Fullerenocene ☆

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A R T I C L E   I N F O

A B S T R A C T

The nature of the molecule $C_{60}CrC_{60}$ was studied from a theoretical point of view. Calculations on this molecule were carried out at the BPW91 level. The results are compared with those from another two molecules, dibenzenechromium that is a known and stable species, and η^6-fullerene chromium(0) η^6-benzene, a nonexisting molecule. This analysis has been carried out in order to study the stability of the target compound and provide useful information for its synthesis. The aromaticity of the rings in the three compounds was analyzed by means of HOMA and NICS methods whereas their intrinsic stability was estimated by means of homodesmotic reactions. The electronic structure of the three molecules was also studied. The results show fullerenocene should be a moderately stable species and should display semiconductor behaviour and some of the interesting properties of fullerene itself.

1. Introduction

Dibenzenechromium is a well known organometallic molecule that has been object of several studies [1]. The large symmetry (D_6h) of this species has its origin in the uniform electronic distribution on both decks arising from the aromaticity that gives place to a π bond with perfect hexahapticity [2]. The aromaticity of both benzene fragments does not seem to be affected by the coordination to the metal centre [3]. This system is analogous to ferrocene except that it contains benzene instead of cyclopentadienyl ions.

All the research groups that have studied this structure experimentally as well as theoretically [1,4], are in agreement about the relatively low energy value of the rotational barrier (≈0.9 kcal/mol) between the eclipsed and the staggered isomers, the former being the more stable one. This compound is very interesting because its strong donor capability can lead to a material with one-dimensional conductivity [1d].

Fullerenes [5] are a set of interesting molecules that have been object of many different studies [6]. Their metallic complexes, endohedral as well as exohedral, have also been studied experimentally and theoretically [7]. In this paper, we focused on compounds where the interaction between the fullerene fragment and a phenyl part occurs through a metal centre [8].

The most interesting experimental results are those obtained by Nakamura and co-workers [9]. In these works, Nakamura reported the first ferrocenoid complexes, including a ferrocene fragment

molecule. The main characteristics of these complexes are that the π bond on one side of the metal centre is focused on a pentagonal face of the fullerene fragment, the other side forms another π bond with a Cp fragment and in the majority of cases the metal atom has an intrinsic positive charge, as in the case of ferrocene, calculations on this species and analogous have been reported. Additionally, there are some very interesting theoretical reports [8], in which the capability of the fullerene fragments to generate this kind of bonds was studied.

The present study is different because the initial proposition is that the molecules have, in all cases, hexahapto π bonds. This feature was proposed and studied by Jemmis et al. and by Stankevich et al. [8]. The formed complexes should be analogous to the dibenzenechromium. Therefore, the π bond on one side of the metal centre is localised on a six-membered face of the fullerene fragment, whereas on the other side the π bond of the metal atom is associated with a benzene molecule or another hexagonal face of a new fullerene fragment. Furthermore, the metal atom has been considered to have not a formal oxidation state, i.e., in all cases Cr(0). Particularly Stankevich and his group carried out a very interesting work [8d] in which they analysed from a theoretical point of view the same systems considered in the present work. They focused in the capability of the fullerene to generate η^6 bonds and suggested that the large size of the fullerene may be the cause of inhibition of the formation of such molecules, and a perturbation of the symmetry of fullerene by substituents is necessary in order to stabilise the complex.

The aim of this work was to perform theoretical studies of two non existing new molecules. $C_{60}CrC_{60}$ is the fullerene analogue to dibenzenechromium; this molecule has been named fullerenocene, there is only one previous experimental report about the possibility of having a sandwich molecule with fullerene decks. It was isolated as a film and the authors claimed that the structure is possibly a

polymer with alternate Pd atoms and fullerene units [10a,b]. However, the nature of the bonding in this species is not totally clear. Besides a polymer which contains C$_{60}$–Co has been studied in a theoretical fashion [10c], the authors suggest these polymers favours ferromagnetic ground states, these results are important for our research because of the emphasis on the electronic mobility in these complexes. Additionally, Stankevich [8d] has studied this molecule (C$_{60}$CrC$_{60}$) in a theoretical way, analyzing its stability and found moderately stability for fullerenocene although he suggests the substituted derivatives should be more stable.

