Steric effects on acyclic diaminocarbenes *vs*. their abnormal cyclic saturated and unsaturated analogues, at DFT

Mohammad Zaman Kassaee [1,*] Neda Khorshidvand [2]

[1] Department of Chemistry, Tarbiat Modares University

ABSTRACT

We used DFT calculations (M06/6-311++G** level) to attain Steric effects on the multiplicity, stability, and reactivity of acyclic diaminocarbene 1_R and its saturated 2_R and unsaturated cyclic 3_R diaminocarbenes in normal and abnormal states. Substituent groups are H, Me, i-Pr, t-Bu. All optimized structures are stable singlet state. Cyclization and aromaticity decrease nucleophilicity (N), proton affinity (PA) and increase the singlet–triplet energy gaps (ΔE_{S-T}) and HOMO-LUMO energy gap (ΔE_{H-L}). In abnormals, ΔE_{H-L}, ΔE_{S-T} decrease and N increase than normal (except acyclic form).For better result on carbene properties, we used 3 series of isodesmic reactions that it is shown stability of carbene structures on cyclic and heterocyclic and unsaturated. It is determined that cyclic carbene stability increase with increase of substitution size. Heteroatom in linear or acyclic structure causes carbene stability that this stability decrease with substitution size increase on heteroatom but in saturated and unsaturated cyclic structures, large substitution on heteroatom causes its corresponding carbene stability.

Keywords: DFT, diaminocarbene, stability, isodesmic reaction

1. INTRODUCTION

Carbenes are divalent species have two covalent bonds and two non-bonding electrons with either antiparallel or parallel spins, singlet and/or triplet states.[1] The stability of carbenes increase because of present of Nitrogen in carbene center neighboring, because of mesomeric effects of amino substituents the first stable singlet cyclic diaminocarbene (I) were stable in 1991.[2]

Alder *et al*. synthesized the first acyclic diaminocarbene (3-*i*pr) In 1996.[3] Also He studied through a theoretical study of his stable carbenes.[4] Alder, Heinemann and Thiel studied on saturated and unsaturated cyclic diaminocarbenes.[5-13] Kassaee 's group studied on the acyclic diaminocarbene to probe the effect of π-donor/σ-acceptor (NH) on the singlet–triplet energy gap ($\Delta E_{S–T}$).[2] We used M06 method for steric effect study and compare in linear, cyclic saturated and unsaturated diaminocarbenes with thermodynamic factors and isodesmic reactions.(Fig.1)

2. COMPUTATIONAL METHODS

All optimized structures are carried out with the Gaussian98 package.[14] using the M06/6-311+G** Pople's basis sets [15] and harmonic vibrational frequencies were calculated at the same level of theory to establish the nature of the stationary points obtained. The nucleophilicity index (*N*) has been calculated as the energy difference between the HOMO energy of the compound and that of tetracyanoetylene (E_{HOMO} (TCNE), $N = E_{HOMO} - E_{HOMO}(TCNE)$) as was proposed by Domingo *et al*.[16] and was successfully used earlier for carbenes as well [17]:

The global electrophilicity, ω,[18] is also calculated following the expression, $\omega=(\mu^2/2\eta)$, where μ is the chemical potential ($\mu= (E_{HOMO} - E_{LUMO})/2$) and η is the chemical hardness ($\eta=E_{LUMO}\_E_{HOMO}$).[19,20]

www.1mrss.ir