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Research Article

Chromium tricarbonyl η⁶-Complexes of (R)-[6]helicene -A DFT Study

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Abstract

Isomeric chromium tricarbonyl η⁶-complexes of (R)-[6]helicene have been considered theoretically at the level of DFT (as B3LYP/6-31G(d,p), B3LYP/LANL2DZ, B3LYP/SBKJC and B3LYP/6-31G(d,p)// B3LYP/SBKJC) in order to investigate some molecular orbital, electronic and thermodynamic properties. The chromium tricarbonyl η⁶-complex is formed each time on different ring of (R)-[6]helicene molecule (on the same side of the molecular surface) to get the isomeric complexes and the effect of complexation on the stability and aromaticity of (R)-[6]helicene has been investigated by means of energy and NICS calculations results. Some geometrical and quantum chemical properties were obtained. Additionally, the calculated vibrational and UV/VIS spectra of the complexes were produced.

Introduction

Helicenes are screw-shaped chiral molecules consisting of *ortho*-fused aromatic rings [1,2]. A striking physical property of helicenes is their optical activity to rotate plane-polarized light with an extraordinarily high specific rotation [3]. The property of super chirality enables helicenes to be used in many applications such as photo-optical switches [4] and enantioselective fluorescence detectors [5]. Hexahelicene ([6]helicene) was the first example of the helicene family that was synthesized and then optically resolved [6].

On the other hand, various η⁶-arene transition metal complexes are known. Of these, the arene-chromium tricarbonyl derivatives have been the most extensively studied ones [7-17]. The linkage of a metal tricarbonyl moiety to an aromatic compound can induce several consequences including, activation of the aromatic ring to nucleophilic attack, steric inhibition of attack on functional groups from the same side as the metal carbonyl group, enhancement of aryl-H acidities, stabilization of any charge on carbons α and β to the arene-metal moiety , etc. [7]. The attachment of $Cr(CO)_3$ groups to an aromatic system leads to an activated attack of nucleophiles because

the metal group acts as a kind of electron sink [7]. Moreover, in some cases, complex formation stabilizes the system which is otherwise unstable.

One of the first striking features of π-coordinated metal complexes, such as the chromium tricarbonyl complex coordinated to polycyclic aromatic hydrocarbons (PAHs), is their ability to undergo thermal η⁶,η⁶-inter-ring haptotropic rearrangements (IRHR). That is the π-coordinated metal migrates between different rings of the PAH [18-26]. Haptotropic shifts can be of the σ–σ (sigmatropic rearrangement), σ–π, or π–π type. The haptotropic shift in organometallic species of π-ligands has been extensively studied in cyclic polyenes, such as cyclopentadienyl, indenyl, and anthracenyl ligands [20]. A reversible haptotropic shift has been applied to molecular switches [20].

The simplest system is to be mentioned where a haptotropic shift of ligand takes place is the (η⁶-naphthalene)-Cr(CO)$_3$ complex and their derivatives. On these species, various mechanistic studies have been performed to investigate the nature of η⁶-coordinated metal binding [27-29]. It has been found that the interactions between low-lying unoccupied orbitals (LUMO) of the $Cr(CO)_3$ and high-lying occupied π-orbit-

als (HOMO) of naphthalene represent the dominant bonding mechanism. It has been observed that the chromium tricarbonyl moiety acting in these complexes as a powerful electron withdrawing group [30]. Moreover, some DFT calculations appeared in the literature recently on the $Cr(CO)_3$ complexes of some polycyclic hydrocarbons [31-35]. The η^6-hexahelicene complexes of iridium and ruthenium have been prepared. The results of final thermodynamic products have indicated that the η^6-coordination of the metal fragment occurs to the helicene terminal ring [36].

Also, some DFT calculations have been performed on hexahelicene derivatives [37-40]. Abbate et al., studied the vibrational circular dichroism (VCD) and IR absorption spectra of the (-)-enantiomer of 2-Br-hexahelicene. They have measured and interpreted the results by use of density functional theory (DFT) calculations [37].

In the present treatise, chromium tricarbonyl η^6-complexes of R-[6]helicene have been considered within the constraints of density functional theory (DFT).

