

Design a donor bridge acceptor system (D-B-A) using quantum mechanics methods

تصميم نظام مانح جسر مستقبل باستخدام طرائق الميكانيك الكمي

Adil Jalel Najim

Karbala University, College of Education for Pure Science, Karbala / raq,
adil.alshimmary@yahoo.com

ABSTRACT:

The geometry optimization for the structures of molecules under study and other properties have been calculated using density functional method with (B3LYP) and 6-31G(d,p) level and Austin model (AM1) semiempirical method. The aim of this work is to calculate the electronic properties for aminotulene molecule as an electron donor molecule, as well as study the electronic properties for bromotulene molecule as an electron acceptor and aminosalicyclic molecule as a bridge between donor and acceptor, then grouping these molecules together in one entity to form donor bridge acceptor system (D-B-A).

The results show that the total energy rises from donor to bridge to acceptor. As regarding to the HOMO energy for donor molecule, the latter was more than that of acceptor molecule and both these HOMO energies are more than that of bridge molecule, but when designing the donor bridge acceptor molecule, the HOMO energy was the least. This result was similar when calculating LUMO energy but the only difference being the LUMO energy for (D-B-A) was a little higher than that of bridge. With respect to electron affinity (E_{ca}), then both donor and acceptor molecules have electron affinity more than that for bridge, but for (D-B-A) molecule the electron affinity was the least, while ionization potential (IP) value increased from donor to bridge to acceptor then decreased again when (D-B-A) was built. The electronegativity property for bridge, acceptor and (D-B-A) is close together, whereas for the donor it was the least. Finally, it have been estimated the vibration spectrum for all donor, bridge and acceptor using DFT-(B3LYP) and for (D-B-A) it is estimated using Austin model (AM1) which they have been illustrated in this paper. These properties make this system a good (D-B-A) for transporting electrons from donor to acceptor throughout the bridge, thus when a photon collides donor molecule, then it will release an electron because donor molecule has lowest ionization potential of about 7.3 eV, on the other hand bridge has more electronegativity than that of donor, and thus it has high tendency to attract this released electron, which in turn will transmit this electron to acceptor molecule.

KEYWORDS: AM1, B3LYP, Energy gap, HOMO, IR spectrum and LUMO.

الخلاصة:

تم حساب الامثلية الهندسية للتراكيب الجزيئية تحت الدراسة وباقي الخواص باستخدام نظرية دالة الكثافة بالمستوي (B3LYP) ودوال اساس من نوع 6-31G(d,p) ، وكذلك تم استخدام الطريقة شبه التجريبية وهي نموذج اوستن (AM1). الهدف من هذه الدراسة هو معرفة خواص جزيئة الامينوتولين كجزيئة مانحة للإلكترونات، بالإضافة إلى دراسة الخواص الالكترونية لجزيئة البروموتولين كجزيئة مستقبلية للإلكترونات، ودراسة جزيئة الامينوسلسايك كجسر بين الامينوتولين (الجزيئة المانحة) والبروموتولين (الجزيئة المستقبلية)، ثم تم ربط هذه الجزيئات مع بعض لتكوين نظام مانح جسر مستقبل (D-B-A).

أظهرت النتائج أن قيمة الطاقة الكلية للجزيئة المانحة اقل من تلك التي للجزيئة الرابطة (الجسر) والتي بدورها لها طاقة كلية اقل منها للجزيئة المستقبلية. فيما يتعلق بأعلى مستوي طاقة مشغول بالالكترونات (HOMO) فقد كانت قيمته للجزيئة المانحة اعلى منها للجزيئة المستقبلية وكلاهما لهما طاقة اعلى منها للجزيئة الرابطة، لكن عند تصميم جزيئة (D-B-A) فقد تناقصت طاقة (HOMO) إلى اقل قيمة من بين الجزيئات المدروسة كلا على حده. هذه النتيجة كانت مشابهة عند حساب طاقة ادنى مستوي غير مشغول بالالكترونات (LUMO) ولكن الفرق الوحيد هو أن طاقته لجزيئة (D-B-A) كانت اكثر بقليل من طاقته للجزيئة الرابطة. فيما يتعلق بالألفة الالكترونية (E_{ca}) كانت قيمتها للجزيئة المانحة والجزيئة المستقبلية اعلى منها للجزيئة الرابطة، لكن لجزيئة (D-B-A) كانت قيمة الألفة الالكترونية هي الاقل من الجزيئات المدروسة، بينما كانت قيمة طاقة جهد

