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### SYNTHESIS AND CONFORMATIONAL ANALYSIS OF 16H-DINAPHTHO AND 12 H-DIBENZO [D,G][1,3,2]DIOXASILOCINE

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## SYNTHESIS AND CONFORMATIONAL ANALYSIS OF 16H-DINAPHTHO AND 12 H-DIBENZO [D,G][1,3,2]DIOXASILOCINE

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The conformation of the heterocyclic eight-membered ring in 16H-dinaphtho and 12H-dibenzo [d,g][1,3,2]dioxasilocine was investigated in solution by  $^1\text{H}$  NMR spectroscopy. The barrier to ring inversion in the 16H-dinaphtho compound **3a** was found to be  $8.6 \pm 0.2$  Kcal/mol and for the 12 H-dibenzo compound **4a**,  $8 \pm 0.2$  Kcal/mol. Molecular mechanics calculations show three energy minima conformations for both compounds, boat chair(BC), twist boat(TB) and twist boat boat(TBB). Twist boat form is estimated to be the global minimum for the dibenzo compounds while TBB is the global conformation of the dinaphtho compounds. The result of molecular mechanics calculations are supported by analysis of the  $^1\text{H}$ -NMR spectra.

**Keywords:** Eight-membered rings; heterocyclic rings; dynamic NMR; silicon compounds; conformations; conformational analysis

### INTRODUCTION

The conformational analysis of eight-membered rings with two torsional constraints has been the subject of a number of investigations<sup>1-6</sup>. The parent hydrocarbon, i.e. 1,4-cyclooctadiene adopts the TB and BC conformations in solution with the BC form being 0.1 Kcal/mol higher in steric energy<sup>1</sup>.

Although less is known about the oxygen containing 1,4-cyclooctadiene heterocycles, conformations of a number of nitrogen containing ones have been determined both in solution and in the solid state. X-ray structure

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analysis of the 12*H*-dibenzo[*d,g*][1,3,2]N-methylazocine<sup>7</sup> shows that this compound exists in the solid state as the rigid boat-chair which in solution is populated to 95.5% with the B form as the very minor form. On the other hand the N-*t*-butylazocine exists in the solid state as well as in solution as enantiomeric pairs of twist-boats<sup>8</sup>.

Variable temperature <sup>1</sup>H NMR studies of 3,4,6,7-diazothia-cyclooctane shows the compound to interconvert rapidly at room temperatures. At lower temperatures, the <sup>1</sup>H NMR is consistent with a rigid boat-chair conformation and rapidly equilibrating boat-boat or twist-boat forms<sup>9</sup>.

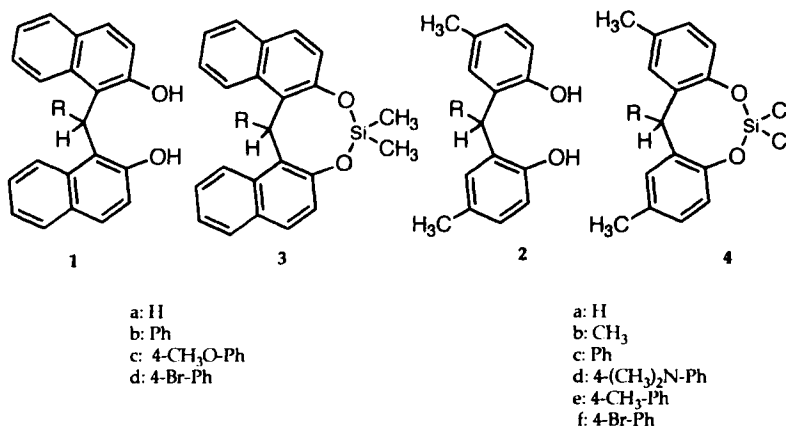
For the phosphorus containing 1,4-cyclooctadiene, the X-ray analysis of the dibenzo derivative of the 1,3,2-dioxaphosphocane ring system proved that the boat chair conformation with C<sub>S</sub> symmetry is adopted in the solid state<sup>10</sup>. For the compounds containing four-coordinated phosphorus, dynamic NMR measurements show the presence of two conformations, a major boat form and a minor boat-chair form<sup>11</sup>.

