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Selectivity of large pore zeolites in the alkylation of naphthalene with *tert*-butyl alcohol: analysis of experimental results by computational modelling

Patrice Moreau*, Zhongmin Liu[1], François Fajula, Jacques Joffre[2]

Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, UMR 5618, Ecole Nationale Supérieure de Chimie,
8 rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France

Abstract

Liquid phase alkylation of naphthalene with *tert*-butanol has been studied using HY and H-beta zeolites with varying silicon to aluminium ratios. Both series of zeolites underwent efficient activities and high selectivities for the mono- and di-(*tert*-butyl) derivatives. In all cases, 2-(*tert*-butyl)naphthalene (2-TBN) was the only monoalkylated product (100%,β-selectivity). Over H-beta zeolites, 2-TBN was obtained as the main product with relatively small amounts of dialkylated compounds. Over HY samples, a 2,6-di(*tert*-butyl)naphthalene (2,6-DTBN) selectivity up to 84% was obtained, with a 2,6-DTBN/2,7-DTBN ratio of 5.6–5.9 and β,β'-selectivity (2,6-+2,7-) of 98–99%. This constitutes the first published observation of such high β,β' selectivity and 2,6-/2,7- ratio in the liquid phase alkylation of naphthalene. In order to understand such a differentiation in the formation of the two di-(*tert*-butyl)naphthalenes over the HY zeolites, computational analysis of both energies and molecular dimensions of these derivatives and of the monoalkylated counterparts has been performed, using quantum mechanics (AM1 and PM3) and molecular mechanics (MM^+) methods. The energy calculations are in agreement with the experimental results regarding the selective formation of the β and β,β' isomers. The determination of the kinetic diameters shows that, in their most stable conformation, 2,6-DTBN has a smaller kinetic diameter (7.1 Å) than 2,7-DTBN (7.5 Å), which may explain the selective formation of the 2,6-isomer against the 2,7- within the faujasite framework. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: 2,6-dialkylnaphthalene; Shape-selectivity; Zeolites; Heterogeneous catalysis; Computational modelling; Kinetic diameter

1. Introduction

In order to avoid the disadvantages and the environmental limitations of conventional Friedel–Crafts catalysts, especially in aromatic electrophilic substitution reactions, it is nowadays necessary to find suitable, recyclable and environment-friendly solid acid catalysts [1]. Due to the interest of 2,6-dialkylnaphthalenes as valuable compounds for the preparation of polyester fibers and plastics with superior properties and of thermotropic liquid crystal polymers [2,3], shape-selective and acid properties of zeolites have been recently exploited in the alkylation of naphthalene, with the aim of achieving both high activity and 2,6-dialkylnaphthalene selectivity. Isopropylation of naphthalene has been especially investigated using different zeolite catalysts in liquid

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* Corresponding author. Tel.: +33-4-67-14-43-23;
fax: +33-4-67-14-43-49.
E-mail address: pmoreau@cit.enscm.fr (P. Moreau)

[1] Permanent address: Dalian Institute of Chemical Physics, P.O. Box 110, Dalian 116023, China.

[2] Co-corresponding author.

