Conformational Preferences of Racemic Ethylene-Bridged Bis(indenyl)-Type Zirconocenes: An ab initio Hartree−Fock Study

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The ab initio Hartree–Fock method has been utilized to rationalize the conformational preferences of racemic ethylene-bridged bis(indenyl)-type zirconocenes in dichloride and cationic methyl forms. This group of catalysts is characterized by conformational isomerism due to fluxionality of the ethylene bridge resulting in two distinct orientations of the indenyl ligands, indenyl-forward (Π) and indenyl-backward (Y). A systematic investigation of the influence of methyl and trialkylsiloxy substitution on the relative stabilities of Π and Y conformations was performed. For the dichloride catalyst precursors the stabilities and orientations of the equilibrium structures are determined on the basis of repulsive interactions within the ligand framework. In the cationic methyl intermediates of the olefin polymerization catalytic cycle, the electron-rich indenyl ligand appears to reduce the electron deficiency of the cation by tilting towards the metal.

Introduction

Homogeneous olefin polymerization catalysis currently represents the most significant application of metallocenes.[1] The field has been extensively studied by experimental techniques[2−4] and, during the last decade, also by theoretical approaches.[5−120] Undoubtedly, the most influential breakthroughs have been the discoveries of isospecific polymerization of propylene by C_2-symmetric racemic *ansa*-metallocenes,[121] together with the activation of metallocene catalyst precursors with methylaluminoxane (MAO) co-catalyst.[122]

A distinct characteristic of two-atom bridged metallocenes is the conformational freedom of their five-membered metallacycles. The combination of an ethylene bridge with bis(indenyl)- or bis(tetrahydroindenyl)-based ancillary ligands results in two limiting conformations, indenyl-forward (Π) and indenyl-backward (Y) (Figure 1). If the barrier for transformation is small, the interconversion between the conformers may be rapid. In such case both conformations exist in solution and the crystal structure solely is inadequate to describe the structure of the catalyst precursor. Furthermore, notwithstanding the maintenance of C_2 symmetry, the polymerization properties, especially the stereoregulating ability of the catalytically active species formed from these two catalyst precursors have been proposed to be different.[123]

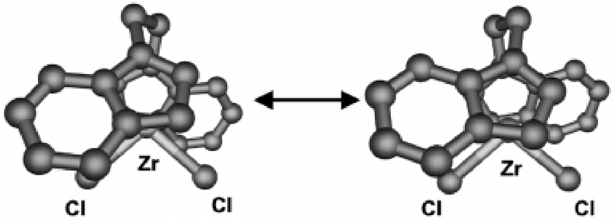

Figure 1. Top view of indenyl-forward (Π) and indenyl-backward (Y) conformations of bis(indenyl)zirconocene dichlorides

In most cases, racemic ethylene-bridged bis(indenyl)-type metallocenes crystallize in the Π conformation,[123−127] apparently due to larger nonbonding interactions within the ligand in the Y conformation.[128] The less favorable Y conformation has been observed for at least some group-IV bis(indenyl) and bis(tetrahydroindenyl) adducts and amido complexes,[129−132] but also for 2,4,7-Me_3-substituted ethylenebis(indenyl)zirconium dichloride[133] as well as for the majority of trialkylsiloxy-substituted metallocenes.[134−138] Hence, the role of ligand substituents in determination of the preferred conformation seems apparent. The aim of the present study is to clarify the relationship between the degree of ligand substitution and the preferred conformation for both dichloride precursors and cationic intermediates of olefin polymerization process.

