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Umbrella inversions of cyclononatetraenylidenes at *ab initio* and DFT

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Abstract

Barriers of umbrella inversions for *non-planar* triplet 2-, 3-, 4-, or 5-X-2,4,6,8-cyclononatetraenylidenes, inverting through *planar* transition states, appear roughly four times lower in energy than their corresponding singlet states, at *ab initio* and DFT levels (X = H, F, Cl, Br). Relative activation energies for these racemization ($\Delta E_r^{\#}$), follow electronegativity for both singlet and/or triplet states of 2-X-2,4,6,8-cyclononatetraenylidenes (F > Cl > Br > H). This trend does not hold for species with halogens further away from the carbenic center: 3-, 4-, or 5-X-2,4,6,8-cyclononatetraenylidenes. Frequency calculations show one negative force constant for all *planar* species (transition states), while they appear positive for *non-planar* minima.

Keywords: Carbene; Singlet; Triplet; Racemization; C_9H_8; C_9H_7Br; C_9H_7Cl; C_9H_7F; 2-, 3-, 4-, or 5-Halo-2,4,6,8-cyclononatetraenylidenes; *Ab initio*; DFT

1. Introduction

Group 14 divalent species continue to attract attention as important reactive intermediates [1–5]. Among them, cyclic completely conjugated carbenes are of particular interest to organic chemists [6–9]. The potential for alternating electrophilicity and/or nucleophilicity adds more theoretical importance to the singlet states of cyclic conjugated carbenes (Scheme 1) [6]. The most interesting and the largest monocyclic, conjugated, *non-planar*, singlet and triplet carbenes, yet generated are the singlet and triplet 2,4,6,8-cyclononatetraenylidenes (**1s-H** and **1t-H**, respectively) [10]. One may describe **1s-H** as a σ^2 or a π^2 carbene (Scheme 2) [6]. When portrayed as a π^2 carbene, it appears *planar*, with a C_{2v} symmetry, showing one negative force constant (a transition state, **1*s-H**). It converts to a lower energy 1,2,4,6,8-cyclononapentaene, which is a *non-planar* allene with a C_2 symmetry (Scheme 3). When C_9H_8 is described as a σ^2 carbene, it appears *non-planar*, with either a C_1 or a C_s symmetry. Neither C_1, nor C_s isomers shows any negative force constant. They both turn out to be *non-planar* intermediates, and more stable than the *planar* C_{2v} isomers.

We have already reported some studies on the group 14 divalent species, including the generation of **1s-H** and **1t-H**, and established the *planar* C_{2v} forms of the latter carbenes, **1*s-H** and **1*t-H**, respectively, as transition states for mirror image conversions of halogenated allenic C_9H_8 [6,8,11–19]. In addition, we have determined the kinetic isotope effects for the dimerization and cyclization of the resulting C_9H_9 radical, but have not yet been able to reach for the possible racemizations of these carbenes experimentally. This required a computational study on the umbrella inversions of four series of singlet *vs.* triplet 2-, 3-, 4-, or 5-X-2,4,6,8-cyclononatetraenylidenes, at *ab initio* and DFT levels, presented in this manuscript (X = H, F, Cl, Br) (Fig. 1).

2. Computational methods

Racemizations of four series of *non-planar* 2-, 3-, 4-, and 5-X-C_9H_7 cyclic conjugated carbenes (**1X**, **2X**, **3X**, and **4X** to **1′ X**, **2′X**, **3′X**, and **4′X**, respectively) are calculated at HF/STO-3G, HF/6-31G*, MP2/6-31G*, B3LYP/6-31G*,

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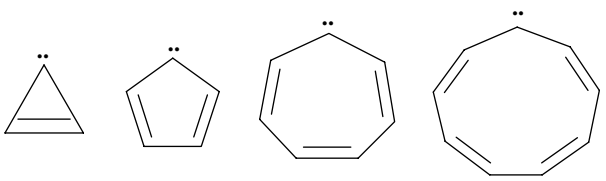
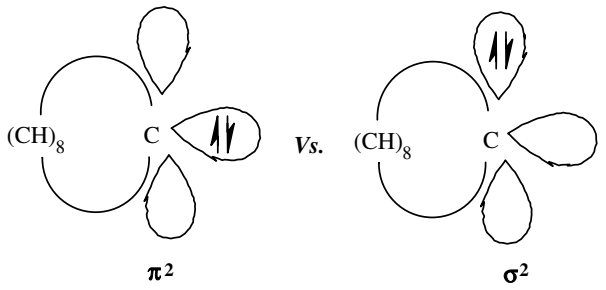


Scheme 1.



