

Preliminary communication

Local and non-local DF calculation of the structure of the helically twisted 1,3-dimethyl- $\{(\eta^6\text{-chromium-tricarbonyl})\text{benzo}\}$ -[b]naphtho[1,2-d]pyran-6-one: a comparison^{1,2}

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Abstract

The ground state structure of the helically twisted, configuratively unstable biaryl lactone 1,3-dimethyl- $\{(\eta^6\text{-chromium-tricarbonyl})\text{benzo}\}$ [b]naphtho[1,2-d]pyran-6-one, the central intermediate in the stereoselective synthesis of axially chiral biaryls, was calculated using the LDA and the NL-DF methods. The results of different functionals were compared with the experimental data from an X-ray structure analysis. The DF geometries, especially those obtained through the non-local BP functional match very well with the X-ray data.

Keywords: Biaryls, configuratively unstable; Biaryls, lactone-bridged; Chromium tricarbonyl arene complex; Density functional calculation

1. Introduction

In the recent literature, density functional (DF) [1] methods are described as attractive ab initio methods that allow the calculation of structures of transition metal complexes with a moderate demand of CPU-time [2,3]. A rewarding, but simultaneously challenging molecule to be calculated by DF methods is the structure of the helically twisted, configuratively unstable biaryl lactone chromium tricarbonyl complex **1** [4,5].

In their free form, lactone-bridged biaryls **2**, and also their carbonyl-activated analogs **3**, constitute important substrates for mechanistic studies and for the preparative atropisomer-selective ring cleavage to give axially chiral target molecules with high asymmetric inductions [6,7] (Fig. 1). On these systems **2** and **3**, we have performed semiempirical calculations concerning the mechanism of the ring cleavage process [8], as well as ab initio HF calculations on structures and dynamics of the free and main group Lewis acid activated species [9,10]. Recently, we have shown that chromium arene

complexes **1**, which undergo a rapid interconversion of the two helimeric forms **1a** and **1b** (Fig. 1), constitute attractive synthetic intermediates, since they can be ring opened with high stereoselectivities, to give virtually one single atropisomeric product exclusively. For a better understanding of this remarkable process, the calculation of the structure of **1** would be highly desirable. However, 1,3-dimethyl- $\{(\eta^6\text{-chrom-tricarbonyl})\text{benzo}\}$ [b]naphtho[1,2-d]pyran-6-one (**1**) constitutes quite a difficult and challenging system for quantum chemical calculations — with its large molecular size, the lacking symmetry (C_1 !), and the flexibility at the stereogenic axis. This molecular flexibility is demonstrated by the occurrence of two slightly different conformers (still with the same axial vs. planar configuration **1a**) in the crystal lattice [4]. In this paper, exemplarily for the chromium tricarbonyl complex **1a**, we report on the calculation of the ground structure of this transition metal activated biaryl lactone using different DFs, and on the comparison of the results with experimental data, showing that the applied methods indeed give reliable results.

2. Computational details

DF calculations were performed on a Cray Y-MP/8-128 computer by means of the program DGauss 2.3

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¹ In memoriam Professor Hidemasa Takaya.

² Novel concepts in directed biaryl synthesis, part 57; for part 56, see Ref. [9].

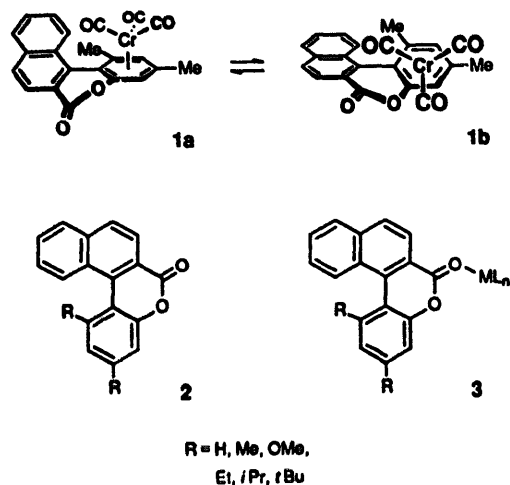


Fig. 1. Structures of 1a, 1b, 2 and 3.