Method

The initial geometry optimizations of all the considered structures leading to energy minima have been achieved by using first MM2 (molecular mechanics) method followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [41,42] at the restricted level [43]. Subsequent geometry optimizations have been achieved by using various restricted Hartree-Fock (RHF) methods successively and finally optimizing within the framework of density functional theory (DFT, B3LYP) [44,45] using LANL2DZ [46,47] and SBKJC [48] and 6-31G(d,p) basis sets. It has to be noted 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 [45,49]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [50] and Lee, Yang, Parr (LYP) correlation correction functional [51].

In the present study, for each set of calculations, also vibrational analyses have been done (using the same basis set employed in the corresponding geometry optimization). The normal mode analysis for each structure yielded no imaginary frequencies for the $3N-6$ vibrational degrees of freedom, where N is the number of atoms in the system. This result indicates that the structure of each molecule corresponds to at least one local minimum on the potential energy surface. All these computations were performed by using the Spartan 06 [52] package program.

Absolute NMR shielding values [53] were calculated using the Gauge-Independent Atomic Orbital method [54] with the restricted closed shell formalism employing B3LYP/6-31G(d,p) type NICS calculations over the B3LYP/SBKJC optimized geometries and LANL2DZ basis set over B3LYP/ LANL2DZ optimized geometries as well as. The NICS values have been obtained by calculating absolute NMR shielding at the ring centers, NICS (0). The NICS calculations of the present systems have been performed by the use of Gaussian 03 package program [55].

Results and Discussion

The present study considers isomeric chromium tricarbonyl η^6-complexes of (R)- [6]helicene. The chromium tricarbonyl moiety has been η^6-complexed with each benzenoid ring of (R)-[6]helicene at a time. The [6]helicene under investigation was constructed in R-stereochemistry ((R)-[6]helicene) and the complexation was achieved in each case on the same surface (upper surface) of the (R)-[6]helicene.

For the calculations, LANL2DZ , SBKJC and also 6-31G(d,p) (as B3LYP/6-31G(d,p) and B3LYP/6-31G(d,p)//B3LYP/SBKJC) basis sets have been employed with the B3LYP functional at the restricted level. Note that these bases sets are suitable for transition metals [46-48,56].

Structures

Figure 1 shows the numbering and some bond lengths of ((R)-[6]helicene [57] and its calculated bond lengths at the levels of B3LYP/ LANL2DZ , B3LYP/ SBKJC and B3LYP/6-31G(d,p). As seen in the figure B3LYP/ LANL2DZ and B3LYP/6-31G(d,p) type calculation yields much closer bond lengths to the experimental values indicated in the figure.

The bond lengths obtained using SBKJC basis set are a little bit longer than the other calculated bond length values. However, LANL2DZ basis set cannot predict the direction of the dipole moments correctly. The attachment of $Cr(CO)_3$ moiety to an aromatic ring attracts electrons acting as a kind of electron sink [7]. Therefore, the tip point of the dipole moment is expected to be somewhere nearby the ligand, whereas LANL2DZ type calculations locate the positive end on the ligand. The other basis sets presently employed with B3LYP functional correctly estimates the dipole moment direction. However, the magnitudes of all the dipole moments are obviously basis set dependent and quite different from each other (just as two examples see Tables 1 and 2).

Table 1 shows some bonding distances and the magnitudes of the dipole moments calculated at the level of B3LYP/SBKJC. The dipole moment values are quite high. The LANL2DZ basis set yields even much greater dipole moment values (106-130 Debye, see Table 2). The high values for dipole moments must be due to the opposite charge centers being far away from each other and also different magnitudes of the charges estimated by different methods for the same centers. The dipole moment orders are as follows; 6>1>2>5>3>4 (B3LYP/SBKJC); 1>2>5>6>3>4 (B3LYP/LANL2DZ); 1>3>5>4>6>2 (B3LYP-6-31G(d,p)); and 5>4>3>2>1>6 (B3LYP-6-31G(d,p)// B3LYP/ SBKJC).

Figure 1. Numbering and some bond lengths of hexahelicene [57] and its calculated bond lengths at various levels.

Figure 2. Optimized structures of the complexes considered (B3LYP/SBKJC).

All the complexes studied presently possess **C1** symmetry. Figure 2 shows the optimized geometries of the complexes presently concerned (B3LYP/SBKJC). Note that dipole moment vector in each case originate somewhere in the helicene structure and aiming to the chromium ligand.

