Molecules for Memory, Logic, and Amplification

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Abstract: The molecules described possess properties of key electronic components as suggested by the title. These molecules are of the π–σ–π, mixed-valence type and provide double-well potentials for single electrons. The σ bridge proposed is a spirocycloalkane, chosen to provide a high potential barrier and unique stereochemistry that makes the molecules suitable for interconnection in future molecular devices. The theoretical models that reveal these properties are presented and critically examined.

The recent surge of activity in the area of molecular electronics[1] is driven by expectation of scientific inroads into the realm of the molecular state and by anticipation of exceptional technological payoff. In the quest for molecular electronics, new ground is being broken that has the overall effect of enriching our scientific knowledge. This study examines a class of molecules that seem to be suitable candidates for computing devices based on molecular properties. Furthermore, detailed study of the proposed molecules can take us one step further toward an understanding of one possible mode of employment of molecules for performing the device functions needed to build a computing machine.

The Model

Intramolecular electron transfer between two or more π electronic systems separated by σ bridges[2] or in mixed-valence organometallic compounds[3] has received considerable attention recently.[4] Numerous reports on experimental aspects[5] served as catalysts for theoretical work that followed. It is interesting to note that the extensive body of work points to a duality in the transfer mechanism namely "through space" and "through bond" transfers.[6]

In most cases electron-transfer problems are studied theoretically in terms of a model one-electron Hamiltonian. These studies are reviewed in a comprehensive survey by Mikkelsen and Ratner,[7] who point out that the method of choice for calculations of electron transfer between two sites is to find a matrix element that conveniently describes the physics of the electron transfer. This matrix element is then used to calculate the electron motion, either by time-dependent perturbation theory (i.e., the Golden Rule) or by determination of the splitting in the energy levels of the donor and acceptor sites.

The related research on organic conductors that originated with the pioneering work of Akamatu and Inokuchi[8] and Eley[9] in the forties has accelerated in recent years with spectacular results. Organic semiconductors, organic metals, and conductive polymers are the outcome of this effort.[10] An interesting aspect of the

results is that organic conductors (C) can be correlated structurally to, what will be termed in this paper, "PRO-CONDUCTORS" (PC) a non-conductive form of the same compounds. For instance, tetrathiafulvalene is a nonconductive compound, but its derivative tetrathiafulvalenium, (+) charged, is a conductor. Pro-conductor and conductor share a relationship, so that one can be obtained from the other by oxidation or reduction, as the case may be.[11] The process of derivatization of the pro-conductor produces a highest occupied molecular orbital, HOMO orbital, in the molecule that is only partially occupied. These electronic states mix in the solid state to form conductive bands that are only partially filled and can serve as solid-state organic conductors. The accepted model for understanding the transport properties of these materials is the one-dimensional tight-binding band theory,[12,13] which is an extension of the Hückel model. In this model, the molecular HOMO's replace the atomic carbon p orbitals as the local basis functions. The electronic Hamiltonian contains two terms: one that corresponds to the binding energy of the electron in the HOMO and the other to the nearest neighbor electronic tunneling matrix element, t, analogous to the Hückel β integral. Formation of dimers leads to splitting the HOMO's by $2t$ and a bandwidth of $4t$.[13]

This study focuses on the molecular state and examines whether a conjugated π molecule, at least 50 Å long, can serve as a pro-conductor or a conductor when placed between two metallic electrodes with the long axis of the molecule perpendicular to the metal surfaces. Figure 1 illustrates the difference between a pro-conductor molecule and a conductor molecule, in the prescribed configuration. In Figure 1a the HOMO molecular orbital of the pro-conductor molecule is situated below the Fermi level of the metals and contains a pair of electrons, so that no tunneling can occur. When a bias voltage is applied, the Fermi level can drop below the HOMO level and allow a current to pass.[14] On the other hand, the case of the conductor molecule differs considerably: the HOMO of the molecule, being only partially filled, can interact as shown in Figure 1b. The molecule can take part in transfer of electrons from side to side, when a small bias is applied. Thus, the difference between the pro-conductor and conductor molecules is that, in the prescribed configuration, the pro-conductor will act as an insulator up to a threshold voltage while the conductor will have no threshold voltage.

