

DF-studies on a ‘stop and go’ rotor: steric and electronic factors determining the regio- and stereochemical position of a $\eta^6\text{-Cr}(\text{CO})_3$ metal fragment on a helically distorted biaryl ligand¹

Gerhard Bringmann^{*}, Ralf Stowasser, Lothar Göbel

Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Received 12 November 1996

Abstract

Ground state structures and relative energies of the regioisomers of 1,3-dialkyl-benzo[*b*]naphtho[1,2-*d*]pyranone chromiumtricarbonyl complexes **2** and **4** (R = Me and *t*Bu) have been calculated by means of DF methods. The thermodynamically most stable regioisomers calculated agree with those found experimentally. Additionally, two atropisomeric minimum structures with different rotating positions of the $\text{Cr}(\text{CO})_3$ rotor were found per regioisomer. The rotor positions governed by electronic and steric factors are compared with experimental results and theoretical predictions. From the periodically increasing steric interactions during the helimerization process, a ‘stop-and-go’ dynamic of the $\text{Cr}(\text{CO})_3$ rotor, depending from the conformation at the biaryl axis, is suggested. © 1997 Elsevier Science S.A.

Keywords: Biaryl lactones; Chromiumtricarbonyl rotor; Correlated dynamics; Density-functional calculation; Regioisomers; Steric and electronic effects

1. Introduction

The atropisomer-selective ring opening of helicene-like twisted, rapidly interconverting lactone-bridged biaryls like **1a** \rightleftharpoons **1b** constitutes a both preparatively efficient and mechanistically interesting concept for the stereoselective synthesis of natural and unnatural biaryls [2–5]. This useful principle was recently extended to the cleavage of transition metal activated biaryl lactones, e.g. in the form of the sterically labile chromiumtricarbonyl complex **2a** \rightleftharpoons **2b**, which, influenced by the additional element of planar chirality, can be opened highly atropo-diastereoselectively, to yield the (stereochemically stable) product **3b** [6].

Besides being useful intermediates for the directed synthesis of stereochemically homogeneous biaryls, such chromiumtricarbonyl biaryl lactone complexes are also interesting with respect to the general topic of the regio- and stereoselectivity of the formation of $\eta^6\text{-Cr}(\text{CO})_3$

coordinated complexes of polycyclic aromatic ring systems, which are intensively discussed in the literature [7–18]. The key question is whether the regioselectivity, perhaps even the stereoselectivity of their formation can be predicted by theoretical methods or empirical rules. Fig. 1 presents (and defines) the possible chromiumtricarbonyl complexes of **2a** and of the related sterically more hindered complex **4a**, with respect to complexation site (I–IV) and helicity (**a**, **b**).

For the lactone complex **2b** (type I) we have recently shown that the DF-approach² constitutes a very good method for the theoretical prediction of the structures of such benzo[*b*]naphtho[1,2-*d*]pyranone chromiumtricarbonyl systems, as demonstrated by comparison of the calculated structure with X-ray crystallographic data [19].

Exemplarily for **2** (R = Me) and for the as yet un-

^{*} Corresponding author.

¹ ‘Novel concepts in directed biaryl synthesis’, part 59; for part 58, see Ref. [1].

² Acronyms used in this paper: BLYP: Becke Lee Yang Parr; BP: Becke Perdew; DF: density functional; DZVP: double zeta valence split and polarization function; EH: Extended Hückel; HF: Hartree Fock; LDA: local density approximation; NL: non local; VWN: Vosko, Wilk, Nusair.

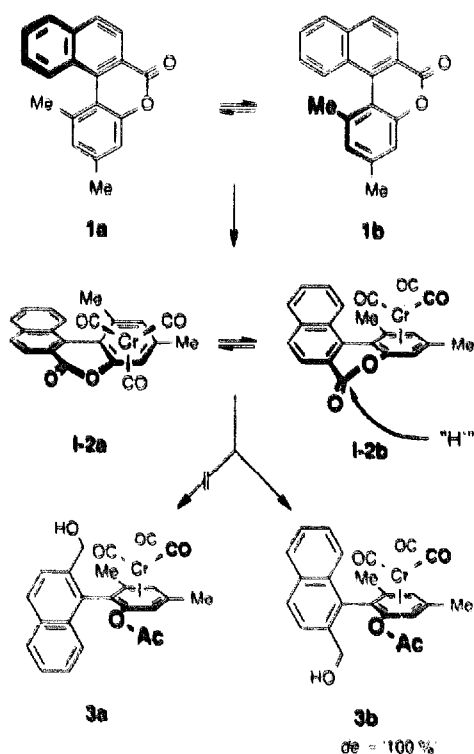
known sterically more hindered representative **4** ($R = t\text{Bu}$), we have now calculated the relative energies of the imaginable regioisomers I–IV, including the stereochemical aspects of the helicity of the polycyclic ring system and the rotor position and their mutual interaction, correctly predicting the experimentally most stable regioisomers for **2** and **4**, as well as the existence of two energetically similar helimeric forms for **2** and only one atropisomer for **4**.