Scheme 2.

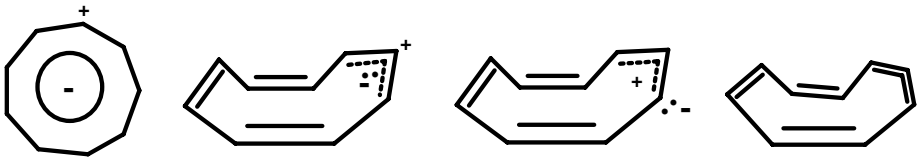
B3LYP/6-311+G*, B3LYP/6-311++G** levels of theory (where X = H, F, Cl, and Br) (Fig. 1). Geometry optimizations are carried out through HF and B3LYP [20,21] methods using 6-31G*, 6-311+G*, and 6-311++G** basis sets of the *Gaussian* 98 system of programs [22]. To assess the performance of this approach, all species are computed at higher theoretical levels; in a way that HF/STO-3G outputs are used as inputs for the HF/6-31G*. Also, HF/6-31G* outputs are used as inputs for the B3LYP/6-31G* and MP2/6-31G*. Consequently, B3LYP/6-31G* outputs are used as inputs for the B3LYP/6-311+G*. Finally, the outputs of the later methods are used in B3LYP/6-311++G** calculations. These are done in order to obtain rather highly accurate values for activation electronic energies ($\Delta E^{\#}$), enthalpies ($\Delta H^{\#}$), and Gibbs free energies ($\Delta G^{\#}$). For calculating energy minima the keyword "FOPT" and for transition states the keyword "FOPT (QST3)" is employed. In order to confirm the nature of the stationary species and evaluate the activation energy barriers between valence tautomers, frequency calculations with the keyword "FREQ = NORAMAN" are carried out at both HF/6-31G* and DFT (B3LYP/6-31G*, B3LYP/6-311+G*, and B3LYP/6-311++G**) levels of theory. The geometry was adjusted until a stationary point on the potential surface was found. Here, the Berny algorithm was employed for all minimizations using redundant internal coordinates [23]. Schlegel QST3 method is employed for determining reaction paths, minima, and transition state geometries [24]. Starting with an approximate path represented by *N* points, the path is iteratively relaxed until one of the *N* points reaches the transition state, the end points optimize to minima and the remaining points converged to a second order approximation of the steepest descent path. The method appears to be more reliable than conventional transition state optimization algorithms, and requires only energies and gradients, but not second derivative calculations.

All minima and singlet transition states are calculated with spin-restricted wave function. For minimum state structures, only real frequency values (with a positive sign), and for the transition states, only a single imaginary frequency value (with a negative sign) is accepted. Minima are calculated with spin-restricted wave function. Triplet transition states are calculated using the UHF, UMP2, and UB3LYP formalisms. Thermodynamic functions, obtained through frequency calculations, are multiplied by Hehre et al. [25] scaling factor of 0.89 for HF/6-31G*. Also, they are multiplied by 0.99 scaling factor of Rauhut and Pulay [26] for B3LYP/6-31G*, B3LYP/6-311+G*, and B3LYP/6-311++G**. Nevertheless, scaling factors fitted to observe (an-harmonic) frequencies may deviate from unity even for exact calculations [26]. Here, a set of molecules containing similar motifs are treated together, where they benefit from similar scaling.

3. Results and discussion

In this section, we begin with listing our results followed by their discussions. Four series of carbenic transition states, including cyclic, *planar*, singlet 2-, 3-, 4-, or 5-X-2,4,6,8-cyclononatetraenylidenes (**1*X**, **2*X**, **3*X**, and **4*X**, respectively), are characterized at 6 levels of theory: HF/STO-3G, HF/6-31G*, MP2/6-31G*, B3LYP/6-31G*, B3LYP/6-311+G*, and B3LYP/6-311++G**, for X = H, F, Cl, Br (Fig. 1). The ball-and-stick geometries of the molecules of the molecules optimized at the highest level of theory (B3LYP/6-311++G**) are shown in the supplementary (Fig. 2).

We discuss the possible involvement of these *planar* **1*X**, **2*X**, **3*X**, and **4*X** transition states in the umbrella inver-



C_{2v} carbene (TS, planar) | **Cs carbene (Min, non-planar)** | **C_1 carbene (Min, non-planar)** | **C_2 allene (Min, non-planar)**

Scheme 3.