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MOLECULAR STRUCTURE, VIBRATIONAL SPECTRA AND IN SILICO EVALUATION OF TRIFLUSULFURON-METHYL

DR.J. CLEMY MONICKA, Assistant Professor, Department of Physics, St. John's College of Arts and Science,

Ammandivilai

DR. T. SUNITHA, Assistant Professor, Department of Physics, St. John's College of Arts and Science,

Ammandivilai

ABSTRACT: Density functional theory calculations have been performed with B3LYP functional and 6-311+G(d,p) basis set implemented in the Gaussian 09 package inorder to support spectral characteristics and geometry of triflusulfuron-methyl, a molecule known for its herbicidal activity. The observed Raman and infrared spectral bands have been assigned in the framework of theoretical frequencies and intensities. Aromaticity of the phenyl and triazine rings has been measured based on harmonic oscillator model of aromaticity index. Natural bond orbital analysis performed on triflusulfuron-methyl has been carried out to reveal various non-bonding interactions present in the molecule. Triflusulfuron-methyl has been tested for its antimicrobial activity and found to exhibit antifungal and antibacterial effects.

KEYWORDS: FTIR; Raman; DFT; NBO; UV.

1. INTRODUCTION

Triflusulfuron-methyl is a triazinylsulfonylurea herbicide which inhibits the activity of acetolactate synthase [1]. It is a post-emergence herbicide that controls annual grasses and broad–leaved weeds like fools parsley, mayweeds, brassica species, or small nettle in sugar beets [2, 3]. In view of the actual importance of this compound, the analyses on the structure and vibrations of the same have been carried out and are presented here. The present study includes theoretical and experimental (FTIR and FT-Raman) techniques for the investigation of triflusulfuron-methyl structure. To the best of our knowledge, DFT assisted vibrational spectral studies of triflusulfuron-methyl have been done yet. Nowadays, the availability of sophisticated computational techniques has made possible the calculation of vibration force fields with less computational effort. In particular, density functional B3LYP method is used to predict vibrational frequencies of triflusulfuron-methyl.

2. EXPERIMENTAL

Triflusulfuron-methyl was purchased from Sigma Aldrich and used without further purification. IR spectra of KBr discs of the samples were recorded on a PerkinElmer Spectrum 2000 spectrometer (2 cm^{-1} resolution) between 400 and 4000 cm^{-1} region. Raman spectrum was obtained using a Bruker Senterra Dispersive Raman microscope spectrometer in the spectral region of 3700–200 cm^{-1} with 3 cm^{-1} resolution. The laser power during signal acquisition was 45 mW. Antimicrobial activity of triflusulfuron-methyl was determined by agar well diffusion method [4] and it was tested against two bacterial strains and two fungal strains. Both, the antibacterial and antifungal activities of the title compound were observed and the mean diameter of the zone of inhibition (in mm) formed around the well was measured.

3. CALCULATIONS

Molecular structure of triflusulfuron-ethyl was fully optimized using DFT method with Becke3Lyp functional and 6-311+G (d, p) basis set as implemented in Gaussian'09 software package . Normal coordinate analysis (NCA) was performed using MOLVIB program version 7.0 of Sundius inorder to obtain detailed description of the molecular motion pertaining to the

normal modes. Pulay's natural internal coordinates] were given as input for NCA analysis. The force field was selectively scaled according to scaled quantum mechanical (SQM) procedure .Charge transfer between atoms provide the evidence for inter and intra molecular hydrogen bondings of the molecule and it was analyzed using natural bond orbital (NBO) analysis.

4. RESULTS AND DISCUSSION

4.1 Molecular structure

Fig. 1 illustrates the optimized molecular structure of triflusulfuron-methyl. The structural parameters obtained from the geometry optimization of triflusulfuron-methyl are listed in Table 1 together with the XRD data .
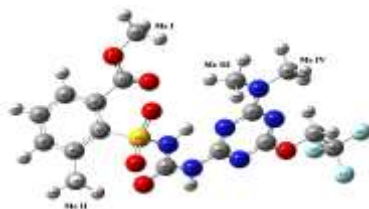

Fig. 1 Optimized molecular structure of triflusulfuron-methyl.