Computational Details

Calculations were carried out with a Gaussian 94 program package,[139] using the restricted Hartree−Fock method with a standard double-zeta basis set, 3-21G*. Earlier work based on a data set of 62 bridged zirconocene dichlorides demonstrated that the HF/3-21G* method pro-

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vides reliable structures for zirconocenes, the accuracy being comparable to the more expensive BLYP,[140,141] B3LYP,[141,142] and MP2 calculations with larger basis sets.[118] The good performance of the HF/3-21G* method is apparently due to small near-degeneracy and relativistic effects in several complexes of zirconium,[143,144] including zirconocenes. Furthermore, the Hartree−Fock method should be reasonable for conformational energetics[145] regardless of the lack of electron correlation, since its influence on rotational barriers is insignificant.[146]

The interconversion barrier between the Π and Y conformations was studied by systematic modification of the torsion angle of the ethylene bridge. The torsion angle was specified to a certain value while the rest of the molecule was fully optimized. The specified torsion angle was changed with intervals of 10°, after which the new constrained structure was optimized. In order to obtain the structures and energies for the local minima, the bridge constraints of the nearest intermediate structures were relieved and a full geometry optimization without symmetry constraints was performed. In order to confirm the local minima and to obtain zero-point corrections to the total energy, frequency calculations were carried out.[147] The influences of zero-point corrections on relative stabilities of the conformers are very small, on average 0.4 kJ/mol and at maximum 0.9 kJ/mol, and are therefore omitted in the interpretation of the calculations.

As a result of the procedure, the structures of the limiting Π and Y conformations and the relative stabilities of the Π−Y transformations were obtained as a function of the ethylene bridge torsion. It should be noted that the relative stability alone does not determine the preferred conformation. Crystal packing effects may be a contributory cause, since the molecules must be accommodated in the crystal lattice.

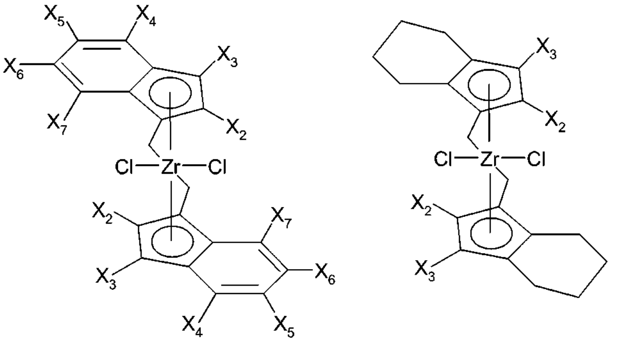
Results and Discussion

Π−Y Transformation in Dichloride Precursors

Schematic structures of the studied racemic zirconocenes are presented in Figure 2. In addition to unsubstituted bis(indenyl) (**1**) and bis(tetrahydroindenyl) (**2**) complexes, various methyl- (**3**) and siloxy-substituted (**4**) complexes were investigated. A detailed interpretation of the results follows.

Unsubstituted Ligands

The energetics for the Π−Y transformation of **1** and **2** are shown in Figure 3. The barriers for rotation are low, as verified experimentally for **1** by NMR at room temperature,[123] suggesting a feasible interconversion between the conformers. The orientation of the ethylene bridge in the Π and Y conformations corresponds to the *gauche* conformation of butane. The rotation barriers of approximately 20 kJ/mol are close to the butane *gauche-cis* energy difference of 22 kJ/mol at the HF/3-21G* level. The limit conformations are somewhat distorted from the optimal *gauche* conformation of 67° due to strain of the metallacycle and nonbonding repulsions between the indenyl ring and the ethylene bridge (Figure 4). In the Π conformation the orientation determining repulsion occurs between the bridge and H(2), whereas the orientation of the Y conformation is limited by H(7)−ethylene bridge interaction.



1: X=H
3a: X_2=Me
3b: X_3=Me
3c: X_4=Me
3d: X_5=Me
3e: X_6=Me
3f: X_7=Me

3g: X_2=X_4=Me
3h: X_2=X_7=Me
3i: X_4=X_7=Me
3j: X_2=X_4=X_7=Me
4a: X_2=O-Si(Me)$_2$(*t*-Bu)
4d: X_2=O-Si(*i*-Pr)$_3$

2: X=H
4b: X_2=O-Si(Me)$_2$(*t*-Bu)
4c: X_3=O-Si(Me)$_2$(*t*-Bu)
4e: X_2=O-Si(*i*-Pr)$_3$

Figure 2. Schematic structures of the studied zirconocene dichlorides; X = H, unless otherwise mentioned