Dibenzenechromium is a very well known molecule [1]. It has been calculated in the present work in the same conditions that the others in order to validate the method of calculation by comparison with published results [1] and for the internal comparisons with the molecules under study.

Finally, the third molecule is a hybrid molecule similar to that studied by Nakamura [9] and Chystiakov [11] that arose for the interaction among a fullerene fragment, a benzene molecule and a Cr(0) atom. This case has been previously studied by Jemmis and Stankevich [8] by using an energy criterium and semiempirical methods in the first case and DFT methods in the second case.

In this work fullerenocene is studied from a theoretical point of view. The present analysis extended the cited works mainly performed by the comparison of the aromaticity results obtained by means of the ASE factor [12] estimated by homodesmotic reactions, HOMA [13] and NICS [14] routines employing other DFT method. The electronic structure of the three molecules was also studied. Furthermore the most relevant features derived from the study are addressed. The results are analysed on the basis of possible preparation and electronic application of these substances.

2. Methods

All structures were optimised in the gas phase using the JAGUAR 4.0 package [15]. A pure DFT method containing Becke's gradient correction [16] for exchange and Perdew–Wang's for correlation [17] was used for the energy evaluations. All calculations were performed using the 6-31G** basis set. The quality of this combination of method and basis set was validated by comparing the result of total energy of dibenzenechromium (−550.675 au) and the heat of formation of C$_6$H$_6$CrC$_{60}$ (947.5 kcal/mol) obtained in this work with the same values obtained by Jemmis (−550.706 au and 977.2 kcal/mol, respectively) [8b]. The frequency calculations were carried out at the same level of theory in order to confirm that the optimised structures were at the minimum of the potential surface. These frequencies were then used to evaluate the zero-point vibrational energy, the thermal vibrational corrections to the enthalpy, and the total enthalpy values. The bond lengths of the optimised structures were used for the HOMA (Harmonic Oscillator Model of Aromaticity) method [13] to study the aromaticity. The NICS (Nucleus Independent Chemical Shifts) [14] is a technique that was proposed by Schleyer as a new aromaticity index. The authors named it 'absolute magnetic shielding' and computed the value at the ring centres, which were determined by the non-weighted mean of the heavy atom coordinates. In this work, NICS calculations were performed following this technique, carried out with GAUSSIAN03 [18] at the BPW91/6-31G∗∗ level.

3. Results and discussion

3.1. Energy and aromaticity comparisons

The results of the energy and aromaticity of the molecules under study are shown in this section Fig. 1.
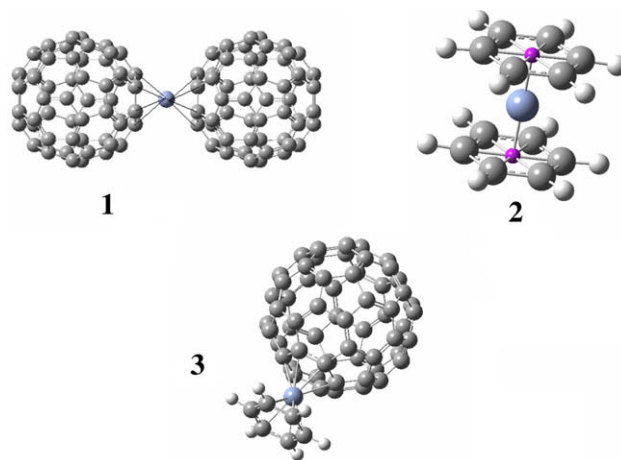

Fig. 1. Molecules under study.

Homodesmotic reactions were developed in order to calculate the ASE (aromatic stabilization energy) [12] in the three cases. In order to develop similar reactions for all cases, a set of two parent molecules were selected for all the species. The first parent molecule is similar to the bis(2,4-dimethylpentadienyl)chromium molecule prepared by Ernst and his group [19], but in our case it is bis(dibutadienyl)chromium. This molecule was chosen because it contains a delocalised electronic system without a clear aromatic scheme, but it has a framework of π bonds and this characteristic makes it suitable for analysing the stabilisation scheme produced by the appearance of aromaticity. The methyl substituents originally found in the compound by Ernst were removed, because these fragments would have been a source of carbon atoms with sp^3 hybridisation, that would be a problem in the definition of homodesmotic reactions. Therefore, the parent molecule is only bis(butadienyl)chromium (C$_8$H$_{12}$Cr) and its geometry is shown in Fig. 2.