The conformation of 12*H*-dibenzo[*d,g*]dioxathiocines in the solid state is shown to be BC by X-ray crystallography. The sulfinyldioxy compound exists as the asymmetric axial boat form<sup>12</sup>.

For the eight membered ring in 12 *H*-dibenzo[*d,g*][1,3,2]dioxasilocine derivatives, boat chair, twist boat and boat conformations are found in the solid state and in solution<sup>13,14</sup>. These compounds have two bulky *t*-Bu groups at the 4 and 8 positions, and in those with a boat conformation in the solid state, methyl groups in 1 and 2 positions are present. It is expected that the conformations of these compounds are affected by the presence of the bulky *t*-Bu groups. To see the effect of the absence of *t*-Bu groups on the conformation and conformational barriers, synthesis and conformational analysis of 16*H*-dinaphtho and 12*H*-dibenzo [*d,g*][1,3,2] dioxasilocines with different substitution at C-16 or C-12 positions are reported (scheme 1).

## RESULTS AND DISCUSSION

The reaction of alkylidene bisnaphthols (**1a-1e**) or bisphenol (**2a-2f**) derivatives (Scheme 1) with dichlorodimethylsilane using triethylamine or hexamethylenetetramine as acid acceptor gave the dioxasilocine (**3a-3e**) and (**4a-4f**) in moderate yields. <sup>1</sup>H NMR spectra of **3a** and **4a** show sharp sin-



SCHEME 1

glet signals at  $\delta$  0.45 and 0.25 respectively for the two equivalent methyl groups bonded to silicon and at  $\delta$  4.76 (**3a**) and 3.87 (**4a**) for the two equivalent protons of the bridging methylenes. The variable temperature  $^1\text{H}$  NMR spectra of **3a** and **4a** were recorded down to  $-100^\circ\text{C}$  and  $-108^\circ\text{C}$ , respectively.

For **3a**, the decoalescence of  $\text{CH}_2$  protons was achieved at  $-93^\circ\text{C}$ , but down to  $-100^\circ\text{C}$  no evidence of decoalescence of the methyl protons bound to silicon was observed; the signals remained quite sharp at this temperature which might be due to the very small difference in their chemical shifts as well. A barrier of  $8.6 \pm 0.2$  Kcal/mol to ring inversion could be derived by spectra simulation. At  $-100^\circ\text{C}$  the signals due to aromatic protons remained sharp and unchanged compared to the ones at ambient temperatures. This requires that either a  $\sigma$  plane of symmetry be present in the molecule like in BC or BB forms, or an average  $\sigma$  plane of symmetry be adopted due to a rapid conformational interconversion like  $\text{TB} \rightleftharpoons \text{TB}^*$  via BB as either an intermediate or a transition state, at  $-100^\circ\text{C}$ .

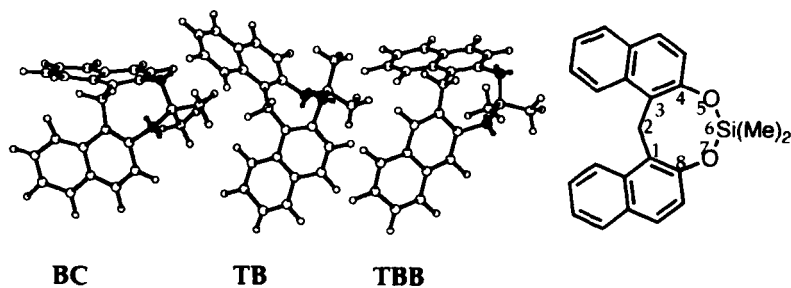
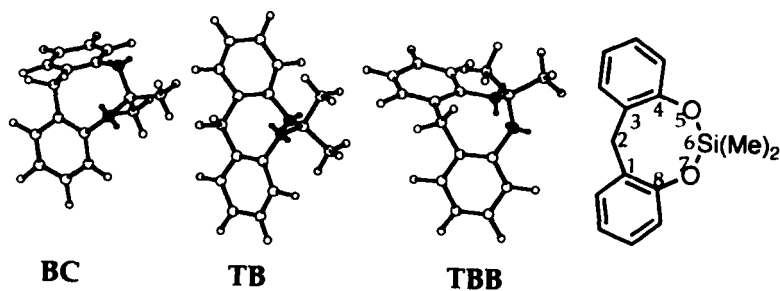
The use of  $^2\text{J}$  magnitude as well as the difference in chemical shifts of  $\text{CH}_2$  protons and methyl protons connected to silicon is believed to be indicative of conformations in solution<sup>14</sup>. A coupling constant of  $15 \pm 1$  Hz could be drawn out from the spectrum at  $-100^\circ\text{C}$ . Efforts to record the spectra lower than  $-100^\circ\text{C}$  was not successful due to the precipitation

