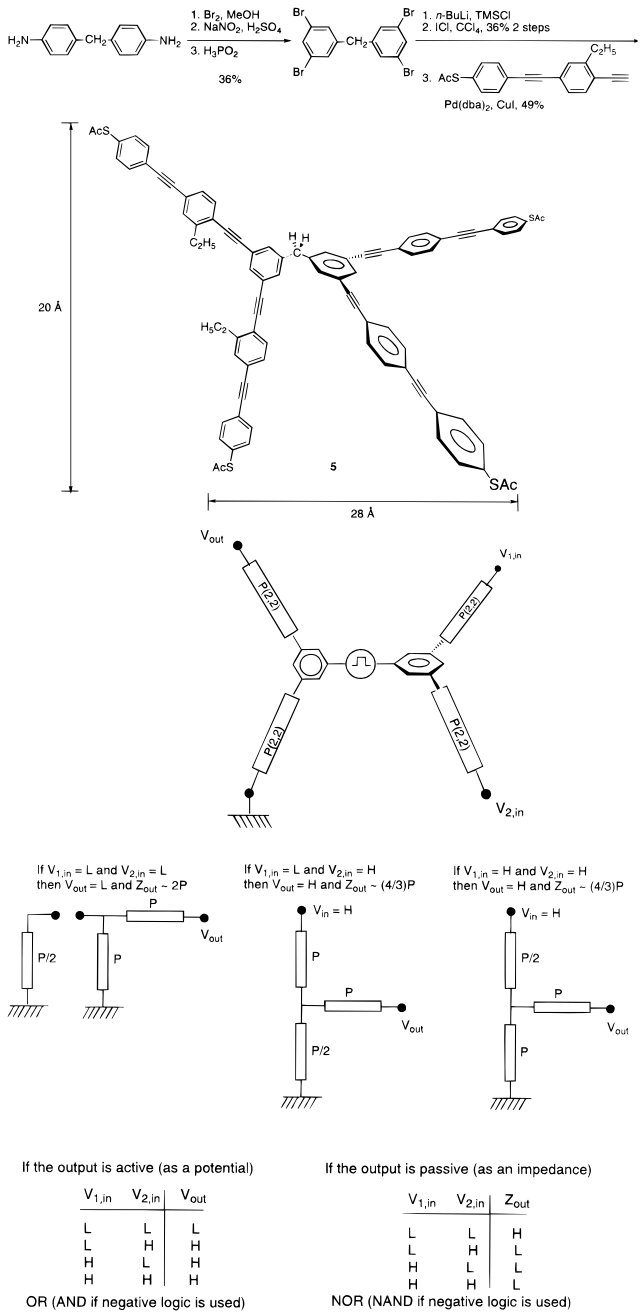
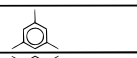
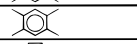
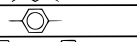
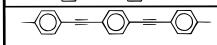



**Figure 5.** Chemical synthesis of **5**, which serves as a molecular logic device, and its corresponding molecular circuit symbol as described in Table 1. Corresponding circuit diagrams are also shown with the derived logic tables.

molecular three-terminal junction that could be used as a molecular interconnect. A common feature of logic circuits is that output from a gate is connected to two or more successive gates.

Compound **4** is a molecular-sized switch for which we have indicated the corresponding equivalent of source, drain, and gate terminals of a bulk solid-state FET. The operation of this device could be in the following manner: A low ($L$) input potential will not be easily transmitted through the barrier. For simplicity, we assume that $P(2,2)$ is approximately equal to $P(3,2)$ so both can be assigned a value $P$. Understanding that all results are approximations, the impedance observed from the output will be equal to $2P$, reminiscent of two impedances connected in series. Conversely, if a high ($H$) input potential is applied such that the threshold imposed by the methylene barrier is exceeded,

**Table 1.** Chemical Symbols and Their Corresponding Molecular Circuit Symbols

| Chemical Symbol | Molecular Circuit Symbol | Description |
|---|---|---|
| —SAc[a] | —● | Contact to input or output |
| —$CH_2$— | —⊓— | Transport barrier |
|  |  | 1,3,5-Trisubstituted benzene or T-junction |
|  |  | 1,2,4,5-Tetrasubstituted benzene or Q-junction |
|  | —P(1,0)— | 1,4-Disubstituted benzene |
|  | —P(2,1)— | 1,4-(Phenylene ethynylene)-1,4-phenylene |
|  | —P(2,2)— | 1,4-(Phenylene ethynylene)-1,4-(phenylene ethynylene) |
|  | —P(3,2)— | 1,4-(Phenylene ethynylene)-1,4-(phenylene ethynylene)-1,4-phenylene |