التأين (IP) تزايد من الجزيئة المانحة للجزيئة الرابطة للجزيئة المستقبلية، لكن قيمته لجزيئة (D-B-A) كانت الاقل. عند حساب خاصية السالبية الالكترونية كانت قيمتها للجزيئة الرابطة والجزيئة المستقبلية وجزيئة (D-B-A) متقاربة مع بعضها، في حين كانت قيمتها للجزيئة المانحة اقل منها لباقي الجزيئات. اخر الخواص التي تم حسابها هي طيف الاهتزاز للجزيئات المدروسة باستخدام نظرية دالة الكثافة ما عدا جزيئة (D-B-A) حيث تم حساب طيف الاهتزاز باستخدام نموذج اوستن (AM1) وهي طريقة شبه تجريبية. أن هذه الخواص التي تم حسابها تجعل جزيئة (D-B-A) ذات خواص مناسبة لأستخدامها كنظام مانج جسر مستقبلي، يعمل على نقل الالكترونات من الجزيئة المانحة للجزيئة المستقبلية عبر الجزيئة الرابطة، حيث عندما يسقط فوتون على الجزيئة المانحة فإنه سوف يحرر الكترون لأن الجزيئة المانحة لها جهد تأين بحوالي 7.3 eV، ثم أن الجزيئة الرابطة تمتلك سالبية الكترونية اقل منها للجزيئة المانحة فأنها لها ميل اكبر لجذب هذا الالكترون المتحرر وتقوم الجزيئة الرابطة بنقل هذا الالكترون إلى الجزيئة المستقبلية.

INTRODUCTION

The study of electron transfer is very important especially in DNA and in organic electronic applications such as solar cells, sensors or organic transistors. The quality of donor bridge acceptor systems depend mainly on electron transfer between molecules, so these types of organic systems have been studied widely in recent years [1-5]. Where some of these studies studied electron transfer from donor to acceptor and these studies show that electron transfer dependent not only on distance between donor and acceptor but also on the electronic structure of the bridge [1]. Other study investigated the influence of orientations of donor and acceptor, and showed that there is a significant effect for the geometry of the fluctuation on electron transfer between donor and acceptor [6]. Some studies investigate the controlling on electron transfer using cross conjugated bridges, implying that cross-conjugation decreases the π orbital contribution to the donor-acceptor electronic coupling [7].

COMPUTATIONAL METHODS

The density functional theory (DFT) (Kohn Sham equations) [8] and semiempirical method Austin model (AM1) programmed using Gaussian 03 package has been used [9]. The initial geometry optimizations have been carried out using Austin model (AM1) [10]. Then density functional method with (B3LYP) level and polarized split valance basis sets 6-31G (d,p) have been used to guess the ground state of neutral molecules under study, as well as the energies of anion and cation of each molecule, which are used to estimate the electron affinity, ionization potential, and electronegativity.

The electron affinity (E_{ea}) and ionization potential have been calculated according to following equations, [11]:

$$E_{ea} = E_{neutral} - E_{anion} \quad (1)$$

$$IP = E_{cation} - E_{neutral} \quad (2)$$

RESULTS AND DISCUSSION

The final geometry optimization structures for all molecules have been performed using density functional theory with (6-31G**) level. These structures are shown in figure (1).

The energy for the highest occupied molecular orbitals (HOMO), the lowest unoccupied molecular orbitals (LUMO), the donor, bridge, acceptor, and (D-B-A) molecules are shown in figures (2) and (3) respectively. From figure (2) we note the HOMO energy for donor molecule is more than that of acceptor molecule and both these HOMO energies are more than that of bridge molecule, but when design the donor bridge acceptor molecule, the HOMO energy was the least but

also it is approaching to that of bridge. This result may appear because as we will see later that HOMO orbital is largely center on the bridge, and less on the donor molecule. With respect to LUMO, we see from figure (3), the pattern variation was similar to that of HOMO but the main difference is LUMO energy for (D-B-A) is little more than that of bridge, and that maybe because the LUMO orbital for (D-B-A) molecule is largely center on the bridge, and less on the acceptor molecule. Like-behavior change for HOMO and LUMO led to the conclusion that the energy gap decreases as shown in figure (4).