2. Computational details

For the investigations, DF methods were chosen, because of their moderate demand of CPU time (scaling factor $N^{2.2-3}$ with N basis functions) and—as shown e.g. in literature [19,20]—because of their capability to describe complexes of chromiumtricarbonyl in good agreement with experimental data. DF calculations were performed on a CRAY YMP/8-128 computer by means of DGauss 3.0 [21,22]. The DF theory is based on the theorem of Hohenberg and Kohn [23] that the ground state energy $E[\rho]$ of a system is an exact functional of the electron density ρ :

$$E[\rho] = T[\rho] + U[\rho] + E_{xc}[\rho]. \quad (1)$$

where T is the kinetic energy of non-interacting electrons, U the Coulomb potential, and E_{xc} the exchange correlation energy. The ground state structures of the



Scheme 1. Dynamic behavior and atropisomer-selective cleavage of chromiumtricarbonyl activated biaryl lactones **2a/b**.

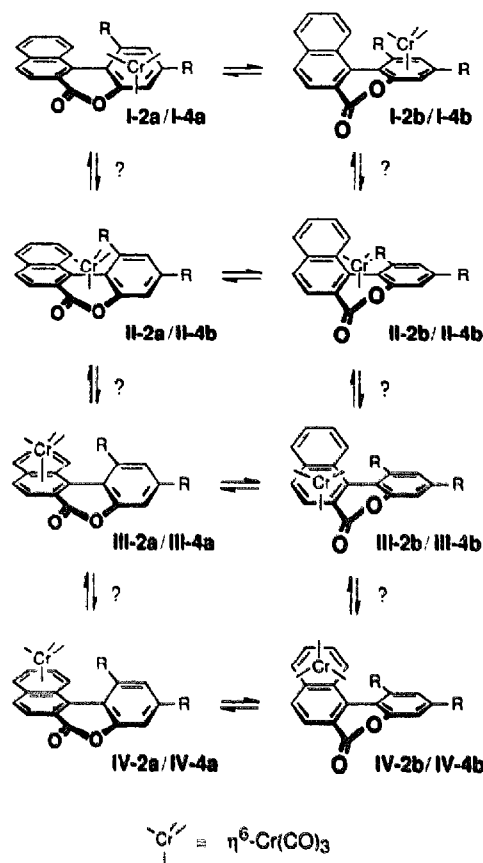


Fig. 1. Possible regioisomeric and helimeric forms of the complexes **2** ($R = \text{Me}$) and **4** ($R = t\text{Bu}$); only one of the two enantiomeric series, with the metal fragment 'above' the ring system, is shown; additional conformers result from the different rotor positions of the $\text{Cr}(\text{CO})_3$ fragment; the helimerization process is blocked for $3a \leftrightarrow 3b$ (see below).

benzo[*b*]naphtho[1,2-*d*]pyranone chromiumtricarbonyl complexes were determined by means of the standard optimization algorithm [24] using the LDA approach [25]. For the calculation of the exchange correlation energy,

$$E_{xc} = \int \rho(r) \epsilon_{xc}^{\text{hom}}[\rho(r)] dr \quad (2)$$

where and $\epsilon_{xc}^{\text{hom}}$ is the exchange correlation energy per particle in an homogeneous electron gas, the VWN potential [26] was used. The non-local DF energy values were determined by single-point calculations using the BP functional [27,28] on LDA geometries. For all calculations, the DZVP [29,30] basis set with the basis functions H (41); C, O (621/41/1); and Cr (63321/531/41) was used. The electronic density and the exchange-correlation potential were fitted by a triple-zeta A1 [29,30] set. Molecular orbitals **8**, **9**, and **10** of the benzonaphthopyranones were calculated with PM3, implemented in the VAMP 5.5 program package [31].

3. Results and discussion

3.1. Calculation of the complexation site and the preferred helimeric form

According to the DF calculations, global minimum³ structures for **2** (R = Me) are the two helimeric forms **I-2a** and **I-2b**, while for **4** (R = *t*Bu) only one helimer (**IV-4b**) was found (see Fig. 2).⁴

This result is in full agreement with previous experimental work [6], which shows that compound **2** exists as the regioisomer **I-2** exclusively, occurring as the two diastereomeric helimers **I-2a** and **I-2b** (s. Scheme 1 and Fig. 2), which rapidly interconvert at room temperature. The stability of the regioisomer **I-2** is chemically plausible, due to the electron-rich character of the oxygen- and alkyl-substituted aromatic ring. The calculations likewise predict the diastereomeric minimum structures to be energetically nearly identical, whereby the **I-2a** helimer was calculated to be more stable than **I-2b** by 0.5 kJ/mol (LDA) and 1.7 kJ/mol (NL-BP). For an isolated molecule—as described by the calculations—this is plausible, since for **I-2a**, steric interactions between the Cr(CO)₃ group and the hydrogen at C-10 are minimized (for the atomic numbering of the molecule, see Table 1).