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phase conditions; high β and β,β′-selectivities were obtained over both large and medium pore zeolites [4–8,24]. Over H-mordenites, β- and β,β′-selectivities were attributed to a shape selective effect. The preferential formation of 2,6-diisopropylnaphthalene (2,6-DIPN) among all isomers has been obtained with H-mordenites when using propene or propanol as alkylating reagent with a 2,6-DIPN/2,7-DIPN ratio in the range of 2–3. Hence, by using partially dealuminated mordenites, over 65% selectivity to 2,6-DIPN was obtained by Song and coworkers [8–10], and up to 70% selectivity was achieved over a highly dealuminated H-mordenite impregnated with a large amount of cerium poisoning external acidic sites [11]. It thus appears that, compared to their parent counterparts, modified, especially dealuminated, mordenites are more effective for shape-selective isopropylation of naphthalene. As for large pore zeolites (HY), the existence of supercages providing enough space for multiple reactions leads to the preferential formation of the thermodynamically stable β- or β,β′-isomers. In that case, no characteristic selective effect of the 2,6-isomer against the 2,7- was observed [6–8]. On the other hand, we recently showed [12–14] that the liquid phase alkylation of naphthalene with cyclohexyl derivatives as alkylating agents could be carried out over HY zeolites, leading to high conversions and efficient β,β′-selectivities. In that case also, no characteristic selective effect of 2,6- against 2,7-isomer was observed (2,6-DCN/2,7-DCN=1), but the easy separation of the crystalline 2,6-dicyclohexylnaphthalene from the reaction mixture constituted an advantage of the cyclohexylation reaction, regarding the production of a pure 2,6-dialkylnaphthalene [15]. Moreover, it was found, by means of a computational analysis of the molecular dimensions of the two isomers, that 2,6-DIPN and 2,7-DIPN on one side and 2,6-DCN and 2,7-DCN on the other side had the same critical diameters (6.6 and 7.1 Å), explaining that no differentiation was obtained between the two isomers within the three-dimensional HY framework [14]. Such a result led us to focus our interest on other hindered alkylating agents, especially *tert*-butyl alcohol, from which it was expected that both high activity and high β- and β,β′-selectivities could be achieved, and which has not been used in the naphthalene alkylation under heterogeneous conditions before; the *tert*-butyl group, being a much bulkier substituent than the isopropyl or cyclohexyl, was supposed to lead to larger degrees of shape-selectivity.

The present work deals with the results obtained in the alkylation of naphthalene over large pore zeolites such as HY and H-beta as catalysts with *tert*-butyl alcohol as alkylating agent, leading to the selective synthesis of either 2-*tert*-butylnaphthalene or 2,6-(di-*tert*-butyl)naphthalene [16] and with a computational analysis of the energies and molecular dimensions of the different isomers, allowing to discuss these experimental results.

2. Experimental and methods of calculation

2.1. Experimental

The catalysts and materials used, the experimental procedure (catalytic runs) and the product analysis and characterisation have been already described in a previous paper [16].

2.2. Methods of calculation

The Hyperchem 5.11 version software package [17] was used for computational modelling analysis. The analysis is based on energies, dimensions and molecular graphics of the molecules implied in the reaction. The energy is computed mainly using semi-empirical quantum mechanics methods with the AM1 and PM3 hamiltonians [18]. For comparisons, molecular mechanics calculations with the MM^+ force field module, an improved version of the MM2 force field [19], was also used. After minimisation of the energy, the kinetic (or critical) diameter of the molecule was determined using the width of the closest box enclosing the molecular system [20], the van der Waals radius of the hydrogen atom (1.2 Å) and a conversion factor $2^{-1/6}$ [21].

3. Results and discussion

3.1. Experimental results

As previously reported [16] and as shown in Table 1, both series of catalysts underwent efficient activities and high β and β,β′-selectivities. In all

Table 1
Results of *tert*-butylation of naphthalene from previous work [16][a]

Catalyst	Naphthalene conversion (%)	Product distribution (wt.%)			β,β′-selectivity in DTBN (%)[b]			2,6-/2,7-
		2-TBN	DTBN	Others	2,6-	2,7-	2,6-+2,7-	
HY (20)	52.4	44.1	53.1	2.7	83.8	14.1	97.9	5.9
HY (6)	44.9	52.1	46.3	1.6	83.8	14.9	98.7	5.6
H-beta (26)	32.6	90.0	9.0	1.0	52.2	47.8	100	1.1
H-beta (13)	16.2	95.2	4.8	/	50.0	50.0	100	1.0

[a] Reaction conditions: catalyst 0.50 g, naphthalene 10 mmol, *tert*-butanol 20 mmol, solvent cyclohexane 100 ml, temperature 160°C, pressure 2 Mpa, reaction time 2 h.

[b] β,β′-DTBN with respect to total DTBN isomers.

cases, 2-(*tert*-butyl)naphthalene (2-TBN) was the only monoalkylated product. Compared with the results of naphthalene isopropylation [6], in which 1-isopropylnaphthalene is initially formed over HY zeolites, the present results clearly show that a remarkable shape-selective effect is in operation on the large pore zeolites for the monoalkylation step, when a hindered molecule such as *tert*-butyl alcohol is used as the alkylating agent.