The other parent molecule was 3-ethylene–butadiene (C$_6$H$_8$), which is an excellent source of carbon atoms containing only sp^2 hybridization. These species are shown in Fig. 3.

These last two compounds were calculated to find their optimised structures, followed by frequency calculations that were carried out in order to obtain their enthalpy values. In these cases, exactly the same methods and level of theory were used. The developed reactions for each case are shown in the next subsections together with the enthalpy analysis.

3.1.1. Homodesmotic reaction for C$_{60}$CrC$_{60}$

The homodesmotic reaction for the fullerenocene complexes is:

$$C_8H_{12}Cr + 59\ C_6H_8 \rightarrow C_{120}Cr + 121\ C_2H_2$$
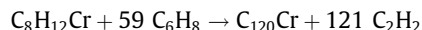
The result is excellent; the ASE value obtained was 7026.698 kJ/mol, which is very large compared with results obtained for fuller-

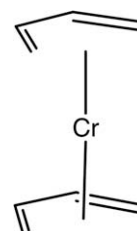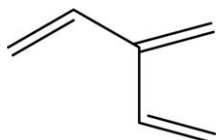Fig. 2. Bis(butadienyl)chomium.

Fig. 3. 3-Ethylene–butadiene (parent molecule).

Table 1
HOMA and NICS results for the molecules under study.

Molecule	$C_{60}CrC_{60}$	$C_6H_6CrC_6H_6$	$C_6H_6CrC_{60}$
HOMA	0.915	0.918	0.874 (ful)
			0.957 (ben)
NICS	−10.08 (centre)	−47.07	−7.95 (ful)
	−61.99 (η^6-face)		−57.90 (ben)
			−47.08 (η^6-face)

ene as 2345.88 kJ/mol [20] or 2509 kJ/mol ± 55 kJ/mol (from seven reports) [12]. Indeed the result should be 3521.349 kJ/mol for each fullerene unit with its respective bonds to the metal atom. This feature suggests the extra electronic flux due to the organometallic bonds help to stabilize the complex.

### 3.1.2. Homodesmotic reaction for dibenzenechromium

In the case of dibenzenechromium ($C_{12}H_{12}Cr$), the reaction was easy and the ASE result was very representative. The corresponding scheme is as follows:

$$C_8H_{12}Cr + 2\ C_6H_8 \rightarrow C_{12}H_{12}Cr + 4\ C_2H_4$$
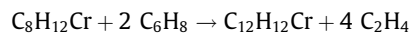
The homodesmotic reaction yielded a value of ASE of 564.49 kJ/mol. Such a value denotes a highly aromatic behaviour and can be compared with coronene, a known aromatic molecule, with a reported value ∼418 kJ/mol [12]. The proposition of Phillips et al. [3] is therefore correct, and hence the coordination on this molecule does not affect the aromaticity of the phenyl ring.

3.1.3. Homodesmotic reaction for $C_6H_6CrC_{60}$

The last homodesmotic reaction is remarkable. The corresponding scheme is

$$C_8H_{12}Cr + 30.5\ C_6H_8 \rightarrow C_{66}H_6Cr + 62.5\ C_2H_4$$
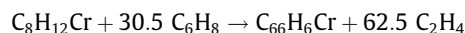
The result is even better than that found for the fullerenocene. The ASE value is 3964.5 kJ/mol.

