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An Orbital Rule for Electron Transport in Molecules

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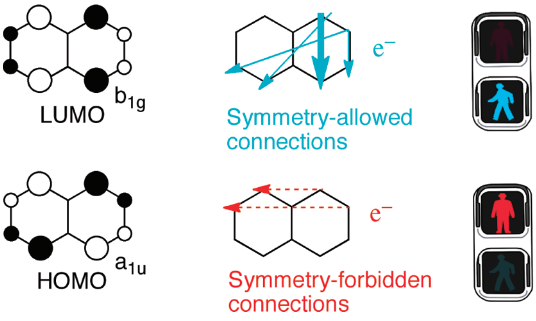

The transfer of electrons in molecules and solids is an essential process both in biological systems and in electronic devices. Devices that take advantage of the unique electronic properties of a single molecule have attracted much attention, and applications of these devices include molecular wire, molecular memory, and molecular diodes. The so-called Landauer formula with Green's function techniques provides a basis for theoretical calculations of coherent electron transport in metal–molecule–metal junctions.

We have developed a chemical way of thinking about electron transport in molecules in terms of frontier orbital theory. The phase and amplitude of the HOMO and LUMO of π-conjugated molecules determine the essential properties of their electron transport. By considering a close relationship between Green's function and the molecular orbital, we derived an orbital rule that would help our chemical understanding of the phenomenon. First, the sign of the product of the orbital coefficients at sites *r* and *s* in the HOMO should be different from the sign of the product of the orbital coefficients at sites *r* and *s* in the LUMO. Second, sites *r* and *s* in which the amplitude of the HOMO and LUMO is large should be connected. The derived rule allows us to predict essential electron transport properties, which significantly depend on the route of connection between a molecule and electrodes. Qualitative analyses of the site-dependent electron transport in naphthalene (as shown in the graphics) demonstrate that connections 1–4, 1–5, 2–3, and 2–6 are symmetry-allowed for electron transmission, while connections 1–8 and 2–7 are symmetry-forbidden. On the basis of orbital interaction analysis, we have extended this rule to metal–molecule–metal junctions of dithiol derivatives in which two gold electrodes have direct contacts with a molecule through two Au–S bonds.

Recently we confirmed these theoretical predictions experimentally by using nanofabricated mechanically controllable break junctions to measure the single-molecule conductance of naphthalene dithiol derivatives. The measurement of the symmetry-allowed 1,4-naphthalene dithiol shows a single-molecule conductance that exceeds that of the symmetry-forbidden 2,7-naphthalene dithiol by 2 orders of magnitude. Because the HOMO and LUMO levels and the HOMO–LUMO gaps are similar in the derivatives, the difference in the measured molecular conductances arises from the difference in the phase relationship of the frontier orbitals. Thus, the phase, amplitude, and spatial distribution of the frontier orbitals provide a way to rationally control electron transport properties within and between molecules.

Introduction

Electron transfer in molecules and solids is an essential process in biological systems and electronic devices.[1] Molecular scale devices that use unique electronic properties of a single molecule have attracted much attention with applications to molecular wires, memory, and diodes in mind.[2] The Landauer formula[3] with Green's function technique[4] is of great use for theoretical consideration of electron transport phenomena in metal–molecule–metal junctions. The nonequilibrium Green's function method combined with density functional theory (DFT) is a popular method at present for reliable calculations of coherent

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electron transmission probability.[5−10] Several important mechanisms that determine fundamental aspects of molecular conductance have been discussed as a function of molecular length, molecular conformation, and applied bias voltage.[11−19] In particular, conduction channel analysis in terms of molecular orbital (MO) amplitude near the Fermi energy has shown good guidelines for understanding molecular conductance. Orbital amplitude analysis based on first principles calculations revealed that the delocalization of the orbital is important to make a good conduction pathway.[5,20−22]

Tada and myself have carefully investigated a relationship between frontier orbitals and electron transport properties of π-conjugated systems,[23−26] where frontier orbitals mean highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The derived rule describes the importance of the orbital phase and the amplitude of the HOMO and LUMO to determine essential features of electron transport in molecules. The orbital analysis is based on Green's function for the molecular part of a metal−molecule−metal junction, in which two gold chains are assumed to have weak contacts with a molecule. By looking at the phase and amplitude of the HOMO and LUMO, we are able to predict good connections for coherent electron transport in π-conjugated systems. The purpose of this Account is to explain the chemical understanding of electron transport phenomena in molecules on the basis of qualitative orbital thinking. The analysis based on special attention to orbital phase with respect to the physical phenomena is in line with the frontier orbital theory[27] and the Woodward−Hoffmann rules[28] for chemical reactions. It is notable that our orbital thinking derives from Green's function theory, while the basis of the chemical reaction theories is on second-order perturbation theory.

