Quantum Chemical Study of Solvent and Substituent Effects on the 1,5-Hydride Shift in 2,6-Dimethyl-2-heptyl Cations

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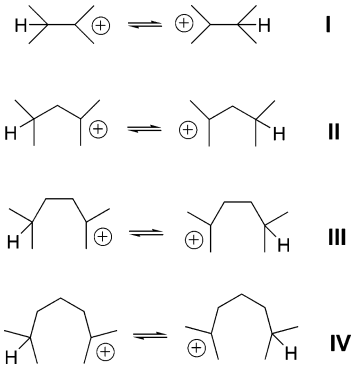
The mechanism of the degenerate 1,5-hydride shift in 2,6-dimethyl-2-heptyl cations has been investigated using ab initio MP2 and density functional theory (DFT) hybrid (B3LYP) calculations. The potential-energy profile for the 1,5-hydride shift consists of three minima corresponding to two equivalent acyclic carbocations and one symmetrically μ-hydrido-bridged carbocation, while two equivalent unsymmetrically hydrido-bridged carbocations were located as transition-state structures. The calculated relative energy differences between acyclic carbocations and symmetrically μ-hydrido-bridged structure are significantly affected by introduction of alkyl and $(CH_2)_n$-substituents at the C_4 position of the 2,6-dimethyl-2-heptyl cation structure. DFT self-consistent isodensity polarizable continuum method (SCI-PCM) and MP2 PCM continuum methods have been used to calculate the effect of solvation on geometries and relative energies of the species involved in the 1,5-hydride shift. It is found that relative energies of acyclic and μ-hydrido-bridged carbocation structures as well as the energy barriers for 1,5-hydride shifts are in accord with experimental data if solvation effects are taken into account.

Introduction

Carbocations are well-established reactive intermediates in chemical and biochemical reactions. The study of carbocation rearrangement reactions has led to a deeper understanding of many fundamental chemical principles including chemical structure and bonding, transition states, and reaction barriers. Various aliphatic carbocations often have a flat potential energy surfaces and are prone to undergo fast degenerate hydride shifts to distant carbons.[1] Hydride shifts in carbocation intermediates are an important propagation step in the biogenetic formation of terpenes and steroids. 1,2-, 1,3-, and 1,4-hydride shifts, **I**, **II**, and **III**, in acyclic tertiary carbocations (Scheme 1) have been described both experimentally[2] and by quantum chemical methods.[3] The potential-energy profiles for the degenerate hydride shifts **I**−**III** have two symmetric global minima potential wells, which correspond to the two interchanging acyclic carbocation structures and a higher energy local minimum for a symmetrically μ-hydrido-bridged carbocation. Transition-state structures for the hydride shifts **I**−**III** are unsymmetrical, μ-hydrido-bridged carbocation structures. The calculated energy barrier values for these hydride shifts increase with increasing size of the ring formed in the bridged transition structures (**I**, 3.9; **II**, 4.2; **III**, 7.5 kcal/mol at MP4/6-311G-(d,p)//MP2/6-311G(d,p) level).[3] This sequence is in line with experimental data obtained form NMR spectroscopic measurements in SbF_5/SO_2ClF solution (**I**, 3.1; **II**, 8.5; **III**, 12 kcal/mol).[2c]

The experimentally determined energy barriers for 1,5-hydride shifts in 2,6-dimethyl-2-heptyl cation **1** ($\Delta G^{\ddagger} = 5.0 \pm 0.5$ kcal/mol)[4] and the 1,6-hydride shift in 2,7-dimethyl-2-octyl cation

SCHEME 1



($\Delta G^{\ddagger} = 8.0 \pm 0.9$ kcal/mol)[5] are significantly lower compared to those for 1,3- and 1,4-hydride shifts. This was attributed either to a presumably linear transitions state[1b] and/or in part to less strain in the six- and seven-membered-ring μ-H-bridged transition state structures. To explore 1,5-hydride shifts in carbocations in some more detail, we have performed a quantum chemical study of the influence of solvent and substituents on structures and reaction barriers in 4-substituted 2,6-dimethyl-2-heptyl cations (Scheme 2).

