

**ACTIVATION PARAMETERS AND RELATION OF  
ACTIVATION ENTROPY WITH SOLVENT POLARITY IN  
THERMAL REARRANGEMENT OF 7,7-DICHLORO-[a,c]-  
DIBENZO-[4,1,0]-BICYCLOHEPTANE**

**Saeed Taghvaei-Ganjali\* and Hassan Kabiri-Fard,**

Department of Chemistry, North Tehran Branch, Islamic Azad University Tehran, Iran

**ABSTRACT**

Thermal rearrangement of 7,7-dichloro-[a,c]-dibenzo-[4,1,0]-bicycloheptane (**1**) to 5,6-dichloro-5H-dibenzo-[a,c]-cycloheptene (**2**) was studied in the solid phase and in solvents with different polarities. The first-order constants at various temperatures for the rearrangement process were evaluated from the absorption time data. The activation parameters for this rearrangement were obtained from the temperature dependent of the rate constants. Variation of solvent polarity has no influence on  $E_a$ , but a marked difference in  $\Delta S^\ddagger$  is observed. Abinitio investigation of the thermal ring-opening support the experimental data. Solvating of  $R^+$ ,  $X^-$  ions in Transition State could explain the trend.

**Keywords:** Arrhenius Parameter; Activation; Transition state

**INTRODUCTION**

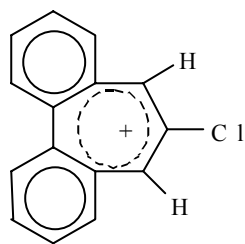
Addition of carben to aromatic and polyaromatic compounds is a well-known reaction<sup>1-5</sup>. One of the simplest way to producing of carben adducts is the reaction of chloroform with conceterated aqueous Sodium hydroxide in the presence of a phase transfer catalyst. The cyclopropane ring thus formed, could be opened by heat.<sup>6-8</sup> Olivella and coworkers who have published a paper on abinitio investigation of the thermal ring-opening cyclopropyl radical to give an allyl radical, predicted a high nonsymmetric structure for the transition state.<sup>9</sup>

Hetrolytic ring-opening of mono and di-substituted cyclopropyl ring with a carbocationic intermediate have been thoroughly studied. The ring opening of known-stereochemical intermediate structure of dichlorocyclopropanes has been carried out in ethanol at 80 °C with silver nitrate.<sup>10</sup>

Rabinovitz *etal* for evaluating the effect of the developed induced ring current resulting from homoaromatic overlap have detected the chemical shifts of the ring opened huckelid Cation **3**.<sup>11</sup>

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\* Corresponding author:



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In this paper we report the results of kinetic and spectral studies concerning the thermal ring opening of cyclopropyl in 7,7- dichloro-[a,c]-dibenzo-[4,1,0]-bicyclopropane in solid state and solution. Variation of solvent polarity has a marked influence on  $\Delta S^\ddagger$  in addition the conversion path of this transformation was simulated by abinitio calculations.

