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Molecular Electrostatics, Energetics, and Dynamics of the Alkylation of Naphthalene: Positional Isomerization of Monoalkylnaphthalenes at Hartree−Fock and Correlated Levels with BSSE Corrections

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The energetics and dynamics of the protonation of the naphthalene molecule were investigated at the Hartree−Fock (HF) and correlated levels. Calculations at correlated levels reproduced the experimental gas-phase proton affinity and basicity of naphthalene quite well. Positional isomerizations of monoalkylnaphthalenes were studied at various theoretical levels. The calculated thermodynamic equilibrium compositions at correlated levels are in good agreement with the experimental results. According to the calculations, intramolecular shifts are possible for the methyl, ethyl, and isopropyl groups. By contrast, the bulky *tert*-butyl group transfers exclusively intermolecularly. In accordance with the experimental results, the activation energies of the 1,2-alkyl shifts decrease with the increase in the size of the alkyl group. This indicates that the rate-determining step of the isomerization reactions is the rearrangement of the monoalkylnaphthalenium ions via 1,2-alkyl shifts. An intermolecular methyl group transfer between two naphthalene molecules is energetically much less favored than the relevant intramolecular one. However, an appropriate basis set superposition error correction to the total energy of the three-body transition state complex is of utmost importance at second-order Møller−Plesset level.

Introduction

Homogeneous and heterogeneous (Brønsted and Lewis) acid-catalyzed alkylation of benzene and naphthalene with various alkylating agents (alkenes, alcohols, alkyl halides, etc.) is of great practical importance.[1] Especially the BTX (benzene−toluene−xylenes) processing is of industrial significance in producing aromatics. Alkylation of naphthalene is just slightly less important than that of benzene from industrial point of view. Among dialkylnaphthalenes, the 2,6-isomers are fundamental starting materials for the preparation of liquid crystal polymers. This is the reason the shape selective production of 2,6-diisopropylnaphthalene over HM zeolite catalyst[2] is remarkable.

However, prompt economic circumstances determine which isomer is the most valuable. Consequently, the control of the alkylation process to get one or several particular components in high yields is of utmost importance. However, if one wants to do that, one should know the details of the reactions occurring in the system.

Today, computational chemistry has become an important research tool complementing and occasionally directing experimental work. For instance, computational thermochemistry affords thermochemical data within experimental precision using sophisticated theoretical (quantum chemical) models.[3] Quantum chemistry is able to provide enormous help in determining and characterizing transition states of elementary reactions hardly accessible for experimental scrutiny.

Acid-catalyzed alkylation of arenes on its own is a very complex reaction system. In general, the following reactions take place: alkylation−dealkylation, positional and side-chain isomerization, and transalkylation−disproportionation. The product distribution first of all depends on the equilibria attained among the pure (neutral) hydrocarbons and their carbocationic derivatives. The impact of the external variables (temperature, pressure, solvent, catalyst, etc.) on the product distribution is realized via changing the state of these equilibria. Usually, the goal is to gain a mixture with composition very different from that of the pure hydrocarbons being in thermodynamic equilibrium.

Suld and Stuart studied the acid catalyzed ($HF-BF_3$) interconversion of methyl- and dimethylnaphthalenes experimentally long ago.[4] In their paper they have put forward two statements: (i) "... the term intramolecular 1,2-methyl shift implies no insight into the mechanism of rearrangement ..." and (ii) "... since neither the π- nor the σ-complex stabilities of dimethylnaphthalenes are presently known, no correlation of the latter with the rates of isomerization is possible ...". According to a current review,[1] these problems have remained unsolved ever since.

First, the protonation of the isolated naphthalene molecule is considered in this paper. By determining the local minima as well as the transition states of the intramolecular hydrogen shifts on the potential energy surface (PES), an overall energetic picture for the protonation of naphthalene is provided. For the mixtures of various monoalkylnaphthalenes (methyl, ethyl, isopropyl, *tert*-butyl), the thermodynamic equilibrium compositions obtained at different theoretical levels are then compared with the experimental values. Furthermore, the transition states of the intramolecular and intermolecular alkyl group migrations

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are localized and characterized. The calculation results allow reasonable estimates to the activation energies for the possible reaction pathways and the most probable mechanisms for the positional isomerization are determined. It turns out that without a proper account of the basis set superposition error (BSSE), the activation energies for the bimolecular alkyl group transfer reactions are misleading at the second-order Møller−Plesset (MP2) level. In addition, we consider how the size of the alkyl group affects the energetics and mechanism of the intramolecular migration.

The influence of the inclusion of various catalysts and solvents in the quantum chemical calculations on the energetics and mechanism of the alkylation of naphthalene will be discussed in forthcoming papers.

Methods and Software Packages

For the semiempirical and ab initio quantum chemical calculations, the following packages were used: *Gaussian 98*,[5] *Gaussian 94*,[6] MOPAC 6.0,[7] and PcMol.[8] To determine the most stable conformers of molecules with conformational flexibility, methods (and the associated software) applied recently for aliphatic alkanes[9] were used. In this work, every molecule is represented by its most stable conformer. For drawing and analyzing molecular structures, the gOpenMol package[10] was applied.

The following notation is used to designate the ab initio quantum chemical computational results: HF: HF/6-31G*//HF/6-31G*, MP2H: MP2(full)/6-31G*//HF/6-31G*, MP2: MP2(full)/6-31G*//MP2(full)/6-31G*, MP2X: MP2(full)/6-311++G**//MP2(full)/6-31G*, and G2(MP2,SVP).[3c] Details concerning the methods and the basis sets applied are given in the literature.[11]

G2(MP2,SVP) energy calculations on MP2(full)/6-31G* optimized geometries approximate energies at the QCISD(T)/6-311+G(3df,2p) level. The evaluation of the G2(MP2,SVP) energy requires two calculations, QCISD(T)/6-31G* and MP2(FC)/6-311+G(3df,2p). For larger molecules (ca. 10−20 heavy atoms), these calculations use huge amounts of CPU time and require large hard disk capacities. For example, a QCISD(T)/6-31G* calculation on 1,2-dihydro-2-naphthyl cation ($C_{10}H_9^+$) on a CRAY C90 computer requires 3.26 GB of disk space and uses about 21 h of the CPU time.