Note that the Cr-CO bond vectors have a staggered arrangement with respect to the carbon atoms of the ring where the complex formation occurred. Tables 1 and 2 show also Cr-CO and η^6-bond lengths and of the complexes considered (B3LYP/SBKJC and B3LYP/LANL2DZ, respectively).

Table 1. Some bond lengths and dipole moments (B3LYP/SBKJC).

No	Cr-CO bonds			η^6-bond	Dipole moment
1	1.83	1.84	1.84	1.84	45.63
2	1.83	1.83	1.84	1.89	42.61
3	1.83	1.84	1.84	1.89	26.96
4	1.83	1.84	1.85	1.93	19.59
5	1.82	1.84	1.85	2.06	41.49
6	1.83	1.83	1.84	1.85	61.23

Dipole moments in Debye. Bond lengths in Å.

Table 2. Some bond lengths and dipole moments (B3LYP/LANL2DZ).

No	Cr-CO bonds			η^6-bond	Dipole moment
1	1.82	1.83	1.83	1.85	130.53
2	1.82	1.82	1.83	1.91	128.89
3	1.82	1.82	1.83	1.92	118.62
4	1.82	1.82	1.84	1.97	106.19
5	1.82	1.82	1.84	2.17	124.69
6	1.82	1.82	1.83	1.87	123.00

Dipole moments in Debye. Bond lengths in Å.

Generally, Cr-CO bond lengths are comparable. The η^6-bond is the longest for structure-**5** followed by structure-**4**. Whereas 1 is characterized with the shortest η^6-bond (Tables 1 and 2). The order is **1<6<2=3<4<5**. The same order is produced by B3LYP/LANL2DZ type calculations (Table 2).

Electronic Energies

Table 3 shows the total electronic energy values for complexes

1-6, calculated at various levels. The corrected total electronic energy (E_{corr}) includes the zero points vibrational energy term (ZPE). The B3LYP/SBKJC and B3LYP/LANL2DZ level of energy calculations (although the magnitudes are very different) produce the same order of stabilities, that is **1>3>2>4>6>5**. Whereas B3LYP/6-31G(d,p) and B3LYP/6-31G(d,p)//B3LYP/SBKJC stability orders are **2>4>5>6>3>1** and **2>1>3>6>4>5**, respectively.

The stabilities of these complexes should be the implicit functions of their gross and fine topologies including curvature of the skeleton, the degree of π-conjugation between the adjacent rings etc. The most stable structure-1 is expected (as produced by B3LYP/SBKJC and B3LYP/LANL2DZ level of calculations) if one considers the number of Clar's sextets [58] in these isomeric structures. In structure-**1**, the Clar's sextet can shift over five rings which contributes to the stability. Whereas in the other isomers less number of Clar's sextets exists along the ribbon of hexagons. In that respect, the order of stability estimation by B3LYP/6-31G(d,p) type calculations should be unlikely. The B3LYP/6-31G(d,p)// B3LYP/SBKJC calculations also yield somewhat unexpected order. However, isomer-5 in all the cases, except B3LYP/6-31G(d,p) is expected to be the least stable one among the isomeric series.

The energy differences between structures **2** and **3** in one hand and **3** and **4** in the other are rather small. Then, if the activation energies for the haptotropic shift of the ligand are favorable, these structures should be pair wise interconvertible.

In general, shifts of the π–π type have relative low activation energies. At room temperature, complexes that present haptotropic phenomena are very fluxional, and it is common to find them in equilibrium[59]. The fluxionality of these complexes gives the possibility to use them as molecular switches. There is at least one example with aromatic polycyclic ligands in which it was possible to control the direction of the equilibrium by changing the conditions of the system [20]. There are several studies of haptotropic shifts in complexes with aromatic polycyclic ligands, like naphthalene or anthracene, where the metal moves across the rings [31,60-62]. Note that the larger the ring, and the larger its **π** system, the easier the slippage becomes [24]. This behavior is explained by the fact that larger rings bind more weakly to the metal centers when they are η^5 coordinated. With cyclopentadienyl ligand, η^3-Cp rings have not often been observed [63]. On the other hand, heterocycles exhibit a marked tendency to coordinate η^1. Clear η^3 coordination has never been observed (and was predicted to be unfavored relative to η^1), although η^5 coordination has been achieved when adequate substituents are. Also, a large number of haptotropic rearrangements in aromatic ligands were disclosed and qualitatively studied for many transition metals including Mo, W, Rh, Pd, Ir, Ni, Mn, Fe, Zr, Ru, and Os [61]. There are two kinds of haptotropic rearrangements: intra-ring haptotropic (when the metal fragment changes its p-coordination to the organic ligand within the same ring) and

