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Modes of Interconversion in the Cycloheptene Ring

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The possible modes of interconversion for cycloheptene have been studied by carrying out calculations in the CNDO/2 and MINDO/2 approximations.

The transition state of lower energy is found along an asymmetrical pathway from the chair form, which is the most stable conformation, to the twist-boat form; the calculated activation energy agrees with the experimental data obtained from DNMR measures. The possibility of a change in the inversion mechanism for benzocycloheptene is also discussed.

Key words: Cycloheptene conformation – Benzocycloheptene, inversion of

1. Introduction

In cycloheptene there are two families of conformations. The chair family contains the regular symmetrical chair (C) which is relatively rigid and cannot undergo pseudorotation [1]. The boat family contains the regular symmetrical boat (B), the twist-boat (TB) having a C_2 axis, and the biplanar form (II) in which carbon atoms C_1, C_2, C_3, C_6, and C_7 are coplanar (Fig. 1); the forms (II) and (TB) are intermediate in the pseudorotation itinerary between the pair of equivalent boat conformations (B and B*).

Several modes of interconversion can be considered with different transition states (Fig. 1).

Our earlier calculations by Hendrickson's treatment [2] found the chair form favoured over the boat by 1.19 kcal/mole and over the twist-boat by 1.71 kcal/mole [3], while previously Pauncz and Ginsburg [4] using only a potential function for nonbonded H...H interactions calculated the boat to be more stable than the chair by 0.67 kcal/mole, and Allinger *et al.* [5] found the boat preferred by 0.94 kcal/mole.

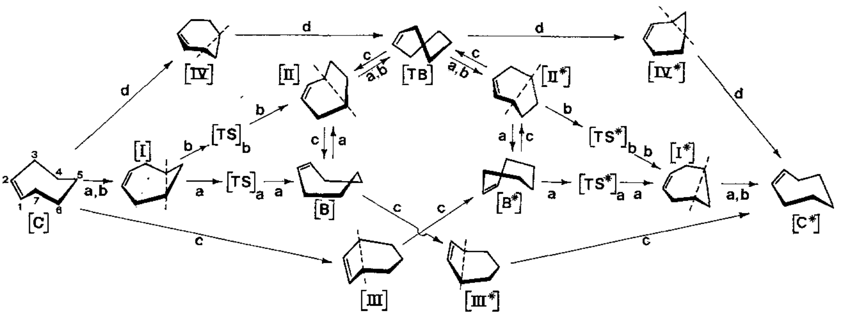


Fig. 1. Interconversion pathways between various forms of cycloheptene

Direct evidence for the structure of cycloheptene was obtained from a study of its Raman and infrared spectra [6]; it was concluded that the cycloheptene exists in the chair conformation in the crystal, while additional bands observed in the liquid at room temperature were attributed to the boat form. Dynamic nuclear magnetic resonance (DNMR) spectroscopy [7] has proven to be a powerful tool for the study of the ring inversion in cyclic molecules; St-Jacques and Vaziri [8] indicate that in 4,4,5,6,6-pentadeuteriocycloheptene there are two equivalent chair forms in equilibrium, separated by an energy barrier of 5.0 ± 0.3 kcal/mole; the free energy profiles corresponding to the interconversion pathway are qualitatively discussed by the same authors.

In a more recent work Allinger and Sprague [9] with an extension of the force field method previously applied to saturated hydrocarbons, calculate the chair favoured by 0.57 kcal/mole over the twist form and by 3.37 kcal/mole over the boat form. Three interconversion pathways are also studied in detail; a symmetrical mode involves wagging of the $C_7C_1C_2C_3$ plane through the form (I) having six coplanar carbon atoms (1, 2, 3, 4, 6, 7) and an energy barrier of 5.16 kcal/mole was calculated; a second symmetrical mode involves wagging of the $C_4C_5C_6$ plane through the form (III) having five coplanar carbon atoms (3, 4, 5, 6, 7); the energy of this form was estimated to be of 10.26 kcal/mole; therefore it is an higher energy pathway contrary to suggestions of Kabuss *et al.* [10] and of Glazer *et al.* [11]. A third asymmetrical mode involves a direct interconversion between the chair and the twist-boat forms through an asymmetrical intermediate (IV) having six coplanar atoms (1, 2, 3, 4, 5, 7), for which an energy of 8.87 kcal/mole was evaluated [9].

