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PCM/TD-DFT analysis of 1-bromo-2,3-dichlorobenzene – A combined study of experimental (FT-IR and FT-Raman) and theoretical calculations

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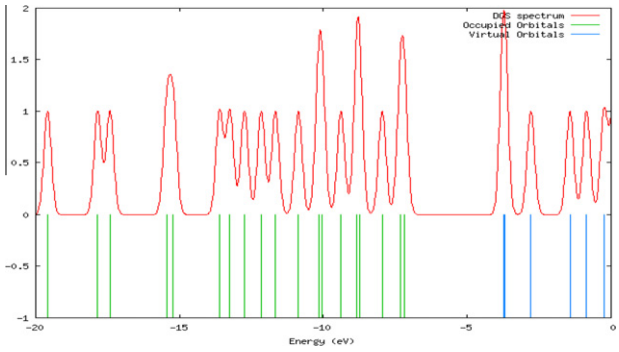
HIGHLIGHTS

- The reactivity sites are identified by MESP.
- Solvent induces a slight blue shift of the transition $S_0 \rightarrow S_1$ going from less polar to more polar solvents.
- HOMO and LUMO levels are illustrated by DOS spectrum.

GRAPHICAL ABSTRACT



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ABSTRACT

This study represents an integral approach towards understanding the electronic and structural aspects of 1-bromo-2,3-dichlorobenzene (BDCB). The experimental spectral bands were structurally assigned with the theoretical calculation, and the thermodynamic properties of the studied compound were obtained from the theoretically calculated frequencies. The relationship between the structure and absorption spectrum and effects of solvents have been discussed. It turns that the hybrid PBE1PBE functional with 6-311+G(d,p) basis provide reliable λ_{max} when solvent effects are included in the model.

The NBO analysis reveals that the studied compound presents a structural characteristic of electron-transfer within the compound. The frontier molecular orbitals (HOMO–LUMO) are responsible for the electron polarization and electron-transfer properties. The reactivity sites are identified by mapping the electron density into electrostatic potential surface (MESP). Besides, ^{13}C and ^{1}H have been calculated using the gauge-invariant atomic orbital (GIAO) method. The thermodynamic properties at different temperatures were calculated, revealing the correlations between standard heat capacity, standard entropy, standard enthalpy changes and temperatures. Furthermore, the studied compound can be used as a good nonlinear optical material due to the higher value of first hyper polarizability (5.7 times greater than that of urea (0.37289×10^{-30} esu)). Finally, it is worth to mentioning that solvent induces a considerable red shift of the absorption maximum going from the gas phase, and a slight blue shift of the transition $S_0 \rightarrow S_1$ going from less polar to more polar solvents.

Introduction

Benzene is mainly used as an intermediate to make other chemicals, its mostly widely-produced derivatives include styrene, which is used to make polymers and plastics, phenol for resins

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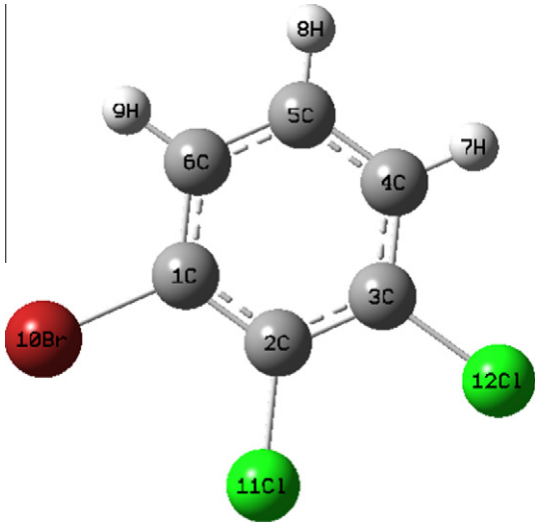

Fig. 1. Optimized structure of 1-bromo-2,3-dichlorobenzene.

and adhesives, and cyclohexane, which is used in the manufacture of nylon [1]. Benzene is a clear, colorless, no corrosive and highly flammable liquid with a sweet odor. It evaporates into the air very quickly and dissolves slightly in water [2]. Benzene is also used to make some types of rubbers, lubricants, dyes, detergents, drugs, and pesticides. Natural sources of benzene include volcanoes and forest fires. Benzene is also a natural part of crude oil, gasoline, and cigarette smoke [3,4]. At one time, chlorobenzene is the main precursor for the manufacture of phenol [5]. The major use of chlorobenzene is an intermediate in the production of commodities such as herbicides, dyestuffs, and rubber. Chlorobenzene is also used as high-boiling solvent in many industrial applications as well as in the laboratory [6]. Interestingly, dichlorobenzene belongs to the group of organic halogen compounds and used in the fumigant and insecticide, solvent, chemical intermediate to manufacture dyes, agrochemical, pharmaceuticals and other organic synthesis.