That still only the slightly less stable atropisomer **I-2b** is found in the crystal, may have to do with the preference of this more symmetric, ellipsoid-shaped helimer in the crystal lattice and the rapid interconversion of the two helimeric forms in the mother liquor, so that ultimately the entire material is converted into crystalline **I-2b**.

While for compound **2**, the regioisomer **I** is the most stable one (followed by isomers **IV** and **III**, see Table 1), it is the regioisomer **IV** in its helimeric form **IV-4b**, which is by far (by a difference of 20 kJ/mol) the most stable species for compound **4**. This may be explained by the steric demand of the *t*Bu group and the resulting steric blocking of the **I**-position.

For **4**, the calculations suggest that at room temperature no rotation at the biaryl axis can take place, because of the steric demand of the *t*Bu group. Likewise, due to this steric hindrance, only one of the two imaginable helimers, viz. only **IV-4b**, is calculated to be thermodynamically stable. This predicted entirely different behavior of **4** compared with **2** warranted the

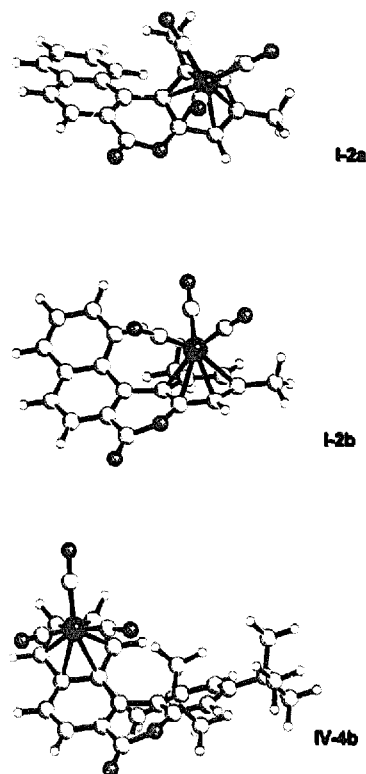


Fig. 2. DF calculated minimum structures **I-2a**, **I-2b**, and **IV-4b**.

experimental investigation for this as yet unknown compound **4**, which was, thus, synthesized from the free parent lactone and naphthalene chromiumtricarboxyl.⁵ It was indeed found to exist as the regioisomeric species, **IV-4**, moreover, only in the predicted atropo-diastereomeric form, **IV-4b**, thus, clearly confirming the results of the calculations presented above.

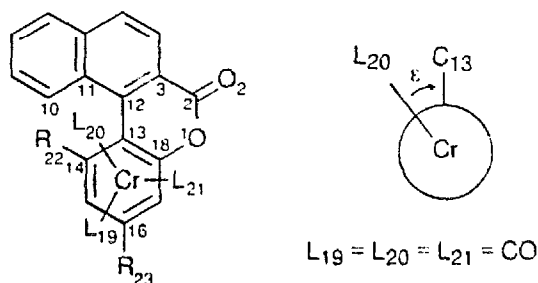
³ In this context, the term 'global minimum' is referred to one of the four possible regioisomers **I-IV**.

⁴ For regioisomers **II-2** and **II-4**, no thermodynamically stable minimum structures were found. For compound **4**, only the data of structures **III-4b** and **IV-4b** are presented in Table 1, because of the high energy and chemically not meaningfully distorted structures of the other regioisomers. For **IV-4a**, it was impossible to locate a stationary point starting from various geometries.

⁵ (8*a*,9,10,11,12,12*a*- η^6 -1,3-di-*tert*-butyl-6H-benzo[*b*]naphtho[1,2*d*]pyranon-6-one) tricarbonyl chromium (**4**). A degassed solution of 720 mg (2.00 mmol) of 1,3-di-*tert*-butyl-6H-benzo[*b*]naphtho[1,2*d*]pyranon-6 one [32] and 550 mg (2.08 mmol) (η^6 -chromiumtricarboxyl)naphthalene in 4 cm³ of dry diethyl ether and 4 drops of dry THF was sealed in an ampulla and heated to 70° for 65 h. After cooling, the solvent was evaporated, the residue was chromatographed on silica gel (petroleum ether/diethyl ether 10:1), and then crystallized from petroleum ether. Yield 5.0 mg (0.5%) of **4** as dark brown crystals, m.p. 150° (decomp.). IR (CCl₄): ν = 3000 cm⁻¹ (m), 2950, 2900, 2850 (m), 1960, 1900, 1880 (s), 1730 (m), 1590 (m). ¹H NMR ([D₆]benzene): δ = 0.94 and 1.19 (2s, 18H, 2C(CH₃)₃), 4.49 and 4.60 (2br t, *J* = 6.3 Hz, 2H, 10H and 11H), 5.12 (d, *J* = 6.3 Hz, 1H, 9H), 5.91 (d, *J* = 6.7 Hz, 1H, 9H), 6.84 (d, *J* = 8.9 Hz, 1H, 8H), 7.21 and 7.54 (2br s, 2H, 2H and 4H), 7.89 (d, *J* = 8.9 Hz, 1H, 7H). MS (70 eV); *m/z* (%): 494 (10) [M⁺], 438 (8) [M⁺ - C₄H₈], 410 (67) [358 + Cr], 382 (87), 358 (89) [M⁺ - 3(CO)], 302 (66) [358 - C₄H₈], 57 (100) [C₃H₃⁺]. HRMS: C₂₈H₂₆CrO, Calc. 494.1185, Found 494.1182; C₂₄H₂₆CrO₂, Calc. 410.1338, Found 410.1350; C₂₄H₂₆CrO, Calc. 382.1389, Found 382.1382.