Since the force field method requires a great amount of parameters and is founded on a classical basis, we will consider energetical and geometrical aspects of the possible modes of interconversion for cycloheptene within the framework of the molecular orbital method by carrying out all-valence electron SCF calculations in the CNDO/2 and MINDO/2 approximations.

2. Method of Calculation

The numbering system adopted is shown in Fig. 2. Bond lengths were assumed invariant as in the previous work [3]. Carbon atoms C_7, C_1, C_2, and C_3 were considered always coplanar.

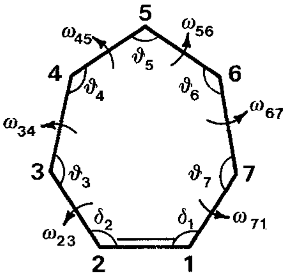


Fig. 2. Numbering system for cycloheptene

The following independently variable parameters were selected for the energy calculations:

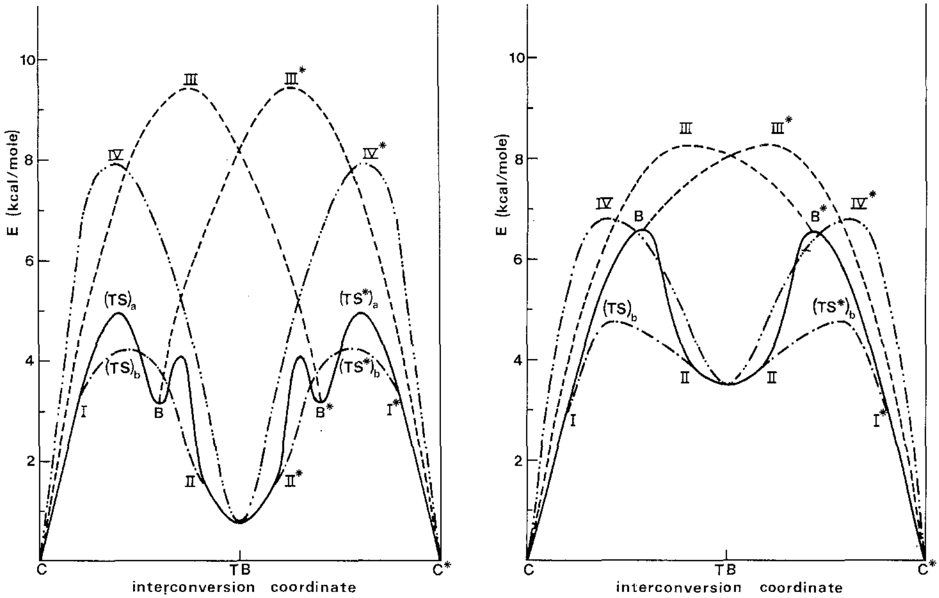
- in the conformations with a plane of symmetry (C, B, I, III), the trigonal angle $\delta_1(=\delta_2)$, the tetrahedral angle ϑ_5 and the dihedral angles φ and φ' (between the plane $C_3C_4C_6C_7$ and the planes $C_7C_1C_2C_3$ and $C_4C_5C_6$ respectively).
- in the TB form, the angles $\delta_1(=\delta_2)$, $\vartheta_4(=\vartheta_6)$ and the dihedral angle between the planes $C_7C_1C_2C_3C_5$ and $C_3C_4C_5$ (or $C_5C_6C_7$).
- in the biplanar form II, the angles $\delta_1(=\delta_2)$, ϑ_3 and $\vartheta_5(=\vartheta_6)$ and the dihedral angle between the two planes. With $\vartheta_5 \neq \vartheta_6$ and $\delta_1 \neq \delta_2$ the energy variation calculated are irrelevant.
- in the other asymmetrical forms, the angles $\delta_1(=\delta_2)$, ϑ_3, ϑ_4, ϑ_5, and the torsional angles ω_{23} and ω_{34}.

