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## MOLECULAR RECTIFIERS

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The construction of a very simple electronic device, a rectifier, based on the use of a single organic molecule is discussed. The molecular rectifier consists of a donor  $\pi$  system and an acceptor  $\pi$  system, separated by a sigma-bonded (methylene) tunnelling bridge. The response of such a molecule to an applied field is calculated, and rectifier properties indeed appear.

### 1. Introduction

The tremendous improvements in reliability, compactness, versatility and range of electronic circuitry due to the widespread manufacture and use of solid-state devices constitutes perhaps the major technological advance of the past quarter century. Within biological systems, however, some tasks performed by solid-state devices in electronic applications are performed, instead, by organic molecules; such tasks include storage and transfer both of energy and of electrons. It has been suggested occasionally [1] that the development of synthetic electronic devices based on organics be attempted. Particular interest has been evinced recently in the use of organic crystals both as semiconductors [2] and as possible superconductors [3]. It seems to us reasonable to examine the potential use of molecules as components of electronic circuitry by looking, as a start, at the current-voltage characteristics of a single molecule acting as a rectifier.

In this article we present semiquantitative calculations that are intended to demonstrate the feasibility of such a molecular device.

### 2. Architecture of the rectifier circuit

Common solid-state rectifiers are based on the use of  $p-n$  junctions. An organic molecule, to show rectifier properties, should have roughly the properties of a  $p-n$  junction. By the use of substituent groups on aromatic systems, it is possible to increase or decrease the  $\pi$  electron density within the organic, and therefore to create relatively electron-poor ( $p$ -type) or electron-rich ( $n$ -type) molecular subunits. Those substituents classified as electron withdrawing (that is, showing positive Hammett constants) [4] will cause their aromatic subunit to become relatively poor in  $\pi$  electron density, thus raising the electron affinity and making the subunit a good electron acceptor. Conversely, electron-releasing substituents will increase the  $\pi$ -electron density, thereby lowering the ionization potential and rendering the subunit a good electron donor [5-7].

Certain solids, the so-called charge-transfer crystals, show high electronic conductivity and spin susceptibility due to the donor-acceptor transfer of electrons [8]. This electron motion suggests that a rectifier could be built in which electrons would be allowed to pass from a cathode to an acceptor site or from a

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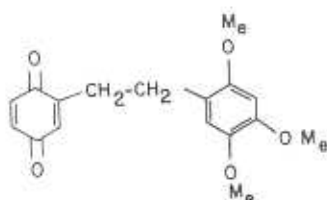


Fig. 1. An example of a hemiquinone.

donor site to an anode, but not in the other sense. If, however, the electronic systems of the donor and acceptor molecular subunits are allowed to interact strongly with one another, a single donor level will exist on the time-scale of any laboratory experiment [9]. Therefore, the donor and acceptor sites should be effectively insulated from one another in order for the device to function. This can be accomplished by the use of a sigma-electron system between the donor and acceptor pi subunits\*. Such a molecule, illustrated in fig. 1, might then be expected to show rectifier properties; electron current would be expected to pass only from left to right in the figure, along the system cathode  $\rightarrow$  acceptor  $\rightarrow$  donor  $\rightarrow$  anode. The hemiquinone molecule shown in fig. 1 may be used as a prototype for understanding rectifier behavior. The quino ( $=O$ ) groups on the left decrease the pi density and raise the electron affinity, whereas the methoxy ( $-OCH_3$ ) groups on the right increase pi density and lower ionization potential. Fig. 2 shows a similar molecule based on the extremely popular acceptor tetracyanoquinodimethane (TCNQ) and the donor tetrathiofulvalene (TTF). In this case, we have indicated a triple, rather than single, methylene ( $-CH_2-$ ) bridge; this will help ensure molecular rigidity. We will refer to the methylene bridge as a  $\Sigma$  bridge henceforth. Its purpose is to cause the pi levels of the donor and acceptor sites to be essentially non-interacting on the time-scale of electronic motion to or from the electrodes.

