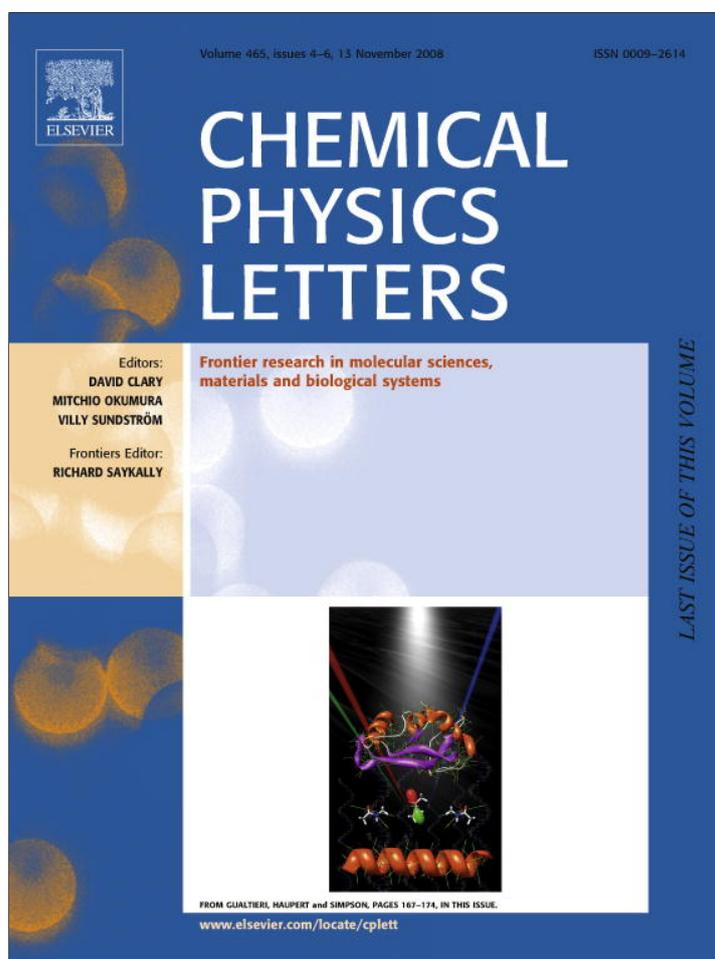


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## Coordination of bis(tricarbonylchromium) complexes to small polycyclic aromatic hydrocarbons: Structure, relative stabilities, and bonding

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## ABSTRACT

Bis(tricarbonylchromium) complexes of two- to four-fused benzenoid rings were investigated by means of the B3LYP method. Our analysis was focused on both the molecular structure of the different isomers and their relative energies. For all the studied cases, the isomer with the lowest energy resulted to be the *anti* where both Cr(CO)<sub>3</sub> units are bonded to the most external rings. According to the calculated dissociation energies for the lowest energy isomers, stabilization due to metal bicomplexation is similar in angular and linear polycyclic aromatic hydrocarbons (PAH), while the less energetically favorable complexation occurs in PAH with a compact arrangement of six-membered rings like in pyrene.

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## 1. Introduction

( $\eta^6$ -Arene)tricarbonylchromium(0) complexes are among the most studied in organometallic chemistry of half-sandwich species because of their useful properties in catalysis and arene activation [1,2]. The effect of complexation of an electron-withdrawing Cr(CO)<sub>3</sub> unit to a polycyclic aromatic hydrocarbon (PAH) entails the expansion of the coordinated ring, a partial localization of the  $\pi$ -bonds, and a slightly bending of this aromatic ring [3–5]. Usually, tricarbonylchromium complexation takes place on the ring with the highest  $\pi$ -electron density [6,7] and once attached, the Cr(CO)<sub>3</sub> group changes dramatically the reactivity of the ring. In addition, Cr(CO)<sub>3</sub> complexation leads to systems with interesting electrochemical properties [8,9].

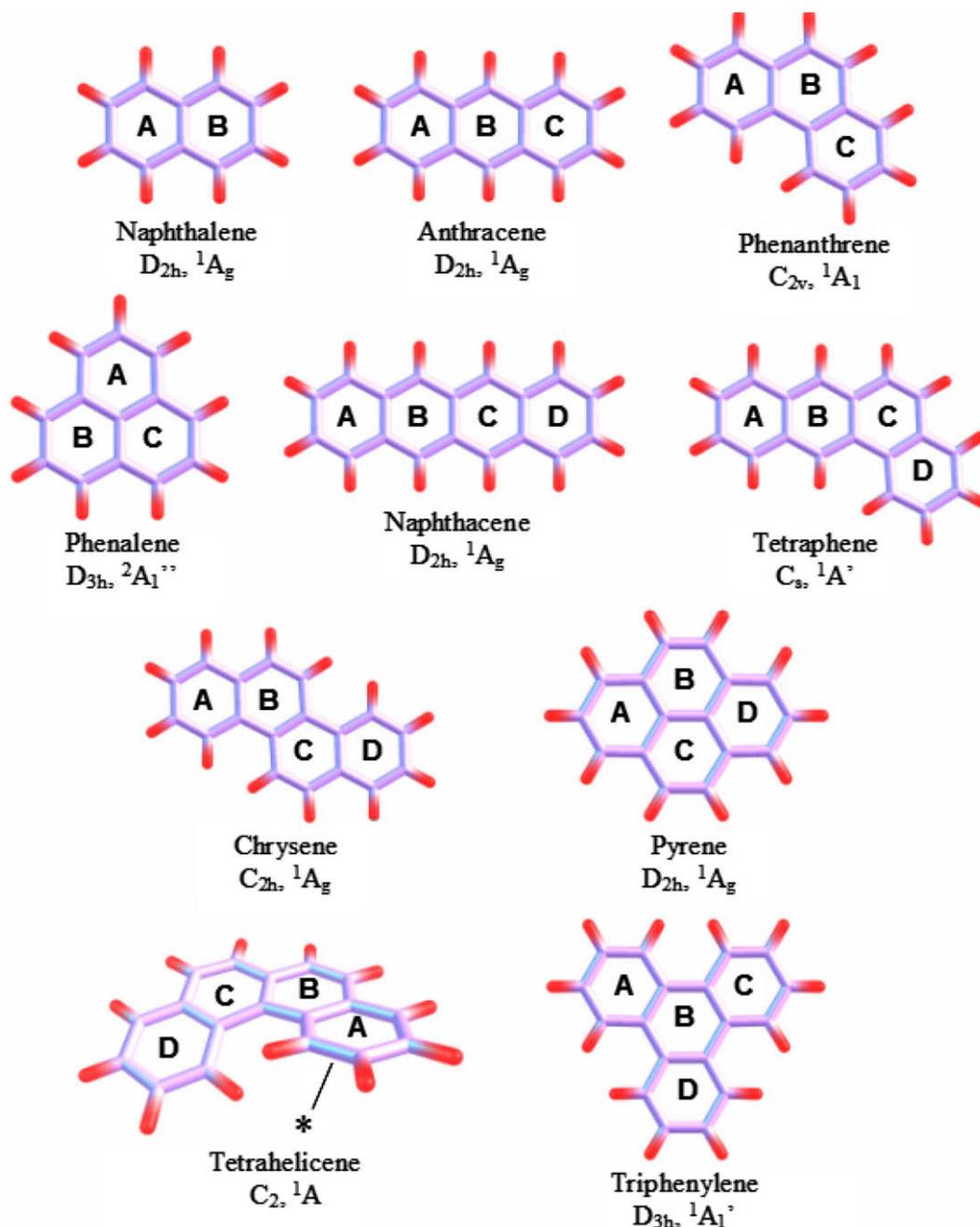
The introduction of two or more Cr(CO)<sub>3</sub> fragments is of great synthetic interest as it can modify at the same time the reactivity of different parts of a given PAH. Bis(tricarbonylchromium) complexes are unique initial substrates for the synthesis of metal-containing polymers [10] and for the preparation of optical stereoisomers and materials for nonlinear optics [2]. The first published X-ray structure of a bis(tricarbonylchromium) complex corresponded to the (biphenyl)bis(tricarbonylchromium) systems [11]. For this species, it was reported that (1) the two phenyl rings were coplanar, (2) the metal fragments were in *anti* position (the two Cr(CO)<sub>3</sub> groups coordinated to opposite faces of the PAH) and symmetrical with respect to the arene plane, and (3) the Cr–C–O directions were approximately staggered with respect to the phenyl ring where each Cr(CO)<sub>3</sub> was coordinated. Other published works of derivatives of (biphenyl)bis(Cr(CO)<sub>3</sub>) also observed simi-