A direct comparison of these results is not obvious. A valid comparison can be carried out by means of the ASE/π index proposed by Liebman [12]. This index indicates a stabilisation energy per carbon atom that contributes to the resonance framework. The ASE/π is 58.55 kJ/mol for fullerenocene, 47.04 kJ/mol for dibenzencrhomium and 60.07 kJ/mol for $C_6H_6CrC_{60}$. The best value is that for the hybrid molecule $C_6H_6CrC_{60}$ but very near to the fullerenocene. It has been proposed that the fullerene molecule is deficient in electrons [21], and present low polarizability [8c,d]. Indeed the nature of Cp and C_{60} is different since the first one is an electron donor whereas de second one is a weak electron acceptor. This feature changes the behaviour of the bond as it is shown in these results. It is important to note that the ASE is a global criterium of aromaticity, therefore it evaluates the whole system but not a specific zone of the molecules. Therefore, the application of some local criteria is important to reach a conclusion.

4. Aromaticity indices

The global aromaticity of the proposed molecules seems to be large on the basis of the results outlined in the last section; however, an energy criterium is not conclusive because global and local aromaticities can show a different behaviour as outlined by Solà and his co-workers [6g], and Chen and King [21]. Therefore, two popular methods to measure local aromaticity were applied; HOMA [13] and NICS [14].

The HOMA and NICS results for the six-membered face joined to the metal atom and in the centre of the fullerene ligands are shown in Table 1 for the three molecules under study.

The results of HOMA show that the dibenzenechromium is the most aromatic system; however the value is very close to that of

fullerenocene and only in the hybrid molecule there is a notable decrease for the fullerene fragment. It is important to note that the large value of aromaticity of the benzene ring joint to the Cr atom is associated with the hybrid molecule. This feature should lead to the full planarity of this ring as compared with the same section in the fullerene fragment, where the phenomenon of pyramidalisation is present. Since HOMA is a geometric criterium, the difference between both kinds of aromatic fragments is emphasised.

The NICS results follow a slightly different trend but are striking. First, the value of the aromatic rings joined to a metal are very large; this feature has been studied previously and discussed on the basis of paratropic and diatropic σ and π contributions [22]. However, in the present case the results are so high for dibenzenechromium that they indicate a large contribution of C–C(π) orbitals from two decks. The result grows significantly in the case of fullerene. There are two computed values, one for the centre of the sphere and the other for the six-membered face joined to the metal atom. The first one depicts the spherical aromaticity and the value is in the normal gap of NICS. This shows that the fullerene fragments of $C_{60}CrC_{60}$ are more aromatic than the same fragment in the hybrid molecule suggesting a larger current in the first. But the large difference appears for the surface where the trend is the same but the values are much higher, showing that there is a large contribution from the C–C(π) orbitals, which are donating electronic charge to the Cr atom.

The hybrid compound shows a peculiar behaviour similar to that found in the HOMA analysis. The NICS of the benzene ring is almost the same than that of the fullerene six-membered face (although this last one value is in itself very high). This feature means it can be expected a similar behaviour of the bonds from the metal centres with single aromatic fragments as well as for fullerenes, although the nature of this bonding is a little different as it will be discussed in the last section.

A conclusion about aromaticity can be reached with these results: based on the global criterium, the trend can be written as $C_6H_6CrC_{60} \approx C_{60}CrC_{60} > C_6H_6CrC_6H_6$. The HOMA and the NICS results show discrepancies mainly due to the pyramidalisation phenomenon present in the aromatic rings belonging to the fullerene fragments. However, in both cases the fullerenocene exhibited values that suggest a good aromatic behaviour on the faces directly joint to the chromium atom, and this result matches well with the global criterium.

5. Electronic structure

The electronic structure of fullerene has been extensively studied [23]. The scheme of molecular orbitals has been the object of particular attention due the I_h point group symmetry, which is not common in other kinds of molecules. The particular characteristic of this molecule is the nature of the frontier orbitals having a five-fold degenerated set for the HOMO which belongs to the irreducible representation h_u (with a very near HOMO-1 being a four-fold degenerated molecular orbital belonging to the g_g irreducible representation) and a triple degenerated set for the LUMO which belongs to the irreducible representation t_{1u}. Such a richness of electron states leads to a very narrow HOMO–LUMO gap. An
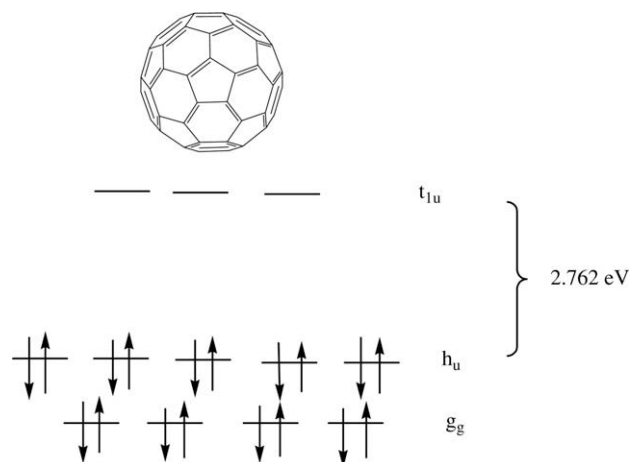
Fig. 4. Frontier molecular orbital scheme for fullerene (results obtained in this work).