[3,11]. The ground state structure of 1,3-dimethyl-((η^6 -chromium-tricarbonyl)benzo)[b]naphtho[1,2-d]pyran-6-one (1) was determined by means of the standard optimization technique using the LDA-VWN, the NL-BLYP, and the NL-BP functionals, as implemented in DGauss. In another calculation, the NL-BP functional with a MCP for Cr [12] was used. The DZVP [13,14] basis set with the basis functions H (41); C, O (621/41/1) and Cr (63321/531/41) was used for all calculations with the functionals. Additionally, a DZVP2 [13,14] basis set with the basis functions H (41/1); C, O (721/51/1) and Cr (63321/5211/41) was used within the LDA approach. The electronic density and the exchange correlation potential were fitted by a triple-zeta A1 [13,14] set. R.m.s. values were determined by the fit atom algorithm of the *SYBYL* [15] program package. For a suitable input geometry, a Li^+ ion was placed η^6 from the *exo*-side [5] on the 1,3-dimethylbenzo[b] part of the calculated [9] structure of 1,3-dimethylbenzo[b]naphtho[1,2-d]pyranone (2, R = Me), and subsequently optimized by PM3 [16,17]. After minimizing this structure by LDA, the Li^+ was substituted by the $\text{Cr}(\text{CO})_3$ fragment and the structure was again further optimized.

3. Results and discussion

As a result of the DF calculations, Fig. 2 shows the optimized geometries typical of an LDA and an NL functional, matched with one of the two conformers of the crystal structures.

The corresponding $r.m.s._{tot}$ values (see Table 1) reveal that the geometries of the NL functionals show a better agreement with the X-ray data [$r.m.s._{tot}(\text{NL-BP}/\text{DZVP}) = 0.157$] than the LDA-optimized structures (e.g. $r.m.s._{tot}(\text{LDA}/\text{DZVP}) = 0.186$), the BP-functional giving a somewhat smaller deviation com-

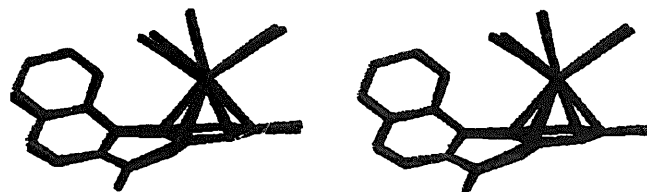


Fig. 2. Matched plots of the LDA and NL-BP optimized structures (red) and the structure in the crystal (blue) of 1.

pared with the BLYP functional ($r.m.s._{tot}(\text{NL-BLYP}/\text{DZVP}) = 0.163$). For the LDA approach, even the use of an enlarged DZVP2 basis set does not give distinctly better $r.m.s._{tot}$ values. The use of a model core potential in the NL-BP approach indeed does diminish the calculatory demand, but also leads to a significant enhancement of the $r.m.s._{tot}$ values (see Table 1).

With respect to the structural data in Table 1, larger differences between calculations and experiments are found only for the dihedral angles α – γ , which, owing to the large molecular ‘leverage’, are most sensitive towards external potentials. This is underlined by the occurrence of two different conformers in the crystal, which mainly differ by these torsion angles [4]. For the possibility of an objective comparison between calculation and crystal structure, the $r.m.s.$ values (see Table 1) for the naphtho[1,2-d] and the chromium tricarbonyl-1,3-dimethylbenzo[b] structural elements were calculated separately. The good agreement is well-demonstrated in Fig. 3.

Interestingly, the LDA approach ($r.m.s._{naph}(\text{LDA}/\text{DZVP}) = 0.020$) more precisely corresponds to the structure of the naphtho[1,2-d] element than the NL approach (e.g. $r.m.s._{naph}(\text{NL-BLYP}/\text{DZVP}) = 0.040$), whereas the benzochromium tricarbonyl subunit is more exactly described by the NL functional (e.g. $r.m.s._{benz}(\text{NL-BP}/\text{DZVP}) = 0.113$ and $r.m.s._{benz}(\text{LDA}/\text{DZVP}) = 0.139$). As already discussed above for the $r.m.s._{tot}$ values, this significantly overcompensates the slightly larger deviation for the naphtho[1,2-d] unit.

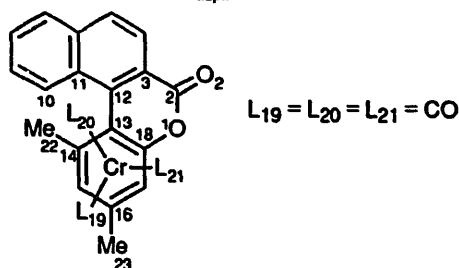
The trend in the $r.m.s.$ values is also reflected by the bond lengths (see Table 1): LDA underestimates the $d_{\text{L,Cr-C}}$ distance by ca. 3–4 pm. This effect is not noticeably changed when using the qualitatively higher



Fig. 3. Plots of the naphtho[1,2-d] and the chromium tricarbonyl-1,3-dimethylbenzo[b] fragments of the calculated LDA structure (red), matched with the corresponding crystal structure fragments of 1 (blue).