Table 1

Ground states of the chromiumtricarbonyl arene complexes **2** and **4**; relative energy values (kJ/mol), distances d (Å), angles φ (deg), dihedral angles α - ε (deg), and overall distortion of the 'inner spiral loop' ($\Sigma_{\alpha\beta\gamma}$): ε is defined as dihedral angle L_{20} -Cr- P_{Cr} - C_{13} (P_{Cr} : projection point of Cr on the aromatic ring (C_{13} - C_{18}))



| Compound | I-2 | | III-2 | | IV-2 | | III-4 | IV-4 |
|--|-------|-------|-------|-------|-------|-------|-------|-------|
| | a | b | a | b | a | b | b | b |
| $E_{LDA-VWN}$ | 0.00 | 0.50 | 37.27 | 33.39 | 36.76 | 13.43 | 20.12 | 0.00 |
| E_{NL-BP} | 0.00 | 1.72 | 46.14 | 30.60 | 43.2 | 10.2 | 19.51 | 0.00 |
| $d_{L_{19}Cr-C}$ | 1.81 | 1.81 | 1.80 | 1.82 | 1.80 | 1.80 | 1.82 | 1.83 |
| $d_{L_{20}Cr-C}$ | 1.81 | 1.80 | 1.80 | 1.81 | 1.82 | 1.81 | 1.82 | 1.81 |
| $d_{L_{21}Cr-C}$ | 1.83 | 1.81 | 1.82 | 1.81 | 1.82 | 1.82 | 1.82 | 1.81 |
| $d_{L_{19}C-O}$ | 1.17 | 1.17 | 1.17 | 1.17 | 1.17 | 1.17 | 1.17 | 1.17 |
| $d_{L_{20}C-O}$ | 1.17 | 1.17 | 1.17 | 1.17 | 1.17 | 1.17 | 1.17 | 1.17 |
| $d_{L_{21}C-O}$ | 1.17 | 1.17 | 1.17 | 1.17 | 1.17 | 1.17 | 1.17 | 1.17 |
| $d_{C_2-O_2}$ | 1.21 | 1.21 | 1.21 | 1.21 | 1.22 | 1.22 | 1.21 | 1.21 |
| $d_{C_2-O_1}$ | 1.38 | 1.38 | 1.37 | 1.37 | 1.37 | 1.37 | 1.37 | 1.38 |
| $\varphi_{L_{19}Cr-C-O}$ | 179.4 | 176.7 | 176.0 | 176.3 | 174.7 | 178.3 | 178.1 | 178.3 |
| $\varphi_{L_{20}Cr-C-O}$ | 176.4 | 179.3 | 177.5 | 177.0 | 178.9 | 178.5 | 177.3 | 177.1 |
| $\varphi_{L_{21}Cr-C-O}$ | 177.5 | 177.0 | 178.9 | 177.7 | 176.7 | 178.3 | 176.6 | 176.2 |
| $\alpha_{C_{12}-C_{13}-C_{14}-C_{12}}$ | 10.3 | 13.3 | 13.0 | 13.0 | 16.5 | 18.0 | 31.1 | 33.2 |
| $\beta_{C_{14}-C_{15}-C_{12}-C_{11}}$ | 33.7 | 32.1 | 35.9 | 35.6 | 33.6 | 30.7 | 39.7 | 35.0 |
| $\gamma_{C_{11}-C_{12}-C_{11}-C_{10}}$ | 13.3 | 12.9 | 7.6 | 13.5 | 11.3 | 11.6 | 9.7 | 12.9 |
| $\Sigma_{\alpha\beta\gamma}$ | 57.3 | 58.3 | 56.5 | 62.1 | 61.4 | 60.3 | 80.5 | 81.1 |
| $\delta_{C_{15}-O_1-C_2-C_1}$ | 29.2 | 23.5 | 25.1 | 24.4 | 22.8 | 23.2 | 23.2 | 25.9 |
| ρ | -79.6 | -36.1 | -39.6 | -76.4 | -97.4 | -29.7 | 30.1 | -23.0 |

3.2. The rotational position of the $Cr(CO)_3$ fragment

Encouraged by this good agreement between theoretical predictions and experimental results, we embarked on the investigation of the $Cr(CO)_3$ group of the minimum structures with respect to its properties as a metal fragment rotor. The rotational positions and barriers of the $Cr(CO)_3$ fragments relative to the condensed polycyclic aromatic system are frequently discussed in the literature, based on numerous X-ray, DNMR, and theoretical investigations⁶ [8-18]. Predominantly from EH calculations, the rotational position of the $Cr(CO)_3$ fragment, as found in crystal structures, has been interpreted by orbital interactions and a rationale for the prediction of the rotor position has been given [12,13]. The helically twisted and potentially regioisomeric species **2** constitute an extremely interesting and versatile system for the investigation of the rotor position of the $Cr(CO)_3$ fragment relative to the aromatic system.