Variation of C-C bond length (1.38−1.41Å) shows asymmetry of the phenyl ring and is due to various substituents in the phenyl ring. Electron donating methyl group substituted in the phenyl ring decrease the bond angles C_2-C_1-C_6 (119.9°), C_1-C_2-C_3 (119.8°), C_1-C_6-C_5 (119.5°), C_3-C_4-C_5 (116.7°) and increase the bond angles C_2-C_3-C_4 (122.4°), C_4-C_5-C_6 (121.3°). Twisting of phenyl ring with respect to sulfonylurea moiety is evident from the large torsional value of 103.6° for C_4-C_5-S_{21}-N_{24}. The $H_{19}...O_{27}$ (2.35 Å) and $H_{47}...O_8$ (2.51 Å) .

4.2 NBO analysis

NBO 3.1 program at DFT/B3LYP level was used to perform NBO calculations to probe the possible interactions between the filled and vacant orbitals of two different subsystems, which is a measure of hyperconjugation or intramolecular delocalization. The stabilization energy E(2) associated with i to j delocalization is given by $E(2) = \Delta E_{ij} = \dfrac{q_i (F_{ij})^2}{\varepsilon_i - \varepsilon_j}$

Table 1: Second order perturbation theory analysis of Fock matrix in NBO basis.

Donor (i)	ED^a (i) (e)	Energy (i) (a.u)	Acceptor (j)	ED (j) (e)	Energy (j) (a.u)	$E(2)^b$ (kJ/mol)	$E(j)-E(i)^c$ (a.u)	$F(i,j)^d$ (a.u)
π (C_1-C_6)	1.660	-0.27852	π* (C_2-C_3)	0.30164	0.01296	85.35	0.29	0.069
π (C_1-C_6)	1.660	-0.27852	π* (C_4-C_5)	0.37673	0.00225	71.83	0.28	0.063
π (C_2-C_3)	1.652	-0.27367	π* (C_1-C_6)	0.33452	0.00881	81.54	0.28	0.066
π (C_2-C_3)	1.652	-0.27367	π* (C_4-C_5)	0.37673	0.00225	101.92	0.28	0.074
π (C_4-C_5)	1.665	-0.28344	π* (C_1-C_6)	0.33452	0.00881	98.15	0.29	0.074
π (C_4-C_5)	1.665	-0.28344	π* (C_2-C_3)	0.30164	0.01296	63.76	0.30	0.060
π (C_{30}-N_{31})	1.773	-0.34375	π* (C_{32}-N_{33})	0.52459	-0.04166	155.89	0.30	0.103

π (C_{32}-N_{33})	1.700	-0.33210	π^* (C_{34}-N_{35})	0.45591	-0.03440	203.92	0.30	0.112
π (C_{34}-N_{35})	1.726	-0.33401	π^* (C_{30}-N_{31})	0.46013	-0.03593	182.92	0.30	0.107
LP (2) O_8	1.842	-0.28842	σ^* (C_6-C_7)	0.06771	0.37703	76.81	0.67	0.101
LP (2) O_8	1.842	-0.28842	σ^* (C_7-O_9)	0.10135	0.35355	131.50	0.64	0.129
LP (2) O_9	1.778	-0.34506	π^* (C_7-O_8)	0.23006	0.00928	191.96	0.35	0.114
LP (2) O_{22}	1.803	-0.30674	σ^* (C_5-S_{21})	0.19976	0.12073	78.49	0.43	0.080
LP (2) O_{23}	1.813	-0.31075	σ^* (C_5-S_{21})	0.19976	0.12073	63.09	0.43	0.072
LP (2) O_{23}	1.813	-0.31075	σ^* (S_{21}-N_{24})	0.26633	0.09245	57.70	0.40	0.068
LP (1) N_{24}	1.752	-0.29883	π^* (C_{26}-O_{27})	0.33414	-0.00884	222.21	0.29	0.113
LP (2) O_{27}	1.847	-0.27407	σ^* (C_{26}-N_{24})	0.07746	0.41204	101.46	0.69	0.117
LP (2) O_{27}	1.847	-0.27407	σ^* (C_{26}-N_{28})	0.08042	0.37846	108.91	0.65	0.118
LP (2) O_{27}	1.847	-0.27407	σ^* (C_{17}-H_{19})	0.01028	0.43124	3.05	0.71	0.021
LP (1) N_{28}	1.667	-0.28833	π^* (C_{26}-O_{27})	0.33414	-0.00884	214.97	0.28	0.107
LP (1) N_{28}	1.667	-0.28833	π^* (C_{30}-N_{31})	0.46013	-0.03593	238.86	0.25	0.111
LP (1) N_{31}	1.877	-0.38734	σ^* (N_{24}-H_{25})	0.04541	0.39389	54.81	0.78	0.092