Fig. 6. Frontier molecular orbital for fullerene–benzene–chromium, the HOMO presents accidental degeneracy between irreducible representations a1 and the set e.

anomalous pyramidalisation of the hybridisation of the sp^2 carbon atoms [24] appears as well. The same scheme was used in the present study through the BPW91/6-31G** method in order to compare the energy values on the same scale; the ordering is the same as well as the separation of levels, which yields a gap of 2.762 eV between the Frontier orbitals (see Fig. 4).

The molecular orbital distribution of dibenzenechromium has also been studied [25]. It belongs to the D_6h point group and its main characteristic is a HOMO-1 double degenerated, which belongs to the irreducible representation e_{2g} that is very near the a_{1g} HOMO. The set of frontier orbitals is shown in Fig. 5; again the system was studied at the same level of theory for comparison purposes and in this case the gap between HOMO–LUMO is 3.946 eV.

The hybrid compound presents a peculiar ordering of its molecular orbitals with the molecule belonging to the C_3v point group. It has been seen that in the case of this point group it is possible to find an accidental degeneracy [26], since the C_3v group does not have triple-folded degenerated irreducible representations. However, the molecular orbital scheme for the hybrid molecule shows, at first sight, a triple degenerated set for the HOMO. This set does not correspond to an irreducible representation but to a mixing of a
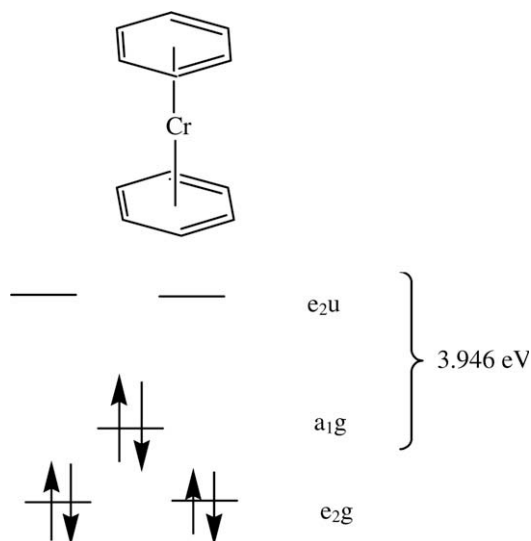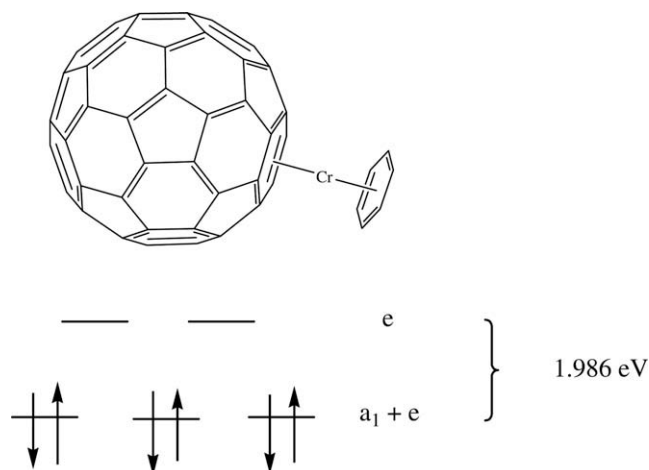
totally symmetric a_1 and a double e irreducible representation. This is a curious example of accidental degeneracy. It is important to note that this set results from the combination of HOMO (a_{1g}) and HOMO-1 (e_{2g}) of the D_6h *dibenzenechromium,* that are two irreducible representations which lie very close together, as pointed out above.

