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## Theoretical investigations on the molecular structure, vibrational spectra, HOMO–LUMO and NBO analysis of 5-chloro-2-((4-chlorophenoxy)methyl)benzimidazole



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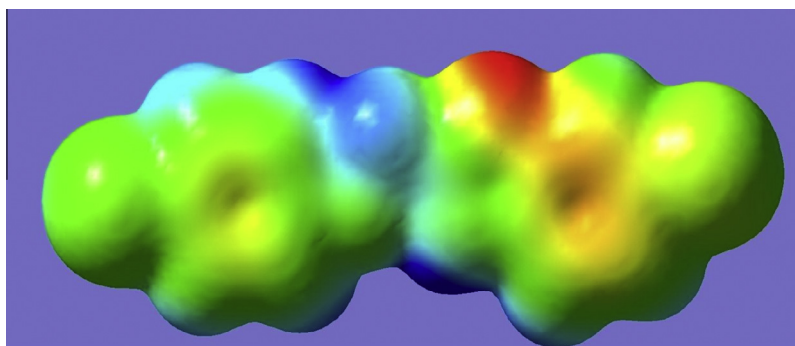
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### HIGHLIGHTS

- IR, Raman spectra and NBO analysis were reported.
- The wavenumbers are calculated theoretically using Gaussian09 software.
- The wavenumbers are assigned using PED analysis.
- The geometrical parameters are in agreement with that of similar compounds.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The optimized molecular structure, vibrational frequencies, corresponding vibrational assignments of 5-chloro-2-((4-chlorophenoxy)methyl)benzimidazole have been investigated experimentally and theoretically using Gaussian09 software package. The energy and oscillator strength calculated by time dependent density functional theory results almost compliments with experimental findings. Gauge-including atomic orbital <sup>1</sup>H NMR chemical shifts calculations were carried out and compared with experimental data. The HOMO and LUMO analysis is used to determine the charge transfer within the molecule. The stability of the molecule arising from hyper-conjugative interaction and charge delocalization has been analyzed using NBO analysis. Molecular electrostatic potential was performed by the DFT method and the infrared intensities and Raman activities are reported. Mulliken's net charges have been calculated and compared with the atomic natural charges. First hyperpolarizability is calculated in order to find its role in non-linear optics.

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### Introduction

Benzimidazole derivatives possess a variety of biological activities and pharmacological effects. Several compounds containing benzimidazole group, have been reported to exhibit antimicrobial [1–3], anticancer [4,5], antifungal [6,7], anti-parasitic [8], antiviral

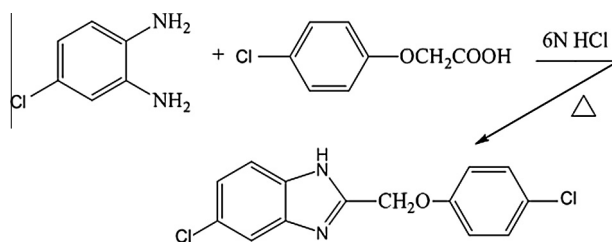
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[9] and anti-inflammatory [10] activities. Benzimidazole and its derivatives show pharmaceutical activity [11–17], such as lowering of blood sugar level, inhibition of phosphodiesterase-5 [18], as well as casein kinase-2 and -5 [19]. Despite a numerous attempts to develop new structural prototype in the search for more effective antimicrobials, the benzimidazoles still remain as one of the most versatile class of compounds against microbes [20–27] and, therefore, are useful substructures for further molecular exploration. Benzimidazole-containing heterocyclic moieties have found extensive uses in agriculture [28]. The benzimidazole scaffold is an accepted pharmacophore and represents an important synthetic precursor in new drug discovery [29–36]. Yildiz-Oren et al. [37] synthesized 5-chloro-2-((4-chlorophenoxy)methyl)benzimidazole for evaluating microbiological activity. The minimum inhibitory concentrations (MIC) of the title compound against *Staphylococcus aureus*, *Streptococcus faecalis*, *Bacillus subtilis* as Gram-positive and *Escherichia coli*, *Klebsiella pneumoniae*, *Pseudomonas aeruginosa* as Gram negative bacteria and *Candida albicans* as a yeast were obtained by using twofold serial dilution technique and compared to ampicillin, amoxycillin, tetracycline, streptomycin, clotrimazole and haloprogin as standard drugs. According to this study, the title structure was found to be moderately potent against *S. aureus*, *S. faecalis*, *B. subtilis*, *E. coli*, *K. pneumoniae*, *P. aeruginosa*, *C. albicans* (MIC values of 50, 50, 25, 50, 25, 25, 12.5  $\mu\text{g}/\text{mL}$ , respectively). Besides, this compound showed more potent than the standard drug streptomycin against *S. faecalis* and *B. subtilis*. Moreover, 5-chloro-2-((4-chlorophenoxy)methyl)benzimidazole exhibited significant antibacterial activity with MIC values of 25  $\mu\text{g}/\text{mL}$  for the Gram-negative enterobacter *P. aeruginosa*, which is effective in nosocomial infections and often resistant to antibiotic therapy, providing higher potencies than the compared standard drugs. Considering the enormous biological importance, 5-chloro-2-((4-chlorophenoxy)methyl)benzimidazole is re-synthesized and the detailed experimental and theoretical normal Raman spectroscopy, and FTIR spectra are reported in the present work.

## Experimental details

The title compound was prepared involving the reaction of 4-chloro-2-phenylenediamine with 4-chloro-phenoxyacetic acid in the presence of dehydrating agents in one step procedure as shown in 'Scheme 1' [37]. During the synthesis of 5-chloro-2-((4-chlorophenoxy)methyl)benzimidazole aqueous hydrochloric acid was used as the condensation reagent according to well-known Philips' method [38]. A mixture of 4-chloro-phenoxyacetic acid (10 mmol) and 4-chloro-2-phenylenediamine (10 mmol) was boiled under reflux with stirring for 19 h in 15 ml 6 N HCl. At the end of the reaction period, the mixture was neutralized with excess of  $\text{NaHCO}_3$ . The collected precipitate washed with water, dried in vacuum, purified by flash chromatography, eluting with  $\text{CHCl}_3$  and recrystallized by using  $\text{EtOH-H}_2\text{O}$ . m.p: 182–183  $^\circ\text{C}$  [37], Yield 35%, Reaction temperature 100  $^\circ\text{C}$ , Elemental analysis: C% 57.33 (Calcu-



Scheme 1. Synthetic pathway of the title compound.

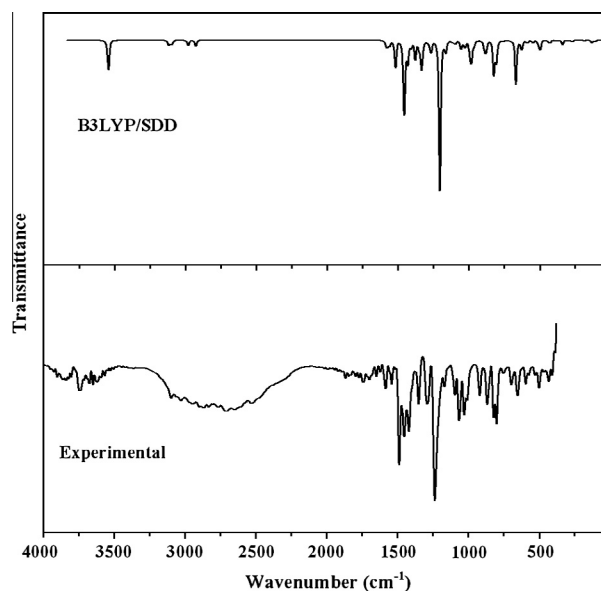


Fig. 1. FT-IR spectrum of 5-chloro-2-((4-chlorophenoxy)methyl)benzimidazole.

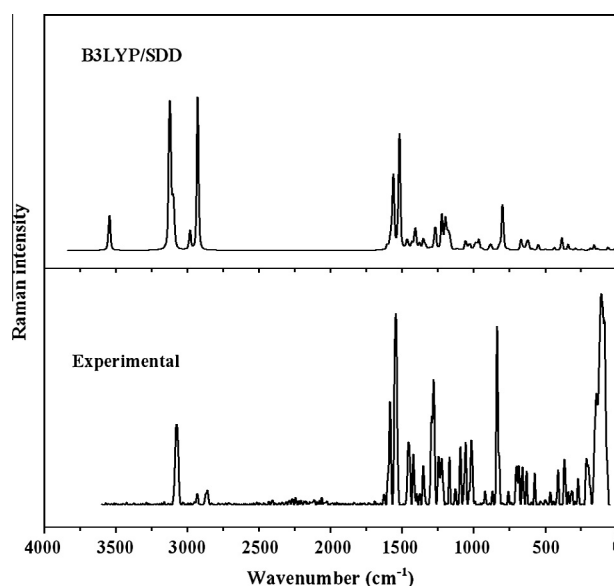


Fig. 2. FT-Raman spectrum of 5-chloro-2-((4-chlorophenoxy)methyl)benzimidazole.

lated) 57.53 (Found); H% 3.41 (Calculated) 3.40 (Found); N% 9.55 (Calculated) 9.51 (Found).

The FT-IR spectrum (Fig. 1) was recorded using KBr pellets on a DR/Jasco FT-IR 6300 spectrometer. The FT-Raman spectrum (Fig. 2) was obtained on a Bruker RFS 100/s, Germany. For excitation of the spectrum the emission of Nd:YAG laser was used, excitation wavelength 1064 nm, maximal power 150mW, measurement on solid sample. <sup>1</sup>H NMR spectra were obtained with a Bruker AC 80 MHz spectrometer and TMS was used as an internal standard. Elemental analyses were carried out with a Perkin–Elmer model 240-C apparatus.

## Computational details

Calculations of the title compound are carried out with Gaussian09 program [39] using the HF/6-31G\*, B3LYP/6-31G\* and

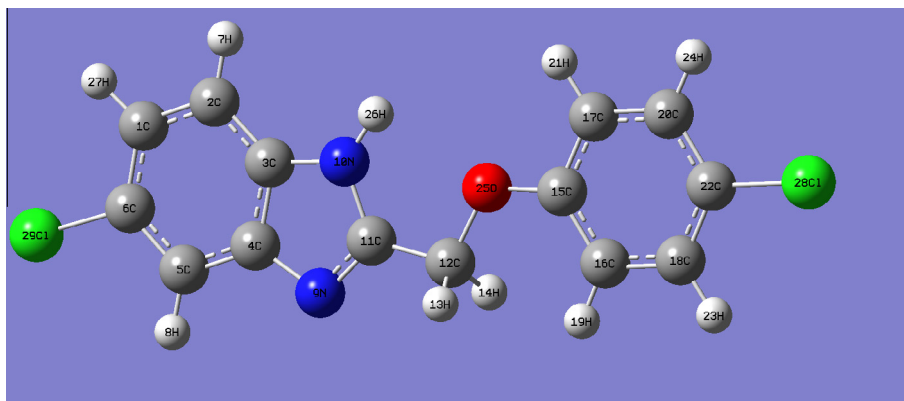


Fig. 3. Optimized geometry (SDD) of 5-chloro-2-((4-chlorophenoxy)methyl)benzimidazole.