[a] Although the acetyl unit was synthetically affixed to provide stability to the precursor systems, it can be removed in situ to afford the free thiol which could bind to a metallic probe or to a second device via, for example, a disulfide linkage.[39]

a further reshape of the electron density is possible since an extra channel $P(3,2)$ is available. Therefore, the molecular impedance observed from the output will be smaller than when the input is low. This effect is qualitatively presented as having the input $P(2,2)$ and the $P(3,2)$ impedances in parallel, yielding an equivalent of $(1/2)P$ to be added to the output $P(2,2)$, affording a total of $3P/2$. These two possible and well distinguishable values of impedances, which are controlled by the input potentials, permit this structure to have switch-like properties, and thus correspond to an active molecular scale electronic device with an inherent power supply (which maintains the device in its operation point but not as a power-producing source). This specific configuration would behave as a NOT logic gate, and it outlines only one of the three possible configurations, similar to a bulk transistor's versatility. Though the impedance relationship between the two states in **4** is small when compared to that in the present bulk devices, it is important to understand that these molecular devices are not used as amplifiers, but logical gates, where it is only necessary to distinguish between the low and high levels of potentials (similar to the 0 or 5 V in some present circuits).

Compound **5** could be viewed as a molecular logic device. The output would be the electrostatic potential, and the level of the electrostatic potential represents the binary information. This circuit can be analyzed analogously to **4** by finding the output impedances (so the molecule is being used as a passive device) as shown in the accompanying circuit diagrams. Alternatively, we can calculate the approximate output potential (so the molecule is being used as an active device) using the same assumptions used for **4** and considering that the low potential $L$ corresponds to a zero potential and that the high potential $H$ corresponds to a positive potential $V_H$. As shown in Figure 5, **5** can be an active OR or a passive NOR gate if positive logic is used ($L = 0$ and $H = 1$). Conversely, **5** can be an AND or NAND gate, respectively, if negative logic is used ($L = 1$ and $H = 0$). This shows only one of the several possible configurations for this device.

## Theoretical Calculations

One of the benefits of molecular electronic systems is the fact that they can be successfully guided by precise calculations. In this section we illustrate how the electrostatic potential of a molecule can be used as the carrier of digital information. The importance of this study focuses on the fact that molecules can be considered active electronic devices able to transfer the information from one molecule to another. The second goal

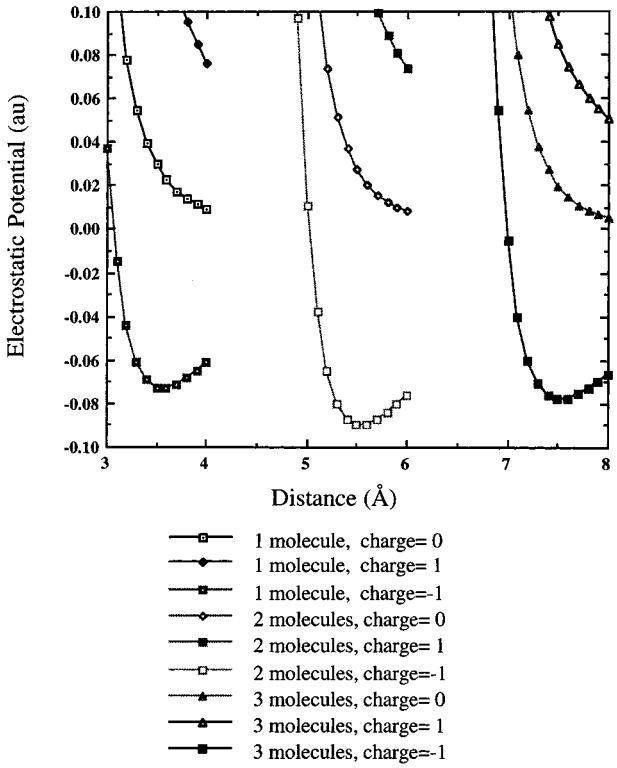



**Figure 6.** Changes in electrostatic potentials that are transmitted from one $H_2$ molecule to another using an external potential on one end of a series of three $H_2$ molecules. When no potential is applied, the central left curve is obtained for a single $H_2$ molecule. When an external positive potential is applied on one side of the bond axis of the $H_2$, the potential on the other side of the axis is increased as shown by the top left curve. When a negative potential is applied instead, the potential on the other side of the $H_2$ is lowered as indicated by the lowest left curve of the figure. The second trio of curves corresponds to the potentials when two $H_2$ molecules are aligned along their bond axes so that a potential on the first molecule is passed onto the second molecule. The third group of lines correspond to the case of three $H_2$ molecules aligned along their bond axes.