The calculated minimum structures for the different regioisomers **I**, **II**, and **IV** of **2** as shown in Fig. 3 can be subdivided into two groups, which will be explained in detail, below: structures with electronically ('group e'; structures **I-2a**, **III-2b**, **IV-2b**) resp. sterically controlled positions of the $Cr(CO)_3$ rotor ('group s'; structures **I-2b**, **III-2a**, **IV-2a**).

'Group e': within this group of isomeric structures, the $Cr(CO)_3$ fragment is throughout located in an *exo*-type manner, i.e. such that it is *anti* with respect to most distant end of the helix. Hence, no steric interaction between this remote aromatic part and the metal fragment has to be expected, so that the $Cr(CO)_3$ rotor should adopt its normal, i.e. electronically governed, rotational position. This is indeed the case. The rotor positions calculated here correspond to those experimentally found for related systems in the literature. Thus, the rotational positions of the $Cr(CO)_3$ fragments coordinated to the outer rings of the minimum conformers **IV-2b** and **I-2a** are near-identical to those in naphthalene chromiumtricarbonyl and the phenanthrene

⁶ For a permanently high barrier, see Ref. [33].

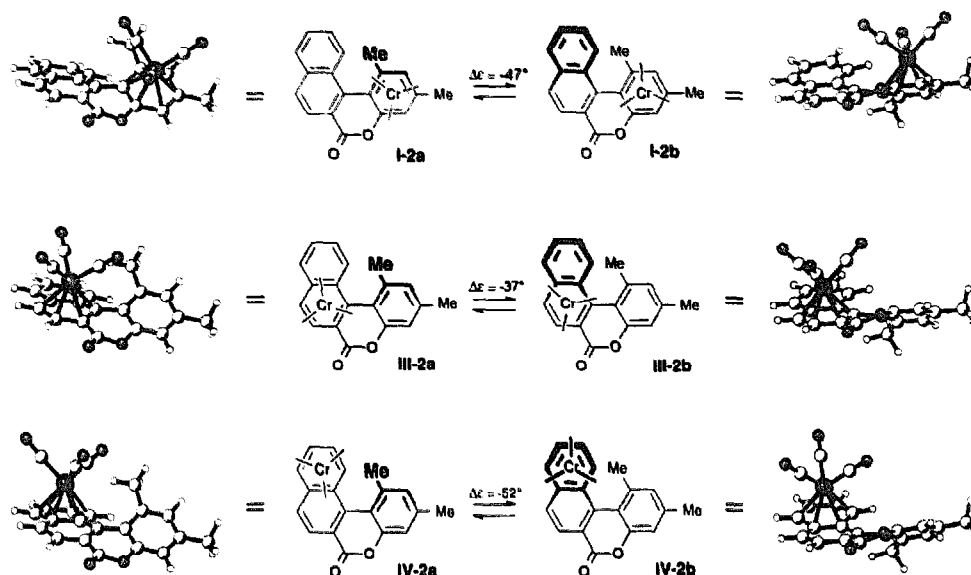


Fig. 3. DF calculated minimum structures of **2**. Mind the different rotational position of the $\text{Cr}(\text{CO})_3$ fragments ($\Delta\epsilon$) in the respective helimeric forms **a** and **b**.

chromiumtricarbonyl with the outer ring coordinated [8–10]. Likewise, the position of the $\text{Cr}(\text{CO})_3$ rotor on ring **III** of the **III-2b** conformer closely corresponds to the (calculated) stereochemical array of the phenan-

threne chromiumtricarbonyl with the coordination on the central ring [12]. In all these cases, both experimentally and from the calculations, the rotor adopts a staggered conformation relative to the condensed ar-