B3LYP/SDD basis sets to predict the molecular structure and vibrational wave numbers. Molecular geometry was fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wave numbers are calculated using the analytic second derivatives to confirm the convergence to minima on the potential surface. The wave number values computed at the Hartree–Fock level contain known systematic errors due to the negligence of electron correlation [40]. We therefore, have used the scaling factor value of 0.8929 for HF/6-31G\* basis set. The DFT hybrid B3LYP functional and SDD methods tend to overestimate the fundamental modes; therefore scaling factor of 0.9613 has to be used for obtaining a considerably better agreement with experimental data [40]. The Stuttgart/Dresden effective core potential basis set (SDD) [41] was chosen particularly because of its advantage of doing faster calculations with relatively better accuracy and structures [42]. Then frequency calculations were employed to confirm the structure as minimum points in energy. Parameters corresponding to optimized geometry (SDD) of the title compound (Fig. 3) are given in Table S1 as supporting material. The absence of imaginary wave numbers on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy. The assignments of the calculated wave numbers are aided by the animation option of GAUSSVIEW program, which gives a visual presentation of the vibrational modes [43]. The potential energy distribution (PED) is calculated with the help of GAR2PED software package [44]. The  $^1\text{H}$  NMR data were obtained from the DFT method using basis set 6-31G\*. The characterization of excited states and electronic transitions were performed using the time-dependent DFT method (TDB3LYP) on their correspondingly optimized ground state geometries. We used the time-dependent density functional theory (TD-DFT), which is found to be an accurate method for evaluating the low-lying excited states of molecules and has been thoroughly applied to solve physical and chemical problems. Vertical excitation energies were computed for the first 30 singlet excited states, in order to reproduce the experimental electronic spectra. Potential energy surface scan studies have been carried out to understand the stability of planar and non-planar structures of the molecule. The HOMO and LUMO are calculated by B3LYP/SDD method.

## Results and discussion

### IR and Raman spectra

The observed IR and Raman bands and calculated (scaled) wave numbers and assignments are given in Table 1. The C=N stretching skeletal bands [45–48] are observed in the range 1650–1500  $\text{cm}^{-1}$ .

For the title compound, the SDD calculations give  $\nu\text{C}=\text{N}$  mode at 1520  $\text{cm}^{-1}$  with a band at 1518  $\text{cm}^{-1}$  in the IR spectrum. Similar values are reported at 1536  $\text{cm}^{-1}$  for 5-nitro-2-(4-nitrobenzyl)benzoxazole [49].

Primary aromatic amines with nitrogen directly on the ring absorb strongly at 1330–1260  $\text{cm}^{-1}$  due to stretching of the phenyl carbon–nitrogen bond [50]. Sandhyarani et al. [51] reported  $\nu\text{CN}$  at 1318  $\text{cm}^{-1}$  for 2-mercaptobenzothiazole. For the title compound  $\nu\text{CN}$  is assigned at 1333, 1199, 1177  $\text{cm}^{-1}$  theoretically (SDD). These modes are not pure but contain a significant contribution from other modes. For 5-nitro-2-(4-nitrobenzyl) benzoxazole C–N stretching vibrations are observed in the region 1228–1195  $\text{cm}^{-1}$  [49]. CN stretching modes are reported at 1268, 1220, 1151  $\text{cm}^{-1}$  theoretically for benzimidazolium salts by Malek et al. [52].

In aromatic compounds the  $\nu\text{NH}$  appears the region 3400  $\pm$  40  $\text{cm}^{-1}$  [53]. The SDD calculations give a value of 3544  $\text{cm}^{-1}$  for this  $\nu\text{NH}$  mode and a band is observed in the IR spectrum at 3548  $\text{cm}^{-1}$  and at 3424  $\text{cm}^{-1}$  in the Raman spectrum. N–H group show bands at 1510–1500, 1400–1300 and 740–730  $\text{cm}^{-1}$  [54]. According to literature, if N–H is a part of a closed ring [54,55] the C–N–H deformation band is absent in the region 1510–1500  $\text{cm}^{-1}$ . For the title compound the C–N–H deformation band assigned at 1409  $\text{cm}^{-1}$  theoretically (SDD). The out of plane NH deformation is expected in the region 650  $\pm$  50  $\text{cm}^{-1}$  [53] and the band at 660  $\text{cm}^{-1}$  in the Raman spectrum and at 669  $\text{cm}^{-1}$  theoretically (SDD) are assigned as this mode. Minitha et al. [56] reported  $\nu\text{NH}$  at 3469  $\text{cm}^{-1}$ ,  $\delta\text{NH}$  at 1300  $\text{cm}^{-1}$  and  $\gamma\text{NH}$  at 535  $\text{cm}^{-1}$ . Panicker et al. reported the out-of-plane bending mode of NH at 746  $\text{cm}^{-1}$ , theoretically [57]. Kim et al. reported [58] NH deformation bands at 549, 1484  $\text{cm}^{-1}$  in the Raman spectrum and at 556, 1495  $\text{cm}^{-1}$  theoretically for benzimidazole and Malek et al. [52] reported modes at 1394, 680  $\text{cm}^{-1}$  theoretically as NH deformation.

The vibrations of the  $\text{CH}_2$  group, the asymmetric stretch  $\nu_{\text{as}}\text{CH}_2$ , symmetric stretch  $\nu_{\text{s}}\text{CH}_2$ , scissoring vibration  $\delta\text{CH}_2$ , appear in the region 2945  $\pm$  45, 2885  $\pm$  45 and 1445  $\pm$  35  $\text{cm}^{-1}$ , respectively [50,53]. The SDD calculations give  $\nu_{\text{as}}\text{CH}_2$  at 2982  $\text{cm}^{-1}$  and  $\nu_{\text{s}}\text{CH}_2$  at 2928  $\text{cm}^{-1}$ . The bands observed at 2974, 2931  $\text{cm}^{-1}$  (Raman) and 2940  $\text{cm}^{-1}$  (IR) are assigned as the stretching modes of  $\text{CH}_2$  group. In the present case, the band observed at 1454  $\text{cm}^{-1}$  in the IR, 1456  $\text{cm}^{-1}$  in the Raman spectrum and 1456  $\text{cm}^{-1}$  (SDD) are assigned as the scissoring mode of  $\text{CH}_2$ . Bands of hydrocarbons due to  $\text{CH}_2$  twisting and wagging vibrations are observed in the region 1180–1390  $\text{cm}^{-1}$  [47,50]. The  $\text{CH}_2$  wagging and twisting modes are assigned at 1382  $\text{cm}^{-1}$  and 1206  $\text{cm}^{-1}$  theoretically (SDD). The band calculated at 966  $\text{cm}^{-1}$  is assigned as the rocking mode of  $\text{CH}_2$ .

