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Hartree Fock Calculations on the Effects of Lewis Acids on the Helimerization Barrier of a Lactone-Bridged Biaryl[1]

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Abstract: Activation barriers for the helimerization process of model Lewis acid complexes of the helically twisted lactone-bridged biaryl, 1,3-dimethyl-benzo[b]naphtho[1,2-d]pyran-6-one, were determined using Hartree Fock (HF) methods and compared with the value calculated for the free lactone.

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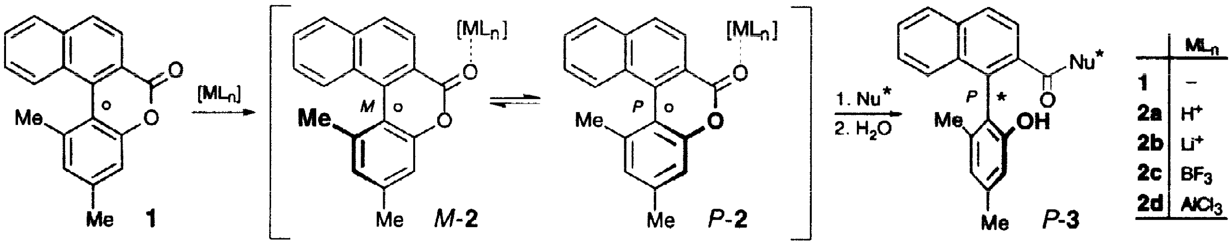
INTRODUCTION

The atropisomer-selective cleavage of configuratively unstable lactone-bridged biaryl compounds of type **1** using chiral *N*-, *O*-, or *H*-nucleophiles, is a preparatively efficient[2,3] and mechanistically interesting[4] method for the stereocontrolled synthesis of chiral biaryls like *P*-**3** (see Scheme 1). Besides the possibility of activating the nucleophile, *e.g.* by deprotonation, the ester carbonyl function (or its thiono analog[5]) can be activated by Lewis acids.[6] In particular, the use of chiral Lewis acids in catalytic amounts is of high interest since it should allow an atropo-enantioselective ring cleavage by non-activated achiral and thus cheap nucleophiles. Within this concept, the atropisomerization equilibrium between the (here diastereomeric) helimeric forms *M*-**2** and *P*-**2** of the intermediate metal-activated lactone plays a crucial role.



Scheme 1. The atropisomer-selective ring cleavage of lactone-bridged biaryls **1**, *via* their metal complexes **2**; labile stereogenic elements (centers or axes) are denoted by 'o', stable ones by '*'.

In previous papers we have described Hartree Fock (HF) calculations[7] on the ground structure of lactone **1**, which gave an excellent agreement with the corresponding crystal structure[8] (RMS = 0.038). Moreover, semiempirical (PM3 and MNDO) and *ab initio* calculations revealed significant structural changes caused by the coordination of $AlCl_3$, which were verified by vibrational spectroscopic experiments.[9] Encouraged by these good results on ground structures, we have now extended our quantumchemical studies to the effects of $AlCl_3$

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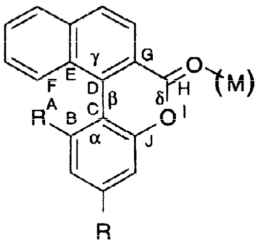
and further main group Lewis acids (H^+, Li^+ and BF_3) on the helimerization barrier of **1**. This barrier is of crucial importance for the dynamic kinetic resolution of *M*-**2** ⇌ *P*-**2**, which requires a rapid isomerization process of the biaryl lactone, also in its Lewis acid coordinated form, **2**.

RESULTS AND DISCUSSION

Table 1 shows selected geometric ground state data of **2a**-**d**, as determined by RHF/3-21G calculations. In comparison to **1**, an increase of the CO_{exo} bond lengths, a contraction of the endocyclic CO_{endo} bonds, and a significant planarization of the central lactone part by the influence of ML_m are observed. The largest increase of the CO_{exo} bond lengths caused by a Lewis acid is found for the protonated lactone **2a**. For this compound the contraction of the CO_{endo} bond, as effected by the proton coordination, is calculated to be 7-8 pm. The planarization of the central lactone ring becomes manifest through the difference of the dihedral angle δ between **1** and **2**, again complex **2a** showing the strongest effect. Still larger effects for the planarization of the heterocyclic lactone ring are detected for the helimerization transition structures, which were found to be, in part, virtually planar (see Fig. 1 and Table 1, last column) with the CO_{exo} and MO bond lengths unchanged and the CO_{endo} bond slightly contracted relative to the ground structures of **1** and **2a**-**d**.