of this section is to demonstrate that the electrostatic potential can also be used as a tool to perform logical operations. The third goal is to computationally demonstrate that the molecules we synthesized could perform the functions for which they were designed.

Specifically, we have used DFT techniques since these are the most powerful tool to deal with a relatively large number of atoms.[35] The use of DFT is fully justified due to the fact that it is an ab initio technique able to deal with a broad variety of systems. Several successful applications of DFT have been reported using the hybrid functionals where a portion of the exchange functional is calculated as a fully nonlocal functional of the wave function of an auxiliary noninteracting system of electrons. Since this resembles the exchange in the HF procedure (actually in any wave function procedure), it is common to refer to this functional, or procedure, as a DFT−HF hybrid. However, we have to consider that the exchange is being calculated using a noninteractive wave function whose density, but not its wave function, corresponds to the real system. A detailed analysis and its theoretical rigor were recently reviewed.[41] The functional that we used is the B3PW91 with the triple splitted valence basis set 6-311G** which includes polarization functions for all atoms.[42−44] All calculations were

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(42) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372−1377.

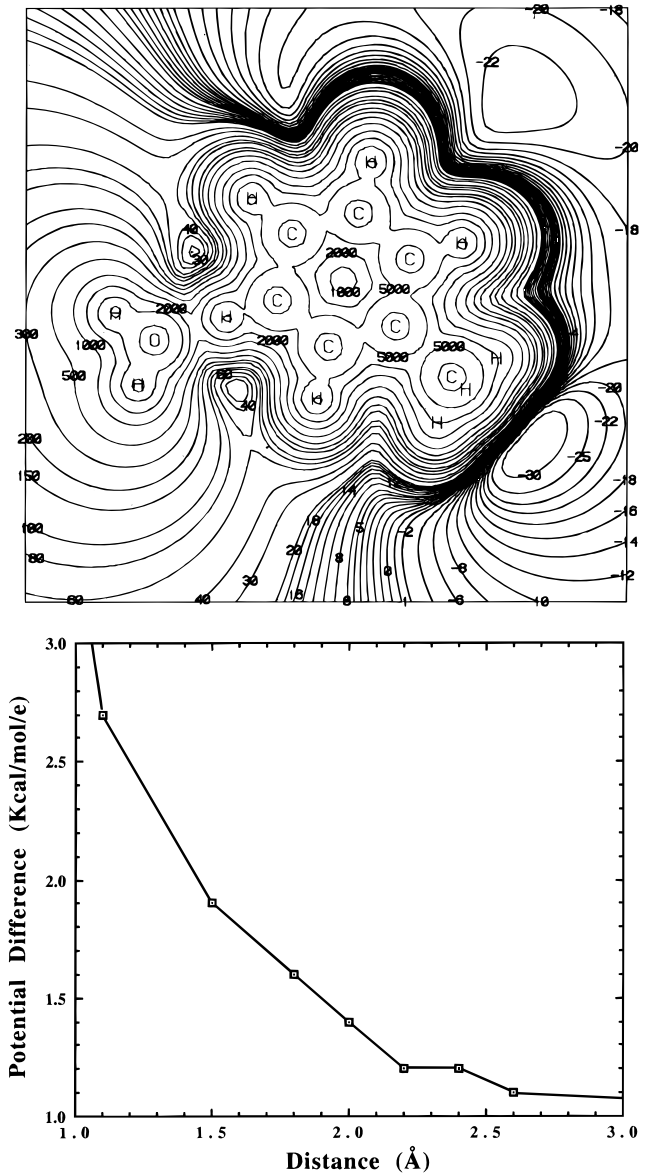


**Figure 7.** The switching properties of **4** are computationally simulated using toluene as the central core of switch **4** and using the oxygen atom of a water molecule as the region of approaching electrostatic potential. (a, top) As the water molecule approaches (2.2 Å) the proton at toluene C3 (source), the electrostatic potentials are monitored at the C5 proton (drain) and the methyl protons (gate). As the input potential increases (at C3), the output potential (at C5) also increases with little potential change at the methyl protons (gate); therefore, the gate circuit is "open". At a threshold input