



Reinvestigation of homoaromaticity of cyclohepta-1,3,5-triene



Preeti Saini, Parul Bhasin, R.K. Bansal*

Department of Chemistry, The IIS University, Jaipur 302 020, India

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ABSTRACT

A reinvestigation of the homoaromaticity of cyclohepta-1,3,5-triene has been done at the DFT (B3LYP/6-31+G*) level. The determination of the aromatic stabilization energies based on the hypohomodesmotic reactions gives either too high value ($-19.58 \text{ kcal mol}^{-1}$ using ethane as the hydrogen donor molecule) or too low values ($-0.46 \text{ kcal mol}^{-1}$ using cycloheptane or $-4.27 \text{ kcal mol}^{-1}$ using cyclopentane molecules as the hydrogen donor molecules), as the ring strains on the two sides of the reactions are not compensated. The isomerisation reaction of methylenecyclohepta-1,3-diene to 1-methylcyclohepta-1,3,5-triene gives a value of $-10.68 \text{ kcal mol}^{-1}$ as the isomerisation energy. Investigation of the valence tautomerization of cyclohepta-1,3,5-triene to norcaradiene and back to cyclohepta-1,3,5-triene reveals that a dynamic equilibrium exists between the two valence tautomers due to small activation energy barriers, which causes strong interactions between the π orbitals of the triene moiety and the $-\text{HC}-\text{CH}_2-\text{CH}-\sigma$ orbitals. The NBO analysis of the two valence tautomers and the transition structure involved therein support these interactions. The Frontier Molecular Orbitals of cyclohepta-1,3,5-triene, norcaradiene and the transition structure depict unambiguously the formation of the annular electron cloud, which confers homoaromatic character on cyclohepta-1,3,5-triene.

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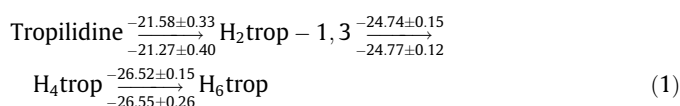
1. Introduction

The molecule of cyclohepta-1,3,5-triene (tropilidene) may perhaps be having the unique distinction of being the subject of the highest number of claims and counter-claims about its homoaromatic stabilization. Thiele for the first time in 1901 attributed the weakly acidic character of the methyl protons of cycloheptatriene to a partial 1,6-interaction conferring “benzene like character” [1]. Doering et al. termed cycloheptatriene as “mono-homobenzene”, and supported the concept of 1,6- π electrons interaction, although its structure was assumed planar incorrectly [2,3].

On the basis of thermochemical and structural evidence, Rogers et al. concluded that a stabilization energy of ca. 6 kcal mol^{-1} of cyclohepta-1,3,5-triene comes mainly from homoaromatic delocalization across the sp^3 carbon [4]. Most recently, Schleyer and co-workers [5] determined various magnetic properties, namely magnetic susceptibility exaltation, NICS values and anisotropy of the current-induced density (ACID) of cyclohepta-1,3,5-triene and its valence-isomer, norcaradiene and concluded that cyclohepta-1,3,5-triene is a neutral homoaromatic system, although norcaradiene does not display aromatic character. However, the transition structure involved in the electrocyclization of the former to the latter is highly aromatic in accordance with the pericyclic mechanism. On the contrary, Conrow [6] attributed homoaromaticity

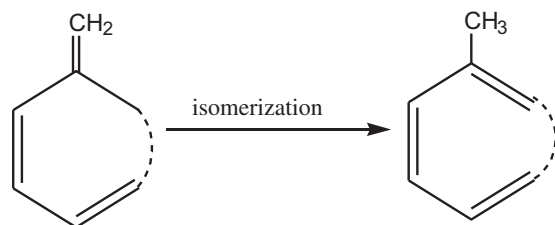
only a minor stabilizing role on the basis of a small $\Delta G_{\text{isom}}^\circ$ in favor of 2,3,7,7-tetramethylcyclohepta-1,3,5-triene than its isomer, 1-methylene-2,6,6-trimethylcyclohepta-2,4-diene. Williams et al. calculated two-centre energy partitioning term for the molecular orbitals of cyclohepta-1,3,5-triene molecule at the semiempirical MNDO and AM1 levels and concluded that there was no appreciable homoaromatic stabilization across the sp^3 carbon atom [7]. Lew and Capon [8] also came to the same conclusion on the basis of electrophilic addition reaction of isomeric cycloheptatrienols. However, Herndon and Párkányi [9] supported homoaromatic stabilization on the grounds of structure resonance theory calculations. Cremer and co-workers [10,11] carried out ab initio calculations and interestingly were cautious in their postulation; they suggested that although the triene part of the seven-membered ring is flattened resulting in the improved π -delocalization and consequently stabilization of cycloheptatriene, it is not necessary to invoke homoaromaticity for it.

Enthalpies of stepwise hydrogenation of polyenes and cyclopolyenes reveal stabilization resulting from the delocalization of the π electrons. Conn et al. [12] reported experimental values of the stepwise hydrogenation of tropilidene obtained in the gas phase at 355 K. These values are shown above the arrows in the following equation.



* Corresponding author. Tel.: +91 141 2651030; fax: +91 141 2652730.

E-mail address: bansalrk43@yahoo.com (R.K. Bansal).

