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# DFT, FT-RAMAN, AND FT-IR INVESTIGATIONS OF 1-CYCLOPROPYLPIPERAZINE

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FT-IR and FT-Raman spectra of 1-cyclopropylpiperazine (1cppp) are experimentally examined in the range 4000—200 $cm^{-1}$. The optimized geometric parameters, conformational equilibria, normal mode frequencies and corresponding vibrational assignments of 1cppp $C_7H_{14}N_2$ are theoretically examined by means of B3LYP hybrid density functional theory (DFT) with the 6-31++G(*d,p*) basis set. Based on the potential energy distribution (PED) reliable vibrational assignments are made and the thermodynamics functions, highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of 1cppp are predicted. Calculations are performed for four different conformations in two point groups of 1cppp in the gas phase. A comparison between the experimental and theoretical results indicates that the B3LYP method is able to provide satisfactory results for the prediction of vibrational frequencies, structural parameters, and assignments. Furthermore, the $C_s$ (equatorial-equatorial) point group is found as the most stable conformer of 1cppp.

**K e y w o r d s:** 1-cyclopropylpiperazine, vibrational spectra, PED, DFT, B3LYP.

## INTRODUCTION

Piperazine and its derivatives have an extensive range of applications in the field of materials science and organic synthesis. Many piperazine derivatives are of great interest in pharmacy and drugs. 1-cyclopropylpiperazine, known in the literature by synonyms such as N-cyclopropylpiperazine and 4-cyclopropylpiperazine, is a piperazine derivative. It has been used in the preparation of some tri- and tetrasubstituted ureas with histamine H3 antagonist receptor activity [ 1 ], 3-amido-4-anilinoquinolines series as CSF-1R kinase inhibitors [ 2 ], for the synthesis of cyclopropyl amines as modulators of the histamine H3 receptor [ 3 ], sulfonamide compounds as cysteine protease inhibitors [ 4 ], N-oxides as antibacterial agents [ 5 ] and in the treatment of the disease caused by helicobacter infection [ 6 ].

Vibrational spectroscopy has been extensively used for the structural characterization of molecular systems by DFT calculations [ 7—11 ]. Unlike Hartree-Fock theory, DFT includes electron correlation in the self-consistent Kohn-Sham procedure through the electron density functions, so it is a cost effective and reliable method [ 7—11 ]. The DFT/B3LYP model shows good performance on electron affinities, bond energies and reasonably good performance on vibrational frequencies and geometries of organic compounds [ 7—15 ].

Even though, 1cppp has wide applications, to the best of our knowledge, there is no information present in literature about its spectroscopic properties. A detailed quantum chemical study is required to make definitive assignments to the fundamental normal modes of 1cppp and to clarify the obtained experimental data for the title molecule. The detailed results of the theoretical and spectroscopic stu-

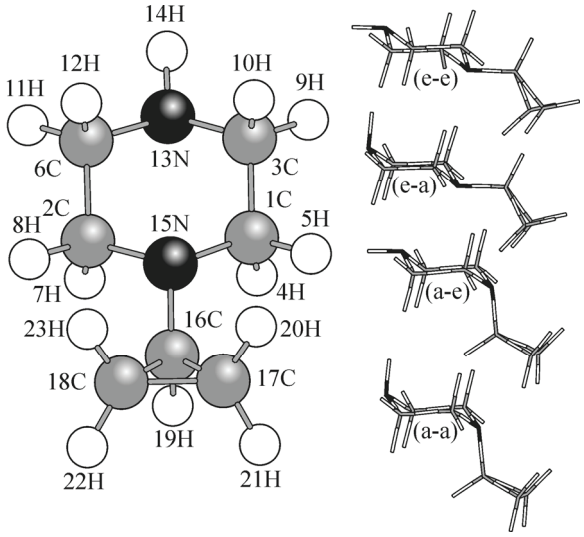


*Fig. 1.* Four different conformations in epy $C_s$ point group and numbering of 1cppp

dies are reported here. In the present study, we have reported the vibrational spectra of 1cppp with PED data and the structural parameters of 1cppp have also been calculated for the most stable conformer in the gas phase at the B3LYP/6-31++G(*d*,*p*) level.

## EXPERIMENTAL

A commercial sample of N-cycloprpopylpiperazine was purchased (Santa Cruz Biotechnology, ≥%98) and used without further purification. FT-MIR and FT-FIR spectra of 1cppp were recorded in the range 4000—200 $cm^{-1}$ with a Bruker Optics IFS66v/s FTIR spectrometer with the resolution of 2 $cm^{-1}$. The FT-Raman spectrum was obtained using a Bruker Senterra Dispersive Raman microscope spectrometer with 532 nm excitation from a 3B diode laser having 3 $cm^{-1}$ resolution in the spectral range 4000—200 $cm^{-1}$.

