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Molecular Scale Rectifier: Theoretical Study

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The geometric and electronic structures of polyphenyl-based conjugated molecules (donor-spacer-acceptor), potential candidates for molecular rectifying devices, have been investigated theoretically using *ab initio* quantum mechanical calculations. The individual donor (n-type) and acceptor (p-type) molecular devices have been designed by substituting one or two of the hydrogen atoms of benzene with $-NH_2$ and $-NO_2$ functional groups, respectively. The molecular rectifier has been modeled by combining donor and acceptor molecules with methylene or dimethylene functional groups. The electronic rectification behavior in these molecules has been analyzed from the molecular orbital energy levels and the spatial orientations of the unoccupied molecular orbitals. The results suggest that in such donor−acceptor molecular complexes, while the lowest unoccupied orbital is localized on the acceptor ring, the highest occupied molecular orbital is localized on the donor ring. The approximate potential differences for mono substituted donor−acceptor complexes have been estimated to be 1.56 and 2.05 eV for the $-CH_2-$ and $-CH_2-CH_2-$ spacers, respectively. It is found that for the disubstituted rectifier complex, the potential difference increases to 2.76 eV.

1. Introduction

Radical developments in the field of molecular electronics during the past few years have opened up enormous possibilities for organic chemists to synthesize suitably tailored organic structures, considered to be potential candidates for the ultimate miniaturization of nano-electronic devices. The excitement is evident from the large number of recent reviews and articles appearing in leading scientific journals.[1−4] A quarter century ago, Aviram and Ratner[5] first theoretically demonstrated the possibility of an organic molecule to function as a molecular rectifying diode. Since then, in a remarkable series of experimental demonstrations, chemists, physicists, and engineers have shown that substituted polyphenylenes and similar small organic molecules can conduct, switch electrical current, and store information.[6−8]

Aromatic molecules such as benzene and polyphenylenes have π-conjugation through which electrons can flow easily. Typically, to show rectifying properties on the molecular scale, a molecule should have roughly the properties of a bulk-effect solid-state p−n junction diode. It is possible to realize p-type (acceptor) and n-type (donor) molecular subunits by substituting benzene or other symmetric aromatic molecules with electron-withdrawing or electron-donating functional groups. Therefore, a molecular rectifier could be built by combining these two donor and acceptor molecular subunits between two electrodes in which electrons can flow from the cathode to the acceptor or from the donor to the anode.

For an active device such as a rectifier diode or transistor, one needs to control the flow of electrons to obtain the desired electronic properties. In the case of a benzene molecule substituted by an electron-withdrawing group, the π -electron density in the benzene ring is reduced, whereas for the substitution of an electron donating group, the π-electron density is enhanced. From theoretical understanding, we know that the effect of the electron density directly reflects on the electronic structure of the corresponding molecules. Hence, the understanding of the discrete molecular orbital energy levels is necessary to manipulate the electron transport across the molecule. In the case of donor substituted benzene, the energy levels of the HOMO and LUMO states increase because of greater electron−electron repulsion, whereas in the case of acceptor substituted benzene, the energy levels of the HOMO and LUMO states decrease due to a relative decrease in the electron density.

In a recent review article by Ellenbogen *et al.*,[9] a number of monosubstituted and disubstituted polyphenyl compounds were chosen to study the rectification behavior in this class of molecules. It is assumed that the unoccupied orbitals provide channels for electron conduction through the molecules. The difference in the energy of the lowest unoccupied levels between the isolated substituted benzene molecules was used to estimate the approximate value of potential drops (P.D.) across the molecule and thereby the effectiveness of the combined molecule to behave as a molecular rectifier. However, for a chemically bonded D−S−A (donor−spacer−acceptor) molecular complex, the potential drop is measured as the difference between the unoccupied orbitals localized on the donor and acceptor sides.

