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Theoretical Study on the Bicyclo[4.1.0]heptatriene Rearrangement in a Molecular Container

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Abstract: The conversion process from bicyclo[4.1.0]heptatriene (BCT) to 1,2,4,6-cycloheptatetraene (CHTE) within a molecular container was studied with AM1 method, and single point energies for all stationary points were evaluated by B3LYP and HF methods. The conversion potential barrier for the encapsulation complex became smooth when compared with that for the rearrangement in free state. The influences of the inner phase of the molecular container on the conversion process were discussed.

Keywords: Cycloheptatetraene, bicyclo[4.1.0] heptatriene, molecular container, rearrangement.

Some molecules or molecular assemblies with special cavities can exhibit interesting proprieties such as accelerating reactions[1-2], stabilizing reactive intermediates[3-6], selectively separating ions[7-8]. These encapsulation complexes, formed through small guests completely surrounded by hosts, generally are too large to treat with time-consumed quantum chemical methods, thus molecular mechanics (MM) is the most widely used method for such systems. Unfortunately, MM method does not involve the motion of the electrons and can not describe the interactions between molecules accurately. Especially, when it comes to the problems with the forming or breaking of chemical bond, MM becomes more incapable. With the rapid progress in computer hardware and software, it becomes possible to explore such complex systems as a chemical reaction in a limited area using quantum chemical methods[9].

Phenylcarbene (PC) rearrangement reaction is a classic reaction, which has aroused extensive interests since the late 1960s. Early theoretical studies showed that 1,2,4,6-cycloheptatetraene (CHTE) is the species with the lowest energy of the PC rearrangement products[10]. Chapman photochemically generated CHTE at 15 K in argon and provided spectroscopic evidence for the formation, but this highly strained allene can not exist in common condition for its rapid dimerization[11]. However, Ralf Warmuth reported the room temperature stabilization of CHTE generated using a novel, fantastic method by incarcerating it in the inner phase of Cram's hemicarcerand[5-6]. This clearly proves the superiority of the inner phase of the molecular container (MC, shown in **Figure 1**) for the investigation of highly strained reaction species. Bicyclo[4.1.0]

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heptatriene (BCT) is the possible intermediate during the conversion from PC to CHTE[10,12], but it has not been observed in any experiment. In this letter, we aim at the study of the encapsulated rearrangement process using the quantum chemistry methods. It is expected that, through comparing the conversion routes for the encapsulated state and the free one, the inner phase's influence on the rearrangement reaction and the mechanism of the stabilization could be understood better.

To save computational time, eight -$(CH_2)_4CH_3$ groups on the acetal carbons of the hemicarcerand were replaced by hydrogen atoms, which would not influence our research aims in that they were attached outside only and got the desired solubility. The structure of the MC optimized by semi-empirical method (AM1) is shown in **Figure 1**. This container is nearly a cylinder with a cavity about 6 Å×6 Å×12 Å. BCT, CHTE, MC, and the complexes of MC-BCT and MC-CHTE formed by enveloping BCT or CHTE in the MC were optimized by AM1. Two structural conversion processes, in which BCT rearranged to CHTE and MC-BCT to MC-CHTE, were employed with the same method as the minimization steps. Intrinsic reaction coordination methods (IRC) were implemented in both reaction courses to confirm the verity of transition states. The energies for the stationary points (shown in **Table 2**) were further evaluated at much higher level of the theory, such as HF/6-31G(d) and B3LYP/6-31G(d).

Figure 2 shows the optimized structures for BCT, TS1 and CHTE, together with their corresponding complexes MC-BCT, TS2 and MC-CHTE from AM1 method. The

Figure 1 Optimized structure of the MC ($C_{80}H_{72}O_{24}$) displayed in ball and stick model

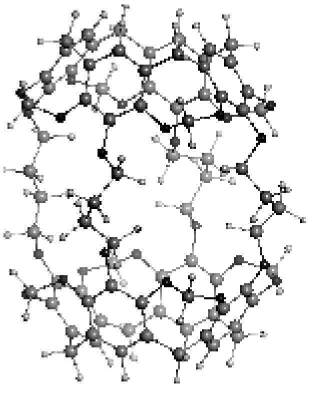


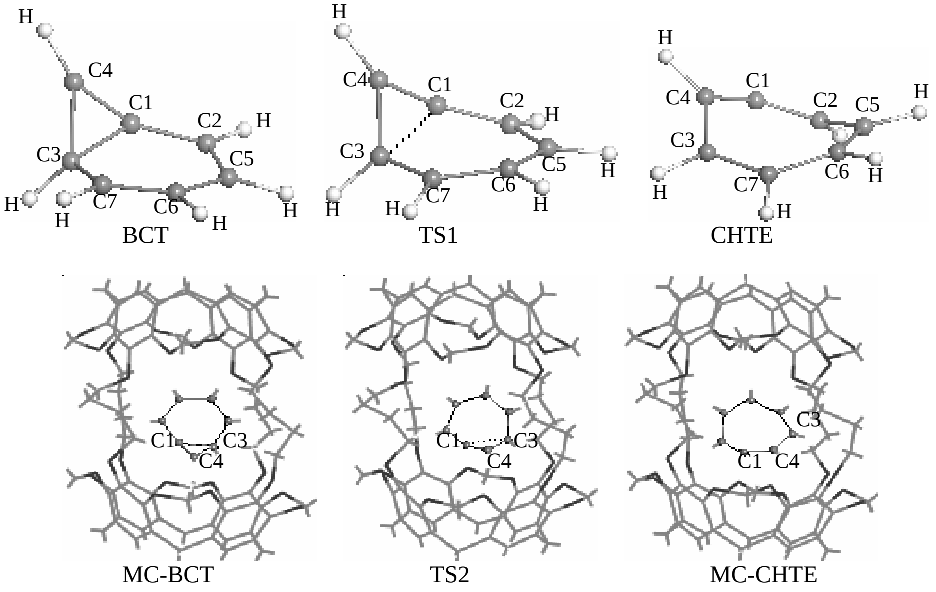
Table 1 Primarily variable parameters along the structure rearranging process (Distance (L) in Å, angle (A) and dihedral (D) in degree)