3.1.1. *Effect of catalyst type on activity*

Concerning the activities of the various catalysts, a 45–52% naphthalene conversion can be achieved after 2 h reaction at 160°C over HY samples (Si/Al ratios of 6, 15, 20), indicating a very interesting catalytic activity in the alkylation reaction of naphthalene with *tert*-butanol.

On the other hand, H-beta samples (Si/Al ratio of 13 and 26) show relatively lower activities (16–32% naphthalene conversion after 2 h reaction) compared with HY samples with corresponding Si/Al ratios.

3.1.2. *Effect of catalyst type on selectivity*

As regards to 2,6-di(*tert*-butyl)naphthalene (2,6-DTBN) selectivity, which is defined as the percent of 2,6-DTBN with respect to all DTBN isomers, the HY samples show a much higher selectivity than the H-beta catalysts (80% for HY against 50% for H-beta).

A 2,6-DTBN selectivity up to 84% was obtained over the HY samples (Si/Al ratio from 6 to 20) with a 2,6-DTBN/2,7-DTBN ratio of 5.6–5.9 and β,β′ selectivity (2,6-+2,7-) of 98–99% after 2 h at 160°C (at a 45–52% naphthalene conversion). This was the first observation [16] of such high β,β′ selectivity and 2,6-/2,7- ratio in the liquid phase alkylation of naphthalene.[3] This could be logically attributed to the pore size effect of the HY zeolite (with its supercages) which is capable of limiting the formation of isomers with relatively large dimensions. In the reaction over H-beta zeolites, 2-(*tert*-butyl)naphthalene (2-TBN) was observed as the main product (about 80% at 45% conversion) with relatively small amounts of DTBN derivatives. This may be due to the different architecture of the pores of zeolite beta (interconnected channels and absence of supercages) in which further alkylation of 2-TBN cannot occur or through which the dialkylated derivatives cannot freely move.

3.2. *Computational modelling results*

It has been clearly established by different authors that the 2,6-diisopropylnaphthalene is favoured by a factor of 2–3 over the 2,7-isomer in the isopropylation of naphthalene over dealuminated modified mordenites [7–11]. Horsley et al. [22] have shown by computer simulation that the diffusion of 2,6-DIPN inside mordenite pore channel is easier than that of 2,7-DIPN. They conclude that such a difference in energy barrier may partially account for the observed higher selectivity of mordenites for 2,6-DIPN, despite the critical diameters of the two isomers being very similar [4]. On the other hand, as said above, we could confirm that the molecular dimensions of not

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[3] K. Smith, S.D. Roberts (oral communication, IVth Europacat Symposium, Rimini, September 1999) have reported an improvement of the selectivity in 2,6-DTBN under different experimental conditions.