Table 1

Ground states of the chromium tricarbonyl arene complex **1**. Total energy (Hartree), r.m.s. values (Å), distances d (Å), angles φ (deg), dihedral angles α – δ (deg), and overall angle of the 'inner spiral loop' [18] ($\Sigma_{\alpha\beta\gamma}$); r.m.s. values refer to the X-ray structure **II** and were calculated for all atoms except hydrogen (r.m.s._{tot}), for the naphtho[1,2-d] part (r.m.s._{naph}) and the chromiumtricarbonyl-1,3-dimethylbenzo[b] part (r.m.s._{benz})



	Density functional method used					Exp. X-ray
	LDA DZVP	LDA DZVP2	NL-BLYP DZVP	NL-BP DZVP	NL-BP(MCP) DZVP	
E_{tot}	-2225.1441	-2255.2797	-2267.2319	-2267.8099	(-1233.2050)	I/II
r.m.s. _{tot}	0.186	0.183	0.163	0.157	0.164	—
r.m.s. _{naph}	0.020	0.019	0.040	0.044	0.043	—
r.m.s. _{benz}	0.139	0.136	0.124	0.113	0.129	—
$d_{L19,Cr-C}$	1.81	1.80	1.85	1.84	1.87	1.84
$d_{L20,Cr-C}$	1.81	1.82	1.87	1.86	1.88	1.85
$d_{L21,Cr-C}$	1.81	1.81	1.86	1.84	1.87	1.84
$d_{L19,C-O}$	1.17	1.18	1.18	1.18	1.18	1.15
$d_{L20,C-O}$	1.17	1.17	1.18	1.18	1.18	1.15
$d_{L21,C-O}$	1.18	1.18	1.18	1.18	1.18	1.15
$d_{C22-C14}$	1.50	1.50	1.52	1.52	1.52	1.52
$d_{C23-C16}$	1.50	1.50	1.52	1.52	1.52	1.52
d_{C2-O2}	1.21	1.21	1.22	1.22	1.22	1.20/1.21
d_{C2-O1}	1.38	1.38	1.42	1.41	1.41	1.39
$\varphi_{L19,Cr-C-O}$	179.3	178.7	178.8	179.2	177.0	178.3/178.6
$\varphi_{L20,Cr-C-O}$	177.0	177.4	177.4	177.4	176.3	176.7/177.8
$\varphi_{L21,Cr-C-O}$	176.6	177.2	176.5	177.0	176.9	178.3/177.3
$\alpha_{C22-C14-C13-C12}$	13.2	12.8	13.3	12.4	13.3	6.1/8.7
$\beta_{C14-C13-C12-C11}$	32.0	31.9	32.9	33.5	32.9	29.4/35.7
$\gamma_{C13-C12-C11-C10}$	12.9	12.9	14.8	15.3	15.5	24.1/20.1
$\Sigma_{\alpha\beta\gamma}$	58.1	57.6	61.0	61.2	61.7	59.6/64.5
$\delta_{C18-O1-C2-C3}$	23.5	23.8	23.4	22.4	20.8	18.3/28.4

DZVP2 basis set. By contrast, the NL approach, in particular in connection with the BP functional, exactly predicts the length of the $d_{L,Cr-C}$ bond (see Table 1). For bond lengths in the carbon framework, LDA delivers very good values (deviations of maximum of 1–2 pm), and also the length of the C2–O1_{endo} bond exactly corresponds to the experimental value, whereas e.g. the NL-BLYP functional overestimates the bond distance by 3 pm. By all the functionals used, the C2–O2_{exo} distance is overestimated by 1–2 pm and the $d_{L,C-O}$ by 3–4 pm.

For the dihedral angles there are no drastic differences in the results, only the angle γ is 'method-sensitive'. For the NL functional it is by 2–3° higher than for the LDA values. Compared with the X-ray data, the calculated dihedral angle α is smaller than in the crystal, whereas γ is larger (compare Table 1). By contrast, the 'inner spiral loop' [18], i.e. the sum of the three angles α , β , and γ is determined quite well by all of the three functionals, whereas the NL results again range above the LDA values by ca. 3°.