Calculation of zero-point vibrational energy (ZPVE) corrections and thermochemical quantities was performed within the rigid rotor−harmonic oscillator (RRHO) approximation.[12] Scaled HF/6-31G*//HF/6-31G* harmonic vibrational frequencies were used in every case, exactly as in the Gaussian methods.[3a−d] Recently, the RRHO approximation was successfully applied for calculating various thermochemical quantities for aliphatic alkanes.[9,13]

It was found that the methods implemented in the Gaussian packages for locating a transition state without having a good initial guess for it failed in our cases. However, we could successfully apply the procedure[14] of Dewar et al. to generate trial geometries for unknown transition state complexes. With the help of the methods SADDLE and TS of the MOPAC package, the transition state geometries were first determined at the AM1,[15] MNDO,[16] and PM3[17] levels. It turned out that the PM3 transition states were usually close enough to the HF/STO-3G ones, therefore, the following route could be followed in determining the ab initio transition states: PM3 → HF/STO-3G → HF/3-21G → HF/6-31G* → MP2(full)/6-31G*. In each step, the optimized geometry of the previous one was used as an initial guess. However, in several cases the trial geometries were manually generated with the help of the PcMol package. The characterization of the stationary points obtained was performed by harmonic vibrational analysis. For every transition state, the local minima connected by the transition state in question were determined by an intrinsic reaction coordinate (IRC) calculation. Thus, it was always checked whether a transition state belongs to an assumed reaction or not.

For the transition states of the intermolecular alkyl group migrations, it is necessary to correct the total energies due to the well-known BSSE problem. As far as the intramolecular migrations are concerned, since the same finite basis set is used for the description of the local minima and for the transition states, these phenomena are free from BSSE problems. The original counterpoise (CP) method[18] of Boys and Bernardi can be used for a system consisting of two subunits. For example, the CP procedure is usually applied to determine the interaction energy of two weakly bonded molecules. However, the transition state of a bimolecular alkyl group transfer reaction consists of three subunits; therefore, the conventional CP method cannot handle this case without an appropriate modification.[19] A generalization of the CP scheme leads to a “19-point” formula to calculate the CP-corrected total energy of a three-body system.[19] Instead of performing an “a posteriori” correction, as in the CP method, the BSSE problem can be handled “a priori” using, for example, the chemical Hamiltonian approach (CHA) formalism.[20] A further very promising alternative to avoid the BSSE problem is the basis set extrapolation of the computational results.[21]

Calculations were performed on CRAY C90 and IBM SP2 mainframe computers as well as on IBM RISC/6000 and PC workstations.

Discussion

Electrophilic aromatic substitution reactions (alkylation, acylation, chlorination, nitration, etc.) are multistep processes involving various cationic intermediates: π- and σ-complexes (see Figure 1). Figure 1 shows one of the three Kekulé structures of the naphthalene molecule. According to its spin-coupled valence bond theoretical description,[22] this is the most stable and, therefore, the most probable Kekulé form of the molecule. Carbon atoms at the junction of the two rings are also numbered as opposed to the conventional numbering scheme. To avoid confusion, these carbon atoms are denoted by γ. Therefore, there are three carbon atoms in different positions with different reactivities in the ground state naphthalene molecule of D_{2h} symmetry: α, β and γ.

Experimental and computational results reveal that the rate-determining steps in the above multistep reaction are the formation and transformation of the σ-complexes.[23] The π-complexes are formed fast, since they require low activation energy. The calculation results reveal that the PES minima corresponding to the π-complexes are weak (flat minima), i.e., the structures are ill-defined. The σ-complexes can take part in further transformations as well. In the alkylation reactions, for instance, the alkylarenium ions may transform to each other via intra- or intermolecular alkyl group migrations. In the discussion to follow, the protonated forms of the naphthalene and monoalkylnaphthalene molecules, σ-complexes or arenium ions, will be named as the derivatives of the dihydronaphthalene molecule.

In general, electrophiles have fractional positive charges (the charge separation is not at all complete in an alkylating agent); however, the assumption of a whole unit positive charge can be accepted as a working hypothesis. Accordingly, MEP maps[24]

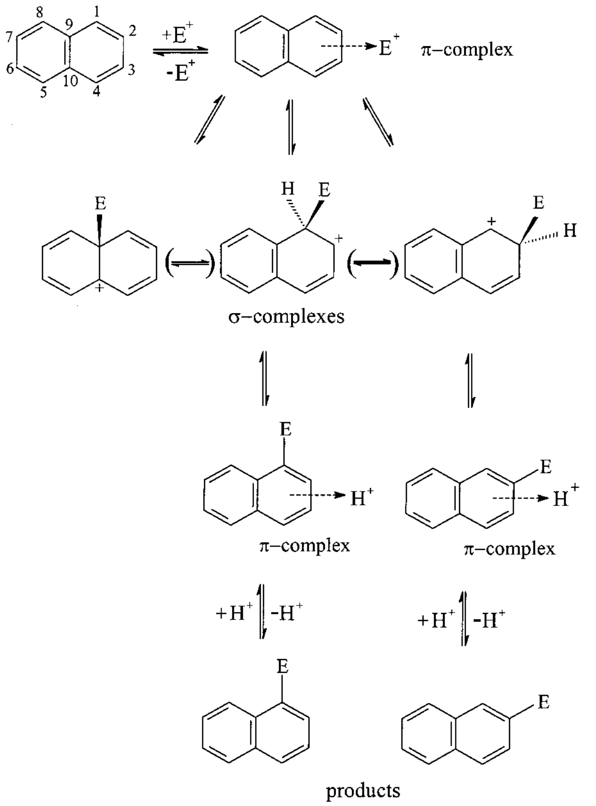

Figure 1. Scheme of the electrophilic substitution reactions of naphthalene. E: an electrophile.

may be of significant help in rationalizing and/or predicting initial (kinetically determined) regioselectivities. In a recent paper,[25] we have shown that a knowledge of all MEP local minima allows good predictions concerning the selectivity in the alkylation reactions of fused N-heteroaromatics. However, since MEP maps display static properties, i.e., they do not reflect polarization and steric effects, information deduced from them should be treated cautiously.

The MEP contour maps of naphthalene at the HF level are depicted in Figure 2. The planes considered are 1.5, 2.0 and 2.5 Å above the molecular plane. With the help of the HF and MP2 electron density functions, we have determined all of the MEP local minima of naphthalene. Calculations provided five minima above and five minima below the molecular plane obeying the D_{2h} symmetry of the molecule. Eight of them are close to the α and β positions (−83.39 kJ/mol at the HF level) and the remaining two weaker ones are located above and below the symmetry center of the molecule (−72.00 kJ/mol at the HF level). EP atomic charges can be derived from MEP maps generated outside the van der Waals surface of the molecule via constrained parameter estimation.[24] The ChelpG method in the Gaussian packages provided the following charges at the HF level on the carbon atoms in the naphthalene molecule: α: −0.294e, β: −0.068e, and γ: +0.222e. On the basis of the electrostatic properties of naphthalene, therefore, one may expect that an electrophilic attack is the most probable in position α and the least probable in position γ.