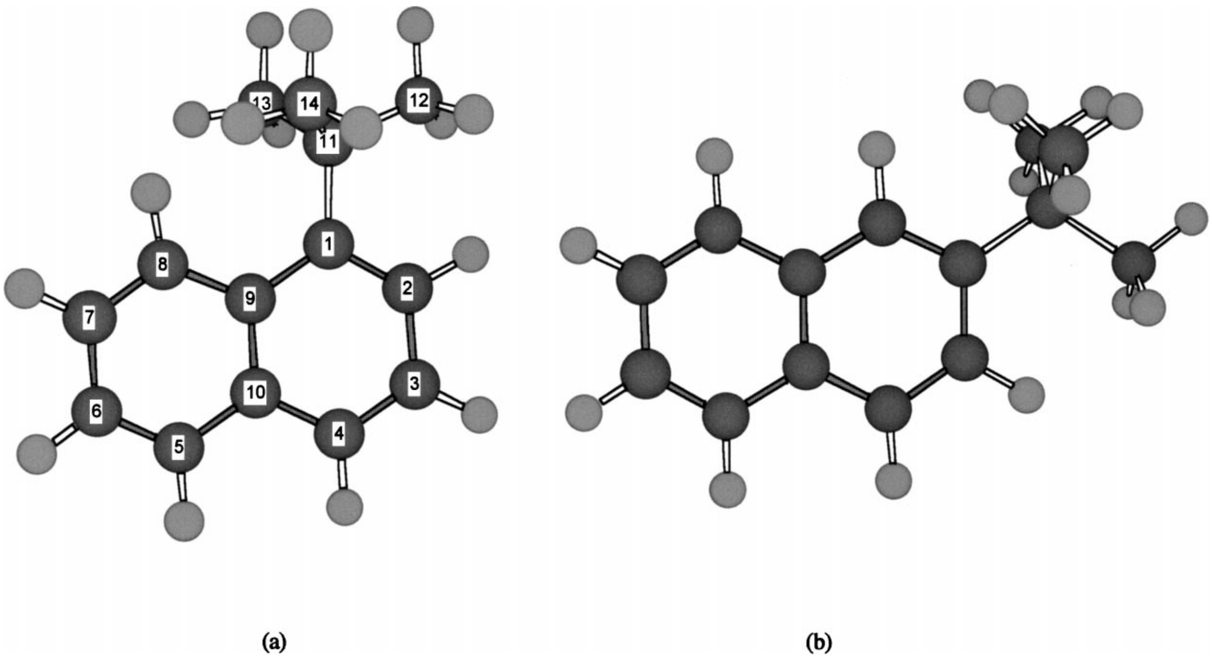

Fig. 1. Molecular representation of 1-(*tert*-butyl)naphthalene (a) and 2-(*tert*-butyl)naphthalene (b).

only 2,6- and 2,7-DIPN, but also of the corresponding 2,6- and 2,7-dicyclohexylnaphthalene derivatives, were effectively of the same magnitude [14]. In order to clarify whether the differentiation between the two isomers was caused by their differences in molecular dimensions or electronic properties, Song et al., in a recent paper [23], performed a computational analysis of these properties for the 2-isopropyl and 2,6- and 2,7-diisopropylnaphthalenes. These authors conclude that the results of the frontier orbital analysis, for which the frontier electron density in position 6 of 2-IPN has been shown to be considerably higher (0.177) than that of position 7 (0.122), on one side, and the fact that 2,6-DIPN has a more linear structure with a slightly smaller critical diameter than 2,7-DIPN, on the other side, may partially account for the enhanced formation of the 2,6-DIPN from 2-IPN inside mordenite channels.

Taking into account the significative value of up to 6 obtained for the 2,6-DTBN/2,7-DTBN ratio, it was thus important for us to determine both molecular dimensions and energies of these derivatives by means of computational modelling.

3.2.1. Monoalkylated compounds: 1- and 2-(tert-butyl)naphthalene's

The mono *tert*-butylated naphthalene's, 1-TBN and 2-TBN, have been first considered in order to explain the remarkable β-selectivity observed experimentally over both HY and H-BEA zeolites. For this purpose, a conformational analysis has been carried out for the two isomers, considering the rotation around the C1–C11 (Fig. 1a) and C2–C11 (Fig. 1b) bonds.

Table 2 shows that, whatever the computational method used, the 2-TBN (β-isomer) is more stable than its α counterpart (1-TBN). It is worth noting

Table 2
Energies in kcal/mol of the stable conformations of 1- and 2-TBN

Molecule	Conformation	Heat of formation		Steric energy
		AM1	PM3	MM^+
1-TBN	C2–C1–C11–C12 (0)	26.1	20.3	3.3
	C2–C1–C11–C12 (60)	30.0	25.0	6.7
2-TBN	C1–C2–C11–C12 (0)	19.8	17.0	−4.4
	C1–C2–C11–C12 (60)	19.9	17.2	−4.5