of **3a** in the NMR tube. The difference in chemical shifts of CH<sub>2</sub> protons in **3a** is about 0.4 ppm. This value is between the values reported for the B and TB conformations in similar compounds<sup>10</sup>. The difference in chemical shifts of the methyl protons connected to the silicon atom was found to be 0.18 for **3b** and 0.16 for **3d**. For **3c** and **3e** both methyls appear at the same chemical shift. The values for **3b** and **3d** are very similar to the reported value for a B conformation<sup>10</sup>.

For **4a**, decoalescence occurs at -103°C for the methylene and at -108°C for the methyl protons bound to silicon, whereas at -108°C, the protons of the two methyl groups connected to the benzene rings appear as a sharp singlet. The barrier to ring inversion was estimated to be 8.7±0.2 Kcal/mol by spectra simulation. A barrier of 13.9 Kcal/mol for a dibenzo analogue with two t-Bu groups at the 4 and 8 positions has been reported<sup>14</sup>. The difference of ~5 Kcal/mol between the barrier to ring inversion in these compounds could be attributed to the presence of the t-Bu groups in the second one.

The <sup>1</sup>H NMR spectra of **4a** below T<sub>C</sub> requires that the ring conformation possesses a σ plane of symmetry passing through the silicon atom and the bridging methylene carbon atom, such as found in the BB or BC conformations or an average plane of symmetry like in **3a** is adopted. The difference in chemical shifts of CH<sub>2</sub> protons of **4e** below T<sub>C</sub> was found to be about 1 ppm. A coupling constant of about ~15 Hz could be derived from the spectrum at -108°C. These values suggest that TB is the dominant form in solution. The chemical shift difference between the anisochronous methyl groups connected to the silicon atom in **4b-4f** is found to be about 0.5 ppm. This is close to the one found for the TB form, therefore a TB conformation for the compounds **4a-4f** in solution is supported.

The conformational space of the dibenzo and dinaphtho[a,d]cyclooctene was explored by molecular mechanics calculations. Three energy minima conformations were found for each i.e. boat chair(BC), twist boat(TB), and twist boat boat(TBB). For the dibenzo compound, BC is the global minimum while in the dinaphtho compound, TBB is the global minimum form. Molecular mechanics calculations on the dibenzo and dinaphtho silocine compounds show that the TB form is the global form for the dibenzo and TBB is the global minimum for the dinaphtho compound. The optimized structures of the energy minima for **3a** and **4a** are depicted in Figures 1 and 2 and the relative steric energies and the torsion angles are given in Tables I and II.

FIGURE 1 The optimized structure of the three energy minima conformations of **3a**FIGURE 2 The three energy minima conformations of **4a**TABLE I The relative steric energies (Kcal/mol) and torsional angles (in degree) of different conformations of the dinaphtho silocine **3a**. For the numbering see Figure 1

<i>Conformation:</i>	<i>BC</i>	<i>TB</i>	<i>TBB</i>
S.E.	0.8	14.3	0.0
$\Phi$			
1234	-82	-42	-105
2345	-11	0.6	5
3456	75	-70	70
4567	-77	88	-15
5678	84	22	-88
6781	-78	-80	57
7812	-3	-7	2
8123	98	98	47

TABLE II The relative steric energies (Kcal/mol) and torsional angles (in degree) of different conformations of the dibenzo silocine **4a**. For the numbering see Figure 1

<i>Conformation:</i>	<i>BC</i>	<i>TB</i>	<i>TBB</i>
S.E.	1.1	0.0	0.9
$\Phi$			
1234	-95	-34	-101
2345	1	2	2
3456	72	-74	68
4567	-78	85	-10
5678	78	26	-83
6781	-72	-84	50
7812	-1	-4	-0.1
8123	95	86	52