Table 1. Selected geometric data of the calculated ground and transition structures (RHF/3-21G) of helimerization of the lactone complexes **1** and **2a**-**d**; distances (pm), angles (deg.), dihedral angles (deg.).

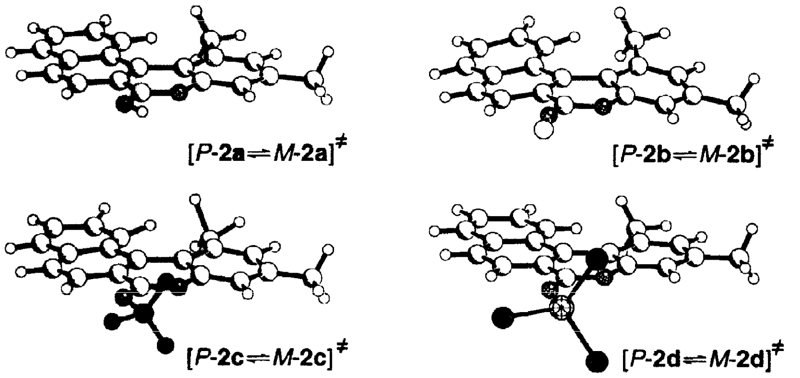


Structure	$d_{CO_{exo}}$	$d_{CO_{endo}}$	d_{MO}	φ_{COM}	α	β	γ	δ
P-**1**[a]	120	137	–	–	13.4	32.9	16.5	22.7
P-**2a**	130	130	97	117.0	14.8	29.8	18.3	12.4
P-**2b**	124	133	168	161.7	14.2	30.8	17.9	15.1
P-**2c**	124	132	163	129.3	13.8	31.1	17.4	16.6
P-**2d**[a]	125	132	180	144.3	14.1	30.6	17.9	14.6
[*P*-**1** ⇌ *M*-**1**]$^{\neq}$[a]	120	134	–	–	-14.4	-4.7	13.9	-4.37
[*P*-**2a** ⇌ *M*-**2a**]$^{\neq}$	130	128	97	116.3	-2.6	-0.6	2.0	-0.18
[*P*-**2b** ⇌ *M*-**2b**]$^{\neq}$	125	131	168	161.3	-14.5	-3.8	12.41	-2.4
[*P*-**2c** ⇌ *M*-**2c**]$^{\neq}$	120	130	163	128.5	-6.7	-1.8	5.86	-1.0
[*P*-**2d** ⇌ *M*-**2d**]$^{\neq}$[b]	125	129	180	142.4	3.4	0.5	-2.9	0.34

[a]see ref. 7; [b]see ref. 9

While the geometric data were found to converge already when using the small basis set 3-21G, a satisfying convergence in terms of the corresponding energy values was obtained only by the use of larger basis sets such as 6-31G*. For this reason, 6-31G* single-point HF-calculations were carried out for the ground *and* transition structures (see Fig. 1) of **2a** - **d**.

For all of the complexes investigated, the RHF/6-31G*//RHF3-21G calculations predict the same order of energetic barriers for the helimerization process. Relative to **1**, the $AlCl_3$-complex **2d** shows the most significant decrease of the isomerization barrier by about 15 kJ/mol (see Table in Fig. 1). The smallest decrease was found for **2a** ('ML_n' = H^+), with a value of about 7 kJ/mol. Interestingly, the barriers are not significantly influenced by taking electron correlation corrections (MP2/6-31G*//RHF/3-21G) into account.