From the total energy shown in figure (5), it is evident that total energy increases from donor to bridge to acceptor, and finally to (D-B-A) molecule which has the largest total energy. This is due to the large number of bonds contained in (D-B-A) relative to these in its constituent molecules.

The electron affinity (E_{ea}) of the molecules, shown in figure (6), has been calculated as a difference between the total energies of neutral and anion molecules. The results show that both donor and acceptor molecules have electron affinity more than that of bridge, but for (D-B-A) molecule the electron affinity is the least, meaning that the amount of energy released when it attracts electron is little compare with released energy by other molecules.

Figure (7) shows the ionization potential (IP). The value of which (IP) increases from donor to bridge to acceptor but falls again when (D-B-A) is built. This indicates that the donor has large ability to give an electron compare with bridge and acceptor when it is subjected to an excitation energy. This released electron will then be transferred through the bridge and acceptor.

Another property that has been calculated is electronegativity (μ) and is shown in figure (8). It is represented as average for (E_{ea}) and (IP), in accordance with equation (3) [12]. As it is clear from this figure, the electronegativity (μ) for donor is less than other molecules whose (μ) is approximately the same.

$$\mu = \frac{E_{ea} + IP}{2} \quad (3)$$

All energies that have been calculated are tabulated in table (1). The total energy for each molecule, the energy of (LUMO), and the energy of (HOMO) have been calculated directly from output files of Gaussian 03. With respect to energy gap E_{gap} , it has been calculated according to equation (4).

$$E_{gap} = E_{LUMO} - E_{HOMO} \quad (4)$$

With regarding to electron affinity (E_{ea}), and ionization potential (IP), they have been calculated according to equations (1) and (2) respectively. Where for the donor, bridge, acceptor, and (D-B-A), they have been calculated three total energies, and they are total energy of neutral molecule, the total energy of cation molecule, and the total energy of anion molecule.

Table (1): The total energy (E_{tot}), E_{LUMO} , E_{HOMO} , E_{Gap} , Ionization potential (IP), Electron affinity (E_{ea}) and Electronegativity (μ) for molecules under study

Molecule	E_{tot} eV	E_{LUMO} eV	E_{HOMO} eV	E_{Gap} eV	IP eV	E_{ea} eV	μ eV
<i>Donor</i>	-8896.59	-5.31	-9.09	3.78	7.30	-2.31	2.49
<i>Bridge</i>	-15005.376	-0.84	-5.77	4.93	7.74	-1.07	3.33
<i>Acceptor</i>	-77355.074	-5.31	-8.57	3.21	8.36	-1.71	3.33
<i>D-B-A</i>	-98073.798	-1.12	-5.70	4.58	6.96	-0.32	3.32

From the table above, it can be concluded that the total energy of (D-B-A) molecule E_{D-B-A} is approximately equal to the sum of total energy of donor E_D , bridge E_B and acceptor E_A . Thus:

$$E_{D-B-A} \approx E_D + E_B + E_A \quad (5)$$

With respect to IR spectrum, all of them have been plotted using DFT/B3LYP with 6-31G (d,p) basis sets, except for (D-B-A) molecule where its IR spectrum is investigated using (AM1) method because it is a large molecule, and DFT method takes a long time to investigate the IR spectrum. Figure (9) illustrates the IR spectrum for donor, bridge, acceptor, and (D-B-A). the number of peaks in IR spectrum proportional with the degree of freedom, where aminotulene has 8 degrees of freedom, aminosalicylic has 14 degrees of freedom, bromotulene has 48 degrees of freedom and (D-B-A) molecule has 34 degrees of freedom. Each degree of freedom allows bending or stretching vibration of bonds between atoms.

Figure (10) shows the HOMO and LUMO shapes of molecules under study. It can be noticed from HOMO and LUMO of aminotulene, that HOMO almost distributes on all portions of molecule, while LUMO distributes only on the ring. The HOMO and LUMO for Aminosalicylic distribute on all molecule planes. The HOMO for bromotulene molecule almost covers all the molecule whereas LUMO spreads only on the ring. Finally, HOMO orbital for (D-B-A) distributes on donor and bridge molecules while LUMO distributes on bridge and acceptor. These shapes of HOMO and LUMO interpret the property of this molecule to be donor bridge acceptor to transport electron from donor to acceptor throughout bridge.