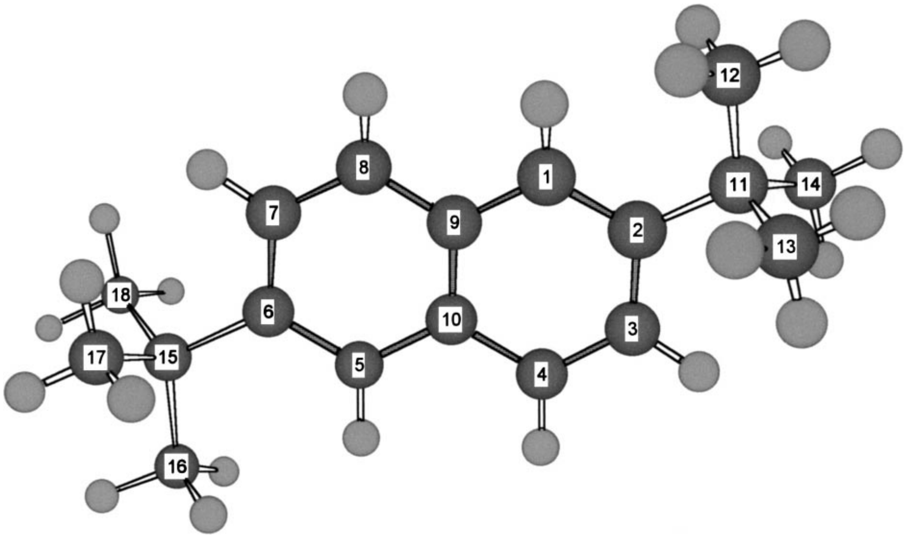

Fig. 2. Molecular representation of 2,6-di(*tert*-butyl)naphthalene.

that AM1 and MM^+ methods lead to energetic differences between the two isomers in the same conformation higher than PM3 method. For example, in the case of the dihedral angles C2–C1–C11–C12 and C1–C2–C11–C12 in the (0) conformation (i.e. where the dihedral angle value is almost zero), such a difference is 6.3 for AM1 and 7.7 kcal/mol, respectively, for MM^+ instead of 3.3 kcal/mol for PM3.

Moreover, concerning the two rotamers of the 2-TBN, it can be seen that the quantum mechanics methods slightly favour the (0) conformation, while molecular mechanics predicts the (60) conformation as the more stable. Despite these small differences, these energy calculations are in total agreement with the experimental results regarding the selective formation of the 2-(*tert*-butyl)naphthalene isomer (2-TBN), and thus rules out the computational studies of the various di-*tert*-butyl isomers, except the 2,6- and 2,7-ones.

3.2.2. Dialkylated derivatives: 2,6- and 2,7-di(tert-butyl)naphthalenes

A similar conformational analysis has been first performed on both 2,6- and 2,7-DTBN, considering the rotation around the C2–C11 and C6–C15 or C7–C15 bonds respectively, as shown in Fig. 2 for the 2,6-isomer given as example.

The energy surface $E=f(\Phi,\Psi)$, with Φ=C1–C2–C11–C12 and Ψ=C5–C6–C15–C16 (2,6- isomer) or C8–C7–C15–C16 (2,7-isomer), corresponding to the heat of formation of each molecule in all the conformations and computed with the AM1 hamiltonian, displays three stable conformations, respectively, (0,0), (0,60) and (60,60). Fig. 3 gives the example of the 2,6-isomer.

Table 3 shows the values obtained for the energies of these stable conformations. It can be seen that the energies of the two isomers, 2,6- and 2,7-DTBN, in a given conformation are very close, and that, for both isomers, the (0,0) conformation is the most stable. Therefore, 2,6- and 2,7-DTBN, which are both β,β' selective products, are equally stable in terms of heat of formation. Consequently, the selective formation of the 2,6-isomer against the 2,7- must be due to another parameter.

Table 3 indicates also the values of the kinetic diameters determined using the AM1 geometry, taking into account the conversion factor described in the experimental part. It is clear, from this table, that, whatever the conformation, the kinetic diameter of the 2,6-isomer is significantly smaller than that of the 2,7-, especially in the most stable (0,0) conformation, for which the difference is 0.4 Å. The same meaningful difference has been found using the MM^+ force field method, as shown in Table 4.

