

## *Short Communication*

# Norcaradiene–Cycloheptatriene Substituted in Position 7: Investigation of the Valence Isomerization Equilibrium

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**Summary.** The valence isomerism of a series of noncaradiene–cycloheptatriene compounds is investigated. Geometry and energy calculations allow to explain the nature of the transitions. Peculiarities of equilibrium shifts between different structures depending on the substituent at position 7 ( $X = \text{CH}_3$ ,  $\text{NH}_2$ ,  $\text{CHO}$ ,  $\text{CN}$ ) are discussed. The nature of the interaction between the substituent  $X$  and the ring ( $\sigma$ - or  $\pi$ -interaction) is investigated.

**Keywords.** Norcaradiene–cycloheptatriene; Valence isomerism; Electronic structure.

### Norcaradiene–Cycloheptatrien mit Substituenten in Position 7: Untersuchungen der Valenzisomeriegleichgewichte (Kurze Mitt.)

**Zusammenfassung.** Es wurden Gleichgewichte zwischen Norcaradien und Cycloheptatrien mit Hilfe der semiempirischen Methoden MNDO und AM1 untersucht. Die Elektronendichteverteilungen und  $\Delta H_f$ -Werte der untersuchten Verbindungen werden in Abhängigkeit der Substituenten diskutiert.

### Introduction

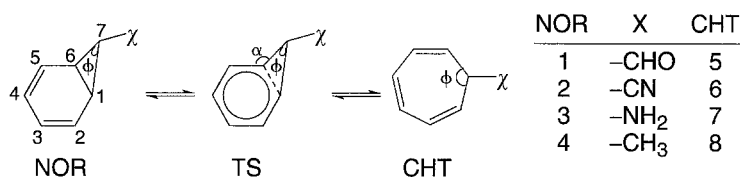
Non-catalytic thermal rearrangements *via* transition states (TS) were studied extensively by suitable experiments. Among them there is the cycloheptatriene (CHT)–norcaradiene (NOR) equilibrium [1, 2]. A few articles are dealing with theoretical studies of cyclopropane ring opening [3–6]. Special attention is paid to the nature of the cyclopropane ring bonds. It has been shown that the cyclopropane ring properties depend substantially on the  $\sigma$ - and  $\pi$ -interactions between the substituent  $X$  and the ring.

*Ab initio* and MNDO molecular orbital calculations on substituted cyclopropyl compounds have been carried out (Ref. [7]). The effect of substitution and its geometrical consequences were analyzed in terms of molecular orbital interactions. It can be shown that the cyclopropyl group is more electronegative than 2-propyl; hence,  $\sigma$ -donors stabilize the ring whereas  $\sigma$ -acceptors destabilize it.  $\pi$ -Acceptors

produce specific stabilization and geometrical effects, and strong  $\pi$ -donors ( $\text{NH}_2$  and  $\text{O}^-$ ) are also able to stabilize cyclopropane. Using the MNDO method and *Hartree-Fock* calculations with minimal basis (STO-3G), the authors of Ref. [8] studied the equilibrium between cycloheptatriene and norcaradiene. The valence tautomerization is characterized by an asymmetric double-well potential. The values of 10 kcal/mol and 5 kcal/mol were found for the energy barriers of the direct and reverse reactions, respectively.

A theoretical study of the substituted norcaradiene with some strong electron withdrawing groups at position 7 (7-cyano, 7,7-dicyano and 7,7-difluoro) was carried out by means of *ab initio* methods and the charge density topological analysis at the 6-31G\*, 6-31G\*\* and MP2/G-31G\*\* levels of theory [9]. The calculated relevant cross sections of the potential energy surface have shown that the 7,7-dicyanonorcaradiene, in which two CN groups act as  $\sigma$ -acceptor and  $\pi$ -acceptor, behaves as a stable neutral homoaromatic compound. For a comparison the destabilized 7,7-difluoronorcaradiene in which fluorine substituents act as  $\sigma$ -acceptor and  $\pi$ -donor was studied as well.

In the present communication, the peculiarities of the *NOR-CHT* transition following the scheme given below are considered.



Substituents with opposite donor-acceptor functions were selected with the aim of studying the nature of the influence of  $X$  on the cyclopropane ring opening reaction. The  $\text{CH}_3$  group is taken as  $\sigma$ -donor,  $\text{NH}_2$  acts as  $\pi$ -donor and  $\sigma$ -acceptor. The groups CN and CHO are both  $\pi$ - and  $\sigma$ -acceptors. These substituents alter the electron state of the cyclopropane ring affecting the equilibrium shown.