In the present work, our interest is to design a new intramolecular complex with donor and acceptor molecular subunits and to explore the possibility of its working as a molecular rectifier device through electronic structure calculations. The donor and acceptor molecules are connected via an aliphatic chain like methylene ($-CH_2-$) or dimethylene ($-CH_2-CH_2-$), which acts like a spacer and provides a potential barrier for the electron transport from one end to other. The plan of this work is as follows. First, we discuss the results of the geometry and electronic structure optimizations of a few individual monosubstituted donor and acceptor benzene molecules. These calculations are necessary to explore suitable combinations in terms of approximate potential differences. The potential drop in a vacuum can be explained as the difference

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in the LUMO energies between the donor and acceptor molecules when they are widely separated ($\Delta E_{\mathrm{LUMO}}(\infty) = E_{\mathrm{LUMO(donor)}} - E_{\mathrm{LUMO(acceptor)}}$). The geometry of the chemically bound donor−spacer−acceptor complex has been optimized to calculate the potential-drop across the central insulating barrier of the aliphatic groups. Second, we have optimized the geometries and energetics of the disubstituted benzene molecular rectifier using the same electron-donating and electron-withdrawing groups connected via the dimethylene spacer group. The motivation for the second part of this work is to design a new rectifier molecule with a larger potential drop by changing the electron density on the donor−acceptor aromatic rings. Qualitatively, it can be imagined that under a bias voltage, an electron passes from one end to other, and therefore, it is expected that, instantaneously, the rectifier molecule will be in a negative charged state instantaneously. To see the effect of the excess negative charge localization on different atoms, we have also performed a geometry optimization for the disubstituted molecular complex having one excess electron.

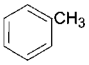
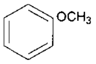
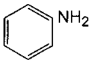
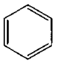
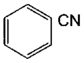
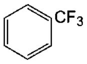
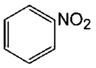
2. Computational Details

The total energy calculations have been performed under density functional theory (DFT) formalism.[10] The exchange and correlation energies have been calculated using a hybrid functional. We have opted to use hybrid functional over Hartree−Fock (HF) method, as it can account for correlation effects also. Although HF describes exchange exactly, it results in unbound LUMO states. In the present calculation, well descriptions of the LUMO states are very important, as the incoming electrons are assumed to pass through it. Therefore, the use of hybrid functional in DFT formalism is fully justified. Several successful applications using hybrid functionals have been reported.[11−12] All calculations were performed using the Gaussian98 program[13] at the B3LYP level of theory.[14−15] The notation B3 indicates a three-parameter Becke exchange functional, where a portion of the exchange contribution has been calculated in the same fashion as that in the Hartree−Fock (HF) procedure but using the Kohn−Sham noninteractive wave function instead of the HF wave function. LYP indicates the Lee−Yang−Parr correlation functional.[16] The 6-311G valence triple-ζ basis set augmented with polarization functions was used.

3. Results

3.1. Preliminary Studies on Monosubstituted Benzene. To precisely understand the dopant-induced effects on benzene molecules, we have first optimized the geometries of a number of monosubstituted benzene molecules with donor and acceptor ligands. The calculated results for the HOMO and LUMO energies are listed in Table 1. The HOMO and LUMO energies obtained for these molecules are different than those recently reported by J. C. Ellenbogen et al. for similar molecules.[9] The reason for this difference is because in the previous calculations the HOMO and LUMO energies were calculated at the Hartree−Fock level, where the LUMO levels tend to be greatly overestimated. The hybrid method, which we have used, results in more physical HOMO−LUMO gaps.[11] Table 1 shows a comparison of the energetics of different monosubstituted benzenes with electron donation and electron-withdrawing groups. It is clear from the table that when electron-donating groups such as $-NH_2$, $-CH_3$, or $-OCH_3$ is attached to the benzene ring, the HOMO and LUMO energy levels increase. The converse is true when an electron-withdrawing group like $-NO_2$, −CN, or $-CF_3$ is attached to the benzene ring. This effect is due to the increase in electron density in the aromatic ring by electron-donating groups and a corresponding decrease by electron-withdrawing groups. Therefore, one can imagine that the substitution of aromatic rings by an electron-withdrawing group can make an aromatic ring behave like a p-type molecular device while substitution of an aromatic ring by an electron-donating group results in an n-type molecular device.