lar trends [12–14]. Other bis complexes involved derivatives of biphenylene [15], benzannulene [16], corannulene [17], and heptalene [18]. Excess quantities of Cr(CO)<sub>3</sub> are needed to afford such binuclear complexes in good yields [19]. The *anti* conformation is the preferential one [20–23]. Few known examples of *syn*-bis(tricarbonylchromium) complexes have been reported [24,25]. The orientation of the Cr(CO)<sub>3</sub> moiety differs in these *syn* complexes: one is positioned in a staggered conformation (with respect to the ring in which it is coordinated) and the other is close to the eclipsed conformation. Such a mutual orientation of the metal fragments minimizes steric repulsions between carbonyl groups of the adjacent Cr(CO)<sub>3</sub> units [25]. It is worth noting that, when the organic substrate is curved, the *syn* isomer where both Cr(CO)<sub>3</sub> groups are attached at the same convex face can be the most favored [17]. Interestingly, coordination of two Cr(CO)<sub>3</sub> moieties on a [3,3]orthocyclophane [26] revealed an important decrease of the dihedral angle between the two aromatic rings. As a result of the Cr(CO)<sub>3</sub> coordination, the two benzene rings become closer. This means that apparently the  $\pi$ - $\pi$  interactions are favored when the PAH rings are coordinated to tricarbonylchromium. Finally, tris(tricarbonylchromium) complexes have been also characterized on trindenyl ligand [27] and coordinated to ruthenium complexes [28].

In this Letter, we analyze by means of theoretical methods all possible isomers that result from the complexation of two Cr(CO)<sub>3</sub> groups to the PAHs with two-, three-, and four-fused benzenoid rings depicted in Scheme 1. In a previous Article, we have discussed all reaction pathways for the haptotropic migrations of Cr(CO)<sub>3</sub> in the same series of PAHs [29]. The aim of the present work is to analyze bis(tricarbonylchromium) complexation in the PAHs of Scheme 1 in order to answer questions such as (i) how many isomers can be located for each PAH?; (ii) for a given PAH,

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**Scheme 1.** Polycyclic aromatic hydrocarbons studied in this work. Complexation face of a second tricarbonylchromium (denoted with *prima* letters in Tables 1 and 2) is pointed out with an asterisk sign for tetrahelicene.

which are the preferred rings for coordination of two  $\text{Cr}(\text{CO})_3$  moieties?; (iii) are the *anti* isomers always the most stable?; (iv) how large is the difference between the first and second dissociation energies of the  $[\mu-(\eta^6:\eta^6)\text{PAH}]\text{bis}(\text{tricarbonylchromium})$  complexes; or (v) is the coordination of two  $\text{Cr}(\text{CO})_3$  units more favored in linear or in kinked PAHs of similar size? To the best of our knowledge, this is the first time that bis(tricarbonylchromium) complexes are theoretically investigated.

## 2. Computational methods

Geometry optimizations were performed using the non-local three-parameter Becke's exchange functional [30] and the gradient-corrected Lee–Yang–Parr correlation functional [31], the so-

called B3LYP hybrid functional, implemented in GAUSSIAN03 [32] program package. For our study, such a well-known functional is quite suitable as the organometallic complexes involved in the haptotropic rearrangement have been shown to possess single reference character [33]. As to the basis, we employed a polarized mixed basis set with the 6-31G(d,p) [34,35] for C, O, and H atoms and for the chromium atom we utilized the Wachters-type basis set with polarization functions [36] (14s9p5d3f)/(8s4p3d1f) using the expanded contraction scheme (62111111/3312/311/3) and we denoted this mixed basis set as Wachters' basis/6-31G(d,p) throughout this work. The addition of polarization functions have been shown to be important to correctly describe the Cr–arene interaction in this kind of complexes [37], whereas relativistic effects are unimportant for accurate calculations of chromium spe-

cies [38] and were neglected in our calculations. Moreover, since actual experiments are typically carried out in rather non polar solvents, solvation effects are small [39] and have not been considered in our study.

All benzenoid compounds considered in this study have a closed-shell singlet ground state and have been treated using the restricted formalism, except phenalene and its bis(tricarbonylchromium) complexes for which the ground state is a doublet. In this latter case, the unrestricted methodology has been used.

We also performed calculations of harmonic frequencies to check the nature of the stationary points located on the potential energy surface (PES) under the method above mentioned. Particu-

larly, non negative frequency values denote minima whereas one negative frequency is expected for a transition state (TS). All relative energy values shown in this work contain the zero-point energy (ZPE) correction, except otherwise noted. Dissociation energies computed at the B3LYP/(Wachters' basis/6-31G(d,p)) were corrected by the basis set superposition error (BSSE) according to the following expression

$$\Delta E = \Delta E_{el} + ZPE(AB) - ZPE(A) - ZPE(B) + \delta^{BSSE} \quad (1)$$

where  $\Delta E_{el} = E_{AB}^{AB}(AB) - E_A^A(A) - E_B^B(B)$ . Here  $E_Y^Z(X)$  represents the energy of subsystem  $X$  at optimized geometry  $Y$  using the basis set  $Z$  and the counterpoise correction is defined as [40,41]

**Table 1**

Ring slippage,  $d$ , and Cr distances perpendicular to the plane of the coordinated ring,  $l$ , for the studied bi- and tricyclic aromatic hydrocarbons calculated at the B3LYP/(Wachters' Basis, 6-31G(d,p)) level of theory. Distances are given in Å. *Prima* letters are used for isomers in *anti* position (see Scheme 1).

