Pergamon

Tetrahedron Letters, Vol. 38, No. 52, pp. 8955-8958, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)10361-6

Ab Initio Molecular Orbital Study on Inversion Mechanism of Trimethylene Bridges of [3$_3$](1,3,5)- and [3$_6$](1,2,3,4,5,6)Cyclophanes[1]

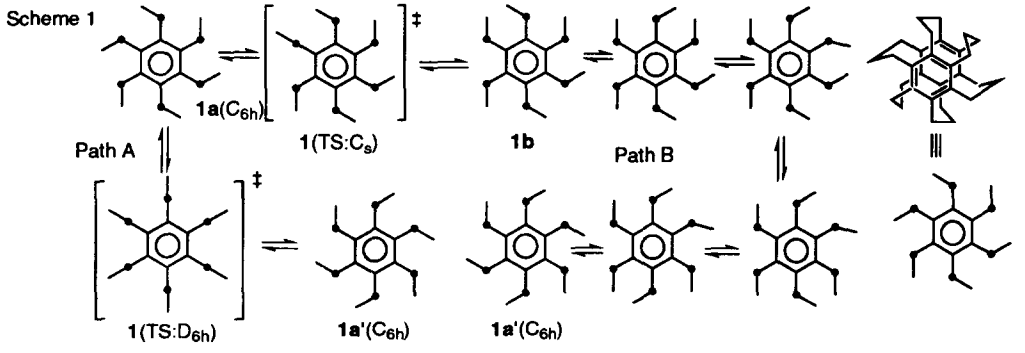
Kenzi Hori,[a,*] Wakana Sentou[b,c] and Teruo Shinmyozu[b]

[a]Department of Applied Chemistry, Faculty of Engineering, Yamaguchi University, Ube 753, Japan,
[b]Institute for Fundamental Research of Organic Chemistry (IFOC), Kyushu University, Hakozaki, Fukuoka 812-81, Japan
[c]Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Fukuoka 812-81, Japan

Abstract: *Ab initio* molecular orbital (MO) study on the inversion process of six trimethylene bridges between two degenerate C_{6h} conformers of [3$_6$](1,2,3,4,5,6)cyclophane suggests that the inversion occurs in a stepwise manner rather than a synchronous mechanism. © 1997 Elsevier Science Ltd.

In the previous papers,[2] we have reported the successful synthesis of a pinwheel molecule with six blades, [3$_6$](1,2,3,4,5,6)cyclophane **1**. Its conformational analysis by the variable temperature (VT) ^{1}H NMR method suggested that the inversion process of the correlated trimethylene bridge was formed between two degenerate C_{6h} conformers (**1a** and **1a'** in Scheme 1) in toluene-d_8. The energy barrier was estimated to be 10.9 kcal mol^{-1} (T_c = -40 ℃). The value was comparable to activation energies for trimethylene bridge inversion processes of [3$_n$]cyclophane (n = 2-5).[2] Although experimental results indicated the presence of the dynamic process, no information was obtained for the mechanism and the transition state (TS) structures.

Scheme 1

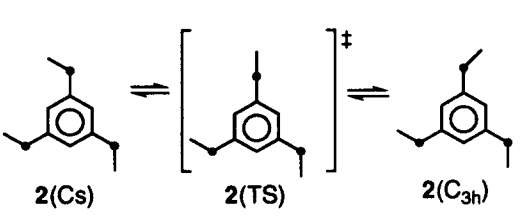


As all the benzene carbons are connected with trimethylene bridges in **1**, the inversion of one bridge should cause some conformational changes of the adjacent bridge. From this point of view, we can assume two types of inversion processes from **1a** to **1a'**. In Path A, six bridges move synchronously and take flat conformations at the TS; **1**(TS:D_{6h}) has D_{6h} symmetry. The trimethylene bridges change their conformation step by step via several unstable intermediates such as **1b** in Path B. On the other hand, the flipping process is so simple that each bridge can proceed its inversion independently in [3$_3$](1,3,5)cyclophane **2** (Figure 1).

In the present study, we investigated the structures of **1** and **2** by use of *ab initio* molecular orbital (MO) calculations. Our attention was also focused on identifying difference of the inversion mechanism for the trimethylene bridges between **1** and **2** by comparing their TS structures.

We used the Gaussian 94 program[3] on the Fujitsu M1800 computer at the data processing center of Kyushu University and the NEC HSP computer at the computer center, Institute for Molecular Science. The 6-31G basis sets were used for optimizing stable and TS structures. In order to estimate the correlation effect between two benzene rings, both RHF and Density Functional calculations (the B3LYP/6-31G level of theory) were employed in optimizing structures of **2** with C_s and C_{3h} symmetries. Table 1 lists optimized parameters of **1a**, **2**(C_s) and **2**(C_{3h}).