## EXPERIMENTAL SECTION

Melting points were determined in capillary tubes on an Electrothermal 9100 melting point apparatus and are uncorrected.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra as well as the temperature dependent  $^1\text{H}$  NMR spectra of **3a** and **4a** were recorded on a Bruker FT-80 spectrometer. The  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are reported in ppm relative to tetramethylsilane. The dynamic NMR spectra were analysed by coalescence approximation<sup>15</sup> as well as line shape analysis which was performed by DNMR-3 program<sup>16</sup>. The errors in the computed free-energy barriers are mainly due to errors in the temperature measurements and are estimated to be less than  $\pm 0.2$  Kcal/mol. Mass spectra were recorded on a Finnigan MAT spectrometer at 70 eV. Elemental analyses were performed by the Analytical group at the Department of Chemistry, Tarbiat Moddarres University, Teheran. Reagents and solvents were purchased from Merck and used without further purification. Bisnaphthols and bisphenols were prepared according to the published procedures<sup>17-21</sup>. The typical procedure outlined below was used for the preparation of **3a-3d** and **4a-4e**. In a modified procedure, for preparation of **3b** and **3d**, hexamethylenetetramine was used instead of triethylamine, in other cases side reactions take place. Molecular mechanics calculations were performed by MMP2-87 program<sup>22,23</sup> using the parameters reported by Burke *et al*<sup>14</sup>.

## GENERAL PROCEDURE

To a solution of 5mmol of the appropriate bisnaphthol **1** or bisphenol **2** and 15 mmol of triethylamine in 20ml of dichloromethane or toluene at room temperature 7mmol of dichlorodimethylsilane was injected slowly. The reaction mixture was stirred at room temperature for several hours and then worked up. The work up procedure was first removing the precipitate by filtration followed by removal of the solvent by rotary evaporation. The residue was purified by flash chromatography except for the dinaphtho compounds which were found to decompose on the column. For dinaphtho compounds fractional crystallization was found usefull.

### 8,8-Dimethtyl-16H-dinaphtho[2,1-d::1,2 -g][1,3,2] dioxasilocine (**3a**)

Recrystallized from hexane/CH<sub>2</sub>Cl<sub>2</sub>; (white crystals, mp 131.5–133.5°C); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.45 (6H, s), 4.76 (2H, s), 7.04–8.25 (12H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: -1.7, 23.9, 122.6, 123.4, 123.7, 126.7, 127.5, 127.8, 130.6, 133.4, 138.0, 151.1; MS m/z: 433(M+1, 34%), 432(M<sup>+</sup>, 100%), 281(24%), 270(81%), 241(17%)

### 8,8-Dimethtyl-16-phenyl-16H-dinaphtho[2,1-d::1,2-g][1,3,2] dioxasilocine (**3b**)

Recrystallized from hexane/CH<sub>2</sub>Cl<sub>2</sub>; (white crystals, mp: 227–228 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.6(3H, s), 0.24(3H, s), 6.91–8.89(m, 18H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: -3.2, -1.6, 42.2, 123.0, 123.4, 123.9, 125.2, 125.7, 127.2, 127.5, 127.8, 128.9, 129.4, 130.6, 134.5, 143.6, 151.2; MS m/z: 357(M+1, 22%), 356(M<sup>+</sup>, 100%), 281(15%).

### 16-(4-Methoxyphenyl)-8,8-dimethtyl-16H- dinaphtho[2,1-d::1,2-g][1,3,2] dioxasilocine (**3c**)

Recrystallized from hexane/CH<sub>2</sub>Cl<sub>2</sub>; (white crystals, decomposed at >100°C); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.11 (3H, s), 0.27 (3H, s), δ 3.73(3H, s), 6.72–7.96 (17H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: -3.2, -1.7, 41.5, 55.0, 113.1, 123.1, 123.4, 123.9, 125.4, 127.1, 128.3, 128.8, 129.3, 130.5, 134.4, 135.7, 151.2, 157.5. Anal. Calcd for C<sub>30</sub>H<sub>26</sub>O<sub>2</sub>Si: C, 77.9; H, 5.7. Found: C, 77.1; H, 5.6.