## Results and Discussion

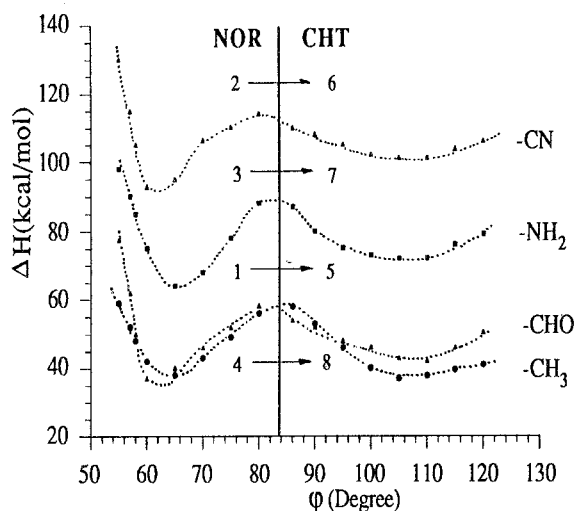
Optimized geometry parameters calculated by the MNDO and AM1 methods for the atoms of the ring are given in Table 1. From the table one can see that bond lengths remain mostly unchanged upon changing the hamiltonian.

There may be differences in the values of the angles  $\phi$  and  $\alpha$  however. For instance, stable structures of *NOR* compounds (1-4) are observed at  $\phi = 60^\circ$  (according to both methods applied). At the same time, the most stable states of *CHT* compounds (5-8) are achieved at  $\phi = 109^\circ$  (MNDO) or at  $\phi = 112^\circ$  (AM1). The latter gives lower values for  $\Delta H_f$ , too. The valency angle  $\phi$ , varying in the limits of  $55^\circ$ - $130^\circ$ , is chosen as a reaction coordinate. In Fig. 1, the energy profile of the reaction at the moment of the cyclopropane ring opening is shown.

As can be seen from the picture, for all *NOR*-systems there exist energy minima at  $\phi = 60$ - $62^\circ$  which do not depend on the nature of the substituent  $X$ . The increase of  $\phi$  causes  $\Delta H_f$  to increase for all systems, under consideration. So, if  $X = \text{CN}$ , the maximum of  $\Delta H_f$  (transition state) is achieved at  $\phi = 86^\circ$ , and the distance  $\text{C}_1 \cdots \text{C}_6$  is equal to 1.94 Å. For  $X = \text{CHO}$ , the critical value of  $\Delta H_f$  is achieved at

**Table 1.** Geometrical parameters, dipole moments and heats of formation ( $\Delta H_f$ ) calculated for compounds 1–8

Hamiltonian		C1–C2 (Å)	C2–C3 (Å)	C1–C6 (Å)	C1–C7 (Å)	C6–C7 (Å)	$\varphi$ (°)	$\alpha$ (°)	IP (eV)	DM (Debye)	$\Delta H_f$ (kcal/mol)
1	MNDO	1.45	1.36	1.53	1.52	1.52	61.8	115.4	9.08	2.42	37.02
	AM1	1.46	1.35	1.52	1.52	1.52	60.0	121.4	9.12	2.39	20.78
2	MNDO	1.51	1.36	1.56	1.52	1.52	61.7	116.3	9.22	2.97	92.81
	AM1	1.46	1.35	1.52	1.52	1.52	60.0	121.4	9.26	3.10	82.56
3	MNDO	1.48	1.36	1.56	1.52	1.52	61.7	116.6	8.85	1.33	64.32
	AM1	1.46	1.35	1.53	1.52	1.52	60.4	121.4	8.81	1.28	53.84
4	MNDO	1.49	1.35	1.51	1.51	1.51	60.0	121.4	8.86	0.12	37.47
	AM1	1.46	1.35	1.53	1.51	1.51	60.9	121.4	8.75	0.35	44.11
5	MNDO	1.34	1.34	2.63	1.51	1.50	121.6	129.8	8.63	2.45	41.86
	AM1	1.34	1.44	2.48	1.49	1.49	112.7	126.1	9.02	2.72	11.50
6	MNDO	1.35	1.43	2.66	1.51	1.53	121.8	129.9	8.96	2.85	101.1
	AM1	1.34	1.44	2.58	1.49	1.49	119.9	128.2	8.96	3.02	76.42
7	MNDO	1.34	1.34	2.66	1.51	1.50	124.2	129.8	8.45	1.38	73.06
	AM1	1.34	1.44	2.47	1.50	1.50	110.8	126.0	8.80	1.22	48.25
8	MNDO	1.34	1.34	2.62	1.52	1.50	120.2	129.4	8.35	0.29	37.76
	AM1	1.34	1.44	2.47	1.49	1.49	112.0	130.2	8.73	0.16	35.51

**Fig. 1.** Potential energy profile depending on the angle  $\phi$  (compounds 1/5, 2/6, 3/7, 4/8)

$\phi = 84^\circ$  ( $r_{C_1 \dots C_6} = 1.93 \text{ \AA}$ ).  $\sigma$ - and  $\pi$ -donor groups like  $\text{CH}_3$  and  $\text{NH}_2$  form TS at  $\phi = 82^\circ$  ( $r_{C_1 \dots C_6} = 1.92 \text{ \AA}$ ).