There is no contribution of the fullerene fragment to this last set of molecular orbitals, as the contribution of the fragment is totally concentrated in the LUMO and this feature confirms the weak electron acceptor nature of fullerene. The HOMO–LUMO gap is 1.986 and this result is interesting because such a value suggests that this molecule should have semiconductor behaviour. The large value of aromaticity found by the HOMA and NICS methods for this species
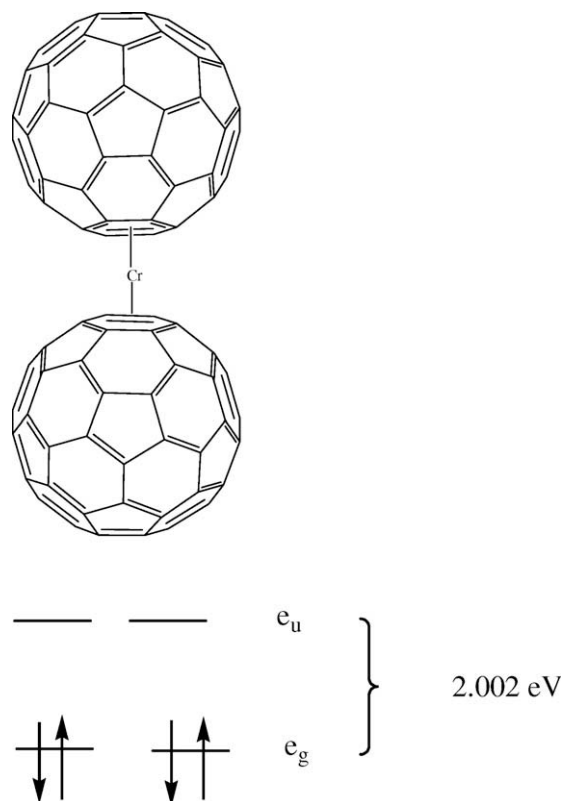

Fig. 5. Frontier orbitals for dibenzenechromium.

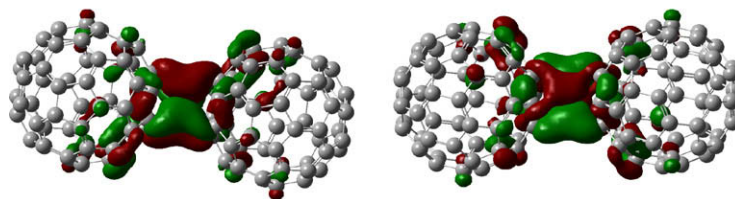**Fig. 7.** Frontier molecular orbitals from fullerenocene.

Fig. 8. Degenerated set for the HOMO of fullerenocene 1.

arise from this phenomenon because the *pseudo* triple degenerated set corresponding to the HOMO contributes with six electrons of the same energy to the aromaticity instead of the same six of dibenzenechromium but at different energy levels. The corresponding molecular orbital interaction is shown in Fig. 6.

Concerning the fullerenocene there are also interesting results. The molecule belongs to the D_3d symmetry group and the large symmetry of fullerene changes dramatically. The HOMO, as well as the LUMO are only two-fold degenerated sets. The HOMO belongs to the e_g irreducible representation, whereas the LUMO belongs to the e_u irreducible representation. The interesting point is that the HOMO–LUMO gap is even smaller than that of free fullerene, at 2.002 eV. This again suggests a semiconductor behaviour and all the known electronic characteristics of fullerene [27] must be found in this molecule. The molecular orbital interaction diagram is shown in Fig. 7.

