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Molecular structure, vibrational spectra, NBO analysis, first hyperpolarizability, and HOMO, LUMO studies of mesityl chloride by density functional methods

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ABSTRACT

The FT-IR and FT-Raman vibrational spectra of mesityl chloride (2,4,6-trimethylbenzyl chloride) were recorded. The optimized geometry and wavenumbers in the ground state were calculated using density functional (B3LYP, and B3PW91) methods with standard 6-311G(d,p) basis set. The computed B3PW91/6-311G(d,p) results show the best agreement with the experimental values over the other methods. Natural bond orbital analysis of mesityl chloride is also carried out, which confirms the occurrence of strong intermolecular bonding, stability of the molecule arising from hyperconjugative interactions, and charge delocalization. The electric dipole moment (μ), polarizability (α), and first hyperpolarizability (β_0) which results also show that the mesityl chloride might have microscopic non-linear optical behavior with non-zero values. The calculated HOMO and LUMO energies show that charge transfer occur in the molecule. The results of the calculations were applied to simulated spectra of the title compound, which show excellent agreement with observed spectra.

1. Introduction

Benzyl chloride or α-chlorotoluene is an organic compound consisting of a phenyl group substituted with a chloromethyl group. It has the molecular formula $C_{10}H_{13}Cl$. This colorless liquid is a reactive organochlorine compound that is widely used chemical building block. Benzyl chloride is used in organic synthesis for the introduction of the benzyl protecting group for alcohols and carboxylic acids. Benzyl chloride also reacts readily with metallic magnesium to produce an ordinary reagent. Because of its utility in the synthesis of amphetamine-class drugs, it is mentioned as List II drug precursor chemical; benzyl chloride is a lachrymator and has been used as a war gas [1].

The compound mesityl chloride is known as 2,4,6-trimethylbenzyl chloride. Due to greater pharmaceutical and industrial importance, mesityl chloride has been taken for the present study. The complete vibrational analysis of mesityl chloride was performed by combining the experimental and theoretical information using Pulay's density functional theory (DFT) based on scaled quantum chemical approach [2]. The DFT calculations are also reported to provide excellent vibrational frequencies of organic compounds if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for the anharmonicity effects [3–6]. The DFT methods are increasingly used by spectroscopists for modeling molecular properties that includes equilibrium structure, vibrational frequencies, and intensities [7].

To our knowledge, no theoretical density functional theory calculations or detailed vibrational infrared and Raman analyses have been performed on mesityl chloride. A detailed quantum chemical study will aid in understanding the vibrational modes of this title compound. So, the aim of the present paper is to predict the molecular structure, vibrational wavenumbers, geometrical parameters, IR intensities, Raman scattering activities are calculated using DFT-B3LYP/B3PW91 levels with 6-311G(d,p) basis set for mesityl chloride. Reduced masses, force constants, depolarization ratios, atomic charges, HUMO, LUMO and thermodynamic parameters of mesityl chloride have also investigated using B3LYP/B3PW91 calculations with standard 6-311G(d,p) basis set. Different scale factors were also used and employed in the predicted frequencies. The calculated harmonic force constants of mesityl chloride were used for predicting the FT-IR and FT-Raman spectra. The calculated vibrational frequencies and band assignment were compared with those observed experimentally. The redistribution of electron density (ED) in various bonding and antibonding orbital and $E^{(2)}$ energies have been calculated by natural bond orbital analysis by B3LYP/6-311G(d,p) method to give clear evidence of stabilization originating from the hyperconjugation of various intermolecular interactions. The HOMO and LUMO analyses have been used to elucidate information regarding charge transfer within the molecule.

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2. Experimental details

Spectroscopically pure mesityl chloride was obtained from Lancaster Chemical Company, UK with a stated purity of greater than 98%, and it was used as such for the spectral measurements. The room temperature Fourier transform infrared spectra of mesityl chloride was recorded in the 4000–400 cm^{-1} region at a resolution of ±1 cm^{-1}, using BRUKER IFS-66V Fourier transform spectrometer, equipped with an MCT detector, a KBr beam splitter and global source. The FT-Raman spectrum was recorded on the KBr instrument with FRA-106 Raman accessories in the region 3500–100 cm^{-1}. Nd:YAG laser operating at 200 mW power with 1064 nm excitation was used as source.