Further lengthening of the bond  $C_1-C_6$  stabilizes the *CHT* system. So, for  $\sigma$ - and  $\pi$ -acceptor groups  $\text{CHO}$  and  $\text{CN}$  the minima of  $\Delta H_f$  are reached at  $\phi = 108^\circ$  and  $\phi = 109^\circ$ , respectively. For  $X = \text{CH}_3$  and  $X = \text{NH}_2$ , these values amount to  $108^\circ$  and  $107^\circ$ . Thus, the substituents influence the *TS* according to their electronic properties. For the compounds discussed here there exist two possibilities of reaction starting from the transition state: to return to the adducts or to pass on to the final

product of the *CHT* ring opening. Calculations show that for the system with  $X = \text{CHO}$  it is easier to return to the initial state because the activation barrier for the direct reaction (17 kcal/mol) is higher than that for the reverse one (14.2 kcal/mol). In contrast, the direct reaction is more profitable when  $X = \text{NH}_2$ . To fix the point, the electron density distribution in the system is considered. The analysis of the frontier orbitals shows the HOMO to be the nonbonding orbital.

Orbital population and stability of the resulting cyclopropane ring depend on the nature of the substituent  $X$ . The additional settlement of the HOMO ( $X = \text{CH}_3$ ,  $\text{NH}_2$ ) causes the antibonding tendency among the interacting atoms of the cyclopropane ring to increase and therefore an easier transition to *CHT*. Electron density acceptance from this orbital ( $X = \text{CHO}$ ) will strengthen the cyclopropane ring bonds.

Therefore, it may be supposed that in the process of the ring opening the doubly occupied HOMO is splitted into two nonbonding orbitals corresponding to electrons with  $\alpha$  and  $\beta$  spins. It results in an instable biradical particle formation with small singlet-triplet splitting in the ground state. The analysis of effective charges on atoms in some critical points of the system shows that the redistribution of the charges occurs mainly at the atoms C1, C6, and C7. The negative charge increase at the atoms C1 and C6 at  $\phi = 80^\circ$  shows that the biradical particle may exist in the TS. At this point, the system begins its rebuilding with respect to the *NOR-CHT* transition. The process splitting of old bonds and formation of new ones is shown in Fig. 2. As can be seen from the Figure, these processes proceed synchronously. At the point of the C1–C6 bond breaking, a new double bond tends to shift to the atoms C3=C4.

The analysis of the charge distribution shows that for  $\phi = 62^\circ$  (*NOR* systems) the HOMO includes orbitals belonging to the atoms forming  $\pi$ -bonds in the cyclopropane ring. The *NOR-CHT* transition changes the structure of the HOMO/LUMO orbitals. After the cyclopropane ring opening, new atoms (C1, C6) are included into the  $\pi$ -conjunction, and the contribution of the atoms C2 and C5 grows. Small differences in the HOMO energies may be observed for the electron donor ( $X = \text{NH}_2$ ,  $\text{CH}_3$ ) and electron acceptor ( $X = \text{CHO}$ ) substituents. When  $X = \text{CHO}$ ,

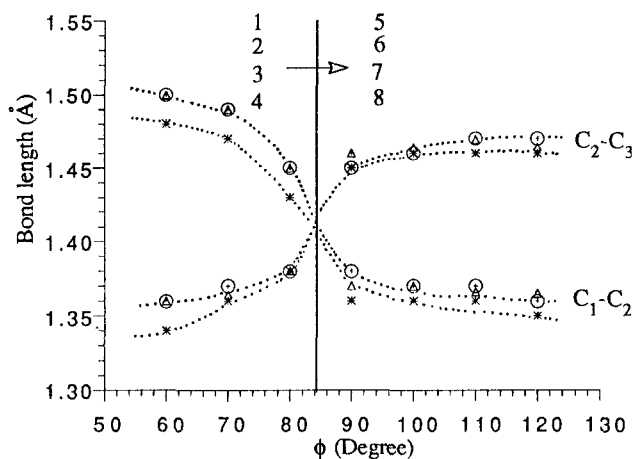


Fig. 2. Bond lengths dependence on the value of the angle  $\phi$

the HOMO energy is a bit lower; this tells in favour of the higher stability of the system with the substituent mentioned.

## Methods

We used standard parameters [10, 11] and programs [11, 12] for the MNDO calculations. All geometries were optimized at the SCF level employing the *Davidon-Fletcher-Powell* algorithm [13, 14] for minima and gradient norm minimization [15] for transitional state. A force constant analysis was performed for all MNDO SCF stationary points. The AM1 [16] calculations were carried out by means of the MOPAC program (version 5.0, QCPE No. 455).

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