# FT-IR, FT-Raman, NMR spectra, and molecular structure investigation of 2,3-dibromo-*N*-methylmaleimide: A combined experimental and theoretical study

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## ARTICLE INFO

## ABSTRACT

In the present work, the experimental and theoretical vibrational spectra and chemical shifts of 2,3-dibromo-*N*-methylmaleimide (2,3DBrNMM, $C_5H_3NO_2Br_2$) were studied. FT-IR and FT-Raman spectra of 2,3DBrNMM in the solid phase were recorded in the region 4000–4400 $cm^{-1}$ and 3500–3550 $cm^{-1}$, respectively. The structural and spectroscopic data of the molecule in the ground state were calculated by using Hartree-Fock and density functional method (B3LYP) with the 6-31G(d), 6-31G(d,p), 6-31+G(d,p), 6-31++G(d,p), 6-311G(d), 6-311G(d,p), 6-311+G(d,p) and 6-311++G(d,p) basis sets. The scaled values have been compared with experimental FT-IR and FT-Raman spectra. The observed and calculated frequencies are found to be in good agreement. The complete assignments were performed on the basis of the total energy distribution (TED) of the vibrational modes, calculated with scaled quantum mechanics (SQM) method. $^{13}$C NMR, $^1$H NMR and DEPT spectra were recorded. $^{13}$C NMR and $^1$H NMR chemical shifts were calculated by using HF and B3LYP methods with 6-311++G(d,p) basis sets. The optimized geometric parameters (bond lengths and bond angles) were given corresponding experimental values of maleimide and 3-benzoylmethyl-2-chloro-*N*-methylmaleimide molecules.

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## 1. Introduction

Derivatives of maleimide have been the subject of investigation for many reasons. The maleimide group is used in many areas such as antibiotic antitumor medicine [1] and biochemical conjugations rings [2]. *N*-Phenylmaleimide serves as an excellent model compound for the important class of resin/fibre advanced materials based on bismaleimides [3–5]. Example of the compound *N*-methylmaleimide is especially preferred from the standpoints of heat resistance, mechanical properties, and transparency.

Because of their spectroscopic properties and chemical significance in particular, maleimide and its derivatives have been studied extensively by spectroscopic (IR and Raman spectra) and theoretical methods. Vibrational modes and frequency analyses have been assigned in extensive recent studies on vibrational spectra of substituted maleimides [3,4,6–8]. Lazslo et al. [8] investigated the molecular structure of maleimide by using electron diffraction experimental method and MINDO/3 and CNDO/2 calculation methods. They determined bond lengths and angles of maleimide and related molecules. Harsányi et al. [7] studied all

vibrations of maleimide experimental and theoretical. Parker studied extensively the vibrational assignments of infrared (IR), Fourier transform Raman (FT-Raman) and inelastic neutron scattering of *N*-methylmaleimide [3]. *N*-Phenylmaleimide and *N*-(perdeuterophenyl)maleimide are investigated experimentally (infrared, Raman and inelastic neutron scattering (INS) spectroscopies) and theoretically with density functional theory (DFT) [4]. The infrared and Raman spectra of *N*-methylmaleimide (solid, solution, gas) and of (π-*N*-methylmaleimide) iron tetracarbonyl (solid, solution) which the assignment of the normal modes of both molecules was offered and compared with the data for (π-maleic anhydride) iron tetracarbonyl are obtained by Lokshin et al. [6]. Steege and Buma [9] investigated the spectroscopic and dynamic properties of the strongly one–photon absorbing S4($\pi$C=C$\pi^*$) state of maleimide and *N*-methylmaleimide with an experimental approach that combined with ab initio calculations of the electronic structure of the molecules. *N*-Phenylmaleimide and *N*-ethylmaleimide are also studied by X-ray crystallography [10–11].