inter-ring haptotropic (involving migration of organometallic group from one of the aromatic ring to the other) [61]. The dynamic behavior of fluxional organometallic systems was tried to be theoretically investigated and all were revised [59]. In the present case, the chromium moiety should undergo 1,2-shift sequentially somewhat parallel to the shift of Clar's sextet. Since strongly aromatic rings will be less willingly to donate electrons and the metal atom acts as an electron sink [7] then the metallic moiety should shift to the comparatively less aromatic ring.

magnetic criteria for aromaticity [71-74]. Resonance energies and magnetic susceptibilities are measures of the overall aromaticity of a polycycle but do not provide information about the individual rings. In contrast, NICS has been proved to be an effective probe for local aromaticity of individual rings of polycyclic systems.

Table 4 shows the NICS(0) values of the (R)-[6]hexahelicene rings of structures **1** (the most stable complex expected by B3LYP/SBKJC and B3LYP/LANL2DZ type calculations) and **5** (the least stable complex estimated by all except B3LY-P/6-31G(d,p) level of calculations).

Table 3. Various energies of the complexes considered calculated at some level of calculations.					
	B3LYP/SBKJC		**B3LYP/LANL2DZ**		**B3LYP/6-31G(d,p)// B3LYP/SBKJC**	
No	E_{total}	E_{corr}	E_{total}	E_{corr}	E_{total}	E_{corr}
1	-807593.66	-806645.15	-3745093.88	-3744135.45	-6261543.33	-6260608.78
2	-807563.97	-806616.19	-3745064.92	-3744107.76	-6261556.26	-6260609.52
3	-807570.30	-806621.54	-3745070.19	-3744112.45	-6261512.83	-6260579.20
4	-807562.60	-806612.17	-3745063.85	-3744105.23	-6261504.78	-6260570.44
5	-807533.34	-806584.66	-3745039.72	-3744081.71	-6261471.58	-6260538.51
6	-807555.27	-806606.66	-3745057.37	-3744099.04	-6261506.90	-6260572.54
Energies in kJ/mol. $E_{corr} = E_{total} + ZPE$, ZPE: Zero point vibrational energy.					

NICS

The simplest criterion for aromatic compounds is that the presence of cyclic conjugated π-systems containing the proper number of π-electrons (i.e., the Hückel rule). While this criterion is enough to predict the aromaticity of a neutral and charged monocyclic ring systems, it is not always a clear indicator of aromaticity for more complex systems.

Aromaticity is expressed by a combination of various properties in cyclic delocalized systems. In general, aromaticity is discussed in terms of energetic, structural and magnetic criteria [64-69]. In 1996, Schleyer has introduced a simple and efficient probe for aromaticity: Nucleus-independent chemical shift (NICS) [70], which is the computed value of the negative magnetic shielding at some selected point in space, generally, in a ring or cage center. It is known in the literature that negative NICS values denote aromaticity (-11.5 for benzene, -11.4 for naphthalene) and positive NICS values denote antiaromaticity (28.8 for cyclobutadiene) while small NICS values indicate non-aromaticity (-2.1 for cyclohexane, -1.1 for adamantane). NICS may be a useful indicator of aromaticity that usually correlates well with the other energetic, structural and

In Table 4, the NICS(0) values are the crop of B3LYP/6-31G(d,p) level of calculations based on B3LYP/SBKJC geometry optimization. Note that the SBKJC and 6-31G(d,p) basis sets predict the direction of dipole moment correctly in contrast to the LANL2DZ basis set. Thus, B3LYP/SBKJC and B3LYP/6-31G(d,p) level of calculations should estimate the charge distribution in the complexes considered better than the B3LYP/ LANL2DZ level. The aromaticity order for the rings (A-F) based on NICS(0) values for complexes **1** and **5** are F>C>D>E>B and A>F>C>B>D, respectively. The common point between the aromaticity order of rings of structures **1** and **5** is that the ring occupying the position farthest away from the complex formed ring is the most aromatic one (namely F and A rings in **1** and **5**, respectively).