To describe simply the response of such a molecular rectifier circuit to an ac signal, we will employ an independent-particle picture for the pi electrons. The empty orbital which accepts electrons from the cathode will be called the affinity state. In the free

\* Compare, e.g., the beautiful experimental work on photoelectron spectra of methylene-bridged aromatics by Berkowitz et al. [10], and related papers.

donor acceptor molecules of the type shown in figs. 1 and 2, the electron affinity of the acceptor will be of order 1–2.5 volt, while the ionization potential of the donor will be of order 6–9 volt. These values are considerably modified in crystals [3], as we might expect them to be in our rectifier circuit, due to interaction with other (in our case metallic electrode) electronic states. For proper rectifier behavior we require the affinity level of the acceptor to be either totally or partially empty, and lie at or slightly above the Fermi level of the electrode (and of course above the ionization level C of the donor) as shown in fig. 3.

Figs. 4 and 6 demonstrate the passage of electron current from cathode to anode and the non-conduction of current on reversal of polarity; that is, they show the rectifier property of the molecule. As soon as the applied field becomes large enough for the cathode levels to overlap the acceptor levels in fig. 4, electron transfer onto the acceptor becomes possible. The threshold for this process will depend on several factors, principally the affinity perturbed level energy  $E_B$  and the work function  $\phi$ . A similar process occurs at the donor end, where electron transfer from the donor orbital C to anode becomes possible when the applied voltage  $V > IP - \phi$ , where IP is the donor ionization potential. Motion of electrons from acceptor to donor will occur under the action of the field. The (now occupied) affinity level and the hole left on the ionized donor are sufficiently close in energy that an electron tunneling process will occur: the tunneling width can be of the order of  $10-5000 \text{ cm}^{-1}$ . This tunneling is generally inelastic as can be observed by glancing at fig. 5. The charged acceptor contains an electron in orbital B, in the ground vibrational state, that tunnels with conservation of energy to the empty orbital C at the donor site. Except in cases of resonant transfer, the level B will lie above C, so that C will be prepared in an excited Franck-Condon state, which will then decay radiationlessly [11]. This process is clearly irreversible so long as B lies above C.

We thus think of current passage through our rectifier molecule as a three-step equivalent-resistance Kirchhoff net, with the three steps being cathode to acceptor, acceptor to donor and donor to anode transfers. Thus when polarity is reversed as shown in fig. 6 level D would have to be lowered to the Fermi level of the metal on the right and the Fermi level of the metal on the left would have to be lowered below

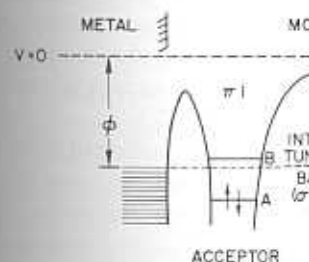
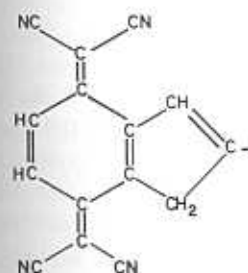


Fig. 3. Energy versus distance of acceptor and donor. A and B are the affinity levels and C is the ionization level, of acceptor and donor, respectively.

level A in order to obtain asymmetry in these levels. As can be seen from fig. 4, a small voltage for this process is sufficient. There may be an additional tunneling step in this direction that has not been counted. The first step of this process is internal tunneling from level C to level B of the acceptor. This would be the initial step, tunneling would then be from levels to and from the metal.

