Rotational Barriers of Vinylsilane Derivatives: *Ab Initio* and MM2 Studies

Soo Gyeong Cho* and One Kwon Rim

Agency for Defence Development, P.O. Box 35, Yuseong, Taejon 305-600

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The importance of the vinylsilane (VS) derivatives has been emphasized due to their versatile utility in synthetic applications.[1] Furthermore, there has been considerable interest in the structure and bonding nature of VS.[2] Especially the possible (p-d) π-bonding participation in Si-C(sp^2) bond has been a controversial subject.[2]

O'Reilly and Pierce measured the rotational barrier of VS, 1.5 kcal/mol, from microwave spectrum.[2a] Shiki *et al.* reinvestigated the microwave spectrum, and determined the rotational barrier of VS as 1.488± 0.024 kcal/mol.[2f] Recent estimate, from combined IR and Raman spectra, was 1.50± 0.05 kcal/mol.[2g] In addition to the experimental data, Oberhammer and Boggs calculated this barrier with modest basis set to be 1.44 kcal/mol.[2d] Thus, obviously it appears to be a good fitting that the recent MM2 force field[3] furnish the rotational barrier of VS with 1.51 kcal/mol.[4]

With regard to the rotational barriers and conformational energies of Me derivatives of VS, experimental data are rare. Of particular interest is the rotational barrier of trimethylvinylsilane (TMVS), 0.73 kcal/mol, from IR and Raman spectra by Durig *et al.*[2e] This value is obviously low compared with the one of VS (1.5 kcal/mol), which is surprising if one considers the increase of the steric hindrance around the Si-C_2 bond. When we apply MM2 method to calculate the rotational barrier of TMVS, it provides 1.7 kcal/mol, which is somewhat higher than the one of VS. The discrepancy between the MM2 result and the experimental data is evident. In addition, MM2 method provides a different trend in the changes of rotational barriers by successive Me substitutions compared with the experimental data.

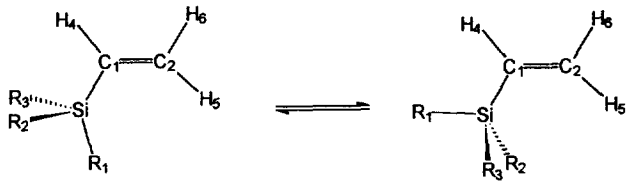
Chemical information derived from molecular mechanics (MM) depends heavily on the force field parameters utilized in that particular package. Most of the force field parameters for geometries such as bond lengths and angles can be acquired from relevant experimental data. However, force field parameters for energetics such as rotational barriers are often problematic due to (1) the lack of experimental data and (2) the inaccuracy of available experimental data. Fortunately, the recent development of *ab initio* molecular orbital calculations appears to be useful in supplementing experimental data. It also provides (1) the chemical insight about magnitudes and possible origins of the rotational barriers and (2) the validity of relevant MM2 torsional parameters.

Ab initio molecular orbital calculations were carried out with 3-21G* and 6-31G* basis sets using the GAUSSIAN-92[5] series of programs on a CRAY YMP computer. The relative conformational energies were further refined with the inclusion of the electron correlation. Vibrational frequencies were calculated at the HF/6-31G*//HF/6-31G* level to determine whether the computed structures correspond to local minima or to transition states. Calculated vibrational frequencies (0.9 scale factor were employed) are in excellent agreement with the ones observed by IR and Raman experiments.[2g] MM calculations were performed with MM2 (85) program.[3] All MM2 parameters were taken from recent publications.[4]

Table 1. Relative Conformational Energies[a] of VS

Calculation level	Eclipsed conformation	Staggered conformation
AM1	0.0	0.20
MNDO	0.0	0.03
PM3	0.0	0.26
HF/3-21G*//HF/3-21G*	0.0	1.48
HF/6-31G*//HF/6-31G*	0.0	1.65
MP2/6-31G*//MP2/6-31G*	0.0	1.60
MP3/6-31G*//MP2/6-31G*	0.0	1.55
MP4(SDTQ)/6-31G*//MP2/6-31G*	0.0	1.51
Experimental data	0.0	1.488(24)[b]
		1.50(5)[c]

[a] Values in kcal/mol. [b] From MW, reference Shiki, Y; Hasegawa, A.; Hayashi, M. *J. Mol. Struct.* **1982**, *78*, 185. [c] From IR and Raman (gas phase), reference Kalasinsky, V. F.; Rodgers, S. E.; Smith, J. A. S. *Spectrochim. Acta, Part A* **1985**, *41*, 155.