Computational Methods

The quantum chemical calculations were performed using the Gaussian98 and Gaussian03 suites of programs.[6] All structures were fully optimized using both density functional theory (DFT) hybrid methods with the B3LYP[7] functional and MP2 (Møller−Plesset) perturbation theory.[8] The standard split valence and polarized 6-31G(d) basis set was used for geometry optimizations and frequency calculations. Optimized coordinates of all structures are included in the Supporting Information. Analytical vibrational analysis at the same level were performed to

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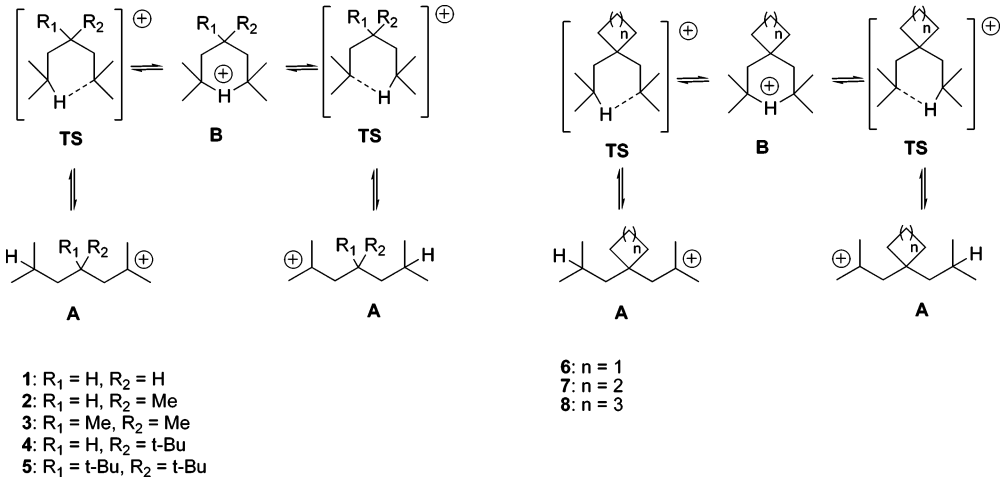
SCHEME 2



determine the zero-point vibrational energy (ZPE) and to characterize each stationary point as a minimum or first-order saddle point. Corrections for ZPE (not scaled) are included in the calculated energies. For carbocations **1** and **3**, where detailed experimental data are available, geometries were also calculated using B3LYP and MP2 methods and the 6-311G(d,p) basis set (see Supporting Information). Extra valence functions and polarization functions as in the 6-311G(d,p) basis set allow a somewhat better modeling of systems with hypercoordinated hydrogens involved in three-center two-electron C−H−C bonds.[3]

Geometry optimization and frequency calculations in the presence of solvent were carried out for all carbocations at the B3LYP/6-31G(d) level. The solvent effects were calculated using the self-consistent reaction field (SCRF) method based on the self-consistent isodensity polarizable continuum method (SCI-PCM),[9] which employs a higher-order cavity whose volume and shape are iteratively computed from the electron density. This method has been proposed as a general-purpose way of calculation the solvent effect on chemical equilibria and reactions.[10] The default value of 0.0004 was used for the isodensity surface, 974 points were used in the special grid option, and surface integrals were evaluated using the single center procedure.[11] The solvent relative permittivity of $\epsilon = 30.0$ was used. It has been suggested[12] that an excess of the strong Lewis acid SbF_5 in SO_2ClF (the solvent mixture used in experiments) would create a more polar medium than that of the pure SO_2Cl_2 ($\epsilon = 9.1$).[13]

Numerical frequencies were calculated for each structure at the B3LYP/6-31G(d) SCI-PCM level, confirming that structures were minima or first-order saddle points.

MP2/6-311G(d,p) single-point energy calculations with a polarized continuum (overlapping spheres) model (SCRF PCM)[14] were performed for MP2/6-31G(d)-optimized geometries (solvent relative permittivity ϵ =30.0).

Results and Discussion

The results of the quantum chemical calculations for the structures involved in the 1,5-hydride shift in 2,6-dimethyl-2-heptyl cations **1**−**8** are in general similar and resemble those for 1,2-, 1,3-, and 1,4-hydride shifts.[3,15]

The reaction profile for the 2,6-dimethyl-2-heptyl cation **1** for example has three potential wells that correspond to two equivalent carbocation structures **1A** and a symmetrical μ-hydrido-bridged structure **1B** and two maxima which correspond to two equivalent unsymmetrically μ-hydrido-bridged transition state structures **1TS** (Scheme 2). The μ-hydrido-bridged structure **1B** has a regular chair conformation with C_s symmetry and shows symmetrical C−H−C bridging with long C−H bonds (1.262 Å) and a bond angle C_2−H−C_6 of 156.4° (MP2/6-311G-(d)) (Figure 1). In the transition structure **1TS** this symmetry is considerably perturbed (C_2−H bond, 1.103 Å; C_6−H distance, 3.308 Å (MP2/6-311G(d))) (Figure 1). The only imaginary vibrational frequency mode (−58 cm^{-1}) of **1TS** is associated with the movement of the bridging hydrogen atom between the C_2 and C_6 carbon atoms. This low imaginary frequency indicates a rather flat potential energy surface.

