On the effects of methyl substituents on chelating ligands in models for homogeneous isospecific Ziegler–Natta catalysis

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A model for homogeneous isospecific Ziegler–Natta polymerization, recently proposed by us, has been tested for its ability to predict the experimentally observed behaviour when the structure of the catalysts is changed by chemical substitution. In particular, conformational energy calculations have been performed on models of the catalytic site containing the ethylene-bis(1-indenyl) ligand substituted in various positions with methyl groups. In agreement with previous experiments, the analysis indicates that the presence of substituents at the 3,3′ positions strongly reduces the isospecific behaviour of this catalyst. On the contrary, calculations performed on model sites containing the non-chiral ethylene-bis(cyclopentadienyl) ligand suggest that the presence of methyl groups at 3,3′ positions should induce a high degree of isospecificity in this otherwise aspecific system. This theoretical prediction has been confirmed by recently announced experimental results.

(Keywords: Ziegler–Natta homogeneous polymerization; non-bonded interactions; chelating ligands; methyl substituents)

INTRODUCTION

Following its recent discovery in 1984, the isospecific polymerization of olefins with soluble Ziegler–Natta catalysts based on chiral group 4A metallocenes in the presence of methylalumoxane[1,2] has been the subject of stimulating experimental and theoretical research. In the hypothesis that the stereochemical behaviour of these catalysts is mainly related to the non-bonded interactions active in the transition state of the insertion step, we have applied the techniques of conformational analysis to investigate the factors that determine the isospecificity of the polymerization reaction. As a result, we have been able to develop a model for the site control of the isospecificity that is in agreement with all the presently available experimental information on the stereochemical behaviour of these systems[3,4].

As in the case of heterogeneous Ziegler–Natta catalysts[5–7], the growing chain plays an essential role. According to the model, the non-bonded interactions with the chelating ligand force the growing chain to choose one of two possible chiral orientations, depending on the (*R*,*R*) or (*S*,*S*) coordination chirality of the ligand. As a consequence, one of the two possible chiral coordinations (*re* or *si*) of the propene molecule is strongly disfavoured with respect to the other by selective repulsive interactions between the methyl group of propene and the atoms of the growing chain. This results in the preferential insertion of monomer always having the same chirality at a given site and explains the high isospecificity of the catalytic systems.

In agreement with experimental findings[8], the model predicts that the insertion of *re* and *si* coordinated olefins is favoured for the (*R*,*R*) and (*S*,*S*) coordinations of the ethylene-bis(1-indenyl) (en(ind)$_2$) ligand, respectively[3]. Moreover, for the initiation step at a Ti–CH$_3$ bond, the model predicts[4] a non-stereospecific behaviour for the insertion of propene and a partial enantioselectivity for the insertion of 1-butene. Both these predictions are in agreement with the experimental results of Zambelli and coworkers[9].

Recent experiments performed by Ewen using catalysts with methyl-substituted en(ind)$_2$ ligands indicate that substituents in suitable positions can play a role in the enantioselective process. In particular, the polymerization of propene in the presence of a catalyst containing the ethylene-bis(3-methyl-1-indenyl) ligand has been found to proceed with almost complete absence of stereospecificity[10].

In order to test the model on the basis of these recent findings, and also to understand better the factors that determine the stereospecificity of homogeneous catalysts of this kind, we have performed conformational energy calculations on model catalytic sites containing the en(ind)$_2$ ligand or the ethylene-bis(cyclopentadienyl) (en(cp)$_2$) ligand, substituted in various positions with methyl groups.

As in our previous work on this subject, we make the fundamental assumption that the model sites are reasonably similar to the transition state of the insertion step. The ability of our calculations to predict behaviour in substantial agreement with experiments can be taken as an indication of the approximate validity of this approach.

MODELS AND METHODS

The basic models of the catalytic site considered in this paper are metal complexes containing three ligands, that is a π-coordinated ethene or propene molecule, a

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σ-coordinated methyl or isobutyl group and a chelating en(ind)$_2$ or en(cp)$_2$ ligand. In order to simplify the description of our calculations and results, model sites containing the en(ind)$_2$ or en(cp)$_2$ ligand are identified in the following as (olefin)(alkyl group)(en(ind)$_2$) or (olefin)(alkyl group)(en(cp)$_2$) sites, respectively. For instance, the notation (*re*-propene)(isobutyl)(en(ind)$_2$) identifies a model site containing the en(ind)$_2$ ligand, a propene molecule coordinated *re* to the metal atom and the growing chain simulated by an isobutyl group. Specification of the coordination chirality of the chelating ligands is omitted, with the understanding that all the calculations have been performed for (*R*,*R*) complexes. Schematic drawings of the (*re*-propene)(isobutyl)(en(ind)$_2$) site and of the (*re*-propene)(isobutyl)(en(cp)$_2$) site are shown in *Figures 1* and *2*, respectively.

All the model sites considered in this work are characterized by a local two-fold symmetry axis (C$_2$; broken lines in *Figures 1* and *2*) relating the two coordination positions available for the olefin and the alkyl group. For this reason, identical results are obtained when the coordination positions of the olefin and the alkyl group are exchanged, as could happen after each insertion step.