## CALCULATIONS

Calculations were performed using the Gaussian 09.A1 program [ 16 ] on a personal computer and GaussView 5.0.8 [ 17 ] was used for the visualization of the structure and simulated vibrational spectra. Many possible conformers could be suggested for 1cppp (Fig. 1), but most of them are energetically not possible, so the investigation was limited to e-e (equatorial-equatorial), e-a (equatorial-axial), a-a (axial-axial), and a-e (axial-equatorial) conformers in both $C_s$ and $C_1$ point groups of the title molecule and where the former represents NH while the latter stands for the cyclopropane group (Fig. 1).

They are considered in axial and equatorial positions according to the plane formed by C1, C2, C3 and C6 carbon atoms of 1cppp. For the calculations, all four forms of 1cppp were first optimized by B3LYP with the 6-31++G(*d*,*p*) basis set in the gas phase. The e-e conformation belonging to the $C_s$ point group (e-e ($C_s$)) was found to be more stable than the other forms (Table 1).

T a b l e 1

*Point groups*, *conformers*, *gibbs free energy*, *relative stability and mole fractions of* 1cppp *by* B3LYP *with* 6-31++G(*d*,*p*) *basis set*

| Point group | Conformers | Δ*G* (Hartree) | Relative stability[a] (δΔ*G*, kcal/mol) | Mole fractions (%) |
|---|---|---|---|---|
| $C_s$ | e-e | –384.485062 | 0.000 | 0.27 |
| | e-a | –384.484347 | 0.449 | 0.24 |
| | a-e | –384.479428 | 3.535 | — |
| | a-a | –384.478329 | 4.225 | — |
| $C_1$ | e-e | –384.484954 | 0.068 | 0.26 |
| | e-a | –384.484345 | 0.450 | 0.23 |
| | a-e | –384.479377 | 3.567 | — |
| | a-a | –384.478171 | 4.324 | — |

[a] Relative stability were calculated compared to $C_s$ (e-e) conformer.

Therefore, for the vibrational calculations, the vibrational frequencies of the e-e($C_s$) conformer of 1cppp were calculated using the same method and basis set under the keyword freq = Raman, pop = full and then scaled by 0.955 (above 1800 $cm^{-1}$) and 0.977 (under 1800 $cm^{-1}$) for 6-31++G(*d*,*p*) [ 13, 14 ]. The polarizable continuum model [ 18 ], which is the default in Gaussian 09.A1, was used for the geometries, free energies, and vibrational frequencies. The absence of imaginary frequencies confirmed that the optimization was successfully performed.

PED calculations; which indicate the relative contributions of the redundant internal coordinates to each normal vibrational mode of the molecule and thus make it possible to identify the character of each mode numerically; were carried out by the VEDA 4 (Vibrational Energy Distribution Analysis) [ 19 ] program. The VEDA program does not scale the elements of fthe orce constant matrix as proposed by Pulay *et al*. [ 20 ]. For details of the PED analysis for the VEDA program, more information was published in [ 21 ].

## RESULTS AND DISCUSSION

The results of the calculations on the molecular conformations and geometrical parameters of 1cppp are discussed first. A brief discussion of the experimental and theoretical vibrational frequencies and intensities is then presented.

**Geometrical structures.** Gibbs free energies, relative stabilities, and molar fractions of the optimized geometries in the gas phase of four conformations in two point groups of 1cppp calculated with DFT/6-31++G(*d*,*p*) are given in Table 1. Regarding the relative stability energies given in Table 1, the molar fractions of a-e($C_s$), a-a($C_s$), a-e($C_1$), and a-a($C_1$) conformers could be ignored since their relative stabilities compared to the e-e($C_s$) conformer are more than 2.0 kcal/mol. The molar fractions for individual e-e($C_s$), e-e($C_1$), e-a($C_s$), and e-a($C_1$) conformers, where *a*, *b*, *c* and *d* respectively, can be calculated with the following equations:

$$a \xleftrightarrow{K_{T1}} b \xleftrightarrow{K_{T2}} c \xleftrightarrow{K_{T3}} d.$$

