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Geometrical isomers of lumogallion and interaction of its *trans* isomer with gallium cations – A DFT treatment

Lemi Türker

Department of Chemistry, Middle East Technical University, Üniversiteler, Eskişehir Yolu No: 1, 06800 Çankaya/Ankara, Turkey
e-mail: lturker@gmail.com; lturker@metu.edu.tr

Abstract

In the present study, first *cis* and *trans*-lumogallion, then the interaction of its *trans* isomer with gallium +1 and +3 cations (one by one) in vacuum conditions have been investigated within the constraints of density functional theory at the level of B3LYP/6-31++G(d,p). The collected data revealed that all the structures considered have exothermic heat of formation and favorable Gibbs free energy of formation values. They are thermally favored and electronically stable at the standard states. Various structural and quantum chemical data have been collected and discussed, including IR and UV-VIS spectra.

1. Introduction

Gallium is a commonly used element in microelectronic components as a main component of semi-conductor material. However, the ionic species of gallium [1-4] tend to enhance the risk of the gallium pollution. The most dominant consumption of gallium is in the form of gallium arsenide (GaAs) and gallium nitride (GaN), which account for 94% of the production share, alongside other minor compounds such as gallium antimonite (GaSb) and gallium phosphide (GaP). GaAs is considered a substrate material in manufacturing semiconductors, as well as in forming ternary compounds like InGaAs and AlGaAs [5].

Furthermore, severe harms will be done to human health if the daily intake amount of gallium nitrate and gallium arsenide is maintained at a high level, especially for the kidneys and haematopoietic system [3,4].

On the other hand, lumogallion (2,2',4'-trioxy-5-chloro-(1-azo-1'-benzene-3-sulphonic acid)) is a highly sensitive fluorescent reagent for the detection of aluminum, gallium and some other metals [6]. Various detection methods have been developed for various elements [6-12].

2. Method of Calculations

In the present study, all the initial optimizations of the structures leading to energy minima have been achieved first by using MM2 method which is then followed by semi empirical PM3 self consistent fields molecular orbital method [13-15]. Afterwards, the structure optimizations have been achieved within the framework of Hartree-Fock and finally by using density functional theory (DFT) at the level of B3LYP/6-31++G(d,p) [16,17]. Note that the exchange term of B3LYP consists of hybrid Hartree-Fock and local spin density (LSD) exchange functions with Becke's gradient correlation to LSD exchange [18]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [19] and Lee, Yang, Parr (LYP) correlation correction functional [20]. In the present study, the normal mode analysis for each

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structure yielded no imaginary frequencies for the 3*N*–6 vibrational degrees of freedom, where *N* is the number of atoms in the system. This search has indicated that the structure of each molecule considered corresponds to at least a local minimum on the potential energy surface. Furthermore, all the bond lengths have been thoroughly searched in order to find out whether any bond cleavage occurred or not during the geometry optimization process. All these computations were performed by using SPARTAN 06 program [21].

3. Results and Discussion

The ground state electronic configuration of gallium is [....$3d^{10}4s^24p^1$] [22]. Gallium atom is electron deficient and its valence shell includes d-orbitals and hence the atom undergoes octahedral hybridization [23]. The univalent Ga^{+1} ion is present in some compounds, such as $Ga[GaCl_4]$, GaI, $Ga[AlCl_4]$ [22-24]. The ionization potentials of Ga are 4s: 30.6 eV, 4s: 20.43 eV and 4p: 5.97 eV [22,24].

Presently, lumogallion, and its *cis* and *trans* isomers are named as, L, *cis*-L and *trans*-L, respectively. Figure 1 shows the optimized structures of lumogallion isomers considered (two different views). Note that the *cis* isomer is not a planar molecule. The figure also displays the direction of the dipole moment vectors. Note that the *cis* isomer was subjected to geometry constraints to keep the *cis* form while the entire optimization process.

