Micellar Aggregation Behavior at Low Ionic Strength of Cyclic Acetal-Type Cationic Surfactants Containing the 1,3-Dioxolane Moiety

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Abstract Published in
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Aggregation studies in water of several cationic acetal-type surfactants having varied hydrophobic chains, [(2-alkyl-1,3-dioxolan-4-yl)methyl]trimethylammonium bromides (Cₙ-D-TAB; where Cₙ = C₉H₁₉, C₁₁H₂₃, C₁₃H₂₇), have been performed by means of dynamic light scattering in the 0.015−0.32 M NaBr concentration range over the temperature limits of 25−45 °C. The aggregation parameters (translational diffusion coefficient of micelle (D₀), hydrodynamic radius (R₀), ionization fraction (α), and aggregation number (n)) have been determined and discussed with respect to the parameters of the “classical” alkyltrimethylammonium bromides (Cₙ-TAB). Additionally, the effect of diastereoisomerism upon surfactant aggregation has been characterized for the trans- and cis-[(2-tridecyl-1,3-dioxolan-4-yl)methyl]trimethylammonium (C₁₃-D-TAB), (2-hydroxyethyl)dimethylammonium (C₁₁-D-HEAB), and triethylammonium (C₁₃-D-TEAB) bromides. Accordingly, the 1,3-dioxolane ring configurations and the size of the head groups do not involve noticeable diastereomeric discrimination in the self-assembling abilities. Because the studied cationic acetal-type surfactants contain a 1,3-dioxolane unit (D), they are an acid hydrolyzable type of chemodegradable surfactant, which is analogous to Cₙ-TAB in terms of the micellar aggregation characteristics.

Introduction

Ionic surfactants bearing an acetal-type 1,3-dioxacyclane ring, i.e., the five -membered 1,3-dioxolane or the six-membered 1,3-dioxane, have attracted much attention in the literature.¹⁻³ Such chemodegradable structures (for an explanation of the term see ref 3a) are susceptible to hydrolysis in acidic media, giving rise to nonsurfactant products: a neutral, water insoluble compound and an ionic, water soluble one.³ᵇ Chemical decomposition of the cyclic acetal-type amphiphiles can be useful for any number of purposes (e.g., micellar/emulsion catalysis of an organic reaction) in order to avoid unfavorable processes such as foaming and emulsification during the separation techniques.⁴⁻⁵

Recently, we have started systematic investigations of the properties of cationic cyclic acetal-type surfactants containing a 1,3-dioxolane moiety in their structure.⁶ The incorporation of a five-membered cyclic acetal grouping between the hydrocarbon chain and the polar ammonium group of “classical” alkyltrimethylammonium bromides causes both the Krafft point and the critical micelle concentration (cmc) to decrease. The values of the standard free energy contribution of the 1,3-dioxolane ring [-D-] in the [(2-alkyl-1,3-dioxolan-4-yl)methyl]trimethylammonium bromides (Cₙ-D-TAB) to micellization and adsorption at the aqueous solution−air interface (∆Gmic[-D-] = −5.7 kJ/mol and ∆Gmic[-D-] = −21.5 kJ/mol, respectively) showed that the [-D-] moiety is approximately 1.7 times more hydrophobic than a methylene group of the alkyl chain in promoting micellization and 6.3 times more effective in promoting adsorption.⁶ It clearly indicates a higher strength of adsorption of the five-membered 1,3-dioxolane grouping at the infinite dilution surface film rather than the tendency to micellization.

Aqueous micelles and oil-in-water microemulsions based on the Cₙ-D-TAB derivatives can be successfully applied as chemodegradable reaction media.⁵ They are liable to chemical degradation in both homogeneous and micellar systems, which makes them most promising components not only of micelles but especially of microemulsions. Additionally, it has been pointed out that the 1,3-dioxolane ring as a portion of Cₙ-D-TAB does not introduce significant changes in the catalytic ability of its micellar aggregates in relation to their hydrophobic analogues, i.e., alkyltrimethylammonium bromides.⁵ᵃ