Two different isomeric structures of type **A** were located (Figure 1): one isomer with C−C hyperconjugation between the C_3C_4 σ-bond and the formally vacant 2p orbital at the C_2 carbon (**1A**) and another with C−H hyperconjugation between one of the C_3−H hydrogen σ-bonds and the formally vacant 2p orbital at the C_2 carbon (**1A$_{CH}$**). Analogous C−H hyperconjugative isomers were not located for smaller alkyl cations undergoing 1,2-, 1,3-, or 1,4-hydride shifts but converged on geometry optimizations to the more stable C−C hyperconjugative isomers.[3] The hyperconjugative interaction in the isomer **1A** is accompanied by a relative lengthening of the C_3C_4 bond to 1.639 Å and a reduced $C_2C_3C_4$ bond angle of 84.1° (MP2/6-311G(d,p)). The C_3−H hydrogen bond involved in hyperconjugation in the isomer **1A$_{CH}$** shows an extended bond length of 1.119 Å and a small C_2C_3H bond angle of 98.5 °.

Solvent Effects. The relative energy differences and the structural parameters of **1**−**8**, **A**, **B**, and **TS** are very dependent on solvent and substituent effects. To estimate the effect of solvation[16] on the relative energies for the structures **A**, **B**, and **TS**, SCRF single-point MP2/6-311G(d,p) calculations with a PCM[14] were performed. Since geometry optimization including the effect of the medium is not available at this level of theory, the SCRF method at B3LYP/6-31(d) level using a SCI-PCM was applied for geometry optimizations. Substituent effects of various alkyl and $(CH_2)_n$ substituents at the C_4 position of cations **2**−**8** are reported in the subsequent section (Scheme 2).

The quantum chemical calculations for the gas-phase structures of **1A** and **1B** (Table 1) show that the μ-hydrido-bridged cation **1B** is 0.7 (B3LYP/6-31G(d)) and 7.4 kcal/mol (MP2/6-311G(d,p)//MP2/6-31G(d)) more stable than the acyclic isomer **1A** (Table 1).

The calculated order of relative energies is not in accord with the experimental observations of kinetic line broadening[2c,17,18,19] and equilibrium isotope effects (EIE) in ^{1}H and ^{13}C NMR spectra of cation **1**,[18,19] which show that the equilibrating acyclic