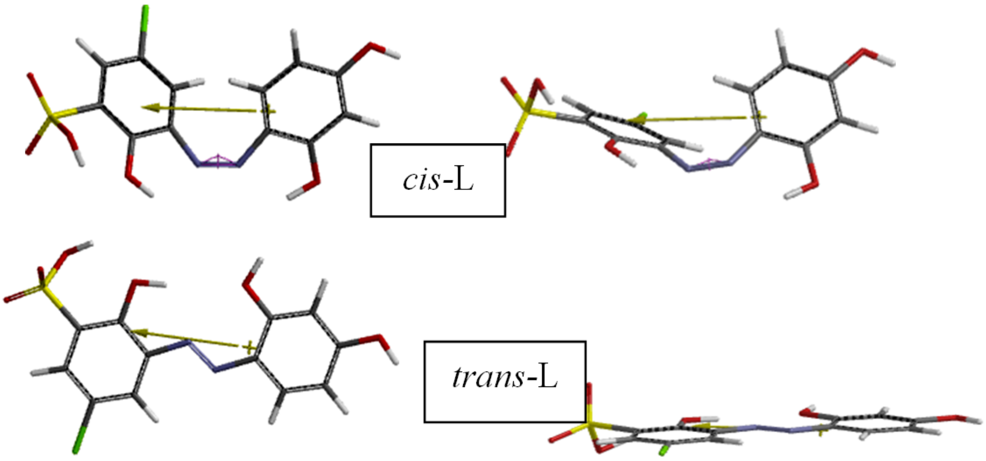
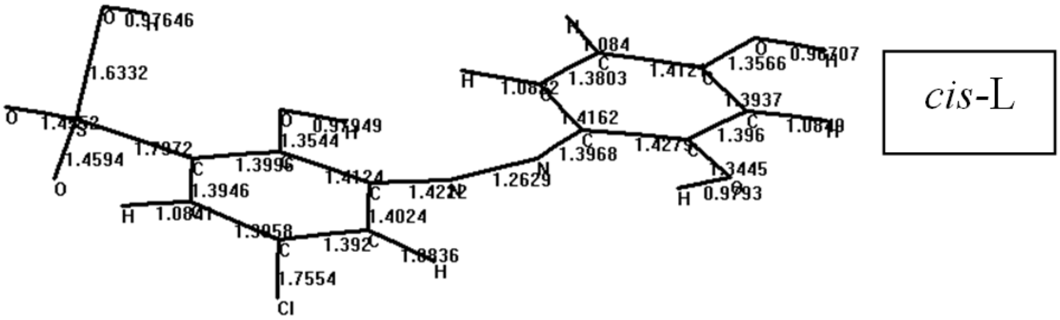


Figure 1. Optimized structures of lumogallion isomers considered (two different views).

Figure 2 displays the calculated bond lengths (Å) of lumogallion isomers considered. Some thermo chemical properties of the geometric isomers of lumogallion considered are shown in Table 1. Whereas, Table 2 includes some energies of lumogallion isomers considered. The data in Table 1 reveal that the standard heat of formation (H°) values of the isomers are exothermic and they are favored according to their G° (Gibbs free energy of formation) values. The algebraic order of H° and G° values are *trans*-L< *cis*-L. Whereas S° values follow the order of *trans*-L> *cis*-L.



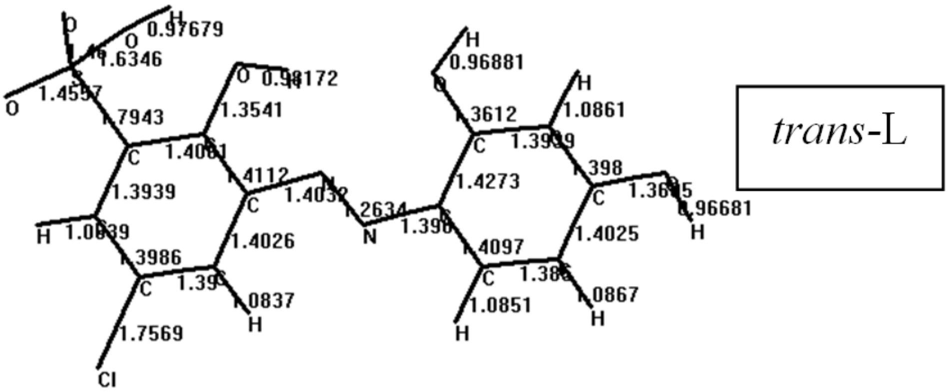


Figure 2. The calculated bond lengths (Å) of lumogallion isomers considered.

Table 1. Some thermo chemical properties of the geometric isomers of lumogallion considered.

Isomers	H°	S° (J/mol°)	G°
cis-L	-4940276.631	533.52	-4940435.685
trans-L	-4940322.079	538.42	-4940482.603

Energies in kJ/mol.

Some energies of lumogallion isomers considered are listed in Table 2 which reveals that they are all electronically stable structures. The stability order is *trans*-L> *cis*-L. Note that E, ZPE and E_C stand for the total electronic energy, zero point vibrational energy and the corrected total electronic energy, respectively.

Table 2. Some energies of lumogallion isomers considered.

Isomers	E	ZPE	E_C
cis-L	-4940824.93	547.78	-4940277.15
trans-L	-4940869.97	546.80	-4940323.17

Energies in kJ/mol.

Figure 3 displays the electrostatic potential (ESP) maps of lumogallion isomers where negative potential regions reside on red/reddish and positive ones on blue/bluish parts of the maps. Thus, the oxy groups donate electrons and sulphonic acid group attracts electrons as also indicated by the direction of dipole moment vectors. Note that the maps based on ESP charges are obtained by the program which uses a numerical method that generates charges thus reproducing the electrostatic potential field from the entire wavefunction [21].