Orbital Rule of Molecular Conductance

We have developed an orbital rule for electron transport properties of single molecules from the analysis of Green's function with the simple Hückel method in terms of the orbital concept for the past decade.[23−26] The orbital rule provides a powerful tool to predict the conductance through a single molecule. The necessary preconditions for the application of the orbital rule can be summarized as follows: (a) the coupling between a molecule and electrodes is weak, (b) there is electron−hole symmetry or pairing theorem[29] in orbital energies and MO expansion coefficients, and (c) the Fermi energy is located in the midgap of HOMO and LUMO. In fact, much of the work on molecular electronics is based on such molecules with large HOMO−LUMO gap and electron−hole symmetry. These assumptions are useful for a better understanding of a comprehensible relationship between the conductance of molecules and the Green's function formalism. According to Landauer's model, the conductance of a metal−molecule−metal junction in the limit of zero temperature and zero bias voltage is written as follows:[8]

$$g = \frac{2e^2}{h} T(E_\mathrm{F}) \tag{1}$$

where e is the magnitude of the charge on electron, h is the Planck constant, T is the transmission probability of electron, and E_F is the Fermi energy of electrodes. We can calculate the transmission probability for a metal−molecule−metal junction using the nonequilibrium Green's function method.[4] For a weak-coupling system, the Green's function of a molecule, what we call zeroth Green's function, plays an essential role in the calculation of electron transimission.[7] At the Fermi energy, the matrix elements of the zeroth Green's function, $G_{rs}^{(0)\mathrm{R/A}}$, which describes the propagation of a tunneling electron from site r to site s through the orbitals in a molecular part, can be written as follows:[32]

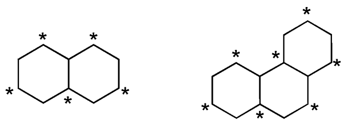
$$G_{rs}^{(0)\mathrm{R/A}}(E_\mathrm{F}) = \sum_k \frac{C_{rk} C_{sk}^*}{E_\mathrm{F} - \varepsilon_k \pm i\eta} \tag{2}$$

where C_{rk} is the kth MO coefficient at site r, asterisk on the MO coefficient indicates a complex conjugate, ε_k is the kth MO energy, and η is an infinitesimal number determined by a relationship between the local density of states and the imaginary part of Green's function.[7] Equation 2 tells us about an important correlation between the MOs and Green's function. The role of the HOMO and LUMO is significant in the zeroth Green's function because the denominators of the two orbitals are small in comparison with those of other MOs in eq 2 when we assume the Fermi energy of electrodes to lie between the HOMO and LUMO. The contributions from the HOMO and LUMO are written as follows:

$$\frac{C_{r\mathrm{HOMO}} C_{s\mathrm{HOMO}}^*}{E_\mathrm{F} - \varepsilon_\mathrm{HOMO} \pm i\eta} + \frac{C_{r\mathrm{LUMO}} C_{s\mathrm{LUMO}}^*}{E_\mathrm{F} - \varepsilon_\mathrm{LUMO} \pm i\eta} \tag{3}$$

Considering the reversed signs in the denominators in eq 3, we can develop an orbital rule that is useful for chemical understanding. To obtain effective electron

SCHEME 1



transport through a single molecule, (1) two atoms in which the sign of the product of the MO expansion coefficients in the HOMO ($C_{r\mathrm{HOMO}}C^*_{s\mathrm{HOMO}}$) is different from that in the LUMO ($C_{r\mathrm{LUMO}}C^*_{s\mathrm{LUMO}}$) should be connected with electrodes and (2) two atoms in which the orbital amplitudes of the HOMO and LUMO are significant should be connected with electrodes.

Electron Transport in π-Conjugated Systems

Having described essential features of the orbital rule, let us next consider electron transport properties in naphthalene that has direct contacts with two electrodes.[26] Naphthalene is an alternant π-conjugated system, in which the carbon atoms can be divided into two groups, *starred* and *unstarred*, in such a way that no two atoms of the same group are directly linked, as shown in Scheme 1.[29]

The MOs of naphthalene are shown in Figure 1, in which β is the resonance integral or transfer integral. Note that there is electron−hole symmetry or pairing theorem with respect to the MO energies and MO expansion coefficients of the alternant hydrocarbon within the framework of the simple Hückel method, in which the overlap integral is neglected. The zeroth Green's function of naphthalene can be easily calculated from the MO energies and MO expansion coefficients according to eq 2. If we assume the Fermi energy to lie in the midgap of the HOMO and LUMO, their contributions are significant in eq 2 since the denominators are small for the HOMO and LUMO. Therefore we can reasonably use eq 3 to intuitively evaluate the zeroth Green's function.

We can successfully predict from their orbital phase and amplitude that the two terms of eq 3 are enhanced in certain connections of atoms and canceled in other connections, as shown in Figure 2.[26] When the sign of the product of the orbital coefficients at sites *r* and *s* in the HOMO is different from the sign of the product of the orbital coefficients at sites *r* and *s* in the LUMO, the contributions from the HOMO and LUMO are constructively enhanced because the signs of the denominators $E_{\mathrm{F}} - \varepsilon_{\mathrm{HOMO}}$ and $E_{\mathrm{F}} - \varepsilon_{\mathrm{LUMO}}$ are different. Here *r* and *s* are connection atoms to electrodes. In order to further enhance the contributions from the HOMO and LUMO, two atoms in which the orbital amplitude of the HOMO and LUMO is large should be connected with electrodes. On the other hand, when the sign of the product of the orbital coefficients at sites *r* and *s* in the HOMO is the same as the sign of the product of the orbital coefficients at sites *r* and *s* in the LUMO, the contributions from the HOMO and LUMO are canceled. This relationship holds true also in a pair of HOMO − 1 and LUMO + 1, a pair of HOMO − 2 and LUMO + 2, and so on, due to the electron−hole symmetry at this level of theory.[29] Thus, electron transport is formally forbidden in such unfavorable connections.