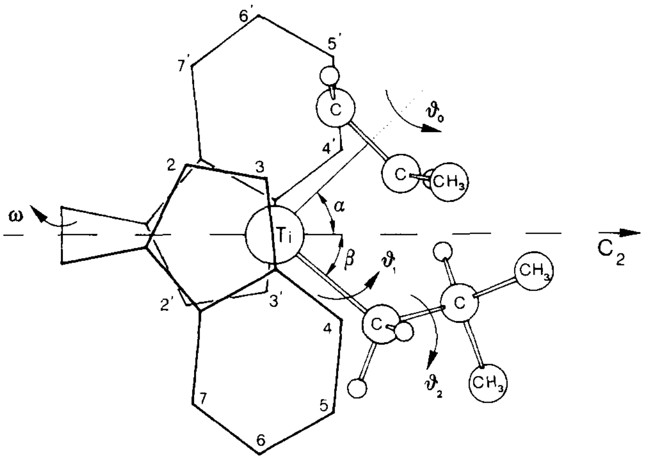

Figure 1 Schematic drawing of the (*R*,*R*)(*re*-propene)(isobutyl)(en(ind)$_2$) model site in the conformation corresponding to $\theta_0 = 0°$, $\theta_1 = -40°$ and $\theta_2 = -20°$. For the aromatic ligand, only the C–C bonds are sketched for clarity. The broken line represents the local C$_2$ symmetry axis. The main internal coordinates that have been varied in the calculations and the labelling scheme for the carbon atoms of the two indenyl groups are also indicated

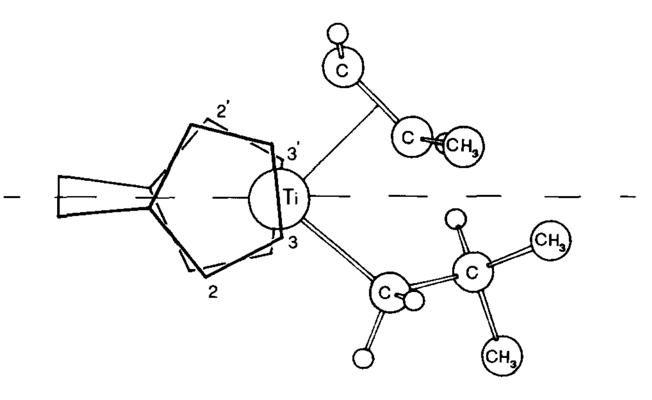

Figure 2 Schematic drawing of the (*R*,*R*)(*re*-propene)(isobutyl)(en(cp)$_2$) model site in the conformation corresponding to $\theta_0 = 0°$, $\theta_1 = -40°$ and $\theta_2 = -20°$. For the aromatic ligand, only the C–C bonds are sketched for clarity. The broken line represents the local C$_2$ symmetry axis

The geometries of the two types of model sites have been constructed using internal parameters coincident with those found by Brintzinger and coworkers in crystalline racemic [TiCl$_2$(en(ind)$_2$)]^{11} for the en(ind)$_2$ sites and in permethylated [TiCl$_2$(en(cp)$_2$)]^{12} for the en(cp)$_2$ sites, respectively. As in ref. 3, the geometric parameters relative to the coordinated olefin have been derived from the crystal structure of bis(pentamethylcyclopentadienyl)(ethene)titanium^{13}. In particular, the distance Ti–C(olefin) has been set equal to 2.17 Å. The distance Ti–C(chain) has been assumed to be 2.15 Å, as observed in some σ-alkyl Ti complexes^{14,15}. The angle Ti–C–C (chain) has been set equal to 118°, as observed for the angle Nb–C–C in the crystal structure of a niobium complex^{16}.

Test calculations on zirconium complexes with the en(ind)$_2$ ligand have been performed assuming the coordination geometry of the en(ind)$_2$ ligand described in the crystal structure of dichloroethylene-bis(3-methyl-1-indenyl)zirconium^{17}. The distance Zr–C(chain) has been set equal to 2.29 Å^{18}, while the distance Zr–C(olefin) has been assumed to be 2.31 Å, that is 0.02 Å bigger than the Zr–C(chain) bond length, to be consistent with the corresponding distances observed in titanium complexes.

We have also examined models in which two aromatic hydrogen atoms related by the local C$_2$ symmetry axis are replaced by methyl groups. These are the 2,2′-, 3,3′-, 4,4′-, 5,5′-, 6,6′- and 7,7′-dimethyl derivatives in the case of en(ind)$_2$ sites and the 2,2′ and 3,3′ derivatives in the case of en(cp)$_2$ sites. Since alkyl groups on the cyclopentadienyl rings in metallocenes are normally bent out of the ring plane, the out-of-plane bending angle (γ) of the methyl substituents is generally assumed equal to that of the corresponding methyl groups in permethylated [TiCl$_2$(en(cp)$_2$)]^{12} (4.7° for position 2 and 6.1° for position 3). Some calculations have also been performed with different values of γ (see later).

The main internal coordinates that have been varied in our calculations are sketched in *Figure 1*: the angle α between the local C$_2$ axis and the axis connecting the metal and the centre of the double bond; the angle β between the local C$_2$ axis and the metal–carbon bond of the growing chain; the dihedral angle θ_0 associated with rotations of the olefin around the axis connecting the metal to the centre of the double bond; and the internal rotation angles θ_1 and θ_2 associated with rotations around the two bonds between the metal atom and the first carbon atom of the growing chain and between the first and second carbon atoms of the growing chain, respectively.