According to the equilibrium given above,

$$K_{T1} = N_b/N_a, \quad K_{T2} = N_c/N_d, \quad K_{T3} = N_d/N_c$$

and

$$N_a + N_b + N_c + N_d = 1$$

can be written, where $K_{T1}$, $K_{T2}$ and $K_{T3}$ are the conformational equilibrium constants between *a*, *b*, *c* and *d* forms, $N_a$, $N_b$, $N_c$ and $N_d$ are the molar fractions of conformers *a*, *b*, *c* and *d*.

$$N_a = \frac{1}{1 + K_{T1} + K_{T1}K_{T2} + K_{T1}K_{T2}K_{T3}},$$

$$N_b = \frac{K_{T1}}{1 + K_{T1} + K_{T1}K_{T2} + K_{T1}K_{T2}K_{T3}},$$

$$N_c = \frac{K_{T1}K_{T2}}{1 + K_{T1} + K_{T1}K_{T2} + K_{T1}K_{T2}K_{T3}},$$

$$N_c = \frac{K_{T1}K_{T2}K_{T3}}{1 + K_{T1} + K_{T1}K_{T2} + K_{T1}K_{T2}K_{T3}}.$$

$K_T = e^{-\Delta G/RT}$, $R = 1.987\times10^{-3}$ kcal/mol·K, $T = 298$ K and $\delta\Delta G = \Delta G_b - \Delta G_a$ [ 22 ].

Regarding the calculated free energies for the gas phase, the following molar fractions were obtained: $N_a = 0.27$ (e-e($C_s$)), $N_b = 0.26$ (e-e($C_1$)), $N_c = 0.24$ (e-a($C_s$)), and $N_d = 0.23$ (e-a($C_1$)). Based on the calculations, the e-e($C_s$) form is most stable and the most abundant conformer in the gas phase. Since $N_a$ is larger than $N_b$, $N_c$, and $N_d$, the approximate mode descriptions were determined considering the e-e($C_s$) conformer.

Some optimized geometric parameters (bond lengths, bond and dihedral angles) calculated by B3LYP/6-31++G(*d*,*p*) are listed in Table 2. To the best of our knowledge, the experimental data on the geometric structure of 1cppp is not available in the literature. Therefore, the theoretical results

T a b l e 2

*Optimized geometric parameters for four conformers of* 1cppp *in gas phase*

| Parameter | Experimental [a,b] | B3LYP/6-31++G(*d*,*p*) | | | |
|---|---|---|---|---|---|
| | | $C_1$ | | $C_s$ | |
| | | e-e | e-a | e-e | e-a |
| Bond Lenghts, Å | | | | | |
| N13—H14 | | 1.02 | 1.02 | 1.02 | 1.02 |
| (C—N)pp | 1.47[a] | 1.47 | 1.47 | 1.47 | 1.47 |
| (C—C)pp | 1.54[a] | 1.53 | 1.54 | 1.53 | 1.54 |
| (C—H)pp | 1.11[a] | 1.10 | 1.10 | 1.10 | 1.10 |
| (C—C)cp | 1.51[b] | 1.51 | 1.51 | 1.51 | 1.51 |
| (C—H)cp | 1.08[b] | 1.09 | 1.09 | 1.09 | 1.09 |
| C16—N15 | | 1.44 | 1.44 | 1.44 | 1.43 |
| Bond Angles, deg. | | | | | |
| (C—C—N)pp | 110.4[a] | 109.8 | 112.2 | 109.8 | 111.1 |
| (C—N—C)pp | 109.0[a] | 111.2 | 111.1 | 111.2 | 111.1 |
| (H—C—H)pp | 109.1[a] | 108.1 | 107.7 | 108.1 | 107.5 |
| (H—C—H)cp | 115.9[b] | 115.1 | 115.0 | 115.0 | 115.0 |
| C17—C16—H19 | | 116.3 | 116.4 | 116.3 | 116.4 |
| C18—C16—H19 | | 116.3 | 116.4 | 116.3 | 116.4 |
| C17—C16—N15 | | 118.4 | 118.4 | 118.3 | 118.4 |
| C18—C16—N15 | | 118.4 | 118.4 | 118.3 | 118.4 |
| C1—N15—C16 | | 112.3 | 112.4 | 112.4 | 112.4 |
| C2—N15—C16 | | 112.3 | 112.4 | 112.4 | 112.4 |
| N15—C16—H19 | | 115.8 | 115.7 | 115.9 | 115.7 |
| Dihedral Angles, deg. | | | | | |
| C1—C3—N13—H14 | | –176.1 | –70.6 | –174.0 | –70.6 |
| C2—C6—N13—H14 | | 176.1 | 70.6 | 177.0 | 70.6 |
| C6—C2—N15—C16 | | 176.0 | 175.9 | 174.7 | 175.9 |
| C3—C1—N15—C16 | | –176.0 | –175.9 | –175.7 | –175.9 |
| C1—N15—C16—C17 | | 82.2 | 82.1 | 82.1 | 82.1 |
| C1—N15—C16—C18 | | 151.8 | 151.7 | 151.6 | 151.7 |
| C2—N15—C16—C17 | | –151.8 | –151.7 | –151.6 | –151.7 |
| C2—N15—C16—C18 | | –82.2 | –82.0 | –82.1 | –82.1 |
| C1—N15—C16—H19 | | –63.0 | –63.1 | –63.1 | –63.1 |
| C2—N15—C16—H19 | | 63.0 | 63.1 | 63.1 | 63.1 |