The model system applied for calculating MEP maps will come closer to reality if the unit positive probe charge is replaced by a point-like (unpolarizable) electrophile and the system is allowed to relax. The smallest agent like this is the proton. By placing protons at the MEP minima and allowing full geometry relaxations, three different naphthalenium ions can be obtained: 1,2-dihydro-2-naphthyl (NC1); 1,2-dihydro-1-naphthyl (NC2); and 9,10-dihydro-10-naphthyl (NC3) cations. Energy data for the naphthalene molecule and its protonated forms calculated at various levels are tabulated in Table 1. It is to be seen that the stability of the cations decreases in the following order: NC1 > NC2 ≫ NC3.

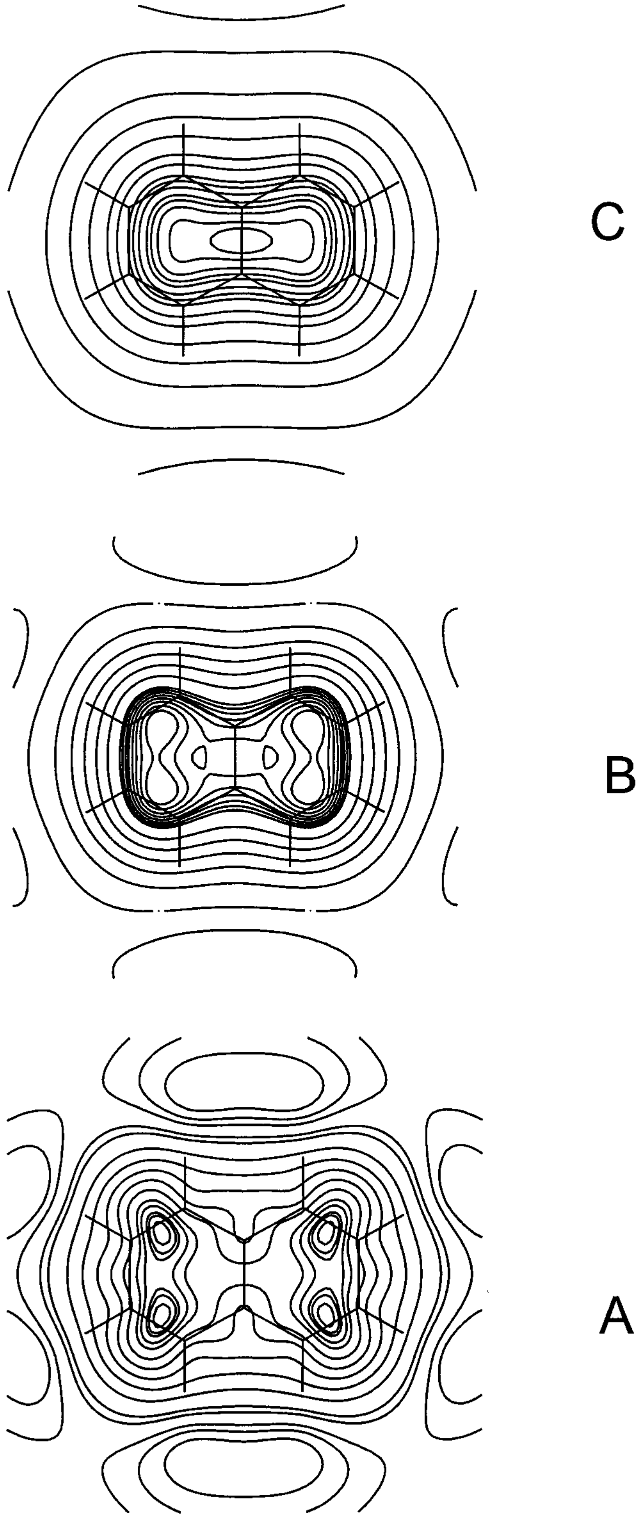

Figure 2. HF MEP contour maps of naphthalene above the molecular plane: A: 1.5, B: 2.0, and C: 2.5 Å.

The cations may transform to each other via 1,2-hydrogen (H) shifts. Energy data of the transition state complexes of 1,2-H shifts are also given in Table 1. The energy diagram of the intramolecular hydrogen migration in Figure 3 was prepared on the basis of Table 1. It is to be seen that the HF results are

TABLE 1: Total Energies (0 K) and ZPVE Corrections for Naphthalene, Its Various Protonated Forms, and for the Transition State Complexes Involved in the Intramolecular Hydrogen Migrations at Different Theoretical Levels (au)[a]

molecule	HF	MP2	G2(MP2,SVP)	ZPVE
naphthalene	−383.3550458	−384.6646049	−385.2733171	0.141219
NC1	−383.6903399	−384.9798548	−385.5864815	0.151695
NC2	−383.684328	−384.9737849	−385.5819629	0.15154
NC3	−383.652058	−384.948626	−385.557145	0.151033
TS(α-β)	−383.6534122	−384.9570482	−385.5640138	0.149094
TS(β-β')	−383.6383638	−384.9503797	−385.5556637	0.148725
TS(α-γ)	−383.6325842	−384.9433729	−385.5498406	0.148554

[a] NC1: 1,2-dihydro-2-naphthyl cation. NC2: 1,2-dihydro-1-naphthyl cation. NC3: 9,10-dihydro-10-naphthyl cation.

very different form those obtained at the MP2 and G2(MP2,SVP) levels; however, even they provide a qualitatively correct picture of the protonation of naphthalene. Activation energies calculated without taking into account electron correlation effects are generally too high. Figure 3 clearly reveals that the naphthalene molecule is protonated almost exclusively in position α under normal conditions. This conclusion coincides with that based on the MEP maps of naphthalene. Of course, the equilibrium composition of the mixture of the protonated forms can be accurately computed. If one assumes that the mixture in question is ideal and the naphthalenium ions can freely transform to each other, Boltzmann statistics will determine their fractions:[26]

$$x_i = \frac{\exp(-\Delta Gi^0/kT)}{\sum_j \exp(-\Delta Gi^0/kT)} \qquad (1)$$

TABLE 2: Standard Gas-Phase Proton Affinity (PA) and Absolute Basicity (B) of Naphthalene with Respect to Its Various Protonated Forms at Different Theoretical Levels (kJ/mol)[a]

	PA			B		
protonated forms	HF	MP2	G2-(MP2,SVP)	HF	MP2	G2-(MP2,SVP)
NC1	204.32 (99.81)	191.74 (99.82)	190.43 (99.09)	198.3	185.7	184.36
NC2	200.64 (0.19)	188.03 (0.18)	187.69 (0.91)	194.5	181.9	181.58
NC3	180.77 (0.00)	172.62 (0.00)	172.50 (0.00)	174.5	166.4	166.26

[a] The numbers in parentheses are the equilibrium fractions of the cations in their mixture under standard conditions.

where x_i is the fraction of cation i in the mixture and ΔG_i^0 is the difference between the Gibbs free energies of cation i and the reference cation (global minimum) at a given T temperature.