VS $R_1=H_1$; $R_2=H_2$; $R_3=H_3'$
MVS cis R_1=Me; $R_2=R_3$=H
skew R_2=Me; $R_1=R_3$=H
DMVS cis R_1=H; $R_1=R_3$=Me
skew R_2=H; $R_1=R_3$=Me
TMVS $R_1=R_2=R_3$=Me
(NOTE: Cis, and skew are applied only to the eclipsed conformations.)

Figure 1. Conformations of VS, MVS, DMVS, and TMVS.

We have employed various levels of theories to predict the rotational barrier of VS including semi-empirical methods. The results are summarized in Table 1. VS is stable in the eclipsed conformation. The SCF calculation with 3-21 G* basis set gives 1.48 kcal/mol, and the SCF result with 6-31G* basis set provides 1.65 kcal/mol, a slightly overestimated value for the rotational barrier of VS. Our best estimate for the energy difference between the staggered and the eclipsed conformation is 1.51 kcal/mol, resulting from MP4(SDTQ) level calculation using the 6-31G* basis set. This result is in excellent agreement with the available experimental data. The SCF result with 3-21G* basis set is also consistent with both our best estimate and the experimental data. This confirms that the 3-21G* basis set is practically useful for the prediction of geometries and energetics in various silicon compounds including force field develop-

Table 2. *Ab Initio* Calculated and Observed Geometries[a] of VS

	HF/ 3-21G*	HF/ 6-31G*	MP2/ 6-31G*	Experimental values[b]
Eclipsed conformer				
Si-C_1[c]	1.867	1.873	1.869	1.853(4)
$C_1=C_2$	1.324	1.325	1.345	1.347(7)
Si-H_1	1.476	1.477	1.486	1.479(5)
Si-H_2	1.477	1.478	1.487	1.478(2)
C_1-H_4	1.080	1.081	1.090	1.089(6)
C_2-H_5	1.075	1.077	1.087	1.094[d]
C_2-H_6	1.075	1.078	1.088	1.094(10)
<Si-$C_1=C_2$	123.74	123.57	122.65	122.43(25)
<C_1-Si-H_1	109.09	109.12	108.41	108.12(25)
<C_1-Si-H_2	110.93	110.93	111.13	110.50(15)
<Si-C_1-H_4	118.24	118.67	119.56	119.42(36)
<C_2-C_1-H_4	118.02	117.76	117.79	117.34(100)
<C_1-C_2-H_5	122.25	122.22	121.85	120.55(52)
<C_1-C_2-H_6	122.24	122.22	122.29	120.21(56)
<H_1-Si-H_2	109.07	109.08	109.18	109.10(18)
<H_2-Si-H_2	107.71	107.64	107.76	108.34(7)
(H_2-Si-$C_1=C_2$)	120.17	120.21	120.00	
Staggered conformer[e]				
Si-C_1	1.874	1.881	1.876	
$C_1=C_2$	1.324	1.324	1.345	
Si-H_1	1.476	1.477	1.486	
Si-H_2	1.477	1.478	1.487	
C_1-H_4	1.079	1.080	1.090	
C_2-H_5	1.076	1.078	1.088	
C_2-H_6	1.075	1.078	1.088	
<Si-$C_1=C_2$	124.34	124.33	123.73	
<C_1-Si-H_1	109.25	109.27	109.33	
<C_1-Si-H_2	111.25	111.30	111.13	
<Si-C_1-H_4	117.77	118.04	118.67	
<C_2-C_1-H_4	117.89	117.63	117.60	
<C_1-C_2-H_5	122.43	122.42	122.14	
<C_1-C_2-H_6	122.18	122.22	122.25	
<H_1-Si-H_2	108.56	108.51	108.59	
<H_2-Si-H_2	107.88	107.87	108.00	
(H_2-Si-$C_1=C_2$)	60.15	60.18	60.15	

[a] Values are lengths in Å, and angles in deg. [b] From r_s. structure/r_s of microwave spectra, reference Shiki, Y; Hasegawa, A.; Hayashi, M. *J. Mol. Struct.* **1982**, *78*, 185. [c] For the numbering scheme, see Figure 1. [d] Assumed parameter. [e] A transition state with one imaginary frequency ($-155.43i$ cm^{-1} in HF/6-31G*).