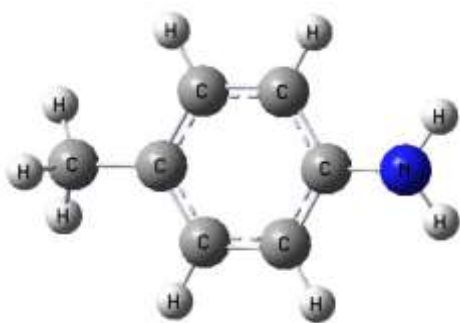
CONCLUSIONS

The (D-B-A) molecule which is designed from aminotulene as electron donor, aminosalicylic as bridge, and bromotulene as electron acceptor is a good donor bridge acceptor system. When total energies have been calculated, the total energy of (D-B-A) molecule has approximately been equal to the sum of total energy of donor, bridge and acceptor. This result is attributed to the acceptable accuracy the density functional method has in estimating energies. When the HOMO and LUMO have been plotted for (D-B-A) molecule the shapes show that (D-B-A) is good electron transporter from donor to acceptor molecule.

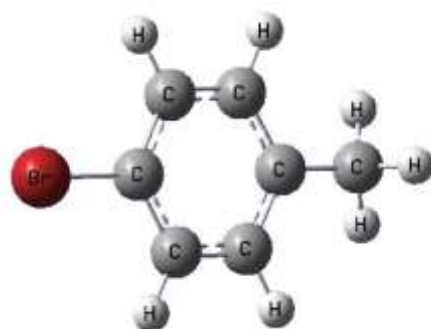
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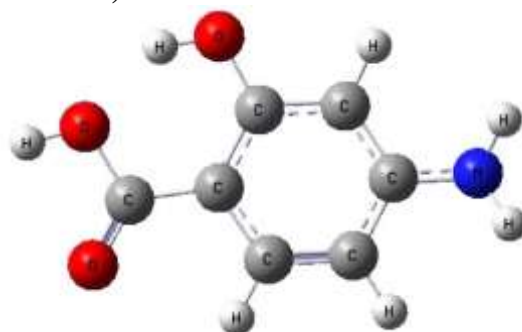
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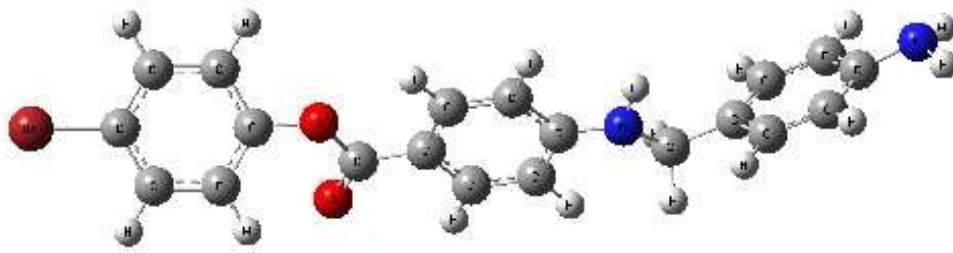
aminotulene (the donor)



bromotulene (the acceptor)



4-Aminosalicylic (the bridge)



D-B-A molecule

Figure (1): the optimized structures for molecules under study.

