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1,3-Dipolar cycloadditions. Part-XVI : Frontier molecular orbitals of *C*-aryl-*N*-methyl nitrones[1,2] – A DFT study

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Abstract : Molecular orbital calculations have been performed by DFT calculations using B3LYP theory and 6-31 G (d) level of approximation for *C*-(4-chlorophenyl)-*N*-methyl nitrone on the basis of its optimised geometry. The effect of substitutions on orbital energies have been deduced by comparison to other nitrones and 1,3-dipoles.

Keywords : *C*-(4-Chlorophenyl)-*N*-methyl nitrone, frontier molecular orbital energies.

Introduction

Huisgen[3] and coworkers led to the general concept of 1,3-dipolar cycloadditions (1,3-DCs) and proposed evidences in favour of concerted mechanism. On the other hand, Firestone[4] proposed his stepwise mechanism involving diradical intermediates to interpret the observed selectivities. However, a concerted transition state model has proved to be the accepted one in 1,3-DCs on account of its wide applicability.

Fukui[5] argued that the prediction of reaction rates and selectivities of 1,3-DCs can be performed by utilizing frontier orbitals on the basis of "the principle of narrowing of inter-frontier level separation". Thus, Houk[6] and coworkers reported a series of CNDO/2[7], INDO[7] and extended Hückel (EH)[8] molecular orbital calculations of several 1,3-dipoles and dipolarophiles to explain the origin of selectivities in 1,3-DCs[9]. However, these methods were semi-empirical and hence do not provide reliable orbital energies as measured by photoelectron spectroscopy[10,11], reduction potential and charge transfer studies[12]. They provide satisfactory relative orbital energies only while working with a narrow range of compounds. The DFT method is based solely on quantum mechanics and includes the effects of electron correlation via general functionals of electron density. So, the method can be exploited to achieve accuracy by a wider margin than semi-empirical and *ab initio* methods. The present communication reports DFT calculations of molecular orbital energies of *C*-aryl-*N*-methyl nitrones and their comparison to other 1,3-dipoles. The study is supported by the experimental UV spectral data of the nitrones under investigation.

Computational details :

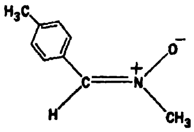
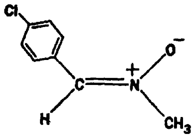
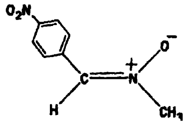
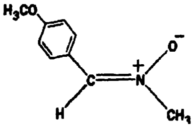
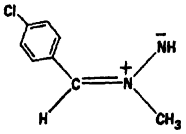
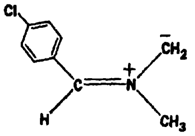
Optimization of the nitrone[13], frontier orbital energy calculations and generation of molecular orbital surfaces were performed by GAUSSIAN 2003 series of programs[14] along with the graphical user interface Gauss View 2003. The calculations were performed using Becke's three-parameter hybrid exchange functional[15] in combination with the gradient-corrected correlation functional of Lee, Yang and Parr[16] (B3LYP) using 6-31 G (d) basis set.

Results and discussion

Table 1 provides the HOMO and LUMO energies of the nitrones under investigation, azomethine ylide and azomethine imine.

Houk *et al.*[6] had estimated the frontier molecular orbital energies of *N*-*tert*-butylmethylene nitrone from its ionization potential, π-π* transition band and a reduced value of Δ ($-J_{ij}$ + $2K_{ij}$), where J_{ij} and K_{ij} are the coulomb and exchange integrals respectively which account for the differences in electron repulsion in the ground states and excited states[17]). The estimates were found to be in qualitative agreement with the calculations. Our previous communication[1] reported UV spectral absorption characteristics of few *C*-aryl-*N*-methyl nitrones in methanol. The absorption spectrum of *C*-(4-chlorophenyl)-*N*-methyl nitrone showed a strong band at 4.11 eV (λ_{max}

Table 1

Entry	1,3-Dipolar species	HOMO energy	LUMO energy (in Hartrees)	Difference (in Hartrees) (LUMO-HOMO)	Difference (in eV) (LUMO-HOMO)
1	*C*-(4-Methylphenyl)-*N*-methyl nitrone 	-0.197	-0.043	0 154	4 19
2	*C*-(4-Chlorophenyl)-*N*-methyl nitrone 	-0.209	-0.056	0 153	4 16
3	*C*-(4-Nitrophenyl)-*N*-methyl nitrone 	-0.229	-0.097	0.132	3 59
4	*C*-(4-Methoxyphenyl)-*N*-methyl nitrone 	-0.189	-0.037	0.152	4.14
5	*C*-(4-Chlorophenyl)-*N*-methyl azomethine imine 	-0.181	-0.444	0.137	3.73
6	*C*-(4-Chlorophenyl)-*N*-methyl azomethine ylide 	-0.158	-0.036	-0 122	3.32

*1 Hartree = 27.21 eV

= 302 nm, log ε_{max} : 4.00) and that of *C*-(4-nitrophenyl)-*N*-methyl nitrone at 3.71 eV (λ_{max} = 335 nm, log ε_{max} : 3.92). The DFT calculated HOMO-LUMO energy differences are 4.16 eV and 3.59 eV for these two nitrones respectively (Table 1, entries 2 and 3). The close correspondence of UV spectral absorptions and theoretically computed frontier orbital energy differences reveals that the consideration of ionization potential and electron repulsion factors can be circumvented by the assistance of DFT calculations.