The standard gas-phase proton affinity[11a] (PA) and basicity (B) of naphthalene with respect to its different protonated forms are listed in Table 2. This table also shows in parentheses the fractions of the cations under standard conditions. It is to be seen that more than 99% of the population of the cations is α-protonated naphthalene at every theoretical level. On the basis of Tables 1 and 2, the gas-phase proton affinity and basicity of naphthalene can be estimated: HF: PA = 204.31, B = 198.24; MP2: PA = 191.73, B = 185.66, and G2(MP2,SVP): PA = 190.41, B = 184.33 kcal/mol. The MP2 and G2(MP2,SVP) results are in very good accordance with the experimental values: [27] PA = 191.9 and B = 186.28 kcal/mol.

Olah and Olah studied in detail the Lewis-acid-catalyzed (Friedel−Crafts) alkylation of naphthalene with alkyl halides

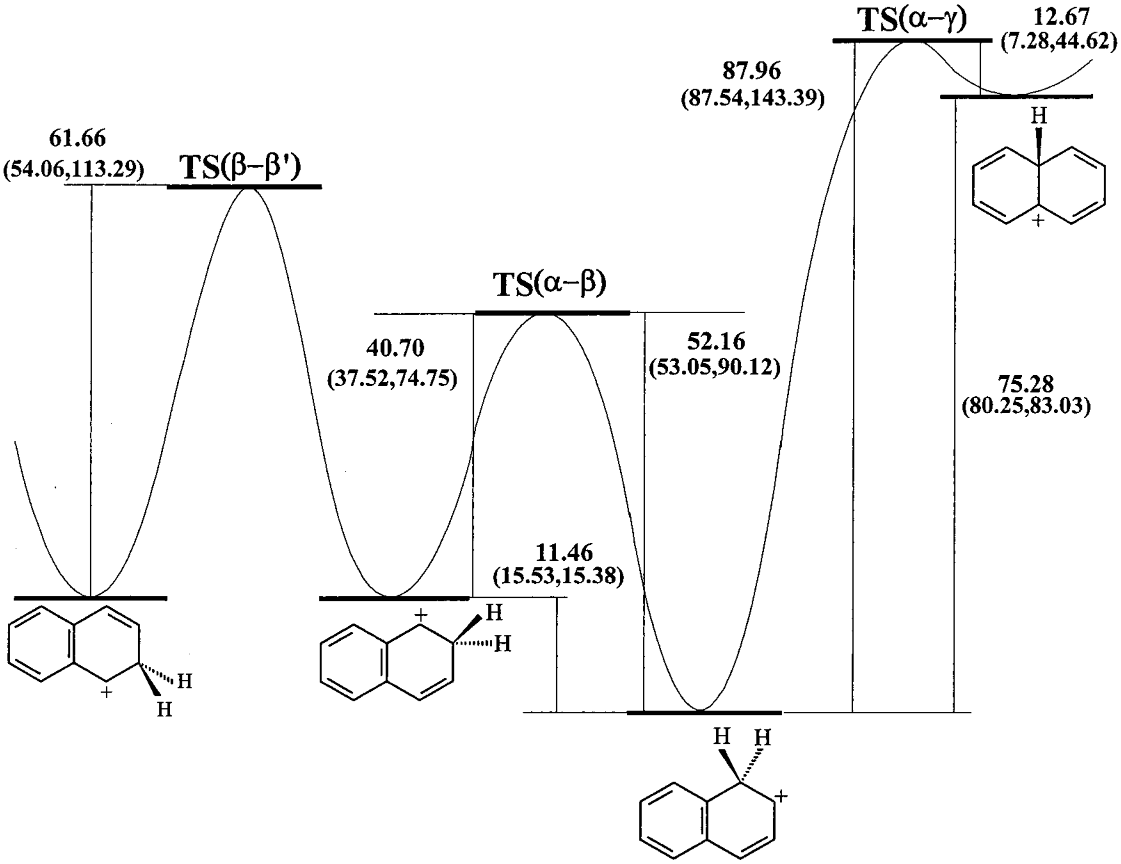

Figure 3. Energy diagram of the protonation of naphthalene at 0 K including ZPVE corrections. The numbers are relative energies in kJ/mol: G2(MP2,SVP) and (MP2,HF).

TABLE 3: Total Energies (0 K) and ZPVE Corrections for Various Monoalkylnaphthalene Molecules at Different Theoretical Levels (au)

	HF		MP2H		MP2		ZPVE	
alkyl group	α	β	α	β	α	β	α	β
methyl	−422.390844	−422.392841	−423.837898	−423.838451	−423.840533	−423.841071	0.1679	0.16747
ethyl	−461.423676	−461.427056	−463.008418	−463.009735	−463.01147	−463.012626	0.19535	0.19495
isopropyl	−500.454777	−500.460681	−502.179819	−502.183031	−502.183085	−502.186144	0.22239	0.22185
tert-butyl	−539.477181	−539.488921	−541.346114	−541.354763	−541.349666	−541.358117	0.24956	0.24881

TABLE 4: Total Energies (0 K) and ZPVE Corrections for the Methylnaphthalene Isomers at Correlated Theoretical Levels (au)

methyl group	MP2	MP2X	G2(MP2,SVP)	ZPVE
α	−423.840533	−424.216791	−424.5287786	0.167902
β	−423.841071	−424.216852	−424.5290119	0.167465

TABLE 5: Equilibrium Compositions of the Mixtures of Various Monoalkylnaphthalenes at Different Theoretical Levels (298.15 K, 1 atm)[a]

alkyl group	HF		MP2H		MP2		exp	
	α	β	α	β	α	β	α	β
methyl	4.38	95.62	17.45	82.55	17.66	82.34	24.5	75.5
ethyl	0.96	99.04	7.98	92.02	9.26	90.74	9.5	90.5
isopropyl	0.06	99.94	1.05	98.95	1.23	98.77	1.5	98.5
tert-butyl	0	100	0	100	0	100	0	100

[a] Experimental values are from ref 28.

