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RESEARCH ARTICLE

Structural and spectroscopic characterisation of dl-alaninium fumarate

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Abstract

In this work, the vibrational spectral analysis of the DL Alaninium fumarate compound was carried out by using FT-Raman and FT-IR spectroscopic techniques. The structure of the compound was optimized and the structural characteristics were determined by density functional theory (DFT) using B3LYP method with 6-311G(d,p) basic set. The observed vibrational wave numbers were compared with calculated results. The molecular stability and bond strength has been investigated by applying the natural bond orbital (NBO) analysis. The calculated HOMO and LUMO energies show that charge transfer occurs with in the molecule and other results observed shows the NLO active nature of DL Alaninium fumarate.

Introduction

Non linear optics (NLO) is a new frontier area of science and technology that is to play major role in the emerging technology of the 21st century. Non linear optical process provides the key function of conversion and optical processes provide the key function of frequency conversion and optical switching [1]. These application depend upon the various properties of the materials, such as transparency, birefringence, refractive index, dielectric constant, thermal and chemical stability. Organic non linear optical materials are attracting great deal of attention, as they have large optical susceptibilities, inherent ultra fast response time and high optical thresholds for laser power as compared with inorganic materials [2]. The optimized structure of DL-Alaninium fumarate is given in **Fig 1.**

Experimental

The quantum chemical calculation of DLAF has been performed using Gaussian 09 program package [3] at the B3LYP level with standard 6-311G (d,p) basis set. This has been successfully applied in order to derive the optimized geometry and vibrational wave number of the normal modes.

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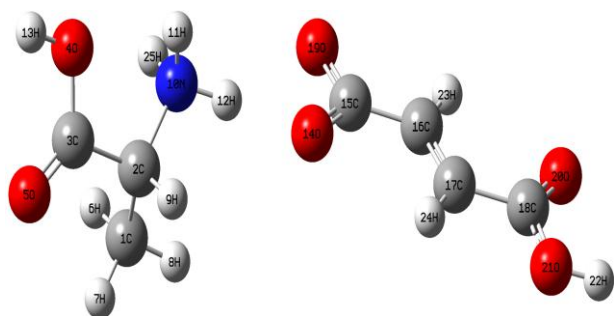
**Fig 1** Optimized structure of DL-alaninium fumarate.

Results and discussion

The optimized geometry parameters of DL-alaninium fumarate at DFT level of computation are listed in **Table1**. The calculated values were compared with experimental values. The experimental and geometric parameters agree well with almost all values.

Table 1 Optimized bond length and bond angle

Bond Length / (Å)			Bond Angle / (°)		
Experimental Value	DLAF	Calculated Value	Experimental Value	DLAF	Calculated Value
1.508	$C_2 - C_3$	1.533	112.8	$C_2 - C_3 - O_4$	111.4
0.980	$C_2 - H_9$	1.094	109.2	$N_{10} - C_2 - C_1$	110.7
0.890	$N_{10} - H_{25}$	1.024	113.8	$C_{16} - C_{15} - O_{19}$	122.9
1.282	$O_{14} - C_{15}$	1.264	123.7	$C_{17} - C_{16} - C_{15}$	120.9
1.233	$C_{15} - O_{19}$	1.272	124.2	$C_{18} - C_{17} - O_{16}$	119.8

The hydroxyl stretching vibrations are generally observed around 3500 cm^{-1} [4]. In DLAF a week band is observed in IR at 3626 cm^{-1}, which corresponds to the O-H stretching Vibration. The corresponding calculated value is found to be at 3630 cm^{-1} with a PED of (100%). Experimental values show that there is a blue shift in the O-H stretching wave number. Bending mode of O-H group usually appears as very strong band in the region 1440-1266 cm^{-1} [5,6]. In DL-alaninnium fumarate compound IR spectrum shows very strong band appear at 1359 cm^{-1} and 1299 cm^{-1}. The carbonyl group vibration is observed in the region 1760-1730 cm^{-1} [7].

In DLAF stretching mode of carbonyl Vibrational appear weak band in Raman at 1742 cm^{-1}.
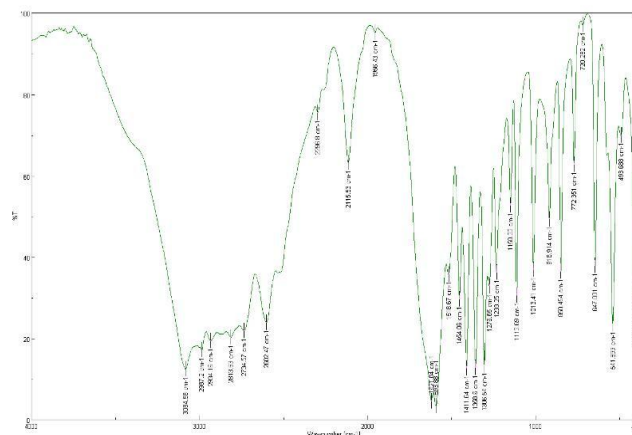
Fig 2 IR Spectrum of DL alaninium fumarate.

The energy involved with the lone pair interaction in between oxygen and carbon atom in fumarate moiety $n_2O_2 \rightarrow \sigma^* (C_1-C_5) = 43.41$KJ/mol appear than that of same type of interaction in alaninium moiety $n_2O_2 \rightarrow \sigma^* (C_1-C_5) = 29.74$ KJ/mol indicating intermolecular charge transfer from fumarate moiety having same energy density (1.995e). Hydrogen Bonds are very important in dipole interaction in stabilizing the protein structures. In amino acid having zwitter ionic forms, the NH_3^+ moiety is a donor and the carbonylate or nitrate group is an excellent acceptor.

In NLO crystals the hydrogen bonds linked with the adjustment molecules ,where O-H---O hydrogen bonds are relatively stronger than N-H—O bonds. In the $n_1O_4 \rightarrow N_{10}$-$H_2$ interactions the bond length O-H is 1.044Å Bond length of N----O is 2.819Å and bond angle of N-H---O is175.3°. The structure is stabilized by strong N-H---O distance remains as 2.819Å shows strong hydrogen bonding. The energies of the HOMO and LUMO based on the optimized structure are computed as 0.336 and 0.216eV respectively. The HOMO-LUMO energy gap in 0.110eV. The calculated HOMO and LUMO energies clearly show that charge transfer occurs with in the molecules.

Conclusions

In DLAF the stretching mode of carbonyl vibration shows the presence of electron donating oxygen .The blue shifting of COO⁻ stretching wave number in DLAF medicates the formation of hydrogen bonding HOMO-LUMO orbitals clearly explicate the charge transfer interaction involving donor and acceptor groups. Which shows more NLO activity.

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