Isomer	$d$	$l$	Isomer	$d$	$l$
[ $\mu$ -( $\eta^6$ : $\eta^6$ )naphthalene]bistricarbonylchromium(0)			[ $\mu$ -( $\eta^6$ : $\eta^6$ )phenanthrene]bistricarbonylchromium(0)		
A-A'	0.089	1.821	A-A'	0.082	1.824
A-B'	0.052	1.768	A-B'	0.055 (0.141) <sup>a</sup>	1.756 (1.813) <sup>a</sup>
			A-C'	0.038 [0.031] <sup>b</sup>	1.770 [1.721] <sup>b</sup>
			A-C	0.031 {0.063} <sup>c</sup>	1.762 {1.762} <sup>c</sup>
			B-B'	0.124	1.857
[ $\mu$ -( $\eta^6$ : $\eta^6$ )anthracene]bistricarbonylchromium(0)			[ $\mu$ -( $\eta^6$ : $\eta^6$ )phenalene]bistricarbonylchromium(0)		
A-A'	0.122	1.844	A-A'	0.113	1.848
A-B'	0.060 (0.092) <sup>a</sup>	1.771 (1.788) <sup>a</sup>	A-B'	0.054	1.799
A-C'	0.115	1.802			
A-C	0.118	1.804			
B-B'	0.010	1.853			

<sup>a</sup> Values for the inner rings are in parentheses.

<sup>b</sup> Experimental values in brackets for the *endo-exo* A-C' isomer from Ref. [45], while theoretical values are for the *exo-exo* A-C' isomer (see text).

<sup>c</sup> Non-symmetric bis-complex.

**Table 2**

Ring slippage,  $d$ , and Cr distances perpendicular to the plane of the coordinated ring,  $l$ , for the studied tetracyclic aromatic hydrocarbons calculated at the B3LYP/(Wachters' Basis, 6-31G(d,p)) level of theory. Distances are in Å. *Prima* letters are used for isomers in *anti* position (see Scheme 1).

Isomer	$d$	$l$	Isomer	$d$	$l$
[ $\mu$ -( $\eta^6$ : $\eta^6$ )naphthacene]bistricarbonylchromium(0)			[ $\mu$ -( $\eta^6$ : $\eta^6$ )tetraphene]bistricarbonylchromium(0)		
A-A'	0.142	1.846	A-A'	0.122	1.838
A-B'	0.104 (0.133) <sup>a</sup>	1.788 (1.800) <sup>a</sup>	A-B'	0.060 (0.044) <sup>a</sup>	1.769 (1.792) <sup>a</sup>
A-C'	0.115 (0.095) <sup>a</sup>	1.811 (1.824) <sup>a</sup>	A-C'	0.113 (0.050) <sup>a</sup>	1.804 (1.862) <sup>a</sup>
A-D'	0.130	1.814	A-D'	0.087 (0.053) <sup>a</sup>	1.788 (1.772) <sup>a</sup>
A-C	0.133 (0.176) <sup>a</sup>	1.800 (1.812) <sup>a</sup>	A-C	0.120 (0.202) <sup>a</sup>	1.801 (1.846) <sup>a</sup>
A-D	0.127	1.809	A-D	0.099 (0.046) <sup>a</sup>	1.790 (1.762) <sup>a</sup>
B-B'	0.062	1.857	B-B'	0.043	1.841
B-C'	0.105	1.787	B-C'	0.162 (0.066) <sup>a</sup>	1.780 (1.838) <sup>a</sup>
			B-D'	0.144 (0.030) <sup>a</sup>	1.798 (1.762) <sup>a</sup>
			B-D	0.119 (0.066) <sup>a</sup>	1.786 (1.764) <sup>a</sup>
			C-C'	0.162	1.878
[ $\mu$ -( $\eta^6$ : $\eta^6$ )pyrene]bistricarbonylchromium(0)			[ $\mu$ -( $\eta^6$ : $\eta^6$ )chrysene]bistricarbonylchromium(0)		
A-A'	0.102	1.828	A-A'	0.091	1.818
A-B'	0.061 (0.080) <sup>a</sup>	1.780 (1.822) <sup>a</sup>	A-B'	0.062 (0.031) <sup>a</sup>	1.769 (1.800) <sup>a</sup>
A-D'	0.054 [0.030] <sup>b</sup>	1.776 [1.762] <sup>b</sup>	A-C'	0.042 (0.088) <sup>a</sup>	1.767 (1.810) <sup>a</sup>
A-D	0.066	1.778	A-D'	0.058	1.780
B-B'	0.137	1.866	A-C	0.089 (0.161) <sup>a</sup>	1.778 (1.809) <sup>a</sup>
B-C'	0.135	1.870	A-D	0.060	1.772
			B-B'	0.098	1.853
			B-C'	0.138	1.810
[ $\mu$ -( $\eta^6$ : $\eta^6$ )tetrahelicene]bistricarbonylchromium(0)			[ $\mu$ -( $\eta^6$ : $\eta^6$ )triphenylene]bistricarbonylchromium(0)		
A-A'	0.103 (0.078) <sup>a</sup>	1.822 (1.831) <sup>a</sup>	A-A'	0.069	1.812
A-B'	0.072 (0.158) <sup>a</sup>	1.757 (1.799) <sup>a</sup>	A-B'	0.052 (0.100) <sup>a</sup>	1.763 (1.861) <sup>a</sup>
A-C'	0.068 (0.121) <sup>a</sup>	1.770 (1.811) <sup>a</sup>	A-C'	0.084	1.758
A-D'	0.080	1.776	A-C	0.062 (0.030) <sup>a</sup>	1.758 (1.758) <sup>a</sup>
A-C	0.103 (0.187) <sup>a</sup>	1.776 (1.800) <sup>a</sup>	B-B'	0.00	1.870
A-D	0.072 (0.100) <sup>a</sup>	1.773 (1.788) <sup>a</sup>			
B-B'	0.118 (0.136) <sup>a</sup>	1.859 (1.850) <sup>a</sup>			
B-C'	0.137	1.808			
B-D	0.142 (0.087) <sup>a</sup>	1.810 (1.772) <sup>a</sup>			
C-B'	0.167	1.819			
A'-B	0.088 (0.133) <sup>a</sup>	1.781 (1.802) <sup>a</sup>			
A'-C	0.058	1.779 (1.820) <sup>a</sup>			
A'-D	0.122 (0.070) <sup>a</sup>	1.788 (1.788) <sup>a</sup>			

<sup>a</sup> Values are given according to the order in the notation of rings (Scheme 1).

