



STRUCTURAL DEFECTS IN IMIDATES : AN AB INITIO STUDY

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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 imidate group. The important vibrational bands, geometrical parameters and thermal parameters are reported. The theoretical calculations were done at the DFT level using Gaussian03 software.

Key words: Imidate, DFT calculations, Hyperpolarizability, Dipole moment.

INTRODUCTION

Imidates are important compounds that find uses in organic synthesis as building blocks and intermediates in many reactions for example in the Mumm rearrangement and the Overman rearrangement. These compounds also find use as ligands¹. The ever increasing demand for the design and synthesis of small molecule peptidomimetics as pharmaceutical probes and drug leads has led to hectic research activities in the area of new drug discovery²⁻⁴. 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 imidate isomer.

Computational details

The vibrational frequencies were calculated using the Gaussian03 software package on a personal computer⁵. 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 $E = E_T + E_V + E_J +$

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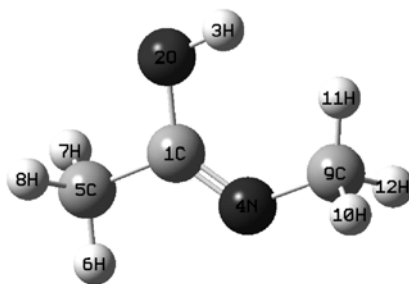
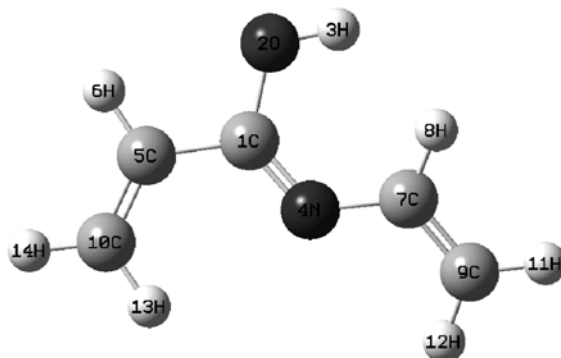
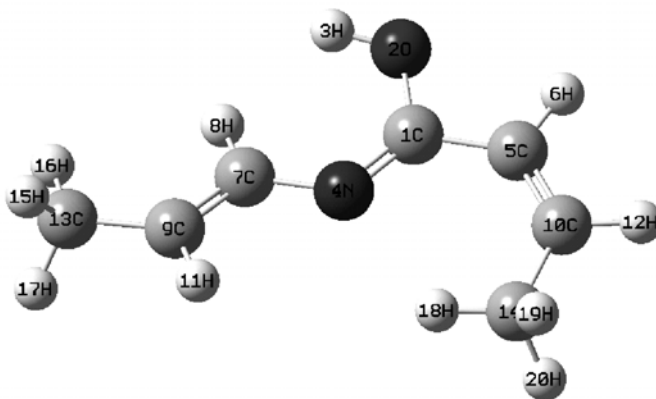
E_{XC} , where E_T , E_V and E_J are electronic kinetic energy, electron nuclear attraction and electron-electron repulsion terms, respectively. The electron correlation is taken into account in the DFT via the exchange-correlation term E_{XC} , which includes exchange energy arising from the anti-symmetry of quantum mechanical wave function and dynamic correlation in the motion of individual electron, and it makes DFT dominant over conventional HF procedure⁶. 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 data⁷. Scaling factor 0.9613 has been uniformly applied for the DFT calculated wavenumbers⁶. The assignment of the calculated wavenumbers is aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes^{8,9}.

RESULTS AND DISCUSSION

Imino carbonates and imidates absorb in the region 1690-1550 cm^{-1} due to C=N stretching vibration¹⁰⁻¹³. The OH stretching vibrations in associated molecules is expected above 3400 cm^{-1} and the in-plane OH deformation is expected in the region 1200-1300 cm^{-1} . The C-O stretching mode interacts with the OH in-plane deformation and is expected in the region¹⁰⁻¹³ 1150-1200 cm^{-1} . In the present case, DFT calculations give the OH stretching mode at 3512, 3674, 3678, 3610 cm^{-1} for $n = 1$ to 4 carbon atoms in the side chain. The C=N stretching modes are 1695, 1671, 1607, 1554 cm^{-1} , for $n = 1$ to 4, respectively. The C-O stretching modes are nearly same for odd number of carbon atoms (1145 and 1144 cm^{-1}) and slightly different for even number of carbon atoms (1196 and 1176 cm^{-1}) in the side chains.

The OH bond lengths are 0.9778, 0.9768, 0.9765, 0.9694 Å for $n = 1$ to 4 and the deviations is minimum, while for $n = 1$ and $n = 3$, C=N bond length increase from 1.2782 to 1.2931 Å. For $n = 2$ and $n = 4$, C=N bond length increase from 1.2903 to 1.2865 Å. The C-O bond lengths are 1.4047, 1.4007, 1.4073 and 1.3721 Å for $n = 1$ to 4 and the deviation is maximum for $n = 4$. The CCO bond angle is nearly same in all cases (except for $n = 4$, 116.6) and lies in the range 109.1-110.1° and the N=CO bond angles are 127.7, 126.8, 125.4,

121.5° for $n = 1$ to 4, which decreases with increase in number of carbon atoms in the side chain. For urea¹⁴ the OCN angle was reported in the range 120.3-122.5°. The COH bond angles are 112.8, 113.0, 112.7 and 109.4° for $n = 1$ to 4.

**Fig. 1****Fig. 2****Fig. 3**

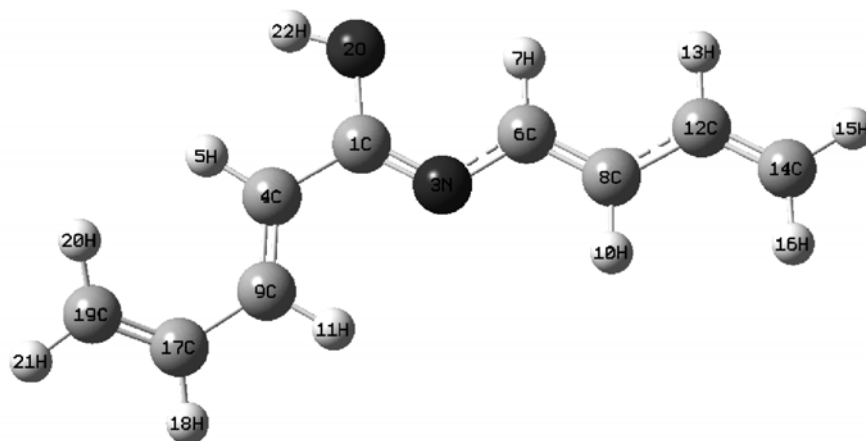


Fig. 4

The thermal energies (E_T), specific heat capacities (C_v), entropy (S), first hyperpolarizability (β), total energy (E) and dipole moment (μ) are given in the Table 1.

Table 1

| n | E_T (KCal/Mol) | C_v (Cal/Mol-kelvin) | S (Cal/Mol-kelvin) | $\beta \times 10^{-30}$ esu | E (a.u.) | μ (Debye) |
|---|---------------------|---------------------------|-----------------------|--------------------------------|-------------|------------------|
| 1 | 67.716 | 21.180 | 79.836 | 0.833 | -248.415 | 1.6713 |
| 2 | 75.071 | 26.750 | 86.223 | 1.71 | -324.567 | 1.0835 |
| 3 | 112.735 | 37.187 | 102.568 | 1.1 | -403.186 | 1.3042 |
| 4 | 119.799 | 43.357 | 110.471 | 36.4 | -479.468 | 3.271 |

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