The molecules that are considered in the following consist of a pro-conductor moiety connected to a rigid σ, nonconjugated bridge, and connected in turn to the respective conductor group. The described molecule can be looked upon as a double-well potential for an electron that can shuttle between the wells at a

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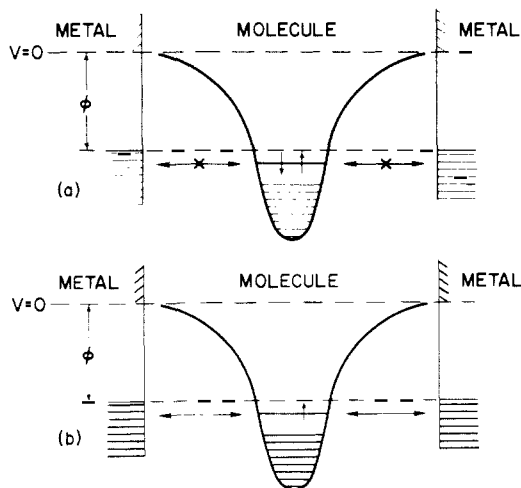
Figure 1. (a) The relative arrangement of energy levels of a pro-conductor between two metallic electrodes and (b) the relative energy levels of a conductor between two metallic electrodes.
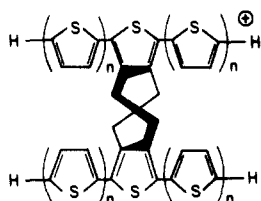

Figure 2. An illustrative example of a PC–σ–C that contains a spiro carbon in the central bridge. The two spiro rings force the two π terminals to be at 90° to each other.

characteristic frequency, particular to the molecule involved.[15] One of many possible molecules that fit this definition is shown in Figure 2 as an illustrative example.

For molecular electronics, the characteristic frequency of tunneling has to be small, and fine tuning of this frequency by structural engineering is a major consideration. Several tools are available for control of the tunneling frequency. One is the obvious separation distance across the σ bridge; another is the symmetry of the double-well potential; and yet another is control of the overlap (direct or bridge-assisted) between the conductor and the pro-conductor. The idea here is that the tunneling is dependent on the local site overlap of the wave functions that constitute the double-well. The best overlap can be obtained when the two π systems are in the same plane, and the least overlap exists when they are structurally orthogonal. Thus, if the σ bridge were to contain a spiro carbon, then compounds can be made that would have a conductor and a pro-conductor at 90° to each other. Figure 2 shows such an example.

As stated previously, the important contribution of "through bond tunneling" in donor- σ bridge-acceptor molecules has been documented. The effect of spiro σ bridging on electron transfer in similar molecules has also been studied to some extent.[16] The experimental results of Stein and Taube[16] document a charge transfer optical absorption between mixed valence ruthenium sites in pentamine-(2,6-dithiaspiro(3,3)heptane)ruthenium(II),I, that indicates a possible through bond electron transfer. The calculated transfer rate is 3.5 × 10⁴ s⁻¹. The authors also calculated the expected rates of transfer over separation distances of 17 Å and found it to be one per second. It seems that while the spiroalkane 90° twist bridge can suppress the tunneling, it may not eliminate it entirely. (This last point requires additional investigation). For practical purposes, the actual bridge may have to be constructed

by blending the twist, the separation, and the off-resonance concepts.

If the interaction between the two π terminals can be made to be weak, then the extra electron that resides on one end can find itself in a deeper well due to colombic interaction with the counter-ion that is present for charge neutrality, or due to relaxation of vibronic modes around it. Such a double-well potential (a two state system) with a localized particle can serve as a bit in a binary system by equating one state with "one" and the other state with "zero".[17] Reading of the information can be achieved by probing of the two separate terminals (which are conveniently separated from each structurally) for conductivity, because, in the process of switching its position, the exchanging electron causes the pro-conductor site to become conductive and the conductive site to become insulating.

One possible mechanism entails an electric field directed along the axis that connects the spiro carbon and the centers of the conductor and the pro-conductor (this axis will be termed henceforth the "z axis"). The double-well potential of the defined molecule will be perturbed due to the polarizability of the π orbitals. This perturbation can have two beneficial effects: one is that of changing the relative depth of the wells and decreasing the height of the barrier, thus creating a driving force for tunneling, i.e., switching, and the other is polarization of the π orbitals in the direction of field, which may lead to electron transfer. The other possible mechanism for switching involves the electrodes that are placed perpendicular to the z axis, in the center of the molecule. These electrodes will be called "switching electrodes". In this case, under the influence of the field, two electrons can be simultaneously transferred, one from the cathode to the partially occupied orbital of the conductor group and the other from the pro-conductor end to the anode. A full discussion of these processes has been advanced in conjunction with the motion of electrons in molecular rectifiers.[14] The overall effect of the two-electron motion is switching of the electronic configuration of the molecule. However, this mechanism can operate only above a certain threshold voltage.[14]

Calculations

While two distinct switching mechanisms have been identified and can be calculated separately, this study concentrates on the region below the threshold for molecule electrode electron transfer. Calculations are presented in an attempt to elucidate the possibility of inducing, by electric fields, meaningful overlaps between the donor and acceptor sites that would lead to enhancement of the electron transfer. Such enhancement is synonymous with intentional switching.