3. Methods of analysis

The molecular geometry optimization and vibrational frequency calculations were carried out for mesityl chloride, with GAUSSIAN 09W software package [8] Becke's three parameter exchange functional (B3) [9,10], and combination with the correlation functional of Lee, Yang and Parr (LYP) [11] and Perdew and Wang's (PW91) [12,13] combined with standard 6-311G(d,p) basis set. The Cartesian representation of the theoretical force constants has been computed at optimized geometry by assuming C_1 point group symmetry. The reduced masses, true rotational force constants, and depolarization ratios were calculated using the GAUSSIAN 09W package. The atomic charges, electric dipole moment, polarizability, first hyperpolarizability, HOMO, LUMO, and other thermodynamic parameters were also calculated theoretically. Scaling of the force field was performed according to the SQM procedure [6,14] using different scaling in the natural internal coordinate representation [15]. Transformation of the force field and subsequent normal coordinate analysis including the least square fit refinement of the scale factors, calculation of the total energy distribution (TED), and the prediction of IR and Raman intensities were done on a PC with the MOLVIB Program (version 7.0-G77) written by Sundius [16,17]. The natural bonding orbital (NBO) calculation [18] were performed using NBO 3.1 program as implemented in GAUSSIAN 09W [8] package at DFT-B3LYP/6-311G(d,p) level in order to understand various second-order interactions between the filled orbital of subsystem and vacant of another subsystem, which is measure of the intermolecular delocalization or hyperconjugation. Finally, the calculated normal mode vibrational frequencies provide thermodynamic properties also through the principle of statistical mechanics.

3.1. Predication of Raman intensities

The Raman activities (S_i) calculated with the GAUSSIAN 09W program and adjusted during the scaling procedure with MOLVIB was subsequently converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering [19,20]:

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

where v_0 is the exciting frequency (in cm^{-1} units), v_i is the vibrational wavenumber of the ith normal mode; h, c, and k are the fundamental constants, and f is the suitably chosen common normalization factor for all peak intensities. The simulated FT-IR and FT-Raman spectra have been plotted using pure normal Lorentizian band shapes, were used with a band width of full width at half maximum (FWHM) of 10 cm^{-1}, and have been shown in Figs. 1 and 2, respectively.

4. Results and discussion

4.1. Molecular geometry

The optimized molecular structure of mesityl chloride is shown in Fig. 3. The most optimized structural parameters (bond lengths, bond angles, and dihedral angles) calculated using DFT-B3LYP/B3PW91 with 6-311G(d,p) basis set are presented in Table S1 (Supplementary material), together with relevant experimental data for comparison [21,22]. Since the exact crystal structure of the title compound is not available till now, the optimized structure can only be compared with other similar system for which the crystal structure have been solved. Therefore optimized geometrical parameters of cis-1,3-dichloropropene and N-(2,4,6-Trimethylphenyl) formamide [21,22] are compared to those of title compound.

From the experimental values of literature [23], C–C single bond length is 1.5037 Å, C–H single bond length is 1.0853 Å, and C–Cl bond length is 1.827 Å for chlorotoluene. The C–Cl bond length (Cl atom of $–CH_2Cl$ group) is 1.821 Å in the earlier work done by Durig et al. [21], and the bond distance is more consistent with the results from the electron diffraction study [24]. From the literature [25], C–C bond length increased from 1.386 to 1.414 Å, while the C–H bond length varies from 1.076 to 1.073 Å. From the literature [26], C–C single bond length is 1.4009 Å, C–H single bond length is 1.0875 Å, and C–Cl bond length is 1.8405 Å for chlorotoluene. Taking account of the effect of conjugation, the calculated values of mesityl chloride are in reasonable agreement with the above-mentioned experimental data. The B3LYP/6-311G(d,p) bond lengths, bond angles and dihedral angles are slightly shorter due to the neglect of electron correlation. The B3PW91/6-311G(d,p) bond lengths, bond angles and dihedral angles are closer to the experimental data due to slightly exaggerated electron correlation effect. So, compared [21,22] with the experimental values, the B3PW91/6-311G(d,p) bond lengths and bond angles are the best. The correlation coefficients (R) for bond lengths were 0.993 for B3LYP, 0.995 for B3PW91 methods. The agreement for bond and bond not as good as for the bond distances. The variations with experimental values are due to fact that the optimization performed in an isolated condition, whereas the crystal environment affected the experimental X-ray diffraction structure.

4.2. Vibrational spectral analysis normal coordinates analysis

The 66 normal modes of mesityl chloride are distributed among the symmetry species. The title molecule belongs to C_1 point group. Under C_1 point group symmetry, the full set of 88 standard internal coordinates containing 22 redundancies were defined and given in Table S2 (Supplementary material). From these, a non-redundant set of local symmetry coordinates was constructed by suitable linear combinations of internal coordinates following the recommendations of Fogarasi et al. [15] and are summarized in Table S3 (Supplementary material). In order to obtain a more complete description of the molecular motion involved in the fundamental modes mesityl chloride, we carried out a normal coordinate analysis. This analysis was performed utilizing DFT-B3LYP/B3PW91 calculations and the Wilson matrix method [27]. The Cartesian coordinates for the mesityl chloride together with the normal modes (in Cartesian coordinates) and frequencies from the GAISSIAN 09W output were used as input in the program. A complete set of internal coordinates (Table S2) was used to make the symmetry coordinates for all the vibrational modes (Table S3). The normal modes were next transformed to mass-weighted Cartesian coordinates, which were then used to calculate the force constant matrix. This was diagonalized and its eigenvectors and