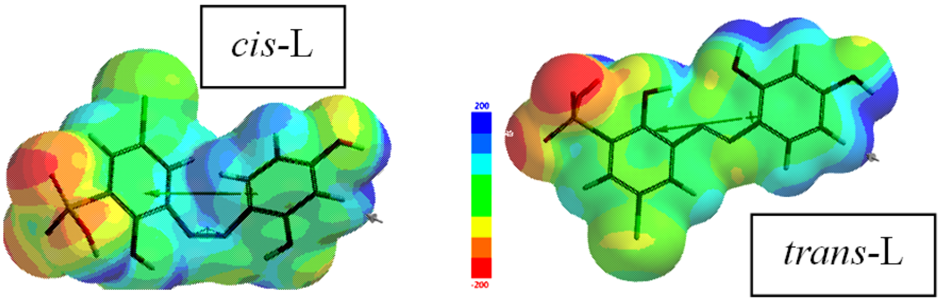


Figure 3. The electrostatic potential maps of lumogallion isomers.

Figure 4 shows the local ionization potential maps of lumogallion isomers where conventionally red/reddish regions (if any exists) on the density surface indicate areas from which electron removal is relatively easy, meaning that they are subject to electrophilic attack. It is worth remembering that the local ionization potential map is a graph of the value of the local ionization potential on an isodensity surface corresponding to a van der Waals surface.

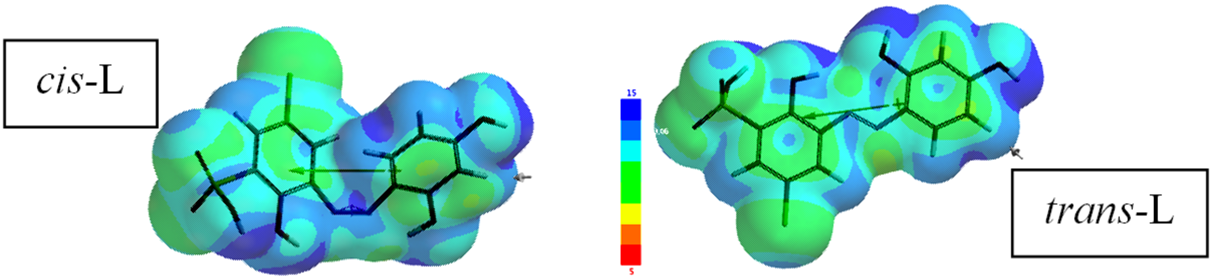


Figure 4. The local ionization potential maps of lumogallion isomers.

Figure 5 shows the LUMO maps of lumogallion isomers. Note that a LUMO map displays the absolute value of the LUMO on the electron density surface. The blue color (if any exists) stands for the maximum value of the LUMO and the red colored region, associates with the minimum value.

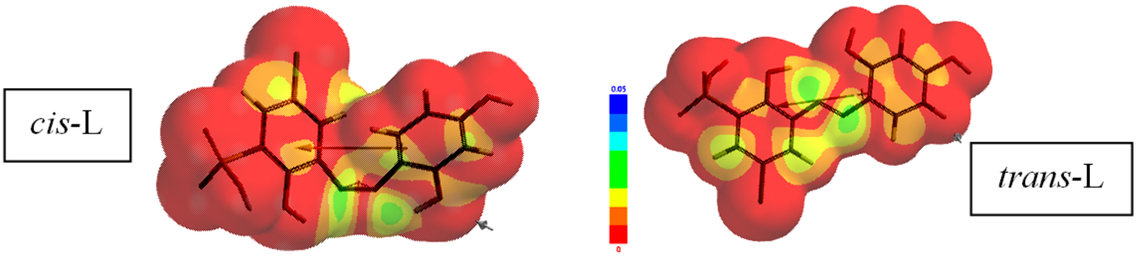


Figure 5. The LUMO maps of lumogallion isomers.

Some properties of lumogallion isomers considered are listed in Table 3. Of the properties mentioned, the polar surface area (PSA) is defined as the amount of molecular surface area arising from polar atoms (N,O) together with their attached hydrogen atoms [21]. Although these compounds are isomeric, their PSA values differ from each other, meaning that the same kind of atoms might be influenced by electronic factors differently at different positions. The polarizability is defined according to a multivariable formula [21] which is the functions of van der Waals volume and hardness, respectively. The later one is dictated by energies of the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals [21]. It is worth mentioning that a negative value for log P means the compound has a higher affinity for the aqueous phase (it is more hydrophilic); when log P = 0 the compound is equally partitioned between the lipid and aqueous phases; whereas a positive value for log P denotes a higher concentration in the lipid phase (i.e., the compound is more lipophilic).