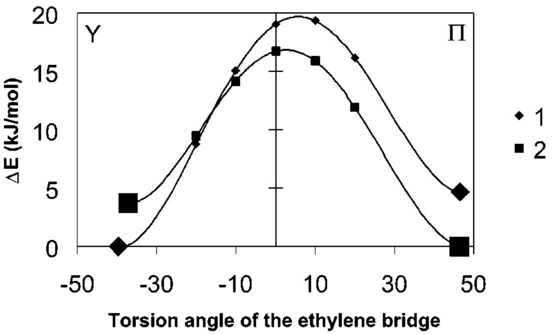


Figure 3. The Π−Y rotation energetics for bis(indenyl)- (**1**) and bis(tetrahydroindenyl)zirconocene dichlorides (**2**); the limiting Π and Y conformations are indicated by larger labels

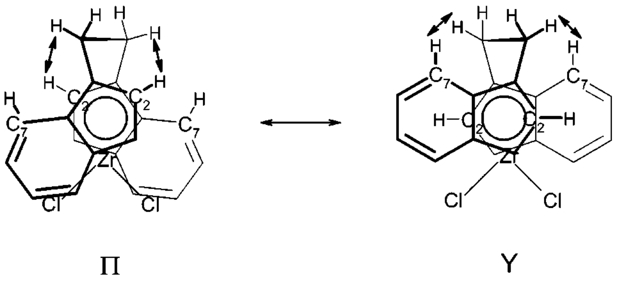


Figure 4. Orientation-determining intramolecular interactions

Both complexes crystallize in the Π conformation,[123,148] apparently due to stronger H(7)−bridge interactions[128] rather than the balancing H(2)−bridge repulsion. The calculations suggest almost identical stabilities for the conformers, in accordance with the earlier molecular mechanics calculations on complex **1**.[133] The small energy differences of approximately 4 kJ/mol are apparently beyond the quantitative accuracy of the method.

Methyl Substituents

The Π−Y transformation energies of monomethyl-substituted bis(indenyl)zirconocene dichlorides are presented in Figure 5. Due to the absence of additional substituent−bridge interactions, the energetics of **3b**−**3e** are nearly identical, also being very similar to the unsubstituted complex **1**. Supposing that the qualitative trends are correct and crystal packing effects are insignificant, **3b**−**3e** should crystallize in the Π conformation similar to **1**, which is true for **3b**, at least.[125] The energetics for **3a** and **3f** are quite different because of a small distance between the substituent and the bridge. The repulsion between the C(2) and the ethylene bridge is the orientation-determining interaction in the Π conformation of **3a**, whereas the Y conformation of **3f** is limited by the C(7)−bridge repulsion.

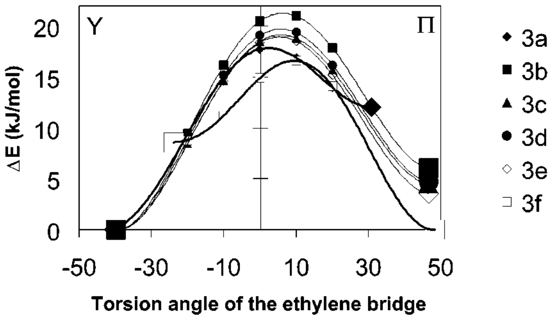


Figure 5. The Π−Y rotation energetics for monomethyl-substituted bis(indenyl)zirconocene dichlorides

Relative stabilities of **3a**−**3f** are given in Table 1. The substituent−bridge repulsion destabilizes the Π conformation of **3a**, while both limit conformations of **3f** become strongly destabilized. This suggests stronger interactions for the latter, hence supporting the earlier proposals.[123,128] Intuitively, it could be assumed that whenever several substituents are simultaneously present, the role of 7-substituent (prefers Π) is the most important, followed by 2-substituent (prefers Y), and that the role of 3-, 4-, 5- and 6-substituents is insignificant.