## RESULTS AND DISCUSSION

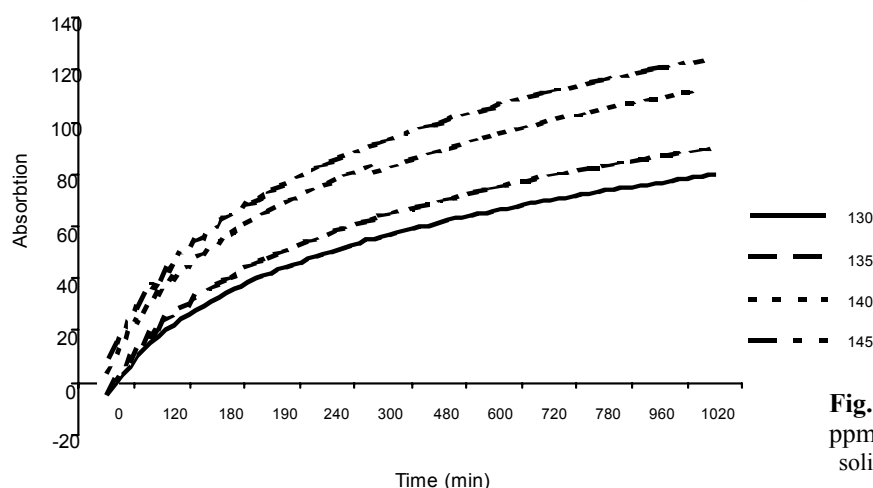
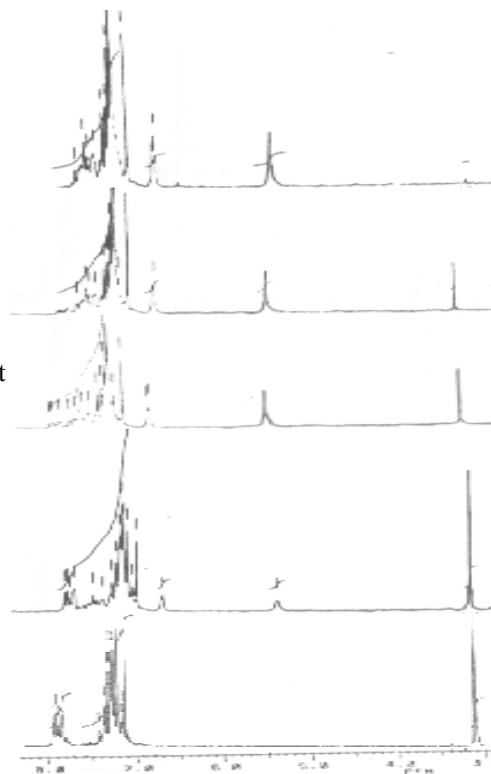
Compound **1** was prepared according to Joshi and etal method.<sup>12</sup> The experimental data shows that

rearrangement of **1** occurred both in solution and in the solid state. Since there are different signals in the <sup>1</sup>H-NMR spectrum of **1** and **2** (rearranged product of **1**), this rearrangement could be followed with respect to the decreasing of intensity in cyclopropyl protons in **1** (singlet, 3.32 ppm) and increasing of intensity in vinylic and allylic protons in **2** (singlet, 6.65 ppm and 5.56 ppm). The increasing of absorption at 5.56 ppm in <sup>1</sup>H-NMR were recorded as a function of time at various temperatures.

Sample <sup>1</sup>H-NMR spectra for the rearrangement process in solid state at 140 °C are shown in Fig.1

In order to obtain further information about the kinetics and mechanism of rearrangement process of **1**, in solid state, the intensity increasing at 5.56 ppm was monitored as a function of time at various temperatures. Sample <sup>1</sup>H-NMR intensity / time plots at different temperatures are shown in Fig. 2

**Fig. 1.** <sup>1</sup>H-NMR spectra for the rearrangement process in solid state at 140 °C in **1** to **2** transformation.

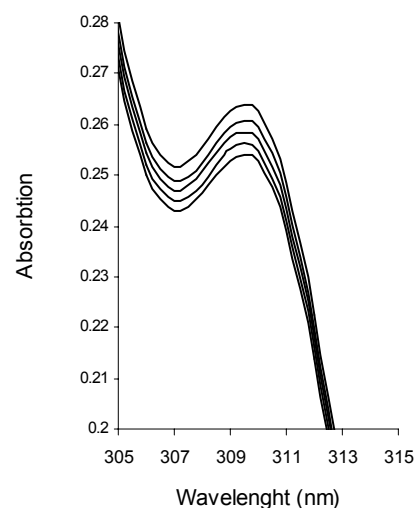


**Fig.2.** Intensity-time plots at 5.56 ppm for rearrangement process in solid state at different temperatures

All of the resulting rate constants in solid state conversion at various temperatures are summarized in table 1. Using the corresponding Arrhenius plots and the Eyring transition state theory<sup>13</sup> the activation parameters ( $E_a$ ,  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$ ) were calculated. The results are also included in table 1.

For detecting of thermal rearrangement process in solution the electronic absorption spectra of heated sample of **1** were recorded as a function of time at various temperatures. Sample spectra for this transformation in DMSO at 80 °C are shown in Fig.3. In this case the decreasing in absorption located at 310 nm was followed.

Table 2 shows the resulting rate constants at various temperatures and activation parameters for thermal rearrangement process in solution.