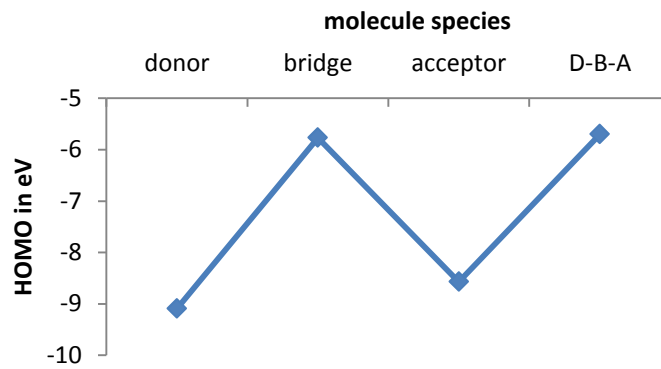


Figure (2) HOMO energy for molecules under study

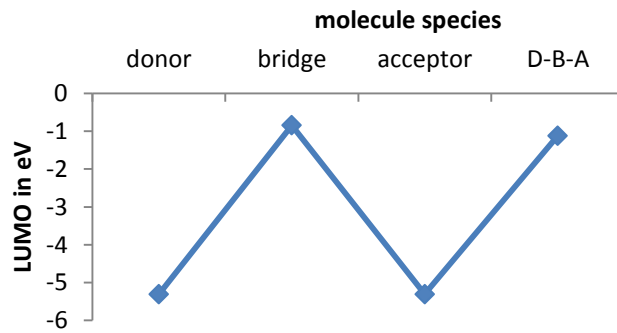


Figure (3) LUMO energy for molecules under study

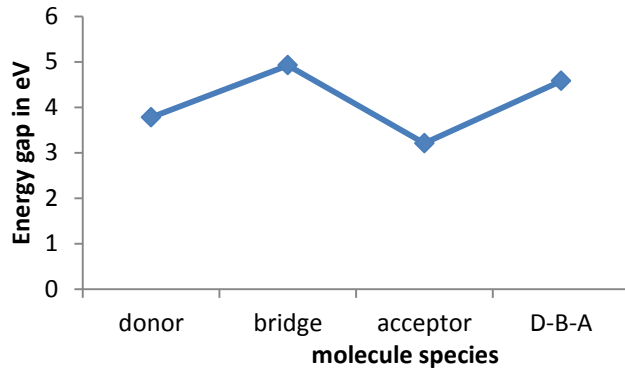


Figure (4) Energy gap for molecules under study

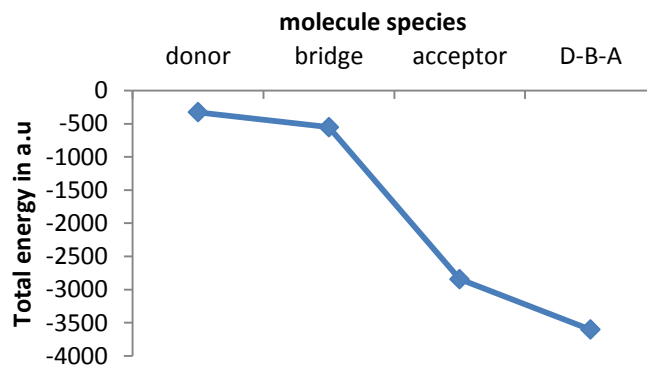


Figure (5) Total energy for molecules under study

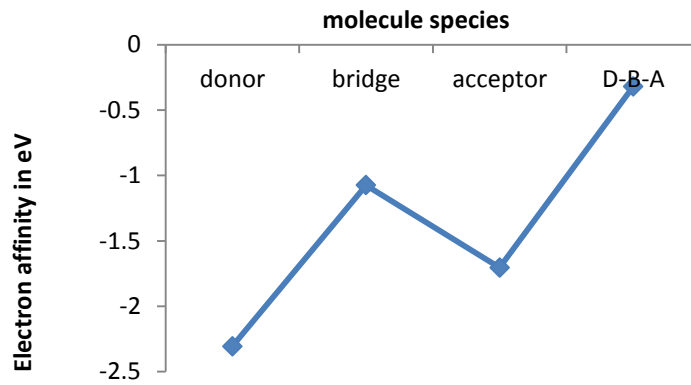


Figure (6) Electron Affinity for molecules under study