The angles α and β have been confined in the plane defined by the two Ti–Cl bonds in the crystal structures of refs. 11 and 12. Moreover, while α and β are varied, their sum is kept in the experimentally observed range 91–99° (refs. 19–21). In particular, various sets of calculations have been performed with $\alpha + \beta = 91, 93, 95, 97$ and $99°$, respectively.

At $\theta_0 = 0°$ the olefin is oriented in a way suitable for primary insertion, while $\theta_0 = 180°$ corresponds to an orientation suitable for secondary insertion. $\theta_1 = 0°$ corresponds to the conformation having the first C–C bond of the growing chain eclipsed with respect to the axis connecting the centre of the double bond to the metal atom. $\theta_2 = 0°$ corresponds to the conformation having the Ti–C bond of the growing chain eclipsed with respect to the C–H bond on the second carbon atom of the chain. The torsional potential for the rotations θ_0 and θ_1 are not known and therefore are not included. While we expect such an energy contribution to be small for θ_1, it may not be so for θ_0. Since deep energy minima are found only for $\theta_0 \simeq 0$, the inclusion of such a torsional potential would not change our conclusions. For the rotation θ_2, the torsional potential reported in ref. 22 is included.

For the internal rotation angle ω around the C–C bond connecting the two cyclopentadienyl rings (*Figure 1*), only the generally favoured[19] G^+ conformation (the $R(\delta)$ complex, according to the nomenclature in ref. 19) has been considered for en(ind)$_2$ sites. On the contrary, both G^+ and G^- conformations have been considered in the energy minimizations for en(cp)$_2$ sites, owing to their rapid interconversion in this case[23]. The bond angles centred on the second carbon atom of the isobutyl group have been optimized in each calculation, the bending contribution to the total energy being evaluated accordng to ref. 22.

The method of calculation of the non-bonded potential energy has been previously described[24] and is not reported here. The results presented in this paper have been obtained with the parameters proposed by Scheraga[25], treating the CH_2 and the CH_3 groups of the chelating ligands, the CH_3 group of the propene and the CH_3 groups of the chain as spherical domains[26]. In order to test the dependence of the results on the particular choice of the parameters in the potential functions, some calculations have also been performed using the parameters proposed by Flory[22,26,27] and/or avoiding the approximation of spherical domains. Although the results are different from the quantitative point of view, the overall trends and the location of the energy minima are practically unchanged.

The numerical results of our calculations cannot be trusted as such. This is especially true for conformations far from the energy minima, because of the inappropriateness of the energy functions in such regions and because of the simplifying assumption of constancy (rather than near-constancy) of most internal coordinates. However, we believe that the trends suggested by our results are realistic, in the sense that conformations having low energy according to our calculations are not likely to be substantially different from the energy minima of the catalytic system. Furthermore, although the numerical values of the energy differences depend on the exact geometry and on the energy parameters adopted in the calculations, no reasonable adjustment of these parameters can modify our conclusions. As far as the results of our calculations are in qualitative, or perhaps semiquantitative, agreement with all the experimental findings, we also believe that such calculations can be used in a predictive way.

RESULTS AND DISCUSSION

Ethylene-bis(1-indenyl) sites

Figure 3 plots as a function of θ_1 the energy, minimized with respect to α, β, θ_0 and θ_2, of the (ethene)(isobutyl)-(en(ind)$_2$) site (*Figure 3A*) and of its 3,3′-dimethyl derivative (*Figure 3B*). The behaviour of en(ind)$_2$ sites without methyl substituents on the aromatic rings has already been discussed in refs. 3 and 4. Although in the present work we have avoided some of the previous simplifications, such as the use of an ethyl group to model the growing chain or the selection of arbitrary fixed values for α and β, the results for this model site are substantially unchanged. In fact, in agreement with our previous calculations, *Figure 3A* shows that the chirality of the en(ind)$_2$ ligand forces the growing chain to assume values of θ_1 close to $-50°$. The energy curves for derivatives with two methyl groups at 2,2′, 4,4′, 5,5′, 6,6′ and 7,7′ are not significantly different, and the corresponding plots are not shown. *Figure 3B* shows instead a remarkable increase of the total energy in the case of 3,3′ derivative (the same reference state is used in all the plots referring to en(ind)$_2$ sites), indicating that methyl groups in these positions interact strongly with the growing chain and/or with the olefin. However, the preference for negative values of θ_1, typical of (R,R) en(ind)$_2$ sites, is not modified by these strong interactions.