<sup>b</sup> Experimental values in brackets from Ref. [45].

$$\delta^{BSSE} = E_{AB}^A(A) + E_{AB}^B(B) - E_{AB}^{AB}(A) - E_{AB}^{AB}(B) \quad (2)$$

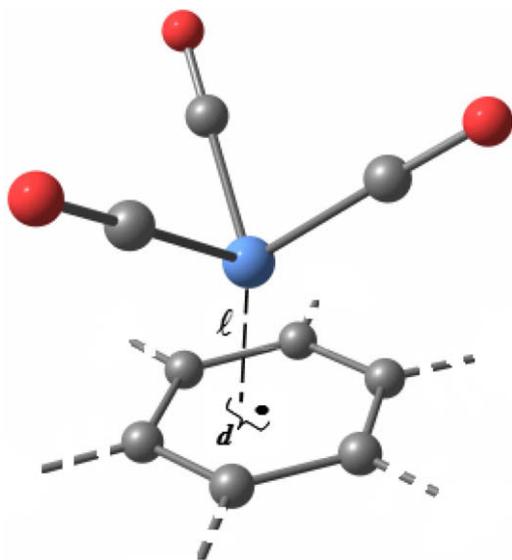
Finally, to evaluate the effect of the basis set in the relative and dissociation energies, single point energy calculations were carried out with the 6-311G(3df,3pd) basis set in all three-fused benzenoid rings and for all species involved in the calculation of the first and second Cr(CO)<sub>3</sub> dissociation energies reported in this work.

In a previous work [42] we have shown that, in the case of the ( $\eta^6$ -naphthalene)Cr(CO)<sub>3</sub> complex, the present method of calculation yields an accurate geometry, which is in good accordance with X-ray data, and a binding energy that is quite close to the experimental value. We expect a similar performance for all systems analyzed in this work.

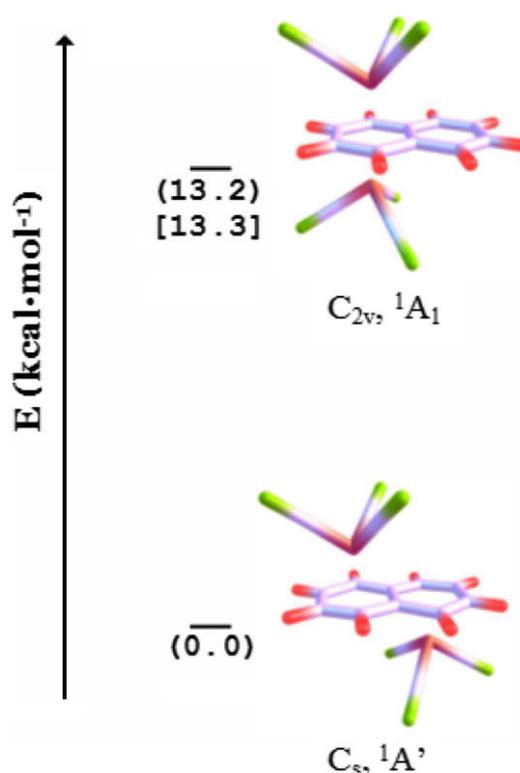
### 3. Results and discussion

All the compounds discussed here are neutral and were calculated without symmetry constraints starting from the highest possible symmetry of each fragment until the optimized geometry (Scheme 1). The rotation of the Cr(CO)<sub>3</sub> tripod about its local approximate C<sub>3</sub> axis generates different stable conformers. In all systems analyzed, we tested different conformations to ensure we got the rotational isomer with the lowest energy. In this search, we found TSs corresponding to the rotational movement of Cr(CO)<sub>3</sub> tripods on the fused ring systems. Energy barriers of rotational isomerization for this kind of compounds are in the range of 0.5–2.2 kcal mol<sup>-1</sup> at the level of theory employed here, and, therefore, the rotational movement of the Cr(CO)<sub>3</sub> tripod is basically free. Thus, in the following we discuss geometrical features of all non-rotational isomers found for each possible coordination of the bis(tricarbonylchromium) complex on these arenes, the energetic stability among these isomers (in a scale ordered from the lowest to the highest in energy) and Cr(CO)<sub>3</sub> dissociation energies of the minima.

Tables 1 and 2 show the more characteristic distances for these complexes in terms of ring slippage (*d*) and coordination distance (*l*) of chromium perpendicular to the plane of the related ring as defined in Scheme 2 (see Scheme 1 for the labels of the rings). For the experimentally synthesized [anti- $\mu$ -(1 $\eta^6$ :3 $\eta^6$ )phenanthrene]bistricarbonylchromium(0) and [anti- $\mu$ -(1 $\eta^6$ :4 $\eta^6$ )pyrene]bistricarbonylchromium(0), the difference between the calculated and experimental *d* and *l* values is less than 0.049 Å. For all



**Scheme 2.** The reported ring slippage, *d*, and the coordination distance, *l* (see the values at Tables 1 and 2) of these arene bicomplexed tricarbonylchromium species are shown.



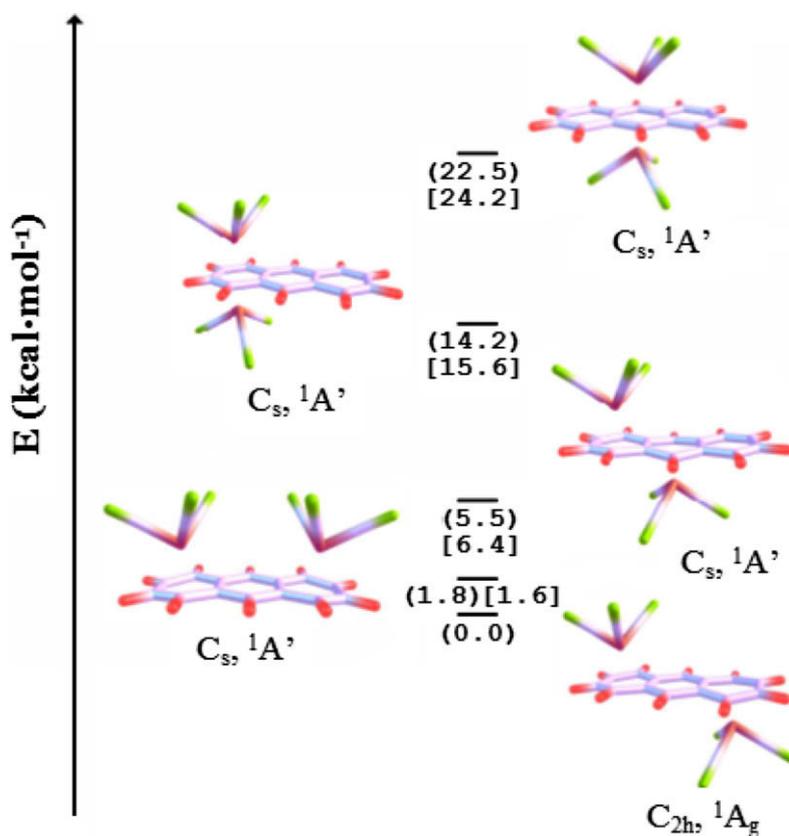
**Fig. 1.** Optimized geometries and energetic scale calculated at B3LYP/(Wachters' Basis, 6-31G(d,p)) level of theory for the possible isomers of [ $\mu$ -( $\eta^6$ : $\eta^6$ )naphthalene]bistricarbonylchromium(0) complex. The value in brackets corresponds to the relative energy calculated at the B3LYP/6-311G(3df,3pd)//B3LYP/(Wachters' Basis, 6-31G(d,p)) level.

two- and three- and for most of the four-fused benzenoid rings, the major *l* distance characterizing the coordination of the metal complexes corresponds to the systems where the two Cr(CO)<sub>3</sub> units are fixed to the same ring. In this case, the coordination of a second Cr(CO)<sub>3</sub> group in the same ring increases the effect of the first coordination [42], *i.e.*, both the expansion and the  $\pi$ -localization of the aromatic ring increase. For the case of tricyclic aromatic hydrocarbons (Table 1) where one Cr(CO)<sub>3</sub> is coordinated to the external ring and the other to the inner one, the largest coordination distances are observed for the Cr(CO)<sub>3</sub> unit interacting with the inner ring. These larger interaction distances are related to the lower  $\pi$ -electron density of the inner rings, which are also the less aromatic [43–45].<sup>1</sup> The inverse trend (*i.e.*, shorter distances) is observed when the tripods are connected to the more distant outer rings. Expectedly, longer Cr-ring distances usually go with larger ring slippages.