Summarizing, the structure of 1,3-dimethylbenzo[b]naphtho[1,2-d]pyranone chromium tricarbonyl (**1**) is very precisely calculated by DF methods. Interestingly, LDA gives a better agreement for the naphtho[1,2-d] structural subunit, whereas NL functionals give better results for the benzochromium tricarbonyl subunit. This short study underlines the excellent capability of DF methods for the prediction of structures of large, non-symmetric and flexible molecules containing transition metals. Work to predict the experimentally observable formation of regio- and stereoisomeric forms depending on the presence of substituents other than R = Me in **1** is in progress.

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References and notes

- [1] In this paper, the following acronyms are used: BLYP: Becke Lee Yang Parr; BP: Becke Perdew; DF: density functional; DZVP: double zeta valence split and polarization function; HF: Hartree Fock; LDA: local density approximation; MCP: model core potential; NL: non-local; r.m.s.: root mean square; VWN: Vosko, Wilk, Nusair.
- [2] T. Ziegler, *Chem. Rev.*, 91 (1991) 651.
- [3] J. Andzelm, in J. Labanowski and J. Andzelm (eds.), *Density Functional Methods in Chemistry*, Springer, New York, 1991 and references cited therein.
- [4] G. Bringmann, L. Göbel, K. Peters, E.-M. Peters and H.G. von Schnering, *Inorg. Chim. Acta*, 222 (1994) 255.
- [5] In order to allow a comparison between calculatory and experimental results, we have performed the calculation on the atropo-diastereomer **1a**, i.e. with a relative exo configuration [4]. Compound **1** crystallizes as two conformers, both corresponding to the helimeric form **1a**, but differing mainly in the dihedral angles α , β , and γ at the biaryl axis (compare Table 1). As an experimental reference structure, the X-ray conformer **II** (see Table 1) was used which, compared with conformer **I**, shows distinctly smaller r.m.s. values (by a factor of ca. 0.5) and thus better agreement compared with the calculated minimum structures.
- [6] G. Bringmann, R. Walter and R. Weirich, *Angew. Chem.*, 102 (1990) 1006; *Angew. Chem. Int. Ed. Engl.*, 29 (1990) 977.
- [7] G. Bringmann and O. Schupp, *South African J. Chem.*, 47 (1994) 83.
- [8] G. Bringmann and D. Vitt, *J. Org. Chem.*, 60 (1995) 7674.
- [9] G. Bringmann, H. Busse, U. Dauer, S. Güssregen and M. Stahl, *Tetrahedron*, 11 (1995) 3149.
- [10] G. Bringmann and U. Dauer, *J. Mol. Mod.*, 1 (1995) 79.
- [11] J. Andzelm, E. Wimmer and D.R. Salahub, in D.R. Salahub and M.C. Zerner (eds.), *The Challenge of d and f Electrons: Theory and Computations*, ACS Symp. Series, No. 394, American Chemical Society, Washington, DC, 1989, p. 228, and references cited therein. DGauss is available as part of the UniChem software from Cray Research Inc., Eagan, MN.
- [12] H. Chen, M. Kvasowski and G. Fitzgerald, *J. Chem. Phys.*, 98 (1993) 8710.
- [13] J. Andzelm, E. Radzio and D.R. Salahub, *J. Comput. Chem.*, 6 (1985) 520.
- [14] N. Godbout, D.R. Salahub, J. Andzelm and E. Wimmer, *Can. J. Chem.*, 70 (1992) 560.
- [15] SYBYL, Tripos Associates, 1699 St. Hanley Road, Suite 303, St. Louis, MO 63114.
- [16] J.J.P. Stewart, *J. Comput. Chem.*, 10 (1989) 209.
- [17] G. Rauhut, J. Chandrasekhar, A. Alex, B. Beck, W. Sauer and T. Clark, VAMP 5.5, available from Oxford Molecular Limited, The Magdalen Centre, Oxford Science Park, Sandford on Thames, Oxford OX4 4GA, UK.
- [18] G. Bringmann, T. Hartung, L. Göbel, O. Schupp, Ch.L.J. Ewers, B. Schöner, R. Zagst, K. Peters, H.G. von Schnering and Ch. Burschka, *Liebigs Ann. Chem.*, (1992) 225.