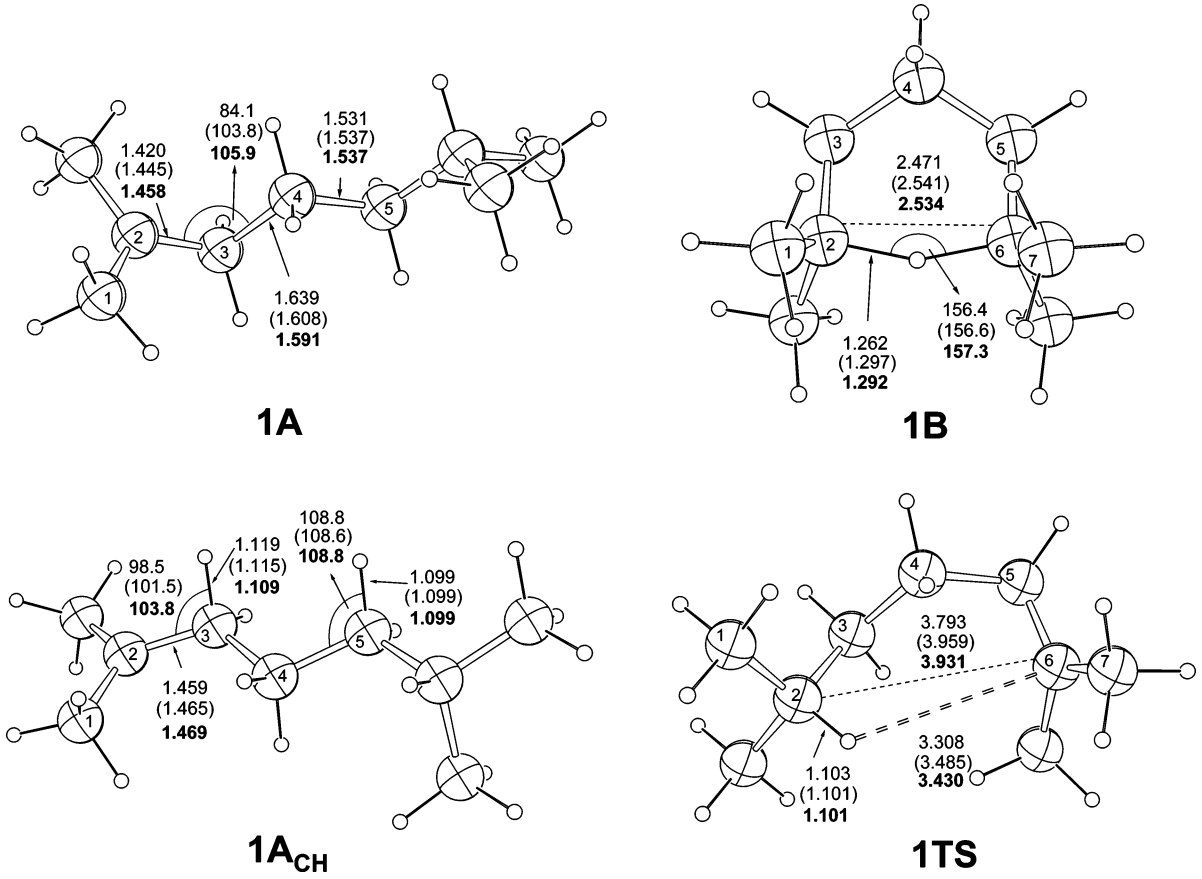


Figure 1. MP2/6-311G(d,p)-optimized geometries of **1A**, **1A$_{CH}$**, **1B**, and **1TS** (B3LYP/6-311G(d,p) values in parentheses and values obtained by B3LYP/6-31G(d) SCI-PCM reaction field model are presented in bold). Distances are in angstroms, and bond angles are in degrees.

TABLE 1: Calculated Relative Energy Differences (with ZPE Corrections) for Carbocation Stuctures 1−8

cation	B3LYP/6-31G(d) (ΔE (kcal))	SCI-PCM B3LYP/6-31G(d), $\epsilon = 30.0$ (ΔE (kcal))	MP2/6-311G(d,p)[a] (ΔE (kcal))	PCM MP2/6-311G(d,p),[a] $\epsilon = 30.0$ (ΔE (kcal))
1A	0	0	0	0
1A$_{CH}$	2.51	0.58	2.69	1.20
1B	−0.71	3.46	−7.44	2.01
1TS	4.75	4.8	3.95	6.90
2A	0	0	0	0
2B	−2.81	0.64	−8.82	1.27
2TS	2.71	4.18	1.99	2.72
3A	0	0	0	0
3B	−1.92	1.11	−8.27	1.10
3TS	4.38	4.67	4.12	4.62
4A	0	0	0	0
4B	−4.49	−2.82	−11.62	−8.02
4TS	2.38	5.55	2.40	3.60
5A	0	0	0	0
5B	−3.69	−1.58	−9.07	−5.80
5TS	8.71	8.75	9.67	9.13
6A	0	0	0	0
6B	−5.22	−2.40	−10.92	−7.03
6TS	2.87	3.03	2.90	3.98
7A	0	0	0	0
7B	−3.08	−0.36	−8.89	−5.89
7TS	3.88	4.31	3.80	4.15
8A	0	0	0	0
8B	−2.25	−0.78	−7.96	−5.42
8TS	4.93	4.20	4.84	5.45

[a] Single-point energy calculations on MP2/6-31G(d) geometries (ZPE corrections from MP2/6-31G(d) frequency calculations are included).

carbocation structure **1A** is preferred in SbF_5/SO_2ClF solution.[20] Likewise the equilibrating acyclic 4,4-dimethyl-substituted 2,6-dimethyl-2-heptyl cation structure **3A** is found experimentally in solution,[4,18] whereas quantum chemical calculations for the gas phase prefer the μ-hydrido bridged structure **3B** by 1.9 kcal/mol (B3LYP/6-31G(d)) and 8.3 kcal/mol (MP2/6-311G(d,p)//MP2/6-31G(d)). This disagreement between calculated gas phase structures and experimentally determined structures in solution was not observed for carbocations undergoing 1,2-, 1,3-, or 1,4-hydride shifts.[3] Apparently calculations of gas-phase structures

are not sufficient to correctly describe the 1,5-hydride shift carbocation system in solution. Inclusion of entropy corrections from vibrational analysis at the MP2/6-31G(d) level (at 198 K: S_{tot} in cal/(mol K) for **1A** = 112, **1B** = 99, **3A** = 120, **3B** = 112) favors the acyclic conformer **1A** but does not alter the trends provided by using only electronic energies.