TABLE 1: Calculated HOMO and LUMO Values of the Monosubstituted Benzenes Using B3LYP/6-311G(d,p) Method for Optimization

system	HOMO (eV)	LUMO (eV)	HOMO−LUMO (eV)
toluene 	−6.71	−0.47	−6.24
methoxybenzene 	−6.22	−0.46	−5.76
aniline 	−5.57	−0.32	−5.25
benzene 	−7.07	−0.46	−6.61
benzonitrile 	−7.62	−1.84	−5.78
triflurotoluene 	−7.67	−1.33	−6.34
nitrobenzene 	−7.95	−2.91	−5.04

The energy difference between the LUMO energies of individual n-type and p-type molecules ($\Delta E_{\mathrm{LUMO}}(\infty)$) can be used as an approximate measure of the potential drops across a molecule chemically bonded by n-type and p-type molecular subunits. From Table 1, it is seen that the potential difference between the LUMO levels of aniline and nitrobenzene is the largest among the different combinations of donor ($-OCH_3$, CH_3, NH_2) and acceptor (−CN, CF_3, NO_2) ligands (($\Delta E_{\mathrm{LUMO}}(\infty) = 2.59$ eV). From these results, it is found that the HOMO and LUMO energy levels of the aniline molecule ($-NH_2$ substitution) increase by 1.50 and 0.14 eV, respectively, as compared to the benzene molecule. Expectedly, for the nitrobenzene ($-NO_2$ substitution) molecule, the HOMO and LUMO energy levels are lowered by 0.88 and 2.45 eV, respectively. However, the effects of both electron withdrawing and electron donating groups are found to be similar with respect to the HLG (HOMO−LUMO Gap); i.e., in both cases the aniline and nitrobenzene molecules reduce the HLG as compared to the unsubstituted benzene. In particular, when an $-NH_2$ or $-NO_2$ group is substituted in the benzene ring, the HLG of the benzene molecule (originally 6.61 eV) is reduced to 5.25 or 5.04 eV, respectively.

On the basis of the above results, it is of interest to investigate the electronic structure for a combined molecular complex of aniline and nitrobenzene subunits. An aliphatic group is required to be attached between the n-type and p-type molecules to act like a spacer and form a potential barrier to electron transport across the molecule. Accordingly, we have decided to use spacers such as $-CH_2-$ or $-CH_2CH_2-$ between the aniline and nitrobenzene subunits to form an intramolecular donor−

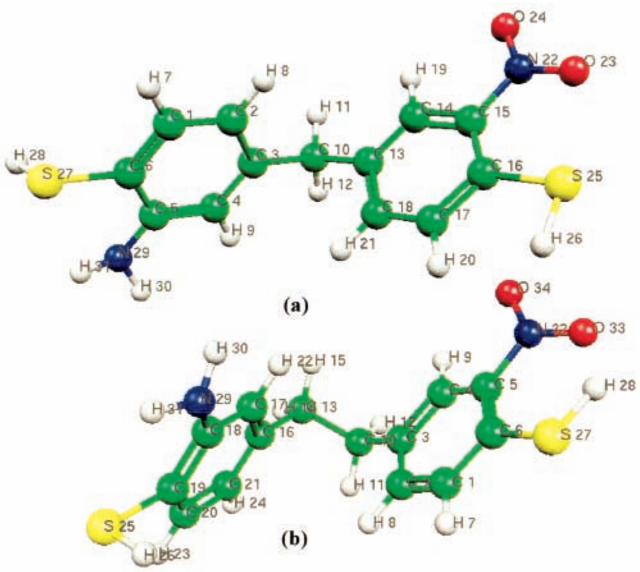


Figure 1. Optimized geometry for the monosubstituted donor−spacer−acceptor molecular complex separated by methylene (1a) and dimethylene (1b) functional groups. The donor and acceptor subunits are created by substitution of the $-NH_2$ and $-NO_2$ functional groups in the benzene ring. The geometry is optimized at the B3LYP/6-311G++(d,p) level of theory.

spacer−acceptor (D−S−A) rectifier. Two different length spacers are chosen to examine the effect on the geometry of the combined molecule and the potential drop across the molecule as the length of the spacer increases. In the following, we discuss about the possibility of the combined molecule to show electrical rectification behavior from the corresponding electronic energy level diagram and orbital spatial orientation. To show electrical rectification, the molecular energy levels should typically orient in such a way that the electrons can flow in one direction while in the other direction the flow of electrons should be blocked.