Rayón and Frenking carried out a very interesting analysis by comparing the nature of the bond in ferrocene and that in dibenzenechromium [28]. In this work the authors showed, by means of

theoretical calculations, that the largest contribution to the orbital interactions in ferrocene comes from the π electronic donation from Cp to Fe. In a different pathway, the main contribution to the orbital interaction in dibenzenechromium is δ back-donation considering the symmetry of the corresponding irreducible representations. A similar analysis in the present case show that the irreducible representations e_g for fullerenocene, corresponding to the degenerated set of the HOMO (into the scheme of D_3d point group) have π symmetry and it contains only the electron donation from fullerene fragments to the d_{xz} and d_{yz} atomic orbitals of the Cr atom (see Fig. 8). On the other hand, the LUMO is again a degenerated set which belongs to the irreducible representation e_u, and this MO has only a contribution from the fullerene fragments without the presence of atomic orbitals coming from the metal atom. The behaviour in this sense is therefore very different than in dibenzenechromium.

Concerning the hybrid molecule, the behaviour is different but not completely defined. The 'actual' HOMO is a MO which corresponds to the irreducible representation a_1. This orbital has a clear symmetry δ where the main contribution to the d_z^2 atomic orbital arises from the Cr atom. However, the accidental degeneracy produces the pseudo triple-folded set, joining to this single orbital the next degenerated set. This set corresponds to the e irreducible representation with π symmetry (see Fig. 9). Besides, the LUMO that should act as the receptor of the back-donation do not participate in the bonding between the metal atom and the ligands. Therefore, this compound should be again a π-bonded molecule.

It is important to note that the latter results for fullerenocene correspond to an eclipsed isomer, therefore the staggered isomer was also calculated leading to a slightly less stable species. The difference in total energy between both isomers is 3.4132 kJ/mol in favour of the eclipsed structure. The staggered isomer belongs to the D_3 point group and its HOMO as well as its LUMO belong to the a_1 and a_2 irreducible representations respectively. Here again there is a curious phenomenon: the lack of symmetry causes the gap between HOMO and LUMO to be much more open than the corresponding value of the eclipsed one (5.898 eV), therefore this species seems less interesting than its isomer.

6. Conclusions

The aromaticity and relative stability of the fullerene analogue of dibenzenechromium was studied as well as a hybrid species which contains a deck of benzene and a deck of fullerene. The energy study carried out by means of homodesmotic reactions showed that the new structures have both large values of ASE as compared with dibenzenechromium itself, suggesting that these fullerene complexes should be as stable as the classically known π bonded organometallic compounds. Besides, the HOMA and NICS analysis suggested a strong aromatic character in both compounds and a reinforcement of the spherical aromaticity. This last condition is more marked in the case of fullerenocene, which showed a very large value of NICS in the face of the sphere joint to the
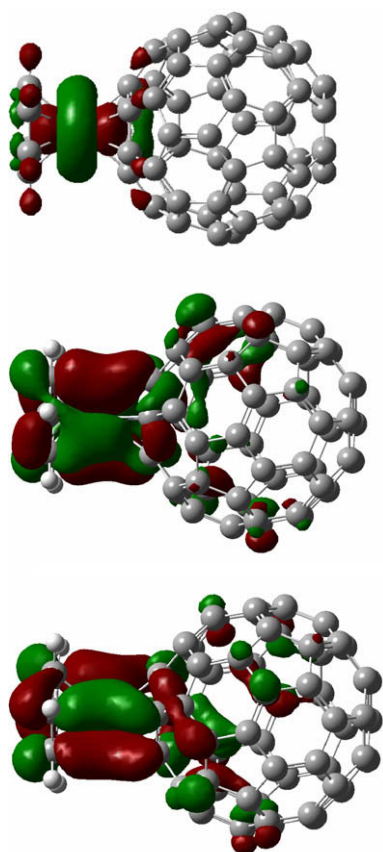

Fig. 9. Degenerated set for the HOMO of molecule 3.

metal atom. The analysis of the electronic structure showed that both molecules have narrow HOMO–LUMO gaps suggesting that these molecules might have a semiconductor character. In particular, the molecular orbital analysis results of the hybrid compound were significant because they showed a triple degenerated set corresponding to the HOMO. However, the corresponding point group does not possess an irreducible representation yielding a triplet; therefore, this is a peculiar example of accidental degeneracy. The phenomenon does account for the size of the energy gap which is even narrower than in the free fullerene itself.

Acknowledgements

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