Table 1. Relative stabilities [kJ/mol] of ethylene-bridged methyl-substituted bis(indenyl)zirconocene dichlorides

	Π	Y
3a	22	10
3b	13	7
3c	5	0
3d	15	11
3e	14	11
3f	39	48

The Π−Y transformation energies are presented in Figure 6 for 2,4-Me_2- (**3g**), 2,7-Me_2- (**3h**), 4,7-Me_2- (**3i**), and 2,4,7-Me_3-substituted (**3j**) complexes. Due to the orientation of 4-methyl groups away from the bridge, the energetics of **3g** and **3i** are identical with the corresponding monomethyl-substituted **3a** and **3b**, respectively. The crystal structure of **3i** is Π,[126] which, as suggested by the calculations, is the more stable conformer due to C(7)−bridge repulsion. This is in accordance with the earlier proposals by Resconi et al.[126]

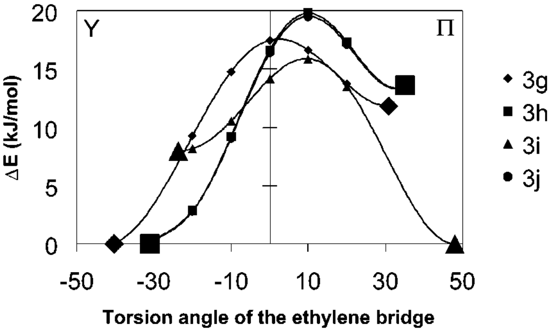


Figure 6. Π−Y rotation energetics for the studied di- and trimethyl-substituted bis(indenyl)zirconocene dichlorides

The presence of both 2- and 7-substituents (**3h** and **3j**) restricts the fluxionality of the ethylene bridge to a narrower area due to methyl−bridge interactions in both conformations. The significant stabilization of the Y conformation despite of generally stronger influence of 7-substituent is not apparent. The explanation is, in fact, further destabilization of the Π conformation, rather than stabilization of the Y conformation. The 2-methyl substituent is forced to interact with the opposite 7-methyl group, and the interaction is much stronger in the Π conformation [see Figure 4 and consider changing the hydrogen atoms of C(2) and C(7) to methyl groups]. Overall, the Y conformation is destabilized due to close contact between 7-Me and the bridge, but the Π conformation is destabilized even more because of the presence of both 2-Me−bridge interactions and the repulsion of the opposite 2-Me and 7-Me substituents. The 4-methyl substituent of **3j** has no relevance. Therefore, as suggested by the calculations, **3j** crystallizes in the Y conformation.[133] This was observed by molecular mechanics calculations as well, even though the local minimum of the unstable Π conformation was not detected.[133]

Siloxy Substituents

Siloxy-substituted zirconocenes represent a uniform group of heteroatom-functionalized group-IV metallocene complexes, showing high activities at reduced co-catalyst concentrations. In the present context, siloxy-substituted zirconocene dichlorides are particularly interesting for two reasons. First, a number of crystal structures are available, making comparisons between stabilities of the limit conformations and identities of the crystal structures possible.

Secondly, most of the crystallographically characterized siloxy-substituted metallocenes favor the generally less common Y conformation. Therefore, the role of the siloxy substituent in determining the preferred conformation deserves a detailed computational investigation.

Five crystallographically characterized siloxy-substituted zirconocenes (**4a−4e**) were selected for the study. Depending on the size and position of the substituents, the following classifications can be made. The attached groups are either *tert*-butyldimethylsiloxy groups (**4a−4c**) or triisopropylsiloxy groups (**4d−4e**), referred to as TBDMS and TIPS, respectively. Depending on the position of the siloxy group, the molecules are denoted 2-siloxy (**4a**, **4b**, **4d**, **4e**) or 1-siloxy (**4c**). The Π−Y transformation energies are presented in Figure 7.