Tetracyclic aromatic hydrocarbons add more details to this scenario. The largest distances of chromium perpendicular to the plane of the coordinated ring are still those when tripods are coordinated to the same ring or for the metal complex coordinated to one of the inner rings (see Table 2). Although ring slippage does not follow a clear trend, for many systems with coordination to outer-inner rings, this value is higher for the Cr(CO)<sub>3</sub>-coordinated inner rings.

Next, we present the relative energies of all possible isomers of naphthalene and anthracene in Figs. 1 and 2. For the [ $\mu$ -( $\eta^6$ : $\eta^6$ )naphthalene]bistricarbonylchromium(0) complex, the *syn* isomer is not stable and it has just two possible *anti* isomers. However, the number of possible isomers grows up when the acene is

<sup>1</sup> For the case of anthracene, the relative aromaticity of the inner and outer rings is a controversial issue. See for instance [43].

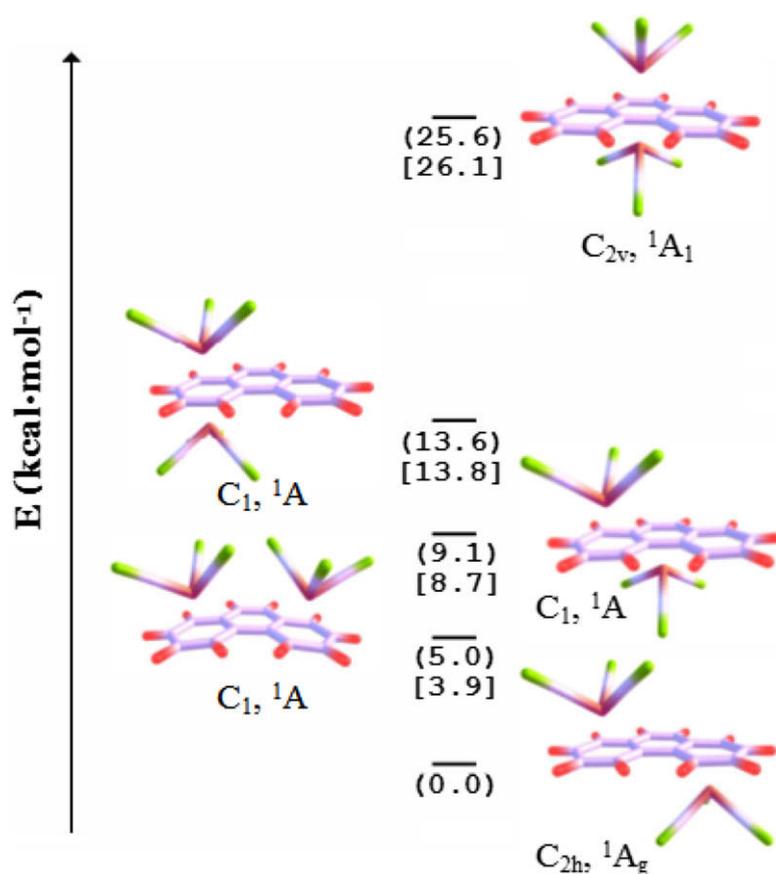


**Fig. 2.** Optimized geometries and energetic scale calculated at B3LYP/(Wachters' Basis, 6-31G(d,p)) level of theory for the possible isomers of  $[\mu-(\eta^6:\eta^6)\text{anthracene}]\text{bistricarbonylchromium}(0)$  complex. The values in brackets correspond to the relative energies calculated at the B3LYP/6-311G(3df,3pd)//B3LYP/(Wachters' Basis, 6-31G(d,p)) level.

bigger (anthracene and naphthalene have five and eight isomers, respectively). Clearly, the *anti* isomer with the two  $\text{Cr}(\text{CO})_3$  units coordinated to two different rings is the most stable. The *anti* isomer with the two  $\text{Cr}(\text{CO})_3$  groups coordinated to the same ring is  $13.2 \text{ kcal mol}^{-1}$  less stable at the B3LYP/(Wachters' basis/6-31G(d,p)) level ( $13.3 \text{ kcal mol}^{-1}$  with the B3LYP/6-311G(3df,3pd)//B3LYP/(Wachters' basis/6-31G(d,p)) method). The  $[\mu-(\eta^6:\eta^6)\text{anthracene}]\text{bistricarbonylchromium}(0)$  complex has four *anti* and one *syn* isomers. Forms *anti* and *syn* between rings A and C (following the notation shown in Scheme 1) differ by just  $1.8 \text{ kcal mol}^{-1}$  ( $1.6 \text{ kcal mol}^{-1}$  at the B3LYP/6-311G(3df,3pd)//B3LYP/(Wachters' basis/6-31G(d,p)) level), the *anti* isomer being the most stable and the *syn* being the second in stability order. An interesting aspect in this *syn* isomer is the bending up of the anthracene fragment. We have used the Pi-Axis Orbital Vector (POAV) analysis implemented by Haddon [46] to get an estimation of the degree of pyramidalization underwent in this bending. In this *syn* isomer, anthracene is in average  $1.2^\circ$  curved to reduce steric hindrance of the carbonyl groups of the two  $\text{Cr}(\text{CO})_3$  moieties. The second introduction of the  $\text{Cr}(\text{CO})_3$  moiety coordinated to the same convex face induces the curvature of this organic fragment. As compared to isolated planar anthracene, this bending has an energetic cost of  $4.9 \text{ kcal mol}^{-1}$ . This effect has been also observed in the bis(tricarbonylchromium)complexes coordinated to the convex face of corannulene [17], in which the addition of a second  $\text{Cr}(\text{CO})_3$  stabilizes the already curved system. The *syn* isomer for this latter system is the lowest in energy. Similar conclusions can be given for  $[\mu-(\eta^6:\eta^6)\text{naphthalene}]\text{bistricarbonylchromium}(0)$  complexes (see Fig. S1 in the Supplementary material) where there are two possible *syn* isomers, **A-D** and **A-C**, coordinated to the

same face of naphthalene. They are only  $0.7$  and  $6.8 \text{ kcal mol}^{-1}$  higher in energy than the global minimum, the *anti-A-D'* bis- $\text{Cr}(\text{CO})_3$  isomer. For the former, the average POAV angle of naphthalene is  $1.7^\circ$  whereas for the **A-C** isomer, this value is  $4.0^\circ$ . Moreover, the energy requirements for this bending in naphthalene are similar to that found in anthracene, that is,  $5.1$  and  $6.4 \text{ kcal mol}^{-1}$  for **A-D** and **A-C**, respectively. Therefore, even when *syn* coordination of a second  $\text{Cr}(\text{CO})_3$  provokes the curvature of the organic molecule (unfavorable change in the isolated PAH), this effect is partially compensated for larger acenes and the *syn* isomer becomes almost as stable as its *anti* counterpart. As shown in a previous work [42], an enhanced curvature favors the interaction between the  $\text{Cr}(\text{CO})_3$  unit and a given PAH because of better orbital interactions.