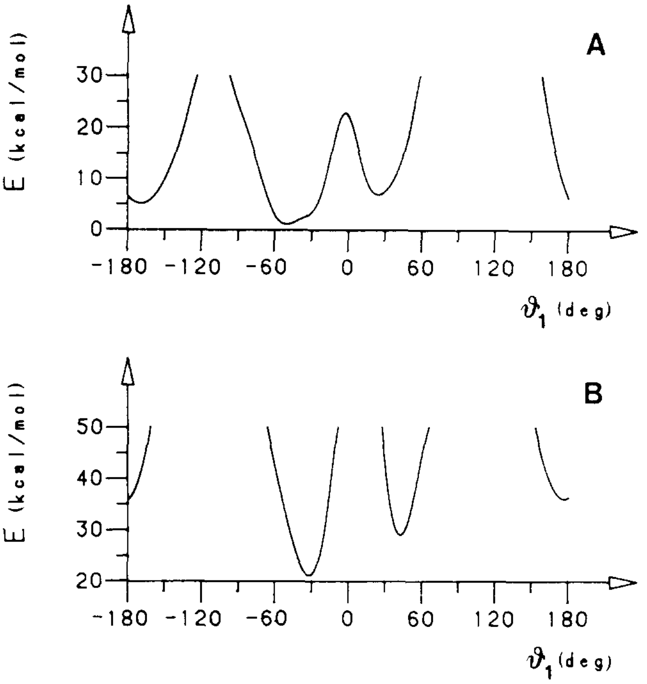

Figure 3 The energy of the (ethene)(isobutyl)(en(ind)$_2$) model site (A) and of its 3,3′-dimethyl derivative (B) as a function of θ_1 after minimization with respect to α, β, θ_0 and θ_2

Figure 4 plots as a function of θ_0 the energy, minimized ith respect to α and β, of the (propene)(methyl)(en(ind)$_2$) site (*Figure 4A*) and of its 3,3′-dimethyl derivative (*Figure 4B*). The full and broken curves refer to *re* and *si* coordinated propene, respectively. In agreement with experimental findings[8] and with previous calculations[3,4], the two chiral coordinations of propene are nearly isoenergetic in *Figure 4A*. This indicates that the chirality of en(ind)$_2$ sites, in the absence of alkyl groups longer than methyl, is unable to generate enantioselectivity in the olefin coordination step. Again, substantially identical results are obtained for all the investigated dimethyl derivatives, with the exception of the 3,3′ disubstituted site. *Figure 4B* shows, in fact, that the *si* coordination of propene is strongly favoured in this case. In practice, the methyl group at position 3 gives rise to large repulsive interactions with the methyl group of *re* coordinated propene, while the energy of the complex with propene in *si* coordination is much less affected.

The effects of the stereochemical environment on the orientation of the growing chain and on the chirality of

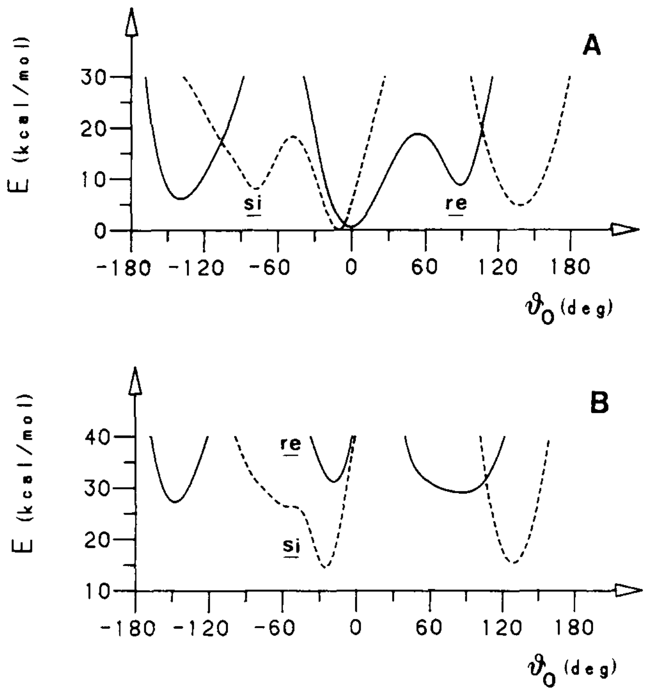

Figure 4 The energy of the (propene)(methyl)(en(ind)$_2$) model site (A) and of its 3,3′-dimethyl derivative (B) as a function of θ_0 after minimization with respect to α and β. The full and broken curves refer to *re* and *si* coordinated propene, respectively

coordination of the propene molecule, considered separately in *Figures 3* and *4*, are combined in *Figure 5*, plotting the minimized energies of the (propene)(isobutyl)(en(ind)$_2$) site (*Figure 5A*) and of its 3,3′-dimethyl derivative (*Figure 5B*) as a function of θ_1. As discussed in a previous work[3], and in full agreement with experiments[1,2], *Figure 5A* shows that the unsubstituted en(ind)$_2$ site is isospecific and that the *re* coordination of propene is greatly favoured for the (*R*,*R*) complex with respect to the *si* coordination. As before, the behaviour of all the dimethyl derivatives considered is strictly analogous, with the exception of the 3,3′ disubstituted model. In fact, the energy minima for the *re* and *si* coordinations of propene (at $\theta_1 \simeq -30°$ and $\theta_1 \simeq +50°$, respectively) are almost isoenergetic in *Figure 5B*, indicating a non-stereospecific behaviour for this model site (the minimum at $\theta_1 \simeq 180°$ is not suitable for monomer insertion according to our model[5,28], and is not considered in this discussion).

