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RESEARCH ARTICLE

Charge transfer interaction on methylphenoxy acetic acid herbicide

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Abstract

Density functional theory and vibrational analysis of Methyl Phenoxy Acetic Acid herbicide has been carried out using FT-IR spectroscopic technique and compared with computational technique. The FT-IR spectra have been recorded in the region 400–4000 cm^{-1}. The geometry has been optimized with complete relaxation on the potential energy surface at B3LYP level of theories using 6-311G (d,p) basis set using Gaussian 09 program and compared with the crystal data. Further, harmonic vibrational frequency calculations have been carried out at B3LYP level and the scaled values were in good agreement with majority of the experimental observations. The theoretically constructed spectra coincide satisfactorily with those of experimental spectra. The relative energies, NBO analysis and structural parameters predicted that steric effect determine the stabilization of the compound. Theoretical methods have been used to study the proper and improper hydrogen bonds, considering the hydrogen bond length and charge transfer. The NBO analysis showed the intra and intermolecular C-H···O hydrogen bonds in the crystal structure of Methyl Phenoxy Acetic Acid Herbicide.

Keywords

Methyl Phenoxy Acetic Acid

FT-IR

NBO analysis

Hydrogen bonds

Introduction

Phenoxy acetic acid is used as a precursor in antibiotic fermentations especially for penicillin V and is a main skeleton of plant growth regulators and herbicides [1]. The presence of phenoxy acid herbicide metabolites were demonstrated in surface water and ground water [2]. The structural and spectroscopic analysis of Methyl Phenoxy Acetic Acid (MPAA) monomer and dimer has been performed using. Computation technique. This work also includes the possibility of hydrogen bonding and charge transfer analysis. The Optimized structure of MPAA dimer in show in **Fig 1.**

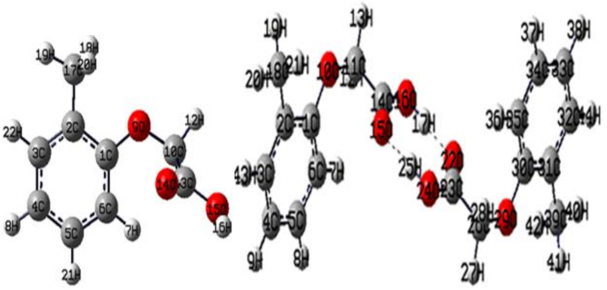

Fig 1 Optimized structure of MPAA dimer.

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Computation

The DFT computation of MPAA monomer and dimer was done using Gaussian '09 program package [3] using B3LYP method with the 6-311G(D,P) basisset, this has been successfully applied in order to derive the optimized geometry and vibrational wavenumber of the normal modes.

Table 1 Optimized parameters of the MPAA**.**

Bond length	Calcd. (Å)	Exp. (Å)
C_1-C_2	1.404	1.405
C_6-H_7	1.080	0.95^0
C_5-H_{12}	1.082	0.95^0
H_7-H_{11}	2.162	2.204

Bond angle (^{o})	Calcd. (Å)	Exp. (Å)
C_5-C_6-C_1	119.8^0	119.9^0
C_6-C_1-C_9	124.1^0	124.1^0
C_{10}-C_{13}-O_{15}	109.8^0	110.8^0
O_{14}-C_{13}-O_{15}	123.8^0	124.3^0

Results and discussion

The optimized parameters of MPAA show that there are some changes observed in C-H bond length due to variation in the charge distribution on the carbon atom of the benzene ring. The significant change identified in C-H bond is 0.13Å. The reduction in the angle C_{10}-C_{13}-O_{15} is 109.8^o from 120^o (**Table 1**) is associated with repulsion between hydroxyl group and H_{11}. The second-order perturbation theory analysis of Fock matrix in NBO of MPAA shows strong intramolecular hyperconjugative interaction. The C-H...O interaction has been identified from DFT calculation, the corresponding intermolecular H...O distance is shorter than that of Van der Waals separation and it indicates the existence of the C-H...O hydrogen bonding in MPAA [4].

Table 2 Vibrational distribution of MPAA monomer and dimer.

Wavenumber calc. (cm^{-1})		Assignments with PED (%)
Monomer	Dimer	
3625	3118	$\upsilon O_{15}H_{16}(100)$
2944	2952	$\upsilon CH_2sy(100)$
1780	1705	$\upsilon C_{13}O_{=}O_{14}(87)$
1592	1654	$8b\upsilon C_1C_6(43)+\upsilon C_{13}=O_{14}(40)$
978	978	$\delta H_{16}O_{15}C_{13}(74)$
630	664	$\tau COOH(75)$

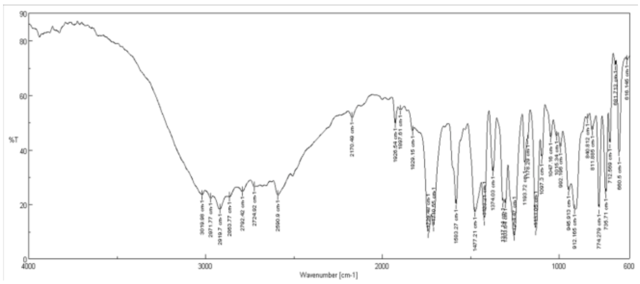

Fig 2 FTIR spectrum of MPAA.

The symmetric CH_2 stretching vibrations [5] are observed at 2853 cm^{-1}. In MPAA the corresponding calculated monomer and dimer values are 2944; 2952 cm^{-1} with PED 100% (**Table 2**). The FTIR spectrum (**Fig 2**) shows the observed position at 2971 cm^{-1}. All these deviations in CH stretching vibration shows blue shifting and the possibility of weak C-H...O hydrogen bonding. The hydroxyl group vibration is observed in the region 3584-3700 cm^{-1}, but the intermolecular hydrogen bond formation lowers the O-H stretching wavenumber in the range 3200-3500 cm^{-1}. The experimental value is identified as weak band at 3020 cm^{-1}. The corresponding calculated value for monomer of MPAA is 3125 cm^{-1}, but in dimer due to red shifting and strong doubly O-H..O hydrogen bond the wave number is reduced to 3118 cm^{-1}.

Conclusions

A strong doubly O-H..O hydrogen bonded system is demonstrated by the red shift in OH stretching wavenumber, weak C-H..O interaction has been identified from NBO analysis in which C-H donor group is strengthened, shorted and blue shifted in the stretching vibrational wave number which shows the herbicidal activity.

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