The cationic quaternary ammonium surfactants Cₙ-TAB form small, spherical micelles in aqueous solution up to quite high concentrations and are adequately described by geometrical arguments of micelle shape and size.⁷ Micellar parameters of aggregates formed by cationic surfactants such as shape, size, aggregation number, and diffusion coefficient can be obtained from various techniques: membrane osmometry,⁸ fluorescence probing,⁹ and quasielastic light scattering (QLS) spectroscopy.¹⁰ In particular, the QLS method has extensively been applied to study structural parameters of surfactant-based systems (e.g., micellar diffusivity,¹¹ intermicellar interactions,¹² average micelle molecular weights¹¹,¹³) since this probe does not disturb the monomer–micelle equilibrium.¹⁰ Many authors have presented dynamic light scattering results of aqueous micelles formed by cationic surfactants: cetyltrimethylammonium bromide (CTAB),¹¹,c,d tetradecyltrimethylammonium bromide (TTAB),¹¹,c,d,¹²b and dodecyltrimethylammonium bromide (DTAB)¹¹,e at low ionic strength, while there is no information about their acetal-type analogues.

Therefore, the main purpose of this investigation was to describe quantitatively the micellar aggregation behavior at low
ionic strength of a series of cationic cyclic acetal-type surfactants

\[ \text{C}_n\text{H}_{2n+1} \text{O} \text{C}_2\text{H}_2\text{OH} \text{Me}_2 \]

or

\[ \text{C}_n\text{H}_{2n+1} \text{O} \text{C}_2\text{H}_2\text{OH} \text{Br} \]

(structures given above) by means of light-scattering measurements and discuss the obtained results in relation to C_{n}-TAB surfactants, since variations in diffusivity, $D$, with respect to either surfactant or salt concentration in the positive slope $D$ vs [surfactant] region has been well-documented for various CTAX + NaX ($X = \text{Br}, \text{Cl}, \text{OH}, \text{SO}_4$) systems.\textsuperscript{11c,d,12b–e}

Generally, the studied surfactants containing the 1,3-dioxolane ring comprise dia stereoisomeric mixtures of approximately constant molar ratios of $cis$ to $trans$ isomers equal to 1.4.\textsuperscript{3b} Furthermore, to justify the assumption that the configurations of the $cis$- and $trans$-2,4-disubstituted-1,3-dioxolane surfactants with the flexible 1,3-dioxolane ring do not significantly affect the micellar aggregation, we extended our scattering studies to the pure $cis$ and $trans$ isomers of the selected 2-tridecyl surfactant derivatives of the structures given below.

\[
\begin{array}{c}
\text{C}_n\text{H}_{2n+1} \text{O} \text{C}_2\text{H}_2\text{OH} \text{Me}_2 \\
\text{C}_n\text{H}_{2n+1} \text{O} \text{C}_2\text{H}_2\text{OH} \text{Br}
\end{array}
\]

This work explores in further detail the role of the 1,3-dioxolane grouping in the cationic cyclic acetal-type surfactants and their aggregation behavior in water in comparison with the classical alkyltrimethylammonium bromides.

**Experimental Section**

The synthesis and properties of [(2-alkyl-1,3-dioxolan-4-yl)-methyl]trimethylammonium bromides were previously described.\textsuperscript{3b,6} [(2-Tridecyl-1,3-dioxolan-4-yl)methyl](2-hydroxyethyl)dimethylammonium (C_{13}-D-HEAB) and [(2-tridecyl-1,3-dioxolan-4-yl)methyl]triethylammonium (C_{13}-D-TEAB) bromides were obtained by quaternization of stoichiometric amounts of 2-tridecyl-4-(bromomethyl)-1,3-dioxolanes with trimethylamine, (2-hydroxyethyl)dimethylamine or triethylamine, respectively, in MeOH in a sealed tube at 90 °C. The surfactants obtained were purified several times by recrystallization from acetone–ethyl ether and dried under vacuum at 100 °C.

The Krafft temperature values of the synthesized compounds were determined as follows. Five milliliters of the 2% aqueous surfactant solution was slowly cooled with constant agitation, and the temperature at which the given surfactant precipitated from the solution was recorded. The obtained temperature was similar to the midpoint of a narrow temperature range over which the solutions clarified on slow warming (at a rate of 1 °C/10 min) and with continuous vigorous shaking.