The introduction of an electron withdrawing *para*-nitro group results in the decrease in HOMO orbital energy by 0.87 eV and that of the LUMO energy by 1.47 eV. As a consequence, the HOMO-LUMO energy gap gets lowered by 0.6 eV in *C*-(4-nitrophenyl)-*N*-methyl nitrone compared to *C*-(4-methylphenyl)-*N*-methyl nitrone (Table 1, entries 1 and 3). On the other hand, the electron donating groups show opposite effects. In case of *C*-(4-methoxy- phenyl)-*N*-methyl nitrone, the HOMO energy is raised by 0.22 eV and the LUMO energy by 0.16 eV (Table 1, entries 1 and 4). However, both electron withdrawing as well as electron donating groups lower the HOMO-LUMO energy gap in case of *C*-aryl-*N*-methyl nitrones. Thus, DFT calculations also support the fact that both electron-releasing and electron withdrawing groups should acce-lerate nitrone reactions. Although the frontier orbital energies of *C*-aryl-*N*-methyl nitrone calculated by semi-empirical methods, Hartree Fock Theory and DFT (using 6-31 G (d) basis set) calculations differ from each other, the qualitative overview of the orbital surfaces remain unaltered in all cases for a particular nitrone. Fig. 1 provides the DFT calculated orbital energy surfaces of *C*-(4-chlorophenyl)-*N*-methyl nitrone. The coefficient at oxygen is larger in the HOMO orbitals of *C*-aryl-*N*-methyl nitrones. Moreover, the node was found to be invariably between nitrogen and oxygen in all the nitrones under investigation. The LUMO orbital surface has a smaller oxygen coefficient with two nodes as shown in Fig. 1. The unequal magnitudes of the terminal coefficients are the keys to the explanation of regioselectivity in 1,3-DCs.

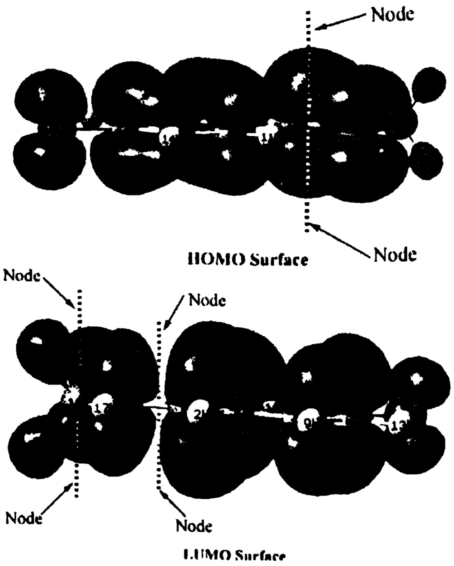


Fig. 1. Frontier molecular orbital surfaces of *C*-(4-chlorophenyl)-*N*-methyl nitrone.

Azomethine ylides are generated as transient intermediates and azomethine imines react readily with dipolarophiles or dimerize reversibly. This fact can be attributed to their narrow frontier orbital separation [3.73 eV in *C*-(4-chlorophenyl)-*N*-methyl azomethine imine, (Table 1, entry 5) and 3.32 eV in case of *C*-(4-chlorophenyl)-*N*-methyl azomethine ylide (Table 1, entry 6)] compared to nitrones (4.16 eV in case of *C*-(4-chlorophenyl)-*N*-methyl nitrone). Thus, the concept of frontier orbital separations can be exploited to assess the relative reactivities of 1,3-dipoles. Fig. 2 and Fig. 3 provide the DFT calculated frontier orbital surfaces of azomethine imines and azomethine ylides respectively. The qualitative view of these surfaces remain similar in semi-empirical, *ab initio* and DFT methods of calculations.

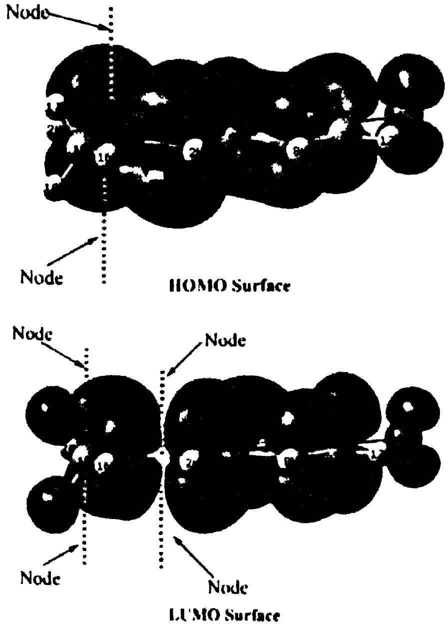
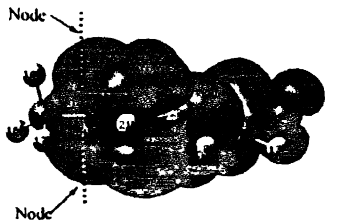
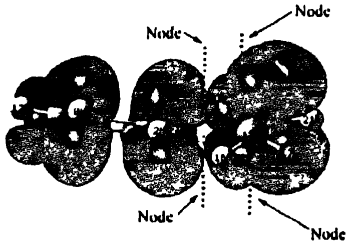


Fig. 2. Frontier molecular orbital surfaces of *C*-(4-chlorophenyl)-*N*-methyl azomethine imine.



HOMO Surface



LUMO Surface

Fig. 3. Frontier molecular orbital surfaces of *C*-(4-chlorophenyl)-*N*-methyl azomethine ylide.

Conclusion :

Frontier orbital calculations of *C*-aryl-*N*-methyl nitrones reported in this communication show close correspondence to the UV spectral absorption data. Thus, DFT calculations using B3LYP theory at 6-31 G (d) level of approximation can be performed to explain the relative reactivities of 1,3-dipoles and selectivities in 1,3-DCs of *C*-aryl-*N*-methyl nitrones. Moreover, ionization potential and electron repulsion correction factors need not be considered in such calculations.

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