**Table 1**  
Vibrational assignments of 5-chloro-2-((4-chlorophenoxy)methyl)benzimidazole.

| HF/6-31G* |                 |                | B3LYP/6-31G* |                 |                | B3LYP/SDD |                 |                | IR    | Raman | Assignments  |
|-----------|-----------------|----------------|--------------|-----------------|----------------|-----------|-----------------|----------------|-------|-------|--|
| $\nu$     | IR <sub>i</sub> | R <sub>A</sub> | $\nu$        | IR <sub>i</sub> | R <sub>A</sub> | $\nu$     | IR <sub>i</sub> | R <sub>A</sub> | $\nu$ | $\nu$ | –  |
| 3524      | 145.14          | 67.74          | 3355         | 96.39           | 102.11         | 3544      | 109.10          | 104.02         | 3548  | 3424  | $\nu$ NH(99)   |
| 3058      | 0.22            | 76.46          | 3133         | 0.12            | 83.42          | 3126      | 0.26            | 88.09          | –     | 3163  | $\nu$ CHI(97)  |
| 3051      | 2.67            | 216.81         | 3125         | 2.11            | 221.61         | 3123      | 1.91            | 235.17         | –     | –     | $\nu$ CHII(99)   |
| 3049      | 4.75            | 13.84          | 3122         | 4.43            | 21.16          | 3119      | 6.96            | 3.07           | –     | –     | $\nu$ CHII(99)   |
| 3046      | 3.82            | 120.52         | 3121         | 3.25            | 131.41         | 3118      | 4.57            | 113.62         | –     | –     | $\nu$ CHI(97)  |
| 3035      | 0.25            | 85.21          | 3109         | 4.36            | 69.78          | 3103      | 6.89            | 46.90          | –     | –     | $\nu$ CHII(98)   |
| 3034      | 8.45            | 8.32           | 3106         | 5.73            | 31.26          | 3102      | 4.92            | 35.72          | 3097  | –     | $\nu$ CHII(98)   |
| 3021      | 4.27            | 61.59          | 3094         | 5.51            | 68.85          | 3092      | 4.26            | 51.44          | 3031  | 3076  | $\nu$ CHII(99)   |
| 2928      | 14.64           | 50.49          | 2966         | 16.09           | 58.15          | 2982      | 16.89           | 44.39          | 2940  | 2974  | $\nu$ CH <sub>2</sub> (100)  |
| 2880      | 7.19            | 142.46         | 2923         | 10.88           | 277.86         | 2928      | 16.33           | 296.68         | –     | 2931  | $\nu$ CH <sub>2</sub> (100)  |
| 1635      | 5.56            | 5.06           | 1614         | 0.24            | 6.01           | 1605      | 0.47            | 5.91           | 1622  | 1626  | $\nu$ PhI(56),<br>$\nu$ PhII(23)                                       |
| 1613      | 37.86           | 22.80          | 1591         | 19.78           | 18.09          | 1582      | 27.94           | 24.10          | 1584  | 1584  | $\nu$ PhII(67),<br>$\delta$ CHII(13)                                   |
| 1596      | 10.46           | 15.42          | 1578         | 19.03           | 37.37          | 1565      | 16.87           | 50.87          | –     | –     | $\nu$ PhII(60)   |
| 1591      | 9.32            | 38.87          | 1571         | 8.04            | 70.94          | 1561      | 5.02            | 73.10          | 1542  | 1544  | $\nu$ PhI(65)  |
| 1569      | 143.45          | 132.51         | 1529         | 98.91           | 181.82         | 1520      | 94.89           | 192.10         | 1518  | –     | $\nu$ PhI(18)  |
| 1505      | 183.16          | 3.18           | 1493         | 47.05           | 20.44          | 1468      | 29.20           | 14.48          | 1489  | –     | $\nu$ PhII(62),<br>$\delta$ CHII(11)                                   |
| 1490      | 60.11           | 10.49          | 1482         | 156.91          | 14.87          | 1456      | 218.66          | 5.19           | 1454  | 1456  | $\delta$ CH <sub>2</sub> (45),<br>$\delta$ CHII(15),<br>$\nu$ PhII(16) |
| 1466      | 77.18           | 6.47           | 1452         | 61.26           | 9.80           | 1433      | 75.72           | 11.65          | 1420  | 1422  | $\nu$ PhI(41),<br>$\delta$ CHI(20)                                     |
| 1446      | 27.64           | 18.46          | 1427         | 16.59           | 47.25          | 1409      | 26.92           | 45.93          | –     | –     | $\delta$ NH(59),<br>$\nu$ PhI(26)                                      |
| 1407      | 21.37           | 1.33           | 1401         | 5.53            | 1.16           | 1382      | 8.97            | 2.06           | –     | 1398  | $\delta$ CH <sub>2</sub> (55),<br>$\nu$ PhII(42)                       |
| 1405      | 87.32           | 5.30           | 1387         | 71.65           | 11.31          | 1379      | 50.78           | 8.23           | –     | 1375  | $\nu$ PhI(53),<br>$\nu$ CN(13),<br>$\delta$ CHI(12)                    |
| 1363      | 142.15          | 6.97           | 1359         | 20.32           | 25.23          | 1351      | 33.04           | 21.67          | 1352  | 1353  | $\delta$ CHI(26),<br>$\nu$ PhI(61)                                     |
| 1328      | 65.44           | 16.54          | 1339         | 116.65          | 9.59           | 1333      | 113.51          | 5.92           | –     | –     | $\nu$ CN(61),<br>$\nu$ PhII(10)  |
| 1318      | 7.45            | 4.88           | 1309         | 0.19            | 2.99           | 1305      | 1.93            | 3.42           | –     | 1296  | $\nu$ PhII(79)   |
| 1253      | 245.14          | 30.09          | 1309         | 2.01            | 1.61           | 1285      | 4.83            | 1.30           | 1292  | 1280  | $\delta$ CHII(87)  |
| 1249      | 122.78          | 6.39           | 1283         | 40.25           | 27.56          | 1270      | 45.78           | 41.13          | –     | 1255  | $\nu$ CN(15),<br>$\nu$ Ph I(22),<br>$\delta$ CHI(40)                   |
| 1242      | 113.62          | 56.73          | 1236         | 9.31            | 34.01          | 1223      | 7.41            | 44.49          | 1237  | 1225  | $\delta$ CHI(47),<br>$\nu$ CN(15)                                      |
| 1227      | 6.16            | 12.38          | 1221         | 440.51          | 4.80           | 1206      | 411.48          | 5.4            | –     | –     | $\delta$ CH <sub>2</sub> (45)  |
| 1209      | 8.24            | 13.64          | 1205         | 28.35           | 53.51          | 1199      | 48.92           | 31.82          | –     | –     | $\nu$ PhI(10),<br>$\delta$ CHI(10),<br>$\nu$ CN(50)                    |
| 1196      | 78.55           | 0.94           | 1194         | 3.22            | 14.56          | 1191      | 1.62            | 12.10          | –     | 1193  | $\nu$ COC(67)  |
| 1189      | 5.63            | 21.25          | 1185         | 17.45           | 23.55          | 1177      | 4.75            | 30.38          | –     | –     | $\nu$ CN(58),<br>$\delta$ PhI(21)                                      |
| 1180      | 10.48           | 6.62           | 1179         | 31.59           | 14.97          | 1165      | 37.50           | 10.40          | 1169  | 1170  | $\delta$ CHII(71)  |
| 1133      | 2.56            | 6.30           | 1133         | 3.46            | 3.07           | 1115      | 5.02            | 2.86           | –     | 1120  | $\delta$ CHI(52),<br>$\nu$ PhI(15)                                     |
| 1104      | 11.08           | 0.04           | 1112         | 9.86            | 0.53           | 1098      | 13.80           | 0.70           | 1095  | 1093  | $\delta$ CHII(60),<br>$\nu$ PhII(27)                                   |
| 1073      | 25.14           | 8.79           | 1068         | 43.69           | 16.51          | 1056      | 35.93           | 18.26          | 1066  | 1056  | $\nu$ PhII(36),<br>$\delta$ CHII(12)                                   |
| 1046      | 34.52           | 7.04           | 1039         | 32.72           | 10.69          | 1029      | 29.51           | 12.02          | 1030  | 1033  | $\nu$ PhI(50),<br>$\delta$ CHI(27)                                     |
| 1038      | 0.11            | 1.52           | 1023         | 0.04            | 0.99           | 1013      | 0.05            | 0.45           | 1008  | 1016  | $\delta$ CHII(83)  |
| 1032      | 82.79           | 3.96           | 1005         | 4.39            | 0.74           | 993       | 65.30           | 9.67           | –     | 992   | $\nu$ COC(54)  |
| 1030      | 0.03            | 0.31           | 999          | 105.71          | 14.37          | 982       | 47.17           | 5.09           | –     | –     | $\delta$ PhI(53),<br>$\nu$ PhII(22)                                    |
| 1020      | 0.01            | 1.21           | 978          | 32.05           | 13.98          | 966       | 16.50           | 16.20          | –     | –     | $\delta$ RingIII(23),<br>$\delta$ CH <sub>2</sub> (63)                 |
| 1018      | 0.20            | 0.11           | 955          | 0.01            | 0.47           | 958       | 0.15            | 0.13           | –     | –     | $\gamma$ CHII(89)  |
| 1009      | 59.09           | 3.13           | 943          | 0.08            | 1.50           | 942       | 0.88            | 2.54           | –     | 951   | $\gamma$ CHI(87)   |
| 993       | 7.20            | 29.24          | 939          | 0.03            | 0.11           | 939       | 0.12            | 0.58           | 921   | 938   | $\gamma$ CHII(78),<br>$\tau$ PhII(18)                                  |
| 964       | 24.36           | 0.07           | 895          | 52.53           | 10.24          | 891       | 23.71           | 1.88           | –     | –     | $\gamma$ CHI(76),<br>$\tau$ PhI(14)                                    |
| 901       | 59.64           | 16.87          | 889          | 19.57           | 0.71           | 882       | 49.50           | 10.72          | 868   | 889   | $\delta$ Ph I(26),<br>$\nu$ CCl (56)                                   |

Table 1 (continued)

| HF/6-31G* |                 |                | B3LYP/6-31G* |                 |                | B3LYP/SDD |                 |                | IR    | Raman | Assignments  |
|-----------|-----------------|----------------|--------------|-----------------|----------------|-----------|-----------------|----------------|-------|-------|--|
| $\nu$     | IR <sub>1</sub> | R <sub>A</sub> | $\nu$        | IR <sub>1</sub> | R <sub>A</sub> | $\nu$     | IR <sub>1</sub> | R <sub>A</sub> | $\nu$ | $\nu$ | –  |
| 879       | 126.85          | 0.86           | 829          | 4.85            | 3.54           | 826       | 96.06           | 0.72           | 823   | 837   | $\gamma$ CHII(23),<br>$\nu$ PhII(42),<br>$\gamma$ COC(12)                        |
| 861       | 6.61            | 1.85           | 826          | 79.31           | 0.98           | 820       | 5.11            | 6.30           | –     | 823   | $\gamma$ CHII(53),<br>$\nu$ CN(15)   |
| 858       | 57.57           | 1.93           | 812          | 3.02            | 59.69          | 809       | 10.64           | 0.03           | –     | –     | $\gamma$ CHII(97)  |
| 829       | 16.06           | 4.10           | 808          | 9.20            | 3.24           | 807       | 54.41           | 0.81           | 802   | –     | $\gamma$ CHI(74)   |
| 814       | 2.05            | 56.92          | 804          | 42.94           | 2.49           | 798       | 4.02            | 61.97          | –     | 799   | $\nu$ CCI(38),<br>$\delta$ PhII(20),<br>$\delta$ CCO(11)                         |
| 783       | 0.71            | 2.09           | 743          | 0.68            | 2.32           | 759       | 2.75            | 1.41           | 755   | 758   | $\tau$ PhI(50),<br>$\tau$ RingIII(33)  |
| 732       | 2.83            | 0.38           | 721          | 1.59            | 0.24           | 710       | 0.72            | 0.10           | –     | 704   | $\delta$ RingIII(26),<br>$\delta$ PhII(13),<br>$\delta$ PhI(12)                  |
| 721       | 3.37            | 0.17           | 696          | 0.07            | 0.19           | 693       | 0.48            | 0.11           | 699   | 685   | $\tau$ PhII(69),<br>$\gamma$ COC(15),<br>$\gamma$ CCI(10)                        |
| 694       | 105.13          | 4.19           | 679          | 29.66           | 9.69           | 669       | 104.36          | 0.34           | –     | 660   | $\gamma$ NH(97)  |
| 682       | 35.62           | 10.53          | 654          | 57.71           | 2.52           | 669       | 27.27           | 13.29          | –     | 660   | $\delta$ RingIII(31),<br>$\delta$ PhI(27),<br>$\nu$ CCI(19)                      |
| 659       | 57.54           | 0.57           | 649          | 76.59           | 0.41           | 655       | 0.85            | 2.02           | 653   | –     | $\tau$ RingIII(54),<br>$\gamma$ CC(24)   |
| 643       | 32.70           | 12.81          | 641          | 38.94           | 8.04           | 630       | 36.43           | 10.81          | –     | 631   | $\delta$ PhII(31),<br>$\nu$ CCI(22),<br>$\delta$ RingIII(26)                     |
| 638       | 1.79            | 6.56           | 634          | 0.03            | 6.18           | 620       | 0.19            | 8.98           | –     | –     | $\delta$ PhII(81)  |
| 621       | 29.04           | 1.27           | 593          | 6.40            | 1.19           | 588       | 10.55           | 2.10           | 596   | 574   | $\gamma$ CCI(10),<br>$\tau$ PhI(52),<br>$\tau$ RingIII(11)                       |
| 556       | 9.43            | 5.04           | 558          | 8.55            | 5.15           | 551       | 6.57            | 6.92           | 534   | 535   | $\delta$ PhI(36),<br>$\delta$ RingIII(16),<br>$\delta$ CCI(15)                   |
| 525       | 17.47           | 0.75           | 515          | 19.16           | 1.04           | 509       | 18.67           | 0.60           | 502   | 522   | $\delta$ CC(22),<br>$\delta$ Ph I(21),<br>$\delta$ COC(21)                       |
| 516       | 18.37           | 0.43           | 502          | 12.25           | 0.62           | 497       | 22.19           | 1.19           | 500   | –     | $\tau$ PhII(36),<br>$\gamma$ COC(31),<br>$\gamma$ CCI(23)                        |
| 448       | 7.86            | 0.52           | 443          | 1.86            | 2.71           | 438       | 2.07            | 3.04           | –     | 443   | $\delta$ COC(43),<br>$\delta$ CCI(15)  |
| 443       | 1.49            | 5.20           | 429          | 5.18            | 0.52           | 431       | 9.48            | 0.39           | 434   | –     | $\tau$ PhII(46),<br>$\tau$ RingIII(27),<br>$\tau$ PhI(12)                        |
| 430       | 0.02            | 0.09           | 419          | 0.05            | 0.09           | 412       | 0.08            | 0.09           | 408   | 411   | $\tau$ PhII(84)  |
| 391       | 2.80            | 14.49          | 391          | 2.26            | 12.15          | 385       | 2.17            | 13.87          | –     | –     | $\delta$ CCI(24),<br>$\delta$ PhI(16),<br>$\delta$ PhII(14),<br>$\delta$ CCO(11) |
| 364       | 0.29            | 0.13           | 350          | 0.13            | 0.01           | 352       | 0.01            | 0.02           | –     | 367   | $\tau$ RingIII(24),<br>$\gamma$ CC(14),<br>$\tau$ PhI(14)                        |
| 346       | 12.73           | 6.90           | 345          | 14.89           | 5.55           | 340       | 13.09           | 6.13           | –     | 339   | $\delta$ CCI(44),<br>$\delta$ PhI(25)  |
| 335       | 1.61            | 1.75           | 321          | 0.75            | 1.36           | 317       | 0.79            | 0.93           | –     | 314   | $\delta$ C=N (39),<br>$\tau$ PhII(25),<br>$\gamma$ CO(13)                        |
| 295       | 1.65            | 2.47           | 296          | 1.22            | 2.03           | 291       | 1.50            | 2.39           | –     | 292   | $\delta$ CCI(52),<br>$\delta$ CC(11)   |
| 284       | 5.66            | 0.64           | 274          | 4.11            | 0.78           | 274       | 4.34            | 0.62           | –     | 271   | $\tau$ PhI(45),<br>$\gamma$ CC(13),<br>$\tau$ RingIII(13),<br>$\gamma$ CCI(10)   |
| 249       | 0.59            | 1.67           | 248          | 0.43            | 1.28           | 244       | 0.52            | 1.43           | –     | 213   | $\delta$ CCI(67)   |
| 186       | 0.76            | 2.46           | 183          | 0.93            | 2.67           | 186       | 1.34            | 2.05           | –     | –     | $\tau$ PhI(34),<br>$\gamma$ CC(13),<br>$\tau$ RingIII(21)                        |
| 159       | 0.03            | 4.16           | 161          | 0.04            | 4.42           | 160       | 0.04            | 4.93           | –     | –     | $\delta$ CCI(33),<br>$\delta$ CCO(20)  |
| 136       | 5.97            | 0.02           | 134          | 1.75            | 1.32           | 133       | 1.78            | 1.49           | –     | 138   | $\delta$ COC(46),<br>$\delta$ CC(16),<br>$\delta$ CCI(10)                        |

