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Molecular structure and vibrational study on 2,3-dihydro-1H-indene and its derivative 1H-indene-1,3(2H)-dione by density functional theory calculations

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ABSTRACT

2,3-Dihydro-1H-indene also known as indan is a simple hydrocarbon petrochemical compound, whereas its derivative 1H-indene-1,3(2H)-dione is an anticoagulant which help prevent the blood coagulation. The equilibrium geometries and harmonic frequencies of both molecules under investigation were determined and analyzed at DFT level employing the basis set 6-311, which is augmented by d and p polarization as well as diffuse functions. The skeleton of both the optimized molecules is non-planar. In general, a good agreement between experimental and calculated normal modes of vibrations has been observed. The calculated frontier orbital energy gap and the dipole moment data also support the fact that the 1H-indene-1,3(2H)-dione is the more reactive molecule and more polar than 2,3-dihydro-1H-indene molecule. The molecular electrostatic potential surface displays how the activity varies from 2,3-dihydro-1H-indene to its derivative 1H-indene-1,3(2H)-dione.

1. Introduction

Anticoagulants are complex organic or synthetic compounds, often carbohydrates, that help prevent the coagulation of blood and stop the new blood clots from forming or an existing clot from enlarging. 2,3-Dihydro-1H-indene is a hydrocarbon petrochemical compound, but its derivative 1H-indene-1,3(2H)-dione is an anticoagulant. Anticoagulants do not dissolve a blood clot, and are given to people at risk, in which there is excessive or undesirable clotting, such as thrombophlebitis, pulmonary embolism and certain cardiac conditions. The structure of the parent molecule 2,3-dihydro-1H-indene and its derivative, which is a vitamin K antagonist anticoagulants, seems to be very interesting as both contain a bicyclic system composed of a five-membered ring fused with a six-membered benzene ring. 1H-indene-1,3(2H)-dione represents a unique class of drugs, due to the presence its two carbonyl groups, and exhibits a unique combination of important physio-chemical and biological properties including the neurotropic, bactericidal, fungicidal activities [1–6].

The aim of the present communication is to investigate the molecular structural, vibrational and energetic data analysis of the molecules under study, in gas phase, due to their biological and pharmaceutical importance. The structure and the ground state energy of the molecules under investigation has been analyzed employing DFT/B3LYP level. In order to obtain a more complete description of molecular motion, vibrational frequency calculation have been carried out at the DFT level. The vibrational analysis also yields the detailed information about the intramolecular vibrations in the molecular fingerprint region. The reported geometries, molecular properties such as equilibrium energy, dipole moment and vibrational frequencies along with the electrostatic potential maps, have also been used to understand the activity of the molecules.

2. Experimental

2.1. Structure and spectra

The model molecular structures of 2,3-dihydro-1H-indene and its derivatives 1H-indene-1,3(2H)-dione have been given in Fig. 1. The FTIR spectra have been obtained from Sigma–Aldrich website [7].

3. Computational methods

The DFT calculations [8] of the title molecules under investigation have been performed by employing Becke's three parameter hybrid exchange functionals [9] with Lee–Yang–Parr functionals (B3LYP) [10,11] method using the Gaussian 03 program [12]. The vibrational frequencies are also calculated and scaled down by the appropriate factor [13]. The vibrational frequency assignments

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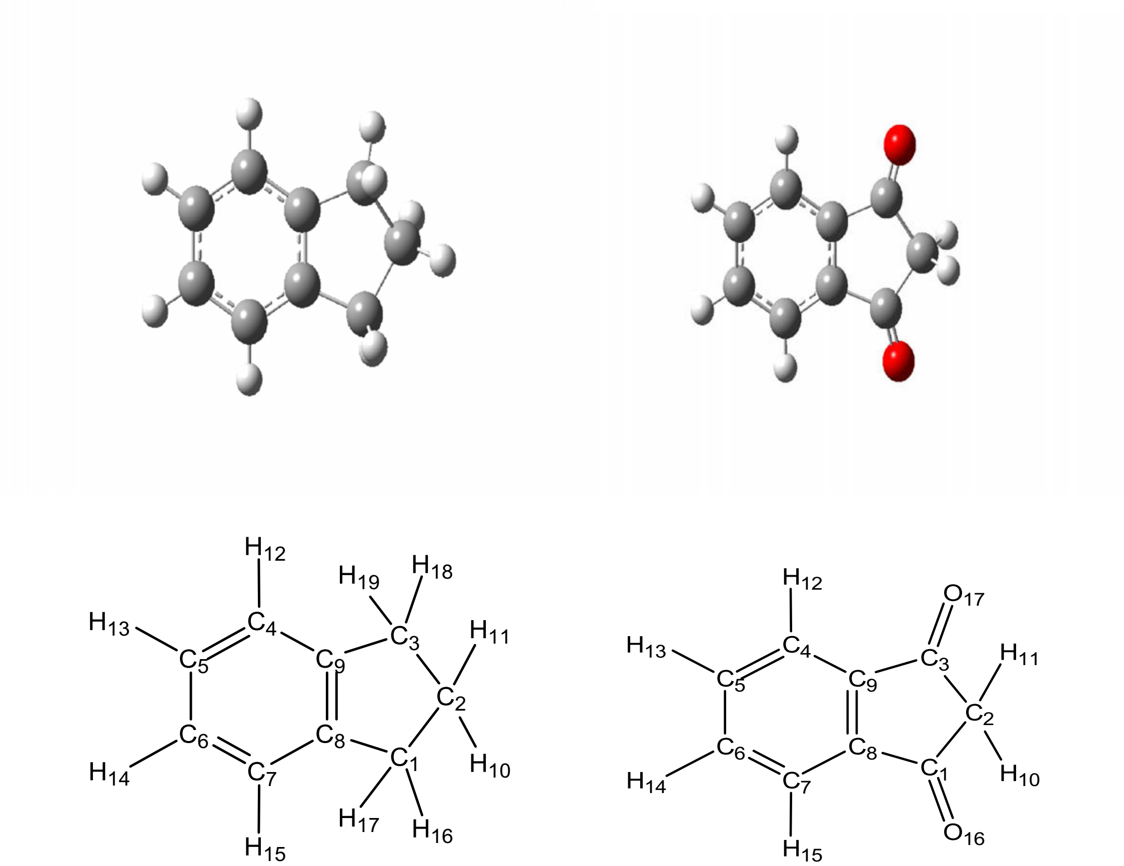

