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DFT and Vibrational Spectroscopic Study on Methyl N-(2-furoyl)-N-(2,6-xylyl)-DL-Alaninate Fungicide

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Abstract

The FTIR and FT-Raman spectra of methyl N-(2-furoyl)-N-(2,6-xylyl)-DL-Alaninate have been recorded in the range 400-4000cm^{-1} and 50-3500cm^{-1} respectively. The fundamental vibrational wavenumbers, intensities of vibrational bands and the optimized geometrical parameters of the compound were evaluated using DFT B3LYP method with 6-311G(d,p) basis set.. The ^{1}H and ^{13}C nuclear spectra have been recorded and chemical shifts of the molecule were also calculated using the gauge independent atomic orbital (GIAO) method. The observed and the calculated frequencies are found to be in good agreement stability of the molecule arising from hyper-conjugative interactions, charge delocalization has been analyzed using natural bond orbital (NBO) analysis.

Keywords: *DFT , FT-IR , FT-Raman, methyl N-(2-furoyl)-N-(2,6-xylyl)-DL-Alaninate*

1. Introduction

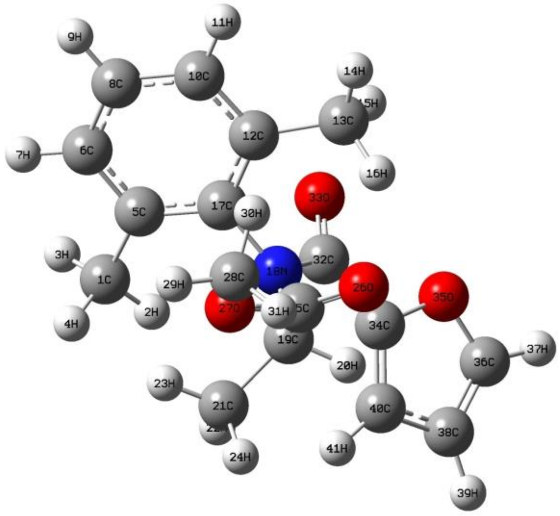

Figure 1 molecular structure of methyl N-(2-furoyl)-N-(2,6-xylyl)-DL-Alaninate.

Furalaxyl is a pesticide active ingredient from the group of acylalanines, specially a 1977 by Ciba Geigy introduced systemic fungicide [1]. Furalaxyl acts both protective and curative and will supply above all in the cultivation of ornamental plants under glass turns. There is the fight against soil fungi (phythium, phytophthora) and Oomceytes such as wrong mildew. David J .Fisher etal. [2] reported the mode of action of the systemic fungicides furalaxyl, metalaxyl and ofurace. Gin.F etal.[3] explained the environmental behavior of benalaxyl and furalaxyl enantiomers in agricultural soils. A.Kerkenaar etal. [4] explained the antifungal activity of metalaxyl and furalaxyl. Figure 1 represents the molecular structure of methyl N-(2-furoyl)-N-(2,6-xylyl)-DL-Alaninate.

2. Experimental details

Furalaxyl was purchased from Sigma Aldrich (St.Louis, MO, USA) and used without further purification. The room temperature fourier transform infrared spectra of the title compound was measured in the region 400-4000 cm^{-1}, at a resolution of +1 cm^{-1}, using Perkin Elmer spectrometer equipped with mercury vapour lamp and globar as source. The ^{1}H and ^{13}C (500MHz:CDCl$_3$) NMR spectra were recorded on a BRUKER AVANCE111 500 MHz (AV500) instrument.

3. Computational details

The combination of spectroscopic methods with DFT calculations are the powerful tools for understanding the fundamental spectral properties and the electronic structure of the compounds. GAUSSIAN 09 software program package was used for theoretical calculation [5]. The quantum chemical calculations were performed by applying density functional theory [6,7] method with the Becke's three parameter hybrid functional (B3) [8,9] for the exchange part and the Lee-Yang-Par(LYP) correlation function [10]. The wavenumber values computed contain known systematic errors and therefore, scaling factor 0.9682 [11] has been used.

4. Results and discussion

4.1 Optimized parameters

The computed and experimental x-ray diffraction data are given in Table 1

Bondlength(Å)			Bond angle(^{0})			Dihedral angle(^{0})		
	Expt.	Comput.		Expt.	Comput.		Expt.	Comput.
C_{17}-N_{18}	1.439	1.443	C_5-C_{17}-N_{18}	120.0	119.5	C_5-C_{17}-N_{18}-C_{19}	115.6	-73.9
N_{18}-C_{32}	1.350	1.379	C_{12}-C_{17}-N_{18}	121.0	119.4	C_5-C_{17}-N_{18}-C_{32}	-72.7	114.4
N_{18}-C_{19}	1.465	1.477	C_{17}-N_{18}-C_{32}	122.2	124.2	C_{12}-C_{17}-N_{18}-C_{32}	106.9	-66.4
C_{17}-C_5	1.392	1.408	C_{17}-N_{18}-C_{19}	122.2	118.4	C_5-C_{17}-N_{18}-C_{19}	115.6	-73.9
C_{17}-C_{12}	1.397	1.411	C_{19}-N_{18}-C_{32}	115.2	116.7	C_{12}-C_{17}-N_{18}-C_{19}	-64.8	105.2
O_{27}-C_{28}	1.454	1.439	N_{18}-C_{32}-O_{33}	122.8	121.6			

Table 1: Optimized parameters

The N_{18}-C_{32} bondlength elongated 0.029Å due to the hyperconjugative interaction between N_{18}-C_{32}. In O_{27}-C_{28} the bondlength contracted 0.015Å due to the interaction between $H_{30}….O_{27}$. The dihedral angle reveals the nonplanarity of the title compound.