Table 3. Some properties of lumogallion isomers considered.

Isomers	Dipole (debye)	Area ($Å^2$)	Volume ($Å^3$)	PSA ($Å^2$)	Ovality	Log P	Polarizability 10^{-30} m^3 units.
cis-L	8.63	299.38	275.45	125.777	1.46	3.02	62.94
trans-L	11.63	307.22	277.12	123.888	1.49	3.02	63.03

The calculated IR spectra of lumogallion isomers considered are included in Figure 6. In the spectrum of *cis* isomer O-H stretchings appear in between 3815-3591 cm^{-1}. Of these peaks the 3815 cm^{-1} and 3591 cm^{-1} stand for O-H groups on the same phenyl ring. The one at 3707 cm^{-1} belongs to sulphonic acid O-H stretching which is followed by the phenolic O-H stretch occurring at 3612 cm^{-1}. The azo group stretches at 1561 cm^{-1} accompanied by bendings of some O-H groups. In the region of 1666-1481 cm^{-1} ring vibrations overlapped with some O-H bendings. In the case of *trans* isomer, the stretchings of two phenolic O-H groups on the same ring happen at 3826 cm^{-1} and 3792 cm^{-1}. The acidic O-H stretches at 3687 cm^{-1} whereas the O-H on the same ring stretches at 3554 cm^{-1}. The azo group of the *trans* isomer stretches at 1555 cm^{-1} and 1528 cm^{-1} overlapped with various ring vibrations and O-H bendings.

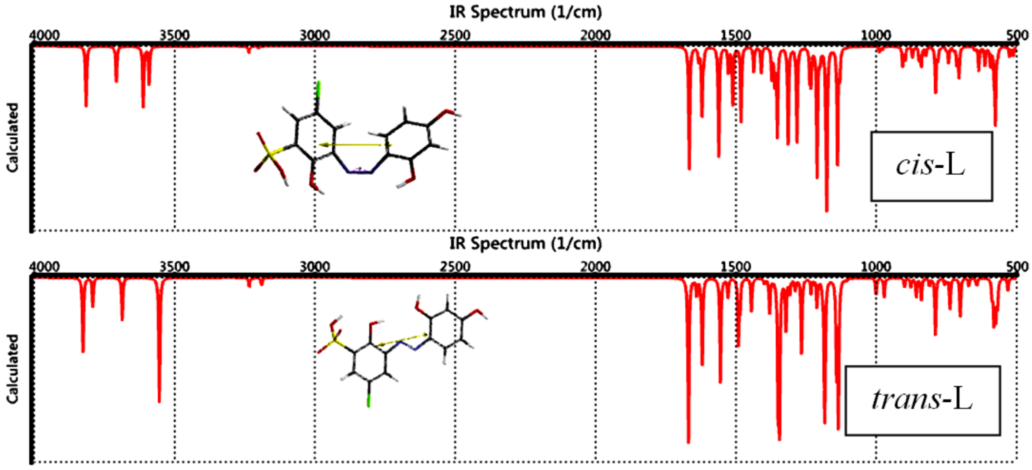


Figure 6. The calculated IR spectrums of lumogallion isomers considered.

Figure 7 shows some of the molecular orbital energy levels of lumogallion isomers considered.

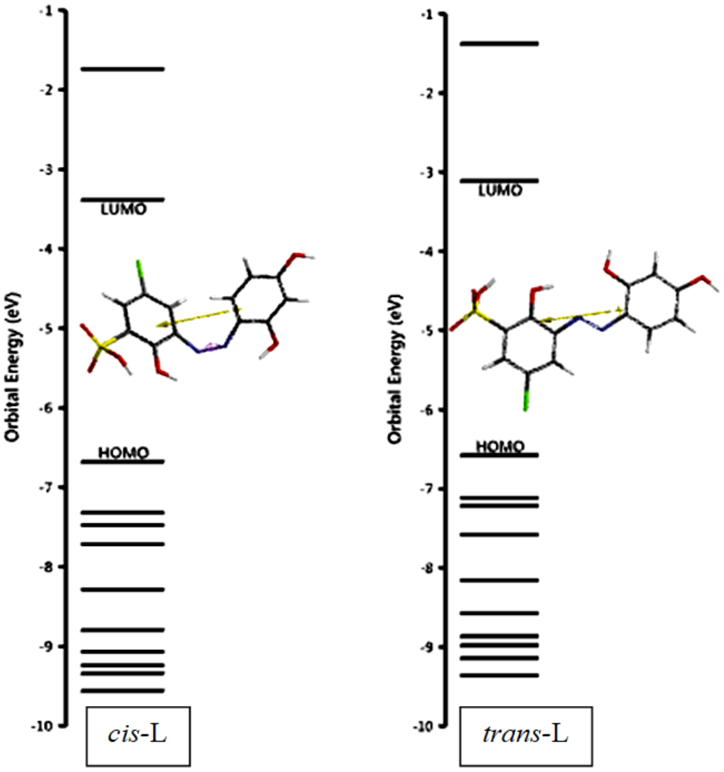


Figure 7. Some of the molecular orbital levels of lumogallion isomers considered.