Table 3. Relative Conformational Energies[a] and Rotational Barriers of Methyl Substituted VS Derivatives

Molecules	3-21G*// 3-21G*	6-31G*// 6-31G*	MP2/6-31G*// 6-31G*	MP3/6-31G*// 6-31G*	MP4(SDTQ)/ 6-31G*//6-31G*	MM2[b]	MM2(85)[c]	Experimental data
VS	1.48	1.65	1.60	1.55	1.52	1.44	1.50	1.488(24)[d] 1.50(5)[e]
MVS								
cis	0.13	0.29	0.18	0.10	0.11	0.02	0.0	
skew	0.0	0.0	0.0	0.0	0.0	0.0	0.12	
cis-skew	1.44	1.64	1.51	1.46	1.43	1.31	1.49	
skew-skew	1.49	1.66	1.66	1.56	1.55	1.39	2.08	
(Me rotation at cis form)								
	1.61	1.66	1.75	1.68		2.05	2.05	1.866(39)[f]
(Me rotation at skew form)								
	1.42	1.45	1.60	1.55		1.54	1.53	1.698(22)[f]
DMVS								
cis	0.0	0.0	0.0	0.0	0.0	0.0	0.09	
skew	0.12	0.28	0.12	0.05	0.05	0.12	0.0	
cis-skew	1.38	1.58	1.47	1.37	1.35	1.27	1.88	
skew-skew	1.39	1.69	1.50	1.44	1.41	1.18	1.28	
TMVS	1.18	1.33	1.33	1.29	1.27	1.02	1.69	0.734[g]
Phenylsilane	0.001							0.035(10)[h], 0.018[i]

[a] Values are relative to the lowest conformational energy (in kcal/mol). [b] This work. [c] Calculated with the parameters of MM2(87) force field distributed by Dr. Allinger; see Table 6 for the details of relevant torsional parameters. [d] From MW, reference Shiki, Y; Hasegawa, A.; Hayashi, M. *J. Mol. Struct.* **1982**, *78*, 185. [e] From IR and Raman (gas phase), reference Kalasinsky, V. F.; Rodgers, S. E.; Smith, J. A. S. *Spectrochim. Acta Part A* **1985**, *41*, 155. [f] From MW, reference Imachi, M.; Nagayama, A.; Nakagawa, J.; Hayashi, M. *J. Mol. Struct.* **1981**, *77*, 81. [g] From IR and Raman, reference Durig, J. R.; Natter, W. J.; Johnson-Streusand, M. *Applied Spectrosc.* **1980**, *34*, 60. [h] From IR (gas phase), reference Fleming, J. W.; Banwell, C. N. *J. Mol. Spectrosc.* **1969**, *31*, 318. [i] From MW, reference Caminati, W.; Cazzoli, G.; Mirri, A. M. *Chem. Phys. Lett.* **1975**, *35*, 475.

Table 4. MM2 Torsional Parameters for VS Derivatives

Torsion	MM2(85)[a]			Frierson's[b]			This work		
	V1	V2	V3	V1	V2	V3	V1	V2	V3
C(sp^2)-C(sp^2)-Si-C	−0.440	−0.240	0.060	0.0	0.0	0.0	0.0	0.0	0.0
C(sp^2)-C(sp^2)-Si-H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H-C(sp^2)-Si-C	0.0	0.0	0.717	0.0	0.0	0.717	0.0	0.0	0.430
H-C(sp^2)-Si-H	0.0	0.0	0.520	0.0	0.0	0.500	0.0	0.0	0.500

[a]Default parameters incorporated in MM2(85) program. [b]Original parameters developed by Frierson *et al.*; see the detail in refs 4 and 8.

ment, although similar results between HF/3-21G* and MP4 (SDTQ)/6-31G* *ab initio* theories may be a coincidence which comes from the compensation of errors caused by truncating the basis set and caused by neglecting the electron correlation. The hamiltonians of the semi-empirical calculations[6] give unacceptably lower rotational barriers, although they predict the eclipsed conformer as a global minimum. This deficiency in semi-empirical methods was also confirmed in other compounds.[7] Thus, we recommend that one should not use the semi-empirical methods to predict the rotational barriers for these particular compounds.