TABLE 6: Equilibrium Composition of the Mixture of Methylnaphthalene Isomers at Different Theoretical Levels (298.15 K, 1 atm)

methyl group	MP2	MP2X	G2(MP2,SVP)	exp[4]	exp[28]
α	17.7	26.25	22.86	23	24.5
β	82.3	73.75	77.14	77	75.5

[a] Experimental values are from refs 4 and 28.

and the isomerization of various monoalkylnaphthalenes in homogeneous phase (nitromethane, CS_2).[28] If it is assumed that the relevant alkyl carbenium ion is the electrophile in the system,[29] the initial regioselectivity will result in the formation of α-alkylnaphthalene molecules on the basis of the electrostatic properties of naphthalene. Experimental results obtained in nitromethane solution, under conditions of minimal product isomerization, fully verify this conclusion (see Table 5 in ref 28).

Tables 3 and 4 contain energy data obtained at different theoretical levels for various monoalkylnaphthalenes. For the methylnaphthalene isomers, calculations were also performed at the MP2X and G2(MP2,SVP) levels. Tables 5 and 6 display the calculated and the experimentally determined equilibrium compositions of the mixtures of the monoalkylnaphthalene isomers. Equation 1 was used for the calculations assuming that the isomers in question can freely transform to each other. It is to be seen that the HF results are generally very different from the experimental values, consequently, dynamic electron correlation effects cannot be neglected.

As far as the methylnaphthalene isomers are concerned, by increasing the basis set size at the MP2 level, the quality of the calculation results is improved. Furthermore, the equilibrium fractions obtained at the G2(MP2,SVP) level precisely match the experimental values[4] of Suld and Stuart. Unfortunately, the application of this high level ab initio methodology is very expensive, therefore, it cannot routinely be used for large alkylnaphthalene molecules.

In general, the equilibrium compositions obtained at the MP2 level are in good agreement with the experimental results. It is to be seen that as the size of the alkyl substituent increases, the β-isomer becomes more and more stable than the α-isomer. For monoalkylnaphthalenes, thermodynamic regioselectivity means dominant formation of the β-isomers. It may be stated that while the α-position is the most reactive, the β-position is the most stable in the naphthalene molecule concerning electrophilic alkylation reactions. However, both the kinetic (initial) and the thermodynamic regioselectivites are rooted in energetic reasons. These two selectivities are different, because the stability order of the monoalkylnaphthalenium ions is just the opposite of that of the pure (neutral) hydrocarbons.

Table 7 contains the calculated energy data of various alkylnaphthalenium ions, which are involved in the alkyl group transfer reactions. It can be seen, for example, that while the β-methylnaphthalene molecule is more stable than the α-methylnaphthalene molecule, the stability order is just the opposite for the protonated forms, i.e., the 1-methyl-1,2-dihydro-2-naphthyl cation is more stable than the 2-methyl-1,2-dihydro-1-naphthyl cation. This holds true at the MP2 level for larger monoalkylnaphthalene molecules.

When the equilibrium compositions of the mixtures of the monoalkylnaphthalene isomers were computed, it was assumed that the isomers can freely transform to each other, i.e., the appropriate transition states are easily formed. If it is not so, e.g., the temperature is too low or there is not enough space for the formation of the transition state complex in question, then the kinetic regioselectivity will predominate in the alkylation. Even the solvent and the amount of the catalyst may cause significant alterations. The pure kinetic and pure thermodynamic regioselectivities are just limiting cases; between them a whole spectrum may occur depending on the actual system and the external conditions.

For the alkylnaphthalenium ions, the alkyl group migration may take place intramolecularly via 1,2-alkyl shifts as well as intermolecularly. While for the methyl- and ethylnaphthalenium ions the migration is assumed to be intramolecular, intermo-

TABLE 7: Total Energies (0 K) and ZPVE Corrections for Various Monoalkylnaphthalenium Ions at Different Theoretical Levels (au)[a]

	HF			MP2			ZPVE		
alkyl group	α	β	γ	α	β	γ	α	β	γ
methyl	−422.7252697	−422.7206729	−422.6848213	−424.1551718	−424.1489446	−424.1267857	0.179049	0.178774	0.178655
ethyl	−461.75994	−461.7556228		−463.3287631	−463.32222		0.206267	0.205941	
isopropyl	−500.7937325	−500.7900557		−502.5033644	−502.4971116		0.233098	0.232761	
tert-butyl	−539.8207375	−539.8216708		−541.6768935	−541.6723575		0.26019	0.259471	

[a] α: 1-alkyl-1,2-dihydro-2-naphthyl cation and β: 2-alkyl-1,2-dihydro-1-naphthyl cation.

TABLE 8: Total Energies (0 K) and ZPVE Corrections of Several Transition State Complexes Involved in Intramolecular Akyl Group Migrations in Monoalkylnaphthalenium Ions (au)[a]

alkyl group migration	HF	MP2	ZPVE
1,2-methyl (α−β)	−422.68508	−424.12957	0.17816
1,2-methyl (β−β')	−422.66265	−424.11295	0.17783
1,2-methyl (α−γ)	−422.65744	−424.10849	0.17739
1,2-ethyl (α−β)	−461.72232	−463.30766	0.20519
1,2-isopropyl (α−β)	−500.76134	−502.48472	0.23146

[a] α: 1-alkyl-1,2-dihydro-2-naphthyl cation and β: 2-alkyl-1,2-dihydro-1-naphthyl cation.