The NICS(0) values of the other rings should be dictated by some subtle factors, such as the bond lengths of the ring, the curvature of the helix at the ring of interest etc. Note that the η^6-bond in structure **5** is notably longer than the respective bond in other complexes (see Tables 1 and 2).

Table 4. NICS(0) values of some of the structures presently considered.

No/Ring	A	B	C	D	E	F
1	-	-7.1441	-7.5061	-7.2333	-7.1571	-10.2247
5	-10.7674	-6.9652	-8.2852	-6.6375	-	-9.7494

B3LYP/6-31G(d,p)//B3LYP/SBKJC

The NICS(0) values calculated by using B3LYP/LANL2DZ level (Table 5) fall into the decreasing order of aromaticity as F>B>C>E>D and A>F>C>D>B for structures **1** and **5**, respectively. Note that the both level of calculations predicts ring-F as the most aromatic in structure-**1**. For structure-**5** the aromaticity order of A>F>C is predicted by the both levels of calculation.

Table 5 . NICS(0) values of some of the structures presently considered.

No/Ring	A	B	C	D	E	F
1	-	-5.0171	-4.4854	-4.2860	-4.3237	-7.0485
1-decomposed	-6.8711	-4.1966	-4.2622	-4.3417	-3.9798	-7.1470
5	-7.3546	-4.0431	-4.8719	-4.3587	-	-6.8947
5-decomposed	-7.1246	-3.9976	-4.5658	-4.6188	-4.2106	-7.2972

B3LYP/LANL2DZ

In Table 5, due to the fastness of computations, LANL2DZ basis set has been employed for comparison purpose of local aromaticity of the rings in the presence and absence of the ligand. In the table, decomposed means the ligand $(Cr(CO)_3)$ moiety has been removed from the complex keeping the geometry of helicene as it was in the complex. The results reveal that the complexation increases the aromaticity of rings so that B>C>E and decreases the aromaticity in rings D and F in structure-**1**. Whereas in **5**, by complexation the aromaticity of rings A,B and C increases but the respective property of rings D and F decreases (F>D). It seems that the complexation increases the aromaticity of the adjacent ring(s) in structure-1 but decreases in structure-**5**. It might be due to the variations in local electron density (caused by the complexation) which is contributed to the π-electron delocalization in each individual ring.

IR Spectra

Table 6 shows some characteristic IR bands for the most stable and least stable isomers (B3LYP/SBKJC), namely **1** and **5**, respectively. Figure 3 shows the IR spectra of (R)- [6]helicene and its complexes **1** and **5** considered presently. Note that they have been the calculated spectra at the same level. The strongest bands in the figure for the complexes stand for the carbonyl stretching.

Table 6. Some bands of IR spectra of complexes 1 and 5 (B3LYP/SBKJC level of calculations).

No	Frequency (cm^{-1})	Remarks
1	3277,3246,3231	C-H stretchings of ring A (complex formation site)
	3236,3210,3187	C-H stretching of the 6th aromatic ring (F)
	3207-3190	C-H stretching of the aromatic rings
	1882-1820	CO stretchings
	1661-1614	Aromatic skeletal breathing
5	3261,3219	C-H stretchings of ring F
	3281,3215,3192	C-H stretchings of ring A
	3211-3174	C-H stretchings of ring E (complex formation site)
	3214-3191	C-H stretching of the aromatic rings
	1879-1808	CO stretchings
	1669-1624	Aromatic skeletal breathing

UV-VIS Spectra

All the calculated UV-VIS spectra presently obtained within DFT approach are actually the product of time-dependent density functional (TD-DFT) treatment. B3LYP/LANL2DZ and B3LYP/SBKJC level of calculations for the UV-VIS spectra yield similar spectra. Figure 4 shows B3LYP/SBKJC spectra for the complexes. The spectrum of complex-**1** spans from 300 nm to 600 nm. As the complexation site moves from ring B to E the spectra exhibit bathochromic shift, eg., spans from 350 nm to 650 nm. For complex-**5** the range covers 375- 750 nm. Note that complex-5 has the longest η⁶-Cr bonding, less electron withdrawing by the ligand and better π-electron delocalization over the helix, thus causing a bathochromic shift. As the complexation occurs at ring-6, the range of absorption wavelengths confines back to 300-640 nm.