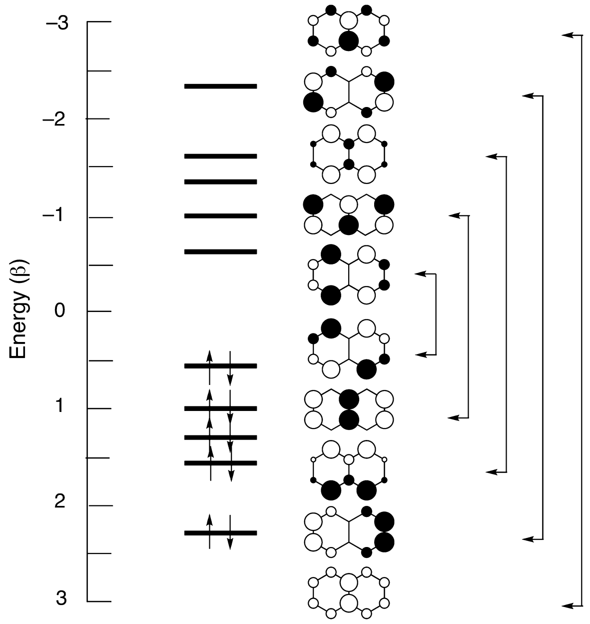


FIGURE 1. πMOs of naphthalene. Note that there is pairing theorem with respect to the MO energies and MO expansion coefficients.

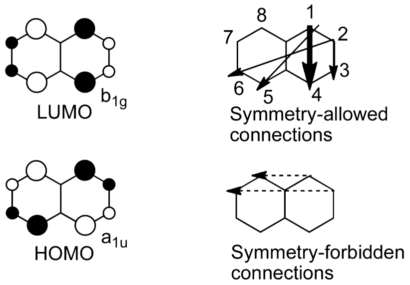


FIGURE 2. HOMO and LUMO of naphthalene and symmetry-allowed and symmetry-forbidden connections for electron transmission.

Thus, the transmission probability depends on how to connect the molecule to two electrodes. On the basis of the qualitative thinking about orbital phase, we can easily predict symmetry-allowed and symmetry-forbidden connections for transmission probability in naphthalene, as shown in Figure 2. The solid arrows show connections in which we expect finite transmission probability and the

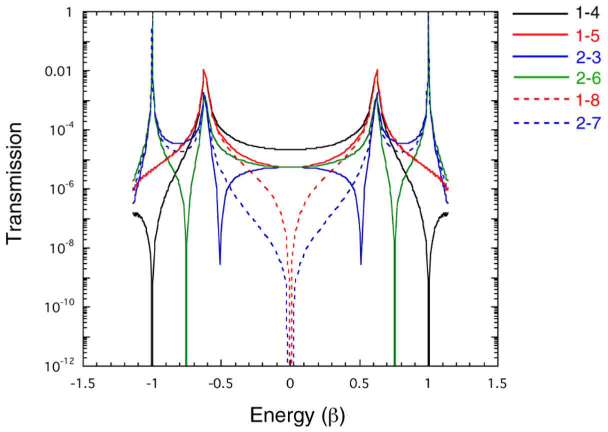


FIGURE 3. Transmission spectra for various connections of a metal–naphthalene–metal junction at the Hückel level of theory. The Fermi energy lies at energy zero. The solid and dotted lines indicate symmetry-allowed and symmetry-forbidden connections for electron transport, respectively.

dotted arrows show connections in which we expect no transmission probability. Note that orbital phase is essential for the characterization of this simple rule. As shown by the thick arrow, connection 1–4 (also 5–8) is predicted to be the best route for electron transport in naphthalene because the sign of the product of the orbital coefficients at sites 1 and 4 in the HOMO is different from that of the product of the orbital coefficients at sites 1 and 4 in the LUMO and at the same time the HOMO and LUMO are significantly localized at sites 1 and 4. Although connection 1–5 is less conductive than connection 1–4, this result is not due to the larger distance in connection 1–5. Partial cancellation occurs in some paired orbitals for connection 1–5 in the zeroth Green's function of eq 2.

Having described the qualitative orbital symmetry rule for the electron transport in naphthalene, we next look at computational results at the simple Hückel level of theory.[26] Computed transmission spectra for various connections of naphthalene are shown as a function of the energy of electron in Figure 3, where the solid lines show symmetry-allowed connections and the dotted lines show symmetry-forbidden connections. The sharp transmission peaks come from the so-called resonance tunneling effect at the location of MO levels. The transmission probability at the Fermi energy ($E = 0$) plays an important role for conductance, as mentioned earlier in eq 1. This computational result is fully consistent with the qualitative prediction based on the orbital symmetry discussion given above. As we expect, connection 1–4 has the largest transmission probability at the Fermi energy, whereas connections 1–8 and 2–7 have no transmission probability. Connections 1–5, 2–3, and 2–6 have similar transmission probabilities at the Fermi energy. The transmission probability in the symmetry-forbidden connections 1–8 and 2–7 is computed to be zero at the Fermi energy because the zeroth Green's function of eq 2 is completely canceled, due to the electron–hole symmetry for the MO energies and expansion coefficients within the framework of the simple Hückel method.