Fig. 1. 3D optimized structures and 2D pictures along with numbering scheme of 2,3-dihydro-1H-indene and 1H-indene-1,3(2H)-dione.

have been carried out by combining the results of the Gaussview 3.07 program [14], symmetry considerations and the VEDA 4 program [15].

4. Result and discussion

4.1. Molecular geometry optimization and energies

The structure of 2,3-dihydro-1H-indene which is the ancestor of the 1H-indene-1,3(2H)-dione has been investigated as a reference, in order to assess the effect of introduction of two electron withdrawing carbonyl groups at it. The equilibrium geometry optimization for both the molecules has been achieved by energy minimization, using DFT at the B3LYP level, employing the basis set 6-311++G(d,p). The optimized geometry of both molecules under study are confirmed to be located at the local true minima on potential energy surface, as the calculated vibrational spectra has no imaginary frequency. Although 1H-indene-1,3(2H)-dione exhibits tautomerism in organic solvents, only the keto form is observed in the crystalline phase. The X-ray diffraction data of indene-1,3-dione from Cambridge Crystallographic Data Centre (CCDC) has been used to optimize its structure. In the case of 2,3-dihydro-1H-indene, the molecule was built using the Gaussview program package then optimized in steps. Initially the optimization of planar structure of 2,3-dihydro-1H-indene resulted in the transition state with a single imaginary frequency. But the gradual changes in dihedral angle, concerned with those atoms which were involved the vibrations corresponding to the single imaginary normal mode frequency, finally optimized the geometry on minima. The molecular symmetry of 2,3-dihydro-1H-indene, rules out the existence of any other conformation, hence the optimized geometry corresponds to the most stable conformation. The optimized molecular structures thus obtained together with the 2D structures representing the numbering scheme of the atoms are shown in Fig. 1. The optimized geometrical parameters of both the molecules have been compared with the previous X-ray study of 1H-indene-1,3(2H)-dione reported by Chetkina and Belsky [16], which further confirm the optimization of both the molecules under investigation. In case of both the compounds, the five-membered ring adopts an envelope conformation, with the C(2) atom, acting as the flap atom, deviating from the plane through the remaining four carbon atoms. In case of 2,3-dihydro-1H-indene/1H-indene-1,3(2H)-dione, the values of the bond lengths of five membered are as follows: C(1)–C(2) and C(2)–C(3), 1.55 Å/1.53 Å; and C(1)–C(8) and C(3)–C(9), 1.51 Å/1.49 Å. The C(1)═O(16) and C(3)═O(17) bond length both equal to 1.21 Å are also found to be close to the standard C═O bond length (1.22 Å) [17,18]. The benzene endocyclic C–C–C angles in 2,3-dihydro-1H-indene/1H-indene-1,3(2H)-dione are found to decrease to 119.2°/118.0° at C(4) and C(7) atoms and increased on an average to 120.4°/121° at C(5), C(6), C(8) and C(9) atoms. For the five-membered ring in both cases, the endocyclic angles are equal to 105.1°/104.3° at C(2), 103.2°/108.0° (on an average) at C(1) and C(3), and 110.5°/109.7° at the C(8) and C(9) atoms. These DFT calculated bond length, bond angles are in full agreement with those reported in Chetkina and Belsky [16]. The skeleton of 1H-indene-1,3(2H)-dione molecule is not strictly planar: the carbonyl groups deviate from the plane of phenyl ring in opposite directions by −0.012° for O(16) atom and by 0.072° for the O(17) atom. The dihedral angles C(9)–C(8)–C(1)–C(2) and C(8)–C(9)–C(3)–C(2) which represent the angular separation/orientation of flap atom C(2) with respect to plane of the molecule, are found to be 0.031° and 0.039° for 1H-in-