	BCT	TS1	CHTE
$L_{1\text{-}3}$	1.518	1.809	2.324
$L_{1\text{-}4}$	1.319	1.305	1.320
$L_{3\text{-}4}$	1.496	1.467	1.454
$A_{1\text{-}4\text{-}3}$	64.888	81.242	113.764
$A_{3\text{-}1\text{-}4}$	63.246	53.287	34.933
$D_{4\text{-}1\text{-}2\text{-}5}$	75.288	30.915	25.856
$D_{4\text{-}3\text{-}7\text{-}6}$	-75.975	-49.926	-1.094

Table 2 Energies (in a.u) for all the species obtained from HF/ 6-31G(d) and B3LYP/ 6-31G(d)

	BCT	TS1	CHTE	MC	MC-BCT	TS2	MC-CHTE
HF	-268.41901	-268.40489	-268.44277	-4867.60276	-5135.98200	-5135.97330	-5135.00770
B3LYP	-270.21307	-270.21135	-270.24023	-4896.06043	-5167.03634	-5167.03743	-5167.06448

Figure 2 Optimized structures for BCT, TS1, CHTE and the complexes derived from AM1 method



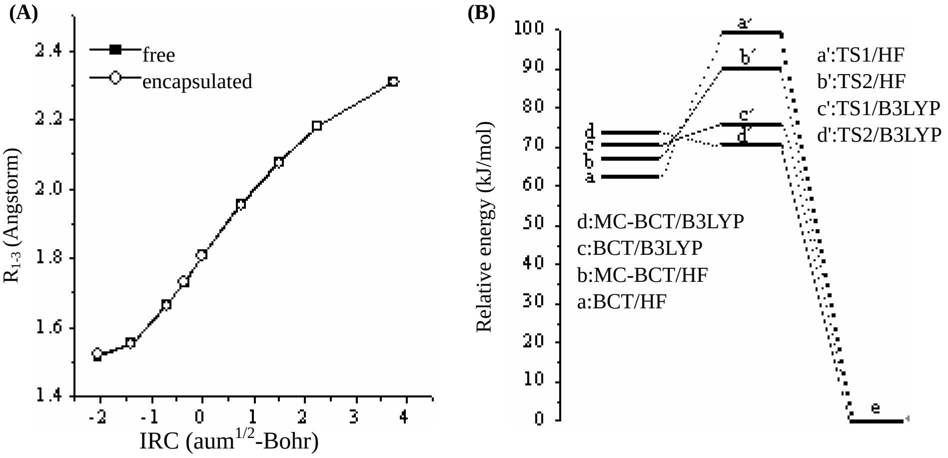
BCT TS1 CHTE

MC-BCT TS2 MC-CHTE

guest lay slightly oblique in the container (shown in **Figure 2**). The rearrangement process was accomplished through the bond breaking (parameters shown in **Table 1**) between C1 and C3. IRC results clearly showed the C1-C3 bond lengthening process, which was very consistent between encapsulated complex and free species (**Figure 3 A**). This indicated that the interaction between guests and hosts was not strong enough to disturb the bond variation. On the other hand, the container's structure also had little change as the overlapped RMSD value between any two molecular containers along the reaction path was less than 0.01 Å.

The potential barriers for both rearrangement courses, encapsulated and free state, are shown in **Figure 3 B**, which were obtained at the level of HF/6-31G(d) and B3LYP/6-31G(d) on the basis of AM1 geometries. HF results showed that the potential barrier of the rearrangement reaction was 37.12 kJ/mol for the free state, and it was reduced to 22.81 kJ/mol when encapsulated in the MC. With a glance at the data from B3LYP, the result seemed a little confusing, that the activation energy was lowered to a negative value of -2.52 kJ/mol compared with that of 4.50 kJ/mol for the free process. In fact, if we considered the computational error, the BCT complex and its transition state were isoenergetic, and the rearrangement in MC was a process of zero potential barrier. After all, both calculation methods tended to give a common tendency that the barrier was lowered when the species were encapsulated in the MC. Concerned with the energies for the complexes, MC-CHTE possessed the lowest energy. The energy difference between the final product and the intermediate species was widened by 5.08 kJ/mol and 2.49 kJ/mol from HF and B3LYP, respectively. It was obvious that the wider gap would be beneficial to stabilize the product, encaged CHTE. So it would be more unfavorable for detecting BCT.

Figure 3 **(A):** C1-C3 bond length variational process for the two states along the IRC; **(B):** The relative energies of the stationary points from HF and B3LYP methods (The energies of the final species CHTE and MC-CHTE were set to zero)



In conclusion, the rearrangement in the MC followed the same route as that in the free state with the slightly lowered potential barrier. Thus the stabilization should be mainly attributed to the MC's sheltering effect, which prevented two CHTE molecules from colliding and combining into one heptafulvalene molecule.

Acknowledgments

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