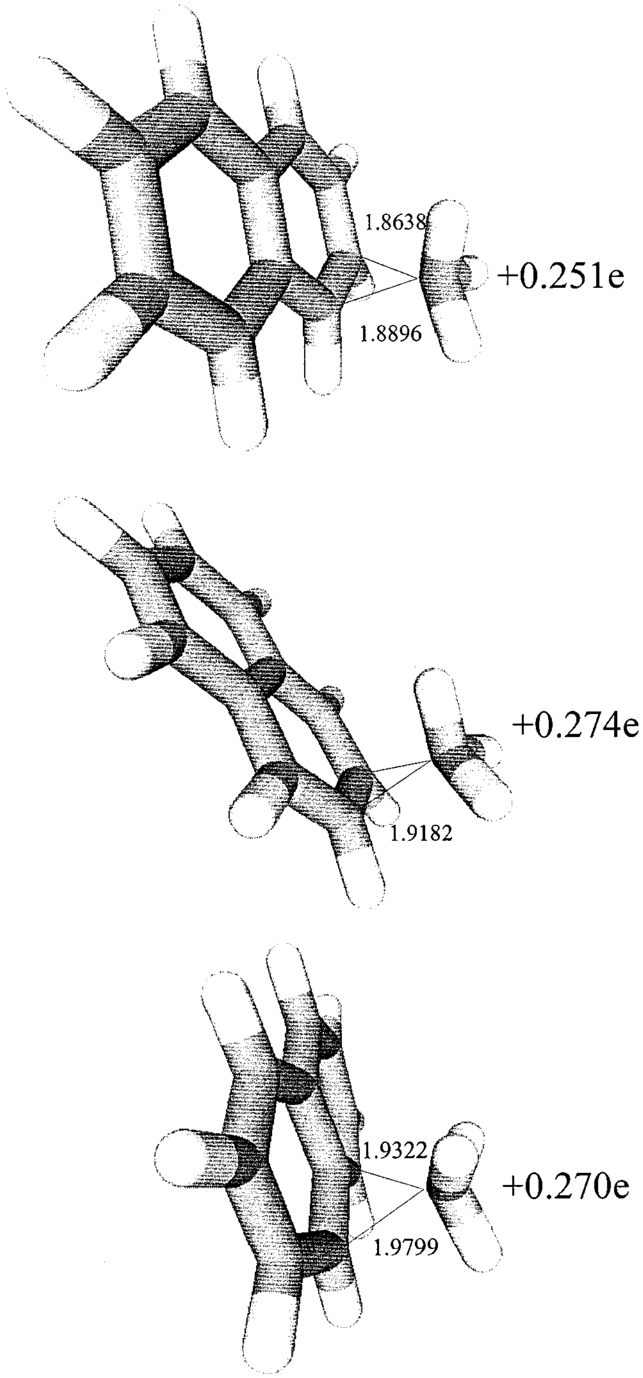

Figure 4. MP2 transition state geometries of the 1,2-methyl shifts. The interatomic distances are in Å.

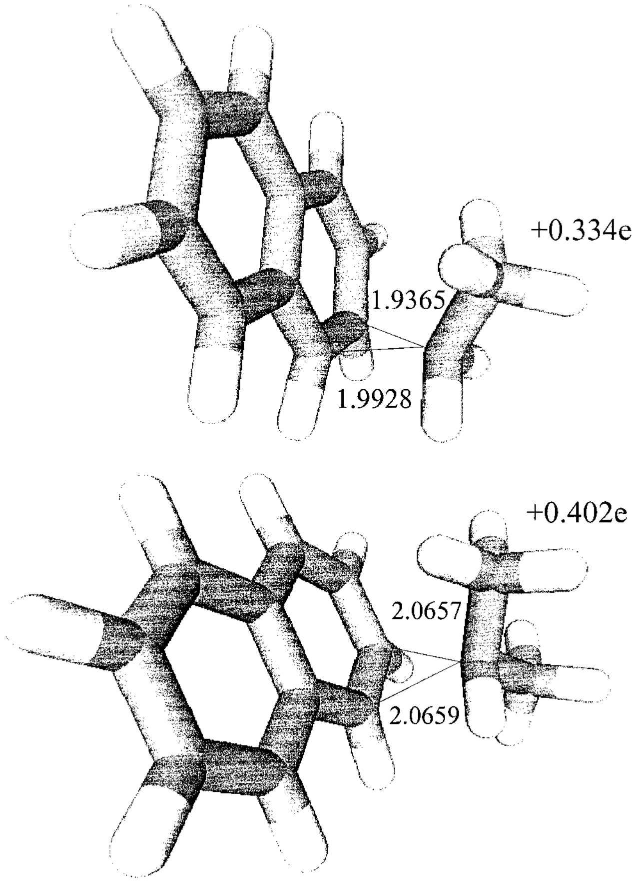

Figure 5. MP2 transition state geometries of the (α,β) 1,2-ethyl and (α,β) 1,2-isopropyl shifts. The interatomic distances are in Å.

lecular group transfers seem to be the most probable for the isopropyl- and *tert*-butylnaphthalenium ions.[28]

For the monoalkylnaphthalenium ions, we have determined all of the possible pathways of the intramolecular alkyl group migrations. Table 8 contains energy data for some transition state complexes. For the methyl group, all of them, for the ethyl and isopropyl groups only the most important ones are listed. It is noteworthy that, according to the calculation results, intramolecular migrations are possible for the isopropyl group. By contrast, despite all the efforts, for the *tert*-butyl group no transition states were found on the PES corresponding to intramolecular shifts. The *tert*-butyl group is too bulky to take part in an intramolecular transfer.

Figures 4 and 5 show the geometries of the transition state complexes listed in Table 8. For the calculation of the charges of the migrating alkyl groups, MP2 EP atomic charges produced by the ChelpG method were used. A detailed energy diagram can be constructed for the 1,2-methyl shifts on the basis of Tables 7 and 8 (see Figure 6).

Calculations reveal that the MP2 activation energies of the 1,2-alkyl shifts decrease with the increase in the size of the migrating alkyl group (α → β: methyl: 64.88, ethyl: 52.60, isopropyl: 44.63 and β → α: methyl: 49.25, ethyl: 36.27, isopropyl: 29.10 kJ/mol. This means that the isomerization reactions may be conducted at lower temperatures for larger alkyl groups if the 1,2-alkyl shifts are the rate-determining steps.

These results are in complete accordance with those of Olah and Olah concerning the isomerization reactions of monoalkylnaphthalenes in CS_2 solution (see Table 6 in ref 28). According to the isomerization experiments, the equilibrium was reached the fastest for *tert*-butylnaphthalene. However, the alkyl group transfer is intermolecular in this case.

As can be seen in Figure 6, the β → α and α → β 1,2-methyl shifts are much more favored energetically than the β → β' and α → γ shifts.