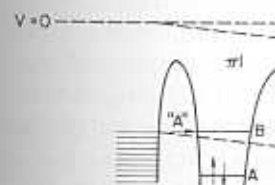


Fig. 4. Energy levels shift with applied voltage. "A", "B", and "C" are three tunneling processes.

ules of the type shown in figs. 1 and 2. The ionization potential of the acceptor will be of the order of 6–9 volt. These values are comparable to the ionization potential of organic crystals [3], as we might expect. In a rectifier circuit, due to interaction with the metallic electrode) electronic rectifier behavior we require the acceptor to be either totally or partially occupied or slightly above the Fermi level (and of course above the ionizing potential) as shown in fig. 3.

To demonstrate the passage of electrons from the donor to anode and the non-conductivity of the molecule, the reversal of polarity; that is, they require the property of the molecule. As soon as the field becomes large enough for the acceptor levels to overlap the donor levels in fig. 4, the process becomes possible. This process will depend on several factors: the affinity perturbed level energy, the ionization potential  $\phi$ . A similar process occurs here where electron transfer from the donor to the acceptor becomes possible when the ionization potential  $\phi$ , where IP is the donor ionization potential.

Motion of electrons from acceptor to donor under the action of the field. The ionization potential level and the hole left on the acceptor are sufficiently close in energy that an electron transfer process will occur: the tunneling process is of the order of  $10^{-5}$ – $10^{-6}$  cm<sup>-1</sup>. This process is inelastic as can be observed by the charged acceptor contains an electron. In the ground vibrational state, the conservation of energy to the empty donor site. Except in cases of resonant energy transfer, so that C will be excited to the Franck-Condon state, which is nonradiative [11]. This process is so long as B lies above C.

If current passage through our rectifier is a three-step equivalent-resistance process, the three steps being cathode to donor, donor to acceptor, and acceptor to anode. When polarity is reversed as shown in fig. 4, the Fermi level of the donor on the right and the Fermi level of the acceptor on the left would have to be lowered below

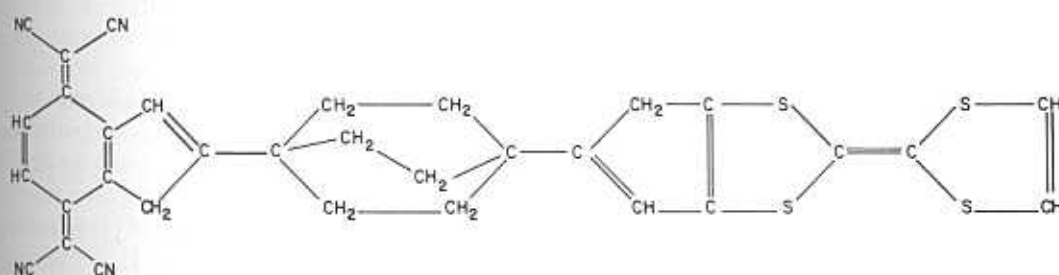


Fig. 2. An example of a rectifier molecule.

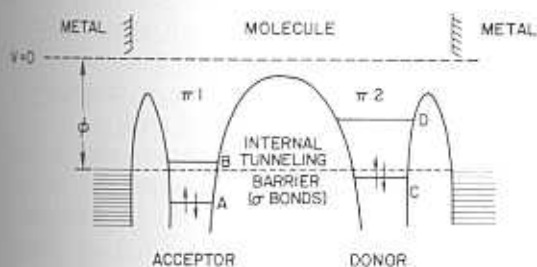


Fig. 3. Energy versus distance of the device (schematic). B and D are the affinity levels and A and C the highest occupied levels, of acceptor and donor, respectively.

level A in order to obtain assisted tunneling through these levels. As can be seen from the figure, the threshold voltage for this process should be relatively high. There may be an additional mechanism for conduction in this direction that has to be taken into account. The first step of this mechanism involves an internal tunneling from level C of the donor to level B of the acceptor. This would lead to a hole at the right side and an electron on the left side. Following this initial step, tunneling would proceed from charged  $\pi$  levels to and from the metals. This mechanism also in-

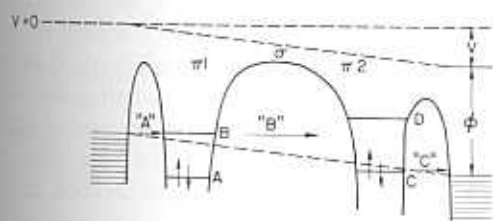


Fig. 4. Energy levels shift with applied voltage. "A", "B", and "C" are three tunneling processes.