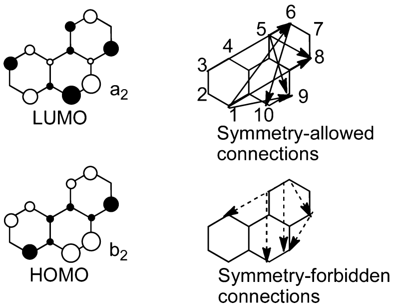


FIGURE 4. HOMO and LUMO of phenanthrene and symmetry-allowed and symmetry-forbidden connections for electron transmission.

In the same way, we are able to distinguish between symmetry-allowed and symmetry-forbidden connections for the transmission probability in phenanthrene, as shown in Figure 4. The qualitative predictions are in excellent agreement with transmission spectra computed at the Hückel level of theory.[26] In phenanthrene, connections 5–8, 5–9, 1–9, 1–6, 1–8, 6–10, and 3–6 show finite transmission probabilities, whereas connections 6–9, 4–6, 6–8, 8–9, and 5–10 have no transmission probabilities at the Fermi energy because the zeroth Green's function is canceled. Connection 9–10 is predicted to be the best route from the rule, but it is too close to construct a metal–molecule–metal junction for this connection.

Thus, the orbital symmetry rule is very useful for the prediction of essential electron transport phenomena in π-conjugated molecules. It has been extended to larger conjugated systems and heteroatomic systems.[33,34] Figure 5 shows HOMOs and LUMOs of various π-conjugated polycyclic aromatic hydrocarbons with acene-edge and phenanthrene-edge type structures and symmetry-allowed and symmetry-forbidden routes for electron transport. The applicability of the derived concept for orbital control of electron transport was tested on larger hydrocarbons in order to estimate its predictive power for different types of π-conjugated molecules.

Favorable connections for effective electron transport in π-conjugated systems with weak coupling between the molecules and electrodes are predicted on the basis of the orbital symmetry rule by looking at the phase and amplitude