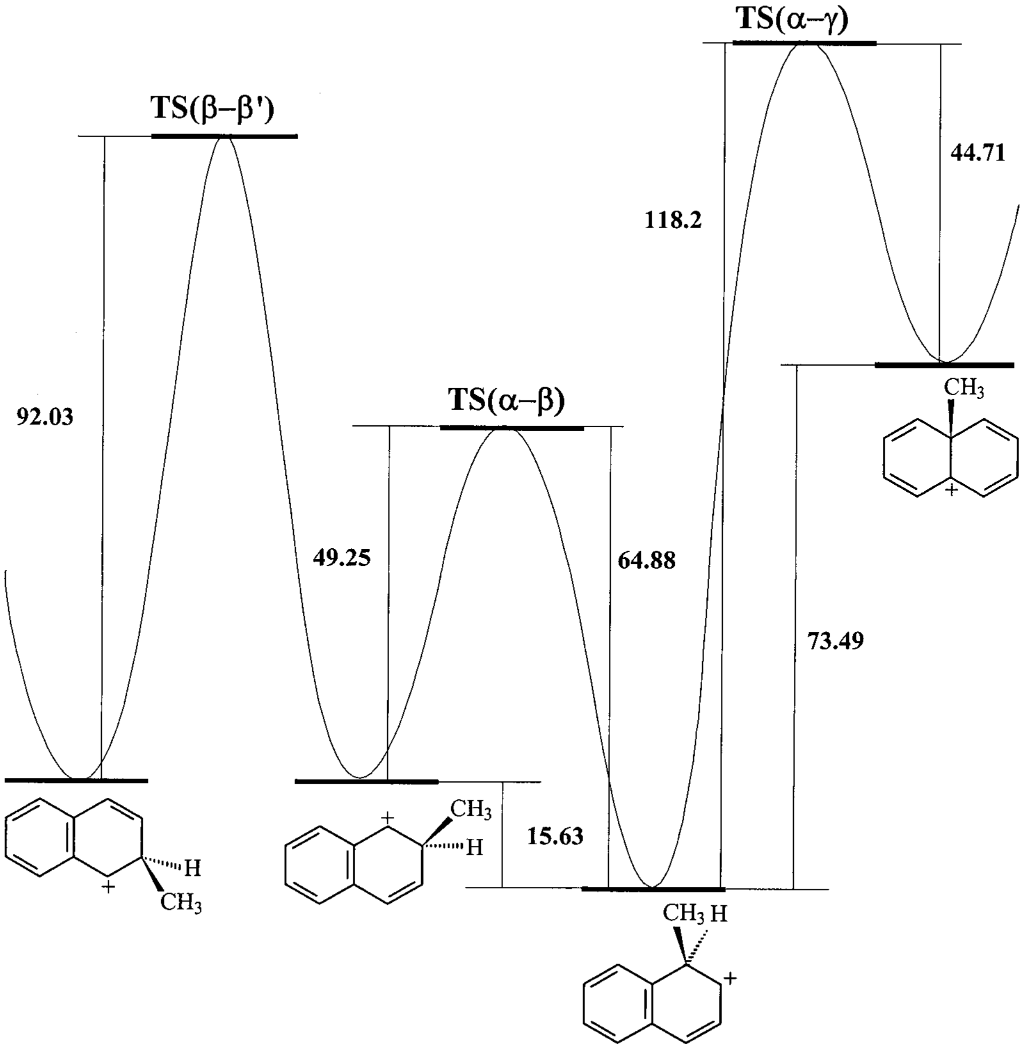

Figure 6. Energetics of the intramolecular methyl group migrations in the methylnaphthalenium ions (0 K, ZPVE corrections are included). The numbers are relative energies in kJ/mol obtained at the MP2 level.

TABLE 9: Energy Components for the Calculation of the CP-corrected Total Energy of the Transition State Complex in the Intermolecular (α,α′) Methyl Transfer Reaction (au)

energy components	HF	MP2
E_{ABC} (ABC)	−806.031548	−808.799123
E_{AB} (ABC)	−422.654636	−424.105171
E_{AB} (AB)	−422.653912	−424.101175
E_{AC} (ABC)	−766.709565	−769.338054
E_{AC} (AC)	−766.706988	−769.327671
E_{BC} (ABC)	−422.65425	−424.105579
E_{BC} (BC)	−422.653527	−424.101741
E_A (AB)	−383.355056	−384.666301
E_A (AC)	−383.353688	−384.662475
E_A (ABC)	−383.355093	−384.667424
E_A (A)	−383.353635	−384.661602
E_B (AB)	−39.2308954	−39.3308783
E_B (BC)	−39.2308949	−39.3309263
E_B (ABC)	−39.2313079	−39.3325558
E_B (B)	−39.2303395	−39.3292391
E_C (AC)	−383.353675	−384.662519
E_C (BC)	−383.355072	−384.666517
E_C (ABC)	−383.355112	−384.667633
E_C (C)	−383.353624	−384.661672

The energetics and mechanism of a bimolecular methyl transfer reaction were also investigated. Figure 7 depicts the transition state geometries obtained at the HF and MP2 levels for the intermolecular (α,α′) methyl group transfer. IRC calculations started from the transition state resulted in a naphthalene molecule and a 1,2-dihydro-1-methyl-2-naphthyl cation in both directions along the reaction coordinate.

The transition state complex consists of three subunits (A, B, and C) and the methyl group between the naphthalene rings is practically planar. It is to be seen that the transition structure obtained at the MP2 level is more compact than that obtained at the HF level: the constituents are closer to each other. The positive charge of the migrating methyl group shows that the extent of the electron donation to the methyl group is slightly larger if two naphthalene molecules participate in the constitution of the transition state complex (compare with Figure 4).

The BSSE-corrected (CP-corrected) total energy of the transition state complex can be calculated by the following, rather clumsy formula:[19]

$$E_{\mathrm{ABC}}^{\mathrm{CP}} = E_{\mathrm{ABC}}(\mathrm{ABC}) - E_{\mathrm{AB}}(\mathrm{ABC}) + E_{\mathrm{AB}}(\mathrm{AB}) - E_{\mathrm{AC}}(\mathrm{ABC}) + E_{\mathrm{AC}}(\mathrm{AC}) - E_{\mathrm{AB}}(\mathrm{ABC}) + E_{\mathrm{BC}}(\mathrm{BC}) - E_{\mathrm{A}}(\mathrm{AB}) - E_{\mathrm{A}}(\mathrm{AC}) + E_{\mathrm{A}}(\mathrm{ABC}) + E_{\mathrm{A}}(\mathrm{A}) - E_{\mathrm{B}}(\mathrm{BC}) + E_{\mathrm{BC}}(\mathrm{ABC}) + E_{\mathrm{B}}(\mathrm{B}) - E_{\mathrm{C}}(\mathrm{AC}) - E_{\mathrm{C}}(\mathrm{BC}) + E_{\mathrm{C}}(\mathrm{ABC}) + E_{\mathrm{C}}(\mathrm{C}) \quad (2)$$

where, for example, E_B(AB) is the total energy of the fragment B using the basis functions of the fragment AB. Values of the energy components in eq 2 are tabulated in Table 9 at the HF and MP2 levels. Table 10 shows the BSSE-corrected and