Table 7 shows the main strong absorption peaks of the complexes. The starred ones are the strongest among the sets. The table also contains the HOMO-LUMO energy gaps (Δε) of the complexes calculated at the level of B3LYP/SBKJC (see Table 8).

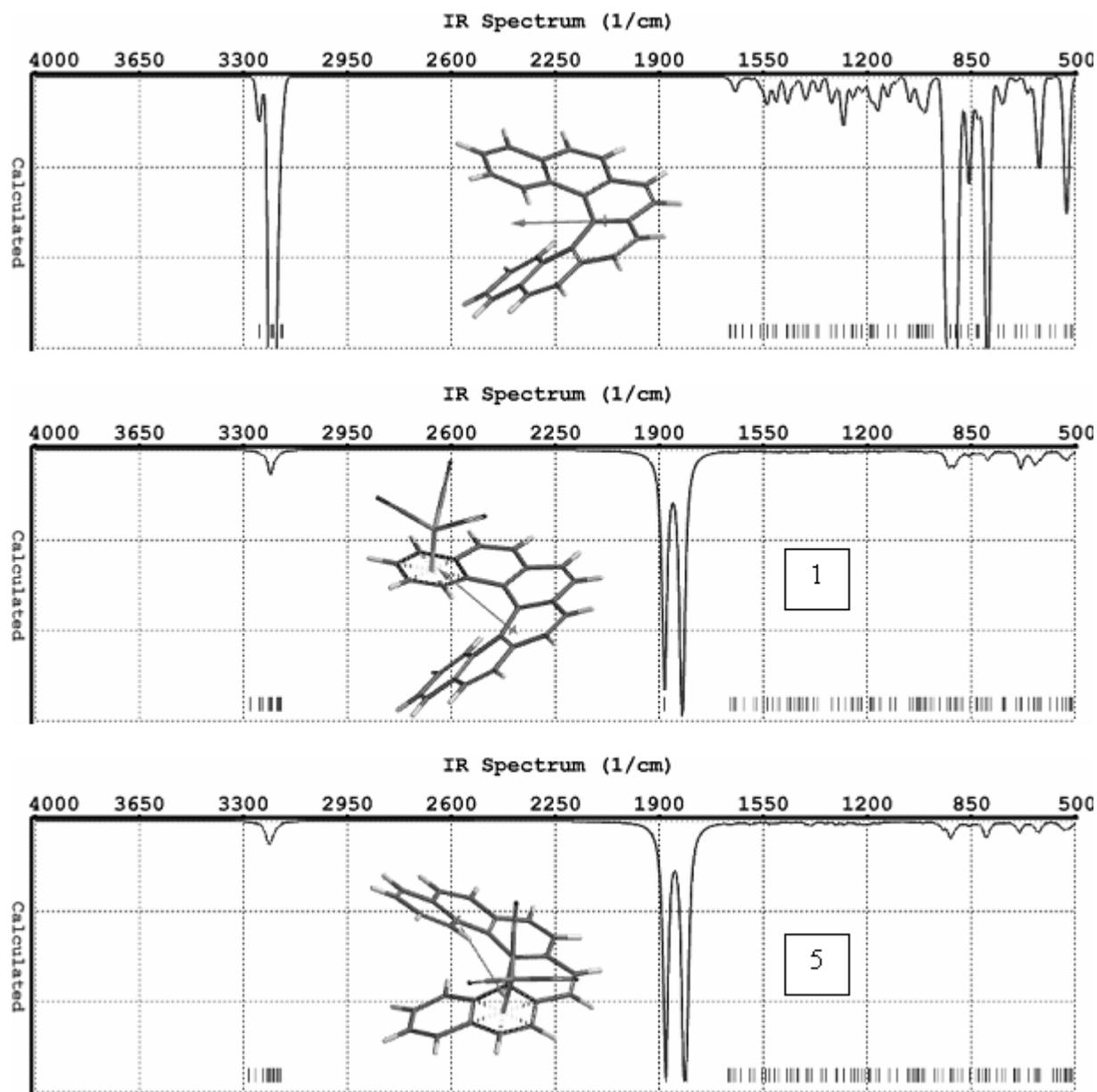**Figure 3.** IR spectra of (R)-[6]helicene and structures 1 and 5 (B3LYP/SBKJC).

Table 7. The λ_{max} and $\Delta\varepsilon$ values for the complexes considered.

