Int. J. Chem. Sci.: 9(4), 2011, 1564-1568
ISSN 0972-768X
www.sadgurupublications.com

AB INITIO MODELING OF THE STRUCTURAL DEFECTS IN AMIDES

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ABSTRACT

A series of models was constructed with varying lengths of conjugated chain containing different carbon atoms on each side of a core containing an amide group. The important amide bands, geometrical parameters and thermal parameters are reported. The theoretical calculations were done at the DFT level using Gaussian03 software.

Key words: Amide, DFT, Hyperpolarizability, Structural defects.

INTRODUCTION

An amide is an organic compound that contains the functional group consisting of a carbonyl group (R-C=O) linked to a nitrogen atom. The lone pair of electrons on the nitrogen is delocalized into the carbonyl; thus, forming a partial double bond between N and the carbonyl carbon. Consequently, the nitrogen in amides is not pyramidal[1]. Because of the greater electronegativity of oxygen, the carbonyl (C=O) is a stronger dipole than the N-C dipole. The presence of a C=O dipole and, to a lesser extent a N-C dipole, allows amides to act as H-bond acceptors. In primary and secondary amides, the presence of N-H dipoles allows amides to function as H-bond donors as well. Thus amides can participate in hydrogen bonding with water and other protic solvents; the oxygen atom can accept hydrogen bonds from water and the N-H hydrogen atoms can donate H-bonds. As a result of interactions such as these, the water solubility of amides is greater than that of corresponding hydrocarbons. The amide I, II and III bands are the most useful in structure designation and correspond to vibrational modes associated with the amide group. The amide I band is the

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most intense and is predominantly C=O stretch. The amide II and III bands arise from the out-of-phase and in-phase combinations of the NH in plane bend and CN stretch, respectively. Besley[2] reported the ab initio modeling of amide vibrational bands in solution. In the present work, a series of models was constructed with varying lengths of conjugated chain containing carbon atoms on each side of a core comprising the amide isomer.

Computational details

The vibrational frequencies were calculated using the Gaussian03 software package on a personal computer[3]. The computations were performed at B3LYP/6-31G* levels of theory to get the optimized geometry (Figs. 1- 4) and vibrational wavenumbers of the normal modes of the title compound. The DFT partitions, the electronic energy $E = E_T + E_V + E_J + E_{XC}$, where E_T, E_V and E_J are electronic kinetic energy, electron nuclear attraction and electron-electron repulsion terms, respectively. The electron correlation is taken into account in the DFT via the exchange-correlation term E_{XC}, which includes exchange energy arising from the anti-symmetry of quantum mechanical wave function and dynamic correlation in the motion of individual electron, and it makes DFT dominant over conventional HF procedure[4]. DFT calculations were carried out with Becke's three parameter hybrid model using the Lee-Yang-Parr correlation functional (B3LYP) method. Molecular geometries were fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wavenumbers were calculated using analytic second derivatives to confirm the convergence to minima in the potential surface. At the optimized structure of the examined species, no imaginary wavenumber modes were obtained, proving that a true minimum on the potential surface was found. The optimum geometry was determined by minimizing the energy with respect to all geometrical parameters without imposing molecular symmetry constraints. The DFT hybrid B3LYP functional tends also to overestimate the fundamental modes; therefore scaling factors have to be used for obtaining a considerably better agreement with experimental data[5]. Scaling factor 0.9613 has been uniformly applied for the DFT calculated wavenumbers[4]. The assignment of the calculated wavenumbers is aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes[6,7].

RESULTS AND DISCUSSION

All amides exhibit a strong band, amide I, due to C=O stretching[8-11] in the range 1680 ± 60 cm^{-1} and in-plane NH deformation band, amide II, in the region 1550 ± 50 cm^{-1}. Like the amide II band, C-N stretching vibration, amide III, appears in the region 1270 ± 55 cm^{-1}. The C=O in-plane deformation, amide IV, is observed in the region 695 ± 75 cm^{-1} and out-of-plane C=O deformation, amide VI, in the region 600 ± 70 cm^{-1}. The out-of-plane NH deformation, amide V, is active in the region[8-11] 735 ± 60 cm^{-1}.