**Results and Discussion**

The dynamic light scattering experiments performed in the first part of this study characterize the size and micellar interactions of C_{n}-D-TAB aqueous micelles as a function of alkyl chain C_{n} ($n = 9$, 11, 13) length, surfactant concentration, and temperature under conditions of moderate ionic strength where there is assumed, as in the case of C_{n}-TAB systems,\textsuperscript{11c–e,12b} little or no spherocylindrical micellar growth. In Figure 1 the concentration dependence of $D$ for C_{13}-D-TAB, C_{11}-D-TAB, and C_{9}-D-TAB is given at 25 °C in the [NaBr] range of 0.015–0.32 M. As shown the diffusivities form a familiar positive slope “fan” of curves which extrapolate to the $D_0$ diffusivity at the cmc (the values are given in SI1); the lower the [NaBr], the larger the slope of lines representing the dependence of the apparent diffusion coefficient on surfactant concentration. The obtained results for our systems are qualitatively similar to those found in\textsuperscript{11c,e,12b} for alkyltrimethylammonium surfactants at low salt concentrations.

Following the classical paper of Corti and Degiorgio\textsuperscript{12a} and subsequent papers by Bunton et al.,\textsuperscript{11c,d,12b} we analyzed quantitatively the concentration dependence of translational diffusion...
Hamaker coefficient $A$ and $R$ and reaches zero slope). $D$ begins. The detailed directions to the method used are given in the Supporting Information (SI2). The mean diffusion coefficient of the micelles at the cmc, $D_{0}$, has been calculated from $D = D_{0}(1 + k_{0}([\text{surfactant}] - \text{cmc})$ where $k_{0}$ (the slope) is the interaction coefficient. The cmc values are given in the Supporting Information (SI1). The apparent mean hydrodynamic radius, $R_{h}$, has been obtained from the Stokes–Einstein relation ($R_{h} = kT/6\pi\eta D_{0}$, where $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $\eta$ is the shear viscosity of the solvent).

The mean diffusion coefficient of the micelles at the cmc, $D_{0}$, has been calculated from $D = D_{0}(1 + k_{0}([\text{surfactant}] - \text{cmc})$ where $k_{0}$ (the slope) is the interaction coefficient. The cmc values are given in the Supporting Information (SI1). The apparent mean hydrodynamic radius, $R_{h}$, has been obtained from the Stokes–Einstein relation ($R_{h} = kT/6\pi\eta D_{0}$, where $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $\eta$ is the shear viscosity of the solvent).

The Hamaker coefficient $A$ of the C$_{n}$-D-TAB micelles in the studied [NaBr] range (Figure 1). The procedure commonly used in such cases is based on the assumption that the interaction potential between micelles (in general, charged spheres) is given by hard sphere interaction plus the electrostatic potential (repulsive forces) and hydrophobic Van der Waals potential (attractive forces). Furthermore, one assumes that the surfactant concentrations under consideration do not exceed the value where nonlinear concentration dependence of $D$ begins. The detailed directions to the method used are given in the Supporting Information (SI2). The values of micellar theoretical interaction parameters (i.e., micellar charge, $q = n\alpha$, where $n$ is the aggregation number and $\alpha$ is the micellar ionization fraction, and the attractive Hamaker coefficient $A$) of the C$_{n}$-D-TAB–NaBr system at 25 °C that the experimental results best fit are summarized in Table 1 (solid lines in Figure 1). As seen, the micellar interaction data of cyclic acetal-type surfactants C$_{n}$-D-TAB correspond well to those found for CTAB.