[a, b] Taken from [ 23, 24 ], respectively. pp, piperazine: cp, cyclopropane.

have been compared with the experimental data for piperazine [ 23 ] and cyclopropane [ 24 ] compounds as given in Table 2. The magnitude of dihedral angles for the optimized 1cppp (the D(2;6;13;14) angles) are found to be 177° in e-e($C_s$) and e-e($C_1$) conformers and also 71° in e-a($C_1$) and e-a($C_s$). Moreover, the D(15;16;2;6) angles are found as 176° in e-e($C_1$) and e-a($C_1$), 175° in e-e($C_s$) and e-a($C_s$).

Several thermodynamic parameters, capacity, zero point energy, entropy etc., calculated by the DFT/B3LYP/6-31++G(*d*,*p*) method are presented in Table 3. The variation in the zero point vibra-

Table 3

*Thermodynamic parameters for four conformers of* 1cppp *in gas phase*

| Parameter | B3LYP/6-31++G(*d*,*p*) | | | |
|---|---|---|---|---|
| | $C_1$ | | $C_s$ | |
| | e-e | e-a | e-e | e-a |
| Thermal total energy, kcal/mol | 136.628 | 136.571 | 136.604 | 136.571 |
| Vibrational energy, kcal/mol | 134.850 | 134.793 | 134.826 | 134.793 |
| Zero point vibrational energy, kcal/mol | 131.366 | 131.292 | 131.330 | 131.292 |
| Dipole moment, D | 0.506 | 1.489 | 0.505 | 1.489 |
| Heat capacity, kcal/mol·K | 0.335 | 0.336 | 0.335 | 0.336 |
| Entropy, kcal/mol·K | 0.890 | 0.891 | 0.891 | 0.891 |

tional energy seems to be insignificant. The total energy and change in the entropy of 1cppp are calculated at room temperature.

## VIBRATIONAL STUDIES OF 1CPPP

To the best of our knowledge, the vibrational frequencies and assignments of 1cppp in the range 4000—200 $cm^{-1}$ have not been reported in the literature. The measured and calculated vibrational frequencies along with the corresponding vibrational assignments and intensities and the theoretical-experimental vibrational spectra of 1cppp are given in Table 4 and Figs. 2 and 3 respectively.

The 1cppp molecule consists of 23 atoms, so it has 63 normal vibrational modes and its most stable form belongs to the point group $C_s$ with the only identity (E) symmetry element or operation. The assignments of vibrational modes of 1cppp in the e-e form have been provided by VEDA 4 [ 19 ] in Tables 4. According to the calculations, 3 normal vibrational modes of 1cppp are below 200 $cm^{-1}$.

The high wavenumber region contains a characteristic NH stretching band of 1cppp attributed to the piperazine group. Free piperazine has a main NH band at 3225 $cm^{-1}$ in the IR spectrum [ 25 ]. The strong broad NH stretching in the title molecule is assigned to 3275 $cm^{-1}$ in the IR spectrum and 3353 $cm^{-1}$ in the Raman spectrum. The corresponding scaled theoretical values of these modes are 3380 $cm^{-1}$ with 0.955 and 3353 $cm^{-1}$ with SQM methodology with a 100 % PED contribution. The asymmetric and symmetric $CH_2$ vibrations in 1cppp arise from both piperazine and cyclopropyl groups. The vibrational bands at 3085 $cm^{-1}$, 3006 $cm^{-1}$ in the IR spectrum and 3084 $cm^{-1}$, 3073 $cm^{-1}$, 3008 $cm^{-1}$, 2986 $cm^{-1}$ in the Raman spectrum are due to symmetric and antisymmetric $CH_2$ vibrations arising from the cyclopropyl group. The corresponding scaled calculated values for these bands were found as between (3087—2997) $cm^{-1}$ with 0.955 and (3087—2996) $cm^{-1}$ with SQM methodology. For the title molecule the $CH_2$ stretching bands in piperazine have been observed at 2939 $cm^{-1}$, 2910 $cm^{-1}$, 2812 $cm^{-1}$ in the IR spectrum and 2945 $cm^{-1}$, 2929 $cm^{-1}$, 2847 $cm^{-1}$, 2806 $cm^{-1}$ in the Raman spectrum, while the present theoretical findings are between (2944—2812) $cm^{-1}$ with 0.955 and (2943—2812) $cm^{-1}$ with SQM methodology. In the high wavenumber region of the spectra, the anharmonicity can explain differences between the experimental and calculated values. Additionally, these differences can be due to the intra- and intermolecular hydrogen bondings or a laser used for Raman.