Literature survey reveals that to the best of our knowledge, no experimental vibrational assignment for 2,3DBrNMM (also known as 3,4-dibromo-*N*-methylpyrrole-2,5-dione) molecule has been performed yet. Also, ab initio Hartree–Fock (HF) and density functional theory (DFT) calculations have not been performed on title

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molecule, and analysis of the vibrational modes of this molecule using quantum chemical methods has not been published in the literature so far.

In this study, we recorded FT-IR, FT-Raman, $^1$H NMR and $^{13}$C NMR spectra of title compound and calculated the vibrational frequencies of 2,3DBrNMM in the ground state to distinguish fundamentals from experimental vibrational frequencies and geometric parameters using HF and DFT/B3LYP (Becke 3-Lee-Yang-Parr) methods. In addition, the gauge-including atomic orbital (GIAO) $^{13}$C and $^1$H chemical shifts calculations of the title compound were calculated by using HF and B3LYP methods with 6-311++G(d,p) basis set. A detailed quantum chemical study will aid in making definite assignments to fundamental normal modes of 2,3DBrNMM and in clarifying the experimental data for this important molecule.

## 2. Experimental

The compound 2,3DBrNMM molecule in solid state was purchased from Sigma–Aldrich chemical company with a stated purity of 99%. The FT-IR spectrum of title molecule was recorded between 4000 cm$^{-1}$ and 400 cm$^{-1}$ on a Perkin Elmer FT-IR System Spectrum BX spectrometer which was calibrated using polystyrene bands. The spectrum was recorded at room temperature, with a scanning speed of 10 cm$^{-1}$ min$^{-1}$ and the spectral resolution of 4.0 cm$^{-1}$. FT-Raman spectra of the sample was recorded on a Bruker RFS 100/S FT-Raman instrument using 1064 nm excitation from an Nd:YAG laser. The detector is a liquid nitrogen cooled Ge detector. Five hundred scans were accumulated at 4 cm$^{-1}$ resolution using a laser power of 100 mW.

NMR experiments were performed in Varian Infinity Plus spectrometer at 300 K. The 2,3DBrNMM molecule was dissolved in chloroform (CDCl$_3$). Chemical shifts were reported in ppm relative to tetramethylsilane (TMS) for $^1$H NMR, $^{13}$C NMR and DEPT NMR spectra. $^1$H and $^{13}$C NMR spectra were obtained at a base frequency of 75 MHz for $^{13}$C and 300 MHz for $^1$H nuclei.

## 3. Calculations

The molecular structure of 2,3DBrNMM in the ground state (*in vacuo*) was determined with HF and B3LYP employing the 6-31G(d), 6-31G(d,p), 6-31+G(d,p), 6-31++G(d,p), 6-311G(d), 6-311G(d,p), 6-311+G(d,p) and 6-311++G(d,p) basis sets. The optimized structural parameters are used in the vibrational frequencies calculations at HF and DFT levels. By using the same methods and basis sets, it was seen that all the vibration frequencies of title molecule were positive. Therefore, we were confident that a definite absolute minimum in the potential energy surface was found. The minimum energy of geometrical structure is obtained by using level 6-311++G(d,p) basis set. Therefore, calculated values by this set are used in discussion. The calculated vibrational frequencies are scaled by 0.9050 for HF [12]. For B3LYP with 6-311++G(d,p) basis set, the wavenumbers in the ranges from 4000 to 1700 cm$^{-1}$ and lower than 1700 cm$^{-1}$ are scaled with 0.958 and 0.983, respectively [13]. The total energy distribution (TED) was calculated by using the SQM program [14] and the fundamental vibrational modes were characterized by their TED. The theoretical results have enabled us to make the detailed assignments of the experimental IR and Raman spectra of title molecule.