Single-point energy SCRF calculations using the PCM model for the carbocation isomers **A** and **B** assuming a solvent with relative permittivity $\epsilon = 30.0$ show the open-chain carbocation **1A** to be 2.0 kcal/mol (MP2/6-311G(d,p)//MP2/6-31G(d)) more stable than the μ-hydrido bridged isomer **1B** (Table 1). This is in accord with the experimental observation of **1A** undergoing fast 1,5-hydride shift in solution.

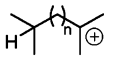
The transition structure **1TS** is calculated 6.9 kcal/mol (PCM MP2/6-311G(d,p)//MP2/6-31G(d)) less stable than cation **1A**. This energy difference corresponds to the barrier for the 1,5-hydride shift of **1A** and is in reasonable agreement with $\Delta G^{\ddagger}$ of ca. 5 kcal/mol estimated experimentally. Similarly, the results of solvent model calculations for cations **3A** and **3B** and the transition structure **3TS** show the preference of structure **3A** and an energy barrier in accord with experiment (Table 1).

The same trends for **1** and **3** are obtained for continuum-based SCI-PCM B3LYP/6-31G(d) geometry optimizations. For example, in a medium of $\epsilon = 30.0$, cation **1A** has a larger stabilization energy (3.5 kcal/mol) than the cation **1B** (Table 1). The energy barrier for the 1,5-hydride shift in **1** of 4.8 kcal/mol (SCI-PCM B3LYP/6-31G(d)) is in fair agreement with the experimental barrier.[18,19] The differential stabilization effect is more pronounced in more polar media. For $\epsilon = 78.0$; the acyclic isomer **1A** is 6.9 kcal/mol more stable than the μ-hydrido-bridged isomer **1B**.

The agreement between the experimental data with both the PCM-MP2/6-311G(d,p)//MP2/6-31G(d) (single-point energy calculation), and SCI-PCM B3LYP/6-31G(d) (geometry optimization) solvation models gives credence to these methods applied to this type of carbocations.[21] These results indicate that solvation effects could change the potential energy surface relative to that of the gas phase. We attribute this to the difference in dipole moment between the acyclic isomers **A** and the μ-hydrido-bridged structures **B**. For the 2,6-dimethyl-2-heptyl cation the dipole moment calculated for the symmetrical bridged structure **1B** is rather small (0.4 D) due to its symmetrical structure, whereas the dipole moment for the acyclic isomer **1A** is more than an order of magnitude larger (11.5 D). Consequently, solvation in a polar solvent has a substantial effect on the relative energies of both isomers.[22] Similar effects were reported for a sila analogue of cation **1** with a symmetrical Si−H−Si bridge.[23] While many experimental solution-phase structures of carbocations appear to be well described by gas-phase calculations,[12,24] recent studies have reported differential solvation in some isomeric carbocation systems[25] solvation effects on closely balanced equilibria of carbocations[26] and on the rate of reorientation of carbocations in solution.[27] A combination of solvent continuum models and explicit solvent molecules is expected to be even more accurate than a continuum model alone.[28]

SCI-PCM B3LYP/6-31G(d) calculated differential solvation energies for acyclic and μ-hydrido-bridged carbocation structures involved in 1,2-, 1,3-, and 1,4-hydride are small and only slightly increase with increasing number of carbon atoms (Table 2). This parallels the increasing difference in dipole moments calculated for the acyclic and bridged structures **A** and **B** (Table 2). The order of relative energy differences between acyclic and μ-hydrido-bridged structures of this smaller carbocations however is not changed compared to the gas phase.

TABLE 2: Dipole Moments and Relative Energy Differences for the Open-Chain and the Cyclic Carbocations Involved in 1,2-, 1,3-, 1,4-, and 1,5-Hydride Shifts, Calculated at the B3LYP/6-31G(d) Level and by the SCRF Method Using SCI-PCM B3LYP/6-31G(d) Model (ϵ =30.0) (Bold)

		 **A**	 **B**
$n = 0$	ΔE	0	7.58
	(kcal/mol)	**0**	**7.83**
	μ (Debye)	2.04	0.31
$n = 1$	ΔE	0	11.35
	(kcal/mol)	**0**	**12.61**
	μ (Debye)	3.79	0.03
$n = 2$	ΔE	0	10.52
	(kcal/mol)	**0**	**13.35**
	μ (Debye)	5.92	0.21
$n = 3$	ΔE	0	-0.71
	(kcal/mol)	**0**	**3.46**
	μ (Debye)	11.50	0.40