Table 4 contains the HOMO, LUMO energies and the interfrontier molecular orbital energy gap ($\Delta\varepsilon=\varepsilon_{LUMO}-\varepsilon_{HOMO}$) values of lumogallion isomers considered. As seen in the table, the *cis* isomer has lower HOMO and LUMO energies compared to the *trans* isomer. Since the *cis* isomer is not coplanar (see Figure 1), it should have a less effective extended conjugation to raise the HOMO energy level as compared to the respective level of the *trans* isomer. Note that electron attracting substituents lower both the HOMO and LUMO energy levels, whereas electron donators have the opposite effect. On the other hand, extended conjugation raises the HOMO but lowers the LUMO energy level in a conjugated system [25]. In lumogallion isomers, all these effects might operate at different extents in an intricate and implicit manner.

Table 4. The HOMO, LUMO energies and Δε values of lumogallion isomers considered.

Isomers	HOMO	LUMO	Δε
cis-L	-644.18	-326.29	317.89
trans-L	-634.58	-300.04	334.54

Energies in kJ/mol.

Figure 8 displays the time dependent density functional (TDDFT) UV-VIS spectra of the lumogallion isomers considered. Since Δε for the *cis* isomer is smaller than the respective value of the *trans* isomer, the spectrum of the *cis* isomer is somewhat shifted to visible part of the spectrum as compared to the *trans* isomer, thus having a more discernable shoulder. Note that due to the nonplanar structure of the *cis* isomer, two different chromophores might be operative. Consequence of these effects, the interfrontier molecular orbital energy gap (Δε) for the *cis* isomer is smaller than the respective value of the *trans* isomer (see Figure 8).

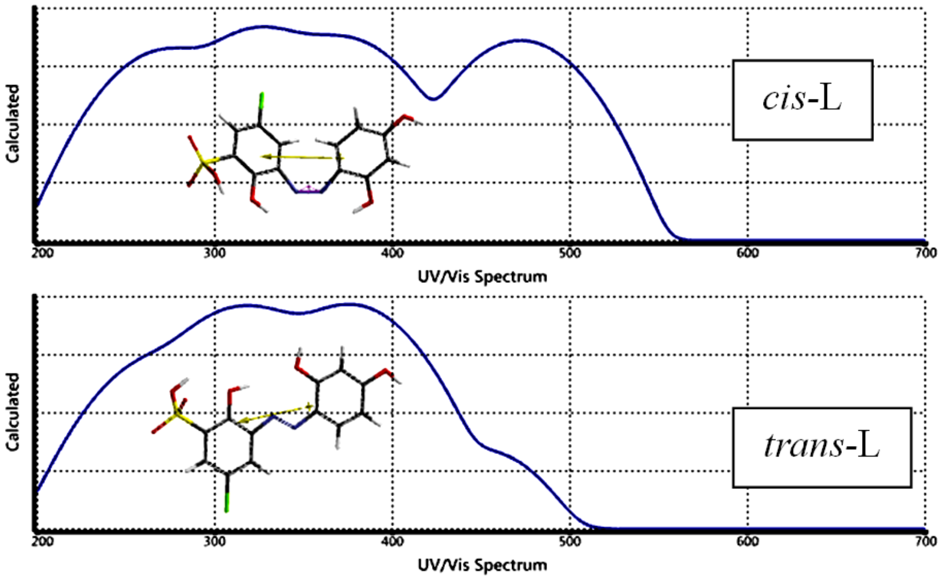


Figure 8. UV-VIS spectra of the lumogallion isomers considered.

Interaction of *trans*-lumogallion with gallium cations

In this section composites of *trans*-lumogallion with gallium cations are abbreviated as L-Ga(I) and L-Ga(III). Figure 9 displays the optimized structures of *trans*-lumogallion with gallium (I) and gallium (III) cations (L-Ga(I) and L-Ga(III), respectively).

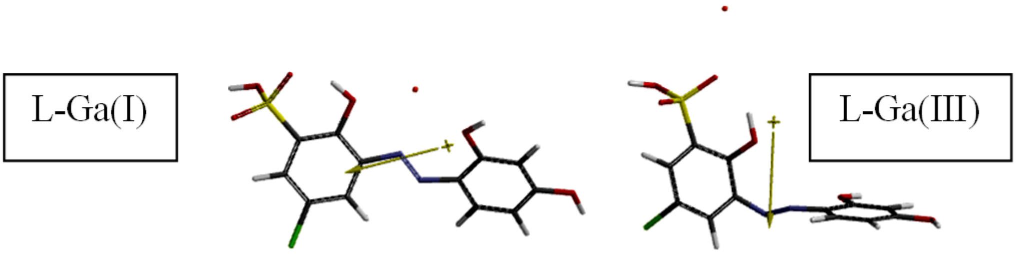


Figure 9. Optimized structures of *trans*-lumogallion with gallium (I) and gallium (III) cations.