**16-(4-Bromophenyl)-8,8-dimethyl-16  
H-dinaphtho[2,1-d::1,2-g][1,3,2] dioxasilocine (3d)**

Recrystallized from hexane/CH<sub>2</sub>Cl<sub>2</sub>; (white crystals, decomposed at >147°C); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.11 (6H, s), 6.94–7.92 (17H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 1.0, 42.1, 119.6, 122.9, 123.4, 123.6, 124.1, 127.3, 128.2, 129.3, 129.7, 129.9, 130.1, 130.9, 132.3, 152.6. Anal. Calcd for C<sub>29</sub>H<sub>23</sub>O<sub>2</sub>SiBr: C, 68.1; H, 4.5. Found: C, 67.6; H, 4.4.

**2,6,6, 10-Tetramethyl-12 H-dibenzo[d,g][1,3,2]dioxasilocine (4a)**

White solid, mp 110°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.25(6H, s), 2.27(6H, s), 3.87(2H, s), 6.64–7.12(6H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: –2.8, 21.3, 33.6, 121.5, 129.0, 131.4, 132.9, 133.3, 150.0. Anal. Calcd for C<sub>17</sub>H<sub>20</sub>O<sub>2</sub>Si: C, 71.7; H, 7.1. Found: C, 71.1; H, 7.1.

**2,6,6,10,12-Pentamethyl-12 H-dibenzo[d,g][1,3,2]dioxasilocine (4b)**

Recrystallized from acetone (white crystals, mp 125°C); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: –0.06(3H, s), 0.53(3H, s), 1.67(3H, d, J=7.2 Hz), 2.28(6H, s), 4.95(1H, q, J=7.2 Hz), 6.62–7.19(6H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: –4.5, –2.2, 18.4, 21.2, 30.1, 120.9, 126.8, 127.9, 132.4, 137.4, 149.1. Anal. Calcd for C<sub>18</sub>H<sub>22</sub>O<sub>2</sub>Si: C, 72.4; H, 7.4. Found: C, 69.5; H, 7.4.

**2,6,6,10-Tetramethyl-12-phenyl-12 H-dibenzo[d,g][1,3,2]dioxasilocine (4c)**

Recrystallized from acetone; (white crystals, mp 154°C); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: –0.04(3H, s), 0.46(3H, s), 2.24(6H, s), 6.25(1H, s), 6.68–7.24(6H, m), 7.28(5H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: –3.8, –1.9, 21.6, 43.8, 121.7, 126.7, 128.52, 129.0, 129.8, 130.8, 133.1, 136.3, 142.8, 150.5. Anal. Calcd for C<sub>23</sub>H<sub>24</sub>O<sub>2</sub>Si: C, 76.6; H, 6.7. Found: C, 75.9; H, 6.6.

**2,6,6,10-Tetramethyl-12-(4-N,N-dimethylaminophenyl)-12 H-dibenzo[d,g][1,3,2] dioxasilocine (4d)**

Recrystallized from acetone; (white crystals, mp 122°C); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.29(3H, s), 0.80(3H, s), 2.55(6H, s), 3.25(6H, s), 6.53(1H, s),

6.95–7.54(10H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : –4.1, –2.0, 21.5, 41.3, 42.0, 112.6, 121.3, 128.5, 130.5, 130.6, 132.7, 136.8, 149.4, 150.4. Anal. Calcd for  $\text{C}_{25}\text{H}_{29}\text{NO}_2\text{Si}$ : C, 74.4; H, 7.2, N, 3.5. Found: C, 74.1; H, 7.2, N, 3.4.

**2,6,6,10-Tetramethyl-12-(4-methylphenyl)-12 H-dibenzo[d,g][1,3,2]dioxasilocine (4e)**

Recrystallized from acetone; (white crystals, mp 105°C);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.20(3H, s), 0.69(3H, s), 2.45(6H, s), 2.57(3H, s), 6.47(1H, s), 6.82–7.5(10H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : –3.9, –2.0, 21.5, 43.1, 121.5, 128.8, 129.2, 129.7, 130.7, 132.9, 135.8, 136.5, 139.7, 150.5. Anal. Calcd for  $\text{C}_{24}\text{H}_{26}\text{O}_2\text{Si}$ : C, 77.0; H, 7.0. Found: C, 76.3; H, 6.9.