The five isomers of the double coordination of  $\text{Cr}(\text{CO})_3$  on phenanthrene can be seen in Fig. 3. As for the previous species, fixation of both  $\text{Cr}(\text{CO})_3$  complexes on the outer rings is preferred over coordination on the inner ring. Here also, the *syn* coordination bends phenanthrene up to  $4.3^\circ$  in average but surprisingly this change takes less energy ( $4.0 \text{ kcal mol}^{-1}$ ) than for the linear counterpart. The *syn* isomer is  $5.0 \text{ kcal mol}^{-1}$  higher in energy than the *anti* form, and, therefore, bicoordination to the planar phenanthrene in an *anti* way is stronger by  $1.0 \text{ kcal mol}^{-1}$  than *syn* bicoordination to the already curved phenanthrene. For anthracene, *syn* bicoordination to the already curved isomer is more favorable by  $3.0 \text{ kcal mol}^{-1}$  than *anti* coordination to the planar one. The reason behind this is because of the steric effects in the *syn* isomer of phenanthrene are stronger than in anthracene since one of the carbonyl groups of the first tripod is closer to another one of the second tripod. In the *syn* isomer of phenanthrene, the first  $\text{Cr}(\text{CO})_3$  is



**Fig. 3.** Optimized geometries and energetic scale calculated at B3LYP/(Wachters' Basis, 6-31G(d,p)) level of theory for the possible isomers of  $[\mu-(\eta^6:\eta^6)\text{phenanthrene}]$ bistricalbonylchromium(0) complex. The values in brackets correspond to the relative energies calculated at the B3LYP/6-311G(3df,3pd)//B3LYP/(Wachters' Basis, 6-31G(d,p)) level.

coordinated in an *exo* staggered position to its associated ring whereas the second almost adopted an *endo* conformation (*vide infra*). In fact, for the *anti* isomers of the PAHs studied here, we observed that the *exo* staggered position is the preferred for all minima.

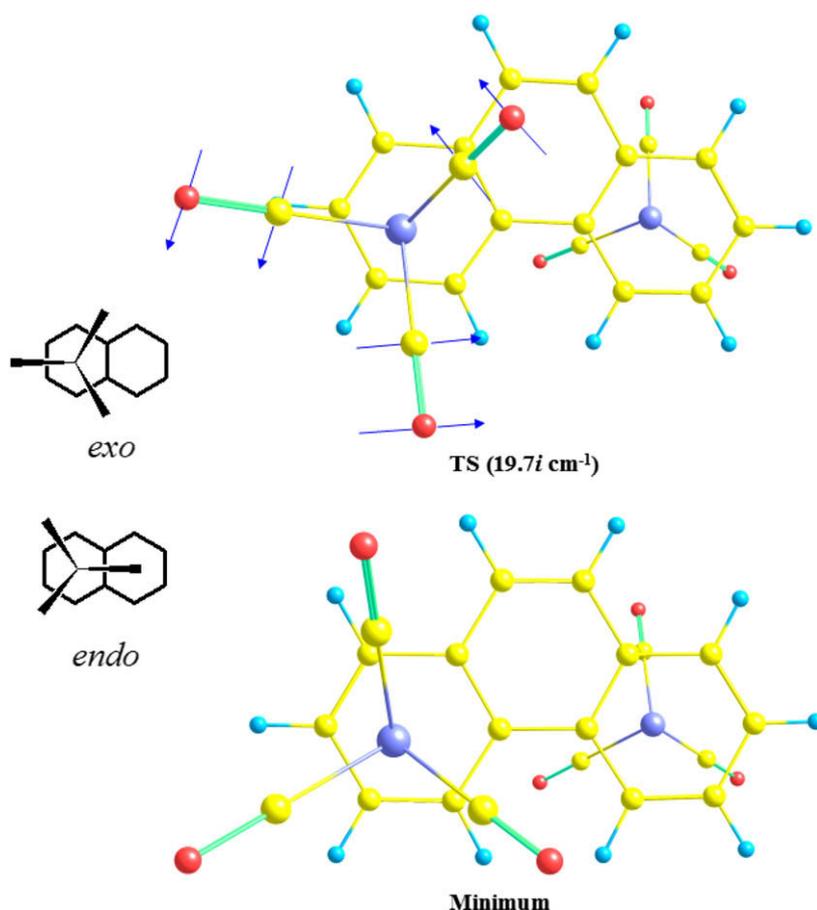
Peitz et al. [47] reported the X-ray crystallographic structure of the facile preparation of bis(tricarbonylchromium) complexes of phenanthrene and pyrene. For phenanthrene, they observed the *endo-exo* staggered conformation of the *anti* **A-C'** isomer shown in Fig. 4 as TS. Our theoretical calculations of this conformer showed that this structure corresponds to a TS of the rotation of the *endo*  $\text{Cr}(\text{CO})_3$ , illustrated in Fig. 4. The energy barrier for the rotation is just  $2.1 \text{ kcal mol}^{-1}$  with respect to the *exo-exo* staggered minimum. We believe that the experimental preference for the *endo-exo* staggered is due to the packing forces present in the solid state. The *endo* to *exo* rotation allows reducing steric hindrance when the  $[\mu-(\eta^6:\eta^6)\text{phenanthrene}]$ bistricalbonylchromium(0) complex is stacked in layers.

In Fig. 5, the optimized geometries of the two possible isomers of the doublet  $[\mu-(\eta^6:\eta^6)\text{phenalene}]$ bistricalbonylchromium(0) complex are shown. The difference in energy between the **A-A'** and **A-B'** isomers are similar to that found in naphthalene ( $13.6 \text{ kcal mol}^{-1}$ , Fig. 1) but somewhat smaller, *i.e.*, the **A-A'** isomer stabilizes slightly by adding a fused ring as compared to **A-B'**.