Tables 5 and 6 stand for some thermo chemical properties of L-Ga(I) and L-Ga(III) and some energies of them, respectively. As seen in Table 5, the algebraic orders of H° and G° values are L-Ga(I)< L-Ga(III). Whereas S° values follow the order of L-Ga(III)> L-Ga(I).

Table 5. Some thermo chemical properties of L-Ga(I) and L-Ga(III).

Composites	H°	S° (J/mol°)	G°
L-Ga(I)	-9993016.071	564.83	-9993184.472
L-Ga(III)	-9990741.420	569.65	-9990911.265

Energies in kJ/mol.

Some energies of lumogallion composites considered are listed in Table 6 which reveals that they are all electronically stable structures. The stability order is L-Ga(I)> L-Ga(III).

Table 6. Some energies of L-Ga(I) and L-Ga(III).

Composites	E	ZPE	E_C
L-Ga(I)	-9993521.01	547.26	-9992973.75
L-Ga(III)	-9991247.75	548.27	-9990699.48

Energies in kJ/mol.

Figure 10 shows the ESP charges on atoms of L-Ga(I) and L-Ga(III) composites. Note that the ESP charges are obtained by the program based on a numerical method that generates charges that reproduce the electrostatic potential field from the entire wavefunction [21]. As seen in the figure in every case the gallium ion has less positive charge than its initial positive value which implies that the lumogallion component donates some electron population to the inorganic component acquiring itself some positive charge.

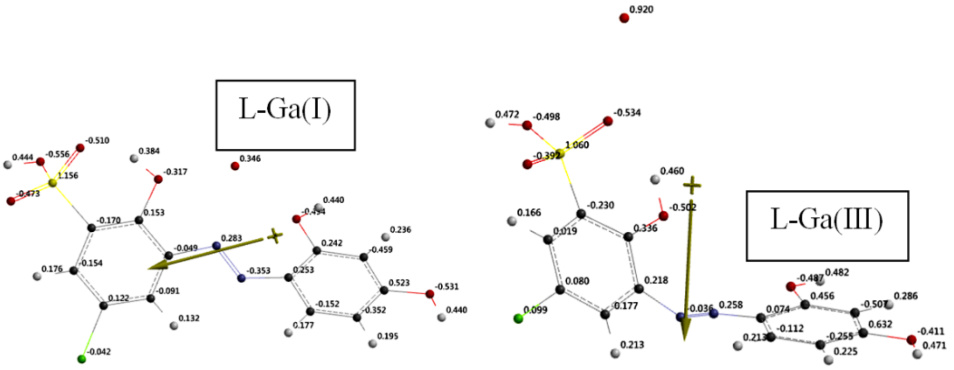


Figure 10. ESP charges on atoms of L-Ga(I) and L-Ga(III) composites.

The electrostatic potential maps of L-Ga(I) and L-Ga(III) composites are displayed in Figure 11.

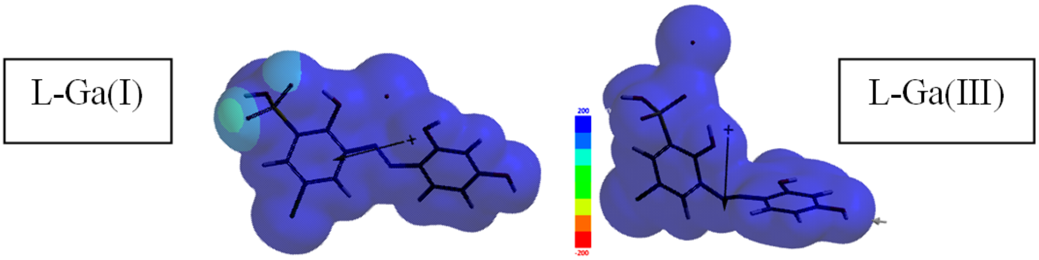


Figure 11. The electrostatic potential maps of L-Ga(I) and L-Ga(III) composites.

Figure 12 shows the bond densities of L-Ga(I) and L-Ga(III). It is clear that the interaction between the partners of the composites does not lead to any bond formations of molecular type. The interaction might be charge-charge or charge -dipole type in nature.