(continued on next page)

Table 1 (continued)

| HF/6-31G* |                 |                | B3LYP/6-31G* |                 |                | B3LYP/SDD |                 |                | IR    | Raman | Assignments   |
|-----------|-----------------|----------------|--------------|-----------------|----------------|-----------|-----------------|----------------|-------|-------|---|
| $\nu$     | IR <sub>I</sub> | R <sub>A</sub> | $\nu$        | IR <sub>I</sub> | R <sub>A</sub> | $\nu$     | IR <sub>I</sub> | R <sub>A</sub> | $\nu$ | $\nu$ | –   |
| 132       | 1.85            | 1.34           | 133          | 4.18            | 0.12           | 133       | 4.57            | 0.21           | –     | –     | $\tau$ CCO(44),<br>$\tau$ PhII(27),<br>$\gamma$ CCl(10)                       |
| 107       | 7.87            | 0.89           | 106          | 5.41            | 0.84           | 112       | 6.03            | 0.79           | –     | 110   | $\tau$ CCO(28),<br>$\tau$ PhI(16),<br>$\gamma$ CCl(11),<br>$\tau$ RingIII(10) |
| 55        | 0.19            | 4.37           | 59           | 0.01            | 4.52           | 62        | 0.06            | 4.02           | –     | –     | $\tau$ CCO(54),<br>$\tau$ RingIII(10)   |
| 39        | 1.54            | 0.05           | 40           | 1.46            | 0.09           | 39        | 1.34            | 0.09           | –     | –     | $\delta$ CCO(31),<br>$\delta$ COC(32),<br>$\delta$ CC(25)                     |
| 20        | 0.49            | 1.03           | 18           | 0.12            | 0.65           | 20        | 0.56            | 0.63           | –     | –     | $\tau$ CCO(66),<br>$\gamma$ CC(18)  |
| 12        | 3.70            | 0.57           | 11           | 4.17            | 1.12           | 16        | 3.38            | 0.59           | –     | –     | $\tau$ CCO(78),<br>$\gamma$ NH(15)  |

$\nu$  – stretching;  $\delta$  – in-plane deformation;  $\gamma$  – out-of-plane deformation;  $\tau$  – torsion; PhI – tri-substituted benzene ring; PhII – para substituted benzene ring; RingIII – benzimidazole ring; IR<sub>I</sub> – IR intensity; R<sub>A</sub> – Raman activity; PED contribution in% is given in brackets in the assignment column.

For the title compound, as expected the asymmetric C–O–C stretching vibration is assigned at 1191 cm<sup>-1</sup> and the symmetric stretching mode at 993 cm<sup>-1</sup> (SDD) theoretically [47]. The C–O–C stretching modes are reported at 1250 and 1073 cm<sup>-1</sup> for 2-mercaptobenzoxazole [59]. Bhagyasree et al. [49] reported C–O–C stretching modes at 1144, 1063 (IR), 1146, 1066 (Raman) and at 1153, 1079 cm<sup>-1</sup> theoretically (SDD).

The vibrations belonging to the bond between the ring and chlorine atoms are worth to discuss here since mixing of vibrations is possible due to the lowering of the molecular symmetry and the presence of heavy atoms on the periphery of the molecule [60]. Mooney [61,62] assigned vibrations of C–Cl, Br, and I in the wave number range of 1129–480 cm<sup>-1</sup>. The CCl stretching vibrations give generally strong bands in the region 710–505 cm<sup>-1</sup>. For simple organic chlorine compounds, CCl absorptions are in the region 750–700 cm<sup>-1</sup>. Sundaraganesan et al. [63] reported CCl stretching at 704 (IR), 705 (Raman), and 715 cm<sup>-1</sup> (DFT) and the deformation bands at 250 and 160 cm<sup>-1</sup>. The aliphatic CCl absorb [53] in the range 830–560 cm<sup>-1</sup> and putting more than one chlorine atom on a carbon atom raises the CCl wave number. The CCl<sub>2</sub> stretching modes are reported at 738 and 284 cm<sup>-1</sup> for dichloromethane [50,64]. Pazdera et al. [65,66] reported the CCl stretching mode at 890 cm<sup>-1</sup>. For 2-cyanophenylisocyanide dichloride, the CCl stretching mode is reported at 870 cm<sup>-1</sup> in the IR spectrum, 877 cm<sup>-1</sup> in the Raman spectrum and at 882 cm<sup>-1</sup> theoretically [67]. Arslan et al. [68] reported the CCl stretching mode at 683 (experimental), and at 711, 736, 687, 697 cm<sup>-1</sup> theoretically. The deformation bands of CCl are reported [68] at 431, 435, 441, and 441 cm<sup>-1</sup>. For the title compound, the bands at 868 cm<sup>-1</sup> in the IR, 889, 799 cm<sup>-1</sup> in Raman and 882, 798 (SDD) are assigned as CCl stretching modes. The deformation bands of CCl are also identified. This is in agreement with the literature data [64,69,70]. For 4-chlorophenylboronic acid, the CCl stretching and deformation bands are reported at 571 (DFT), and at 287 and 236 cm<sup>-1</sup>, respectively [71].

Since the identification of all the normal modes of vibration of large molecules is not trivial, we tried to simplify the problem by considering each molecule as substituted benzene. Such an idea has already been successfully utilized by several workers for the vibrational assignments of molecules containing multiple homo and hetero aromatic rings [72–76]. In the following discussion, the tri-substituted and para substituted phenyl rings are designated as rings PhI and PhII, respectively and benzimidazole as ringIII. The modes in the two phenyl rings will differ in wave

number and the magnitude of splitting will depend on the strength of interactions between different parts (internal coordinates) of the two rings. For some modes, this splitting is so small that they may be considered as quasi-degenerate and for the other modes a significant amount of splitting is observed. Such observations have already been reported [72–76].

The existence of one or more aromatic rings in a structure is normally readily determined from the C–H and C=C–C ring related vibrations. The C–H stretching occurs above 3000 cm<sup>-1</sup> and is typically exhibited as a multiplicity of weak to moderate bands, compared with the aliphatic C–H stretch [77]. In the present case, the SDD calculations give  $\nu$ C–H modes in the range of 3126–3092 cm<sup>-1</sup>. The bands observed at 3097, 3031 cm<sup>-1</sup> in the IR spectrum and at 3163, 3076 cm<sup>-1</sup> in the Raman spectrum are assigned as the  $\nu$ C–H modes of the benzene rings.

The benzene ring possesses six ring stretching vibrations, of which the four with the highest wave numbers (occurring respectively near 1600, 1580, 1490 and 1440 cm<sup>-1</sup>) are good group vibrations. In the absence of ring conjugation, the band near 1580 cm<sup>-1</sup> is usually weaker than that at 1600 cm<sup>-1</sup>. The fifth ring stretching vibration is active near 1355 ± 35 cm<sup>-1</sup>, a region which overlaps strongly with that of the CH in-plane deformation and the intensity is in general, low or medium [53,64]. The sixth ring stretching vibration or ring breathing mode appears as a weak band near 1000 cm<sup>-1</sup> in mono-substituted benzenes [53].

For the title compound, the bands observed at 1622, 1542, 1420, 1352 cm<sup>-1</sup> in the IR and 1626, 1544, 1422, 1375, 1353 cm<sup>-1</sup> in the Raman spectrum are assigned as  $\nu$ PhI modes with 1605, 1561, 1433, 1379, 1270, 1351 cm<sup>-1</sup> as SDD values. For the title compound, PED analysis gives the ring breathing mode of PhI at 1029 cm<sup>-1</sup> [78]. For the phenyl ring PhI, the bands observed at 1237 cm<sup>-1</sup> in the IR spectrum and at 1255, 1225, 1120 cm<sup>-1</sup> in the Raman spectrum are assigned as in-plane CH deformation modes. Also SDD calculations give these modes at 1270, 1223, 1115 cm<sup>-1</sup> which are in agreement with literature [78].

For para substituted benzenes, the  $\delta$ CH modes are seen in the range 995–1315 cm<sup>-1</sup> [53]. Bands observed at 1292, 1169, 1095, 1008 cm<sup>-1</sup> in the IR spectrum and at 1280, 1170, 1093, 1016 cm<sup>-1</sup> in the Raman spectrum are assigned as  $\delta$ CH modes for the ring PhII. The corresponding theoretical values (SDD) are 1285, 1165, 1098 and 1013 cm<sup>-1</sup>. For the para substituted di-heavy phenyl ring, the ring stretching modes  $\nu$ Ph modes are expected in the range 1280–1620 cm<sup>-1</sup> [53]. In this case  $\nu$ PhII modes are assigned at 1582, 1565, 1468, 1382, 1305 cm<sup>-1</sup>

theoretically and observed at 1584, 1489  $\text{cm}^{-1}$  in IR spectrum and at 1584, 1398, 1296  $\text{cm}^{-1}$  in Raman spectrum. The ring breathing modes for the para di-substituted benzenes with entirely different substituent [64] have been reported to be strongly IR active with typical bands in the interval 740–840  $\text{cm}^{-1}$ . For the title compound, the ring breathing mode is assigned at 823  $\text{cm}^{-1}$  in the IR spectrum which finds support from the theoretical value 826  $\text{cm}^{-1}$  which has high infrared intensity. Ambujakshan et al. [79] reported a value 792  $\text{cm}^{-1}$  (IR) and 782  $\text{cm}^{-1}$  (HF) as ring breathing mode.