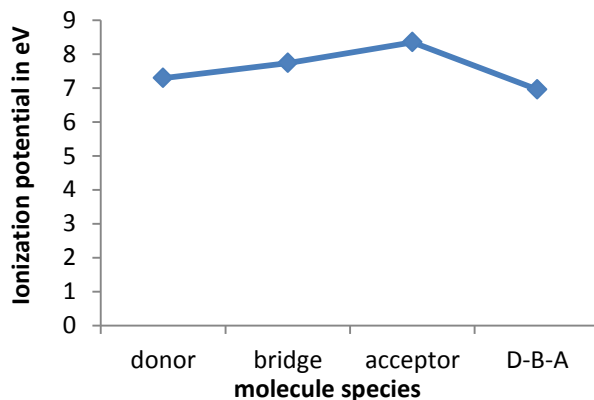


Figure (7) Ionization potential for molecules under study

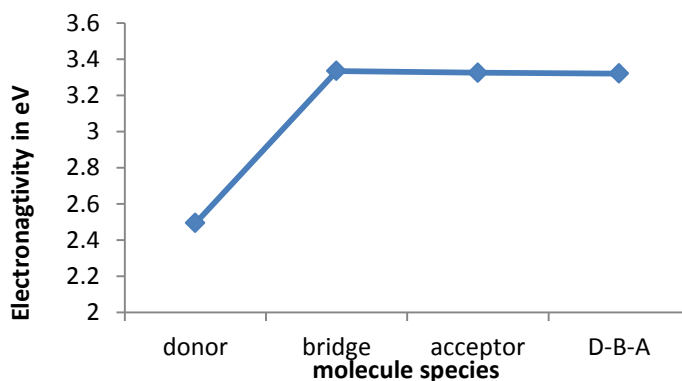
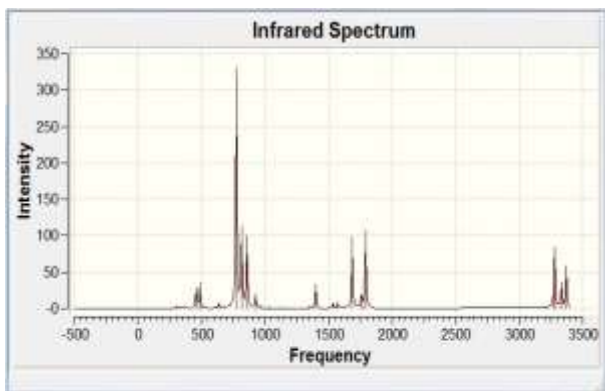
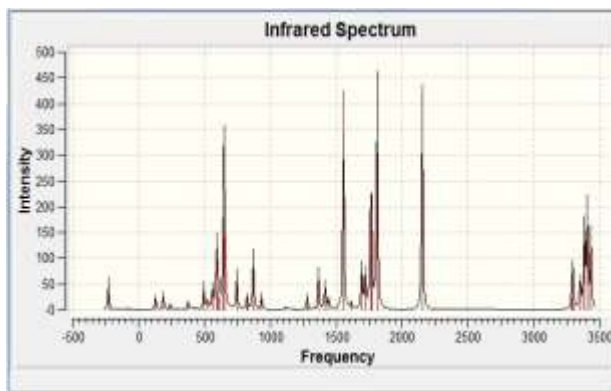


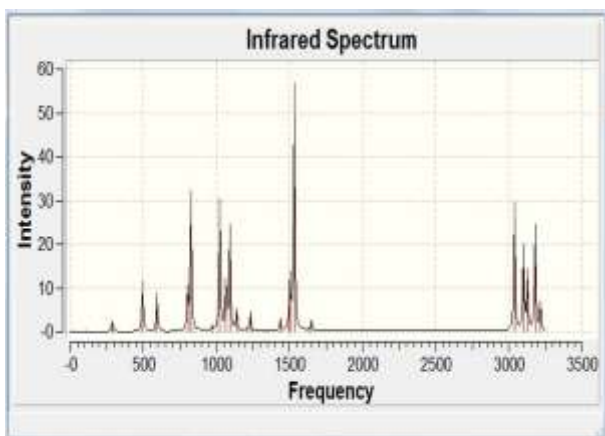
Figure (8) Electronegativity for molecules under study



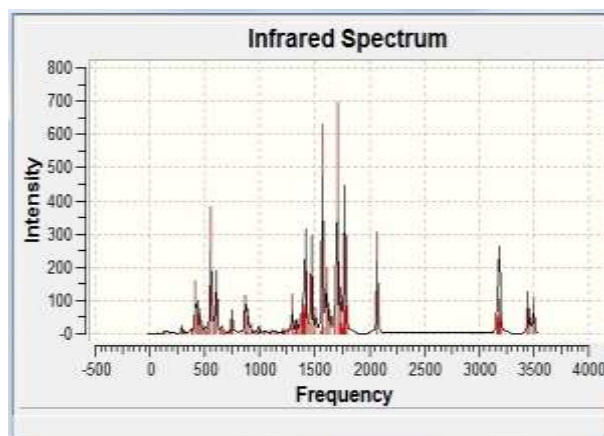
(a) Aminotulene (the donor)



(b) Aminosalicic (the bridge)

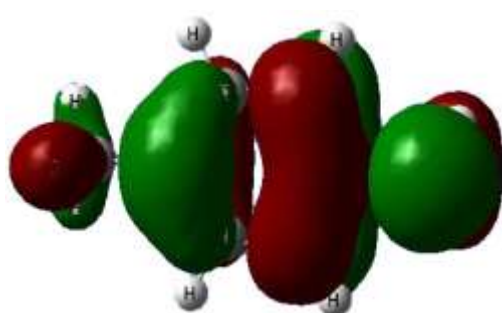


(c) Bromotulene (the acceptor)