The fundamental $CH_2$ vibrations, which are scissoring, twisting, wagging, and rocking, appear in the expected frequency region 1600—800 $cm^{-1}$ [ 26 ]. These vibrations were revealed to be mixed $CH_2$ wagging, $CH_2$ twisting, $CH_2$ rocking, $CH_2$ scissoring, CNH bending, CC or CN stretching. Experimental/calculated (0.977, SQM) δ(CH2) scissoring modes arising from both piperazine and cyclopropyl groups are found as 1453/1454 (0.977, SQM) $cm^{-1}$ in the IR spectrum and 1455/1459 (0.977, SQM) $cm^{-1}$, 1477/1472 (0.977) $cm^{-1}$, 1475 (SQM) $cm^{-1}$ in the Raman spectrum. The bands appeared at 1440 (R) $cm^{-1}$, 1416 (IR, R) $cm^{-1}$, 1383 (IR) $cm^{-1}$ are mainly due to CNH bending vibrations calculated as (1447—1383) $cm^{-1}$ with 0.977 and (1442—1381) $cm^{-1}$ with SQM methodology. Based on the PED assignments, the bands at 1362 $cm^{-1}$ in both IR and Raman spectra mainly arise from the mixed

Table 4

*Comparison of the experimental and calculated vibrational wavenumbers* ($cm^{-1}$) *of* 1cppp *in gas phase*