Thus two questions were addressed: (a) What is the influence of the electric field (EF) on the electron transfer rates and (b) what is the stability of the flexomeric state? (Each of the states in bistable molecules can be called "Flexomer".) Obviously the answer to question b is related to the electron-transfer rates in the absence of a field.

We chose to describe the solutions in terms of the independent-particle approach and used self-consistent-field (SCF) calculations to obtain the necessary matrix elements and the overlap integrals. A particular molecular orbital (MO) ϕ_i, as defined by linear combination of atomic orbitals (LCAO–MO), can be written as

$$\phi_i = \sum_\alpha C_{i\alpha} u_\alpha \qquad (1)$$

where u_α is the αth atomic orbital in the ith molecular orbital. The $c_{i\alpha}$'s can be obtained by MO calculation. For molecules of the general class shown in Figure 2, and for those that will be described in the "Results" section, the notation used for the diabatic initial state is $\psi_{(PC-\sigma-C)} = \psi_i$ and that for the final state is $\psi_{(C-\sigma-PC)} = \psi_f$. With EF applied in the z direction, the coefficients $c_{i\alpha}$ for the HOMO pπ orbitals of both pro-conductor and conductor

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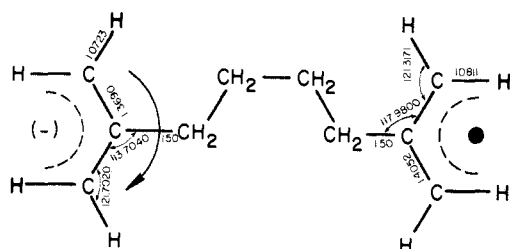*J. Am. Chem. Soc., Vol. 110, No. 17, 1988* 5689

Figure 3. The molecule used in our calculations. Note the arrow that indicates the twist angle variation. The indicated bond angles and bond lengths were obtained by ab initio STO-3-G and STO-4-31-G calculations, UHF for the allyl radical and RHF for the allyl anion.

ends have to change. These changes are then reflected in the overlap S_{if}, where

$$S_{if} = \int \sum_\alpha C_{i\alpha} u_\alpha \sum_\alpha C_{f\alpha} u_\alpha \, d\tau \qquad (2)$$

and in the energies of the initial and final states. The matrix element H'_{if} that contains the information about the electron coupling between the initial state and the final state can be written[18] as

$$H'_{if} = \frac{H_{if} - S_{if}(H_{ii} + H_{ff})/2}{1 - S_{if}^2} \qquad (3)$$

where $H_{if} = \int \psi_i H_{el} \psi_f \, d\tau$ and H_{el} is the electronic (Born–Oppenheimer) Hamiltonian for the molecule described, $H_{ii} = \int \psi_i H_{el} \psi_i \, d\tau$, and $H_{ff} = \int \psi_f H_{el} \psi_f \, d\tau$. The matrix element H_{if} can be estimated by using the Mulliken approximation, i.e.

$$H_{if} = CS_{if}(H_{ii} + H_{ff}) \qquad (4)$$

where C is a constant. It follows that

$$H'_{if} = \frac{S_{if}}{1 - S_{if}^2}(H_{ii} + H_{ff})\left(C - \frac{1}{2}\right) \qquad (5)$$

This equation can be used conveniently to calculate the electron-transfer rates in the presence and absence of an EF. The required matrix elements and wave functions are obtained with MO calculations. For the present work we used a new version of the HONDO–MO program which contains a uniform field in the one-electron Hamiltonian.[19]

The electron-transfer rates can be calculated by using the time-dependent perturbation theory (i.e., the Golden Rule) or the Rabi equation[20] in conjunction with the matrix elements defined by eq 5. Logan, Marshall, and Newton,[18] who used a similar approach for calculation of Fe^{2+}/Fe^{3+} electron exchange, also used a site-separation dependence (r) that scales H'_{if} as a function of distance by $|H'_{if}(r)|^2$, where (r) is an exponentially decaying function of r. In our work the overlap S_{if} is explicitly shown to dominate the coupling H'_{if}, through eq 5, thus it acts as a scaling factor. Therefore the overlap is the physical entity that controls the electron transfer and together with ΔE_o, the "Exoergicity",[7] will determine the rate.

