Research paper

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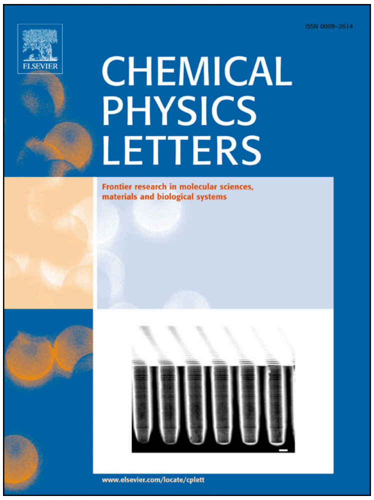

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Research paper

A LFER analysis of the singlet-triplet gap in a series of sixty-six carbenes

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ABSTRACT

Ab initio G4 calculations have been performed to investigate the singlet-triplet gap in a series of 66 simple carbenes. Energies and geometries were analyzed. An additive model has been explored that include four interaction terms. An abnormal behavior of the cyano group has been found. The ^{13}C absolute shieldings of the carbenic carbon atom were calculated at the GIAO/B3LYP/6-311++G(d,p).

Keywords: Carbenes, singlet-triplet gap, G4, excluded regions, ^{13}C NMR, GIAO

1. Introduction

The existence in carbenes of two spin states, singlet and triplet, is of paramount importance and for this reason has been extensively studied experimental and theoretically [1,2,3,4,5]. As hydrogen bond acceptors (HBA), singlets having a lone-pair are rather good HBA [6], while triplets with their solitary electrons are biradicals with poor HBA abilities [7]. Most the cited books on carbenes and on *N*-Heterocyclic Carbenes (NHC) discuss this aspect. For recent works not included in these books, see [8,9]. For most simple hydrocarbons, the triplet is the ground state and the singlet the excited state, but this depends on the phase (gas phase vs. solvents) and on the substituents.

The present work is related to a field known by different acronyms: LFER (Linear Free Energy Relationships) [10], QSAR (Quantitative Structure Activity Relationships) [11], Correlation Analysis in Chemistry [12] and Extra Thermodynamic Relationships [13].

The most important contributions considering the aims of the present work can be found in Bertrand book [2] and in a series of papers by Gronert, Keefe and O'Ferrall [14,15,16]. In the first one, Fleming's classification of substituents [17] is used to predict that X-substituents (p-electron donors, such as OR, NR_2, F, Cl) should stabilize the singlet while Z-substituents (p-electron acceptors, NO_2, CN) and C-substituents (conjugating, like C_6H_5) should stabilize the triplet. Fleming, in his book [17], considers that the alkyl groups (CH_3) belong to the X-type by hyperconjugation. LFER using Hammett (for aryl carbenes) or Taft (for simple carbenes) have been used for homogeneous series [18,19,20,21]. Sauers analyzes the stability of singlet carbenes using linear free energy methods with moderate success [22].

2. Methods

All geometries were fully optimized at the G4 computational level [23] (Table S1 of the Supporting Information). Table S2 reports the corresponding values of the singlet-triplet gap, ΔE_{ST}. The vibrational normal modes within the G4 framework were checked to confirm that the