For the studied C$_{n}$-D-TAB + NaBr systems, the $\alpha$ values lie in a narrow range: 0.19 for C$_{13}$-D-TAB + NaBr and 0.20 for both C$_{11}$-D-TAB + NaBr and C$_{9}$-D-TAB + NaBr. The ionization fraction for CTAB + NaBr and TTAB + NaBr is slightly higher, 0.22. The values of $A$ in units of $kT$ at 25 °C range from 2.5 for C$_{13}$-D-TAB to 3 for both C$_{11}$-D-TAB and C$_{9}$-D-TAB + NaBr. Also listed in Table 1 are the values of [NaBr]$_{v=0}$, which define the range of NaBr concentrations for which the interaction remains net repulsive. A larger value of [NaBr]$_{v=0}$ observed for C$_{9}$-D-TAB + NaBr in comparison to C$_{11}$-D-TAB + NaBr, indicates that over a larger range of NaBr concentrations the micelles of C$_{9}$-D-TAB may remain substantially minimum spheres.

According to the literature data, dimensions of spherical micelles are temperature dependent parameters. The translational diffusion coefficients of the C$_{n}$-D-TAB aqueous micelles at a fixed 0.08 M [NaBr] have been determined at 25, 35, and 45 °C (Figure 2). The values of $D_{0}$ and $k_{0}$ deduced from linear least-squares fit to the data of Figure 2 appear in Table 2. The $R_{h}$ values listed in the final column indicate that the increase of

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**TABLE 1: Micellar Theoretical Interaction Parameters of the Surfactant + NaBr System at 25 °C**

<table>
<thead>
<tr>
<th>surfactant</th>
<th>$n$</th>
<th>$\alpha$</th>
<th>$A$</th>
<th>[NaBr]$_{v=0}$, M</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{13}$-D-TAB</td>
<td>70</td>
<td>0.19</td>
<td>2.5</td>
<td>0.015–0.32</td>
</tr>
<tr>
<td>C$_{11}$-D-TAB</td>
<td>70</td>
<td>0.20</td>
<td>3</td>
<td>0.015–0.32</td>
</tr>
<tr>
<td>C$_{9}$-D-TAB</td>
<td>70</td>
<td>0.20</td>
<td>3</td>
<td>0.03–0.32</td>
</tr>
<tr>
<td>CTAB$^d$</td>
<td>120</td>
<td>0.22</td>
<td>15</td>
<td>0.05–0.10</td>
</tr>
<tr>
<td>TTAB$^d$</td>
<td>90</td>
<td>0.22</td>
<td>7</td>
<td>0.15–0.20</td>
</tr>
<tr>
<td>DTAB$^d$</td>
<td>70</td>
<td>0.14</td>
<td>0.01–0.20</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Best-fit parameters according to directions given in SI2. $^b$ Hamaker coefficient in $kT$ units. $^c$ This parameter denotes [NaBr] which marks the boundary of the net repulsive region (i.e., where $D$ vs [surfactant] reaches zero slope). $^d$ Calculated using linear interaction theory (ref 11b). $^e$ Calculated using an approach of Stephen (ref 11d).

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**Table 2: Micellar Aggregation Parameters of [(2-Alkyl-1,3-dioxolan-4-yl)methyl]trimethylammonium bromides (C$_{n}$-D-TAB) at a Fixed 0.08 M [NaBr]**

<table>
<thead>
<tr>
<th>compound</th>
<th>temp °C</th>
<th>$D_{0}$$^{a}$ 10$^{-7}$ cm$^{2}$ s$^{-1}$</th>
<th>$k_{0}$$^{a}$ M$^{-1}$</th>
<th>$R_{h}$$^{a}$ Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{13}$-D-TAB</td>
<td>25</td>
<td>7.56</td>
<td>3.95</td>
<td>32.3</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>10.1</td>
<td>4.79</td>
<td>30.9</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>13.7</td>
<td>6.26</td>
<td>28.4</td>
</tr>
<tr>
<td>C$_{11}$-D-TAB</td>
<td>25</td>
<td>9.20</td>
<td>4.51</td>
<td>26.5</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>12.4</td>
<td>4.72</td>
<td>25.2</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>16.7</td>
<td>4.94</td>
<td>23.3</td>
</tr>
<tr>
<td>C$_{9}$-D-TAB</td>
<td>25</td>
<td>11.0</td>
<td>5.10</td>
<td>22.4</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>14.9</td>
<td>4.71</td>
<td>21.1</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>19.8</td>
<td>4.40</td>
<td>19.7</td>
</tr>
</tbody>
</table>