Geometries of VS calculated by *ab initio* methods are summarized in Table 2 along with the one observed from microwave data.[2f] Three levels of calculations - HF/3-21G*, HF/6-31G*, and MP2/6-31G* - were conducted to predict geometries of VS. Overall, the *ab initio* calculated geometric parameters are in excellent agreement with the one observed by the experiment, and slight improvement is noticed as the size of the basis set gets larger or the electron correlation is included. One significant change is the C=C bond length, which is elongated dramatically from 1.325 Å at the HF/6-31G* level to 1.345 Å at MP2/6-31G* level.

Relative energies of Me substituted VS derivatives are shown in Table 3. In methylvinylsilane (MVS) and dimethylvinylsilane (DMVS), the energy difference between the H eclipsed and the Me-eclipsed conformation appears to be almost none. The value at the MP4(SDTQ)/6-31G* level is about 0.1 kcal/mol favoring the H-eclipsed conformation. MM 2 calculations by Frierson *et al.*[4] have provided that the Me-eclipsed conformer of MVS is favorable to the H-eclipsed conformer by 0.12 kcal/mol.[8] Frierson's results have not been proved by either experimental data or high level MO calculations. Frierson's insistence on the conformational preference of Me substituted VS derivatives does not agree with both our *ab initio* calculations and the carbon analog, 1-butene.[9] In addition, the rotational barrier of TMVS calculated with Frierson's parameters is much higher than the one observed from IR and Raman spectra by Durig *et al.*[2e] The rotational barrier of TMVS obtained by the experiment is only half to that of VS ! The reduced rotational barriers of congested systems are often noticed in various organosilanes. This trend may arise from the attenuation of the repulsive van der Waals interactions between atoms in the 1,4 relationship due to the longer C-Si or Si-Si bond.[10,11] Sometimes, van der Waals interactions may fall in the attractive region. Hexamethyldisilane serves another example of silicon compounds. Despite of the presence of the six Me groups, the rotational barrier of hexamethyldisilane is not higher than the one of the parental disilane (Both are *ca.* 1.0 kcal/mol).[10,12] Our high level *ab initio* theories confirm that the rotational barrier of TMVS is lower than the one of VS (see Table 3), although the magnitude of the *ab initio* calculated value remains 0.5 kcal/mol higher than the one from the experimental data. Our best energy estimate with MP4(SDTQ) level theory predicts the rotational barrier of TMVS as 1.2 kcal/mol. Since both the calculations and the experiments apparently confirm that the Me substitution reduces the torsional barriers in VS derivatives, we suggest that the MM2 torsional parameters for Me substituted VS derivatives should be corrected without sacrificing the current result in the rotational barrier of parental VS (see the detail in Table 4).

A number of theoretical studies have been undertaken in order to provide possible explanations about rotational barriers of a single bond adjacent to a double bond.[13-15] One of popular explanations is the relative stabilization in the orbital interactions between the eclipsed and staggered conformation. This nature of delocalizations appears to be retained in VS. We have performed the natural bond orbital (NBO) analyses of the Hartree-Fock wave functions for VS and TMVS. The Fock matrix analyses were carried out with the NBO program,[16] which is implemented in the GAUSSIAN-92.[5] The stabilizations of π(C=C) and σ(Si-H) orbitals by empty "Rydberg-type" orbitals in vicinal bonds are summarized in Table 5. As changing from the staggered conformation to the eclipsed conformation by the rotation of Si-C(cp^2) bond, the π orbital of the double bond (π(C=C)) is effectively delocalized by the vacant σ^* orbitals of the adjacent Si-H bonds (σ^*(Si-H)), and two σ orbitals of the adjacent bond (σ(Si-H)) are also strongly delocalized by the vacant π^* orbital (π^*(C=C)). In both VS and TMVS, the energy differences between the eclipsed and staggered conformation by vicinal bonds delocalization (mainly, π(C=C)→σ^*(Si-C/H) and σ(Si-C/H)→π^*(C=C) orbital interactions) are close to the resultant rotational barriers. Therefore, our NBO analysis of VS displays that the rotational barriers of VS derivatives mainly arise from the relative bond delocalizations due to the different orientation between vicinal bonds. NBO analysis further implies that the steric effect around Si-C(sp^2) bond seems to the insignificant. The reduced rotational barriers in Me substituted VS derivatives can be explained by the poorer directionality of σ(Si-C) bond (compared with σ(Si-H) bond) in interacting with the π orbital in a neighboring C=C bond.