The equations mentioned can be employed to determine the dependence of the transfer rates on applied field. Though eq 5 is not explicitly dependent on field, this dependence is invoked through the MO calculations that lead to both the field-dependent overlap and the field-dependent energies.

Equation 5 could be used conveniently to probe the ability of an electric field to induce electron transfer in appropriate systems. One has to calculate the matrix elements expressed in the equation by computing first the diabatic initial and final states. A de-
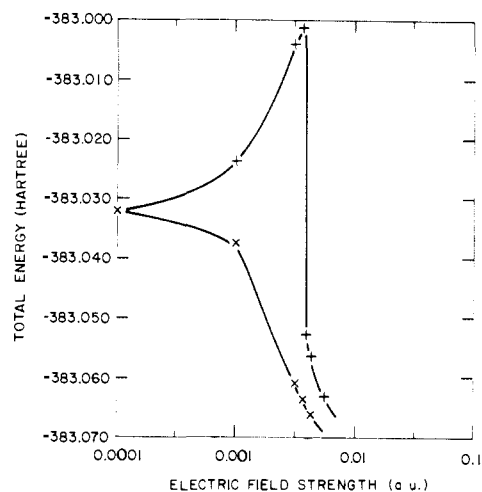

Figure 4. Total energy vs electric field strength for the two molecular configurations. (Only one is shown in Figure 3.) The upper curve represents ψ_i, and the lower curve represents ψ_f. The tendency of the energies of both configurations to converge implies that above the threshold the barrier collapses and the molecule becomes a single-well molecule. The calculations (UHF) were carried out with the HONDO program with the STO-3-G basis set.

scription of suitable wave functions is given in Newton's paper on electron exchange,[21] which can be implemented by ab initio techniques, as was done in a number of examples.[18] For practical considerations, the calculations should also be carried out on relatively small molecules, rather than the huge ones proposed in the model. However, any simplification should retain the essence, namely the electron double-well potential and the 90° twist.

A molecule that fits this description is shown in Figure 3. The allyl end parts of the molecule represent the π orbitals of the pro-conductor and conductor of the molecular switch, and the butyl bridge (with all the carbons in one plane) represents the central tunneling bridge. The effect of spatial non-orthogonality is achieved by keeping one of the allyls in the same plane as the butyl bridge while rotating the other allyl terminal as the arrow in the figure indicates. The localization of charge on the desired end of the molecule was achieved by separate optimizations of bond angles and bond lengths for the allyl radical and the allyl anion. This information was subsequently used to construct the full molecular geometry. Two sets of calculations were carried out, one on the above-mentioned molecule and the other on the allyl pairs in the same geometry, but without the butyl bridge. In the last pair mentioned, two hydrogen atoms took the place of the bridge, but the distance between the central carbons of the individual allyls in the pair was exactly their distance in the full molecule in Figure 3. The calculations consisted of ab initio STO-3-G and STO-4-31-G calculations, UHF for the allyl radical and RHF for the allyl anion. The final optimized geometries are included in the full molecule displayed in Figure 3.

Results

The calculations were carried out in the range of electric fields of 0.0 to 0.01 (au), (one au of electric field strength equals 1.715 × 10⁷ statV/cm), using the HONDO program, UHF with STO 3-G basis set. The effect of the EF on the total energy of the molecule with the ψ_i configuration is shown in the upper curve of Figure 4, while the lower curve in the figure belongs to ψ_f. The energy is given in hartree (1 hartree = 27.21 eV). As the field is raised, the total energy of ψ_i increases up to a threshold, where it abruptly drops. From this EF value and on, the total energy of the molecule with the ψ_i configuration converges with the total energy of ψ_f. The small difference can be attributed to the geometry differences between the two wave functions, one that was

