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Experimental and DFT studies on the vibrational, electronic spectra and NBO analysis of ethyl N-[2-[4-(4-methylphenoxy)phenoxy]ethyl]carbamate

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ABSTRACT

FT IR spectra of Ethyl N-[2-[4-(4-methylphenoxy) phenoxy]ethyl] carbamate has been recorded. Quantum chemical calculations of energies, geometrical structure and vibrational wave number of (EMPEC) were carried by B3LYP/6-311G(d,p) basis set. A study on the electronic properties such as HOMO and LUMO energies are performed by time dependent DFT approach.NBO analysis were used to find the presence of Hydrogen bonding.

Keywords: *DFT, HOMO-LUMO, NBO Charge analysis*

Introduction

Carbamates are used as pesticides. They offer certain environmental and toxicological properties which are especially important in public health use. Density functional theory (DFT) is widely used quantum chemical method for geometry optimization and calculation of molecular properties [1,2]. Most are highly toxic to humans and other mammals by all routes of exposure. When inhaled, the effects are usually respiratory and may include bloody or runny nose, coughing, chest discomfort, difficult or short breath and wheezing due to constriction or excess fluid in bronchial tubes. Spectral analysis have been carried out using computation and experimental methods.DFT with the B3LYP method using Guassian '09 programs package is used for calculation. Hence, the present investigations aim to interpret the vibrational characteristics of ethyl N-[2-[4-(4-methylphenoxy)phenoxy]ethyl]carbamate using their FT-IR,FT-Raman,HOMO-LUMO enegies and NBO analysis.

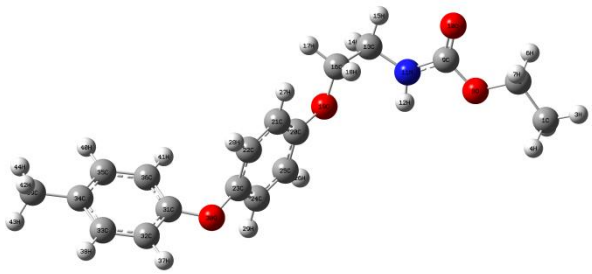


Fig1: Structure of ethyl N-[2-[4-(4-methylphenoxy)phenoxy]ethyl]carbamate

Experimental details

ethyl N-[2-[4-(4-methylphenoxy)phenoxy]ethyl]carbamatewas purchased from Sigma-Aldrich(St.Louis,MO,USA) anused without further purification. The IR spectrum of each sample was recorded using a PerkinElmer Spectrum One FTIR spectrometer in the region 400-4000 cm^{-1},using a KBr sample pellet. The resolution of the spectrum was 4 cm^{-1}.

Computation

The DFT computations for the ethyl N-[2-[4-(4-methylphenoxy)phenoxy]ethyl]carbamate was carried out in the Gaussian 09 program package using "ultrafine" integration grids. The calculations were performed at the B3LYP level with the standard 6-311 G(d,p) basis set in order to derive the optimized geometry, vibrational wave numbers and natural bond orbital analysis of ethyl N-[2-[methylphenoxy)phenoxy]ethyl]carbamate.

Result and Discussion

Optimized geometry

The calculated data of ethyl N-[2-[4-(4-methylphenoxy)phenoxy]ethyl]carbamate are in close agreement with the experimental values [table1]. The bond length C_20-C_{25} is increased by 1.399Aº because of the substitution of ethyl carbamate. The C_{34}-C_{36}(1.326 Aº) of vinyl group is relatively short compared to other C-C bonds.This shows the double bond character also.[4]The various bond angles and dihedral angles are found to be satisfactory agreement with the reported standard values.