**Fig. 3.** UV-VIS spectra of rearrangement process in DMSO at 80 °C, 310 nm, various time intervals

**Table 1.** Calculated rate constant at various temperatures and Arrhenius Parameters for transformation in solid state

Temp / °C	K / s <sup>-1</sup>	E <sub>a</sub> / Kcal mol <sup>-1</sup>	ΔH <sup>‡</sup> / Kcal mol <sup>-1</sup>	ΔS <sup>‡</sup> / cal mol <sup>-1</sup> K <sup>-1</sup>
130	2.1 × 10 <sup>-3</sup>	31 ± 1	30 ± 1	4.7 ± 1
135	3.2 × 10 <sup>-3</sup>			
140	7.1 × 10 <sup>-3</sup>			
145	7.3 × 10 <sup>-3</sup>			

**Table 2.** calculated rate constants at various temperatures and activation parameters for transformation in solution

Temp / °C	K / S <sup>-1</sup>	E <sub>a</sub> / Kcal mol <sup>-1</sup>	ΔH <sup>‡</sup> / Kcal mol <sup>-1</sup>	ΔS <sup>‡</sup> / cal mol <sup>-1</sup> K <sup>-1</sup>
60	1.1 × 10 <sup>-5</sup>	18 ± 1	15 ± 1	34.5 ± 1
65	1.7 × 10 <sup>-5</sup>			
70	2.3 × 10 <sup>-5</sup>			
75	3.1 × 10 <sup>-5</sup>			

The positive entropy of solid phase was predicted because there were two constituents in transition state in transformation process.

The activation entropy in solution (DMSO) is negative (table 2), because there are two factors which affect on determining of activation entropy in solution:

A: The positive entropy of transformation, according to increasing in constituents in transition state.

B: The ionic character of transition state in this rearrangement is better solvated by polar solvents such as DMSO. The transition state would be more ordered and there will be a negative entropy.

For detecting process of solvent polarity effects on activation entropy the thermal rearrangement of **1** was studied in different mixtures of DMSO and Xylene (table 3). Of course the mixing of solvents is accompanied by mixing entropy which is positive. The amount of mixing entropy is dependent on the mole fraction of solvent in mixture. Table 4 shows the dependence of ΔS<sub>mix</sub> to mole fraction of Xylene ( $n_{\text{Xylene}}$ ).

Data in table 3 and 4 shows that the mixing entropies of solvents could be neglected.

**Table 3.** Dependence of activation Entropy to molefraction of Xylene

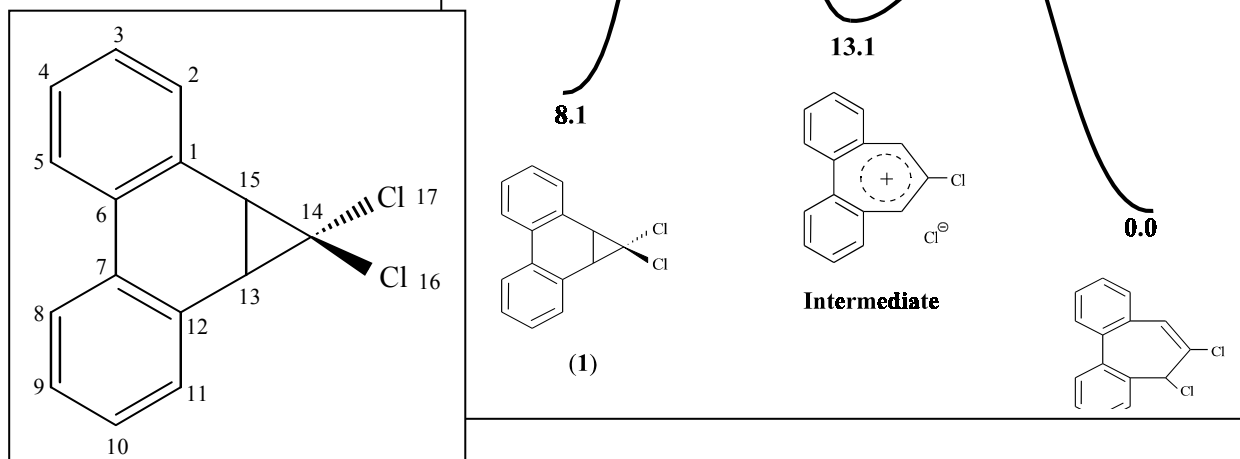
$n_{\text{Xylene}}$	$S$ (cal/mol.K)
0	-34.5
9.2	-31.8
15.9	-30.7
23.4	-24.2
36.2	-17.1
46.3	-11.2
63.3	-9.4
83.8	-6.9
100	-5.8