Table 5. Bond Orbital Delocalizations[a] for VS; Analysis of the NBO-Fock Matrix by Second-Order Perturbation Theory at HF/6-31G*

Molecules Donor NBO	Acceptor NBO	Eclipsed Conformation	Staggered Conformation	ΔE
VS				
π(C=C)	σ*(Si-H)×2	3.67×2	3.15×2	0.52×2
σ(Si-H)×2	π*(C=C)	1.45×2	1.14×2	0.31×2
σ(Si-H)×2	σ*(C=C)	0.65×2	0.68×2	−0.03×2
Total ΔE's				1.60
Rotational Barrier				1.65
TMVS				
π(C=C)	σ*(Si-C)×2	3.88×2	3.49×2	0.39×2
σ(Si-C)×2	π*(C=C)	1.17×2	0.95×2	0.22×2
σ(Si-C)×2	σ*(C=C)	0.64×2	0.62×2	−0.02×2
Total ΔE's				1.18
Rotational Barrier				1.33

[a] Values in kcal/mol.

In conclusions, we have demonstrated that the conformational potential surfaces calculated by MM method depend heavily on the force field parameters utilized. Thus, the force field parameters should be carefully checked, if the accurate potential surface is necessary. About the conformational preference of VS, the eclipsed conformer is favorable to the staggered conformer. *Ab initio* calculations reproduce rotational barriers of parental VS and Me substituted VS derivatives. Semi-empirical methods show serious deficiencies in predicting rotational barriers of VS derivatives. *Ab initio* methods predict that the rotational barrier becomes lower on successive Me substitutions. This trend supports the rotational barrier of TMVS observed by Durig *et al.*, 0.734 kcal/mol.[2e] NBO analysis shows that the vicinal bond delocalizations are the main origin for the rotational barrier of VS. The poor directionality in the vicinal bond stabilization between σ(Si-C) bonds and π(C=C) bond seems to be the reason for the reduced rotational barreir in TMVS. The MM2 results with default force field parameters (incorporated in the MM2(85) program) fail to give a reasonable value for the rotational barrier of TMVS, while its result in the rotational barrier of VS is in excellent agreement with both the experimental data and the high level *ab initio* calculations. Thus, we propose the new value of MM2 torsional parameter for Me substituted VS derivatives, namely V3=0.430 for H-C(sp^2)-Si-C (see Table 4).

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8. During the course of this study, we have found some errors in Frierson's MM2 calculational results for methyl substituted VS derivatives. With Frierson's original parameters, we cannot reproduce his result for MVS, namely that H-eclipsed conformer is more stable than the Me-ecliped conformer by 0.12 kcal/mol (see the descriptions in the main text (p 5255) of ref. 4(b)). Frierson's parameters provide the energy difference between the H-eclipsed conformation and the Me-ecliped conformation to

be almost none, *i.e.* 0.02 kcal/mol. However, the slight modification of recent MM2 (87) parameters for MVS can remedy Frierson's error.
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Unusual Transacetylation in 3,4-Difunctionalized Pyrrolidine

Kee-In Lee*, Young Key Shim, and Wan Joo Kim

Korea Research Institute of Chemical Technology
P.O. Box 107, Yuseong, Taejon 305-606