4.3 UV-vis spectroscopy

Usually, molecules undergo π- π^*, n- π^* and π^*-π type electronic transitions with high extinction coefficients in the UV-vis region. Hence, time-dependent density functional theory (TD–DFT) calculations were carried out inorder to understand the nature of electronic transitions in terms of their energies and oscillator strengths. In view of calculated absorption spectra, the wavelength 260 nm corresponds to HOMO→LUMO+1 transition with 86 % contribution. The molecular orbital plot representing the HOMO→LUMO and HOMO→LUMO+1 transitions is as illustrated in Fig 3.
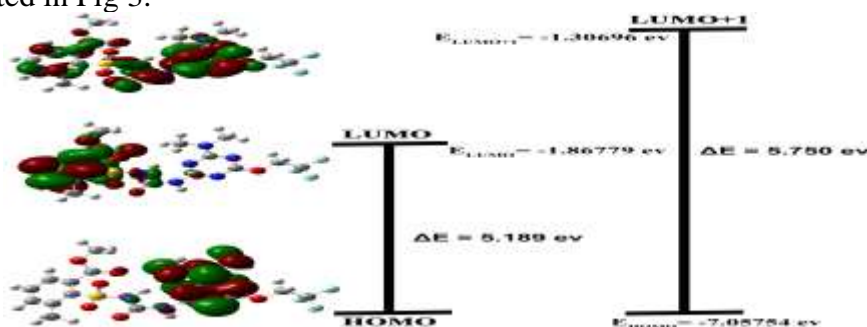

Fig. 3 Molecular orbital plot representing the HOMO→LUMO and HOMO→LUMO+1 transitions.

4.4 IR and Raman studies

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The assignment of IR and Raman bands to the normal modes of vibration of triflusulfuron-methyl was based on the results of the calculations (B3LYP/6-311+G (d, p)). The overall appearance of the Raman and infrared spectra of the title compound are found in Fig. 4.

Fig. 4 Simulated Raman spectrum of triflusulfuron-methyl.

The frequency interval of all C-H stretching vibrations is 3120-3000 cm^{-1} in the spectra of all benzene derivatives .For vicinal trisubstitution, the selection rule allows three C–H stretching vibrations, viz. 2, 13 and 20b. Raman bands situated at 3063 (2), 3082 (20b) and 3017 (13) cm^{-1} and the IR bands situated at 3073 (2) and 3031 (13) cm^{-1} have been assigned to C-H stretching mode. There are five normal modes (8a, 8b, 19a, 19b and 14) characterizing C-C stretching for the trisubstituted benzene derivatives.

5. CONCLUSIONS

Experimental and theoretical, structural and vibrational spectral analyses of triflusulfuron-methyl molecule were carried out. Hyperconjugative interaction between the phenyl ring and the strong electron donating dimethylamino group shortens the C-N bond length. On the basis of the SQM force field obtained by DFT calculations, vibrational wavenumbers, infrared and Raman intensities of triflusulfuron-methyl molecule were calculated and a complete vibrational analysis was performed. The experimentally observed Raman and FTIR spectra showed good correlation with the computed values. NBO analysis identifies the presence of intra-molecular N−H...N interaction. Substitution of strong electron donating dimethylamino group increases the aromatic behavior of triazine ring. Antimicrobial study reveals that the title compound possesses moderate antimicrobial activity.

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