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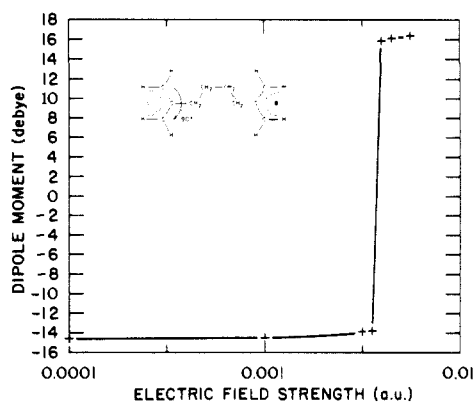
Figure 5. Dipole moments variation vs electric field strength for the molecule shown in Figure 3. The calculations (UHF) were carried out with the HONDO program with the STO-3-G basis set.
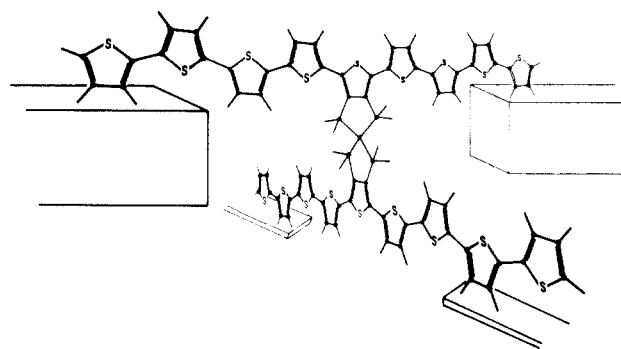

Figure 6. A proposed molecular switch with the proper electrode connections (excluding the two switching electrodes). The number of thiophene rings shown is below the number needed to form oligomers that are adequately long.

used to localize the electron on the left and one for the right. What is rather interesting is that the HOMO orbital of ψ_i is populated exclusively on the left allyl group in p_x atomic orbitals, without EF or with EF below threshold. On the other hand, above the EF threshold, the HOMO orbital is populated on the right allyl group in p_y atomic orbitals, just as the HOMO orbital of ψ_f is populated under all field conditions. The change that occurs abruptly above a threshold field indicates that a transformation takes place at the threshold that leads to stabilization of the molecular energy. This transformation is due to redistribution of charge in the molecule. This also implies that at threshold and beyond, the barrier in the double well collapses and the molecule becomes a single-well potential molecule. This contention is corroborated by the behavior of the calculated dipole moments as a function of electric field, which are plotted in Figure 5, for the molecule shown in Figure 3. It is instructive to note that the dipole moment of the molecule in the z direction changes gradually up to the threshold field and then, suddenly, changes sign and magnitude. This sudden change is due to the migration of charge from one side of the molecule to the other side. This migration implies, in our model, spatial interchange of conductor and proconductor.

The EF calculations mentioned above were also carried out for the allyl radical–allyl anion un-bridged pair, where the allyls were situated at a right angle to each other, along the same axis as in the bridged molecule. They were separated exactly as in the bridged molecule. The results of the field induced dipole moment switching and the double well collapse into a single well were also obtained in this case. The results are very similar to the results of the bridged molecule. However, the threshold field was at 0.0065 au rather than 0.0055 au, which was obtained for the bridged molecule. This might be an indication of the difference of the through-bond vs through-space charge transfer. In this context one should not lose sight that the calculations performed report equilibrium outcomes and do not directly indicate kinetics of electron transfer. Therefore, the comparison does not give a precise answer about the two mechanisms.

Equation 5 indicates that the matrix element for electron transfer is linearly dependent on the sum of energies $H_{ii} + H_{ff}$. These terms change due to the influence of the field, as can be seen in Figure 4. The two curves in the figure describe H_{ii} and H_{ff} independently. The difference between the curves is the field-dependent exoergicity of the double-well potential that grows from zero to its maximum value at threshold field. Thus the field can influence H'_{if} at less than threshold value and accelerate the electron transfer. This implies that the field does not necessarily have to reach the threshold in order to induce electron motion. According to Figures 4, and 5, the threshold field is 2.829 × 10⁶ V/cm, but for more polarizable molecules than the one used as a model in our calculations, the value may be less.