Solvation modeling (SCI-PCM B3LYP/6-31(d)) has small but noticeable effects on the calculated geometries. The calculated changes between gas phase and solution for structures **1A**, **1B**, and **1TS** are given in Figure 1. The structural changes accompanying hyperconjugation in **1A** and $\mathbf{1A_{CH}}$ are somewhat smaller in a model solvent (Figure 1). For **1A** the C_3-C_4 bond involved in β-CC hyperconjugation with the formally vacant 2p orbital at C_2 is slightly shortened (1.59 Å) compared to the gas-phase structure (1.61 Å) and the corresponding $C_2-C_3-C_4$ bond angle is slightly enlarged (105.9 vs 103.4°). Small changes are calculated for the transition structure **1TS**. The distance between C_2 and C_6 in **1TS** is shortened by 0.03 Å, and the corresponding bond angle C_2HC_6 is increased by 2°. The energy barriers for 1,5-hydride shifts in carbocations **1**−**8** are somewhat higher that in the gas phase (Table 1 and Figure 1). This is comparable to calculations reported for hydride transfers from alkanes to carbocations in the gas phase and in a solvent model.[29]

Substituent Effects. Experimental data from dynamic NMR spectroscopy and measurement of deuterium EIE[18] indicate that the relative energy difference between the acyclic (**A**) and the bridged isomers (**B**) of carbocations undergoing a 1,5-hydride shift is susceptible to substituent effects. The energy barrier for the 1,5-hydride shift in the 4,4-dimethyl-substituted 2,6-dimethyl-heptyl cation (**3**) (4.6 kcal/mol) is calculated to be somewhat lower compared to the parent cation **1** (6.9 kcal/mol; PCM MP2/6-311G(d,p)//MP2/6-31G(d) (Table 1). For the 4-penta-methylene-substituted 2,6-dimethyl-2-heptyl cation **8** (Scheme 2), experimental deuterium EIE indicate a slight preference for the symmetrically μ-hydrido-bridged form **8B** over the acyclic structure **8A**,[30] which is calculated to be 5.4 kcal/mol (PCM MP2/6-311G(d,p)//MP2/6-31G(d). Sorensen and Sun[17] reported that μ-hydrido-bridged structures **10** (R = H, CH_3) are favored over the acyclic isomers **9** (R = H, CH_3) in the 1,5-hydride shift equilibria of 2,6-dimethyl-4-isobutylheptane-2,6-diyl dication (**9,** R = H) and 2,4,6-trimethyl-4-isobutylheptane-2,6-diyl dication (**9,** R = CH) (Scheme 3).

The effect of various alkyl and $(CH_2)_n$-substitution at C_4 on the 1,5-hydride shift in 2,6-dimethyl-heptyl cations **2**−**8** (Scheme

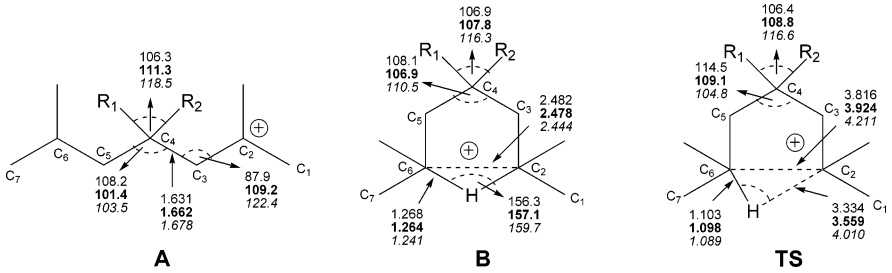
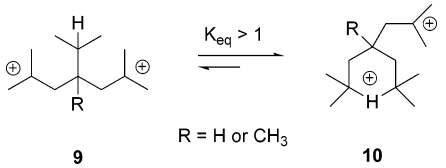


Figure 2. Selected geometrical parameters for the carbocation **1** ($R_1 = R_2 = H$) calculated at the MP2/6-31G(d) level. Optimized values for the C_4-dialkyl-substituted carbocations **3** ($R_1 = R_2 =$ Me) and **5** ($R_1 = R_2 =$ *t*-Bu) are presented in bold and italics, respectively.