The different aspects of the curves in *Figures 5A* and *5B* can be explained on the basis of two opposing steric effects acting in 3,3′ disubstituted en(ind)$_2$ sites. The conformational arrangement corresponding to the two minima at $\theta_1 \simeq \pm 50°$ in *Figure 5A*, as well as in *Figure 5B*, is such that the methyl group of the coordinated propene and the second carbon atom of the isobutyl group are located on opposite sides with respect to the plane defined by the metal atom, the centre of the double bond and the first carbon atom of the isobutyl group. This arrangement is typical of all the model sites in conformations of low energy suitable for monomer insertion[3,5,6]. In the case of the unsubstituted (*R*,*R*) en(ind)$_2$ site, *Figures 3* and *5* show that the growing chain assumes the $\theta_1 \simeq -50°$ orientation. As a consequence, the *si* coordination of propene is disfavoured with respect to the *re* coordination (*Figure 5A*), since the methyl group of a *si* coordinated propene is closer to the crowded region occupied by the second carbon atom of the growing chain (the two situations are almost equivalent in the absence of the growing chain; *Figure 4A*). The former interactions, favouring the $\theta_1 \simeq -50°$ orientation of the chain, are active also in the case of 3,3′ disubstituted (*R*,*R*) en(ind)$_2$ sites (*Figure 3B*). However, the methyl group of a *re* coordinated propene interacts in this case much more repulsively with the substituent at 3 than the methyl group of a *si* coordinated propene (*Figure 4B*). This counterbalances the preference of the growing chain for the $\theta_1 \simeq -50°$ orientation and makes the two possible situations (*re* olefin with chain at $\theta_1 \simeq -50°$ and *si* olefin with chain at $\theta_1 \simeq +50°$) almost isoenergetic (*Figure 5B*).

As one would expect, the relative strength of the two opposing effects depends on the exact values of some of the geometric parameters of the model sites, like for instance the out-of-plane bending angle (γ) of the methyl substituents with respect to the plane of the cyclopentadienyl rings. *Figure 6* shows the energy of the 3,3′ disubstituted (propene)(isobutyl)(en(ind)$_2$) site, minimized with respect to all the variables in *Figure 1*, as a function of γ (curves c and d). For comparison, the lower part of *Figure 6* also shows the energy of the unsubstituted site as a function of the out-of-plane bending angle of the two hydrogens in positions 3 and 3′ (curves a and b). As in the previous plots, the full curves refer to *re* coordinated propene and the broken curves to *si* coordinated propene. While in the unsubstituted site the *re* coordination of the olefin is strongly favoured

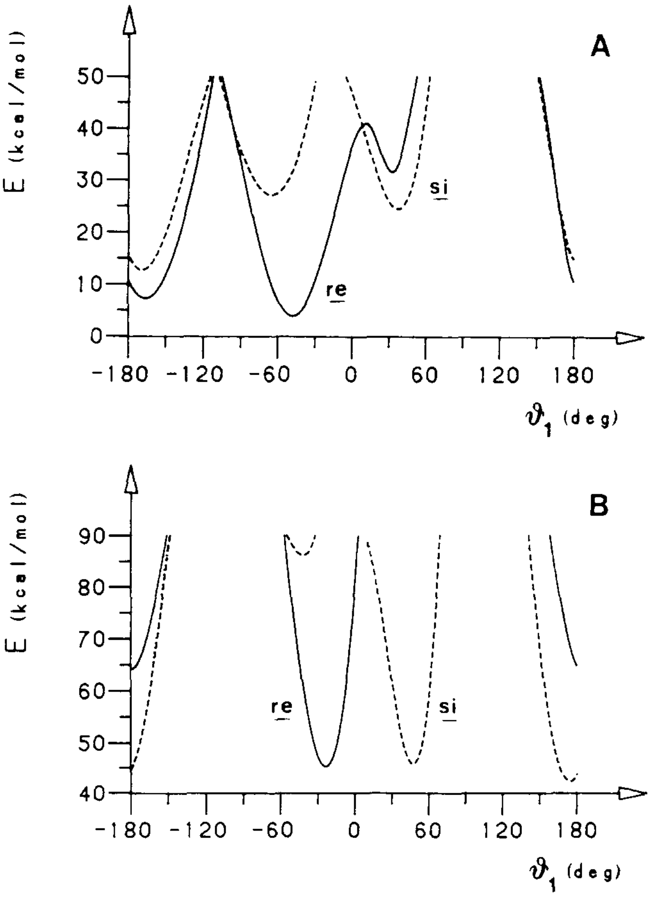

Figure 5 The energy of the (propene)(isobutyl)(en(ind)$_2$) model site (A) and of its 3,3′-dimethyl derivative (B) as a function of θ_1 after minimization with respect to all the other variables indicated in *Figure 1*. The full and broken curves refer to *re* and *si* coordinated propene, respectively

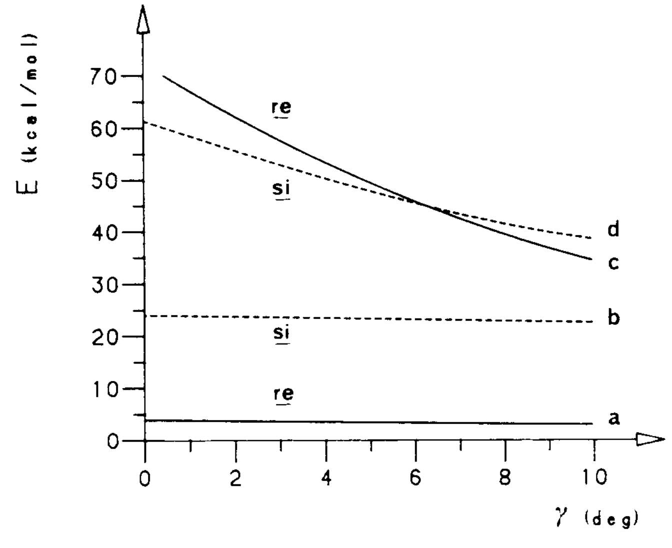

Figure 6 The minimized energy of the (propene)(isobutyl)(en(ind)$_2$) model site (curve a, *re* propene; curve b, *si* propene) and of its 3,3′-dimethyl derivative (curve c, *re* propene; curve d, *si* propene) as a function of the out-of-plane bending angle γ of the two hydrogen atoms (curves a and b) or methyl groups (curves c and d) at positions 3 and 3′