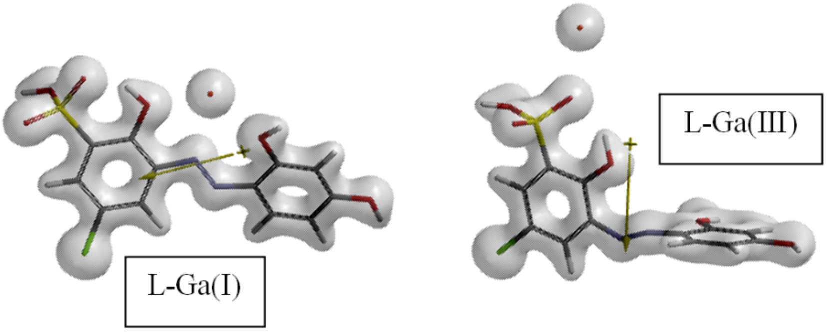


Figure 12. The bond densities of L-Ga(I) and L-Ga(III).

Figure 13 displays some of the molecular orbital energy levels of *trans*-lumogallion, and L-Ga(I) and

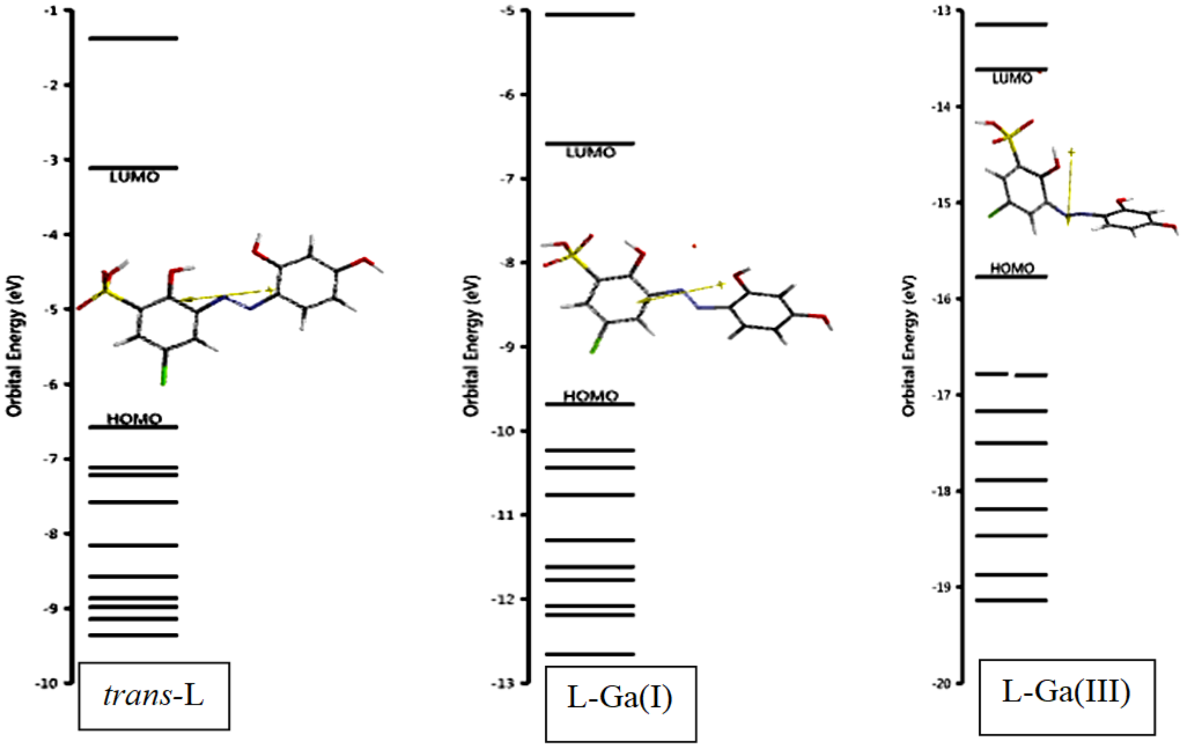


Figure 13. Some of the molecular orbital energy levels of *trans*-lumogallion, L-Ga(I) and L-Ga(III) composites.

L-Ga(III) composites. The figure reveals that the perturbational effect of Ga(III) on molecular orbital energy levels of *trans*-lumogallion is more pronounced compare to Ga(I). Both of the ions lower the molecular orbital energy levels of the *trans*-lumogallion but the interspacing of the levels are quite different in the composites, especially the LUMO-NEXTLUMO spacing are noticeable.

The HOMO and LUMO patterns of L-Ga(I) and L-Ga(III) composites are shown in Figure 14. They have π-symmetry in great extent. Note that in L-Ga(III) case one of the ring moieties contribute very little to the HOMO orbital.