3.2. Calculations for the Monosubstituted Molecular Rectifier. Figure 1a,b shows the structures of the two proposed molecular rectifiers chemically bonded by n-type (aniline) and p-type (nitrobenzene) molecular subunits. Methylene and dimethylene groups are used as spacer groups to combine the aniline and nitrobenzene molecules. Both ends of these molecules are terminated using thiol (−S−H) groups, which are known to have a high electron affinity for Au electrodes. The geometries of molecules 1a and 1b have been optimized at the B3LYP/6-311G++(d,p) level of theory. Significant effects from the polarization functions as well as the diffuse functions are observed in the ground-state geometry and the electronic structure of the molecules. For example, when the geometries are optimized excluding the polarization functions (B3LYP/6-311G), the H atoms of the NH_2 group lie in the same plane as the adjacent ring. However, when polarization functions are included, the optimized geometry of molecule 1a shows that the H atoms of NH_2 group make a dihedral angle of 20° with respect to the adjacent benzene ring. The angles ∠CCN, ∠CNH, and ∠HNH are 120°, 116°, and 114°, respectively. For molecule 1b, the optimized geometry shows that the H atoms of the NH_2 group and the O atoms of the NO_2 group orient similar to the orientation obtained for molecule 1a. The angle between the planes of the two benzene rings becomes almost perpendicular. Figure 2 shows the molecular orbital energy levels of the individual donor and acceptor molecules as compared to those of the intramolecular donor−acceptor molecular complexes corresponding to molecules 1a and 1b. From this figure, it is clear that the while the $-NH_2$ group increases the energy levels, the $-NO_2$ group has an opposite effect. It is interesting to note here that while the LUMO energy levels of molecules 1a and 1b compare well with the LUMO energy level of the nitrobenzene molecule, the HOMO energy levels of molecules 1a and 1b are closer in energy with the HOMO energy level of the aniline donor. This can be attributed to the localization of the HOMO and LUMO energy levels on the donor and acceptor sides of the D−S−A molecular complex, respectively.

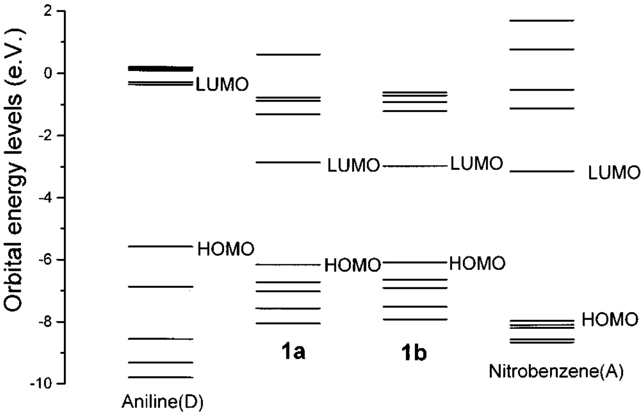


Figure 2. Comparison of the five highest occupied and five lowest unoccupied orbital energy levels for aniline (donor), nitrobenzene (acceptor) and molecules 1a and 1b (shown in Figure 1).