The hydrogen atom positions were determined as functions of internal angles ϑ by imposition of orthogonality between the hybrid orbitals on the carbon atom. The convention defined by Hendrickson [2] was used for the torsional angle signs.

The total energy was minimized with respect to couples of variables interpolating the function with an elliptical paraboloid. The CNDO/2 calculations were performed by emploing the program QCPE 91 with usual parametrization; the MINDO calculations by modifying the program QCPE 137 (MINDO/1) in a MINDO/2 version with the parametrization indicated in Ref. [12].

3. Results

Interconversion pathway **a**. Symmetrical mode from the chair (C) to the boat (B) through the form (I) having six coplanar atoms and the transition state $(TS)_a$, followed from pseudorotation to the twist-boat (TB) form. The potential function for this pathway is shown in schematic Fig. 3, and detailed in Fig. 4A for the rate



[A] [B]

Fig. 3A and B. Schematic interconversion pathways. (A) CNDO/2 method, (B) MINDO/2 method. —— pathway **a**, —·—·— pathway **b**, — — — pathway **c**, —··—··— pathway **d**

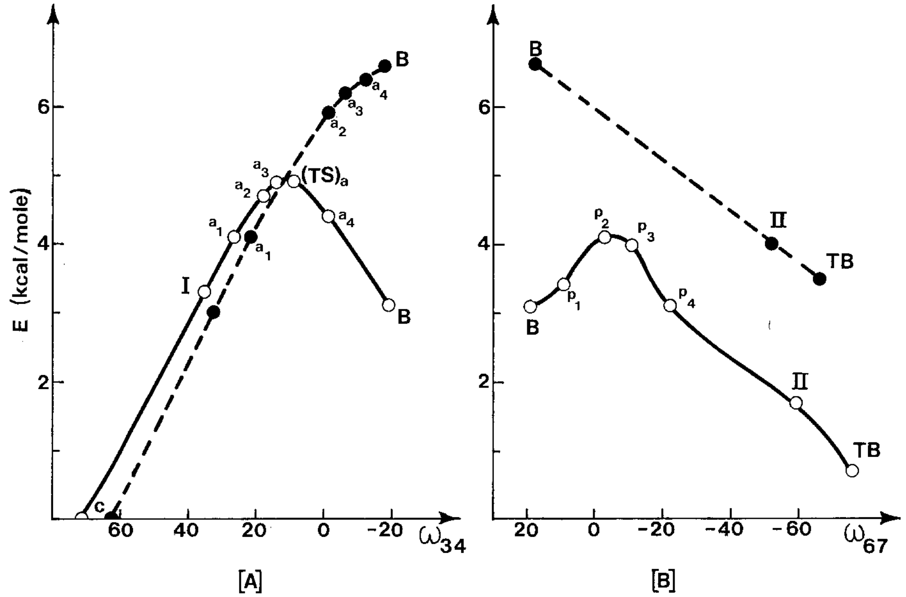


Fig. 4. (A), Symmetrical mode in pathway **a**; (B) Pseudorotation in pathway **a**.
o—o—o CNDO/2 method, ●---●---● MINDO/2 method

Table 1. Geometry (angles in degrees) and energies (in kcal/mole) in the symmetrical mode of interconversion pathway **a** (CNDO/2 method)