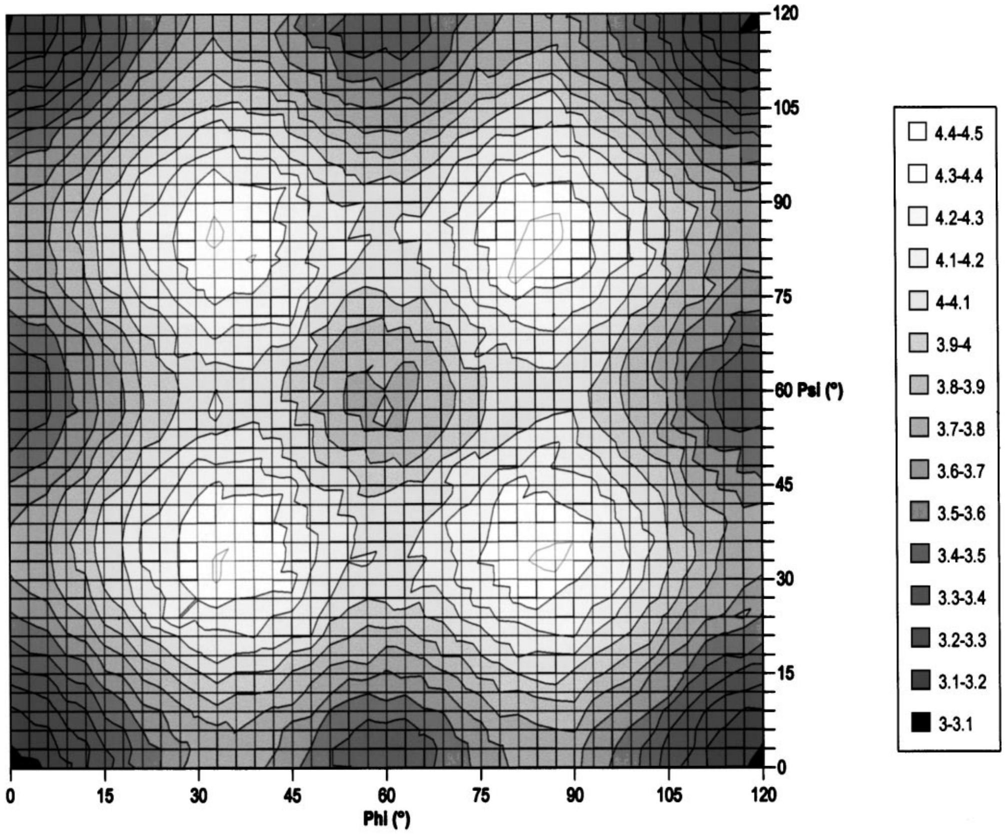

Fig. 3. Energy surface (heat of formation in kcal/mol) of 2,6-di(*tert*-butyl)naphthalene (AM1 method).

From this computational analysis, it appears first that the 2,6- and 2,7-DTBN are equally thermodynamically stable, which does not allow to conclude about selectivity. On the contrary, the difference in the steric hindrance of the two isomers, in terms of their kinetic diameters, is significant enough to explain the selective formation of the 2,6-isomer. Such a difference is illustrated by the molecular graphics representations of the two isomers inside the 12-member ring pore of the faujasite framework, which show that 2,6-DTBN (Fig. 4) fits better in the faujasite window than the 2,7-DTBN (Fig. 5).

Table 3
Energies in kcal/mol and dimensions in Å of the stable conformations of 2,6- and 2,7-DTBN (AM1 method)

Molecule	Conformation (Φ,Ψ)	Heat of formation	Interatomic distances			Kinetic diameter
			Length	Width	Thickness	
2,6-DTBN	(0,0)	3.04	11.7	5.5	4.3	7.1
	(0,60)	3.37	11.9	5.5	4.3	7.1
	(60,60)	3.72	11.5	5.5	4.3	7.1
2,7-DTBN	(0,0)	3.06	11.1	5.9	4.3	7.5
	(60,60)	3.39	11.4	6.0	4.3	7.5
	(60,60)	3.73	11.8	5.6	4.3	7.2

Table 4
Comparison of energies and kinetic diameters of 2,6- and 2,7-DTBN in the most stable conformation (0,0) computed by AM1 and MM^+

Molecule	Conformation (Φ,Ψ)	Method	Energy (kcal/mol)	Kinetic diameter (Å)
2,6-DTBN	(0,0)	AM1	3.04[a]	7.1
		MM^+	0.20[b]	7.1
2,7-DTBN	(0,0)	AM1	3.06[a]	7.5
		MM^+	0.22[b]	7.5

[a] Heat of formation.
[b] Steric energy.