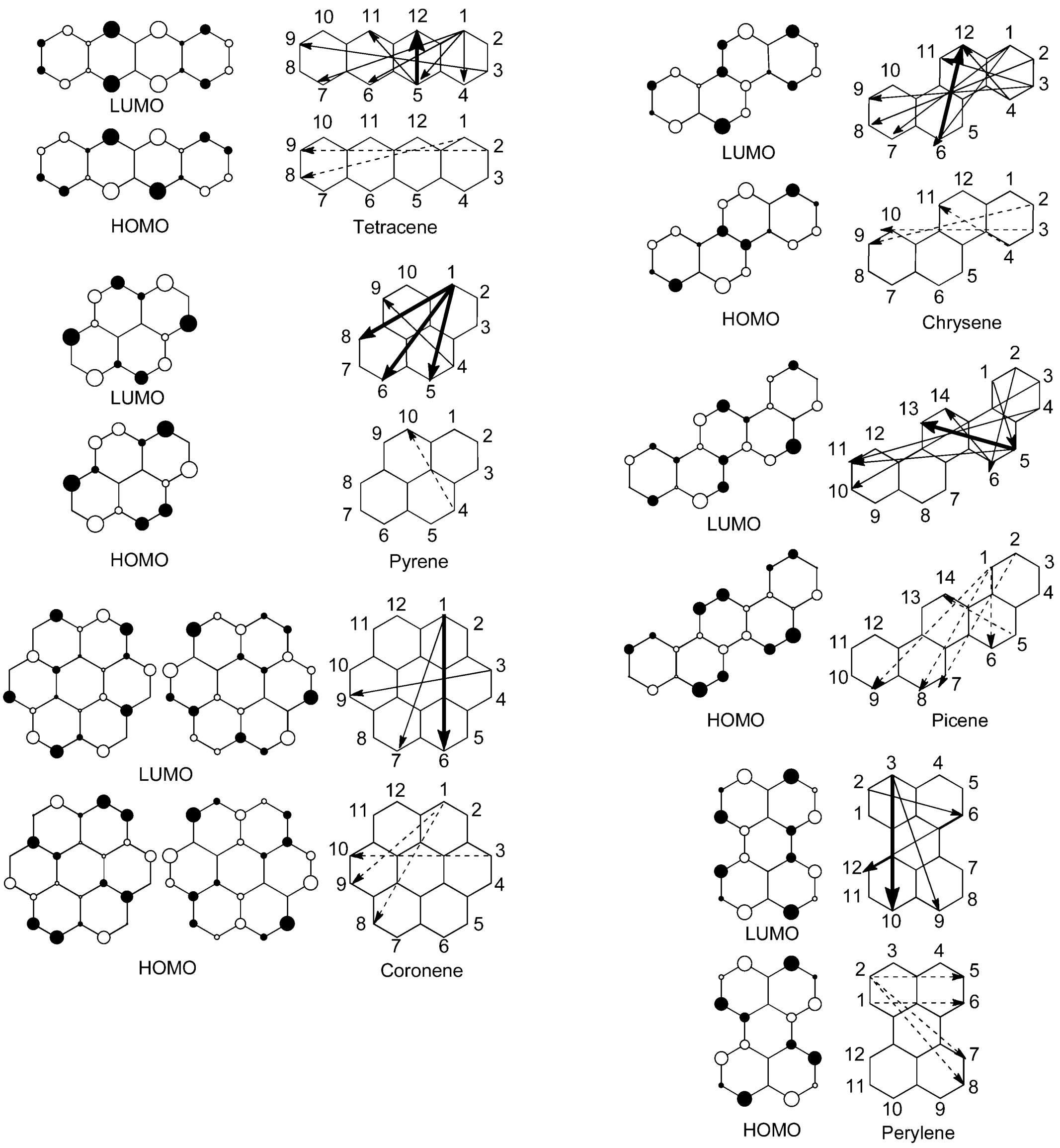


FIGURE 5. Frontier orbitals and symmetry-allowed and symmetry-forbidden connections for electron transport in acene-edge (left) and phenanthrene-edge (right) structures.

of the frontier orbitals. Qualitative predictions based on frontier orbital analysis were compared with DFT calculations for realistic molecular junctions with chemical bonds between a molecule and two gold electrodes.[33] Obtained results are in good agreement with the orbital rule predictions, which makes the frontier orbitals' analysis a powerful tool in electron transport studies in π-conjugated systems.

This rule is again summarized as follows: (1) the sign of the product of the orbital coefficients at sites *r* and *s* in the HOMO should be different from the sign of the product of the orbital coefficients at sites *r* and *s* in the LUMO, and (2) sites *r* and *s* in which the amplitude of the HOMO and LUMO is large should be connected. We might mention condition 1 in another way in terms of alternant hydrocarbon; *starred* and *unstarred* atoms should be connected, as shown in Scheme 1.[26] Since the transmission probability of an electron is determined by electronic states in the vicinity of the Fermi energy, where π orbitals are dominant, the simple Hückel method should work well for good understanding of the electron transport in π-conjugated systems. Essential orbital natures are similar among simple Hückel, extended Hückel, Hartree–Fock, and DFT calculations especially about symmetry;[35] therefore the qualitative orbital views are useful in rationalizing electron transport phenomena in molecules.

Perturbation by Anchoring Atoms

In an actual metal–molecule–metal junction, anchor groups play a crucial role in the fixing of molecule to metal

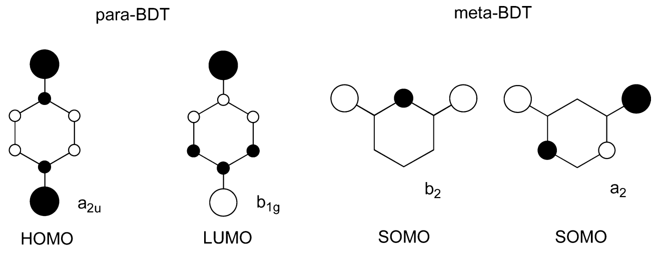


FIGURE 6. Frontier orbitals of *para*- and *meta*-benzene dithiols (BDTs) calculated with the HMO theory. The SOMOs are degenerate nonbonding orbitals.

electrodes. The most widely used anchor group that is tightly bound to gold electrodes is thiol because of the high binding affinity of sulfur atom with the gold surface, where Au−S chemical bonds are formed.[36−43] Sulfur atoms should influence the spatial distribution of the frontier orbitals and the energy level alignment of a molecule. Let us look at the frontier orbitals of benzene dithiol (BDT) derivatives with two anchoring sulfur atoms.[44] Figure 6 shows that in *para*-BDT the product of the MO coefficients on the two anchoring sulfur atoms in the HOMO is different in sign from that in the LUMO and the orbital amplitudes of the HOMO and LUMO on those atoms are sufficiently large. Therefore the electron transport through *para*-BDT is also symmetry-allowed. The orbital rule holds true for the *para*-dithiol derivative.