SCHEME 3



2) was studied by gas-phase and solvent model calculations. The relative energy differences between acyclic structures of type **A** and μ-hydrido bridged structures of type **B** changes with increasing size of the C_4 substituents favoring the symmetrically μ-hydrido-bridged structure type **B** (Table 1). For the parent 2,6-dimethyl-2-heptyl cation (**1**), the μ-hydrido-bridged structure **1B** is calculated 2.0 kcal/mol less stable, while for the C_4-di-*tert*-butyl substituted cation **5** the bridged structure **5B** is 5.8 kcal/mol (PCM MP2/6-311G(d,p)//MP2/6-31G(d) more stable than the **5A**. The relative preference of the bridged form in structures with bulky alkyl group at the C_4 position is consistent with the Thorpe−Ingold effect or *gem*-dialkyl effect.[31] The effect of one or two alkyl group is nonadditive (see Table 1).

The introduction of C_4-alkyl substituents in cations **2**−**5** has distinct effects on the structural parameters. In the acyclic structures of type **A** steric repulsive interaction of two C_4-substituents causes an increase of the $R_1-C_4-R_2$ bond angle (106.3° in **1A**, 111.3° in **3A**, 118.5° in **5A**) and a decrease of the corresponding $C_3-C_4-C_5$ bond angle (Figure 2). The repulsion of the C_4 substituents could reduce β-CC-hyperconjugation and disfavor the acyclic conformation. The $C_2-C_3-C_4$ bond angle of the hyperconjugative three-center two-electron moiety is 87.9° in structure **1A** and is enlarged to 109.2° and 122.4° in **3A** and **5A.** On the other hand, alkyl substituents should stabilize the partial positive charge at C4, thus enhancing β-CC hyperconjugative charge delocalization.

Successive introduction of alkyl groups at C_4 favors the μ-hydrido C_2-H-C_6 bridging. The bridging CH bonds become shorter (1.268 Å in **1B**, 1.241 Å in **5B**), the distance between the C_2 and C_6 carbon atoms decreases (2.482 Å in **1B**, 2.444 Å in **5B**), and the corresponding C_2-H-C_6 bond angle slightly increases (156.3° in **1B**, 159.7° in **5B**) with bulkier substituents (Figure 2). All structures of type **B** adopt a regular chair conformation, except **5B**, which has a twisted conformation due to two bulky *tert*-butyl substituents.

Substitution at C_4 also changes the geometrical parameters of transition-state structures **TS** (Figure 2). The distance between C_2 and C_6 is 3.816 Å in **1TS** (R_1, $R_2 = H$) and increases to 4.211 Å in **5TS** (R_1, $R_2 =$ *t*-Bu). The changes of the energy profile (**A**−**TS**−**B**−**TS**−**A**) for the 1,5-hydride shift with C_4-alkyl substituents (H, Me, *t*-Bu) are schematically depicted in Figure 3. The energy difference between **A** and the transition state structure **TS** decreases with the introduction of two methyl groups at C_4. (**1**, 6.9 kcal/mol; **3**, 4.6 kcal/mol; PCM-MP2/6-311G(d,p)//MP2/6-31G(d)). Introduction of two *tert*-butyl groups at C_4, however, increases the relative energy of the transition state structure **5TS** (Table 1 and Figure 3). This is not consistent with the normal Thorpe−Ingold effect. It is likely that the introduction of two *tert*-butyl groups shifts the transition structure to an earlier stage of the ring closure reaction **A** → **B**.

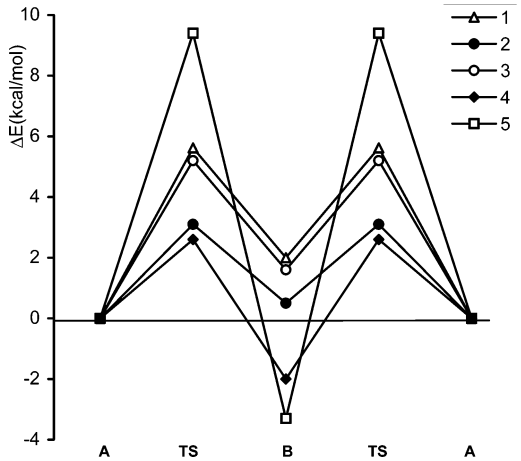


Figure 3. Reaction profiles for 1,5-hydride shift in the C_4-alkyl substituted 2,6-dimethyl-2-heptyl cations (**1**, **2**, **3**, **4**, and **5**) calculated at the MP2/6-31G(d) level using PCM ($\epsilon = 30.0$).