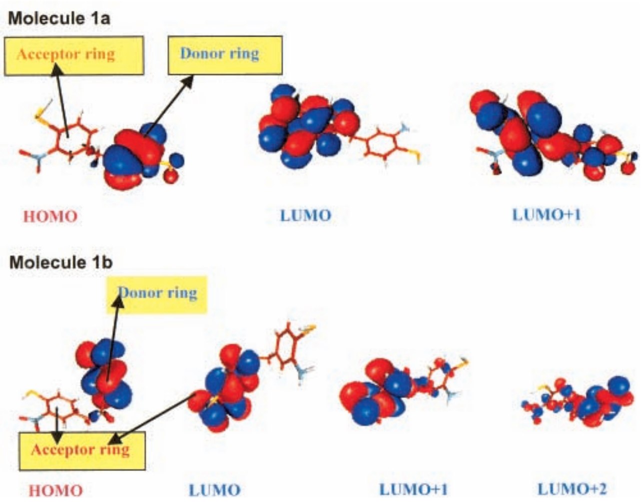


Figure 3. Orbital spatial orientation of HOMO, LUMO, and LUMO+1 for molecule 1a and HOMO, LUMO, LUMO+1, and LUMO+2 for molecule 1b. Molecules 1a and 1b are shown in Figure 1.

To understand the electron transport through this molecule, we have analyzed the spatial extent of the frontier orbitals (HOMO and LUMO), which provides a strategy by which the rectifying properties of this molecular system can be understood. Figure 3 shows the HOMO and LUMO+K (K = 0, 1, 2) plots of molecules 1a and 1b. It has been suggested[9] that the potential drop ΔE_{LUMO} across each molecular rectifier is determined from the difference between E_{LUMO} and the $E_{\mathrm{LUMO}+K}$ for an unoccupied orbital localized on the opposite (donor) side of the molecule from the LUMO. It is generally observed that while the HOMO is localized on the donor ring, the LUMO is localized on the acceptor ring. Therefore, in a rectifying diode, the electrons are injected from the cathode to the LUMO state on the acceptor side. The incoming electron on the acceptor LUMO is then transferred to the lowest unoccupied orbital localized on the donor ring. Therefore, if one can apply a bias voltage, the value of which is E_{LUMO} (donor) − E_{LUMO}

TABLE 2: Mulliken Point Charge Distributions for the Neutral and Singly Negatively Charge Molecules Proposed as Molecular Rectifiers as Shown in Figures 1 and 4[a]

molecule 1a (neutral)		molecule 1a (anion)		molecule 1b (neutral)		molecule 1b (anion)		disubstituted molecular rectifier (neutral)		disubstituted molecular rectifier (anion)	
1C	−0.103	1C	−0.111	1C	−0.076	1C	−0.088	1C	0.095	1C	0.180
2C	−0.082	2C	−0.070	2C	−0.011	2C	−0.093	2C	0.035	2C	−0.027
3C	0.023	3C	0.033	3C	−0.124	3C	−0.109	3C	−0.349	3C	−0.251
4C	−0.192	4C	−0.194	4C	−0.020	4C	−0.081	4C	0.203	4C	0.212
5C	0.535	5C	0.534	5C	0.195	5C	0.196	5C	−0.048	5C	−0.028
6C	−0.484	6C	−0.484	6C	−0.194	6C	−0.215	6C	−0.066	6C	−0.143
10C	−0.532	10C	−0.536	10C	−0.184	10C	−0.183	9N	−0.474	9N	−0.529
								12N	−0.487	12N	−0.530
13C	0.033	13C	0.055	13C	−0.167	13C	−0.158				
14C	−0.160	14C	−0.221					15C	−0.246	15C	−0.169
15C	0.315	15C	0.323	16C	−0.118	16C	−0.106				
16C	−0.264	16C	−0.286	17C	−0.030	17C	−0.015	18C	−0.100	18C	−0.176
17C	−0.156	17C	−0.166	18C	0.225	18C	0.215				
18C	−0.030	18C	−0.103	19C	−0.347	19C	−0.335	21C	−0.072	21C	−0.085
				20C	−0.015	20C	−0.017	22C	0.121	22C	0.010
22N	−0.003	22N	−0.050	21C	−0.082	21C	−0.078	23C	−0.002	23C	−0.015
23O	−0.260	23O	−0.424					24C	−0.220	24C	−0.248
24O	−0.274	24O	−0.440	25S	−0.018	25S	−0.063	25C	0.209	25C	−0.043
				27S	0.048	27S	−0.115	26C	−0.032	26C	0.043
25S	0.2005	25S	0.093								
27S	0.023	27S	−0.012	29N	−0.470	29N	−0.472	29N	0.180	29N	0.255
								30O	−0.263	30O	−0.313
29N	−0.907	29N	−0.916	32N	0.171	32N	0.118	31O	−0.265	31O	−0.283
								32N	0.147	32N	0.177
				33O	−0.300	33O	−0.454	33O	−0.250	33O	−0.291
				34O	−0.252	34O	−0.428	34O	−0.241	34O	−0.306
								35S	0.173	35S	−0.002
								37S	−0.018	37S	−0.057