Form	(C)	(I)	a_1	a_2	a_3	$(TS)_a$	a_4	(B)
$\delta_1=\delta_2$	127.3	134.8	134.8	133.4	132.7	131.9	129.5	124.8
$\vartheta_3=\vartheta_7$	113.0	118.5	118.0	118.0	117.5	117.0	116.0	113.0
$\vartheta_4=\vartheta_6$	115.5	115.5	116.0	116.0	116.0	116.0	115.5	116.5
ϑ_5	115.5	113.0	113.0	113.0	112.5	113.5	114.5	116.0
$\omega_{23}=-\omega_{71}$	− 55.0	0.0	+ 11.0	+ 22.0	+ 27.5	+ 33.0	+ 44.0	+ 60.5
$\omega_{34}=-\omega_{67}$	+ 71.5	+ 35.0	+ 26.5	+ 18.0	+ 14.0	+ 9.0	− 1.5	− 19.0
$\omega_{45}=-\omega_{56}$	− 68.5	− 82.0	− 81.5	− 79.5	− 79.0	− 76.5	− 72.5	− 60.0
E	0.0	3.3	4.1	4.7	4.9	4.9	4.4	3.1

determining step (symmetrical mode) as function of the torsional angle ω_{34} and in Fig. 4B for the pseudorotation step as function of the torsional angle ω_{67}. Geometrical data and energies relative to the form (C), which is the most stable conformation, are reported in Tables 1–3. Angle values are rounded off to 0.5 degrees since smaller angular variations do not affect the energy significantly.

Interconversion pathway **b**. Symmetrical mode from the chair (C) to the form (I), followed by asymmetrical mode to the TB form through the transition state $(TS)_b$ (Fig. 3). The potential energies for this pathway are detailed in Fig. 5 as a function of ω_{34} as the reaction coordinate. Geometrical data and energies of some conformations are reported in Table 4.

Table 2. Geometry and energies in the pseudorotation itinerary (CNDO/2 method)

Form	(B)	p_1	p_2	p_3	p_4	(II)	(TB)
$\delta_1=\delta_2$	124.8	125.8	129.2	129.8	129.4	128.3	128.9
ϑ_3	113.0	114.0	114.0	113.5	115.0	111.0	113.5
ϑ_4	116.5	115.5	116.5	118.0	117.0	116.0	115.5
ϑ_5	116.0	115.0	115.5	114.5	115.0	116.0	116.5
ϑ_6	116.5	115.5	115.5	115.5	115.5	115.0	115.5
ϑ_7	113.0	115.0	115.5	116.0	116.5	115.5	113.5
ω_{23}	+ 60.5	+ 58.5	+ 51.0	+ 51.0	+ 53.5	+ 57.0	+ 32.0
ω_{34}	− 19.0	− 17.5	− 12.0	− 15.5	− 25.0	− 66.5	− 76.0
ω_{45}	− 60.0	− 63.0	− 65.5	− 61.0	− 52.0	0.0	+ 42.0
ω_{56}	+ 60.0	+ 68.5	+ 75.0	+ 78.0	+ 82.0	+ 73.5	+ 42.0
ω_{67}	+ 19.0	+ 9.0	− 3.0	− 11.0	− 22.0	− 59.5	− 76.0
ω_{71}	− 60.5	− 54.0	− 43.0	− 38.0	− 30.0	0.0	+ 32.0
E	3.1	3.4	4.1	4.0	3.1	1.7	0.7

Table 3. Geometry and energies in the interconversion pathway **a** (MINDO/2 method)