It was ascertained that the RHF/6-31G calculation gave geometrical parameters very similar to those obtained from Density Functional calculations. The largest difference of bond lengths were seen in the C-C bond lengths of the benzene ring in **2**, although the differences were less than 0.02 Å. Both calculations estimated that the two conformers **2**(C_s) and **2**(C_{3h}) have almost the same stability. This is consistent with the result of the VT ^{1}H NMR experiment which indicated that the C_s conformer was more stable than the C_{3h} conformer by only 0.4 kcal mol^{-1}.[4] Next, we optimized the TS connecting the C_s and the C_{3h} conformers in order to estimate the activation energy (Ea) of the inversion process. As was easily expected, the transition state **2**(TS) had only one flat bridge whose dihedral angle was calculated to be 180.0°. We would like to emphasize that one of three bridges can change its conformation without influences of other bridges.



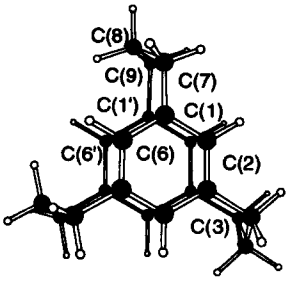


Figure 1 Mechanism of the inversion of one trimethylene bridge and the optimized structure of **2**(C_S)

Table 1 Calculated geometrical parameters of cyclophanes, **1a**, **2**(C_s) and **2**(C_{3h}).

	1a	**2**(C_S)		**2**(C_{3h})	
Method	RHF	RHF	B3LYP	RHF	B3LYP
Bond Length(Å)					
C(1)-C(2)	1.400	1.387	1.402	1.385	1.398
C(2)-C(3)	1.401	1.391	1.401	1.394	1.404
C(1)-C(1')	2.972	3.149	3.152	3.162	3.163
C(6)-C(6')	2.972	3.187	3.181	3.223	3.220
C(1)-C(7)	1.527	1.518	1.522	1.518	1.522
C(7)-C(8)	1.557	1.550	1.557	1.551	1.559
Dihedral angel(°)					
C(1)-C(7)-C(9)-C(8)	141.7	123.3	123.4	123.2	123.7
C(6)-C(1)-C(2)-C(7)	5.7	8.3	8.4	8.2	8.2

The RHF/6-31G level of theory estimated the Ea to be 13.3 kcal mol^{-1} which was almost the same as the experimental value ($\Delta G^{\ddagger}$ = 12.4 kcal mol^{-1}). [5] Therefore, the RHF/6-31G level of theory was considered to be enough quality to discuss the inversion process in **1**.

A preliminary calculation of **1**(TS:D_{6h}) using the PM3 method[6] showed that this geometry with the high symmetry had six imaginary frequencies, i.e., this geometry is not a TS on the potential surface. In order to check the stability of the D_{6h} molecule, the geometry with the fixed dihedral angels $\angle C(1_n)$-$C(7_n)$-$C(9_n)$-$C(8_n)$ =180.0° (n=1-6)[7] was optimized at the RHF/6-31G level of theory. The total energy of the geometry was calculated to be -1156.42388 Hartree. This geometry is, therefore, much less stable by 34.3 kcal mol^{-1} than the C_{6h} one although the vibration frequency calculation was not performed. This value is larger by more than 20 kcal mol^{-1} than the activation energy for the step-by-step mechanism as will be discussed below. Therefore, the D_{6h} geometry cannot be the TS for the inversion of trimethylene bridges.

The *ab initio* MO calculations did not optimize a geometry such as **1b** in Scheme 1. This conformation should be unstable because two trimethylene bridges contact within van der Waals radii of hydrogen atoms of $C(8_1)$ and those of $C(8_2)$. Instead of this unstable structure, we obtained three stable structures (**1a**, **1d**, **1e**) and a TS structure (**1c**) shown in Figure 2. The distance between two benzene rings of **1a** is 2.972 Å which is shorter by ca. 0.2 Å than that of **2**(C_S). This geometrical difference reduces the strain around the benzene carbon in **1a** since its dihedral angle $\angle C(1)$-$C(2)$-$C(6)$-$C(7_1)$ is smaller by ca. 2.6° than that in **2**(C_S). The dihedral angles $\angle C(1)$-$C(7_1)$-$C(9_1)$-$C(8_1)$ in the first bridge of **1a** and **1d** are calculated to be 218.3 (or -141.7) and 140.6°, respectively. Both bridges take similar conformations except for tilted directions. It should be noted that **1d** and **1e** are not TS's but local minima on the potential surface at the RHF/6-31G level of theory, although they have one almost flat trimethylene bridge such as **2**(TS). In order to avoid steric repulsion with the first bridge, the second bridge takes a flat conformation with the dihedral angel $\angle C(2)$-$C(7_2)$-$C(9_2)$-$C(8_2)$ being almost 180°; this angle was estimated to be 185.0° in **1d**. As discussed before, **2** can change the conformation of its trimethylene bridges independently. On the other hand, none of the six bridges of **1** can proceed the inversion without causing steric repulsion with an adjacent bridge. These differences in the environment of the bridges cause a narrower $\angle C(1)$-$C(7_1)$-$C(9_1)$-$C(8_1)$ angle of **1** in the TS than that of **2**; the dihedral angles in **1c**(TS) and **2**(TS) are calculated to be 155.5° and 180.0°, respectively.