| Mode | Assignment | Experimental | | B3LYP/6-31++G(*d*,*p*) e-e ($C_s$) in gas phase | | | | |
|---|---|---|---|---|---|---|---|---|
| | PED (≥ 5 %) | IR | Raman | $\nu^{\alpha}$ | $\nu^{\beta}$ | $\nu^{\varphi}$ | $I_{IR}$ | $I_R$ |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| $\nu_1$ | ν(NH) 100 | 3275 s | 3353 wb | 3539 | 3380 | 3353 | 0.01 | 24.52 |
| $\nu_2$ | ν(CH) 100 | 3085 s | 3084 m | 3233 | 3087 | 3087 | 20.37 | 7.93 |
| $\nu_3$ | ν(CH) 100 | — | 3073 m | 3220 | 3075 | 3075 | 0.30 | 14.86 |
| $\nu_4$ | ν(CH) 99 | 3006 s | 3008 vs | 3142 | 3001 | 3000 | 9.49 | 41.80 |
| $\nu_5$ | ν(CH) 100 | — | 2986 s | 3138 | 2997 | 2996 | 21.42 | 8.03 |
| $\nu_6$ | ν(CH) 94 | 2939 vs | — | 3083 | 2944 | 2943 | 59.91 | 4.30 |
| $\nu_7$ | ν(CH) 90 | — | 2945 s | 3076 | 2938 | 2937 | 42.74 | 17.86 |
| $\nu_8$ | ν(CH) 93 | 2910 vs | 2929 m | 3076 | 2937 | 2937 | 35.29 | 26.48 |
| $\nu_9$ | ν(CH) 99 | — | 2847 m | 3028 | 2891 | 2891 | 75.28 | 27.40 |
| $\nu_{10}$ | ν(CH) 95 | 2812 vs | 2806 m | 2945 | 2812 | 2812 | 234.32 | 11.41 |
| $\nu_{11}$ | δ(HCH) 89 | — | 1477 m | 1507 | 1472 | 1475 | 1.61 | 7.82 |
| $\nu_{12}$ | δ(HCH) 91 | 1453 vs | 1455 m | 1489 | 1454 | 1459 | 0.16 | 13.00 |
| $\nu_{13}$ | δ(HCN) 82 | — | 1440 m | 1481 | 1447 | 1442 | 3.25 | 1.06 |
| $\nu_{14}$ | δ(HCN) 64 | 1416 m | 1416 m | 1432 | 1399 | 1398 | 3.92 | 2.51 |
| $\nu_{15}$ | δ(HCN) 62 | 1383 m | — | 1415 | 1383 | 1381 | 1.06 | 0.82 |
| $\nu_{16}$ | δ(HCN) 57 + ν(NC) 17 | 1362 vs | 1362 m | 1397 | 1365 | 1364 | 56.04 | 2.53 |
| $\nu_{17}$ | δ(HCC) 73 | 1339 s | 1322 w | 1371 | 1340 | 1337 | 15.81 | 0.57 |
| $\nu_{18}$ | δ(HCC) 61 | 1317 s | 1301 m | 1350 | 1319 | 1315 | 26.94 | 1.32 |
| $\nu_{19}$ | δ(HCN) 76 | — | 1295 vw | 1329 | 1299 | 1295 | 1.96 | 11.70 |
| $\nu_{20}$ | δ(HCN) 74 | 1264 vs | — | 1299 | 1269 | 1267 | 10.56 | 1.04 |
| $\nu_{21}$ | δ(HCC) 54 + ν(NC) 15 | 1251 s | — | 1277 | 1247 | 1243 | 15.19 | 0.14 |
| $\nu_{22}$ | ν(NC) 57 + δ(HCH) 10 + δ(HCN) 10 | 1214 vs | 1213 vs | 1244 | 1215 | 1213 | 22.45 | 17.94 |
| $\nu_{23}$ | δ(HCN) 85 | — | 1201 m | 1220 | 1192 | 1191 | 0.02 | 7.79 |
| $\nu_{24}$ | ν(CC) 37 + δ(HCC) 13 | 1183 s | 1187 m | 1207 | 1180 | 1179 | 10.27 | 5.77 |
| $\nu_{25}$ | δ(HCC) 81 | — | 1166 w | 1195 | 1168 | 1169 | 0.87 | 1.93 |
| $\nu_{26}$ | ν(NC) 52 + δ(HCC) 16 | — | 1151 w | 1169 | 1142 | 1140 | 0.04 | 5.23 |
| $\nu_{27}$ | ν(NC) 75 | 1140 vs | 1133 m | 1162 | 1135 | 1135 | 50.10 | 0.30 |
| $\nu_{28}$ | τ(HCNC) 57 | 1125 s | — | 1140 | 1113 | 1125 | 0.55 | 4.14 |
| $\nu_{29}$ | τ(HCNC) 68 | — | 1105 w | 1132 | 1106 | 1100 | 0.46 | 1.07 |
| $\nu_{30}$ | δ(HCC) 81 | 1063 s | 1057 m | 1081 | 1056 | 1056 | 0.37 | 0.08 |
| $\nu_{31}$ | τ(HCCC) 83 | 1016 vs | 1019 w | 1050 | 1026 | 1021 | 14.66 | 1.53 |
| $\nu_{32}$ | ν(CC) 17 + ν(NC) 42 + δ(HCC) 11 | 990 s | 984 m | 1006 | 982 | 983 | 6.71 | 4.19 |
| $\nu_{33}$ | ν(CC) 51 + τ(HCCC) 17 | 967 m | 963 vw | 984 | 961 | 958 | 2.52 | 2.40 |
| $\nu_{34}$ | ν(NC) 77 | 899 s | 896 m | 915 | 893 | 893 | 20.09 | 5.03 |
| $\nu_{35}$ | ν(CC) 71 | 860 vs | 870 m | 908 | 887 | 884 | 0.25 | 2.89 |
| $\nu_{36}$ | ν(NC) 13 + δ(HCC) 48 | — | 843 s | 867 | 847 | 847 | 0.35 | 0.83 |
| $\nu_{37}$ | ν(CC) 76 | — | 824 m | 864 | 845 | 845 | 7.56 | 15.33 |
| $\nu_{38}$ | τ(HCCC) 59+ τ(HCNC) 10+ ν(CC) 23 | 822 vs | 809 m | 835 | 816 | 810 | 8.41 | 4.09 |
| $\nu_{39}$ | ν(NC) 14 + δ(HCC) 35 | 777 vs | 793 m | 803 | 785 | 783 | 24.76 | 3.19 |
| $\nu_{40}$ | δ(HCC) 48 + ν(CC) 13 | 747 s | 747 m | 754 | 737 | 736 | 4.99 | 6.84 |