The C–H out-of-plane deformations are observed between 1000 and 700  $\text{cm}^{-1}$  [53]. Generally the C–H out-of-plane deformations with the highest wave numbers have a weaker intensity than those absorbing at lower wave numbers. The out-of-plane  $\gamma\text{CH}$  modes are observed at 802  $\text{cm}^{-1}$  in the IR spectrum for PhI and at 921, 802  $\text{cm}^{-1}$  in the IR spectrum, 938, 823  $\text{cm}^{-1}$  in the Raman spectrum for PhII. The corresponding SDD values are 942, 891, 807  $\text{cm}^{-1}$  for PhI and 958, 939, 820, 809  $\text{cm}^{-1}$  for PhII. A very strong CH out-of plane deformation band, occurring at  $840 \pm 50 \text{ cm}^{-1}$  is typical for 1,4-disubstituted benzenes [53]. For the title compound, a very strong  $\gamma\text{CH}$  observed by calculation gives at 942  $\text{cm}^{-1}$ . Again according to literature [50,53] a lower  $\gamma\text{CH}$  absorbs in the neighborhood  $820 \pm 45 \text{ cm}^{-1}$ , but is much weaker or infrared inactive and the corresponding theoretical mode is 809  $\text{cm}^{-1}$ .

#### Optimized geometry

A detailed potential energy surface (PES) scan on dihedral angles  $\text{C}_4\text{--N}_9\text{--C}_{11}\text{--C}_{12}$ ,  $\text{N}_9\text{--C}_{11}\text{--C}_{12}\text{--O}_{25}$ ,  $\text{C}_{11}\text{--C}_{12}\text{--O}_{25}\text{--C}_{15}$  have been performed at B3LYP/6-31G(d) level to reveal all possible conformations of 5-chloro-2-((4-chlorophenoxy)methyl)-benzimidazole. The PES scan was carried out by minimizing the potential energy in all geometrical parameters by changing the torsion angle at every  $10^\circ$  for a  $180^\circ$  rotation around the bond. The results obtained in PES scan study by varying the torsion perturbation around the methyl bonds ( $\text{CH}_2$ ) are given as supporting information in Figs. S1–S3. For the  $\text{C}_4\text{--N}_9\text{--C}_{11}\text{--C}_{12}$  rotation, the minimum energy was obtained at  $180.0^\circ$  in the potential energy curve of energy  $-1644.6314$  Hartrees. For the  $\text{N}_9\text{--C}_{11}\text{--C}_{12}\text{--O}_{25}$  rotation, the minimum energy occurs at  $180.0^\circ$  in the potential energy curve of energy  $-1644.6313$  and for  $\text{C}_{11}\text{--C}_{12}\text{--O}_{25}\text{--C}_{15}$  rotation, the minimum energy was obtained at  $0.0^\circ$  in the potential energy curve of energy  $-1644.6314$  Hartrees.

To the best of our knowledge, no X-ray crystallographic data of this molecule has yet been established. The optimized molecular structure of 5-chloro-2-((4-chlorophenoxy)methyl)-benzimidazole was determined by using Gaussian09 program. From Table S1, it is clearly seen that the dihedral angles  $\text{C}_6\text{--C}_5\text{--C}_4\text{--N}_9$  and  $\text{C}_4\text{--N}_9\text{--C}_{11}\text{--C}_{12}$ ,  $\text{C}_1\text{--C}_2\text{--C}_3\text{--N}_{10}$ ,  $\text{C}_2\text{--C}_3\text{--N}_{10}\text{--C}_{11}$  are  $180^\circ$ . This indicates that the benzene ring I and the benzimidazole ring moieties of the title compound are planar as in the case of 2-amino-6-methylbenzothiazole [80]. For 2-amino-6-methylbenzothiazole [81] the bond lengths  $\text{C}_4\text{--C}_5$ ,  $\text{C}_4\text{--C}_3$ ,  $\text{C}_3\text{--C}_2$ ,  $\text{C}_4\text{--N}_9$  are respectively, 1.4145, 1.4333, 1.4066, 1.4110 Å. The corresponding values for the title compound are 1.4083, 1.4311, 1.4044, 1.41 Å. The ab initio calculations give the bond angles  $\text{C}_3\text{--C}_4\text{--N}_9$ ,  $\text{C}_4\text{--N}_9\text{--C}_{11}$ ,  $\text{C}_3\text{--N}_{10}\text{--C}_{11}$ ,  $\text{N}_9\text{--C}_{11}\text{--N}_{10}$  as  $110.0^\circ$ ,  $104.9^\circ$ ,  $107.2^\circ$  and  $113.1^\circ$  for the title compound. These values are in agreement with the bond angles reported for 2-amino-6-methylbenzothiazole [81] and for 2-amino-4-ethylbenzothiazole [82]. For 2-amino-4-methylbenzothiazole [82] the bond lengths  $\text{C}_3\text{--C}_4$ ,  $\text{C}_{11}\text{--C}_{12}$ ,  $\text{C}_4\text{--N}_9$  are 1.3916, 1.2962, 1.4173 Å respectively.

Purkayastha and Chattopadhyay [83] reported  $\text{N}_9\text{--C}_{11}$ ,  $\text{N}_9\text{--C}_4$  bond lengths as 1.3270, 1.400 Å for benzothiazole and 1.3503, 1.407 Å for benzimidazole compounds. For the title compound

we have obtained these values as 1.331 and 1.41 Å. The carbon–carbon bond lengths in the phenyl ring PhI lies between 1.3965 and 1.4152 Å while for phenyl ring PhII, the range is 1.399–1.4094 Å. The CH bond lengths lies between 1.0839 and 1.086 Å for Ph I and 1.0847–1.0855 Å for PhII. These changes in bond lengths for the title compound can be attributed to the conjugation of the phenyl ring. Here for the title compound, benzene is a regular hexagon with bond lengths somewhere in between the normal values for a single (1.54 Å) and a double (1.33 Å) bond [84].

For the title compound, the bonds  $\text{C}_{11}\text{--N}_9 = 1.331$  Å show typical double bond characteristics. However,  $\text{C}_4\text{--N}_9 = 1.41$ ,  $\text{C}_3\text{--N}_{10} = 1.3985$ ,  $\text{C}_{11}\text{--N}_{10} = 1.3874$  Å bond lengths are shorter than the normal C–N single bond length of about 1.48 Å. The shortening of the C–N bonds reveal the effects of resonance in this part of the molecule [68] and this situation can be attributed to the difference in hybridization of the different carbon atoms. The imine  $\text{C}_{11}\text{=N}_9$  bond length is expected to be shorter than the amine C–N bond length. In the present case  $\text{C}_{11}\text{--N}_9$  and  $\text{C}_{11}\text{--N}_{10}$  bond distances are 1.3310 and 1.3874 Å respectively. The essential skeletal angles of  $\text{C}_3\text{--N}_{10}\text{--C}_{11}$ ,  $\text{C}_4\text{--N}_9\text{--C}_{11}$  are  $107.2^\circ$  and  $104.9^\circ$ . These values are particularly in excellent agreement with benzimidazole derivatives  $1.316^\circ$ ,  $1.376^\circ$ ,  $106.2^\circ$ ,  $105.2^\circ$  [85],  $1.315^\circ$ ,  $1.387^\circ$ ,  $106.2^\circ$ ,  $105.2^\circ$  [86]. The close proximity of the values with each other may be due to the electronic delocalization effect resulted from the super conjugation system formed in the title compound as reported in literature [87].

Lifshitz et al. [80] reported the bond lengths for  $\text{N}_9\text{--C}_{11}$ ,  $\text{C}_3\text{--C}_2$ ,  $\text{C}_4\text{--C}_5$ ,  $\text{C}_3\text{--C}_4$ , and  $\text{N}_9\text{--C}_4$  as 1.291, 1.374, 1.4, 1.403 and 1.401 Å. The corresponding values in the present case are 1.331, 1.4044, 1.4083, 1.4311 and 1.41 Å. Corresponding values are reported as 1.2753, 1.3492, 1.359, 1.3768, 1.3879, 1.3784, 1.3892 Å [79] and 1.2727, 1.347, 1.3594, 1.3884, 1.3777, 1.3776, 1.3903 Å [45]. The bond lengths  $\text{C}_4\text{--N}_9$ ,  $\text{N}_9\text{--C}_{11}$  and  $\text{C}_3\text{--C}_4$  are found to be 1.3436, 1.3804 and 1.3827 Å for mercaptobenzoxazole [47]. For the title compound these values are respectively, 1.41, 1.331 and 1.4311 Å. Chlorine is highly electronegative and tries to obtain additional electron density. It attempts to draw it from the neighboring atoms which moves closer together in order to share the electrons more easily as a result. Due to this the bond angles,  $\text{A}(1,6,5)$  and  $\text{A}(18,22,20)$  are found to be  $123.5^\circ$ ,  $121.5^\circ$  in the present calculation, which is  $120^\circ$  for normal benzene. The CCl bond lengths,  $\text{C}_{22}\text{--Cl}_{28} = 1.8238$ ,  $\text{C}_6\text{--Cl}_{29} = 1.8292$  Å given by SDD calculation are in agreement with CCl bond lengths given by Madhavan et al. [74].

#### First hyperpolarizability

Nonlinear optics deals with the interaction of applied electromagnetic fields in various materials to generate new electromagnetic fields, altered in wavenumber, phase, or other physical properties [88]. Organic molecules able to manipulate photonic signals efficiently are of importance in technologies such as optical communication, optical computing, and dynamic image processing [89,90]. In this context, the dynamic first hyperpolarizability of the title compound is also calculated in the present study. The first hyperpolarizability ( $\beta_0$ ) of this novel molecular system is calculated using SDD method, based on the finite field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyperpolarizability is a third rank tensor that can be described by a  $3 \times 3 \times 3$  matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [91]. The components of  $\beta$  are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the electric field is weak and homogeneous, this expansion becomes

$$E = E_0 - \sum_i \mu_i F^i - \frac{1}{2} \sum_{ij} \alpha_{ij} F^i F^j - \frac{1}{6} \sum_{ijk} \beta_{ijk} F^i F^j F^k - \frac{1}{24} \sum_{ijkl} \gamma_{ijkl} F^i F^j F^k F^l + \dots$$

where  $E_0$  is the energy of the unperturbed molecule,  $F^i$  is the field at the origin,  $\mu_i$ ,  $\alpha_{ij}$ ,  $\beta_{ijk}$  and  $\gamma_{ijkl}$  are the components of dipole moment, polarizability, the first hyper polarizabilities, and second hyperpolarizabilities, respectively. The calculated first hyperpolarizability of the title compound is  $2.7 \times 10^{-30}$  esu, which comparable with the reported values of similar derivatives [92] and which is 20.77 times that of the standard NLO material urea ( $0.13 \times 10^{-30}$  esu) [93]. We conclude that the title compound is an attractive object for future studies of nonlinear optical properties.