potential when the water molecule approaches C3 to within 2.2 Å, the methyl (gate) closes, producing a drop in the output potential. (b, bottom) Output transition at C5, with respect to the reference ($CH_3$), over a series of approaching water molecule distances. Notice the drop in the output as soon as the methyl (gate) circuit closes due to the increase in the input.

performed using the Gaussian-94 program.[45] All geometry optimizations were performed via the Berny algorithm in redundant internal coordinates.[46] The thresholds for convergence were 0.000 45 and 0.0003 au for the maximum force and root-mean-square (RMS) force, respectively. The self-consistency of the noninteractive wave function was performed with a requested convergence on the density matrix of $10^{-8}$, and $10^{-6}$

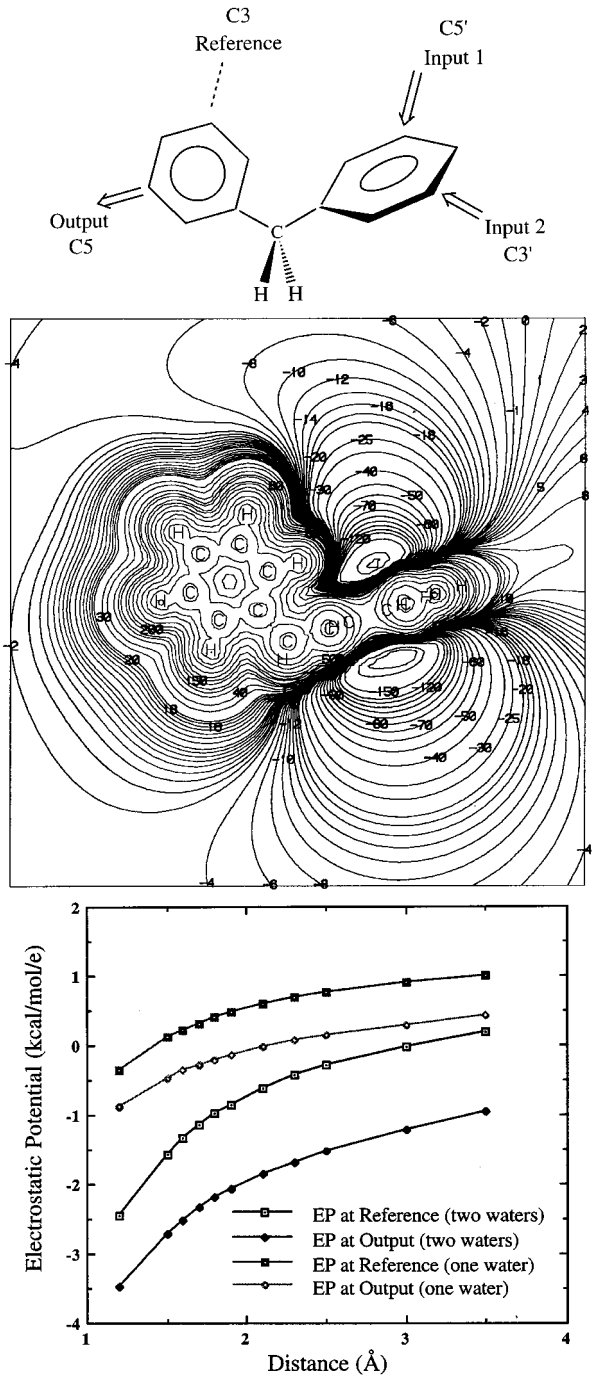


**Figure 8.** (a, top) Diphenylmethane served as the model system for the ab initio calculations of logic device-like properties on **5**. The orientation of the diphenylmethane shows the minimized structural form where the two aryl rings are in orthogonal planes. The C3 diphenylmethane proton is the reference or ground, the C5 proton is the output, and the C3′and C5′ protons are inputs. (b, middle) The electrostatic potential of the diphenylmethane wherein the negative electrostatic potential regions of the input phenyl ring (right) are seen because the input ring is perpendicular to the plane of the paper (as in (a)). Also depicted is one water molecule approaching at 2.5 Å to the input proton at C3′ (input = *L*, *H*), and it is able to induce an electrostatic potential output (*H*) at the C5 proton. A second water molecule approaching the C5′ input proton (input = *H*, *H*) at 2.5 Å was calculated, and it complements the output at the C5 proton (data not shown). Therefore, either one or two *H* inputs induces an output much greater than zero, namely, *H*. (c, bottom) A plot of 11 input distances for both one and two water molecules approaching diphenylmethane. The electrostatic potential outputs are higher than the corresponding references when one or two *H* inputs are added, respectively.