4.2Vibrational spectral analysis

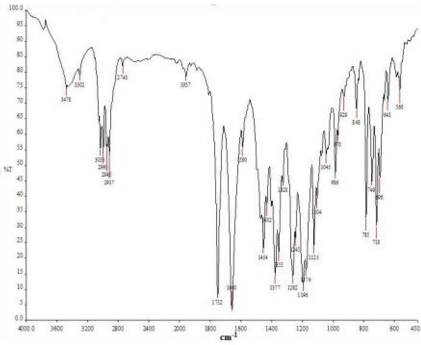

Fig 2: FT-IR spectrum of methyl N-(2-furoyl)-N-(2,6-xylyl)-DL-Alaninate.

The vibrational spectra were analyzed based on the FT-IR spectra aswellas the vibrational wavenumbers computed at the DFT level with the scaled wavenumbers. The FT-IR spectra are given in Fig 2.IR spectral analysis is based on the vibrational modes of phenylring vibrations, methyl group vibrations, carbonyl group vibrations, C-N vibrations and C-O vibrations. The amide band due to the C=O stretching vibration is often referred to as the amide 1 band. Primary amides have a very strong band due to the C=O stretching at 1670-1650 cm^{-1}[12]. The IR spectrum shows a very strong band at 1686 cm^{-1} (PED 85%) which corresponds th carbonyl group C=O stretching.

4.3 *NBO Analysis*

The natural bond orbitals (NBO) calculations were performed using NBO 3.1 program as implemented in the Gaussian 09 package at the DFT/B3LYP level. The NBO analysis is a tool for understanding hydrogen bonding interactions and delocalization of electron density from occupied donor and unoccupied acceptor within the molecule. The second order Fock-matrix was carried out to evaluate the donor-acceptor interactions in the NBO basis. The interactions result in a loss of occupancy from the localized NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor (i) and acceptor (j) the stabilization energy $E^{(2)}$ associated with the delocalization $i \rightarrow j$ determined as

$$E(2) = \Delta E_{ij} = q_i \frac{F(i,j)^2}{E_i - E_j}$$

In NBO analysis large $E^{(2)}$ value shows the intensive interaction electron donors and electron-acceptors, and greater the extent of conjugation of the whole system, the possible intensive interaction are given in Table 2. The second order perturbation theory analysis of Fock matrix in NBO basis shows strong intramolecular interactions of electrons.NBO analysis clearly manifests the evidence for the formation of H-bonded interactions between oxygen lonepair and $\sigma^*(C_{28}\text{-}H_{29})$ antibonding orbital (Table 3) which quantify the extend of intramolecular hydrogen bonding. The difference in $E^{(2)}$ energies are reasonably due to the fact that the accumulation of electron density in the C-H bond is noticed as 2.88e.

Table 2: Second order perturbation theory Analysis

Compound	Donor NBO(i)	E.D/e	Acceptor NBO(j)	E.D/e	$E^{(2)}$ (kJ/mol)
Furalaxyl	$\sigma_{(C5\text{-}C6)}$	1.969 -0.679	$\sigma^*_{(C17\text{-}N18)}$	0.041 0.381	20.50
	$\sigma_{(C5\text{-}C17)}$	1.967 -0.688	$\sigma^*_{(C12\text{-}C17)}$	0.037 0.574	22.80
	$\sigma_{(C10\text{-}C12)}$	1.969 -0.680	$\sigma^*_{(C17\text{-}N18)}$	0.041 0.381	20.08
	$\sigma_{(C12\text{-}C17)}$	1.966 -0.681	$\sigma^*_{(C5\text{-}C17)}$	0.365 0.045	23.26

Table 3 : Possible hydrogen bonding

Compound	Donor NBO(i)	E.D/e	Acceptor NBO(j)	E.D/e	$E^{(2)}$ kJ/mol	H...O	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A $(^0)$
Furalaxyl	O_{26}	1.841 -0.262	$\sigma^*_{(C28\text{-}H29)}$	0.009 0.393	3.05	$sp^{3.08}$	1.087	3.710	2.658	12.3

The formation of intramolecular C-H...O hydrogen bonding interaction in compound1 is due to the presence of phenylamide and the alaninate group, which is very important in the enhancement of the biological activity of this compound. The increased electron density at the oxygen atom (O_{26}) leads to the elongation of $C_{25}\text{-}O_{26}$ bond. The electron density is transferred from $n(O_{26}) \rightarrow \sigma^*(C_{28}\text{-}H_{29})$ showing 1.841e→ -0.262e which leads to the high interaction energy (3.05kJ/mol). The intramolecular charge transfer is one of the causes for fungicidal activity of the compound. These charge transfer interactions of compound1 are responsible for the fungicidal activity.

Conclusion

Vibrational wavenumbers and infrared intensities calculated by B3LYP/6-311G(d,p) level agrees well with the experimental data. The bondlength $N_{18}\text{-}C_{32}$ increased due to the hyperconjugative interaction. NBO analysis shows that the intramolecular C_{28}-H_{29}…O_{26} hydrogen bond due to the interaction between the oxygen lonepair and the C-H antibonding orbital. The possibility of hydrogen bonding and charge transfer shows the fungicidal nature of title compound.

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