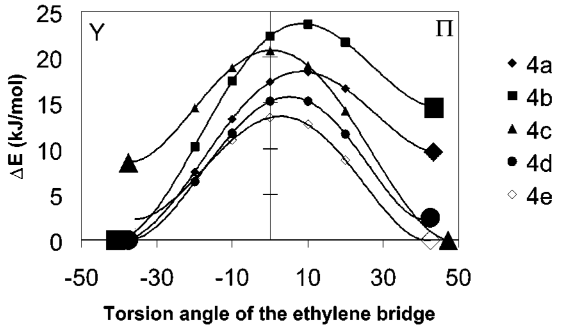


Figure 7. Π−Y rotation energetics for siloxy-substituted zirconocene dichlorides

The 2-TBDMS-substituted complexes (**4a** and **4b**) favor the Y conformation because of repulsions due to the siloxy groups. Each siloxy substituent participates in three close repulsive interactions, namely with one chlorine ligand and with both bridge carbon atoms (Figure 8). However, since the distance between the siloxy substituent and C(1) is constant in both limit conformations, only the repulsions with the oxygen atom and C(2) are orientation-determining. The Cl−O distance of 3.7 Å for the Y conformations and 4.0 Å for the Π conformations indicate smaller repulsions for the latter. On the other hand, the C(2)−O distance is 1.0 Å shorter in the Π conformation. Apparently, the repulsions at the bridge side are more significant than the balancing siloxy−chlorine repulsions. The calculations are in good agreement with experimental observations, since both **4a**[134] and **4b**[135] crystallize in the energetically favored Y conformation.

Increasing the size of the 2-siloxy substituent (TBDMS → TIPS) results in substantial repulsive interactions between the chlorine atom and the carbon atoms of the siloxy group. The Π conformation has more space to accommodate the bulky substituent, as suggested by longer Cl−C(3) distances (Figure 8). Consequently, both limit conformations become destabilized: Π due to the presence of the 2-substituent and Y because of its bulkiness. The destabilization of both conformers leads to lower rotation barriers and to almost equal stabilities. Consequently, **4d**[136] crystallizes in the Π conformation while **4e**[136] crystallizes in the Y conformation.

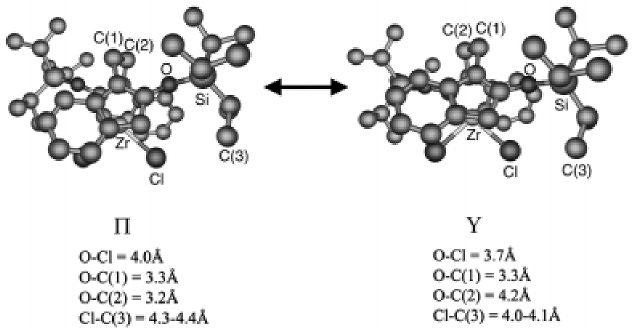


Figure 8. Orientation-determining repulsions in 2-siloxy-substituted zirconocene dichlorides

Due to the absence of substituent−bridge interactions, these interpretations are not valid for the 1-siloxy-substituted complex **4c**, in which the siloxy group is directed towards the chlorine atoms. Repulsions with the chlorine atoms are relevant, but constant. Hence, the 1-siloxy substituent has a marginal effect on the preferred limit conformation, and Π is preferred because of its general preference over the Y conformation. This is in agreement with the experimentally determined crystal structure of **4c** (Π).[138]

Cationic Methyl Intermediates

Cationic methyl complexes represent the simplest approximations of the active species. Since the catalytic system is influenced by a number of other components, such as co-catalyst, an accurate consideration of all effects present is not quantitatively feasible. Whenever quantitative accuracy is unattainable, qualitative observations are generally useful. After all, many of the molecular properties are not influenced by the counter ion. In large co-catalyst molecules the negative charge is evenly distributed to a large space. The resulting complex is not a tight ion pair, but can be regarded as a positive complex surrounded by a uniform cloud of negative charge. The structure of such a cation is primarily determined by the internal bonding, which could be qualitatively modeled by the cation itself. It was thus decided to start from the simplest approximation, i.e., the cationic monomethyl metallocene.

Schematic structures of the studied cationic methyl intermediates are presented in Figure 9. The barriers for Π−Y transformation (Figure 10) are slightly lower than for the corresponding dichloride forms. The Π conformation is generally favored, even by the 2-substituted compounds **7** and **8**, despite of substituent−bridge repulsions.