**Table 4.** Mixing entropy

$n_{\text{Xylene}}$	$S_{\text{Mix}}$	$n_{\text{Xylene}}$	$S_{\text{Mix}}$
0	0	31.7	1.24
2.9	0.15	36.2	1.29
6.0	0.22	46.3	1.37
9.2	0.53	57.3	1.35
12.6	0.75	69.7	1.22
15.9	0.87	83.8	0.87
19.5	0.98	91.6	0.57
23.4	1.07	98.3	0.17
27.4	1.16	100	0

Fig. 4 shows the energy diagram of thermal rearrangement and table 5 shows the calculated heats of formation, total and zero-point vibrational energies, relative energies and structural parameters for **1**, **2**, intermediate and transition states.

**Fig.4.** thermal rearrangement of 7,7-dichloro-[a,c]-dibenzo-[4,1,0]-bicycloheptane (**1**) to 5,6-dichloro-5H-dibenzo-[a,c]-cycloheptene (**2**).



**Table 5.** Calculated total and zero-point vibrational energies (*Hartree*; zero-point vibrational energy is scaled by a factor of 0.9135 to eliminate known systematic errors in calculations), relative energy (including zero-point energy, kcal mol<sup>-1</sup>) and structural parameters

Feature	(1)	TS1	Intermediate	TS2	(2)
HF/6-31G*//HF/6-31G*	-1492.794493	-1492.711387	-1492.786356	-1492.776312	-1492.807619
ZPE	0.219496	0.216355	0.219237	0.219572	0.219686
$E_{rel}^a$ /kCal.mol <sup>-1</sup>	8.13	58.48	13.09	19.58	0.0
$r_{67}$	1.494	1.429	1.495	1.497	1.492
$r_{1213}$	1.490	1.384	1.485	1.543	1.508
$r_{1314}$	1.498	1.413	1.461	1.517	1.506
$r_{1415}$	1.498	1.415	1.320	1.321	1.319
$r_{1416}$	1.763	1.750	1.763	1.759	1.479
$r_{1417}$	1.748	2.263	2.549		
$r_{1317}$				1.829	1.817
$\theta_{567}$	121.9	119.7	117.3	117.5	118.2
$\theta_{678}$	121.9	118.9	117.1	114.5	118.2
$\theta_{111213}$	118.3	113.5	114.6	115.3	117.2
$\theta_{121314}$	121.9	128.9	120.6	119.1	112.1
$\theta_{131415}$	60.3	114.9	131.5	130.6	126.0
$\theta_{131416}$	116.2	113.8	116.2	114.7	114.5
$\theta_{131417}$	121.6	27.3	118.9		
$\theta_{121317}$				108.0	112.5
$\phi_{4567}$	180.0	163.7	-173.6	174.7	-175.5
$\phi_{5678}$	0.0	7.0	35.4	-32.3	39.2
$\phi_{6789}$	180.0	169.3	-177.2	169.5	-178.7
$\phi_{10111213}$	180.0	170.1	-175.0	174.8	-177.4
$\phi_{11121314}$	-111.6	171.7	141.7	-158.2	122.3
$\phi_{12131415}$	-106.4	-47.5	27.1	-22.0	55.8
$\phi_{12131416}$	147.0	178.9	-146.4	164.8	-124.1
$\phi_{12131417}$	4.5	69.1	123.7		
$\phi_{11121317}$				-36.0	-111.6

<sup>a</sup>Relative energy with respect to the most stable conformation from HF/6-31G\*//HF/6-31G\* calculations.

## CALCULATIONS

Semiempirical calculations were carried out using AM1 method<sup>14, 15</sup> with the MOPAC 6.0 program package<sup>16, 17</sup>. Energy minimum geometries were located by minimizing energy, with respect to all geometrical coordinates, and without imposing any symmetry constraints. The geometry of the transition states for conformational interconversion

of the equilibrium structures were obtained using the optimized geometry of the equilibrium structures according to procedure of Dewar et al<sup>18</sup> (keyword SADDLE).

The AM1 results were used as input for the abinitio molecular orbital calculations, which were carried out using the GAUSSIAN 98] program<sup>19</sup>. Geometries for all structures were fully optimized by means of analytical energy gradients by Berny optimizer with no geometrical constrain.<sup>20, 21</sup> The

restricted Hartree-Fock calculation with the split-valence 6-31 G\* basis set which include a set of d-type polarization function on all non-hydrogen atoms were used in these calculation<sup>22</sup>. Single point energy calculations at MP2/6-31G\* //HF/6-31G\* level were used to evaluate the electron correlation effect in the energies and order of stability of conformers.