For the case of the systems with four-fused benzenoid rings complexed to two  $\text{Cr}(\text{CO})_3$  units, adding a new ring leads to a much larger number of possible isomers (8, 13, 8, 6, and 13 for naphthalene, tetraphene, chrysene, pyrene, and tetrahelicene, respectively) than in tricyclic PAHs, but the energetic pattern followed is similar. So, in all cases the *anti* isomer with the two  $\text{Cr}(\text{CO})_3$  groups coordi-

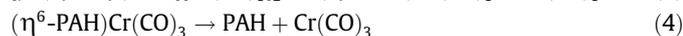
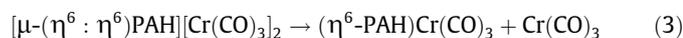
nated to the outer rings is the most stable. With the exception of tetrahelicene, the next most stable isomer corresponds to the *syn* isomer with the two  $\text{Cr}(\text{CO})_3$  units attached to the outer rings. As found before, for the linear and kinked PAHs with four-fused rings, the PAH is curved in the most stable *syn* geometry of the  $[\mu-(\eta^6:\eta^6)\text{PAH}]$ bistricalbonylchromium(0) complex. The most stable *syn* and *anti* isomers are almost isoenergetic (energy differences of about  $1 \text{ kcal mol}^{-1}$ ) in naphthalene, tetraphene, and chrysene and they are separated by 2–4  $\text{kcal mol}^{-1}$  for the rest. For the *syn* **A-D** isomers in angular PAHs, not only the pyramidalization angle is smaller but also the energetic cost of bending is lower as compared to linear acenes. However, despite of this deformation energy is less in angular PAHs, their *syn* conformations are not specially favored in comparison with linear acenes. It is likely that for angular benzenoids, bis(tricarbonylchromium) complexes in the *syn* conformation have higher steric impediment for complexation, so the lower deformation energy needed is compensated by the higher steric hindrance in such a way that the energy difference between the *syn* and *anti* isomers increases from linear to angular acenes. For further details about the systems with four-fused benzenoid rings, the reader is addressed to the [Supplementary material](#) (Figs. S1–S6).

Finally, we selected the isomers with the lowest energy in the series of PAHs analyzed and we calculated its first ( $\Delta E_1^0$ ) and second ( $\Delta E_2^0$ )  $\text{Cr}(\text{CO})_3$  dissociation energies defined according to Eqs. (3) and (4), respectively. Tetraphene has two values of the dissociation energies because the result depends on the choice of the two different  $\text{Cr}(\text{CO})_3$  units. In a previous work, we have obtained that the BSSE for the dissociation energy of naphthalene in  $(\eta^6\text{-C}_{10}\text{H}_8)\text{Cr}(\text{CO})_3$  amounts  $5.45 \text{ kcal mol}^{-1}$  [29,42]. For the dissocia-



**Fig. 4.** The (*endo*, *exo*) isomer (up) and the (*exo*, *exo*) structure (down) of the [anti- $\mu$ -(1 $\eta^6$ :3 $\eta^6$ )phenanthrene]biscarbonylchromium(0) complex calculated at the B3LYP/(Wachters' Basis, 6-31G(d,p)) level of theory. Blue arrows show the momentum vector of the atoms implicated in the vibrational mode. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

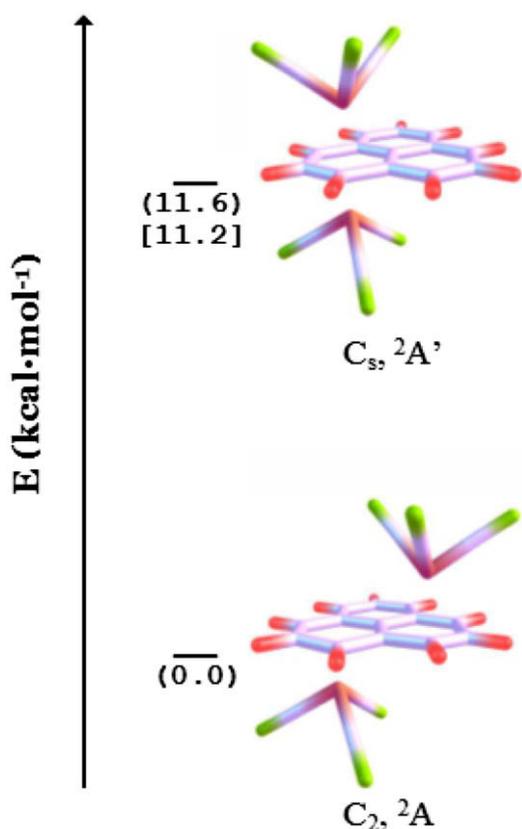
tion energies listed in Table 3 we have computed both the BSSE-corrected and uncorrected values at the B3LYP/(Wachters' basis/6-31G(d,p)). The sum of these first and second BSSE corrected dissociation energies has been plotted in Fig. 6 for the most stable isomer of each PAH studied. As can be seen in Table 3, the BSSE error is smaller for the calculated first dissociation energies, Eq. (3), than for the second ones, Eq. (4). In fact, for using the Wachters' basis/6-31G(d,p) basis set, we can say it is in the range of 5–6 kcal mol<sup>-1</sup> for ( $\eta^6$ -arene)Cr(CO)<sub>3</sub> complexes and of 3–5 kcal mol<sup>-1</sup> for ( $\eta^6$ : $\eta^6$ -arene)[Cr(CO)<sub>3</sub>]<sub>2</sub> species:



Those PAHs having the highest total BSSE-corrected dissociation energies are phenanthrene ( $\Delta E_1^0 + \Delta E_2^0 = 82.7$  kcal mol<sup>-1</sup>), naphthalene ( $\Delta E_1^0 + \Delta E_2^0 = 82.3$  kcal mol<sup>-1</sup>), and anthracene and triphenylene ( $\Delta E_1^0 + \Delta E_2^0 = 82.2$  kcal mol<sup>-1</sup>). Note that the benzenoid rings with the lowest values are precisely the more compact fused-ring structures, *i.e.*, phenalene ( $\Delta E_1^0 + \Delta E_2^0 = 74.7$  kcal mol<sup>-1</sup>) and pyrene ( $\Delta E_1^0 + \Delta E_2^0 = 73.2$  kcal mol<sup>-1</sup>). It is also noteworthy that angular PAHs present similar stability towards Cr(CO)<sub>3</sub> dissociation than the linear counterparts. Moreover, our results suggest that the bis(tricarbonylchromium) complexes are slightly weaker interacting species when the arene grows up (for instance, compare acenes series show in Fig. 6).

Unexpectedly, the order in magnitude of the B3LYP/(Wachters' basis/6-31G(d,p)) BSSE corrected and uncorrected dissociation energies,  $\Delta E_1^0 > \Delta E_2^0$ , predicts that the coordination of a second

Cr(CO)<sub>3</sub> complex has a larger binding energy than that of the first arene + Cr(CO)<sub>3</sub> complexation (see Table 3). This result is counterintuitive, since it is known that after first Cr(CO)<sub>3</sub> complexation there is a stabilization of the HOMOs of the formed complex [42,48], which should make the second coordination less favorable. In order to validate this theoretical result, we have performed a comparative study of  $\Delta E_1^0$  and  $\Delta E_2^0$  with different basis sets and levels of theory for the case of naphthalene. Table S2 in the Supplementary material shows that using the B3LYP hybrid functional and varying the choice of basis sets in the geometry optimization procedure, the order is inverted when using some particular basis sets. More interestingly, Table S3 reveals that for some tested GGA, metaGGA or hybrid functionals keeping constant our Wachters' basis/6-31G(d,p) basis sets, one finds different trends. Thus, BLYP, BP86, OLYP and PBE0 density-functionals give  $\Delta E_1^0 > \Delta E_2^0$  whereas VS98 and 2PLYP density-functionals invert the trend. So, it is clear that the trend in dissociation energies depends on the functional and the basis set used. Since the 6-311G(3df,3pd) basis sets in conjunction with the B3LYP method give the apparently correct order in dissociation energies, we have carried out single-point calculations using this bigger all-electron basis sets. The results are listed in Table 3. Although the numerical results are not dramatically changed, the chemical intuitively expected order ( $\Delta E_1^0 < \Delta E_2^0$ ) is observed. Finally, we have checked how the ordering given by the relative energies is affected by using a more polarized and bigger basis set. Figs. 1–3 and 5 also show the relative energies obtained by single-point calculations with the 6-311G(3df,3pd) basis set. It is found that in all cases changes in relative energies are small and the same ordering predicted by the Wachters' basis/