independently of the out-of-plane bending of the two hydrogens, *Figure 6* shows that for values of γ in the range 4–8°, typical of metallocenes with alkyl groups on the rings[12,29], the energy difference of the two diastereoisomeric disubstituted en(ind)$_2$ sites is always smaller than 3 kcal mol^{-1}. Furthermore, their relative stability is inverted for $\gamma \simeq 6°$.

We have also performed calculations with a different coordination geometry of the disubstituted en(ind)$_2$ ligand, equal to that found in the crystal structure of ethylene-bis(3-methyl-1-indenyl)ZrCl$_2$ (ref. 17). In spite of the different geometry and of the higher distance of the ligands from the metal centre, the results of these calculations are similar to those obtained with the previous geometry. For instance, the energy difference in favour of the *re* coordination of propene is found to be 9.0 kcal mol^{-1} for the unsubstituted (*R,R*) en(ind)$_2$ site and only 2.5 kcal mol^{-1} for the 3,3′-dimethyl derivative. As discussed in the previous section, the rigidity of the models leads to energy differences that are somehow overestimated. However, the almost complete absence of stereospecificity experimentally observed in the case of 3,3′ disubstituted en(ind)$_2$ catalysts[10] is reasonably accounted for by our calculations.

Ethylene-bis(cyclopentadienyl) sites

The conformational energy of the (ethene)(isobutyl)-(en(cp)$_2$) site, minimized with respect to α, β, θ_0 and θ_2, is plotted as a function of θ_1 in *Figure 7A*. *Figures 7B* and *7C* show the corresponding plots obtained for the (*R,R*) 2,2′- and 3,3′-dimethyl substituted sites. As previously specified, all the calculations on en(cp)$_2$ sites have been performed for both the conformers with the torsion identified by ω (see *Figure 1*) in the G^+ and in the G^- state, respectively. For each value of θ_1, *Figure 7* then shows the smaller of the two energies. As in the case of en(ind)$_2$ sites, the energy minima for en(cp)$_2$ sites occur at $\theta_1 \simeq +50°$ and $\theta_1 \simeq -50°$ (corresponding to G^+ and G^- states of ω, respectively), as well as at $\theta_1 \simeq 180°$. Conformations with $\theta_1 \simeq 180°$ are not suitable for monomer insertion according to our model[5,28], and are not considered in the following discussion. The equal depth of the minima at $\theta_1 \simeq \pm 50°$ in *Figure 7A* is an obvious consequence of the absence of chirality in the unsubstituted en(cp)$_2$ site. *Figure 7B* shows, on the other hand, that the behaviour of the 2,2′ derivative is very similar, that is the minima at $\theta_1 \simeq \pm 50°$ are approximately isoenergetic. Also, the energies in *Figure 7B* are almost coincident with those in *Figure 7A* (the same reference state is used in all the plots referring to en(cp)$_2$ sites). These results indicate that the methyl substituents at positions 2 and 2′ do not interact significantly with the ethene molecule or with the growing chain, whatever the orientation of the latter. On the contrary, the stereochemical environment of the growing chain is substantially altered by the placement of methyl groups at positions 3 and 3′, since the energy curve shown in *Figure 7C* for the 3,3′ disubstituted en(cp)$_2$ site is much more similar to that of *Figure 3A* (relative to the unsubstituted en(ind)$_2$ site) than to those in *Figures 7A* and *7B*. In fact, also in the case of the 3,3′ disubstituted (*R,R*) en(cp)$_2$ site, the growing chain is forced to $\theta_1 \simeq -50°$, while values of θ_1 close to $+50°$ are substantially forbidden.

Figure 8A plots the energy of the (propene)(methyl)-(en(cp)$_2$) site, minimized with respect to α and β, as a function of θ_0. The corresponding plots for the 2,2′- and