Form	(C)	(I)	a_1	a_2	a_3	a_4	(B)	(II)	(TB)
$\delta_1=\delta_2$	127.4	132.3	132.3	129.5	128.5	127.0	125.6	127.9	128.2
ϑ_3	120.5	122.5	122.5	121.5	121.0	120.5	120.0	118.0	120.0
ϑ_4	118.5	119.0	119.5	120.0	120.0	119.5	119.5	118.5	119.0
ϑ_5	116.0	113.5	115.5	117.0	119.0	119.0	119.5	118.5	119.0
ϑ_6				$=\vartheta_4$				119.0	119.0
ϑ_7				$=\vartheta_3$				120.5	120.0
ω_{23}	− 44.0	0.0	+ 11.5	+ 35.0	+ 41.0	+ 47.5	+ 52.5	+ 51.0	+ 28.5
ω_{34}	+ 62.5	+ 32.5	+ 22.0	− 1.0	− 6.0	− 12.0	− 18.0	− 60.5	− 66.0
ω_{45}	− 62.0	− 72.0	− 69.0	− 61.5	− 56.5	− 53.5	− 49.0	0.0	+ 35.0
ω_{56}				$=-\omega_{45}$				+ 62.5	+ 35.0
ω_{67}				$=-\omega_{34}$				− 52.0	− 66.0
ω_{71}				$=-\omega_{23}$				0.0	+ 28.5
E	0.0	3.0	4.1	5.9	6.2	6.4	6.6	4.0	3.5

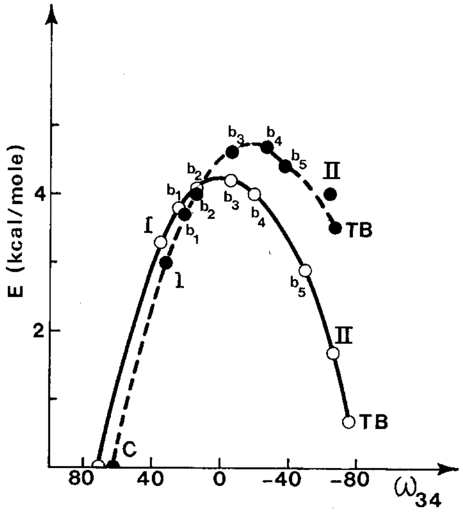


Fig. 5. Interconversion pathway **b**. ○—○—○ CNDO/2 method; ●- - -●- - -● MINDO/2 method

Table 4. Geometry and energies in the interconversion pathway **b**

Form	CNDO/2 method					MINDO/2 method				
	b_1	b_2	b_3	b_4	b_5	b_1	b_2	b_3	b_4	b_5
$\delta_1=\delta_2$	133.8	133.6	133.0	132.2	130.8	131.7	131.6	130.8	130.5	130.0
ϑ_3	121.0	121.5	122.5	122.0	115.5	125.0	125.5	127.0	124.5	122.0
ϑ_4	116.5	117.5	117.0	119.0	118.0	120.0	119.5	119.0	120.5	121.5
ϑ_5	112.5	112.5	113.0	116.5	120.5	113.5	113.5	114.5	120.5	119.5
ϑ_6	115.5	115.5	114.0	115.5	115.0	119.0	119.0	118.5	119.0	119.0
ϑ_7	118.0	116.5	116.5	116.5	116.5	122.0	121.5	121.5	121.0	121.0
ω_{23}	+ 7.5	+ 13.5	+ 20.0	+ 33.0	+ 48.0	+ 7.0	+ 11.0	+ 17.0	+ 33.5	+ 39.0
ω_{34}	+ 24.0	+ 15.5	− 5.5	− 19.5	− 49.5	+ 22.0	+ 15.5	− 5.5	− 26.5	− 37.5
ω_{45}	− 74.5	− 69.0	− 63.5	− 41.0	− 13.0	− 65.0	− 62.0	− 56.0	− 28.5	− 18.5
ω_{56}	+ 85.5	+ 88.0	+ 90.5	+ 84.0	+ 74.0	+ 74.5	+ 77.0	+ 78.0	+ 69.0	+ 66.5
ω_{67}	− 40.0	− 43.5	− 46.5	− 49.5	− 53.0	− 37.0	− 39.5	− 42.0	− 44.5	− 47.0
ω_{71}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
E	3.8	4.1	4.2	4.0	2.0	3.7	4.0	4.6	4.7	4.4