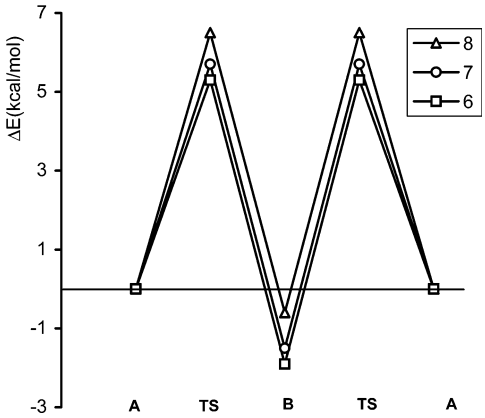


Figure 4. Reaction profiles for 1,5-hydride shift in the C_4-polymethylene-substituted 2,6-dimethyl-2-heptyl cations (**6**, **7**, and **8**) calculated at the MP2/6-31G(d) level using PCM ($\epsilon = 30.0$).

Introduction of C_4-$(CH_2)_n$-substituents in **6**−**8** stabilizes the μ-hydrido structure of type **B** (Figure 4). For gas-phase and solvent-model calculations, the bridged structures **6B**, **7B**, and **8B** are more stable than the corresponding acyclic cation structures **6A**, **7A**, and **8A** (Table 1). The relative stability (PCM MP2/6-311G(d,p)//MP2/6-31G(d) of **B** increases with decreasing length of the methylene chain; **6B** is 7.0 kcal/mol more stable

than **6A**, and **8B** is only 5.4 kcal/mol more stable than **8A** (Table 1 and Figure 4).

The energy barriers **A** → **B** decrease with decreasing length of the methylene chain from **8** to **7** to **6**, suggesting the same origin (*gem*-dialkyl effect) for stabilization of the intermediates **6B**, **7B**, and **8B** and the transitions state structures **6TS**, **7TS**, and **8TS** leading to that intermediates**.**

Conclusion

The potential-energy surface for degenerate 1,5-hydride shifts in 2,6-dimethyl-2-heptyl cations **1**−**8** is rather shallow and consists of three minima corresponding to two equivalent acyclic carbocation structures (**A**) and one symmetrically μ-hydrido-bridged carbocation structure (**B**) and two first-order saddle points corresponding to equivalent unsymmetrically μ-hydrido-bridged transition-state structures. The results of the quantum chemical calculations for the 1,5-hydride shift in cations **1**−**8** are in principle similar to those reported for lower-order 1,2-, 1,3-, and 1,4-hydride shifts in acyclic tertiary carbocations [3], except that for the heptyl cations **1**−**8** the symmetrically μ-hydrido-bridged structures **B** are energetically favored over equilibrating acyclic carbocation structures **A** in the gas phase. The rather small dipole moment for the symmetrically μ-hydrido-bridged dimethylheptyl cation structures **B** and the order of magnitude larger dipole moment for the acyclic dimethylheptyl cations structures **A** led to differential solvation effects. These can change a flat potential-energy surface of carbocations relative to that of the gas phase. SCI-PCM B3LYP/6-31G(d) and PCM MP2/6-311G(d,p)//MP2/6-31G(d) calculations for a model solvent ($\epsilon = 30.0$) show that in solution contrary to the gas phase the equilibrating acyclic cation structures **1A**, **2A**, and **3A** are favored over symmetrical μ-hydrido-bridged structures **1B**, **2B**, and **3B**, whereas for cations **4**−**8** the μ-hydrido-bridged structures are favored over equilibrating structures in the gas phase and in solution. The quantum chemical results are in accord with the experimental observations of kinetic line broadening and EIEs in ^{1}H and ^{13}C NMR spectra of cations **1** and **3** in SbF_5/SO_2ClF solution and reproduce the experimentally observed energy barriers. In general accord with the Thorpe−Ingold effect large C_4-alkyl and C_4-$(CH_2)_n$-substituents lower the barrier for formation and favor the μ-hydrido bridged structures of type **B** over the acyclic carbocation structures A.

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Supporting Information Available: Optimized coordinates of all structures are available free of charge at http://pubs.acs.org.

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(21) The SCI-PCM model was tested calculating the relative energy difference between the open-chain and cyclic form of the 2,6-dimethyl-4-isobutylheptane-2,6-diyl dication. The experimental results[17] showed that the cyclic form is by 0.6 kcal/mol more stable species, and the solvent models reproduced well this result calculating the cyclic form to be 1.6 kcal/mol more stable than open-chain form.

(22) Even larger differential solvation effect of 9 kcal/mol was calculated for the 2,7-dimethyl-2-octyl cation ($n = 4$). This is consistent with the larger difference of the calculated dipole moments for the corresponding open-chain and ring structure (1.7 and 14.7 D, respectively) for this cation.

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