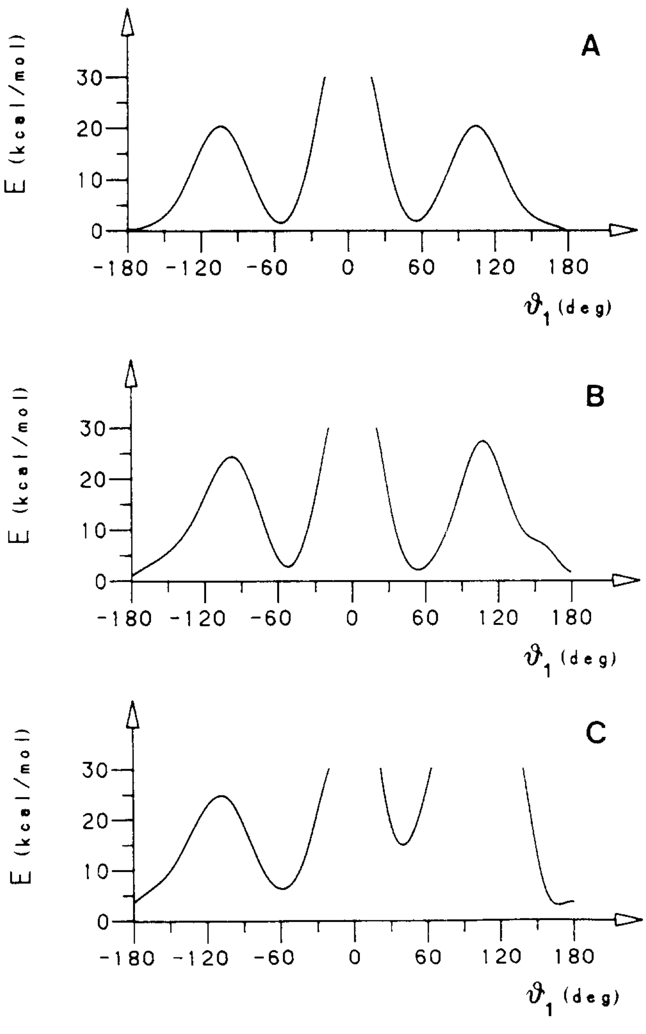

Figure 7 The energy of the (ethene)(isobutyl)(en(cp)$_2$) model site (A) and of its 2,2′- and 3,3′-dimethyl derivatives (B and C, respectively) as a function of θ_1 after minimization with respect to α, β, θ_0 and θ_2

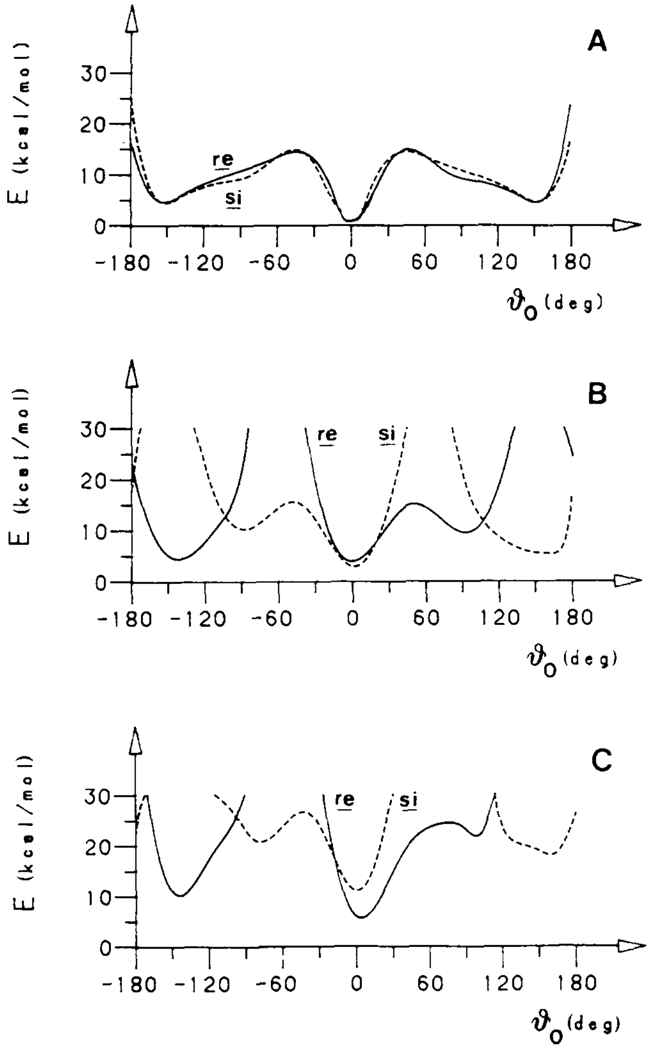

Figure 8 The energy of the (propene)(methyl)(en(cp)$_2$) model site (A) and of its 2,2′- and 3,3′-dimethyl derivatives (B and C, respectively) as a function of θ_0 after minimization with respect to α and β. The full and broken curves refer to *re* and *si* coordinated propene, respectively

3,3′-dimethyl derivatives are shown in *Figures 8B* and *8C*, respectively. As in the previous plots, the full and broken curves refer to *re* coordinated and *si* coordinated propene, respectively. Energy minima are found for $\theta_0 \simeq 0°$ and $\theta_0 \simeq \pm 150°$. The latter correspond to conformations that are geometrically unsuitable for the insertion of monomer. The equal depth of the minima in *Figure 8A* for the two chiral *re* and *si* coordinations of the propene molecule to the unsubstituted site is obvious, since the two models are enantiomeric and not diastereoisomeric. The approximately equal depth of the two minima in *Figure 8B*, relative to the 2,2′ disubstituted en(cp)$_2$ site, indicates that the chirality of this site is not sufficient to generate enantioselectivity in the olefin coordination step. On the contrary, *Figure 8C* shows that the *re* coordination of propene to the 3,3′ disubstituted (*R*,*R*) en(cp)$_2$ site is favoured with respect to the *si* coordination.