The equilibrium structures of **5** and **6** are presented in Figure 11. In **5Π** the electron deficiency is reduced by electron donation from the indenyl ring to the metal center, resulting in "bending" of the indenyl ring. A similar type of stabilizing interaction has been recently observed in benzyl-substituted zirconocenes.[149,150] The indenyl−metal interaction is less significant in the Y conformation due to closeness of the opposite cyclopentadienyl ring, and espe-

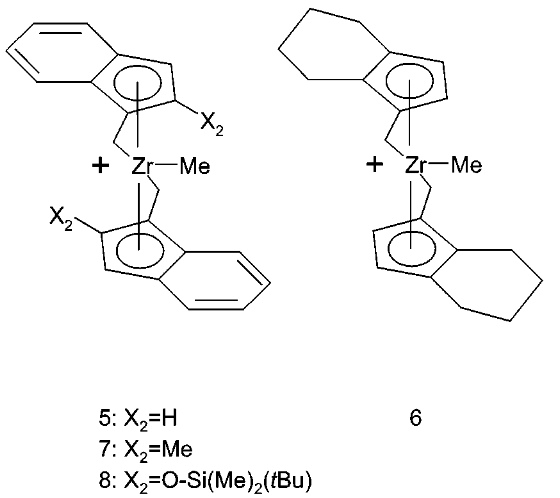


Figure 9. Schematic structures of the studied cationic zirconocenes

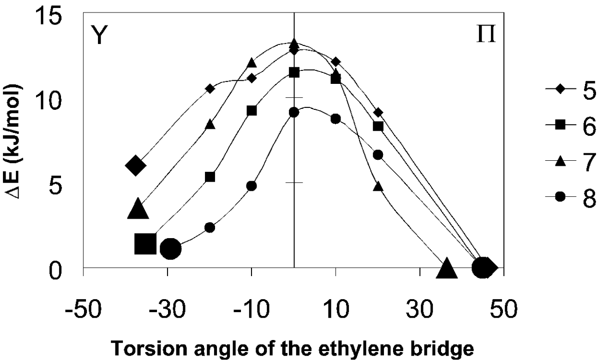


Figure 10. The Π−Y transformation energies for cationic methyl complexes

cially the carbon atom in position 2. The electron donation to the metal ion is absent in **6** as well, due to the saturated tetrahydroindenyl ligand.

By bending towards the metal ion, the quaternary carbon atoms connecting the five- and six-membered rings must distort from the optimal sp^2 hybridization. A number of crystal structures for strained metallocenes showing such distortion are available.[151−157] A direct consequence of the distortion is destabilization of the structure, which in the case of cationic **5Π** is cancelled by greater stabilization due to carbon−metal interaction. In order to verify the relevance of the phenomenon, the energy required for bending of the ring was calculated for the anionic indenyl fragment. The degree of bending, 26°, that was observed for **5Π** leads to destabilization of the structure by 34 kJ/mol. Considering the energy of approximately 80 kJ/mol gained by coordination of C=C double bond of the monomer to the metal center, the tilting of the aromatic ligand seems relevant. Apparently, the degree of bending in **5Π** represents an optimal compromise between destabilization due to distortion from the sp^2 hybridization and stabilization due to electron donation from indenyl to the electron-deficient metal ion.