[a] The charges on the H atoms are not shown for the sake of simplicity. The numbering of the atoms is shown in Figures 1 and 4.

(acceptor), then the tunneling of electrons from one end to the other is possible. From Figure 3, it is clear that for molecule 1a, the LUMO is localized on acceptor, while the LUMO+1 is localized on the donor, thereby resulting a potential drop of $\Delta E_{\mathrm{LUMO}} = E_{\mathrm{LUMO+1}} - E_{\mathrm{LUMO}} = 1.56$ eV. For molecule 1b, the LUMO is localized on the acceptor, and the LUMO+2 is localized on the donor. The resulting potential drop thus increases to 2.05 eV. The increase in the potential barrier for molecule 1b is important and can be attributed to the following reasons. Spacers are typically aliphatic groups with sigma bonds that lie along the axis of the atoms. Such bonds create obstacles for the transport of negatively charged electrons. Therefore, such functional groups are used as electrical registers in a molecular circuit. This could be the reason for the increase of the potential barrier for molecule 1b as compared to that for molecule 1a.

Single-point energy calculations on the optimized geometries of molecules 1a and 1b were performed for the corresponding anions to understand the localization of the excess charge on these molecules. The Mulliken charge distribution for molecules 1a and 1b and their corresponding negative ions is shown in Table 2. It is seen that the excess charge is mainly localized on the NO_2 group attached to the acceptor ring and does not affect the donor ring. This result further corroborates the localization of the lowest unoccupied orbital on the acceptor side.

3.3. Calculations for a Combined Molecular Rectifier with Disubstituted Benzenes. A large potential drop across a rectifier molecule is desirable to ensure robust operation under a range of voltages in molecular circuits. To increase the intrinsic potential drop across the molecular rectifiers, we have studied the disubstituted donor−acceptor complex where one benzene ring is substituted by two $-NO_2$ groups at the 1,4 positions and another benzene ring is substituted by two $-NH_2$ groups also at the 1,4 positions. The HOMO and LUMO energies for 1,4 diamino benzene is found to be 0.84 and 0.19 eV higher than those of the corresponding monosubstituted amino benzene (aniline). For 1,4 dinitrobenzene, the HOMO and LUMO energies are lowered by 1.02 and 0.63 eV, respectively, as compared to those of monosubstituted nitrobenzene. The approximate potential drop across the donor−acceptor molecular complex is obtained by the difference between the LUMO energies of the donor and acceptor individual molecular subunits. The approximate value of the potential drop for 1,4 diaminobenzene and 1,4 dinitrobenzene is calculated to be 3.31 eV.

On the basis of the above results, it is expected that the substitution of benzene by two electron donating and electron-withdrawing functional groups could lead to an effective increase in the potential drop ($E_{\mathrm{LUMO(acceptor)}} - \mathrm{E}_{\mathrm{LUMO(donor)}}$) across the molecular complex as compared to that of the monosubstituted donor−acceptor complex. In the present calculation, the dimethylene group is used as a spacer to combine the substituted donor−acceptor benzene molecules. The ends of the benzene rings are terminated by thiol (−SH) groups, which pave the path for injection and ejection of electrons to and from the metal electrodes.