No	λ_{max} (nm)	$\Delta\varepsilon$
1	402*,430, 477	8.9
2	423, 438*,501	4.83
3	430, 440*,517	14.98
4	434*, 516	17.15
5	429, 561*, 670	6.58
6	400*,410,551	8.44

B3LYP/SBKJC level of calculations. $\Delta\varepsilon$ is in kJ/mol.

In the case of polycyclic benzenoid hydrocarbons, α-bands are often the longest wavelength bands in their spectra [75]. The p-bands are moderately strong whereas mostly β-bands are very intense. The p-bands are generally more sensitive to structural changes than the α-bands. When the order of $\Delta\varepsilon$ values in Table 7 (see also Table 8) are compared with the order of the strongest bands of the complexes, one finds not a direct parallelism comprising all the complexes considered. However, the strongest peak of structures **1,2,5** and **6** exhibit some correlation with $\Delta\varepsilon$, the interfrontier molecular orbital energy gap. Their longest wavelengths also show bathochromic shift as $\Delta\varepsilon$ values decreases, thus they should be the p-bands, originating from the HOMO-LUMO transition.

Figure 5 shows some of the molecular orbital energies of (R)-[6]helixcene and its considered complexes **1** and **5**.

Note that the HOMO and LUMO energy levels are closer to each other in complex-**5** than the complex-1 and (R)-[6]helicene (see Figure 5).
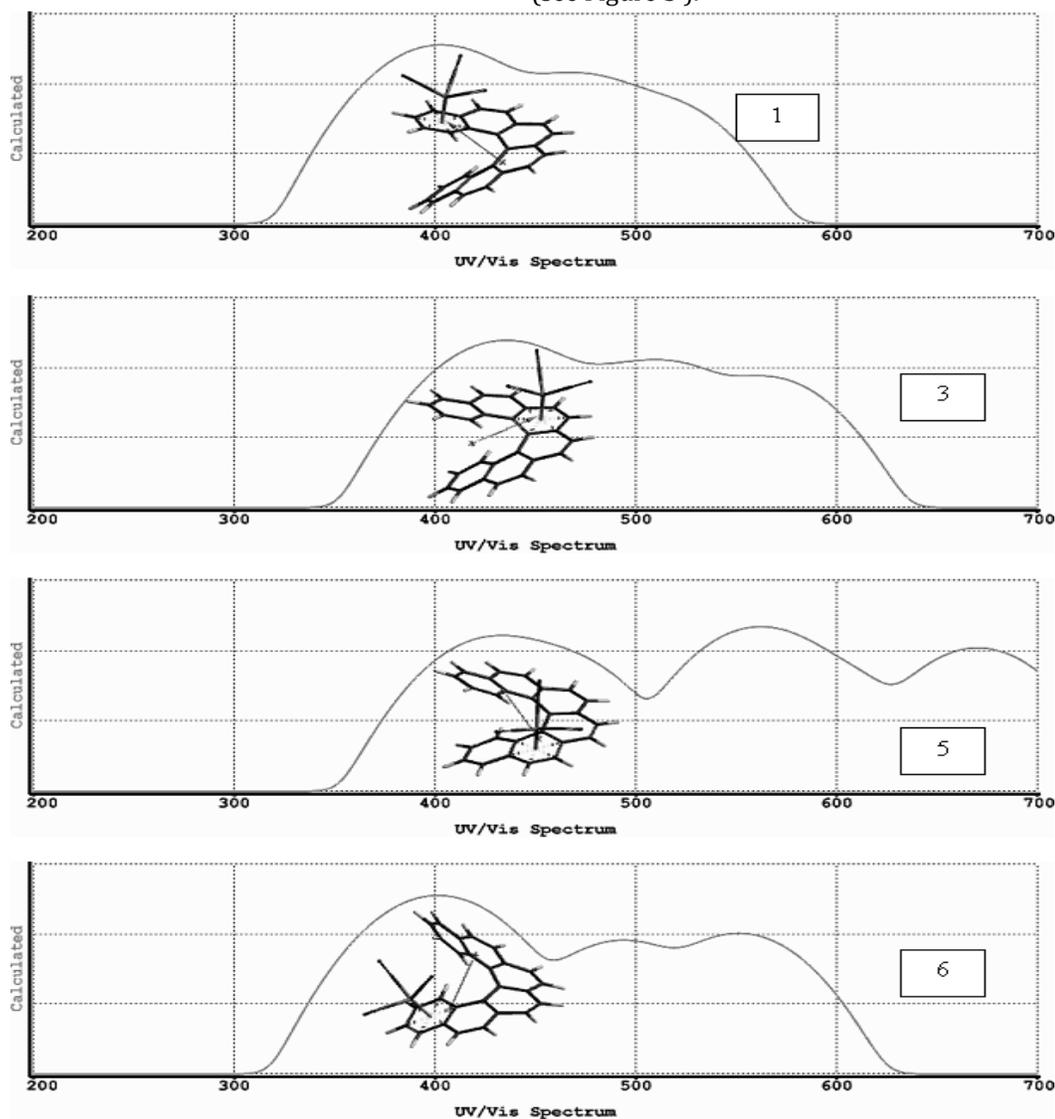