For NMR calculations, the title molecule was firstly optimized at HF and B3LYP methods with 6-311++G(d,p) level. After optimization, $^1$H NMR and $^{13}$C NMR chemical shifts ($\delta_H$ and $\delta_C$) were calculated using the GIAO method [15] in chloroform (CDCl$_3$) at HF and B3LYP methods with 6-311++G(d,p) basis set. Relative chemical shifts were then estimated by using the corresponding TMS shield-

ing calculated in advance at the same theoretical level as the reference. $^{13}$C and $^1$H isotropic magnetic shielding (I.M.S.) of any X carbon (or hydrogen) atom was made according to the value $^{13}$C IMS of TMS: $CS_x = IMS_{TMS} - IMS_x$ ($^1$H IMS of TMS: $HS_x = IMS_{TMS} - IMS_x$). Calculated $^1$H and $^{13}$C isotropic chemical shieldings for TMS at HF and B3LYP methods with 6-311++G(d,p) level in CDCl$_3$ by using the IEFPCM method were 32.421 ppm, 31.884 ppm and 196.365 ppm, 184.252 ppm, respectively. The experimental values for $^1$H and $^{13}$C isotropic chemical shifts for TMS were 30.84 ppm and 188.1 ppm, respectively [16].

The calculations are performed by using GaussView molecular visualisation program [17] and *GAUSSSIAN 03* program package on the personal computer [18].

## 4. Results and discussion

The present molecule 2,3DBrNMM which the five membered ring had an envelope from retaining the planarity of the C–C=C–C part belongs to C$_s$ point group symmetry. The title molecule consists of 13 atoms, so it has 33 normal vibrational modes which fall into 22 in-plane vibrations of the A′ species and 11 out-plane vibrations of the A″ species. All the 33 fundamental vibrations are active in both IR and Raman. Calculated energies for title molecule, determined by HF and B3LYP/all basis sets are presented in Table 1. As clearly seen from the values given in Table 1, on the calculated energies, there is a little difference between basis sets for 6-311 (or 6-31), use of the basis sets of larger sizes give rise to increases in the differences between the calculated energies of the title molecule. However, when we compared the 6-31 and 6-311 basis sets the difference is large.

The molecular structure and numbering of the atoms of 2,3DBrNMM is shown in Fig. 1. Since the crystal structure of the title compound is not available in the literature till now, the geometric parameters compared with the maleimide [7,8], *N*-phenylmaleimide [10] and 3-benzoylmethyl-2-chloro-*N*-methylmaleimide (3BM2ClNMM) [19] bond lengths and bond angles. The calculated vibrational frequencies are compared with the experimental FT-IR and FT-Raman spectra of title molecule.

### 4.1. Geometrical structure

The first task for a computational work was to determine the optimized geometry of 2,3DBrNMM. Calculations on 2,3DBrNMM have been performed under the restriction of C$_s$ symmetry with the mirror plane perpendicular to the ring. The optimized structure parameters calculated ab initio HF and DFT (B3LYP) with the 6-31++G(d,p) and 6-311++G(d,p) basis sets are listed in Table 2 in accordance with the atom numbering scheme given in Fig. 1.

As discussed in our previous paper [20,21], it is well known that HF methods underestimate bond lengths; DFT method predicts bond lengths which are systematically too long, particularly the

**Table 1**
Calculated energies for 2,3DBrNMM by HF and B3LYP methods

| Basis sets | HF | B3LYP |
|---|---|---|
| | Energy (Hartree) | Energy (Hartree) |
| 6-311++G(d,p) | −5540.10192571 | −5545.93978485 |
| 6-311+G(d,p) | −5540.10185337 | −5545.93972968 |
| 6-311G(d,p) | −5540.09486481 | −5545.93082322 |
| 6-311G(d) | −5540.09046665 | −5545.92685895 |
| 6-31++G(d,p) | −5535.10910380 | −5541.01802170 |
| 6-31+G(d,p) | −5535.10886019 | −5541.01781144 |
| 6-31G(d,p) | −5535.05066724 | −5540.94816480 |
| 6-31G(d) | −5535.04587248 | −5540.92685895 |