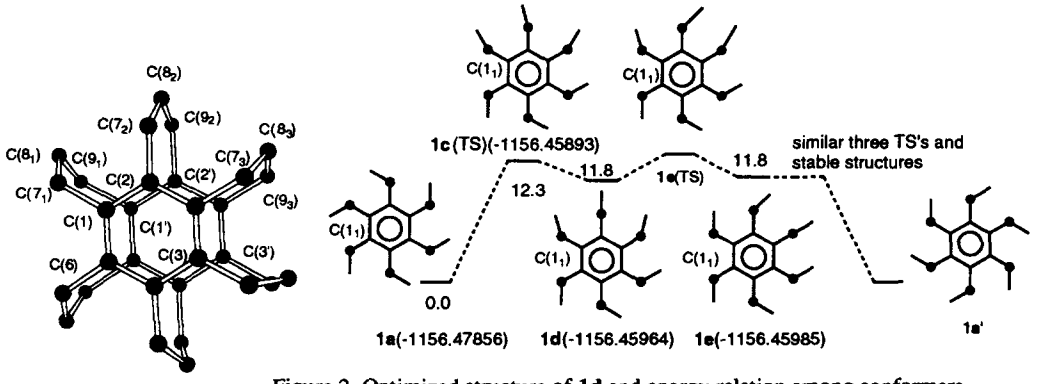


Figure 2 Optimized structure of **1d** and energy relation among conformers related to the inversion of trimethylene bridges

Figure 2 displays total energies in Hartree unit and energies relative to that of **1a** in kcal mol^{-1} unit. The Ea from **1a** to **1d** via **1c**(TS) with only one imaginary frequency (-137.3 cm^{-1}) was calculated to be 12.3 kcal mol^{-1} which was similar to the corresponding Ea of **2** as well as the observed $\Delta G^{\ddagger}$. The energy difference between **1c**(TS) and **1d** was turned out to be only 0.5 kcal mol^{-1}. Moreover, another stable conformer **1e** with the flat third bridge is almost as unstable as **1d**. The instability of these conformers should be due to one flat bridge. Although we did not calculate the TS geometry, **1e**(TS), connecting **1d** and **1e**, such structure probably is as unstable as **1c**(TS). The inversion between **1d** and **1e** and subsequent ones are expected to be very fast. The inversion of the first bridge causes the inversion of the second bridge and the second causes the third, and so on. Therefore, the interconversion between **1a** and **1a'** occurs in a stepwise manner via Path B.

Acknowledgment:

The authors thank to the Computer Center, Institute for Molecular Science at the Okazaki National Research Institutes for the use of the NEC HSP computer and the Library Program GAUSSIAN94. The authors also thank to the data processing center of Kyushu University for the use of the Fujitsu M1800 computer and the library program GAUSSIAN94. TS gratefully acknowledges financial support by the Grant-in-Aid for Scientific Research (B) (no. 09440221) from the Ministry of Education, Science, Sports, and Culture, Japan.

References and Notes:

1. Multibridged [3_n]cyclophanes, Part 5. This work was presented at the Symposium on Computational and Theoretical Chemistry, 1997, July 23, Tokyo.

2. (a) Sakamoto, Y.; Miyoshi, N.; Shinmyozu, T. *Angew. Chem. Int. Ed. Engl.*, **35**, 549 (1996) (b) Sakamoto, Y.; Miyoshi, N.; Hirakida, M.; Kusumoto, S.; Kawase, H.; Rudzinski, J. M. Shinmyozu, T. *J. Am. Chem. Soc.*, **1996**, 118, 12267.

3. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh PA, **1995**.

4. Meno, T.; Sako, K.; Suenaga, M.; Mouri, M.; Shinmyozu, T. *Can. J. Chem.*, **1990**, 68, 440.

5. Total energies of **2**(C_s), **2**(C_{3h}) and **2**(TS) at the RHF/6-31G (B3LYP/6-31G) level of theory are -808.90527 (-814.50887), -808.90536 (-814.50882) and -808.88415 Hartree, respectively.

6. Stewart, J. J. P., MOPAC93, **1993**, Fujitsu, Tokyo, Japan.

7. The subscripts in parenthesis indicate the order of bridges relative to one which changes its conformation first, i.e., C(7_1) means the C(7) in the first bridge.

(*Received in Japan* 28 *August* 1997; *revised* 6 *October* 1997; *accepted* 9 *October* 1997)