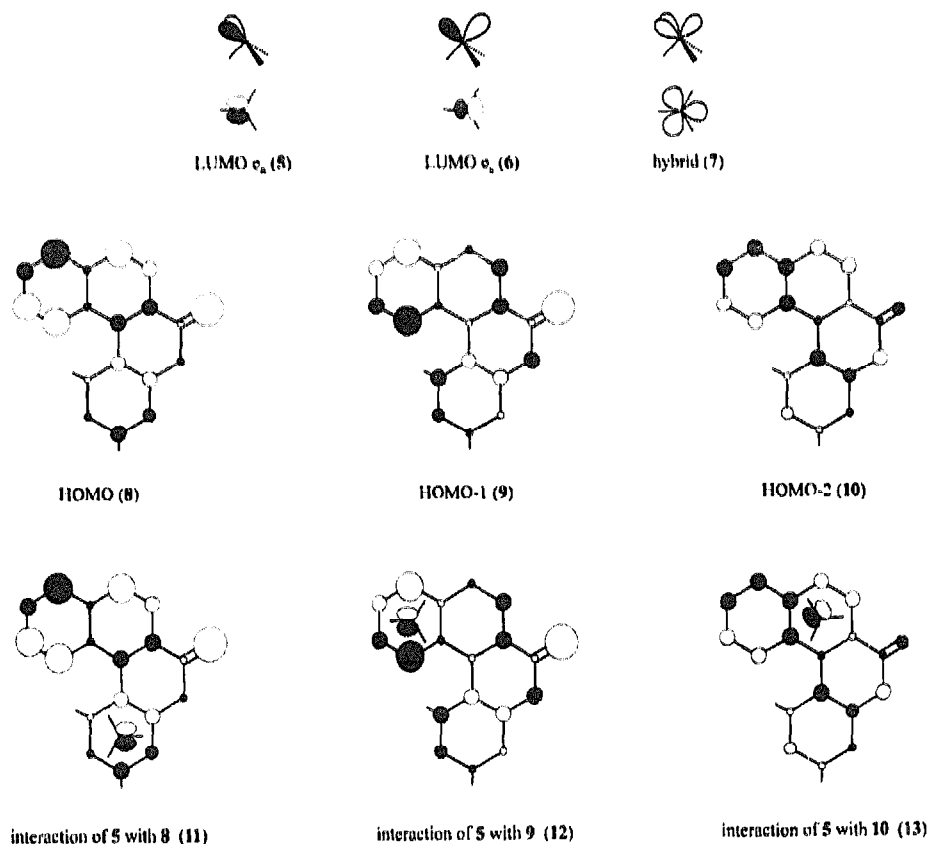


Fig. 4. Empty orbitals **5**, **6**, and **7** of the $\text{Cr}(\text{CO})_3$ fragment [12], the semiempirically calculated highest occupied orbitals **8**, **9**, and **10** of the lactone **1a/b** as well as the important orbital interactions **11**, **12**, and **13**, which determine the orientation of the $\text{Cr}(\text{CO})_3$ fragment.

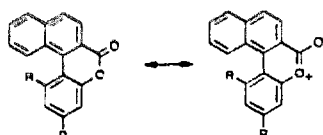


Fig. 5.

matic system [13], such that the three CO groups are located above those three formal, alternating double bonds of those non-metallated ligand that show the lowest averaged bond order.

If one considers the $\text{Cr}(\text{CO})_3$ fragment as derived from the octahedral $\text{Cr}(\text{CO})_6$ by removal of three neighbouring ligands, the tripodal array becomes plausible. The resulting empty hybrid orbital **5** can interact with filled π orbitals of the aromatic system [12]—all the better the higher the electron density (here corresponding to the bond order) of those three (formally localized) π orbitals of the aromatic ring is, above which the rotor is *not* positioned.

In analogy to the brilliant reflections by Rogers et al. and Albright et al. [12,13], the orientations of $\text{Cr}(\text{CO})_3$ fragments relative to the benzonaphthopyranone ligand can also be rationalized by interactions of the highest occupied π orbitals—e.g. the HOMO **8** and the energetically lower orbitals **9** and **10**—(cf. Fig. 4) with empty $2e_u$ orbitals (**5** and **6**) of the CrL_3 fragment. The $2e$ orbitals **5** and **6** shown in Fig. 4 are tilted, i.e. they are not 'left-right symmetric' [13]. The $2e_u$ orbital **5** is decisive for the orientation of the $\text{Cr}(\text{CO})_3$ fragment.

The rotor adopts an array such that the overlap of the (known) empty $2e_u$ orbitals **5** with the semiempirically calculated orbitals **8**, **9**, and **10** (cf. Fig. 4) becomes a maximum. According to Ref. [12], the $\text{Cr}(\text{CO})_3$ rotor is positioned *exo* relative to an annulated $4n\pi$ system (resp. *endo* to a $4n\pi + 2$ system). This rationale is successfully applicable to **2** if its aromatic dipolar resonance structure (with a negative charge on the exocyclic and a positive one on the endocyclic O-atom, see Fig. 5, right) is considered, exclusively. Using VB-model **7** [12] (cf. Fig. 4), also the slight twisting of the $\text{Cr}(\text{CO})_3$ fragment in the non-hindered, electronically governed species **I-2a** and **III-2b** (cf. Fig. 3) may be rationalized. On anisol, with its high electron-excess in *ortho*- and *para*-positions relative to the methoxy group, for example, the rotor adopts an entirely eclipsed position in order to achieve optimum interaction [15,17]. Analogously, influenced by the adjacent lactone ring in **2**—the rotor is twisted by 11° (**I-2a**) resp. 14° (**III-2b**) out of the expected electronically governed position, whereas for **IV-2b** (no influence by donors or acceptors), the array perfectly corresponds to the predicted ideal value.