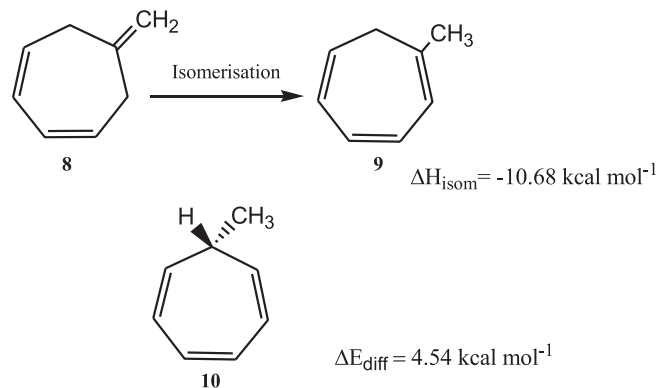


Scheme 1. Isomerisation of non-aromatic methylene derivative to aromatic methyl derivative.

These values agree well with the data (shown below arrows in Eq. (1)) determined calorimetrically using glacial acetic acid [13] after making solvent correction [14].

Isodesmic reactions were introduced by Pople [15] as “the examples of (hypothetical) chemical changes in which there is retention of the number of bonds of a given formal type (C–H, C–C, C≡C) but with a change in their formal relation to one another.” The quantum and thermochemical errors cancel, so “the energies of isodesmic reactions measure deviations from the additivity of bond energies.” Difference of the enthalpies obtained from the isodesmic reaction(s) and independently measured heats of formation gives a very good approximation of the ring strain or the resonance energy. Although isodesmic reactions are not a substitute for quantum mechanical calculations of the energies, they have been used conveniently for the estimation of ring strain and conjugation energies of a large number of systems without much computational costs [16,17]. Following this approach, Rogers et al. [4] calculated 6 kcal mol⁻¹ as the stabilization energy of cyclohepta-1,3,5-triene at the MM2ERW level.

Recently Schleyer and Puhlhofer [18] reported a simple and computationally inexpensive method for determining resonance energies (RE). This method is based on determining isomerisation energy (ISE) of methylene derivatives of a non-aromatic system to its methyl derivative of the aromatic system (Scheme 1). The



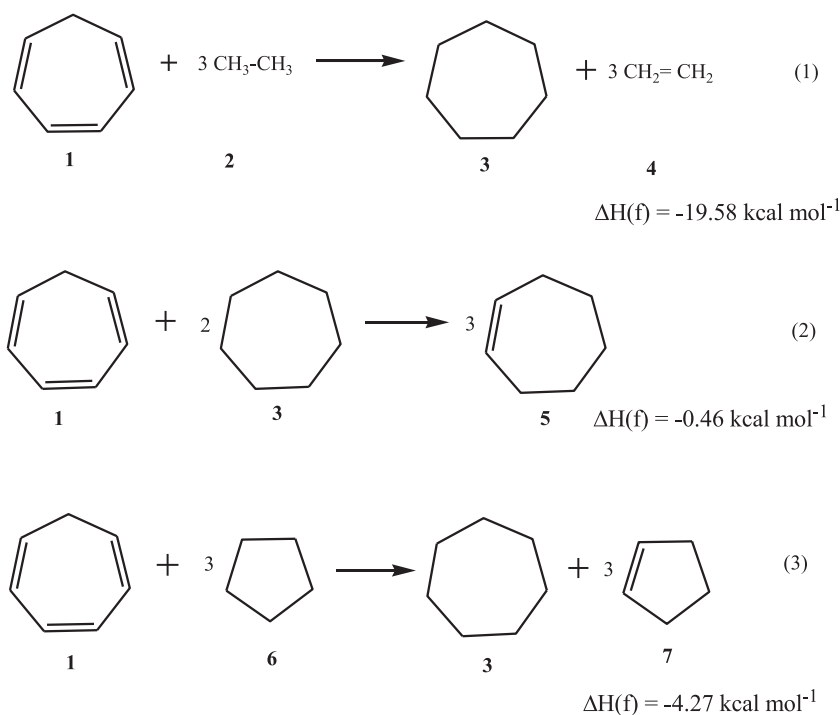
Scheme 3. Isomerisation of methylenecyclohepta-1,3-diene to 1-methylcyclohepta-1,3,5-triene.

ISE so obtained compared well with the resonance energies of the corresponding aromatic systems.

By following this approach, a resonance energy of -9.8 kcal mol⁻¹ was determined as the stabilization energy of cyclohepta-1,3,5-triene at the B3LYP/6-311+G(d,p) level. However, in this approach, contribution of the hyperconjugation has not been taken into account.

Although these studies either establish cyclohepta-1,3,5-triene to be homoaromatic or otherwise, the question, “why is cyclohepta-1,3,5-triene homoaromatic at all?” has not been addressed to.

In order to get answer to this question, the process of valence tautomerization [19] of cyclohepta-1,3,5-triene to bicyclo[4.1.0]hepta-2,4-diene (norcaradiene) and back to the former and the FMOs involved therein need to be investigated and analyzed. In the present studies, we first determined stabilization energy of cyclohepta-1,3,5-triene by the methods of isodesmic reaction and isomerisation and then analyzed the FMOs involved in the valence tautomerization process along with natural bond orbital (NBO) analysis.



Scheme 2. Hypohomodesmotic reactions of cyclohepta-1,3,5-triene at the B3LYP/6-31+G(d) level.

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