$^a$ The mean diffusion coefficient of the micelles at the cmc, $D_{0}$, has been calculated from $D = D_{0}(1 + k_{0}([\text{surfactant}] - \text{cmc})$ where $k_{0}$ (the slope) is the interaction coefficient. The cmc values are given in the Supporting Information (SI1). $^b$ Calculated using an approach of Stephen (ref 11d).
the extrapolated diffusion coefficient is caused not only by the decrease of solvent viscosity and the increase of aggregate mobility in solution with increasing temperature but also by the decrease of aggregate dimensions. It is also significant that, for \( C_n\)-D-TAB (\( C_9 \) \( \sim \) \( C_{19} \)), \( C_9 \)-D-TAB and \( C_{11} \)-D-TAB, \( C_9 \)-D-TEAB and \( C_{13} \)-D-TAB, as well as \( C_9 \)-D-TAB and DTAB, \( C_9 \)-D-HEAB and CTAB (\( C_9 \)) at a fixed 0.08 M [NaBr]. The \( R_h \) values were calculated according to footnote \( b \) of the Table 1.

Thus far, the equilibrium mixture of cis- and trans-\( C_n \)-D-TAB (\( cis/trans = 1.4 \)) has been applied in the aggregation studies. In the following section we characterize the dependence of aggregate behavior upon the surfactant stereoisomer. It has been found for symmetrical 1,3-dioxolanes that the five-membered 1,3-dioxolane ring exists in the planar envelope configuration. The free energy differences \( \Delta G^\circ (\text{trans} \leftrightarrow \text{cis}) \) obtained for the diastereoisomeric cis- and trans-2,4-disubstituted-1,3-dioxolanes are relatively small—the energies themselves are slightly higher for the trans isomers than those for the cis ones independent of the bulk of the substituent at the C-2 atom of the 1,3-dioxolane ring. Burczyk et al. first described surface activities of pure cis- and trans-2-alkyl-4-

![Figure 3](image)

**Figure 3.** Plots of micellar hydrodynamic radius \( R_h \) versus temperature for \( C_9 \)-D-TAB (\( \bullet \)), \( C_{11} \)-D-TAB (\( \mathbb{D} \)), \( C_{13} \)-D-TAB (\( \square \)), DTAB (\( \mathbb{A} \)), TTAB (\( \square \)), and CTAB (\( \mathbb{C} \)) at a fixed 0.08 M [NaBr]. The \( R_h \) values were calculated according to footnote \( b \) of the Table 1.

![Figure 4](image)

**Figure 4.** Translational diffusion coefficient \( D \) versus concentration of cis isomer (\( \mathbb{C} \)), trans isomer (\( \mathbb{D} \)), and cis/trans mixture, molar ratio 1.4 (\( \bullet \)) of \( C_9 \)-D-TAB (a), \( C_{13} \)-D-HEAB (b), and \( C_{13} \)-D-TEAB (c) at a fixed 0.08 M [NaBr] and at 25 °C.

**TABLE 3:** Micellar Aggregation Parameters of Pure cis- and trans-[(2-Tridecyl-1,3-dioxolan-4-yl)methyl]trialkylammonium Bromides and Their Diastereomeric Mixtures at a Fixed 0.08 M [NaBr] at 25 °C