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(44) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244−13249.

for the RMS and maximum density matrix error between iterations, respectively. These settings provide correct energies within the level of theory of, at least, five decimal figures, and geometries of approximately three decimal figures.

The electrostatic potentials are well-proven tools for the study of molecular systems[47,48] and utilizing these computational methods. Figure 6 shows how the changes in electrostatic potential are transmitted from one molecule to another using an external potential. Although there may be decay of the electrostatic potential in some regions of space when small portions of the electron density are transferred between molecules, there is always a corresponding electrostatic potential region that compensates for such a decay since the electrostatic potential depends directly on the electron density and the latter holds to an evident conservation law. In fact, as one region decreases, the electrostatic potentials conformably increase in other regions. Thus, their arrangements in a circuit can be exploited in order to obtain the best signal transfer. In addition, the natural decay on the electrostatic potential can always be restored by a process similar to that proposed by Lent,[49] where the part of the molecule producing the barrier between the input and output (the gate branch in **4**) is connected to a periodic external potential, via the underlying substrate. This would permit the barrier between the input and output states to be increased, thereby changing the input/output signals to specific relative values. Although this potential restoration would permit the long-range transfer of the signal, it would not suffer from the typical heat-dissipation problems that a current-based system would inflict.

Figure 7 shows the functioning of the switch **4**. This is simulated using toluene as the central core of switch **4** and using the oxygen atom of a water molecule as the region of approaching negative electrostatic potential. The transition in the output is noted by the slope change when plotted in Figure 7b, indicating the switch-like properties of this molecular system. The use of these molecules for binary circuit applications is only one possible scheme. The variety of shapes available on the electrostatic potentials could give rise to several higher levels of computational design that cannot be readily compared to macroscopic devices.

Compound **5** is a prototype for a logic device based upon a single molecule rather than the typical arrangement of several transistors. There are two equivalent inputs, one output, and one reference or common terminal. This is simulated using diphenylmethane (Figure 8a) as the central core of **5** for the DFT calculations of the electrostatic potentials, one point of which is shown in Figure 8b. The entire sequence with several added data points is plotted in Figure 8c, which shows that the electrostatic potential outputs are higher than the corresponding references when one or two *H* inputs are added, respectively, thereby demonstrating that an OR gate can be obtained since either one *H* input or two *H* inputs will induce an *H* output. Hence, ab initio calculations on the cores of the synthesized switch (**4**) and logic device (**5**) demonstrated the possibility for these molecules to be used as digital components via perturbations of their electrostatic potentials.

## Future Considerations

When molecular scale electronic systems are considered, it is important to recall the historic steps that took electronics from the vacuum tube to semiconductor devices. Likewise, when moving from semiconductors to molecules, we can expect radical new changes in device architectures and philosophies. Since we are only at the beginning of a systematic science in molecular scale electronics, several targets of research must be projected in order to have single molecules perform realistic device functions. For instance, one of the systems needed is a molecular regulator, a molecule able to produce a constant electrostatic potential output regardless of the value of the electrostatic potential input. We must also have a better understanding of surface chemistry and methods to precisely order and position the adjacent molecular units using thermodynamically driven processes such as self-assembly. The effects of conformational changes in molecules must be systematically delineated by constructing ladder oligomers that have restricted rotation about single bonds. The effects of differing isotopes on electrostatic transport must be studied. On the side of short-range testing, it is imperative to develop an SPM-like device to analyze three- and four-terminal molecules so that we can assess precise single-molecule device functionalities. Despite these hurdles, the enormity of Avogadro's number, the richness of the shapes of the electrostatic potentials, and the physical advantages of using systems in a quantized regime make the prospects of molecular scale electronics eminently attractive for the next generation of ultracomputing.

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