Lastly, *Figure 9* plots as a function of θ_1 the energy of the (propene)(isobutyl)(en(cp)$_2$) model site (*Figure 9A*) and of its 2,2′- and 3,3′-dimethyl derivatives (*Figures 9B* and *9C*, respectively). For each value of θ_1, the energy has been minimized with respect to all the other variables shown in *Figure 1*. The effects of the stereochemical environment on the orientation of the growing chain and on the chirality of coordination of the olefin, considered separately in *Figures 7* and *8*, are of course combined in *Figure 9*. It is clearly seen that, according to our calculations, the 2,2′ derivative should have the same non-stereospecific behaviour of the non-chiral unsubstituted en(cp)$_2$ site. On the other hand, the model predicts a strong preference for *re* coordinated propene in the case of the 3,3′-dimethyl (*R*,*R*) derivative. In fact, the disubstituted ligand by itself favours the *re* coordination of propene, and this effect is further reinforced by the orientation of the growing chain at $\theta_1 \simeq -50°$. This is at variance with the results for unsubstituted en(ind)$_2$ sites, in which the stereospecificity originates from the chiral orientation of the growing chain only. Hence, the model predicts that catalysts containing the 3,3′-dimethyl derivative of en(cp)$_2$ should be roughly as isospecific as those containing the en(ind)$_2$ ligand.

This prediction, based on calculations on simple models of the catalytic site, has been confirmed by the results of recent experiments performed by Ewen[30].

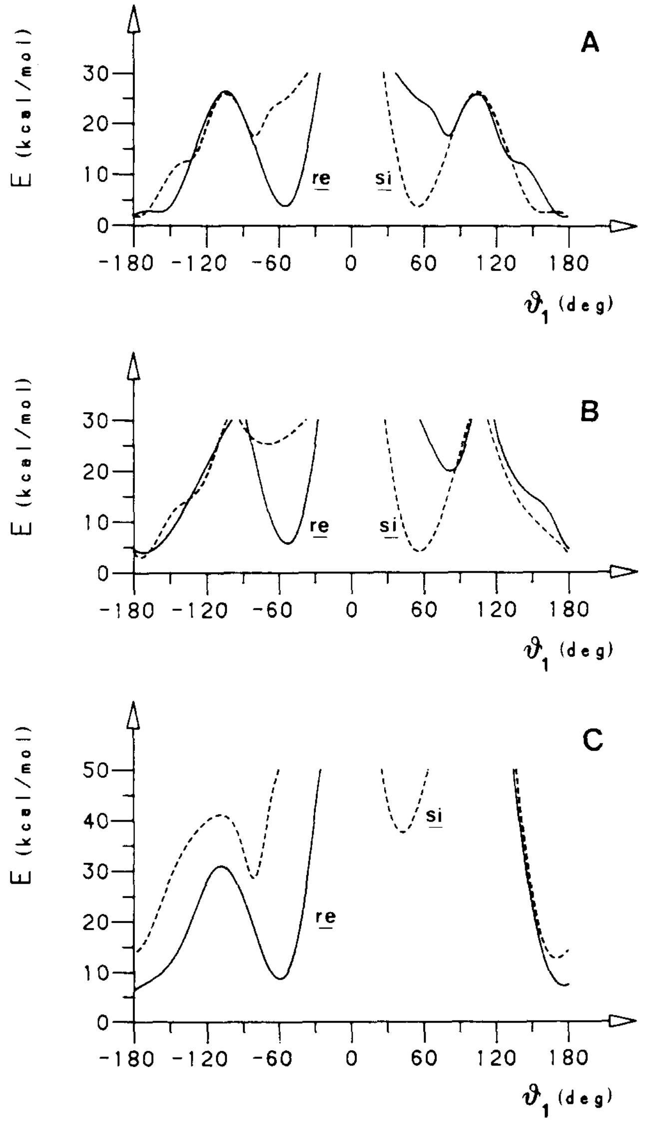

Figure 9 The energy of the (propene)(isobutyl)(en(cp)$_2$) model site (A) and of its 2,2′- and 3,3′-dimethyl derivatives (B and C, respectively) as a function of θ_1 after minimization with respect to all the other variables indicated in *Figure 1*. The full and broken curves refer to *re* and *si* coordinated propene, respectively

CONCLUSIONS

We have performed conformational energy calculations on models of homogeneous Ziegler–Natta catalysts containing the en(ind)$_2$ ligand or the en(cp)$_2$ ligand, substituted in various positions with methyl groups.

According to our model, the presence of methyl substituents on the en(ind)$_2$ ligand influences the stereospecificity only when the methyl groups are at positions 3 and 3′. The principal effect in the latter case is to enhance the energy of the (R,R) model with propene in *re* coordination, since the methyl group of the *re* coordinated olefin comes in close contact with one of the substituents. This counterbalances the steric effects of the C(4) and C(4′) atoms of the en(ind)$_2$ ligand, indirectly favouring the *re* coordination of the olefin, and leads to the non-stereospecific behaviour that has been experiment ally observed for catalysts containing the 3,3′ disubstituted en(ind)$_2$ ligand.

Catalysts containing the unsubstituted en(cp)$_2$ ligand are non-chiral, and then aspecific. This situation is not modified when the aromatic hydrogens at positions 2 and 2′ are substituted by methyl groups. However, according to our model, the substitution in positions 3 and 3′ leads to a highly isospecific behaviour, comparable with that of catalysts containing the unsubstituted en(ind)$_2$ ligand. The fact that this prediction has been confirmed by very recent experiments indicates that the ideas underlying our model are substantially correct and that conformational energy calculations analogous to those reported in this paper can be used as a predictive tool in the study of catalytic systems in which the stereospecificity is mainly determined by non-bonded interactions.

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