#### NBO analysis

The natural bond orbital (NBO) calculations were performed using NBO 3.1 program [94] as implemented in the Gaussian09 package at the DFT/B3LYP level in order to understand various second-order interactions between the filled orbital of one subsystem and vacant orbital of another subsystem, which is a measure of the intermolecular de-localization or hyper conjugation. NBO analysis provides the most accurate possible 'natural Lewis structure' picture of 'j' because all orbital details are mathematically chosen to include the highest possible percentage of the electron density. A useful aspect of the NBO method is that it gives information about interactions of both filled and virtual orbital spaces that could enhance the analysis of intra and inter molecular interactions. The second-order Fock-matrix was carried out to evaluate the donor-acceptor interactions in the NBO basis. The interactions result in a loss of occupancy from the localized NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor ( $i$ ) and acceptor ( $j$ ) the stabilization energy ( $E(2)$ ) associated with the delocalization  $i \rightarrow j$  is determined as

$$E(2) = \Delta E_{ij} = q_i \frac{(F_{ij})^2}{(E_j - E_i)}$$

$q_i$  is the donor orbital occupancy;  $E_i$ ,  $E_j$  the diagonal elements and  $F_{ij}$  the off diagonal NBO Fock matrix element

In NBO analysis large  $E(2)$  value shows the intensive interaction between electron-donors and electron-acceptors and greater the extent of conjugation of the whole system, the possible intensive interactions are given in Table 2. The second-order perturbation theory analysis of Fock matrix in NBO basis shows strong intra molecular hyper conjugative interactions of  $\pi$  electrons. The intra molecular hyper conjugative interactions are formed by the orbital overlap between  $n$  (Cl) and  $\pi^*$  (C–C) bond orbital which results in ICT causing stabilization of the system. The strong intra molecular hyper conjugative interaction of  $C_{18}$ – $C_{22}$  from of  $n3(Cl_{28}) \rightarrow \pi^*(C_{18}$ – $C_{22})$  which increases ED (0.38e) that weakens the respective bonds leading to stabilization of 9.61 kcal mol<sup>-1</sup>. Another intra molecular hyper conjugative interactions are formed by the orbital overlap between  $n$ (Cl) and  $\pi^*$ (C–C) bond orbital which results in ICT causing stabilization of the system. The strong intra molecular hyper conjugative interaction of  $C_5$ – $C_6$  from of  $n3(Cl_{29}) \rightarrow \pi^*(C_5$ – $C_6)$  which increases ED (0.36 e) that weakens the respective bonds leading to stabilization of 9.36 kcal mol<sup>-1</sup>. Also  $n$ (N) and  $\pi^*$  (N–C) bond orbital which results in ICT causing stabilization of the system. The strong intra molecular hyper conjugative interaction of  $N_{10}$ – $C_{12}$  from of  $n1(N_{10}) \rightarrow \pi^*(N_9$ – $C_{11})$  which increases ED (0.35 e) that weakens the respective bonds leading to stabilization of 50.23 kcal mol<sup>-1</sup>. These interactions are observed as an increase

in electron density (ED) in C–C, N–C anti bonding orbital that weakens the respective bonds.

The increased electron density at the oxygen atom leads to the elongation of respective bond length and a lowering of the corresponding stretching wavenumber. The electron density (ED) is transferred from the  $n$ (Cl),  $n$ (N) to the anti-bonding  $\pi^*$  orbital of the C–C, N–C explaining both the elongation and the red shift. The –CH<sub>2</sub>O stretching modes can be used as a good probe for evaluating the bonding configuration around the corresponding atoms and the electronic distribution of the benzene molecule. Hence the 5-chloro-2-((4-chlorophenoxy)methyl)-benzimidazole structure is stabilized by these orbital interactions. The NBO analysis also describes the bonding in terms of the natural hybrid orbital  $n2(Cl_{28})$ , which occupy a higher energy orbital (–0.32212 a.u.) with considerable p-character (100.00%) and low occupation number (1.97849 a.u.) and the other  $n1(Cl_{28})$  occupy a lower energy orbital (–0.93930) with p-character (58.96%) and high occupation number (1.99441 a.u.),  $n2(Cl_{29})$ , which occupy a higher energy orbital (–0.310652 a.u.) with considerable p-character (100.00%) and low occupation number (1.97933 a.u.) and the other  $n1(Cl_{29})$  occupy a lower energy orbital (–0.92760) with p-character (14.15%) and high occupation number (1.99446 a.u.). Also  $n1(N_{10})$ , which occupy a higher energy orbital (–0.261864 a.u.) with considerable p-character (100.00%) and low occupation number (1.60853 a.u.) and the other  $n1(N_9)$  occupy a lower energy orbital (–0.35666) with p-character (66.42%) and high occupation number (1.92622 a.u.). Thus, a very close to pure p-type lone pair orbital participates in the electron donation to the  $\sigma^*(C$ – $C)$  orbital for  $n2(Cl_{28}) \rightarrow \sigma^*(C$ – $C)$ ,  $\sigma^*(C$ – $C)$  orbital for  $n2(Cl_{29}) \rightarrow \sigma^*(C$ – $C)$  and  $\sigma^*(N$ – $C)$  orbital for  $n1(N_{10}) \rightarrow \sigma^*(N$ – $C)$ ,  $n1(N_9) \rightarrow \sigma^*(N$ – $C)$  interactions in the compound. The results are tabulated in Table S2 as supporting material.

#### Mulliken charges

The calculation of atomic charges plays an important role in the application of quantum mechanical calculations to molecular systems. Mulliken charges are calculated by determining the electron population of each atom as defined in the basis functions. The charge distributions calculated by the Mulliken [95] and NBO methods for the equilibrium geometry of 5-chloro-2-((4-chlorophenoxy)methyl)-benzimidazole are given in Table S3 as supporting information. The charge distribution on the molecule has an important influence on the vibrational spectra. In 5-chloro-2-((4-chlorophenoxy)methyl)-benzimidazole, the Mulliken atomic charge of the carbon atoms in the neighborhood of C3, C4, C11, C15 become more positive, shows the direction of delocalization and shows that the natural atomic charges are more sensitive to the changes in the molecular structure than Mulliken's net charges. The results are given as supporting material in Fig. S4. Also we done a comparison of Mulliken charges obtained by different basic sets and tabulated it in Table S4 as supporting material in order to assess the sensitivity of the calculated charges to changes in (i) the choice of the basis set; (ii) the choice of the quantum mechanical method. The results are in given graphical form as supporting information in Fig. S5. We have observed a change in the charge distribution by changing different basis sets.

MEP is related to the ED and is a very useful descriptor in understanding sites for electrophilic and nucleophilic reactions as well as hydrogen bonding interactions [96,97]. The electrostatic potential  $V(r)$  is also well suited for analyzing processes based on the "recognition" of one molecule by another, as in drug-receptor, and enzyme-substrate interactions, because it is through their potentials that the two species first "see" each other [98,99]. To predict reactive sites of electrophilic and nucleophilic attacks for



**Table 2**

Second-order perturbation theory analysis of Fock matrix in NBO basis corresponding to the intramolecular bonds of the title compound.

| Donor(i) | Type     | ED (e) | Acceptor(j) | Type       | ED (e) | $E(2)^a$ | $E(j)-E(i)^b$ | $F(i, j)^c$ |
|----------|----------|--------|-------------|------------|--------|----------|---------------|-------------|
| C1–C2    | $\sigma$ | 197.0  | C1–C6       | $\sigma^*$ | 0.02   | 3.04     | 1.24          | 0.06        |
| –        | –        | –      | C2–C3       | –          | 0.02   | 3.22     | 1.26          | 0.06        |
| –        | –        | –      | C3–N10      | –          | 0.03   | 6.69     | 1.12          | 0.08        |
| –        | –        | –      | C6–Cl29     | –          | 0.04   | 4.54     | 0.78          | 0.05        |
| C1–C2    | $\pi$    | 1.72   | C3–C4       | $\pi^*$    | 0.48   | 19.67    | 0.27          | 0.07        |
| –        | –        | –      | C5–C6       | –          | 0.36   | 18.35    | 0.27          | 0.07        |
| C1–C6    | $\sigma$ | 1.98   | C1–C2       | $\sigma^*$ | 0.01   | 2.49     | 1.29          | 0.05        |
| –        | –        | –      | C2–H7       | –          | 0.01   | 2.10     | 1.17          | 0.04        |
| –        | –        | –      | C5–C6       | –          | 0.02   | 3.94     | 1.29          | 0.06        |
| –        | –        | –      | C5–H8       | –          | 0.01   | 2.07     | 1.19          | 0.04        |
| C1–H27   | $\sigma$ | 1.98   | C2–C3       | $\sigma^*$ | 0.02   | 3.53     | 1.09          | 0.06        |
| –        | –        | –      | C5–C6       | –          | 0.02   | 3.97     | 1.10          | 0.06        |
| C2–C3    | $\sigma$ | 1.98   | C1–C2       | $\sigma^*$ | 0.01   | 2.55     | 1.29          | 0.05        |
| –        | –        | –      | C1–H27      | –          | 0.01   | 2.10     | 1.19          | 0.05        |
| –        | –        | –      | C3–C4       | –          | 0.04   | 4.61     | 1.24          | 0.07        |
| –        | –        | –      | C3–N10      | –          | 0.03   | 2.55     | 1.14          | 0.05        |
| C2–H7    | $\sigma$ | 1.98   | C1–C6       | $\sigma^*$ | 0.02   | 3.64     | 1.08          | 0.06        |
| –        | –        | –      | C3–C4       | –          | 0.04   | 4.08     | 1.06          | 0.06        |
| C3–C4    | $\sigma$ | 1.97   | C2–C3       | $\sigma^*$ | 0.02   | 4.55     | 1.25          | 0.07        |
| –        | –        | –      | C2–H7       | –          | 0.01   | 2.45     | 1.14          | 0.05        |
| –        | –        | –      | C4–C5       | –          | 0.02   | 3.72     | 1.26          | 0.06        |
| –        | –        | –      | C5–H8       | –          | 0.01   | 2.18     | 1.16          | 0.05        |
| –        | –        | –      | N10–H26     | –          | 0.02   | 4.10     | 1.13          | 0.06        |
| C3–C4    | $\pi$    | 1.60   | C1–C2       | $\pi^*$    | 0.33   | 19.36    | 0.28          | 0.07        |
| –        | –        | –      | C5–C6       | –          | 0.36   | 20.57    | 0.27          | 0.07        |
| –        | –        | –      | N9–C11      | –          | 0.35   | 13.97    | 0.25          | 0.05        |
| C3–N10   | $\sigma$ | 1.98   | C2–C3       | $\sigma^*$ | 0.02   | 2.43     | 1.37          | 0.05        |
| –        | –        | –      | C4–C5       | –          | 0.02   | 2.54     | 1.38          | 0.05        |
| –        | –        | –      | C11–C12     | –          | 0.03   | 3.91     | 1.22          | 0.06        |
| C4–C5    | $\sigma$ | 1.97   | C3–C4       | $\sigma^*$ | 0.04   | 3.58     | 1.22          | 0.06        |
| –        | –        | –      | C4–N9       | –          | 0.02   | 2.20     | 1.13          | 0.05        |
| –        | –        | –      | C5–C6       | –          | 0.02   | 3.08     | 1.27          | 0.06        |
| –        | –        | –      | C6–Cl29     | –          | 0.04   | 5.53     | 0.78          | 0.06        |
| C4–N10   | $\sigma$ | 1.98   | C2–C3       | $\sigma^*$ | 0.02   | 2.48     | 1.33          | 0.05        |
| –        | –        | –      | C4–C5       | –          | 0.02   | 2.39     | 1.33          | 0.05        |
| –        | –        | –      | C11–C12     | –          | 0.03   | 7.01     | 1.17          | 0.08        |
| C5–C6    | $\sigma$ | 1.98   | C1–C6       | $\sigma^*$ | 0.02   | 3.83     | 1.27          | 0.06        |
| –        | –        | –      | C4–C5       | –          | 0.02   | 2.81     | 1.30          | 0.05        |
| –        | –        | –      | C4–N9       | –          | 0.02   | 4.94     | 1.16          | 0.07        |
| –        | –        | –      | C5–H8       | –          | 0.01   | 2.05     | 1.20          | 0.04        |
| C5–C6    | $\pi$    | 1.73   | C1–C2       | $\pi^*$    | 0.33   | 19.49    | 0.29          | 0.07        |
| –        | –        | –      | C3–C4       | –          | 0.49   | 16.88    | 0.28          | 0.07        |
| C5–H8    | $\sigma$ | 1.98   | C1–C6       | $\sigma^*$ | 0.02   | 4.06     | 1.06          | 0.06        |
| –        | –        | –      | C3–C4       | –          | 0.04   | 4.01     | 1.04          | 0.06        |
| C6–Cl29  | $\sigma$ | 1.99   | C1–C2       | $\sigma^*$ | 0.01   | 2.60     | 1.22          | 0.05        |
| –        | –        | –      | C4–C5       | –          | 0.02   | 2.74     | 1.22          | 0.05        |
| N9–C11   | $\sigma$ | 1.98   | C4–C5       | $\sigma^*$ | 0.02   | 4.92     | 1.43          | 0.08        |
| –        | –        | –      | N10–H26     | –          | 0.02   | 2.16     | 1.30          | 0.05        |
| N9–C11   | $\sigma$ | 1.88   | C3–C4       | $\sigma^*$ | 0.49   | 17.60    | 0.32          | 0.08        |
| N10–C11  | $\pi$    | 1.99   | C2–C3       | $\pi^*$    | 0.02   | 4.83     | 1.39          | 0.07        |
| N10–H26  | $\sigma$ | 1.99   | N9–C11      | $\sigma^*$ | 0.01   | 2.34     | 1.23          | 0.05        |
| C11–C12  | $\sigma$ | 1.98   | C4–N9       | $\sigma^*$ | 0.02   | 2.49     | 1.12          | 0.05        |
| –        | –        | –      | C15–O25     | –          | 0.03   | 2.20     | 0.98          | 0.04        |
| C12–H13  | $\sigma$ | 1.98   | N9–C11      | $\sigma^*$ | 0.35   | 3.70     | 0.54          | 0.04        |
| –        | –        | –      | N10–C11     | –          | 0.05   | 2.21     | 0.96          | 0.04        |
| C12–H14  | $\pi$    | 1.98   | N9–C11      | $\pi^*$    | 0.35   | 3.70     | 0.54          | 0.04        |
| –        | –        | –      | N10–C11     | –          | 0.05   | 2.21     | 0.96          | 0.04        |
| C12–O25  | $\sigma$ | 1.99   | N9–C11      | $\sigma^*$ | 0.01   | 2.92     | 1.34          | 0.06        |
| –        | –        | –      | C15–C17     | –          | 0.02   | 2.33     | 1.36          | 0.05        |
| C15–C16  | $\sigma$ | 1.98   | C15–C17     | $\sigma^*$ | 0.02   | 4.36     | 1.28          | 0.07        |
| –        | –        | –      | C16–C18     | –          | 0.02   | 2.74     | 1.28          | 0.05        |
| C15–C16  | $\pi$    | 1.67   | C17–C20     | $\pi^*$    | 0.32   | 17.81    | 0.29          | 0.06        |
| –        | –        | –      | C18–C22     | –          | 0.38   | 21.93    | 0.28          | 0.07        |
| C15–C17  | $\sigma$ | 1.97   | C12–O25     | $\sigma^*$ | 0.01   | 2.69     | 0.93          | 0.05        |
| –        | –        | –      | C15–C16     | –          | 0.03   | 4.16     | 1.26          | 0.07        |
| –        | –        | –      | C16–H19     | –          | 0.01   | 2.23     | 1.17          | 0.05        |
| –        | –        | –      | C17–C20     | –          | 0.01   | 2.46     | 1.28          | 0.05        |
| –        | –        | –      | C20–H24     | –          | 0.01   | 2.13     | 1.18          | 0.05        |
| C16–C18  | $\sigma$ | 1.97   | C15–C16     | $\sigma^*$ | 0.03   | 3.17     | 1.25          | 0.06        |
| –        | –        | –      | C15–O25     | –          | 0.03   | 4.87     | 1.00          | 0.06        |
| –        | –        | –      | C18–C22     | –          | 0.02   | 3.24     | 1.26          | 0.06        |
| –        | –        | –      | C22–Cl28    | –          | 0.04   | 5.23     | 0.78          | 0.06        |
| C16–H19  | $\sigma$ | 1.98   | C15–C17     | $\sigma^*$ | 0.02   | 3.81     | 1.09          | 0.06        |
| –        | –        | –      | C18–C22     | –          | 0.02   | 3.53     | 1.10          | 0.06        |