**Fig. 5.** Optimized geometries and energetic scale calculated at B3LYP/(Wachters' Basis, 6-31G(d,p)) level of theory for the possible isomers of  $[\mu-(\eta^6:\eta^6)\text{phenalene}]$ bis(tricarbonylchromium(0)) complex. The value in brackets corresponds to the relative energy calculated at the B3LYP/6-311G(3df,3pd)//B3LYP/(Wachters' Basis, 6-31G(d,p)) level.

6-31G(d,p) basis set is obtained with the B3LYP/6-311G(3df,3pd)//B3LYP/(Wachters' basis/6-31G(d,p)) method.

#### 4. Summary

We have analyzed the molecular structure and the relative stability of different isomers of  $[\mu-(\eta^6:\eta^6)\text{PAH}]$ bis(tricarbonylchromium(0)) complexes. For all the studied cases, the isomer with the

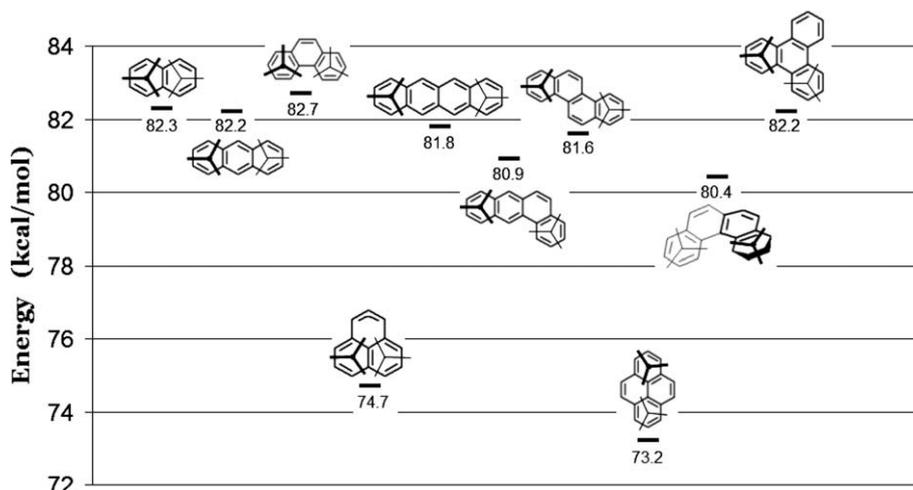
**Table 3**

First ( $\Delta E_1^0$ ) and second ( $\Delta E_2^0$ ) tricarbonylchromium dissociation energies (in  $\text{kcal mol}^{-1}$ ) of the most stable bicoordinated complexes calculated at the B3LYP/(Wachters' Basis, 6-31G(d,p)) level of theory according to Eqs. (3) and (4), respectively. The sum of the two dissociation energies is also given. Values in italics are B3LYP/(Wachters' Basis, 6-31G(d,p)) dissociation energies corrected by BSSE. Values in parenthesis correspond to single point energy calculations with the B3LYP/6-311G(3df,3pd)//B3LYP/(Wachters' Basis, 6-31G(d,p)) method.

Arene	$\Delta E_1^0$	$\Delta E_2^0$	$\Delta E_1^0 + \Delta E_2^0$
Naphthalene	48.1	44.7	92.9
	43.1	39.2	82.3
	(46.2)	(48.3)	(94.5)
Anthracene	48.6	42.6	91.2
	45.0	37.2	82.2
	(47.7)	(48.2)	(95.9)
Phenanthrene	49.8	43.7	93.5
	44.6	38.1	82.7
	(47.5)	(49.4)	(96.9)
Phenalene	44.0	41.2	85.2
	39.0	35.7	74.7
	(35.8)	(45.9)	(81.7)
Naphthacene	49.3	40.7	90.0
	46.5	35.3	81.8
	(48.2)	(48.4)	(96.6)
Tetraphene	50.6 49.2 <sup>a</sup>	40.6 42.0 <sup>a</sup>	91.2
	45.7 44.5 <sup>a</sup>	35.2 36.4 <sup>a</sup>	80.9
	(49.4) (48.1) <sup>a</sup>	(48.5) (49.8) <sup>a</sup>	(97.9)
Chrysene	49.8	41.4	91.1
	45.4	36.2	81.6
	(48.7)	(49.1)	(97.8)
Pyrene	46.4	37.9	84.3
	40.9	32.3	73.2
	(45.5)	(47.9)	(93.4)
Tetrahelicene	49.5	41.1	90.6
	44.8	35.6	80.4
	(48.6)	(49.0)	(97.6)
Triphenylene	51.1	42.6	93.7
	45.4	36.8	82.2
	(49.9)	(50.1)	(100.0)

<sup>a</sup> Value depends on the choice of the  $\text{Cr}(\text{CO})_3$  fragment when calculating this energy.

lowest energy resulted to be the *anti* isomer where both  $\text{Cr}(\text{CO})_3$  complexes are bonded to the most external and distant rings. While the *anti* isomer is always present, the *syn* isomer only appears when the complexed rings are separated by at least another fused ring. In this case, energy differences between *anti* and *syn* conformations of the same isomer are usually not very large (less than  $5 \text{ kcal mol}^{-1}$ ) especially when the PAH is linear and the two rings complexed are the outer rings. The less energetically favored



**Fig. 6.** Sum of the B3LYP/(Wachters' Basis, 6-31G(d,p)) first and second BSSE corrected dissociation energies for the most stable isomer of the bicoordinated complexes ( $\Delta E_1^0 + \Delta E_2^0$ ) studied in this work.

isomer is, in general, that having the metal tripods fixed to the same internal ring (and the less aromatic one). Finally, according to the calculated BSSE-corrected total dissociation energies for the global minima found, stabilization due to the formation of the  $[\mu-(\eta^6:\eta^6)\text{PAH}]\text{bistricarbonylchromium}(0)$  complexes from free PAH and  $\text{Cr}(\text{CO})_3$  is similar for linear and kinked benzenoid rings while it is smaller when the benzenoid rings are grouped in a compact arrangement like in phenalene or pyrene.

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### Appendix A. Supplementary material

Optimized geometries and energetic scales for all the possible isomers of bis(tricarbonylchromium) complexes of six-membered aromatic hydrocarbons of four rings. Cartesian coordinates of all these species reported here and tables of dissociation energies discussed in this Letter. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.cplett.2008.10.001](https://doi.org/10.1016/j.cplett.2008.10.001).

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