In *meta*-BDT the b_2 SOMO and the a_2 SOMO are degenerate, which is accidental degeneracy from the nonbonding character. The *meta*-isomer belongs to the group of *non-Kekulé* molecules,[29] for which no classical structure can be drawn. It is impossible to draw a structure in which the constituent atoms are all linked in pairs by double bonds. Alternant hydrocarbons with n^* starred atoms and n unstarred atoms have ($n^* - n$) nonbonding MOs (NBMOs). Longuet−Higgins proposed a similar rule to predict the existence of NBMOs; alternant hydrocarbons have at least ($N - 2T$) NBMOs, in which N denotes the number of carbon atoms in the conjugated system and T denotes the maximum number of double bonds occurring in any resonance structure.[45] The degeneracy of NBMOs is called topological degeneracy since it is determined by the sequence of carbon atoms forming the conjugated system. This topological rule gives us a general strategy for the synthesis of organic ferromagnets.[46−49] We can regard the b_2 SOMO and the a_2 SOMO as degenerate NBMOs by expanding the concept of the topological degeneracy to the molecules having heteroatoms. The two MOs are in fact degenerate in energy at any level of calculation, due to the nonbonding character, that is, no nearest neighboring interactions. This molecule is thus a diradical species. It is reasonable to treat the molecule as a diradical species rather than a dianionic species because such a dianion is supposed to be formed as a result of interaction with electrodes. In order to apply the orbital rule to the degenerate system, let us look again at the zeroth Green's function. In the sense of eq 3, the values of the denominators of the b_2 SOMO and the a_2 SOMO are the same because of the degeneracy, and the sign of the product of the orbital coefficients at the sulfur sites in the b_2 SOMO is different from the sign of those at the sulfur sites in the a_2 SOMO. As a consequence, cancellation occurs between the b_2 SOMO and the a_2 SOMO, and we can therefore predict that the electron transport through *meta*-BDT is symmetry-forbidden. The orbital symmetry rule for electron transport in *para*-BDT and *meta*-BDT is consistent with the quantum interference discussion about the transport properties in the molecules.[50−53]

In terms of orbital interactions, one can reasonably characterize the difference between the electronic structures of *para*-BDT and *meta*-BDT, which can be theoretically built up from the benzene molecule and a virtual disulfur molecule. Let us apply the fragment molecular orbital (FMO) method[54] for this purpose. An orbital interaction diagram based on extended Hückel calculations[55] for *para*-BDT is shown in Figure 7, where only π orbitals are considered.[44]

Since the interaction between the two sulfur atoms is negligible due to the large distance, the π_u and π_g orbitals consisting of the $3p_z$ AOs of the sulfur atoms are nearly degenerate. The $e_{1g}{}^1$ HOMO of benzene and the π_g orbital of the disulfur molecule interact at the *para* sites so that the out-of-phase combination b_{1g} orbital, which results in the LUMO of *para*-BDT, is destabilized. Since the $e_{2u}{}^1$ LUMO of benzene and the π_u orbital of the disulfur molecule also interact nicely, the in-phase combination a_{2u} orbital, which results in the HOMO of *para*-BDT, is stabilized. As a consequence, the symmetry of the HOMO and LUMO of benzene is switched in *para*-BDT. Thus, the orbital rule is conserved in *para*-BDT since the combination of symmetry in the HOMO and LUMO remains unchanged.

Figure 8 shows an orbital interaction diagram for *meta*-BDT, in which the a_2 SOMO and the b_2 SOMO are degenerate, due to the nonbonding character.[44] In the case of *meta*-BDT, both the $e_{1g}{}^1$ HOMO and the $e_{2u}{}^1$ LUMO of benzene interact with the π_u orbital of the virtual disulfur to form the b_2 SOMO. In a similar way, both the $e_{1g}{}^2$ HOMO and the $e_{2u}{}^2$ LUMO of benzene mix with the π_g orbital of disulfur to form the a_2 SOMO. Thus, the two SOMOs of *meta*-BDT are generated as a consequence of the mixture of the

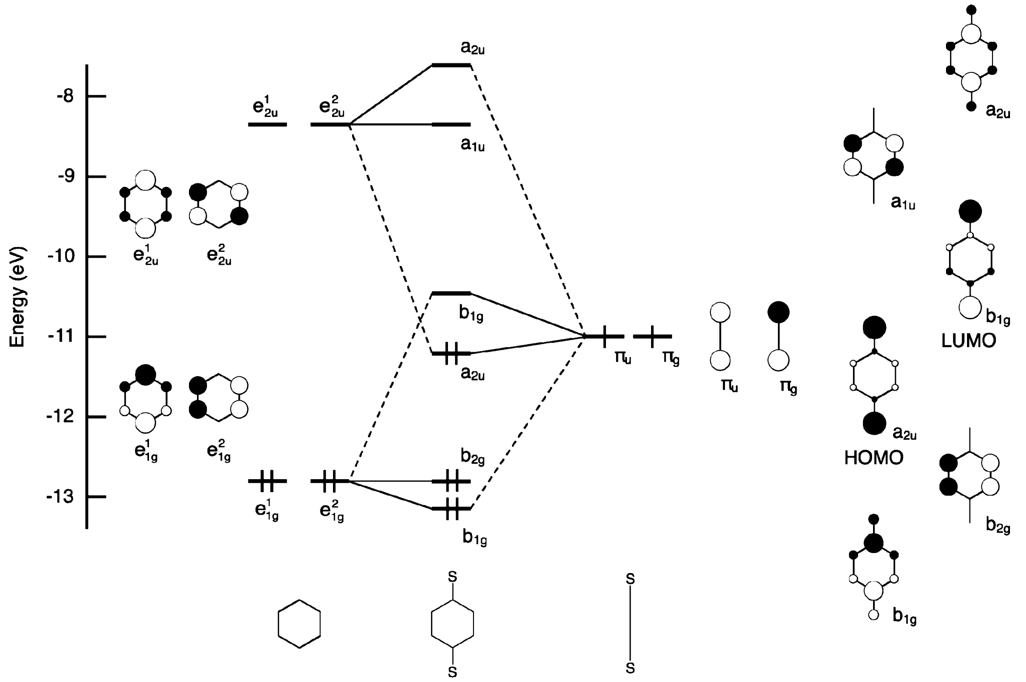


FIGURE 7. Orbital interaction diagram for *para*-BDT partitioned into benzene and a virtual disulfur molecule.