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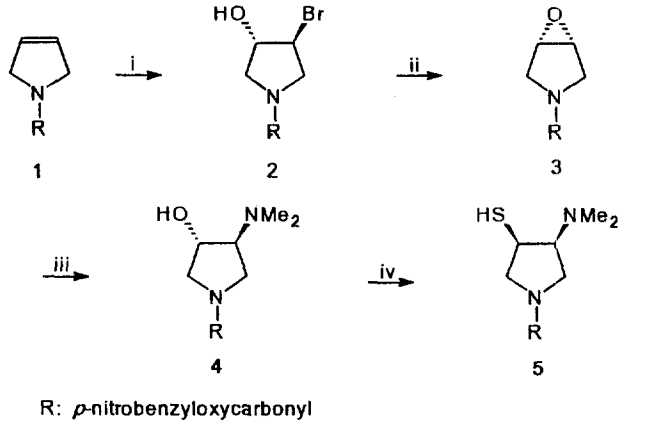
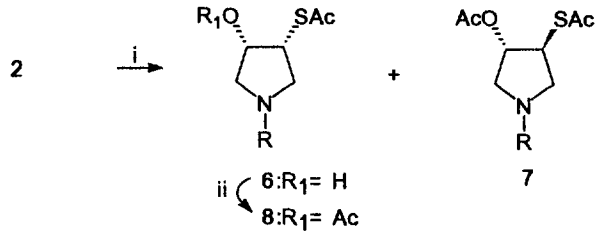
There are considerable interests in the chemistry of natural pyrrolidines and polyhydroxylated pyrrolidine derivatives. Anisomycin[1] and codonopsin[2] are well known biologically active natural pyrrolidines containing 3,4-dihydroxy group. Furthermore, a number of biological activities such as inhibition of glycosidase and inhibition of human immunodeficiency virus (HIV) replication[3] depend on the stereochemistry of polyhydroxylated pyrrolidines. And also they are utilized as useful intermediates for the synthesis of various alkaloids. Recently the pyrrolidine moieties in non-classical β-lactam antibiotics show very potent antimicrobial activities[4] and many investigations of the modified new pyrrolidine substituents are giving a great progress. In the process of preparing various 3,4-difunctionalized pyrrolidines, we isolated a transacetylated compound unexpectedly. Now we are presenting the preparation of the various pyrrolidine derivatives, and possible mechanistic pathway of the unexpected transacetylated compound in the reaction of halohydrin with potassium thioacetate.

The pyrrolidine epoxide **3** was prepared from the reaction of N-*p*-nitrobenzyloxycarbonyl(PNZ)-3-pyrroline **1** with NBS and perchloric acid[5], followed by the treatment of the resulting bromohydrin derivative **2** with 5% KOH. Different kinds of nucleophiles can be used to give new substituted pyrrolidines also. The aminohydroxy compound **4** was obtained from the reaction of pyrrolidine epoxide **3** and the dimethylamine. The amino-thio compound **5** can be obtained from the reaction of the amino-hydroxy compound **4** under Mitsunobu condition[6] as shown in Scheme 1. Our attempts to get hydroxy-thio compound *via* ring opening of **3** with thiolacetic acid in the presence or in the absence of Lewis acid, and potassium thioacetate were unsuccessful.



Scheme 1. Reagents and conditions: i, NBS, aq. $HClO_4$, THF, 80%; ii, 5% KOH, MeOH, 98%; iii, aq. $NHMe_2$, THF, reflux, 95%; iv, PPh_3, $(Pr^iOOCN=)_2$, AcSH, THF, then 4N NaOH, 72%.



Scheme 2. Reagents and conditions; i, KSAc, DMF-toluene, 80 ℃, 2-5 hr, 72%; ii, Ac_2O, Pyridine, DMAP, CH_2Cl_2, 92%.

When bromohydrin **2** was treated with potassiun thioacetate, a separable mixture of thioacetyl compound **6** and unexpected transacetylated compound **7** in *ca.* 1 : 2 molar ratio was obtained. The expected thioacetyl compound **6** can be easily confirmed, but unexpected new compound **7** was identified from ^{1}H-NMR, mass, and NOE experiment. ^{1}H-NMR spectrum of **7** clearly showed two methyl peaks centered at δ 2.36 and 2.12. In general, it is difficult to determine the stereochemistry in substituted pyrrolidine systems by using the chemical shifts and coupling constants when their conformations are flexible[7]. For clarity, thioacetyl compound **6** was further acetylated to the diacetyl compound **8** under the standard condition (Scheme 2). The compound **7** and **8** was identified by NMR and the stereochemistry was confirmed by NOE experiment. From NOE experiment, 2.6% enhancements of C-3 and C-4 signals were observed from the *cis* compound **8** by irradiation on the 4-H and 3-H, respectively, but there was no enhancement from the *trans* compound **7**. Interestingly two hydrogens which are positioned