Continued Table 1

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|
| $\nu_{41}$ | δ(HNC) 65 | 565 s | 544 w | 562 | 549 | 546 | 35.65 | 7.14 |
| $\nu_{42}$ | τ(HCNH) 66 | 490 w | 481 m | 483 | 472 | 470 | 0.01 | 8.73 |
| $\nu_{43}$ | τ(HCCN) 54 + τ(HCNC) 10 | 467 w | 444 m | 464 | 453 | 454 | 1.96 | 9.39 |
| $\nu_{44}$ | τ(HCNC) 63 | 422 vw | 400 w | 420 | 410 | 416 | 2.96 | 10.07 |
| $\nu_{45}$ | τ(HCNC) 52 | 352 vs | 324 w | 347 | 339 | 340 | 3.30 | 15.84 |
| $\nu_{46}$ | τ(HCCN) 79 | — | 297 w | 269 | 263 | 269 | 0.86 | 0.52 |
| $\nu_{47}$ | τ(HCNC) 75 | 274 vs | 268 w | 263 | 257 | 261 | 4.88 | 1.56 |

Note: $\nu^{\alpha}$: Unscaled wavenumbers. $\nu^{\beta}$: scaled with 0.955 above 1800 $cm^{-1}$, 0.977 under 1800 $cm^{-1}$. $\nu^{\varphi}$: scaled by SQM methodology. $I_{IR}$ and $I_R$: Calculated infrared and Raman intensities. PED data are taken from VEDA4. v: very, s: strong, m: medium, w: weak, b: broad.

type combination of CN(15) stretching and HCN(15) bending, which are theoretically calculated at 1365 $cm^{-1}$ with 0.977 and 1364 $cm^{-1}$ with SQM. The NC stretching in the piperazine ring is 1140 $cm^{-1}$ in the IR spectrum, 1133 $cm^{-1}$ in the Raman spectrum, while the present theoretical findings is 1135 $cm^{-1}$ with both 0.977 and SQM methodology with a 75 % PED contribution. Moreover, the NC

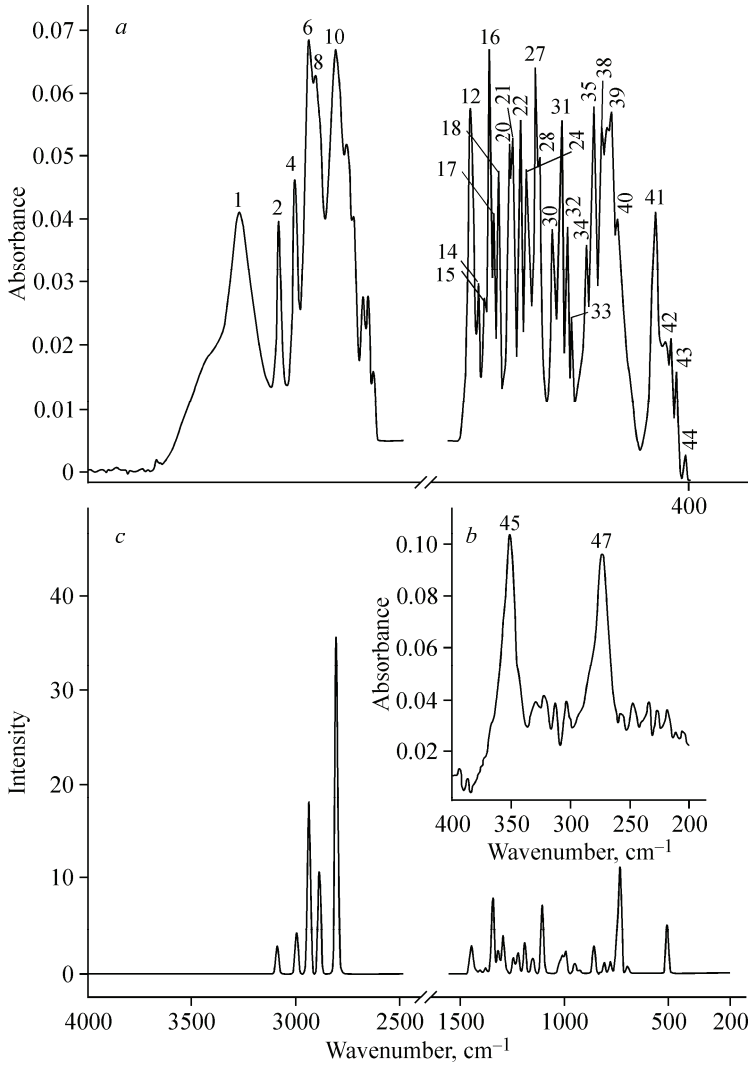


*Fig. 2.* Experimental (*a* and *b*) and scaled calculated (*c*) IR spectra of 1cppp