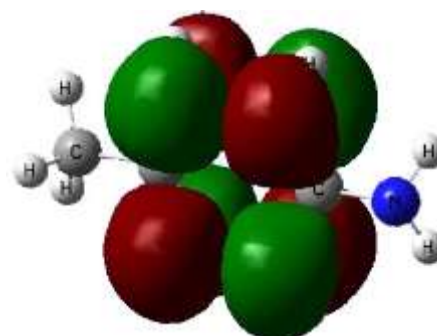


(d) (D-B-A)

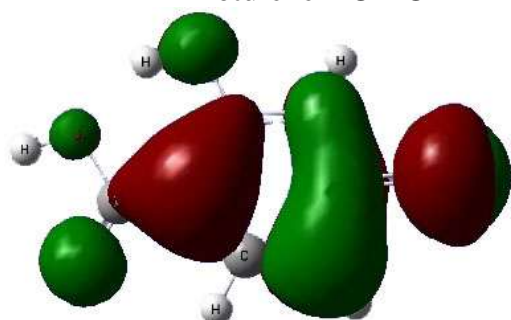
Figure (9) The IR spectrum for aminotulene molecule (the donor), frequency in (cm⁻¹) and intensity in (KM/Mole).



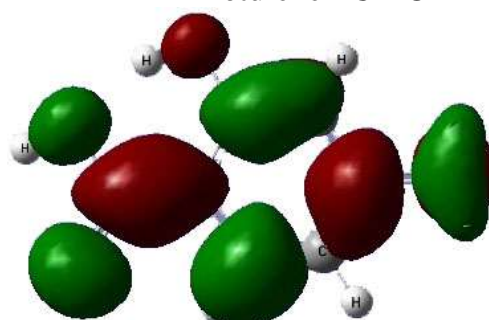
Aminotulene HOMO



Aminotulene LUMO



Aminosalicylic HOMO



Aminosalicylic LUMO

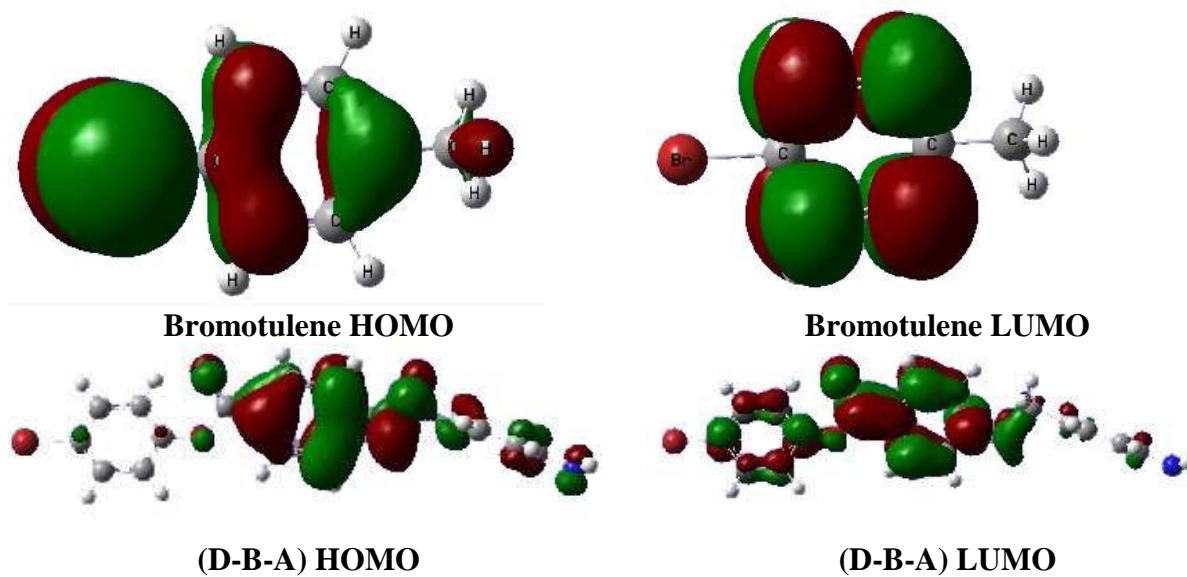


Figure (10) HOMO and LUMO Shapes of molecules under study