**12-(4-Bromophenyl)-2,6,6,10-tetramethyl-12 H-dibenzo[d,g][1,3,2]dioxasilocine (4f)**

Recrystallized from acetone; (white crystals, mp 173°C);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : –0.06(3H, s), 0.43(3H, s), 0.43(3H, s), 2.22(6H, s), 6.11(1H, s), 6.66–7.44(10H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : –3.8, –2.1, 21.5, 43.9, 120.4, 121.8, 129.2, 130.7, 131.5, 131.6, 133.2, 135.7, 141.8, 150.4. Anal. Calcd for  $\text{C}_{23}\text{H}_{23}\text{O}_2\text{SiBr}$ : C, 62.9; H, 5.3. Found: C, 62.3; H, 5.4.

**References**

- (1) Anet, F. A. L.; Yavari, I. *J. Am. Chem. Soc.* **1977**, *99*, 6986.
- (2) Renaud, R. N.; Bovenkamp, J. W.; Fraser, R. R.; Rouston, J.-L. A. *Can. J. Chem.* **1977**, *55*, 3456.
- (3) Barfield, M.; Grant, D. M. *J. Am. Chem. Soc.* **1963**, *85*, 1899.
- (4) Pople, J. A.; Bothner-By, A. A. *J. Chem. Phys.* **1965**, *42*, 1339.
- (5) Barfield, M.; Sternhell, S. *J. Am. Chem. Soc.* **1972**, *94*, 1905.
- (6) Barfield, M.; Grant, D. M. *J. Am. Chem. Soc.* **1964**, *83*, 4726.
- (7) Hardy, A. D.; Ahmed, F. R. *Acta Cryst.* **1974**, *B3*, 1670.
- (8) Hardy, A. D.; Ahmed, F. R. *Acta Cryst.* **1974**, *B3*, 1674.
- (9) Ollis, W. D.; Stoddart, J. F.; Sutherland, J. O. *Tetrahedron* **1974**, *30*, 1903.
- (10) Litvinov, I. a.; Struchkov, Y. T.; Arbuzov, B. A.; Arshinova, R. P.; Ovodova, O. V. *Zhur. Strukt. Khim.* **1984**, *25*, 118.
- (11) Arshinova, R. P.; Danilova, O. I.; Ovodova, O. V. *Dokl. Akad. Nauk SSSR* **1986**, *287*, 1135.
- (12) Hug, P.; Kolly, S.; Meier, H.; Pitteloud, R.; Poppinger, D.; Rihs, G. *Helv. Chim. Acta* **1990**, *73*, 618.
- (13) Clark, F. H.; Fuhrer, H.; Meier, H.; Pastor, S. D.; Rist, G.; Shum, S. P. *Helv. Chim. Acta* **1993**, *76*, 1476.
- (14) Burke, L. P.; DeBellis, A. D.; Fuhrer, H.; Meier, H.; Pastor, S. D.; Rihs, G.; Rist, G.; Rodebaugh, R. K.; Shum, S. P. *J. Am. Chem. Soc.* **1997**, *119*, 8313.
- (15) Sandstrom, J. *Dynanic NMR Spectroscopy*, Academic, London, 1982.

- (16) Binsch, G. and Kleier, D. A. *J. Mag. Res.*, **1970**, 3, 146.
- (17) Mironov, G.S.; Budnji, I. V.; Cherniakovskaya, K. A.; Farberov, M. I. *Zh. Org. Khimi.* **1972**, 8, 597.
- (18) Hewitt, J. T.; Turner, A. J. *Chem. Ber.* **1901**, 34, 202.
- (19) Kharasch, M. S.; Porsche, J. *J. Org. Chem.* **1936**, 1, 265.
- (20) Bonnet, D. I.; Dean, F. M.; Herbin, G. A.; Matkin, D. A.; Price, A. W.; Robinson, M. L. *J. Chem. Soc. Perkin Trans. 1* **1980**, 9, 1978.
- (21) Cordula, G.; Volker, B.; Rosemarie, A.; Sabine, S. *J. Chem. Soc. Perkin trans. 1* **1995**, 2, 93.
- (22) Burkert, U. and Allinger, N. L. *Molecular Mechanics*, American Chemical Society, Washington DC, 1982.
- (23) Liljefors, T.; Tai, J.; Li, S. and Allinger, N. L. *J. Comput. Chem.* **1987**, 8, 1051.