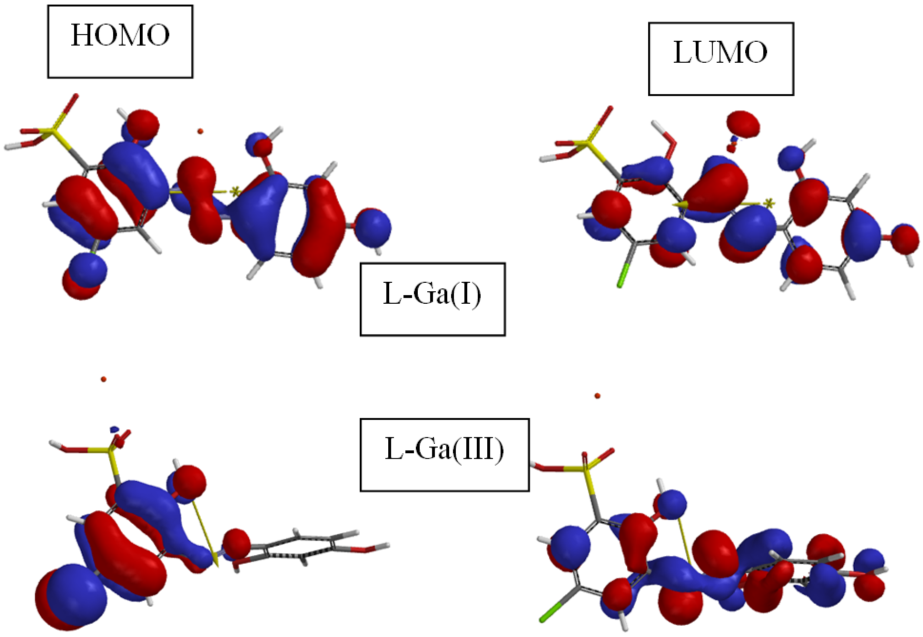


Figure 14. The HOMO and LUMO patterns of L-Ga(I) and L-Ga(III) composites.

The UV-VIS (TDDFT) spectra of L-Ga(I) and L-Ga(III) composites are shown in Figure 15. The spectrum of L-Ga(III) composite is greatly shifted to visible part of the spectrum as compared to the L-Ga(I) spectrum and exhibits some discernable shoulders. Although it is less stable compare to the composite of the *cis* case, the perturbational effect of Ga(III) on molecular orbital energy levels, thus on the spectrum of *trans*-lumogallion is more pronounced compare to Ga(I).

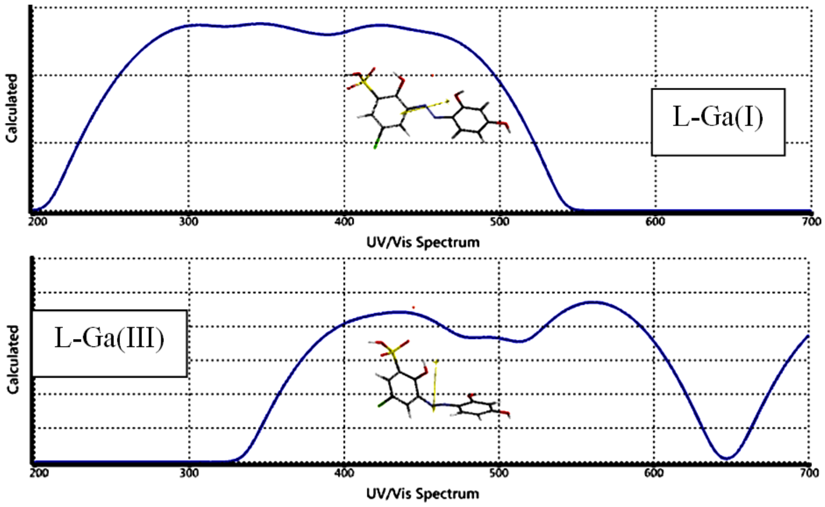


Figure 15. The calculated UV-VIS spectra of L-Ga(I) and L-Ga(III) composites.

4. Conclusion

The present computational DFT study on lumogallion geometrical isomers, within the restrictions of theory and basis set used, has revealed that although the *trans* isomer is coplanar, the *cis* is not. In the vacuum conditions, for both of the isomers it is found that the standard heat of formation (H^o) values are exothermic and they are favored according to their G^o values. Although they are electronically stable structures, the *trans* isomer being more stable than the *cis* isomer as expected. The composites of *trans* lumogallion with Ga(I) and Ga(III) ions are also stable structures having exothermic standard heat of formation values and favorable G^o values. However, lumogallion composite with Ga(I) is more exothermic and favorable and more stable compared to the respective values of Ga(III) case. Although the cations attract some electron population from lumogallion partner, there is no bonding of molecular type between them. However, the perturbational effect of Ga(III) on molecular orbital energy levels of *trans*-lumogallion is more pronounced compare to Ga(I) case.

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