The set of molecular orbitals ψ_i and ψ_f is two sets of non-orthogonal spin-orbital Slater determinants. As such, these orbitals cannot be used directly to obtain the overlap S_{if}. To compute the

overlap one has to use the "Corresponding Orbital Transformation".[22]

The data for calculation of the overlap were obtained from the MO calculations. However, the actual calculations are not trivial. The difficulty arises from the fact that, for calculation of the "D" overlap matrix in ref 22, one has to calculate the eigenvector matrix of the coefficients $[C_{j\alpha}]_i$, the matrix of the overlap integrals of the basis sets $[\int (u_\alpha)_i(u_\beta)_f \, d\tau]$, and the transposed matrix of the coefficients of eigenvectors $[C_{k\beta}]_f$. To obtain the correct matrix of the overlap of the basis set, a separate computation was carried out, with double the number of atoms, where the initial state and the final state, with their respective geometries, were overlayed. The input coordinates presented to the program were coordinates of the initial molecule, followed by the coordinates of the final molecule. The HONDO program of course did not calculate this structure, but it did produce the one-electron overlap integral matrix that contained the matrix that was needed. That matrix was one of the off-diagonal quadrants.

This method did not directly provide the induced change in the overlap due to the action of the field. The reason for this is the fact that above threshold field, ψ_i contains the extra electron on the right side allyl group, and the state that we designated as "initial" cannot be computed. Rather the SCF calculations produce the most stable electronic configuration for the geometry coordinates that are presented to the HONDO program. Obviously, while we inputted the geometry of the initial state with the electron on the left side, the calculated results were those of the final state, ψ_f, with just minor variations. Thus comparison between the orbitals that are computed as initial and final states, in this region of the field, leads to the apparent 1:1 correspondence of the eigenvectors. We did not find a way to localize the electron in the initial geometry in EF above threshold. Thus, the overlap of the HOMO electron below the EF threshold between ψ_i and ψ_f is zero, and according to eq 5 it implies that in this range the coupling is very small, leading to localization of the electron in the initial state. On the other hand, above the EF threshold, since the barrier collapses, the electron migrates to the other end of the molecule (this being energetically the favored position) at a minimum rate of vibrational relaxations.

In effect these results give the answers to the two questions that were posed above: the initial state is stable up to the threshold field and switches abruptly at or above the threshold.

Additional Device Functions

It is interesting to examine some additional properties of this unique type of molecule. Figure 6 shows a model of the molecule that was presented in Figure 2, including the electrodes that would have to be connected to it to form devices (The switching electrodes, perpendicular to the z axis, are not shown.) This com-

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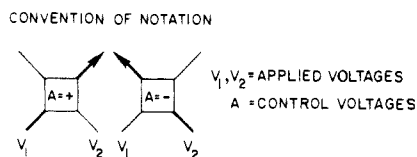
CONVENTION OF NOTATION

V_1, V_2 = APPLIED VOLTAGES
A = CONTROL VOLTAGES

Figure 7. Schematic representation of the molecular switch shown in Figure 6, as it would be seen by an observer looking down at the surface. The square represents the top switching electrode. The arrows represent the conductive (thicker line) and the nonconductive (thinner line) segments.
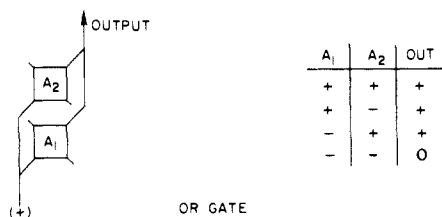

A_1	A_2	OUT
+	+	+
+	−	+
−	+	+
−	−	0

OR GATE

Figure 8. The wiring diagram of two molecules to obtain "OR" gates.

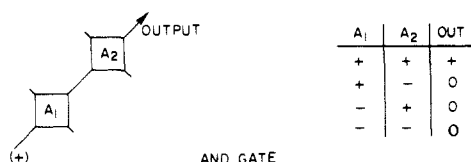| A_1	A_2	OUT
+	+	+
+	−	0
−	+	0
−	−	0

AND GATE

Figure 9. The wiring diagram of two molecules to obtain "AND" gates.

plicated assembly can be represented in the somewhat simpler notation that is given in Figure 7. According to this notation the arrows represent the conductive and the non-conductive π systems. The square denotes a top view of the switching electrode. The character "A" inside it denotes the voltage polarity of that top electrode. "A" is the control voltage, because it influence which of the segments conducts. The other voltages that are specified as V1 and V2 are permanently applied voltages. With use of this simplified notation it is possible to show some additional properties that these molecules possess.

"OR" Logic Gate. Figure 8 represents the wiring of two molecules in a four-terminal device that produces the function of an "OR" gate. The sign (+) indicates that a positive voltage is permanently applied to the terminal as indicated. It works as follows: When the control voltages at "A1" or/and "A2" are positive, a conductive path is available for conduction across the connected chains (arrows). If both "A1" and "A2" are negative no current will pass. The truth table shown in Figure 8 belongs to the molecular device and is identical with the truth table of an "OR" logic device.