The modelling computational analysis thus confirms that the 2,6-DTBN selective formation is mainly due to a product shape-selectivity. Moreover, the higher reactivity of position 6 compared to that of position 7, as estimated by the frontier molecular orbital theory in the isopropyl series [23], leads also to the preferred formation of the 2,6-isomer. Consequently, the combination of the steric and electronic factors accounts for the enhanced formation of the 2,6-DTBN against the 2,7- within the tridimensionnal HY zeolite framework.

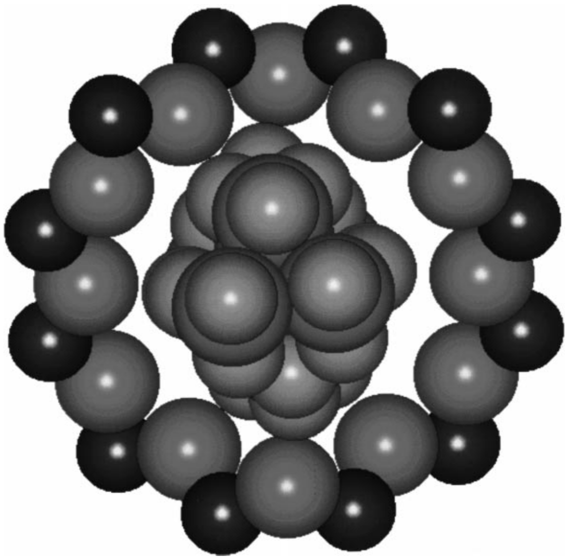

Fig. 4. Molecular graphics representation of 2,6-DTBN in 12 m pore of faujasite; H: cyan, C: violet, O: red, Si: blue.

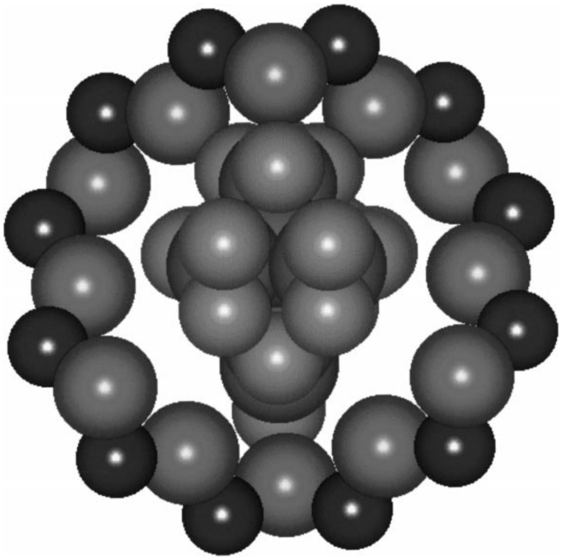

Fig. 5. Molecular graphics representation of 2,7-DTBN in 12 m pore of faujasite; H: cyan, C: violet, O: red, Si: blue.

4. Conclusion

In the liquid phase alkylation of naphthalene with *tert*-butanol, HY and H-beta zeolites undergo efficient activities and high selectivities for the mono- and di-(*tert*-butyl)derivatives. Over H-beta zeolites, 2-TBN is obtained as the main product with relatively small amounts of dialkylated compounds, whereas, over HY samples, a 2,6-di(*tert*-butyl)naphthalene (2,6-DTBN) selectivity up to 84% is obtained, corresponding to a 2,6-DTBN/2,7-DTBN ratio near 6. Such a result constituted the first published observation of such high β,β' selectivity and 2,6-/2,7- ratio in the liquid phase alkylation of naphthalene. The computational analysis of both energies and molecular dimensions of these derivatives and of the monoalkylated counterparts has been performed, using quantum mechanics (AM1 and PM3) and molecular mechanics (MM^+) methods. The energy calculations are in agreement with the experimental results, but do not allow to conclude about the selective formation of both β and β,β' isomers. On the contrary, the determination of the kinetic diameters show that, in its most stable conformation, 2,6-DTBN has a smaller kinetic diameter (7.1 Å) than 2,7-DTBN (7.5 Å), which may explain, by itself, the selective formation of the 2,6-isomer against the 2,7- within the faujasite framework. Such modelling analysis appears thus useful to understand the experimental results, and confirms other computational results in the field of the shape-selective alkylation of naphthalene [23].

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