'Group s': distinctly divergent from these electronically dictated $\text{Cr}(\text{CO})_3$ arrays are the calculated rotor positions within this group, which can be explained by steric interactions. Thus, the twisting of the $\text{Cr}(\text{CO})_3$

group out of the electronically favored position for **IV-2a** and **III-2a** can be rationalized by the destabilizing interaction of the respective CO group of the metal fragment with the methyl group at C-22 (cf. Table 1). Analogously the interaction with the *peri*-hydrogen at C-10 of the naphthalene part should be responsible for the position of the rotor in **I-2b** (cf. Table 1). This rotor position calculated for **I-2b** nearly perfectly (deviation 6°) corresponds to the one found experimentally, by an X-ray structure analysis [19].

As a result of the calculations, the isomerization process, which interconverts the optimized helimeric structures **a** and **b** (see Fig. 3), is—because of the steric and electronic constraints—combined with a variation of the angle of the $\text{Cr}(\text{CO})_3$ rotor by $\Delta\epsilon = -47^\circ$ (**I**), -37° (**III**) and -52° (**IV**), respectively. As shown for several cases in the literature [11,13], barriers for the $\text{Cr}(\text{CO})_3$ rotor at aromatic, delocalized and sterically non-hindered systems are small; they may distinctly increased for sterically crowded arene complexes [32]. Here, by contrast, two drastically different rotational barriers are found⁷: < 20 kJ/mol for group **e** and the extraordinarily high value of > 130 kJ/mol for group **s**. For the dynamics of the system, one may hence conclude the following: Within the state **e**, the $\text{Cr}(\text{CO})_3$ fragment rotates rapidly, with the calculated minimum structures as the averaged rotor position. In the course of the beginning helimerization process, the system moves towards the **s**-state, whereby gradually the rotational barrier is enhanced and the rotor movement is increasingly slowed down by the steric hindrance. After the system has reached the **s**-state, the tripodal rotation is entirely blocked and the rotors adopt the positions of the calculated **s**-structures. Subsequently the process is reversed, whereby the beginning helimerization process towards the **e**-state again deblocks the 'molecular brake'⁸ and allows the metal fragment to start rapidly rotating again.

4. Summary and outlook

This theoretical study shows that DF methods are capable of reliably predicting correct relative stabilities of regioisomeric benzo[*b*]naphtho[1,2-*d*]pyranone chromiumtricarbonyl complexes. Thus, in agreement with experimental data, **I-2a** and **I-2b** were found to be global minima for $\text{R} = \text{Me}$ and **IV-2b** for $\text{R} = \text{tBu}$. For each of the regioisomers **I**, **III**, and **IV** of **2**, two

⁷ The barriers were estimated by a set of single point calculations, by allowing the $\text{Cr}(\text{CO})_3$ fragment to rotate by 5° steps above the aromatic ring.

⁸ For an inducible molecular brake triggered by addition of a metal salt to a conformationally labile bipyridyl system, see Ref. [34].

atropisomeric minimum structures were found, with different positions of the rotors. These structures can be subdivided into two groups, one with electronically determined and one with sterically dictated rotor positions. The electronically governed rotor arrays can be rationalized by interactions of calculated orbitals and correspond to those of analogous non-hindered rotors in the literature [12], whereas the sterically hindered ones show unprecedentedly high rotational barriers. From the different rotor positions for the helimers and an estimation of their rotational barriers we conclude a correlated dynamic process that couples the $\text{Cr}(\text{CO})_3$ rotation with the helimerization process, leading to exceptionally high rotational barriers for one of the two atropisomers, thus, giving rise to a 'temporary molecular brake' and hence to a 'stop-and-go rotor'. It has, however, to be pointed out that due to the size of the molecules the calculations are based on the assumption of a $\text{Cr}(\text{CO})_3$ fragment with only the possibility of rotating about the (hypothetical) Cr-arene 'axis'. The possibility of bending away the fragment from the sterically demanding *peri*-hydrogen at C-10 might lead to greatly decreased rotational barriers. Further calculations as well as experimental work to investigate this more closely, are in progress.

Acknowledgements

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (SFB 347 'Selektive Reaktionen Metall-aktivierter Moleküle') as well as the Fonds der Chemischen Industrie (financial support and a generous fellowship to R.S.). Thanks are due to the Leibnitz-Rechenzentrum (München), the Konrad-Zuse-Rechenzentrum (Berlin), and the Höchstleistungsrechenzentrum (Jülich) for providing computational time on CRAY computers.