"AND" Logic Gate. Figure 9 is a wiring diagram for an "AND" gate. For the type of connection shown, the control voltages on "A1" and "A2" have to have the same positive polarity in order for the device to pass current. The truth table shown is that of the molecular device and corresponds to an "AND" logic gate.

An "Inverter" and an "Amplifier". The wiring of the molecule that produces inversion of currents sent across the device is shown in Figure 10. The (+) and (−) signs denote permanent applied voltages with the specified polarity. The function of the device is as follows: Assuming that for "A" = (+) the left to right chain is conductive, then this chain is connected to a permanent negative voltage and therefore the output of the device will be negative, since the corresponding chain is conductive. (The other chain is insulating.) When the polarity of "A" is reversed to (−), the device switches, and the other chain, which is connected to a positive voltage, becomes conductive while the one that was connected to the negative terminal is rendered insulating. Thus the output of the device becomes positive, always inverse to the input of "A". Note that if the polarities of the permanent applied voltages are reversed, then the device acts as an amplifier: provided that the applied voltages "V" are larger than the voltage "A", and then a small control voltage "A" can modulate the output that would

A	OUT
−	+
+	−

INVERTER

Figure 10. The wiring diagram of one molecule to obtain an "INVERTER".

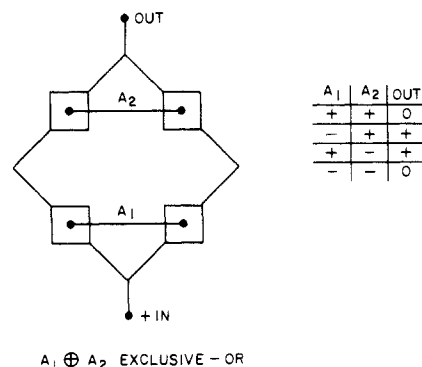| A_1	A_2	OUT
+	+	0
−	+	+
+	−	+
−	−	0

$A_1 \oplus A_2$ EXCLUSIVE − OR

Figure 11. The molecular "EXCLUSIVE OR" gate.

be equal to V_1 or V_2, both in sign and magnitude.

"EXCLUSIVE OR" Logic Gate and a "HALF ADDER". The "EXCLUSIVE OR" gate is one of the most useful logic gates for device applications. A "HALF ADDER" for binary addition of two inputs can be obtained from one "AND" gate together with an "EXCLUSIVE OR" gate as is well-known in the art.[23] Thus, a possible "wiring" of spiro molecules to form an "EXCLUSIVE OR" gate is shown in Figure 11. Four molecules were required to produce the necessary function. The operation of this aggregate is described below: there are two possible conduction pathways from "+ IN" to "OUT". These two branches are the left-side clockwise "C" pathway, and the right-side anti-clockwise "AC" pathway. The analysis is as follows:

$$A_1 +, A_2 +$$

C branch bottom is insulating and AC branch top is also insulating, therefore, the output is zero.

$$A_1 +, A_2 -$$

AC branch bottom and top are conductive; therefore, the output is +.

$$A_1 -, A_2 +$$

C branch bottom and top is conductive; therefore, the output is +.

$$A_1 -, A_2 -$$

AC branch bottom is insulating and C branch top is also insulating; therefore, the output is zero.

The whole table is identical with the truth table of an "EXCLUSIVE OR" logic gate.[24] This gate, together with a molecular "AND" gate, can be utilized to construct a molecular "HALF ADDER" for twin input signals A_i and B_i and the added output $C_{i+1}; S_i$. The adder consists of the two logic gates "AND" and "EXCLUSIVE-OR". The molecular "HALF ADDER" is shown in Figure 12.