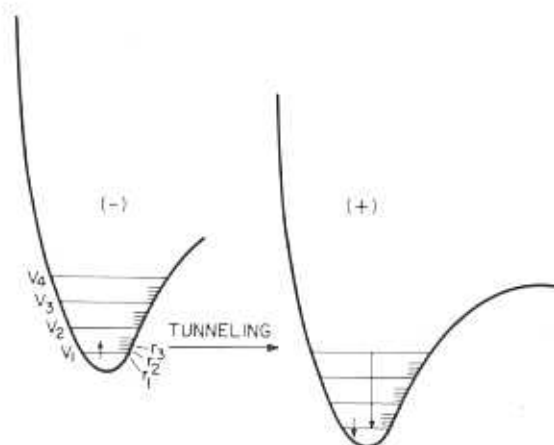


Fig. 5. Internal tunneling.

volves a threshold voltage, since it is imperative that the donor highest occupied molecular orbital C, on the right, be energetically at or above the acceptor  $\pi$  affinity orbital B, before tunneling would occur. It is the nonreversibility of the internal tunneling (for small applied fields) that yields the rectification properties of these molecules. It is thus possible to

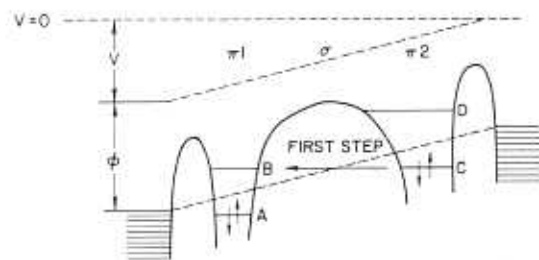


Fig. 6. Reverse applied voltage.

design materials that would have a larger threshold voltage for conduction in one direction than for the other direction; that is, rectifiers.

### 3. Calculations

The passage of electric current through a molecular system can generally be considered simply from the viewpoint of perturbation theory, with the total molecular wavefunction perturbed by the applied field. In the case of our A- $\Sigma$ -D system, however, the  $\Sigma$  bridge effectively separates the pi units, and the concept of a total molecule wavefunction to describe the response to an external field is no longer necessarily the most convenient starting point. Instead, we now choose to consider the three steps of cathode  $\rightarrow$  A, A  $\rightarrow$   $\Sigma \rightarrow$  D, and D  $\rightarrow$  anode as processes in an equivalent resistance network; arguments for the use of this method have been given by Mott and Twose, Kirkpatrick and others [12]. The essential reason for the use of this model is really based on time-scales; the electrode and bridge processes occur on such different time-scales that each one is really not dynamically coupled to the others. We will also choose to ignore, in our present crude independent-particle description, any direct excitonic interactions of the donor hole with the acceptor electron. The electronic eigenenergies (donor acceptor levels) as well as the effective tunneling matrix-elements can be roughly estimated using self-consistent field molecular orbital calculations. Alternatively, and preferably, these levels can be found from photoelectron spectra of the molecule. Our SCF calculations, which were carried out for the molecule of fig. 1 using the INDO semi-empirical method [13], give rough one-electron energies for the molecule alone; interaction shifts and broadening must then be added.