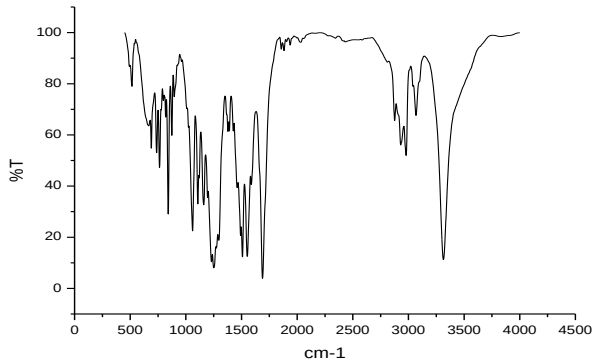
Table 1: Selected optimized parameters of for ethyl N-[2-[4-(4methylphenoxy)phenoxy]ethyl]carbamate

Parameter	Experimental value	Calculated value
C1-C5	1.497	1.515
N_{11}-H_{12}	0.86	1.008
C20-C25	1.386	1.399
C_{30}-C_{31}	1.392	1.428
N_{11}-C_{13}-H_{15}	109	107.2
C_{16}-O_{19}-C_{20}-C_{21}	-5.6	.3
$C_2$4-C23-O30-C31	177.3	179.7

Vibrational analysis

The C=C stretching wavenumber of ethyl group which is an electron withdrawing substituent have two bands which occur near 1645-1640cm^{-1}[5].The aliphatic CH stretching bands are expect between 3030cm^{-1} and 2995 cm^{-1}. The corresponding calculated value lies at 3006 cm^{-1}.

Figure: 2 FTIR Spectrum for ethyl N-[2-[4-(4-methylphenoxy)phenoxy]ethyl]carbamate



NBO analysis

The interaction of $\sigma(C_{20}-C_{25})$ distribute to $\sigma^*(C20-C_{21})$ leading to high stabilization energy of 4.47 $KJmol^{-1}$[5].The lone pair to antibonding orbital interaction LP $(1)N_{11}\rightarrow\sigma^*(C9–O_{10})$ have high delocalisation energy 0.68 $KJmol^{-1}$[6]. The intermolecular hyperconjugation interaction (C16 –H18...O19) is formed.

The energies of HOMO-LUMO based on the optimized structure are computed as 0.3213and 0.1869 respectively. The HOMO-LUMO energy gap is 0.134eV.The calculated HOMO and LUMO energies clearly shows that charge transfer occurs within the molecule.

Table 2: NBO analysis for for ethyl N-[2-[4-(4-methylphenoxy)phenoxy]ethyl]carbamate

Donor NBO(i)	ED(i) (e)	Acceptor NBO(j)	ED(j) (e)	E^2 (KJ/mol)
$\sigma(C_1–H_3)$	1.982 -0.504	$\sigma^*(C_5$- H8)	0.029 0.265	4.13
$\sigma(C_{20}-C_{25})$	1.972 -0.702	$\sigma^*(C20-C_{21})$	0.029 0.555	4.47
$\sigma(C13-H_{14})$	1.979 -0.514	$\sigma^*(C9–N_{11})$	0.072 0.467	2.65
$LP(1)O_{19}$ LP $(1)N_{11}$	1.964 -0.555 1.745 -0.026	$\sigma^*(C_{16}$- $H_{18})$ $\sigma^*(C9–O_{10})$	0.025 0.382 0.025 0.208	0.81 26.73

Conclusion

The equilibrium geometries of ethyl N-[2-[4-(4-methylphenoxy) phenoxy]ethyl]carbamate were determined and analyzed at the DFT level. The DFT calculated values of the Vibrational wave number are well ageed with experimental data. The HOMO–LUMO energy gap clearly reveals the structure activity relation of the molecule.

References

1.J.Goose,Cmbridge Animal and Public health Ltd.Vol.3,issue 8.P257.
2.Viktor N.Anishchenko,Vladimir I.Rybachenko:Central European Journal of Chemistry 12(2) 2014 153-163.
3.A.Nataraj,V.Balachandran:Journal of molecular structure 1022 (2012) 94-108.
4. Bismi Edwin,I.Hubert Joe, Spectrochimica partA:Molecular and Biomolecular Spectroscopy 114(2013) 633-641.
5.G.Socrates Infrared and Raman characteristic group frequencies tablesand charts,third edu.wiley Chichester,2001.
6.Akhil R.Krishnan,H.Saleem: Spectrochimica partA:78(2011) 582-589.