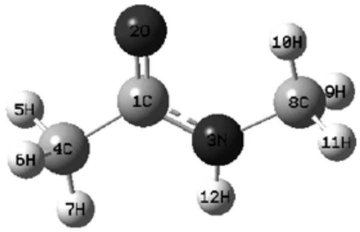

Fig. 1

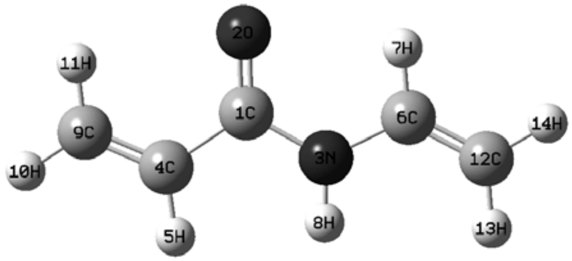

Fig. 2

The DFT calculations give the bands, amide I (C=O stretching), at 1640, 1612, 1711, 1590 cm^{-1}, amide II (NH in-plane deformation), at 1527, 1495, 1489, 1495 cm^{-1}, amide III (CN stretching) at 1259, 1229, 1194, 1233 cm^{-1}, amide IV (in-plane C=O deformation) at 605, 668, 730, 721 cm^{-1}, amide V (out-of-plane NH deformation) at 845, 712, 783, 663 cm^{-1} and amide VI (out-of-plane CO deformation) at 598, 609, 669, 707 cm^{-1}, for n = 1 to 4, respectively. The calculated NH stretching modes for n = 1 to 4 carbon atoms in the chain are found to be 3509, 3480, 3469 and 3493 cm^{-1}.

For the amide groups with n = 1 to 4, the C=O bond lengths are 1.2515, 1.2520, 1.2268 and 1.2527Å. For odd numbers of carbon atoms in the chain, C=O bond length decreases, while the length increases in the case of even number of carbon atoms in the chain. But the CN bond length in the amide moiety, shows an increasing tendency with increase in the number of carbon atoms in the chain. The CN bond lengths for n = 1 to 4 are 1.3722, 1.3873, 1.3838 and 1.3901Å. For urea[12], the C=O and CN bond lengths are in the range 1.221-1.265 and 1.349-1.394Å. The other CN bond lengths, C_8-N_3 = 1.4601 (n = 1), C_6-N_3 = 1.4017 (n = 2), C_6-N_3 = 1.3965 (n = 3) and C_6-N_3 = 1.3956Å (n = 4), which shows a decreasing effect as the number of carbon atoms in the chain increases. The NH bonds give nearly the same value. The bond angles, OCN = 122.6, 121.8, 122.1, 121.3°, OCC = 121.7, 123.4, 123.8, 121.1° and CCN = 115.7, 114.8, 114.1, 117.6° for n = 1 to 4 carbon atoms in the chain. The changes in the angles are due to presence of carbon atoms in the side chain. The reported values of C=O, C-N bond lengths and OCN bond angle are 1.2003, 1.3549 Å, 122.1°[13] and 1.221, 1.3973Å, 122.1°[14].

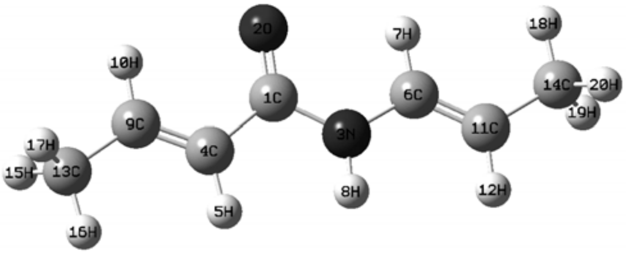

Fig. 3

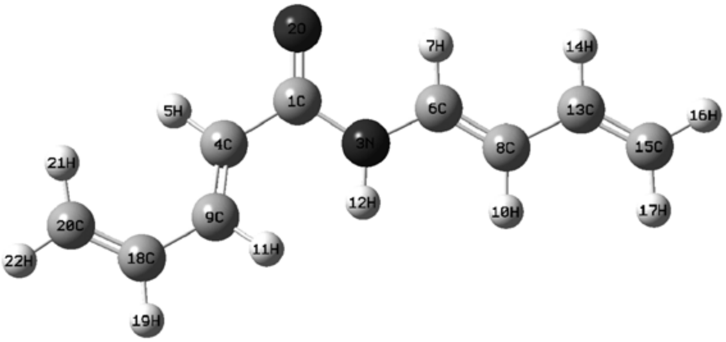

Fig. 4

The thermal energies (E_T), specific heat capacities (C_v), entropy (S), first hyperpolarizability (β), total energy (E) and dipole moment (μ) values are given in the Table 1. As the number of carbon atoms increases in the side chain, the thermal parameters are also increasing.

Table 1

n	E_T (KCal/Mol)	C_v (Cal/Mol-Kelvin)	S (Cal/Mol-Kelvin)	$B \times 10^{-30}$ esu	E (a.u.)	μ (Debye)
1	68.836	20.403	79.645	0.431	-248.45	3.969
2	76.166	25.827	83.744	6.2	-324.60	3.54
3	113.060	37.052	100.364	8.8	-403.330	3.343
4	121.368	42.036	109.911	22	-479.37	4.302

ACKNOWLEDGEMENT

The authors thank University Grants Commission, India for a research grant.

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Accepted : 12.08.2011