Transition structure	$\Delta E^{\neq}$ [kJ/mol][a]
[P-1⇌M-1]$^{\neq}$	90.80[b]
[P-2a⇌M-2a]$^{\neq}$	83.76
[P-2b⇌M-2b]$^{\neq}$	78.39
[P-2c⇌M-2c]$^{\neq}$	76.05
[P-2d⇌M-2d]$^{\neq}$	75.34

a) Obtained by RHF/6-31G*//RHF/3-21G calculations
b) see ref. 7

Fig. 1. RHF/3-21G transition structures of the helimerization process of the complexes **2a** - **d** and their 6-31G* energies relative to the corresponding ground structures ($\Delta E^{\neq} = \Delta H^{\neq}_{\text{transition structure}} - \Delta H^{\neq}_{\text{ground structure}}$).

The fact that the atropisomerization of the activated complexes **2a** - **d** occurs even more rapidly than for the non-complexed parent compound, **1**, underlines the suitability of such lactone complexes as useful chemically activated and stereochemically even more flexible synthetic intermediates for the atropisomer-selective ring cleavage presented in Scheme 1.

COMPUTATIONAL METHODS

The *ab initio* calculations were performed on a CRAY Y-MP/8-128 computer using the Gaussian 92 program.[10] All ground and transition structures were determined using input geometries obtained from semiempirical PM3[11] geometry optimization calculations performed by means of the VAMP 5.0[12] program. The RHF/3-21G geometries of the ground structures were determined using the default optimization algorithm as implemented in Gaussian 92. Calculations on **1**, **2a**, and **2b** using successively increasing basis sets proved to reach satisfying geometric convergence with the basis sets 3-21G. For the HF calculations the TS optimization algorithm by Baker[13] was used after full calculation of the hessian matrix.

The RHF/6-31G* energies were determined by single point calculations on RHF/3-21G geometries and corrected by the zero point energies as obtained from RHF/STO-3G force calculations. Higher level force calculations on the basis of RHF/3-21G* for the compounds **1**, **2a**, and **2b** revealed the RHF/STO-3G force calculations to be of sufficient quality. All minima and transition structures were characterized by calculation of their normal vibrations.

ACKNOWLEDGEMENTS

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REFERENCES

1. "Novel Concepts in Directed Biaryl Synthesis", part 73; for part 72, see Bringmann, G.; Breuning, M. *Synlett*, **1998**, 634-636.
2. Bringmann, G.; Harmsen, S.; Schupp, O.; Walter, R. In *Stereoselective Reactions of Metal-Activated Molecules*, Werner, H.; Sundermeyer, J., Eds.; Vieweg: Braunschweig, 1995; pp. 137-142.
3. Bringmann, G.; Schupp, O. *S. Afr. J. Chem.* **1994**, *47*, 83-102.
4. Bringmann, G.; Güssregen, S.; Vitt, D.; Stowasser, R. *J. Mol. Model.* **1998**, *4*, 165-175.
5. Bringmann, G.; Schöner, B.; Schupp, O.; Schenk, W. A.; Reuther, I.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *J. Organomet. Chem.* **1994**, *472*, 275-284.
6. Seebach, D.; Jaeschke, G.; Gottwald, K.; Matsuda, K.; Formisano, R.; Chaplin, D. A.; Breuning, M.; Bringmann, G. *Tetrahedron* **1997**, *53*, 7539-7556.
7. Bringmann, G.; Busse, H.; Dauer, U.; Güssregen, S.; Stahl, M. *Tetrahedron* **1995**, *11*, 3149-3158.
8. Bringmann, G.; Hartung, T.; Göbel, L.; Schupp, O.; Ewers, Ch. L. J.; Schöner, B.; Zagst, R.; Peters, K.; von Schnering, H. G.; Burschka, Ch. *Liebigs Ann. Chem.* **1992**, 225-232.
9. Bringmann, G.; Dauer, U.; Schupp, O.; Lankers, M.; Popp, J.; Posset, U.; Weippert, A.; Kiefer, W. *Inorg. Chim. Acta* **1994**, *222*, 247-253.
10. Gaussian 92: Trucks, G. W.; Head–Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh PA, **1992**.
11. Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209–220.
12. G. Rauhut, J. Chandrasekhar, A. Alex, B. Beck, W. Sauer, T. Clark, VAMP 5.0, available from Oxford Molecular Ltd., The Medewar Centre, Oxford Science Park, Sandford-on-Thames, Oxford, OX4 4GA, England.
13. Baker, J. *J. Comput. Chem.* **1987**, *8*, 563–571.