#### 3.1. The cathode $\rightarrow$ acceptor step

To estimate the rate of this transition in an applied field, we have employed a variant of the transfer-hamiltonian method originally proposed by Oppenheimer [14] to treat field ionization. In this method, the expression for the transition probability per unit time is simply

$$P = \frac{2\pi}{\hbar} \sum_f |\langle f | -Fz | 0 \rangle|^2 \delta(E_f - E_0). \quad (1)$$

Here  $|f\rangle$  is the final eigenstate (in our case, the vibronic state on the A site),  $|0\rangle$  is the initial eigenstate (the metallic wavefunction), and the electric field of strength  $F$  is directed along the  $z$  axis. Duke [15] has shown the equivalence of (1) to Bardeen's calculation of junction tunneling [16]. The only difference between (1) and the usual golden-rule result is that  $|f\rangle$  is associated with the unperturbed hamiltonian on the final site, rather than with the original unperturbed hamiltonian of which  $|0\rangle$  should be an eigenstate. The state  $|0\rangle$  has simply been taken as a plane-wave state (Bloch states within the electrode would of course be more correct, but we do not expect this to make much difference in our final result).

For the states  $|f\rangle$ , however, the unperturbed state of the pi system of the acceptor are not good enough. As studies of molecular adsorption have shown, the molecular eigenstates undergo both shift and broadening due to interaction with the electrodes. Gadzuk [17] presented an early treatment of these effects in the case of an atom interacting with a metallic surface. He showed that the concept of image charges could be taken over from classical electrostatics, and that an estimate of both the shift and the broadening could be obtained from perturbation theory. For the case of an alkali atom adsorbed on a metal, he showed that correct semiquantitative results could be obtained by using as an unperturbed basis set the bare atom  $s$ -function and the free-electron states within the metal. The level shift is then simply

$$\Delta E = \langle s | H_{a-\text{met}} | s \rangle / \langle s | s \rangle, \quad (2)$$

where  $|s\rangle$  is the atomic function and  $H_{a-\text{met}}$  is the electron interaction with the image charges in the metal. For the adsorption of K on Pt, he finds that  $\Delta E$  drops off slowly with distance, from 0.3 volt at 3 Å separation to 0.1 volt at 15 Å\*. Similar values had been previously suggested by Rasor [18] and by Levine [19], while Gomer [20] had proposed the essential shape of the  $\Delta E$  curve as a function of distance.

For our molecule-metal interaction, we first compute the shift for each atomic basis function. The

\* For slightly smaller distances, the shift goes up dramatically for distances of order 2.5 Å, values of 1.5–2 volt seem reasonable.

total shift of the molecular orbital donor and acceptor ends will then be combinations of these basis-function shifts. We say, for a particular molecular

$$\phi_i = \sum_{\alpha} C_{i\alpha} u_{\alpha},$$

where  $u_{\alpha}$  are the atomic basis functions by  $H_{m-\text{met}}$  the molecule-metal interaction.

$\langle \phi_i | H_{m-\text{met}} | \phi_j \rangle = \sum C_{i\alpha} C_{j\alpha} \langle u_{\alpha} | H_{m-\text{met}} | u_{\alpha} \rangle$ . We find the coefficients  $C_{i\alpha}$  using the initial matrix elements in (1) while the final matrix elements in (1) using the image-charge procedure of

Thus far, the calculations have been for either elastic electron tunneling (transfer hamiltonian) or adsorption (broadening of molecular levels). There is, however, a complication brought about by the broadening due to interaction with the electrodes. If this broadening has been included, there are important contributions from vibrational tunneling; that is, a contribution to the tunneling possibility can arise from transfer from the cathode to a vibrationally excited state of the acceptor. On the basis of strong evidence [11] and assuming, as is generally true, that one particular normal mode (1400  $\text{cm}^{-1}$  stretch) is far more strongly coupled than any other, one can evaluate the relative probabilities to various vibrational states. This is a standard problem in electron-transfer theory. In our present calculations, we have taken the Frölich-type coupling constant as 1.0, which is a spectroscopic value. The contribution of this component is in fact small for the elastic step, but it makes its major contribution in the inelastic step.