Nonlatching Switches. The description so far centered around spiro switches that constitute symmetric double-well potentials that result from utility of twin pairs for conductor and pro-conductor combinations. However, if instead of twins, different classes of constituents were to be employed, for instance pyrrols on one side and thiophenes on the other, or thiophenes on one side and

(23) Taub, H. *Digital Circuits and Microprocessors*; McGraw-Hill: New York, 1982; p 196.
(24) Taub, H. *Digital Circuits and Microprocessors*; McGraw-Hill: New York, 1982; pp 25 and 26.
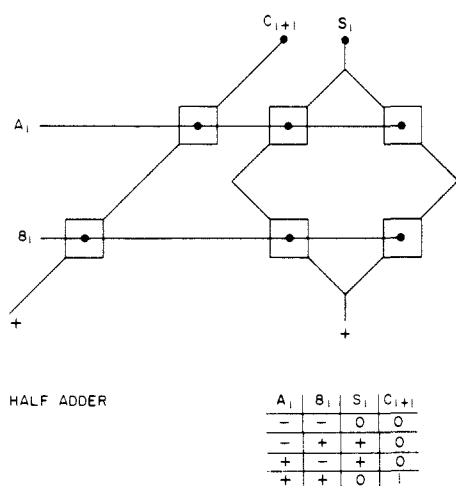
Figure 12. A molecular "HALF ADDER" for two input signals A_i and B_i and the added output C_{i+1}; S_i. The adder consists of the two logic gates "AND" and "EXCLUSIVE OR".

tetrathiafulvulenes on the other, some variations in the operation would result, such as nonlatching switches, which may have beneficial properties. These embodiments will be discussed in subsequent publications.

Conclusions

The spiro bridge that was proposed in this work is rather unique. It is capable of localizing an electron on one side of a molecule by providing a large tunneling barrier. On the other hand the same bridge is flexible toward electron transfer in electric fields, above threshold. Another important feature of the molecules studied is the exchange of the conductivity properties of the terminal groups. This interchange leads to possible device application in areas of signal processing on the molecular level.

The results of the dipole switching due to the action of the field above threshold and the simultaneous collapse of the tunneling barrier are complementary to each other. While the dipole reorientation emphasizes a static equilibrium outcome, the change from a double-well to a single-well molecule implies that the electron transfer will occur at a high rate, comparable at least to vibrational relaxations.

Our calculations show that the model proposed in this article does have the device properties that were presented. Actual implementation of some of the ideas outlined in this paper will be preceded by careful and laborious verifications, both theoretical and experimental, aimed at a deeper understanding of the basic principles involved. Clearly we need more profound knowledge of the through-bond vs through-space electron transfer and of the influence of electric fields on these types of mechanisms of electron transfer. Furthermore, practical molecules should be endowed with large polarizabilities in order to obtain switching with low fields. In short, we face a challenge and there is plenty to be done before we reap the technological benefits that might emerge.

The perceived novelty that the described model offers is the possible molecule-to-molecule communication that can lead to the synthesis of logic and amplification. One should not lose sight of the possible suitability of the proposed molecules for cellular automata. It is felt that the model could serve as a blueprint for molecular electronics.

Experimental and Theoretical Study of Excimer Formation in 1-Azabicyclo[*l.m.n*]alkanes: Interpretation of Binding Energies Using a 3-Electron-Bond Model

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Abstract: The excited dimer (excimer) of 1-azabicyclo[3.2.2]nonane (**322**) is reported. The binding energy is determined from a combination of transient and stationary photophysical measurements and found to be 22.2 kJ/mol in *n*-hexane solution. The binding energy of **322** is compared to those of other 1-azabicyclo[*l.m.n*]alkanes, **221** (51.0 kJ/mol) and **222** (36.8 kJ/mol). The observed changes are explained in terms of steric hindrance posed by the α-C hydrogen atoms, as excimer stability is achieved at close N–N approach. A theoretical model of an amine excimer, based on a neutral–radical cation pair, was used in conjunction with MNDO and AM1 calculations. Results of these calculations show that this type of 3-electron bonding is consistent with observed trends in the excimer stability. The failure of 1,4-diazabicyclo[2.2.2]octane (**DA222**) to manifest evidence of excimer formation, which is consistent with MNDO results, is rationalized in terms of the resonance stabilization of the **DA222** radical cation.

There has been long-standing interest in the structural dependence of molecular photoassociation.[1–3] Our particular concerns have centered on the photophysics and photoassociation of saturated amines in both the vapor and condensed phases. This

paper is primarily concerned with three homologous compounds of the 1-aza bicyclic series (so-called "cage amines") and the excimers (*excited dimers*) of those species in alkane solution. Specifically, the amines examined are those for which [*l.m.n*] are **221**, **222**, or **322** and will be denoted as such throughout. In addition, experiments were performed on 1,4-diazabicyclo-[2.2.2]octane (**DA222**).

Interest in the structural effects on photoassociation arises for at least three reasons: (1) From the results of such studies, one can infer the consequences of similar structural features on any

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