References

- [1] H. Lanig, M. Hof, U. Bringmann, F.W. Schneider, *Chem. Phys. Lett.*, in press.
- [2] G. Bringmann, R. Walter, R. Weirich, *Angew. Chem., Int. Ed. Engl.* 29 (1990) 977.
- [3] G. Bringmann, T. Hartung, *Tetrahedron* 49 (1993) 7891.
- [4] G. Bringmann, S. Harmsen, O. Schupp, R. Walter, in: H. Werner, J. Sundermeyer (Eds.), *Selective Reactions of Metal-Activated Molecules*, Vieweg, Braunschweig, 1995, p. 137.
- [5] G. Bringmann, O. Schupp, *South African J. Chem.* 47 (1994) 83.
- [6] G. Bringmann, L. Göbel, K. Peters, E.-M. Peters, H.G. von Schnering, *Inorg. Chim. Acta* 222 (1994) 255.
- [7] B. Deubzer, H.P. Fritz, C.G. Kreiter, K. Öfele, *J. Organomet. Chem.* 7 (1967) 289.
- [8] V. Kunz, W. Nowacki, *Helv. Chim. Acta* 106 (1967) 1052.
- [9] F. Hanic, O.S. Mills, *J. Organomet. Chem.* 11 (1968) 151.
- [10] J.M. Guss, R. Mason, *J. Chem. Soc., Dalton Trans.* (1973) 1834.
- [11] M. Nambu, D.L. Mohler, K. Hardcastle, K.K. Baldrige, J.S. Siegel, *J. Am. Chem. Soc.* 115 (1993) 6138.
- [12] R.D. Rogers, J.L. Atwood, T.A. Albright, W.A. Lee, M.D. Rausch, *Organometallics* 3 (1984) 263.
- [13] T.A. Albright, P. Hofmann, R. Hoffmann, *J. Am. Chem. Soc.* 99 (1977) 7546.
- [14] T.A. Albright, P. Hofmann, R. Hoffmann, C.P. Lillya, P.A. Dobosh, *J. Am. Chem. Soc.* 105 (1983) 3396.
- [15] E.L. Muetterties, J.R. Blecke, E.J. Wucherer, T.A. Albright, *Chem. Rev.* 82 (1982) 499.
- [16] K.K. Baldrige, J.S. Siegel, *J. Phys. Chem.* 100 (1996) 6111.
- [17] G. Huttner, E.O. Fischer, R.D. Fischer, O.L. Carter, A.T. McPhail, G.A. Sim, *J. Organomet. Chem.* 6 (1966) 288.
- [18] K. Schlögl, *J. Organomet. Chem.* 300 (1986) 219.
- [19] G. Bringmann, R. Stowasser, D. Vitt, *J. Organomet. Chem.* 520 (1996) 261.
- [20] A. Berces, T. Ziegler, *J. Phys. Chem.* 98 (1994) 13233.
- [21] J. Andzelm, E. Wimmer, D.R. Salahub, in: D.R. Salahub, M.C. Zerner (Eds.), *The Challenge of d and f Electrons: Theory and Computations*, ACS Symposium Series, No. 394, American Chemical Society, Washington, DC, 1989, p. 228, and refs. therein. *DGauss* is available as part of the *UniChem* software from Cray Research, Eagan, MN.
- [22] J. Andzelm, E. Radzio, D.R. Salahub, *J. Comput. Chem.* 6 (1985) 520.
- [23] P. Hohenberg, W. Kohn, *Phys. Rev. B* 136 (1964) 864.
- [24] H.B. Schlegel, in: K.P. Lawley (Ed.), *Ab initio Methods in Quantum Chemistry*, Wiley, NY, 1987, p. 249 and ref. therein.
- [25] W. Kohn, L.J. Sham, *Phys. Rev. A* 140 (1965) 1133.
- [26] S.H. Vosko, L. Wilk, M.W. Nusair, *Can. J. Phys.* 58 (1980) 1200.
- [27] A.D. Becke, *Phys. Rev. A* 38 (1988) 3098.
- [28] J.R. Perdew, *Phys. Rev. B* 33 (1986) 8822.
- [29] J. Andzelm, E. Radzio, D.R. Salahub, *J. Comput. Chem.* 6 (1985) 520.
- [30] N. Godbout, D.R. Salahub, J. Andzelm, E. Wimmer, *Can. J. Chem.* 70 (1992) 560.
- [31] G. Rauhut, J. Chandrasekhar, A. Alex, B. Beck, W. Sauer, T. Clark, VAMP 5.5, available from Oxford Molecular, Magdalen Centre, Oxford Science Park, Sandford on Thames, Oxford OX4 4GA, England.
- [32] G. Bringmann, T. Hartung, L. Göbel, O. Schupp, C.L.J. Ewers, B. Schöner, R. Zagst, K. Peters, H.G. von Schnering, C. Burschka, *Liebigs Ann. Chem.* (1992) 225.
- [33] P.A. Downton, B. Mailvaganam, C.S. Frimpton, B.G. Sayer, M.J. McGlinchey, *J. Am. Chem. Soc.* 112 (1990) 27.
- [34] T.R. Kelly, M.C. Bowyer, K.V. Bhaskar, D. Bebbington, A. Garcia, E. Lang, M.H. Kim, M.P. Jette, *J. Am. Chem. Soc.* 116 (1994) 3657.