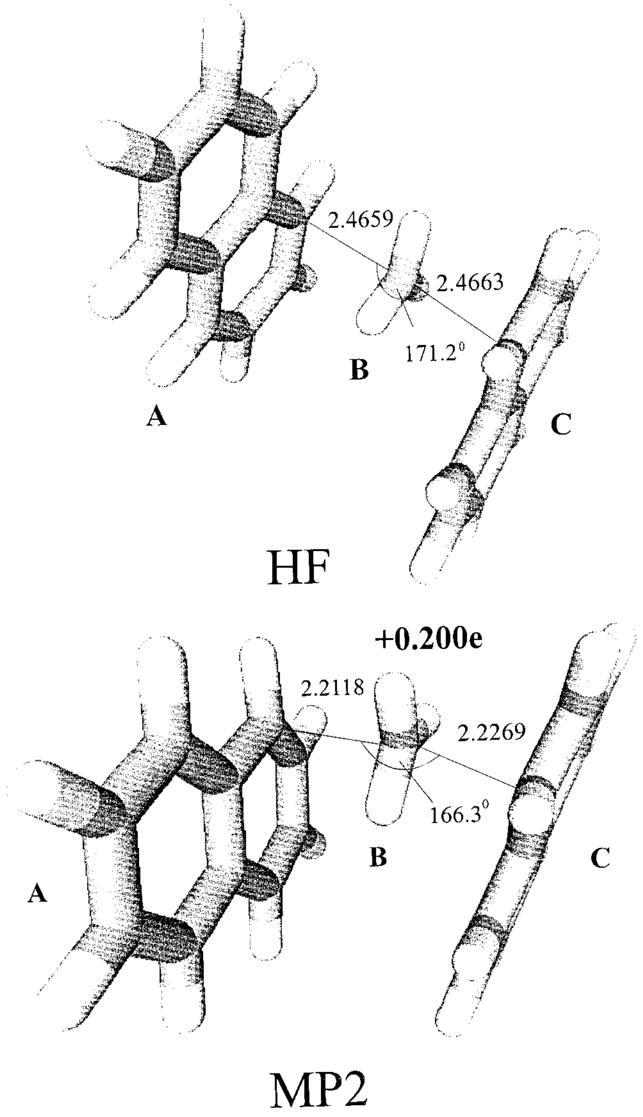

Figure 7. Geometry of the transitions state complex of the intermolecular (α,α′) methyl group transfer reaction at the HF and MP2 levels. A, B, and C denote the various subunits of the complex. The interatomic distances are in Å.

uncorrected total energies and the relevant activation energies. On calculating the activation energies, the reference system was the naphthalene molecule and the 1,2-dihydro-1-methyl-2-naphthyl cation being isolated from each other. The activation energy will only be increased if the formation of a pre-reaction complex is assumed.

It is noteworthy that the BSSE correction is much more important at the MP2 level than at the HF level. Due to the BSSE correction, the activation energy is increased by 46.49 and 11.02 kJ/mol at the MP2 and HF levels, respectively. The uncorrected MP2 activation energy is between those of the α → *β* and the *β* → α 1,2-methyl shifts. On this basis one may assume that the inter- and the intramolecular transfers are competitive reactions. However, the CP-corrected value unambiguously shows that the intramolecular methyl transfer is energetically much more favored than the intermolecular one.

From the energetic patterns of the 1,2-methyl shifts (Figure 6) and the intermolecular methyl group transfer (Table 10), one may assume that, for example, the dimethylnaphthalene (or other polymethylnaphthalene) isomers will belong to discrete equilibrium groups. Isomers from different groups do not transform to each other and transformations within a group are possible via the energetically favored α → *β* and *β* → α 1,2-methyl shifts under normal conditions. The situation of the 1,2-dimethylnaphthalene molecule is unique in this respect. Neither an α → *β* nor a *β* → α 1,2-methyl shift is possible in this case; thus, the molecule will be trapped from the point of view of positional isomerization. Experimental findings support the above reasoning: the dimethylnaphthalene isomers belong to four discrete equilibrium sets and the 1,2-dimethyl isomer is isolated from the others.[4] This coincidence also supports that the rate-determining step of the isomerization reactions is the rearrangement of the σ-complexes via 1,2-methyl shifts. Computational results concerning dimethylnaphthalenes and diisopropylnaphthalenes and their transformations will be published elsewhere.

Our calculation results reveal that it is very important to take the electron correlation effects into account with the proper handling of the BSSE problem in the theoretical investigation of the alkylation reactions of naphthalene. Recent calculations prove that both the CHA and CP schemes handle the BSSE problem correctly.[20]

Conclusion

The electrostatic properties of the naphthalene molecule were studied by means of MEP maps. Computations provided five-five MEP local minima above and below the plane of the molecule. The deepest minima are located in the vicinity of the α and *β* carbon atoms. The MEP maps and the EP atomic charges derived from them reveal that the α carbon atoms are the most probable sites for an electrophilic attack.

By placing protons at the MEP minima and allowing full geometry relaxations, we studied the protonation of the naphthalene molecule at different theoretical levels. Calculations at correlated levels reproduced the gas-phase proton affinity and basicity of naphthalene quite well.

Positional isomerizations of monoalkylnaphthalenes were investigated at the HF, MP2, and G2(MP2,SVP) levels. Generally, the thermodynamic equilibrium compositions obtained at correlated levels reproduce the experimental results correctly. For the methylnaphthalene isomers, the G2(MP2,SVP) data precisely match the experimental values.

According to the calculations, intramolecular migrations are possible for the methyl, ethyl, and isopropyl groups. In contrast, the bulky *tert*-butyl group transfers intermolecularly. In accordance with the experimental results, the activation energies of the 1,2-alkyl shifts decrease with the increase in the size of the alkyl group.

An intermolecular methyl group transfer between two naphthalene molecules is energetically much less favored than an

TABLE 10: BSSE-Corrected and Uncorrected Total Energies (0 K), Activation Energies (0 K), and ZPVE Corrections for the Transition State Complex of the Intermolecular (α,α′) Methlyl Group Transfer[a]

	total energy			activation energy	
method	uncorrected	CP-corrected	ZPVE	uncorrected	CP-corrected
HF	−806.0315476	−806.0273513	0.318938	124.55	135.57
MP2	−808.7991231	−808.7814157		50.73	97.22

[a] Total energies and ZPVE corrections are in au, activation energies in kJ/mol.

intramolecular one. However, the BSSE correction for the total energy of the transition state complex consisting of three subunits is of utmost importance at the MP2 level of theory.

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