Computational and Theoretical Chemistry 1059 (2015) 18–26

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

The effect of fullerene and some electron donating/withdrawing substituents on the molecular orbitals, strength and the nature of C=N bond in a number of RCH=NR′ imines: A theoretical study

Farahnaz Maleki, Sadegh Salehzadeh *

Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran

ARTICLE INFO

Article history:
Received 7 December 2014
Received in revised form 6 February 2015
Accepted 6 February 2015
Available online 26 February 2015

Keywords:
Theoretical study
Imine
Fullerene
Electron donating/withdrawing
Anomeric effect

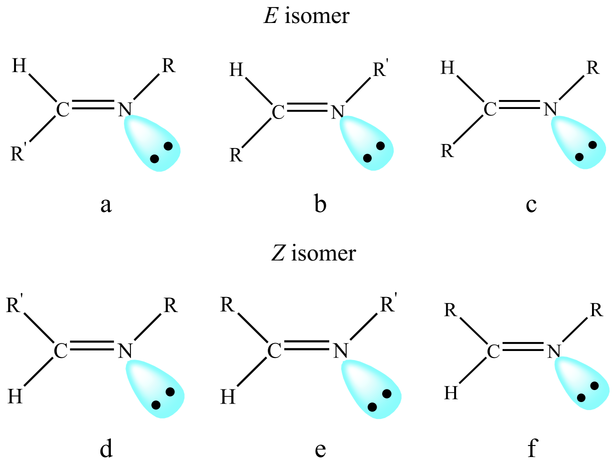
ABSTRACT

A theoretical study on the E and Z isomers of R—CH=N—R′ compounds (R = R′, R ≠ R′; R or R′ = CH_3, CF_3, ph or t-Bu) as well as E isomer of R—CH=N—CH_3 and CH_3—CH=N—R (R = $C_{60}H$ or $C_{60}CH$) molecules is reported. NBO analysis and DFT calculations were used to investigate the effect of R and R′ groups on the strength and the nature of C=N bond in above imines. The relative stabilities of R—CH=N—R′ and R′—CH=N—R isomers is also compared. Furthermore, in all compounds the type of π and π^* and also HOMO and LUMO molecular orbitals and the energy gap between them is studied. Also three types of anomeric effect in imine compounds having CH_3, CF_3, ph or t-Bu substituted groups have been assigned.

1. Introduction

The imines with general formula $R^1R^2C{=}NR^3$ are known also as Schiff bases, named after the German chemist, Hugo Schiff, who discovered the reaction in 1864 [1]. During the past decade, the imine compounds and their metal complexes have been the subject of numerous investigations, both experimentally and theoretically. A few examples of most important features of Schiff bases and/or their metal complexes are their catalytic [2–10] and biological activities [11–17], their application as sensors for the metal ions [18–27], as molecular switches [28–31], and also as anticancer agents [32–37].

Our research group has been interested in synthesis and characterization of Schiff bases and their metal complexes [38–44] and also in pure theoretical studies on their metal complexes [45–47]. The formation of [1 + 1] versus [2 + 2] Schiff base complexes [45,46] and the nature of metal-imine bond in some Schiff base complexes [47] have been studied in our group. Other researchers have been also reported some studies on the kinetics and mechanism of E/Z isomerization of imines and the substituent effects on structures and stabilities of imines [48–55]. The above studies mostly centered on the imines with either N-substituted or C-substituted C=N bond separately. However, in this paper we report the effect of substituent groups on the stability of imine compound and the nature of C=N bond where the substituents are attached to both the carbon and nitrogen atoms. Indeed, the purpose of the present work is to study the effects of fullerene (C_{60}) and electron donating/withdrawing substituents on the nature and strength of C=N double bond in R—CH=N—R′ compounds.



Scheme 1. The schematic representation of chemical structures of E and Z isomers of three types of imine compounds studied here when R and/or R′ are Me, Ph, t-Bu and CF_3.

---

* Corresponding author. Fax: +98 (81) 38380709.
E-mail address: saleh@basu.ac.ir (S. Salehzadeh).

http://dx.doi.org/10.1016/j.comptc.2015.02.005
2210-271X/

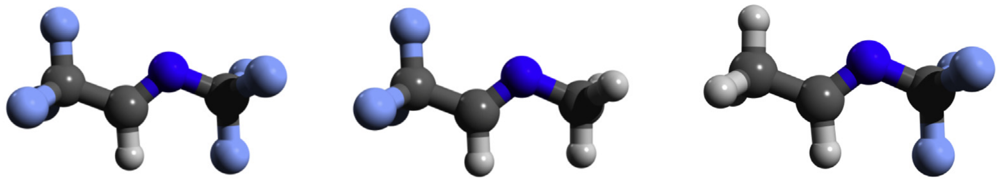
To achieve this, we considered the R and/or R′ groups as Me, t-Bu, Ph, CF_3 and also two derivatives of fullerene molecule including $C_{60}H$ and $C_{60}CH$. To gain more insight into substituent effects on the strength of C=N bond, the interaction energy between two R—CH and N—R′ fragments in R—CH=N—R′ compounds has been calculated. In addition, the origin of substituent effects is explored by means of natural bond orbital (NBO) and molecular orbitals analyses. Also the anomeric effect in imine compounds having R and R′ groups has been assigned.