(continued on next page)

Table 2 (continued)

| Donor(i)    | Type | ED (e) | Acceptor(j) | Type | ED (e) | E(2) <sup>a</sup> | E(j)–E(i) <sup>b</sup> | F(i, j) <sup>c</sup> |
|-------------|------|--------|-------------|------|--------|-------------------|------------------------|----------------------|
| C17–C20     | σ    | 1.97   | C15–C17     | σ*   | 0.02   | 2.60              | 1.26                   | 0.05                 |
| –           | –    | –      | C15–O25     | –    | 0.03   | 3.81              | 1.00                   | 0.06                 |
| –           | –    | –      | C20–C22     | –    | 0.02   | 3.21              | 1.26                   | 0.06                 |
| –           | –    | –      | C22–Cl28    | –    | 0.04   | 5.15              | 0.78                   | 0.06                 |
| C17–C20     | π    | 1.70   | C15–C16     | π*   | 0.39   | 21.81             | 0.27                   | 0.07                 |
| –           | –    | –      | C18–C22     | –    | 0.38   | 18.80             | 0.27                   | 0.07                 |
| C17–H21     | σ    | 1.98   | C15–C16     | σ*   | 0.03   | 4.11              | 1.08                   | 0.06                 |
| –           | –    | –      | C20–C22     | –    | 0.02   | 3.63              | 1.08                   | 0.06                 |
| C18–C22     | σ    | 1.98   | C16–C18     | σ*   | 0.02   | 2.59              | 1.29                   | 0.05                 |
| –           | –    | –      | C20–C22     | –    | 0.02   | 3.97              | 1.28                   | 0.06                 |
| –           | –    | –      | C20–H24     | –    | 0.01   | 1.99              | 1.20                   | 0.04                 |
| C18–C22     | π    | 1.70   | C15–C16     | π*   | 0.39   | 16.56             | 0.28                   | 0.06                 |
| –           | –    | –      | C17–C20     | –    | 0.32   | 21.01             | 0.29                   | 0.07                 |
| C18–H23     | σ    | 1.98   | C15–C16     | σ*   | 0.03   | 3.64              | 1.08                   | 0.06                 |
| –           | –    | –      | C20–C22     | –    | 0.02   | 3.95              | 1.08                   | 0.06                 |
| C20–C22     | σ    | 1.98   | C17–C20     | σ*   | 0.01   | 2.56              | 1.30                   | 0.05                 |
| –           | –    | –      | C17–H21     | –    | 0.02   | 2.13              | 1.19                   | 0.05                 |
| –           | –    | –      | C18–C22     | –    | 0.01   | 4.00              | 1.29                   | 0.06                 |
| –           | –    | –      | C18–H23     | –    | 0.01   | 2.07              | 1.20                   | 0.05                 |
| C20–H24     | σ    | 1.98   | C15–C17     | σ*   | 0.02   | 3.62              | 1.08                   | 0.06                 |
| –           | –    | –      | C18–C22     | –    | 0.02   | 3.84              | 1.09                   | 0.06                 |
| C22–Cl28    | σ    | 1.99   | C16–C18     | σ*   | 0.02   | 2.63              | 1.22                   | 0.05                 |
| –           | –    | –      | C17–C20     | σ*   | 0.01   | 2.50              | 1.23                   | 0.05                 |
| LP (1)N9    | n    | 1.93   | C3–C4       | σ*   | 0.04   | 5.89              | 0.87                   | 0.06                 |
| –           | –    | –      | N10–C11     | –    | 0.05   | 10.09             | 0.76                   | 0.08                 |
| LP (1)N10   | n    | 1.61   | C3–C4       | π*   | 0.49   | 33.54             | 0.29                   | 0.09                 |
| –           | –    | –      | N9–C11      | –    | 0.35   | 50.23             | 0.27                   | 0.11                 |
| LP (1)O25   | n    | 1.96   | C15–C16     | σ*   | 0.03   | 6.11              | 1.11                   | 74.00                |
| LP (2)O25   | n    | 1.86   | C12–H13     | σ*   | 0.02   | 4.49              | 0.74                   | 0.05                 |
| –           | –    | –      | C12–H14     | –    | 0.02   | 4.49              | 0.74                   | 0.05                 |
| –           | –    | –      | C15–C16     | π*   | 0.39   | 26.65             | 0.33                   | 0.09                 |
| LP (1)Cl 28 | n    | 1.99   | C18–C22     | σ*   | 0.02   | 0.95              | 1.48                   | 0.03                 |
| –           | –    | –      | C20–C22     | –    | 0.02   | 0.94              | 1.47                   | 0.03                 |
| LP (2)Cl28  | n    | 1.98   | C18–C22     | σ*   | 0.02   | 3.06              | 0.87                   | 0.05                 |
| –           | –    | –      | C20–C22     | –    | 0.02   | 3.06              | 0.86                   | 0.05                 |
| LP (3)Cl28  | n    | 1.95   | C18–C22     | π*   | 0.38   | 9.61              | 0.31                   | 0.05                 |
| LP (1)Cl29  | n    | 1.99   | C1–C6       | σ*   | 0.02   | 0.86              | 1.46                   | 0.03                 |
| –           | –    | –      | C5–C6       | –    | 0.02   | 0.87              | 1.49                   | 0.03                 |
| LP (2)Cl 29 | n    | 1.98   | C1–C6       | σ*   | 0.02   | 2.92              | 0.84                   | 0.04                 |
| –           | –    | –      | C5–C6       | –    | 0.02   | 2.93              | 0.87                   | 0.05                 |
| LP (3)Cl29  | n    | 1.95   | C5–C6       | –    | 0.36   | 9.36              | 0.32                   | 0.05                 |

<sup>a</sup> E(2) means energy of hyper conjugative interactions (stabilization energy).

<sup>b</sup> Energy difference between donor and acceptor i and j NBO orbitals.

<sup>c</sup> F(i, j) is the Fock matrix element between i and j NBO orbitals.

the investigated molecule, MEP at the B3LYP/6-31G(d,p) optimized geometry was calculated. The negative (red and yellow)<sup>1</sup> regions of MEP were related to electrophilic reactivity and the positive (blue) regions to nucleophilic reactivity (Fig. 4). From the MEP it is evident that the negative charge covers the –CH<sub>2</sub>O– group and the positive region is over the methoxyl group. The more electro negativity methoxy makes it the most reactive part in the molecule.

### <sup>1</sup>H NMR spectrum

The experimental spectrum data of 5-chloro-2-((4-chlorophenoxy)methyl)-benzimidazole in DMSO with TMS as internal standard is obtained at 400 MHz and is displayed in Table 3. The absolute isotropic chemical shielding of 5-chloro-2-((4-chlorophenoxy)methyl)-benzimidazole was calculated by B3LYP/GIAO model [100]. Relative chemical shifts were then estimated by using the corresponding TMS shielding:  $\sigma_{\text{calc}}(\text{TMS})$  calculated in advance at the same theoretical level as this paper. Numerical values of chemical shift  $\delta_{\text{calc}} = \sigma_{\text{calc}}(\text{TMS}) - \sigma_{\text{calc}}$  together with calculated values of  $\sigma_{\text{calc}}(\text{TMS})$ , are reported in Table 3. It could be seen from Table 3 that chemical shift was in agreement with the experimental <sup>1</sup>H NMR data. Thus, the results showed that the predicted

proton chemical shifts were in good agreement with the experimental data for 5-chloro-2-((4-chlorophenoxy)methyl)-benzimidazole.