#### 3.2. A $\rightarrow$ D motion

Within our equivalent-resistance network model, we have effectively

\* Gurney [21] has pointed out that, due to the broadening of one-electron levels will in fact become broadening is negligible at our assumed



$$E_f - E_0) \quad (1)$$

genstate (in our case, the A site),  $|0\rangle$  is the initial eigenfunction, and the electric field is directed along the  $z$  axis. Due to the equivalence of (1) to Bardeen's theory of tunneling [16]. The only difference from the usual golden-rule result is that the unperturbed hamiltonian is the original unperturbed hamiltonian of which  $|0\rangle$  should be an eigenfunction. This has simply been taken as a plane wave within the electrode would of course be correct, but we do not expect this to be in our final result).

However, the unperturbed states of the acceptor are not good enough. Similar adsorption have shown, the molecule undergoes both shift and broadening with the electrodes. Gadzuk's early treatment of these effects for a molecule interacting with a metallic surface. The concept of image charges could be used in classical electrostatics, and that an image charge shift and the broadening could be treated by perturbation theory. For the case of a molecule adsorbed on a metal, he showed that similar results could be obtained using a plane wave basis set the bare atom  $s$ -function within the metal. The unperturbed eigenfunction is simply

$$|s\rangle, \quad (2a)$$

the unperturbed eigenfunction and  $H_{a-met}$  is the interaction with the image charges in the metal. In the case of K on Pt, he finds that the shift of the  $s$ -level with distance, from 0.3 volt at 1.5 Å to 1.1 volt at 15 Å. Similar values are suggested by Rasor [18] and by Gomer [20] had proposed the  $\Delta E$  curve as a function of distance. In the case of metal interaction, we first consider the atomic basis function. The

shift of the  $s$ -level with distance, from 0.3 volt at 1.5 Å to 1.1 volt at 15 Å. Similar values are suggested by Rasor [18] and by Gomer [20] had proposed the  $\Delta E$  curve as a function of distance.

total shift of the molecular orbitals on the rectifier donor and acceptor ends will then be given by linear combinations of these basis-function shifts. That is, if we say, for a particular molecular orbital  $\phi_i$

$$\phi_i = \sum_{\alpha} C_{i\alpha} u_{\alpha} \quad (2b)$$

where  $u_{\alpha}$  are the atomic basis functions, then, denoting by  $H_{m-met}$  the molecule-metal interaction, we have

$$\langle \phi_i | H_{m-met} | \phi_j \rangle = \sum_{\alpha} C_{i\alpha} C_{j\alpha} \langle u_{\alpha} | H_{m-met} | u_{\alpha} \rangle. \quad (3)$$

We find the coefficients  $C_{i\alpha}$  using the INDO procedure, while the final matrix elements in (3) are evaluated using the image-charge procedure of Gadzuk\*.

Thus far, the calculations have been based on those for either elastic electron tunneling (Oppenheimer transfer hamiltonian) or adsorption (shift and broadening of molecular levels). There is, however, one extra complication brought about by the fact that, even after broadening due to interaction with metallic electrodes has been included, there can still be important contributions from vibrationally inelastic tunneling; that is, a contribution to the electron transfer possibility can arise from transfer of an electron from the cathode to a vibrationally excited level of the acceptor. On the basis of strong-coupling theory [11] and assuming, as is generally the case for aromatic molecules, that one particular normal mode (usually the  $1400 \text{ cm}^{-1}$  stretch) is far more strongly coupled than any other, one can evaluate the relative transition probabilities to various vibrational states. This is a standard problem in electron-transfer reactions. For our present calculations, we have taken the diagonal Frölich-type coupling constant as 1.5, the standard spectroscopic value. The contribution of the inelastic component is in fact small for the electrode process; it makes its major contribution in the internal tunneling step.