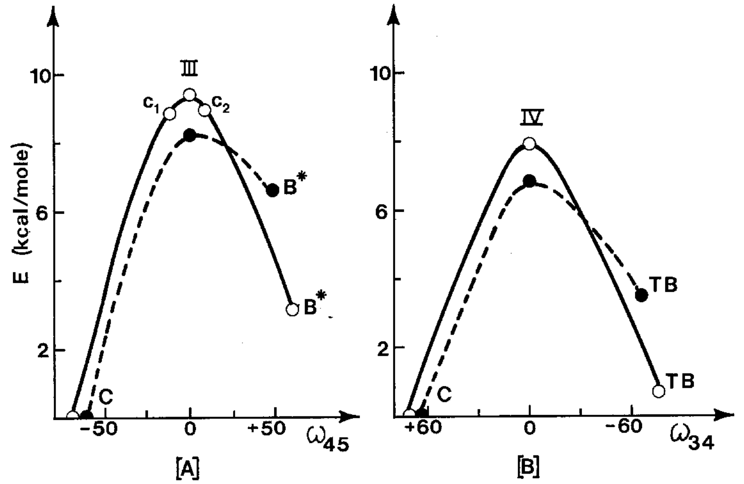


Fig. 6. (A) pathway **c**; (B) pathway **d**. ○—○—○ CNDO/2 method; ●- - -●- - -● MINDO/2 method

Other Interconversion Pathways. The symmetrical mode which involves wagging of the $C_4C_5C_6$ plane through the form (III) having five coplanar carbon atoms (pathway **c**) and the asymmetrical mode with direct interconversion between the chair and the twist-boat forms through an intermediate (IV) having six coplanar atoms (atom 6 out of plane) (pathway **d**) are higher energy processes; the partial data obtained are shown in Fig. 6 and reported in Table 5.

4. Discussion

The transition state of lower energy is found along the pathway **b** with both methods of calculation (Fig. 3). The calculated values of $\Delta H^{\neq}$ for the chair inversion (4.25 kcal/mole by the CNDO/2 method and 4.75 kcal/mole by the MINDO/2 method) are slightly lower than the experimental value of $\Delta G^{\neq} = 5.0$

Table 5. Geometry and energies in the interconversion pathways **c** and **d**

Form	CNDO/2 method				MINDO/2 method	
	c_1	(III)	c_2	(IV)	(III)	(IV)
$\delta_1=\delta_2$	121.9	121.5	121.1	133.3	121.5	133.5
ϑ_3	112.0	112.0	112.0	124.0	118.0	124.5
ϑ_4	120.5	120.5	120.5	121.0	122.0	121.0
ϑ_5	125.0	125.5	124.5	121.0	123.5	125.5
ϑ_6		$=\vartheta_4$		112.5	$=\vartheta_4$	114.5
ϑ_7		$=\vartheta_3$		110.5	$=\vartheta_3$	114.5
ω_{23}	− 70.5	− 71.0	− 71.5	0.0	− 65.5	0.0
ω_{34}	+ 58.5	+ 54.0	=+ 49.0	0.0	+ 51.0	0.0
ω_{45}	− 11.5	0.0	+ 11.5	− 35.5	0.0	− 33.0
ω_{56}		$=-\omega_{45}$		+ 80.0	$=-\omega_{45}$	+ 71.0
ω_{67}		$=-\omega_{34}$		− 72.0	$=-\omega_{34}$	− 63.5
ω_{71}		$=-\omega_{23}$		+ 32.0	$=-\omega_{23}$	+ 29.0
E	8.8	9.4	8.9	7.9	8.2	6.8

± 0.3 kcal/mole found in pentadeuteriocycloheptene [8]. Since $\Delta G^{\neq}$ and $\Delta H^{\neq}$ are expected to be essentially equal, probably within experimental errors [8] (and indeed $\Delta S^{\neq}=0.2$ eu. in 5,5-difluorocycloheptene [11]), the agreement is very satisfactory. It is noteworthy that in proximity of the transition state $(TS)_b$ one observes a change in the sign of the dihedral angle ω_{34} (Fig. 5); it means that there is a biplanar conformation with the atoms $C_2C_3C_4C_5$ and $C_6C_7C_1C_2C_3$ in two planes intersecting across the straight line C_2C_3.