Vibrational frequencies were calculated at the 6-31G\* level for all minimum energies and transition states, which were confirmed to have zero and one imaginary frequency, respectively. The frequencies were scaled by a factor of 0.91<sup>23</sup> and used to compute the zero-point vibrational energies.

## EXPERIMENTAL

Compound **1** was prepared according to published procedure.<sup>12</sup> Reagent-grade DMSO and para-Xylene (both from Merck) were used without any further purification. <sup>1</sup>H-NMR spectra were recorded on a Bruker 400 and UV-VIS spectra were recorded on a Shimadzu Spectrophotometer and absorbency measurements were made with a

Shimadzu spectrophotometer equipped with a temperature controlled cell holder.

In all experiments the temperature was kept constant at the desired temperature at 0.1 °C using an L-Temprol thermostat.

## Spectra data of **1** and **2**.

7,7-dichloro-[a,c]-dibenzo-[4,1,0]-bicycloheptane (**1**) <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ (ppm), 7.78 – 7.98 (m, 8H, Ar), 3.32 (s, 2H, cyclopropyl protons).

5,6-dichloro-5H-dibenzo-[a,c]-cycloheptene (**2**) <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ (ppm), 7.18-7.76 (m, 8H, Ar), 6.67 (s, 1H, Vinyl proton), 5.54 (s, 1H, Allyl proton).

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## REFERENCES

1. L. Hoffman, *Angew. Chem. Int. Ed. Engl.* **1971**, 10, 529 – 537.
2. L. Hoffman, *Acc. Chem. Res.* **1985**, 18, 248 – 253.
3. H. Singh, P. Singh, *Tetrahedron*, **1981**, 37, 6, 1215 – 1219.
4. M. Makosza and M. Wawrzyniewicz, *Tetrahedron Letters*, **1969**, 10, 53, 4659 – 4662.
5. C. Wenstrup, *C. Tetrahedron*, **1974**, 30, 1301-
6. L. Ghosez, P. Laroche and G. Slinckx, *tetrahedron Letters*, **1967**, 8, 29, 2767-2771.
7. W. M. Jones, *Acc. Chem. Res.* **1974**, 7, 415-421.
8. W. M. Jones, *Acc. Chem. Res.* **1977**, 10, 353-364.
9. S. Olivella and N. Lopez, *Chem. Eur. J.*, **2001**, 7, 3951-3960.
10. J. M. Harris, C.C. Wamser, "Fundamental of organic reaction mechanism".
11. I. Willner, A. Minsky and M. Rabinovitz, *J. Org. Chem.* **1979**, 44, 24, , 4440-4443.
12. G. Joshi, N. Singh, L. Pande, *Synthesis*, **1972**, 317-319.
13. S. H. Lin, K. P. Li and H. Eyring, in "Physical Chemistry an advanced treatise", ed by H. Eyring, D. Handerson and Yost, Academic press, New York, **1977**, vol2, p.1.
14. M. J. S. Dewar, E. G. Zeobish, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.*, **1985**, 107, 3907-3921.
15. M. J. S. Dewar and K. M. Dieter, *J. Am. Chem. Soc.*, **1986**, 108, 8072-8091.
16. J. J. P. Stewart, QCPE 581, Department of Chemistry, Indiana University, Bloomington, IN.
17. J. J. P. Stewart, *J. Comput. Aided Mol. Des.*, **1990**, 4, 1.
18. M. J. S. Dewar, E. F. Healy, and J. J. P. Stewart, *J. Chem. Soc., Faraday Trans.*, **1984**, 80, 227-246.
19. Gaussian 98, Revision A. 6, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Startmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rubuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Comperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA **1998**.
20. F. Jensen, "Introduction to Computational Chemistry", Wiley, New York, **1999**.
21. W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople., "Ab Initio Molecular Orbital Theory", Wiley, New York, **1986**.
22. P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, **1973**, 28, 213 - 221.
23. R. S. Grev, C. L. Janssen, and H. F. Schaefer, *Chem. Phys.*, **1991**, 95, 5128 – 5137.