2. Computational methods

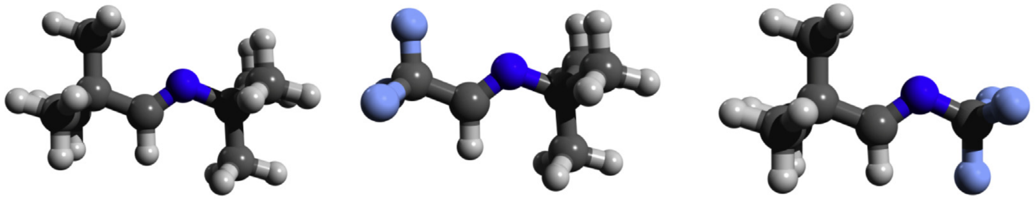
Calculations were carried out with the Gaussian09 program [56]. The DFT studies have been performed by means of B3LYP and the newly developed M06 [57–59] functional. The geometries of the E/Z isomers of R—CH=N—R′ (R, R′ = Me, Ph, t-Bu and CF_3) compounds have been optimized at the B3LYP and M06 levels with 6-311++G**, def2-TZVP and aug-cc-pVDZ basis sets. The single point calculations and NBO analysis were performed at the same level of theory.

The structures of compounds having fullerene moiety were fully optimized at the B3LYP and M06 levels using 6-31G** basis set and also at B3LYP/def2-SVP level of theory. Furthermore, in the case of fullerene containing compounds, the single point calculations and NBO analysis, were performed at B3LYP/6-311++G**//B3LYP/6-31G**, M06/6-311++G**//M06/6-31G** and B3LYP/def2-TZVP//B3LYP/def2-SVP levels of theory.

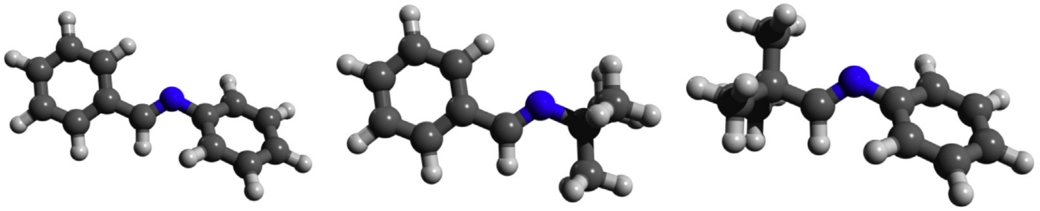
In all cases the vibrational frequency analyses, calculated at the same level of theory, indicated that the optimized structures are at the stationary points corresponding to local minima without any imaginary frequency. The interaction energy was calculated with the following equation:



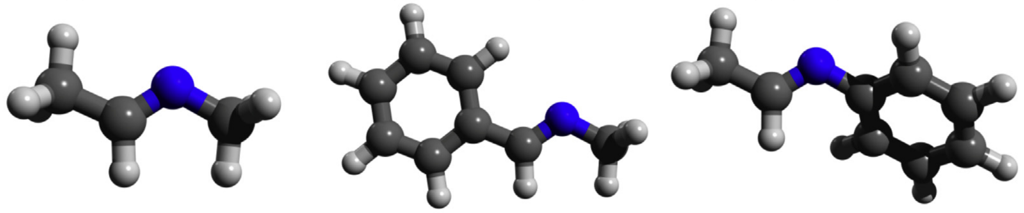
(E)-CF_3-CH=N-CF_3 **(E)-CF_3-CH=N-Me** **(E)-Me-CH=N-CF_3**



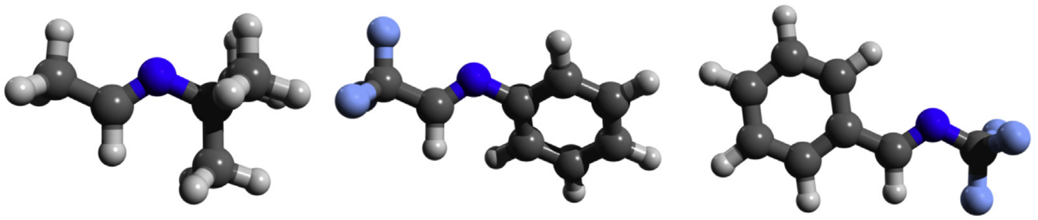
(E)-(t-Bu)-CH=N-(t-Bu) **(E)-CF_3-CH=N-(t-Bu)** **(E)-(t-Bu)-CH=N-CF_3**



(E)-Ph-CH=N-Ph **(E)-Ph-CH=N-(t-Bu)** **(E)-(t-Bu)-CH=N-Ph**



(E)-Me-CH=N-Me **(E)-Ph-CH=N-Me** **(E)-Me-CH=N-Ph**



(E)-Me-CH=N-(t-Bu) **(E)-CF_3-CH=N-Ph** **(E)-Ph-CH=N-CF_3**

Fig. 1. The optimized structures of (*E*)—R—CH=N—R′ compounds (R and/or R′ = Me, Ph, t-Bu and CF_3) at B3LYP/def2-TZVP level of theory.