The transition state $(TS)_a$ suggested by Allinger [9] is found only by the CNDO/2 method with energy somewhat higher (5 kcal/mole); its structure is about biplanar with atoms $C_2C_3C_4C_5$ and $C_5C_6C_7C_1$ in two planes with the atom C_5 alone in common; also in the lower-energy pseudorotation process, the coformation with the highest energy value is characterized by a change in the sign of the torsional angle ω_{67} (Fig. 4B). The MINDO/2 method, on the contrary, along the pathway **a** suggests that the boat form is the transition state, but it is reasonable to suppose that the inversion, after the form I is reached advances along the previously mentioned pathway **b** which is energetically preferred.

Also the biplanar intermediates (III) and (IV) are higher energy conformations and probably coincide with the transition states of the pathways **c** and **d** respectively.

As for the geometrical data, the small differences in the values calculated by the two methods are a consequence of the intrinsic properties of methods; really, higher bending constants are to be expected from CNDO/2 than from MINDO/2 and consequently the angles calculated for the minimum energy forms by the former method are generally smaller than those obtained from the latter method. A comparison with experimental data is not possible because they are not known, but the MINDO values should be the more reliable.

A recent proton magnetic resonance study of benzocycloheptene [12] showed unambiguously that the seven-membered ring exists as a chair conformation and a value of 74–76° was obtained for the torsional angle ω_{34} from the coupling constants. In the chair form of cycloheptene we calculate a value of 71.5° by the CNDO/2 method and of 62.5° by the MINDO/2 method; the agreement is fair when one takes into account that the trigonal angles in cycloheptene should be larger than in benzocycloheptene and consequently a diminution of torsional angles ω_{34} and ω_{67} is necessary for the ring closing.

The higher $\Delta G^{\neq}$ value observed in the inversion of benzocycloheptene (10.9 kcal/mole [8]) was qualitatively interpreted previously [8, 9] on a different basis. We think that the replacement of the double bond by the benzene ring should stretch the bond C_1C_2 and decrease the internal angles $C_1\widehat{C_2}C_3$ and $C_2\widehat{C_1}C_7$. By going from the chair (C) to the transition states $(TS)_a$, $(TS)_b$, and (IV), a remarkable increase in the value of trigonal angles in the seven-membered ring occurs, whilst a decrease is observed in the transition state (III). Then in benzocycloheptene an increase in the inversion barrier along the pathways **a**, **b**, and **d** is very likely; the pathway **c** might become the most probable.

The possibility of this change in the inversion pathway would be able to account for the different values of $\Delta G^{\neq}$ in some disubstituted benzocycloheptenes (10.3 kcal/mole in 3,3-dimethyl-, 11.3 kcal/mole in 4,4-dimethyl-, and 11.8 kcal/mole in 5,5-dimethyl-1,2-benzocycloheptene [10]). An increase of the internal tetrahedral angle on the carbon atom with geminal methyl groups brings an energetically unfavoured approaching of the substituents; in the transition state $(TS)_b$ we remark (Table 4) that $\vartheta_3 > \vartheta_4 > \vartheta_5$; on the contrary, in the intermediate (III) the magnitude order (Table 5) $\vartheta_5 > \vartheta_4 > \vartheta_3$ is in agreement with the observed free activation enthalpies.

We are planning to test if the same calculation methods can confirm this change of inversion mechanism in benzocycloheptene, in spite of the bigger molecular entity and of the higher energy values; preliminary results agree with our previsions.

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