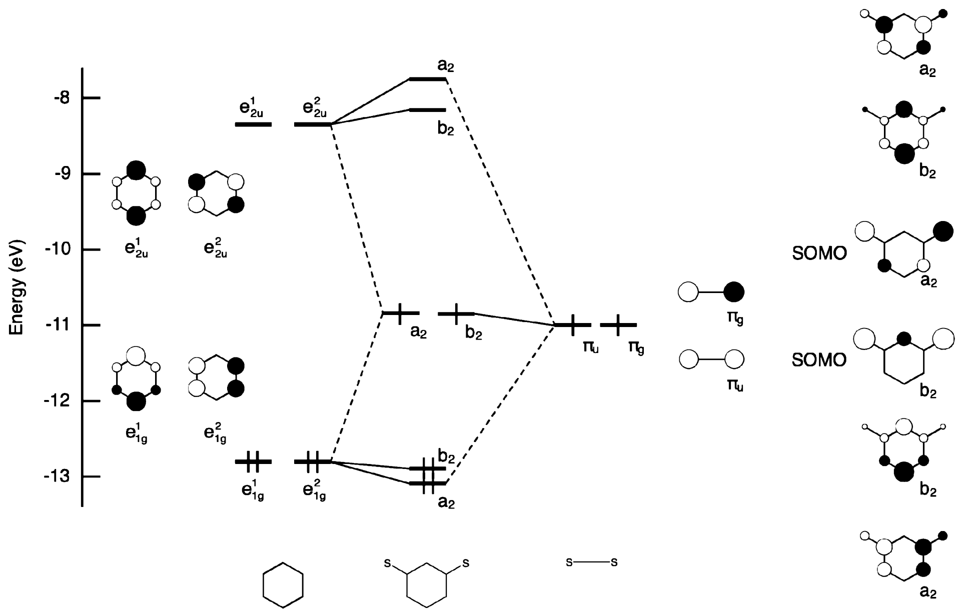


FIGURE 8. Orbital interaction diagram for *meta*-BDT partitioned into benzene and a virtual disulfur molecule.

degenerate HOMOs and LUMOs of benzene and the bonding and antibonding π orbitals of the disulfur molecule.

The validity that the orbital rule can work in molecules including the anchoring sulfur atoms lies in the energy level locations of the sulfur and gold atoms. The 3p AO in sulfur is very close to that of the 2p AO in carbon. The levels of the 3p AO in sulfur and the 2p AO in carbon are −11.0 and −11.4 eV, respectively.[56] Since the two π orbitals of the disulfur molecule are located nearly in the midgap of the degenerate HOMOs and LUMOs of benzene, the two π orbitals can almost equally interact with the degenerate HOMO and LUMO of benzene. As a consequence, the MOs perturbed by the anchoring sulfur atoms still retain the electron−hole symmetry.[44] Since the Au−S bond is weak compared with the C−C and C−S bonds, we can reasonably use the zeroth Green's function of eq 2 on the basis of the weak coupling assumption. The 6s AO in gold (-10.9 eV) is located close to both the 3p AO in sulfur and the 2p AO in carbon. It is reasonable to assume the Fermi energy to lie between the HOMO and LUMO in general. We can therefore use the necessary preconditions for the application of the orbital-based arguments for electron transport in π-conjugated molecules.

Experimental Confirmation of the Orbital Rule

To confirm the orbital rule experimentally, we carried out the syntheses and conductance measurements of 1,4-, 1,5-, 2,6-, and 2,7-naphthalene dithiol (NDT) derivatives by collaboration with experimental groups of the University of Tokyo and Osaka University.[57] Figure 9 shows HOMOs and LUMOs and measured conductances for the four kinds of NDT derivatives. Only 2,7-NDT is symmetry-forbidden for electron transport. It has 2-fold degenerate SOMOs, which are singly occupied. The values of the denominators in eq 3 are same, due to the degenerate SOMOs, and the sign of the product of the orbital coefficients at the sulfur sites in one SOMO is different from that in the other SOMO. Therefore cancellation occurs between the two SOMOs in the sense of eq 3, and we therefore expect that the electron transport through 2,7-NDT is symmetry-forbidden. One can thus apply the orbital rule to the molecule with anchoring sulfur atoms just like the molecule without anchors, that is, naphthalene, as shown in Figure 2.