As a continuation of our recent studies on structural and theoretical investigations of some substituted benzene derivatives, the main aspects of this study are: (i) Structural investigation of BDCB (Fig. 1) by FT-IR and FT-Raman spectra, ^{13}C and ^{1}H NMR and UV/vis. (ii) The molecular geometries and vibrational spectra of the title compound were calculated by applying density functional theory (DFT) computations. (iii) The solvent effect on ^{13}C and ^{1}H NMR data were introduced by applying the integral equation formalism-polarizable continuum model (IEF-PCM). (iv) HOMO–LUMO, and NBO analysis have been used to give more information regarding charge transfer within the molecule. One key approach to understand solvent effects is the solvent-induced changes in the electronic transition of solutes generally referred to as solvatochromism. This present paper aims at reporting the effect of various solvents on the electronic and NMR spectra of the compound.

Experimental details

The pure sample of BDCB was obtained from Lancaster chemical company, UK and used as such for the spectral measurements. The FT-IR spectrum of the compound was recorded in the region 4000–400 cm^{-1} using the BRUKER IFS-66V model FT-IR spectrometer. The FT-Raman spectrum of compound was recorded on BRUKER IFS-66V model interferometer equipped with an FRA-106 FT-Raman accessory in the stokes region (3500–50 cm^{-1}) with Nd:YAG laser operating at 200 mV power continuously with 1064 nm excitation. The calibrated wave numbers are expected to be accurate within ±1 cm^{-1}.

Computational detail

The gas phase geometry of the compound in the ground state was optimized by using HF/6-311++G(d,p) and DFT 6-311++G(d,p) methods using GAUSSIAN 09W [7] program. For this optimized geometry, vibrational frequencies were calculated analytically at the same level of theory to ensure it to be a true local minimum.

In NMR calculations, the optimized molecular geometry of BDCB was first obtained at 6-311++G(d,p) basis level in $CDCl_3$ ($\varepsilon = 4.9$) by using integral equation formalism polarizable continuum model (IEFPCM) method. Similarly, the optimized molecular geometry of BDCB was obtained in DMSO ($\varepsilon = 46.7$) by the same method. Then, ^{1}H and ^{13}C NMR chemical shifts for BDCB were calculated at B3LYP/6-311++G(d,p) levels in solvent by using gauge invariant atomic orbital (GIAO) method .

Additionally, HOMO and LUMO energy values and energy gap for BDCB were calculated by using B3LYP method with 6-311++G(d,p) basis set. Furthermore, molecular electrostatic potentials (MEPs) of BDCB were plotted in 3D by using optimized structures at B3LYP/6-311++G(d,p) level.

After the ground state geometry optimization, the excitation spectrum of the compound has been computed with at PBE1PBE/6-311+G(d,p) level. This selection of basis set and functional clearly indicates that; (a) the addition of polarization functions does not bring any significant improvement to the calculation of excitation energies; (b) adding extra polarization function increases the λ_{max} by only 1 nm, suggesting that second set of polarization function is unnecessary; (c) pure DFT functionals provide too small excitation energies where as the best accuracy is reached by using the 25% functionals, especially PBE1PBE. Since solvent effects play an important role in absorption spectrum of the compound, in this paper, the integral equation formalism polarizable continuum model (IEFPCM) dealing with solvent effect was chosen in excitation energy calculations. In IEFPCM, one divides the problem into a solute part lying inside a cavity, and a solvent part represented as structureless material, characterized by its dielectric constant as well as other macroscopic parameters. Also, thermodynamic properties of the compound at different temperatures was calculated by B3LYP method at the same level of basis set.

Prediction of Raman intensities

The Raman activities were subsequently converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering [8–10]:

$$I_i = \frac{f(v_0 v_i)^4 S_i}{v_i[1 - \exp(-hcv_i/kT)]}$$

where v_0 is the laser exciting wavenumber in cm^{-1} (in this work, we have used the excitation wavenumber $v_0 = 9398.5$ cm^{-1}, which corresponds to the wavelength of 1064 nm of a Nd:YAG laser), v_i is the vibrational wavenumber of the ith normal mode (cm^{-1}), while S_i is the Raman scattering activity of the normal mode v_i. f (is a constant equal to 10^{-12}) is a suitably chosen common normalization factor for all peak intensities. h, k, c and T are Planck and Boltzmann constants, speed of light and temperature in Kelvin, respectively.

Results and discussion

Molecular geometry

Before computing the frequencies and electronic properties, it is necessary to analyze the molecular structure of the compound. So that the structure is optimized at DFT level of theory and numbering scheme is represented in Fig. 1 and the calculated optimized geometrical parameters are presented in Table 1.