### Electronic absorption spectra

Electronic transitions are usually classified according to the orbitals engaged or to specific parts of the molecule involved. Common types of electronic transitions in organic compounds are  $\pi-\pi^*$ ,  $n-\pi^*$  and  $\pi^*(\text{acceptor})-\pi(\text{donor})$ . The UV–visible bands in 2-(phenoxymethyl) benzimidazole are observed at 282, 274, 256, 244, 241

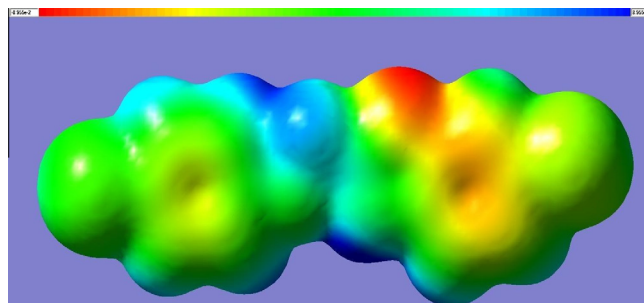


Fig. 4. Molecular electrostatic potential calculated at B3LYP/SDD level.

<sup>1</sup> For interpretation of color in Fig. 4, the reader is referred to the web version of this article.

**Table 3**  
Experimental and calculated  $^1\text{H}$  NMR parameters (with respect to TMS).

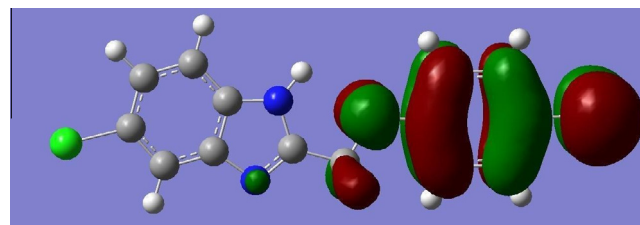
| Proton | $\sigma_{\text{TMS}}$ | B3LYP/6-31G | $\delta_{\text{calc}} (\sigma_{\text{TMS}} - \sigma_{\text{calc}})$ | Exp. $\delta_{\text{ppm}}$ |
|--------|-----------------------|-------------|---|----------------------------|
| H7     | 32.7711               | 25.0012     | 7.7699  | 7.623                      |
| H8     | –                     | 25.1410     | 7.6301  | 7.619                      |
| H13    | –                     | 27.3393     | 5.4318  | 5.336                      |
| H14    | –                     | 27.3398     | 5.4313  | 5.336                      |
| H19    | –                     | 25.8111     | 6.96  | 7.096                      |
| H21    | –                     | 25.3522     | 7.4189  | 7.389                      |
| H23    | –                     | 25.3454     | 7.4257  | 7.579                      |
| H24    | –                     | 25.3384     | 7.4327  | 7.558                      |
| H26    | –                     | 23.2316     | 9.5395  | 9.246                      |
| H27    | –                     | 25.4487     | 7.3224  | 7.350                      |

and 240.8 nm. Observed band at 240.8 nm is due to the  $\pi$ – $\pi^*$ . The less intense band centered at 256 nm is due to the partly forbidden  $n$ – $\pi^*$  transition from HOMO to LUMO. The more intense band observed at 282 nm belonged to the dipole-allowed  $\pi$ – $\pi^*$  transition.

In order to understand the electronic transitions of 5-chloro-2-((4-chlorophenoxy)methyl)-benzimidazole, TD-DFT calculation in vacuum was performed. TD-DFT calculation is capable of describing the spectral features of 5-chloro-2-((4-chlorophenoxy)methyl)-benzimidazole because of the qualitative agreement of line shape and relative strength as compared with experiment. The absorption spectra of organic compounds stem from the ground-to-excited state vibrational transition of electrons. The intense band in the UV range of the electronic absorption spectrum is observed at 282 nm, which is indicating the presence of – OPh entity in the compound. The calculated six lowest-energy transitions of the molecule from TD-DFT method and the observed electronic transitions are listed in Table 4.

**Table 4**  
Calculated electronic absorption spectrum of 5-chloro-2-((4-chlorophenoxy)methyl)-benzimidazole using TD-DFT/B3LYP/SDD.

| Excitation             | CI expansion Coefficient | Energy (eV) | Wavelength nm | Wavelength Expt. nm | Oscillator Strength (f) |
|------------------------|--------------------------|-------------|---------------|---------------------|-------------------------|
| <i>Excited state 1</i> |                          |             |               |                     |                         |
| 73 → 80                | 0.11094                  | 4.8257      | 256.92        | 282                 | 0.1090                  |
| 74 → 80                | 0.29439                  | –           | –             | –                   | –                       |
| 75 → 76                | 0.56018                  | –           | –             | –                   | –                       |
| 75 → 77                | 0.26345                  | –           | –             | –                   | –                       |
| <i>Excited state 2</i> |                          |             |               |                     |                         |
| 72 → 78                | 0.28824                  | 4.9854      | 248.69        | 274                 | 0.0295                  |
| 73 → 76                | 0.40769                  | –           | –             | –                   | –                       |
| 73 → 77                | –0.27779                 | –           | –             | –                   | –                       |
| 74 → 76                | –0.32885                 | –           | –             | –                   | –                       |
| 74 → 77                | 0.18226                  | –           | –             | –                   | –                       |
| 75 → 77                | 0.11123                  | –           | –             | –                   | –                       |
| <i>Excited state 3</i> |                          |             |               |                     |                         |
| 73 → 76                | 0.16279                  | 5.0327      | 246.36        | 256                 | 0.0820                  |
| 73 → 77                | –0.17278                 | –           | –             | –                   | –                       |
| 74 → 76                | 0.53969                  | –           | –             | –                   | –                       |
| 74 → 77                | 0.11638                  | –           | –             | –                   | –                       |
| 75 → 77                | 0.21674                  | –           | –             | –                   | –                       |
| 75 → 80                | –0.17270                 | –           | –             | –                   | –                       |
| <i>Excited state 4</i> |                          |             |               |                     |                         |
| 73 → 76                | –0.11699                 | 5.0626      | 244.90        | 244                 | 0.0096                  |
| 74 → 76                | –0.10726                 | –           | –             | –                   | –                       |
| 74 → 77                | –0.18373                 | –           | –             | –                   | –                       |
| 75 → 76                | –0.32530                 | –           | –             | –                   | –                       |
| 75 → 77                | 0.54186                  | –           | –             | –                   | –                       |
| <i>Excited state 5</i> |                          |             |               |                     |                         |
| 73 → 76                | –0.44194                 | 5.1293      | 241.72        | 241                 | 0.0050                  |
| 73 → 77                | –0.18128                 | –           | –             | –                   | –                       |
| 74 → 77                | 0.48871                  | –           | –             | –                   | –                       |
| <i>Excited state 6</i> |                          |             |               |                     |                         |
| 73 → 76                | 0.19995                  | 5.1541      | 240.55        | 240.8               | 0.0400                  |
| 73 → 77                | 0.51524                  | –           | –             | –                   | –                       |
| 74 → 77                | 0.33644                  | –           | –             | –                   | –                       |
| 75 → 80                | –0.14400                 | –           | –             | –                   | –                       |

**Fig. 5.** HOMO plot of 5-chloro-2-((4-chlorophenoxy)methyl)benzimidazole.

From the table the calculated energy transitions are red shifted from the experimental value, because these bands are observed in gas phase without considering the solvent effect.

HOMO and LUMO are the very important parameters for quantum chemistry. The conjugated molecules are characterized by a highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) separation, which is the result of a significant degree of ICT from the end-capping electron-donor groups to the efficient electron-acceptor groups through  $\pi$ -conjugated path. The strong charge transfer interaction through  $\pi$ -conjugated bridge results in substantial ground state donor–acceptor mixing and the appearance of a charge transfer band in the electronic absorption spectrum. Therefore, an ED transfer occurs from the more aromatic part of the  $\pi$ -conjugated system in the electron-donor side to its electron-withdrawing part. The atomic orbital components of the frontier molecular orbital are shown in Figs. 5 and 6. The HOMO–LUMO energy gap value is found to be 3.916 eV, which is responsible for the bioactive property of the compound 5-chloro-2-((4-chlorophenoxy)methyl)-benzimidazole.

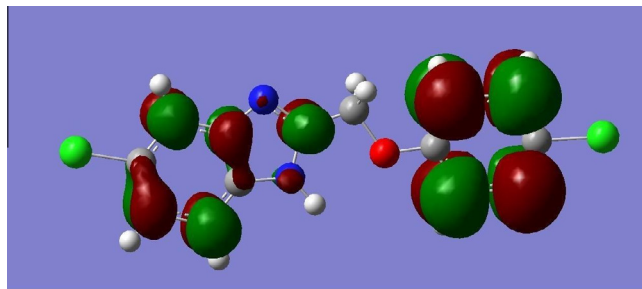


Fig. 6. LUMO plot of 5-chloro-2-((4-chlorophenoxy)methyl)benzimidazole.

## Conclusion

The present investigation thoroughly reports the vibrational spectra, both infrared and Raman of the title compound. All the vibrational bands observed in the FT-IR and FT-Raman spectra of the title compound are assigned to various modes of vibration. Most of the modes have wave numbers in the range suggested by previous assignments found in literature in the case of related molecules. The simultaneous activation of the phenyl ring stretching modes in the IR and Raman spectra can be interpreted as the evidence of intra molecular charge transfer between the donor and the acceptor group via conjugated ring path, which is responsible for hyperpolarizability enhancement, leading to non-linear optical activity. The NBO analysis confirms the ICT formed by the orbital overlap between  $n(\text{Cl})$  and  $\sigma^*(\text{C}-\text{C})$ ,  $n(\text{N})$  and  $\sigma^*(\text{N}-\text{C})$ . A very close to pure p-type lone pair orbital participates in the electron donation to the  $\sigma^*(\text{C}-\text{C})$  orbital for  $n2(\text{Cl}28) \rightarrow \sigma^*(\text{C}-\text{C})$ ,  $\sigma^*(\text{C}-\text{C})$  orbital for  $n2(\text{Cl}29) \rightarrow \sigma^*(\text{C}-\text{C})$  and  $\sigma^*(\text{N}-\text{C})$  orbital for  $n1(\text{N}10) \rightarrow \sigma^*(\text{N}-\text{C})$ ,  $n1(\text{N}9) \rightarrow \sigma^*(\text{N}-\text{C})$  interaction in the molecule. Overall, the TD-DFT calculations on the molecule provided deep insight into their electronic structures and properties. GIAO NMR calculations provided chemical shift values that were in excellent agreement with experimental data. In addition, the calculated UV-Vis results are all in good agreement with the experimental data. The lowering of HOMO-LUMO band gap supports bioactive property of the molecule. MEP predicts the most reactive part in the molecule.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.saa.2013.11.025>.

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