Figure 4a shows the optimized geometry for the combined disubstituted molecule proposed to behave like a prototype molecular rectifier. After the geometry optimization, the angle between the planes of two benzene rings is found to be 110°. The O atoms of the NO_2 group lie in the same plane as the adjacent benzene ring; however, the H atoms of the NH_2 group do not remain in the same plane, thus forming a dihedral angle of 25° with respect to the plane of the benzene rings. Figure 5 shows the molecular energy level plots for the five highest occupied and lowest unoccupied energy levels for the individual

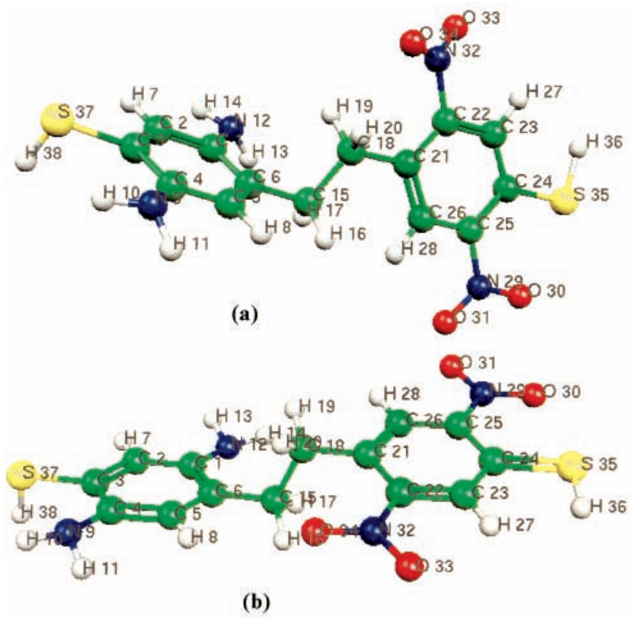


Figure 4. Optimized geometry for the disubstituted donor−spacer−acceptor molecular complex separated by methylene (1a) and dimethylene (1b) functional groups. The donor and acceptor subunits are created by substitution of the two $-NH_2$ and $-NO_2$ functional groups at the 1,4 positions in benzene ring. The geometry is optimized using at the level of theory.

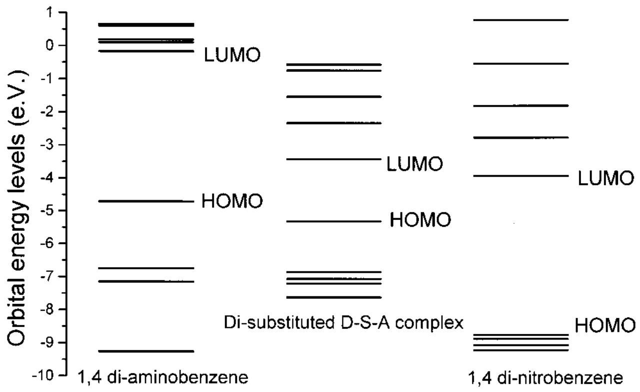


Figure 5. Comparison of the five highest occupied and five lowest unoccupied orbital energy levels for 1,4 diaminobenzene (donor), 1,4 dinitrobenzene (acceptor) and the donor−spacer−acceptor molecular complex (shown in Figure 4).

disubstituted molecules, along with the combined D−S−A molecular complex. It is clear from the figure that the HLG of the combined molecule is significantly smaller than those of the constituents.

To understand the charge localization across the molecule, we have analyzed the Mulliken charge population on each atom and compared the results for the neutral molecule with the anion. For this purpose, we have performed a single-point energy calculation on the optimized structure for the neutral molecule as the starting configuration. The values of the point charges truncated up to third decimal places are shown in Table 2. It is found that the instantaneous extra charges are mainly localized on the S atom and the O atoms of the NO_2 group residing on the acceptor side of the molecule. Unlike molecules 1a and 1b, here we find that a significant amount of charge has been transferred to the donor side also.

It is known that the bias voltage applied across a molecular diode tends to raise the Fermi level of metal electrodes in the low voltage contact and lower the Fermi level on the other side.