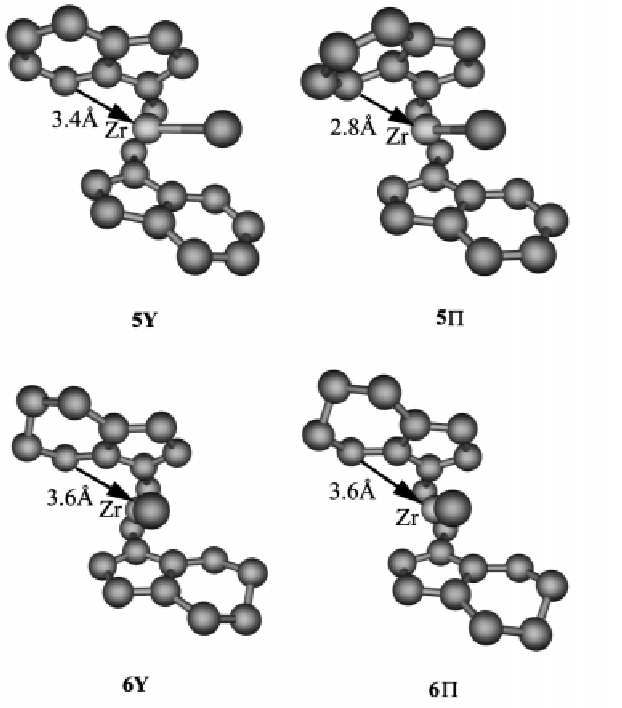


Figure 11. Optimized equilibrium structures of **5** and **6**

The influences of the selected 2-substituents on capability for indenyl bending were studied as well (Figure 12). The stabilization due to ligand−metal interaction is the least significant for unsubstituted **5**, followed by methyl-substituted **7**. The coordination energies for **5** and **7** are very small, less than 5 kJ/mol, and therefore hardly affect the coordination of the incoming monomer. Instead, the coordination energies for siloxy-substituted **8** are much larger, more than 10 kJ/mol for the Π conformation. The presence of indenyl−metal interaction in a real catalytic system would affect the polymerization process in many ways. In addition to minor blocking of the metal center, such interaction would stabilize the cation resulting in higher concentration of cationic metal centers available for the incoming monomer. Possibly, the ligand−metal interaction in combination with the electron-donating siloxy substituent[119] results in an unusually stable active species,[117] as indicated by high catalytic activities at low MAO concentrations.[135,137,158] A third possible consequence could be the increase in the number of different active species with potentially different stereoregulating abilities, possibly resulting in broadening of the molecular weight distributions of the produced polymers.[159]

Conclusion

The indenyl-forward (Π) and indenyl-backward (Y) conformations are relatively similar in energy. Furthermore, the interconversion between the conformers is rapid as also verified experimentally by Resconi et al.[123] Consequently, both conformations can be readily available in the solution,

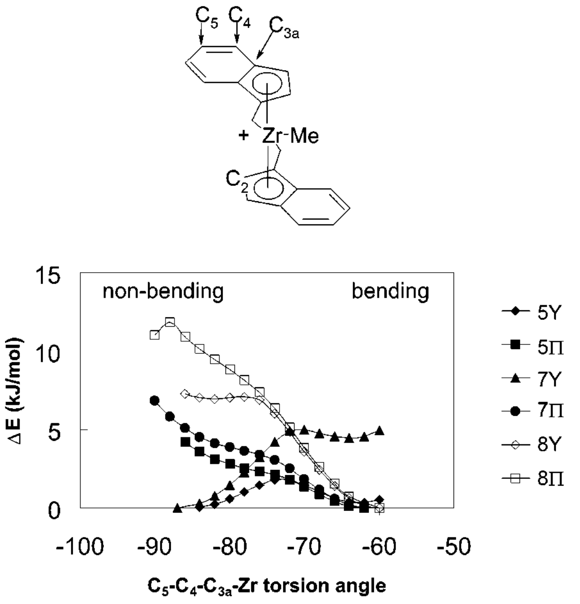


Figure 12. Energetics for the indenyl ring bending

making the crystal structure of the complex alone an inadequate representation for the structure of the precatalyst.

Conformational freedom of dichloride precursors is limited mainly by repulsions within the ligand. In the Π conformation, the most significant repulsion occurs between the bridge and the 2-substituent of the indenyl ring. In the Y conformation, the strongest repulsion can be observed between the bridge and the 7-substituent. These particular repulsions determine the orientations of the ethylene bridge in the limit conformations.

The identities and relative stabilities of the Π and Y conformations are notably changed when the corresponding cationic methyl intermediates of the olefin polymerization catalyst cycle are considered. The electron-rich indenyl ligand donates electrons to the electron-deficient metal ion by tilting towards it. The coordination is less significant for the Y conformation, resulting in general preference of the Π conformation for cations. The strength of the interaction can be controlled by substituents attached to 2-position of the indenyl ligand. The coordination energies are low with hydrogen and methyl substituents, but increase significantly by the introduction of a siloxy group.

Acknowledgments

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