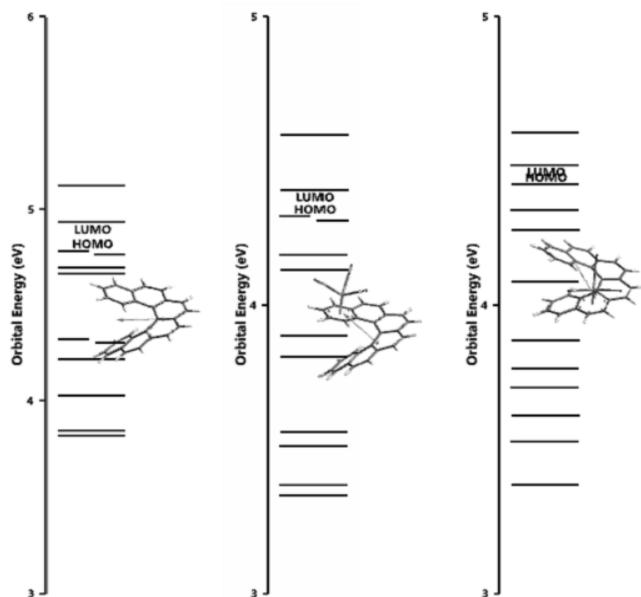**Figure 4.** UV-VIS spectra of some of the complexes (B3LYP/SBKJC).

Figure 5. Some of the molecular orbital energy levels of hexahelicene and structures-1 and 5 (B3LYP/SBKJC).

No	HOMO	LUMO	Δε
Table 8. The HOMO, LUMO energies and interfrontier energy gaps for the structures considered.			
1	415.71	424.61	8.9
2	415.31	420.14	4.83
3	415.78	430.76	14.98
4	422.27	439.42	17.15
5	426.47	433.05	6.58
6	436.04	444.48	8.44
Energies in kJ/mol. B3LYP/SBKJC level of calculations.			

Note also that the η^6-bond in structure-**5** has the longest one. Thus the ligand attracts the electrons less effectively. Consequently, perturbation in the electron population in other rings is less which means relative to structure-**1**, better conjugation exists in structure-**5**. The other factor might be the curvature of the helix in each complex. Depending on it, the π-electron conjugation between the rings might vary. Note that the increased conjugation causes the narrowing of the interfrontier molecular orbital energy gap, resulting in a bathochromic shift [76].

The Δε order is estimated as **4>3>1>6>5>2** by B3LYP/SBKJC type calculations.

Conclusion

The isomeric chromium tricarbonyl η^6-complexes of (R)-[6] helicene have been subjected to DFT treatment at the different level of calculations. Except for LANL2DZ basis set, the others presently employed predict the direction of dipole moments correctly. However, SBKJC and LANL2DZ basis sets predict the same stability order which seems in accord with some of the literature data of other types of complexes of helicene. Of the present complexes, the most stable and least stable ones are considered for NICS(0) calculations that the values show variation depending on the site of complexation. The order of NICS(0) values of the rings are basis set dependent, however, both the methods used for that purpose indicate that F-ring in structure-**1** and A-ring in structure-**5** are the most aromatic ones, respectively.

The calculated UV-VIS spectra, generally exhibit some slight bathochromic effect as the complexation site varies from ring-A to ring-D, gets the maximum value for ring-E and then the domain of wavelengths shrinks almost to the range of structure-**3**.

All these observations show that not only the gross but also the fine topology of these complexes are important factors dictating various properties of them.

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