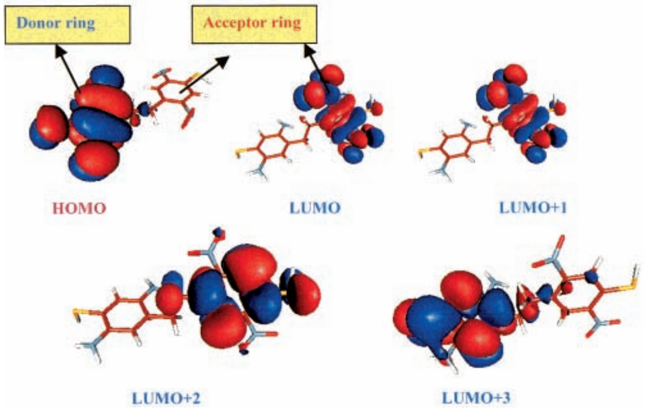


Figure 6. Orbital spatial orientation of HOMO, LUMO, LUMO+1, LUMO+2, and LUMO+3 for molecular complex corresponding to Figure 4.

Therefore, when a forward bias voltage is applied to the disubstituted donor−acceptor complex with higher voltage on the donor side and lower voltage on the acceptor side, the electrons can flow from the acceptor side to the donor side. At this point, one can qualitatively imagine that when a bias voltage is applied the molecule instantaneously becomes negatively charged. Therefore, it is of interest to optimize the geometry of the molecular complex in the presence of an extra electronic charge. Hence, we have performed the geometry optimization of the negatively charged disubstituted donor−acceptor molecule having one excess electron at the B3LYP/6-311++G (d,p) level of theory. Figure 4b shows the optimized geometry of the singly negatively charged disubstituted molecular rectifier. Interestingly, it is found that, unlike the case of the neutral molecule where the two benzene rings are almost perpendicular, the rings are now nearly parallel. The angle between the two rings is calculated to be 10°. To confirm this result, we have calculated the total energies of the neutral and anion with parallel and perpendicular configurations. The results show that for the anion, the parallel configuration is 0.6 eV more stable than the perpendicular geometry. However, for the neutral molecule, the perpendicular configuration is 0.32 eV more stable than the corresponding parallel configuration of the anion. This finding is very important as the orbital overlaps are expected to be maximal in the parallel orientation.

To understand the electronic transport and potential drop through this molecule, we have plotted the orbital spatial distribution for the five lowest unoccupied orbitals. Figure 6 shows the LUMO and LUMO+K (K = 0, 1, 2, 3) levels for the combined neutral disubstituted rectifier molecule. It is seen from this figure that the LUMO is localized on the acceptor ring and the LUMO+3 state is localized on the donor ring, thereby resulting in a higher potential difference of 2.76 eV. The significant increase of ∼40% in the potential drop for the doubly substituted donor−acceptor molecular complex indicates that disubstituted intramolecular complexes could be a better choice for the robust operation of the molecular rectifiers. In addition, the larger number (total four) of localized unoccupied orbitals on the donor side also provides more channels for the electron transport from one side to the other.

4. Summary

We have performed ab initio density functional theory calculations to study the geometries and electronic structures of a group of substituted benzene molecules that can be realized as D−S−A type molecular rectifiers. We have substituted the benzene ring by one or two $-NH_2$ and $-NO_2$ functional groups to form donor and acceptor molecular subunits, respectively. Methylene and dimethylene aliphatic groups have been used as spacers between the donor and acceptor molecules. The electron transport in these molecules has been analyzed based on the spatial distribution of the frontier orbitals (HOMO and LUMO). It is seen that while the HOMO's are always localized on the donor side, the LUMO's are localized on the acceptor side. However, the localization of the LUMO state on the donor side depends on the number of substituents and the length of the spacers, leading to different potential drops across the molecules. In the case of monosubstitued donor−acceptor complexes, the potential drop is 1.56 and 2.05 eV for methylene and dimethylene spacers, respectively. The potential drop for the disubstituted donor−acceptor complex separated by the dimethylene group is found to be 2.76 eV. The significant increase in the potential drop by ~40% for the disubstituted donor−acceptor complex as compared to the monosubstituted complexes indicates that it can be used for wide range of bias voltages.

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