### 3.2. A → D motion

Within our equivalent-resistance scheme and one-electron model, we have effectively chosen to write

\*Gurney [21] has pointed out that, due to tunneling, the one-electron levels will in fact become broadened. This broadening is negligible at our assumed 3 Å separation.

the electronic hamiltonian of the entire molecule as

$$H_{el} = H_D + H_A + V_{DA} \quad (4)$$

$$V_{DA} = \sum_{i \in D} \sum_{j \in A} T_{ij} a_i^{\dagger} a_j + \text{c.c.} \quad (5)$$

The  $H_A$  and  $H_D$  are the subunit electronic hamiltonians for the A, D ends, and of course include two-electron terms. The  $i, j$  in (5) run over the one-electron  $\pi$  states of the donor and the acceptor†, respectively;  $T_{ij}$  is an effective one-electron transfer, or tunneling matrix element, and  $a_j^{\dagger}$  is a Fermion creation operator for orbital  $j$ . Using simple molecular-orbital splitting considerations (or, more elaborately, a canonical transformation), the size of the tunneling elements  $T_{ij}$  can be estimated from separate SCF-type calculations on D, on A, and on A-Σ-D. The element  $T_{da}$  was evaluated in this fashion for the molecule of fig. 1 using the INDO parametrization, and found to be  $360 \text{ cm}^{-1}$ . While this is certainly not quantitatively correct, it is in qualitative agreement with expectations as to the transfer probability for a Σ bridge, and we will use it without further correction††.

When the rectifier molecule is placed between electrodes, the one-electron levels will, as stated above, shift and broaden. The transfer probability for an electron passing from A to D will still be proportional to  $|T_{da}|^2$ , but it will also contain density-of-states factors on the final state, as well as Franck-Condon factors describing the possibility of inelastic transfer. Both the electronic changes and the vibronic factors were discussed above in connection with cathode → acceptor motion.

### 3.3. Donor → anode motion

This is treated in a transfer-hamiltonian procedure, very similar to the cathode → acceptor calculation.

## 4. Results

A current-voltage characteristic can be calculated along the lines described above. The true characteristic

† We have assumed that the  $i, j$  states are approximately orthogonal, so that  $[a_i, a_j^{\dagger}]_{+} = \delta_{ij}$ .

†† The  $\pi$ -Σ- $\pi$  idea was first suggested to us by P.E. Seiden.



presented the calculated  $I-V$  curves for various choices of donor ionization energy, electron affinity, and electrode work function. Complete calculations, including the dependence of the current on these parameters, will be published subsequently. The important question to be made about the present results is indeed a rectification evident: the current flows preferentially to the right in fig. 1. The calculated potential for passage of current is controlled by the voltage at which the broadened states (B) and the metallic states occur. In our calculations, it has been found to be negligible, the distance from the electrode, so that the current is nearly discontinuous near threshold. As the voltage, this onset of current flow will occur. If the reverse voltage is pushed, the current will indeed begin to flow through the anode to cathode; for the present calculations, this occurs at an applied voltage of about 1 V.

One of the materials and synthesis problems that must be overcome before such a molecular device can be tested in the laboratory. Efficient rectification of these problems are the subject of our work. In addition, there are several other problems to the present semiquantitative calculations. The neglect of direct energy transfer between the electrodes, however, can be minimized if the electrodes are properly aligned (properly), possible Jahn-Teller distortions with electrode polarization, and, finally, the correlation effects. Some of these problems are the subject of further work. The essential question, however, is that these calculations are based on a properly constructed single-orbital model. It is indeed exhibit useful device properties. These properties may aid in our further understanding of the molecular electronic structure.

This work was undertaken after a series of discussions with the concept of molecular rectifiers with M.J. Fréchet and especially P.E. Seiden of the University of California; we are very appreciative of

their advice and suggestions. MR is indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research, to B.M. Hoffman for discussions of ref. [9], and to J.R. Sabin for help with the INDO calculations. We are also grateful to Dr. H. Kuhn for his helpful suggestions.

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