<table>
<thead>
<tr>
<th>compound</th>
<th>cmc, ( 10^{-4} ) M</th>
<th>SE, ( \kappa ) kcal mol(^{-1} )</th>
<th>( R_h ), Å</th>
<th>( D_m ), ( 10^{-7} ) cm(^2) s(^{-1} )</th>
<th>( k_0 ), M(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-( C_{13} )-D-TAB</td>
<td>1.13</td>
<td>13.8</td>
<td>30.0</td>
<td>8.14</td>
<td>3.11</td>
</tr>
<tr>
<td>trans-( C_{13} )-D-TAB</td>
<td>0.75</td>
<td>14.5</td>
<td>34.5</td>
<td>7.09</td>
<td>4.81</td>
</tr>
<tr>
<td>( C_9 )-D-TAB</td>
<td>0.96</td>
<td>32.3</td>
<td>7.56</td>
<td>3.94</td>
<td></td>
</tr>
<tr>
<td>cis-( C_{13} )-D-HEAB</td>
<td>0.95</td>
<td>13.9</td>
<td>31.5</td>
<td>7.76</td>
<td>14.9</td>
</tr>
<tr>
<td>trans-( C_{13} )-D-HEAB</td>
<td>0.81</td>
<td>14.6</td>
<td>34.7</td>
<td>7.03</td>
<td>16.8</td>
</tr>
<tr>
<td>( C_9 )-D-HEAB</td>
<td>0.87</td>
<td>33.4</td>
<td>7.32</td>
<td>15.7</td>
<td></td>
</tr>
<tr>
<td>cis-( C_{13} )-D-TEAB</td>
<td>0.76</td>
<td>14.1</td>
<td>27.5</td>
<td>8.88</td>
<td>2.01</td>
</tr>
<tr>
<td>trans-( C_{13} )-D-TEAB</td>
<td>0.65</td>
<td>15.2</td>
<td>29.5</td>
<td>8.28</td>
<td>2.78</td>
</tr>
<tr>
<td>( C_9 )-D-TEAB</td>
<td>0.70</td>
<td>28.5</td>
<td>8.56</td>
<td>2.64</td>
<td></td>
</tr>
</tbody>
</table>

* Strain energies (SE) comprise the energies corresponding to the deformations that are calculated in the course of the energy minimization. The energy of all hydroxymethyl)-1,3-dioxolanes as determined by either the efficiency of surface tension reduction or the standard free enthalpy of adsorption; they are not very different. Accordingly, both diastereoisomers with substratients at C-2 and C-4 carbon atoms occupy almost the same surface area, indicating small conformational differences. Furthermore, Jaeger et al. have recently proved that there are no detectable differences in the energetics of compression for monolayer films cast from either cis- or trans-[(2-heptadecyl-2-methyl-1,3-dioxolan-4-yl)methyl]trimethylammonium bromides. The monolayer characteristics of cis and trans isomers were identical, but slightly different than that of a 50:50 mixture of the two.

The diffusion coefficient dependence upon the surfactant concentration of pure cis and trans isomers of the selected surfactants (\( C_{13} \)-D-TAB, \( C_{13} \)-D-HEAB, and \( C_{13} \)-D-TEAB), as well as their diastereomeric mixtures (cis/trans = 1.4), is shown in Figure 4, while the micellar aggregation parameters are summarized in Table 3. Included values of the surfactant strain energy (SE) that describe the strain present in rings are
not very different within the selected trans/cis forms of surfactants, and only a small diastereoisomeric differentiation is introduced by the bulk of the head group substituent. As shown the aggregation behavior is slightly altered for the sets of pure diastereoisomers respective to the C_{13}-D-TAB, C_{13}-D-
HEAB, and C_{13}-D-TEAB derivatives. The extrapolated diffusion coefficients found for the cis and trans isomers of C_{13}-D-
TAB, C_{13}-D-HEAB, and C_{13}-D-TEAB differ approximately 15, 10, and 7%, respectively.

Evidently, both diastereoisomers of each surfactant series in the micellar state take up conformations in which there is little compression involving the tridecyl substituent, and furthermore the very flexible 1,3-dioxolane ring adjusts itself to the steric requirements of the methyltriaalkylammonium head group. Thus, as the substituents around the quaternary nitrogen atom at the C-4 atom become larger, the differences between cis and trans isomers seem to disappear in respect to their micellar aggregation behavior.

Acknowledgment. This work was supported by grants of the Chemistry Department, Technical University of Wrocław, Poland.

Supporting Information Available: Values for cmc as a function of [NaBr] and temperature (SI1) and calculation of the Hamaker coefficient (SI2) (6 pages). Ordering information is given on any current masthead page.

References and Notes


(16) (a) Burket, U.; Allinger, N. L. Molecular Mechanics, ACS Monograph 177; American Chemical Society: Washington, DC, 1982. (b) All calculations of the strain energy (SE) were performed with HyperChem version 4.0. Geometry optimization was performed using the MM+ force field with the energy convergence criterion 0.01 kcal/mol, and then semiempirical calculations were carried out using the AM3 method.