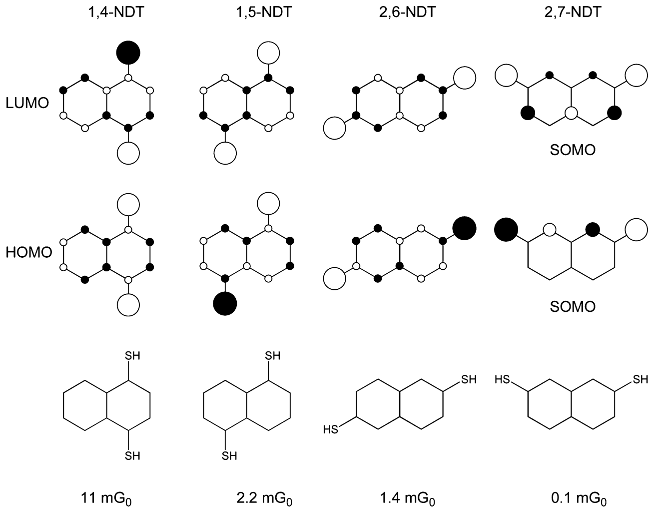


FIGURE 9. Frontier orbitals of naphthalene dithiol (NDT) derivatives and their measured conductances. Conductance g is proportional to the transmission probability at the Fermi energy $T(E_F)$; $g = G_0T(E_F)$, where G_0 is the quantum conductance constant ($2e^2/h$).

The molecular conductance of the NDT single-molecule junctions was measured at room temperature in vacuum using the nanofabricated mechanically controllable break junction technique.[58] As shown in Figure 10, measured conductance histograms of the 1,4-, 1,5-, and 2,6-NDT junctions show pronounced peaks at 11, 2.2, and 1.4 mG$_0$, respectively, whereas the 2,7-NDT junction shows a low peak at 0.1 mG$_0$.[57] We can reasonably conclude that the significant difference in the molecular conductances should come from the difference in the phase relation of the frontier orbitals, as discussed earlier in this Account. The remarkable response of the molecular conductance to the orbital phase demonstrates that single-molecule junctions are applicable to quantum devices. We also investigated voltage

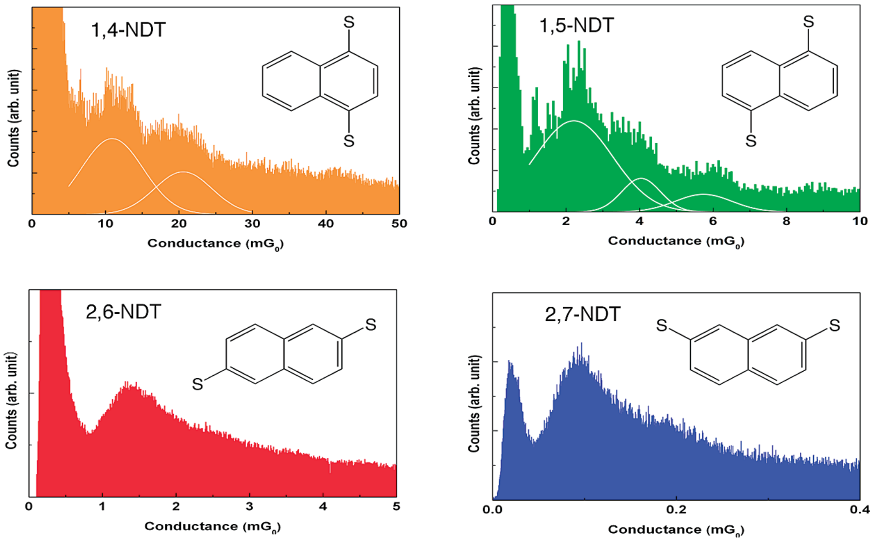


FIGURE 10. Measured conductance histograms of 1,4-, 1,5-, 2,6-, and 2,7-NDT junctions. White lines in 1,4- and 1,5-NDT are Gaussian fits to the peak profiles.

dependence of single-molecule conductance by measuring current−voltage characteristics in a bias region of −0.8 to 0.8 V when the nanoelectrode gaps were fixed in the distance where single-molecule conductance was obtained. In the voltage window, the current−voltage characteristics also showed a single-molecule conductance order of 1,4-NDT > 1,5-NDT > 2,6-NDT > 2,7-NDT. The simple orbital rule for electron transport in single-molecule junctions provides a guiding principle for designing molecules that yield desirable molecular conductance.

Summary and Conclusions

In this Account, chemical understanding of electron transport properties in molecules is presented in terms of the orbital concept. We propose an orbital rule for electron transport properties in π-conjugated molecules, demonstrating that the phase and amplitude of HOMO and LUMO play an essential role in the physical phenomena. Qualitative predictions based on the orbital concept would help our intuitive understanding of the electron transport phenomena in single-molecular devices. The orbital thinking directly derives from Green's function theory while the frontier orbital theory[27] and the Woodward−Hoffmann rules[28] for chemical reactions are based on second-order perturbation theory. We investigated the applicability of the theoretical concept on aromatic hydrocarbons with anchoring units by analyzing effects of the sulfur atoms on orbitals and electron transport properties.[44] The results clearly demonstrate that the orbital view predictions hold true for molecules perturbed by the anchoring units. We experimentally confirmed the orbital rule from the direct comparison of measured conductances of naphthalene dithiol derivatives.[57] Dependence of molecular wire length,[59,60] molecular photoresponsibility,[61−63] and molecular rectification[64,65] were investigated on the basis of the orbital discussion. The rule was recently extended to electron transport properties of cyclophanes for a better understanding the intermolecular interaction in molecular crystals.[66]

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BIOGRAPHICAL INFORMATION

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FOOTNOTES

The authors declare no competing financial interest.

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