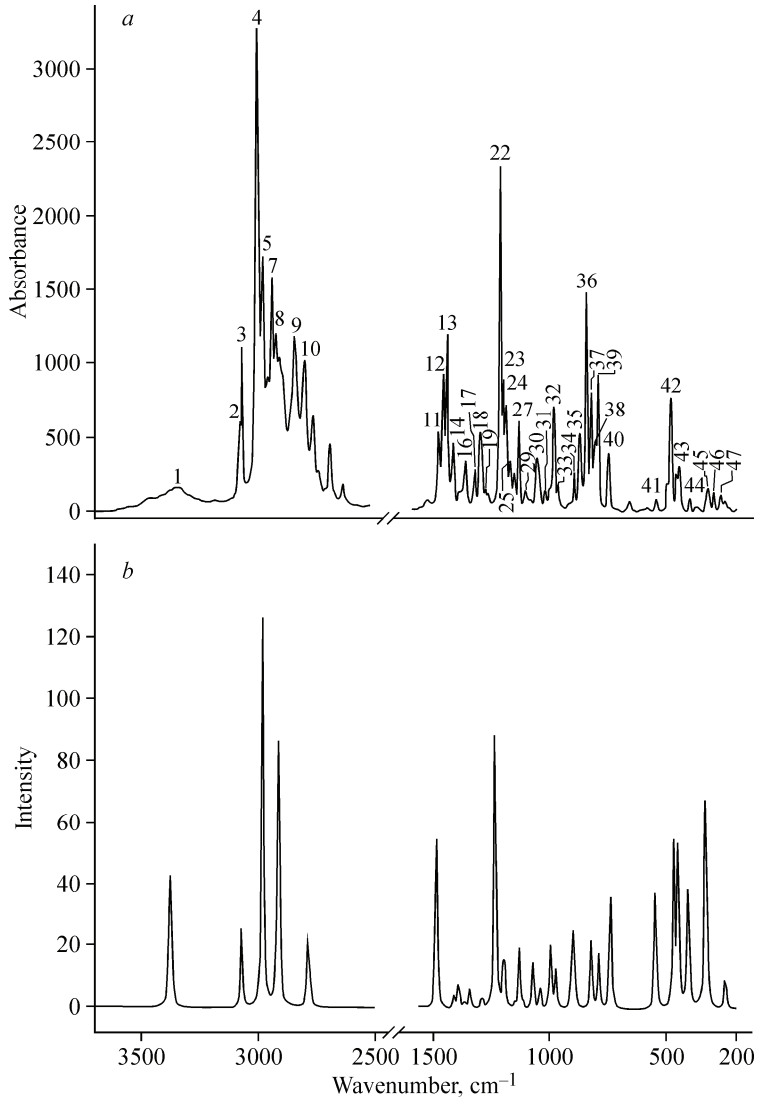


*Fig. 3.* Experimental (*a*) and scaled calculated (*b*) Raman spectra of 1cppp

and CC stretching modes, which are arise from both piperazine and cyclopropyl groups, are also observed at 899 $cm^{-1}$, 860 $cm^{-1}$ in the IR spectrum and 896 $cm^{-1}$, 870 $cm^{-1}$ in the Raman spectrum. The corresponding scaled theoretical values of these modes are 893 $cm^{-1}$, 887 $cm^{-1}$ with 0.977 and 893 $cm^{-1}$, 894 $cm^{-1}$ with SQM methodology.

CC or CN stretching, CCC or CCH bending, and some torsion modes dominate the region of 1000—500 $cm^{-1}$, while CCC or CCN bending and CCCN, CCNH, CCCH or CCCC torsion modes are seen in the low-frequency region. Similar situations have been shown for the calculations. Vibrational modes in the low wavenumber region of the spectrum contain contributions of several internal coordinates and their assignments have a reduction approximation to one of two of the internal coordinates.

It can be drawn from Tables 4 and Figs. 2 and 3 that there is good agreement between the experimental and theoretical vibrational frequencies. In order to compare the experimental frequencies, we have found the correlation graphics based on the calculations (Fig. 4).

The correlation values between the experimental and calculated vibrational frequencies are found to be 0.9996 (IR) and 0.9997 (R) with 0.955—0.977 and 0.9998 (IR) and 0.9997 (R) with SQM.

It can be seen that the B3LYP/6-31++G(*d*,*p*) calculation is reliable for the vibrational spectra.

Calculated Raman activities are converted to relative Raman intensities using the following relationship derived from the intensity theory of Raman scattering:

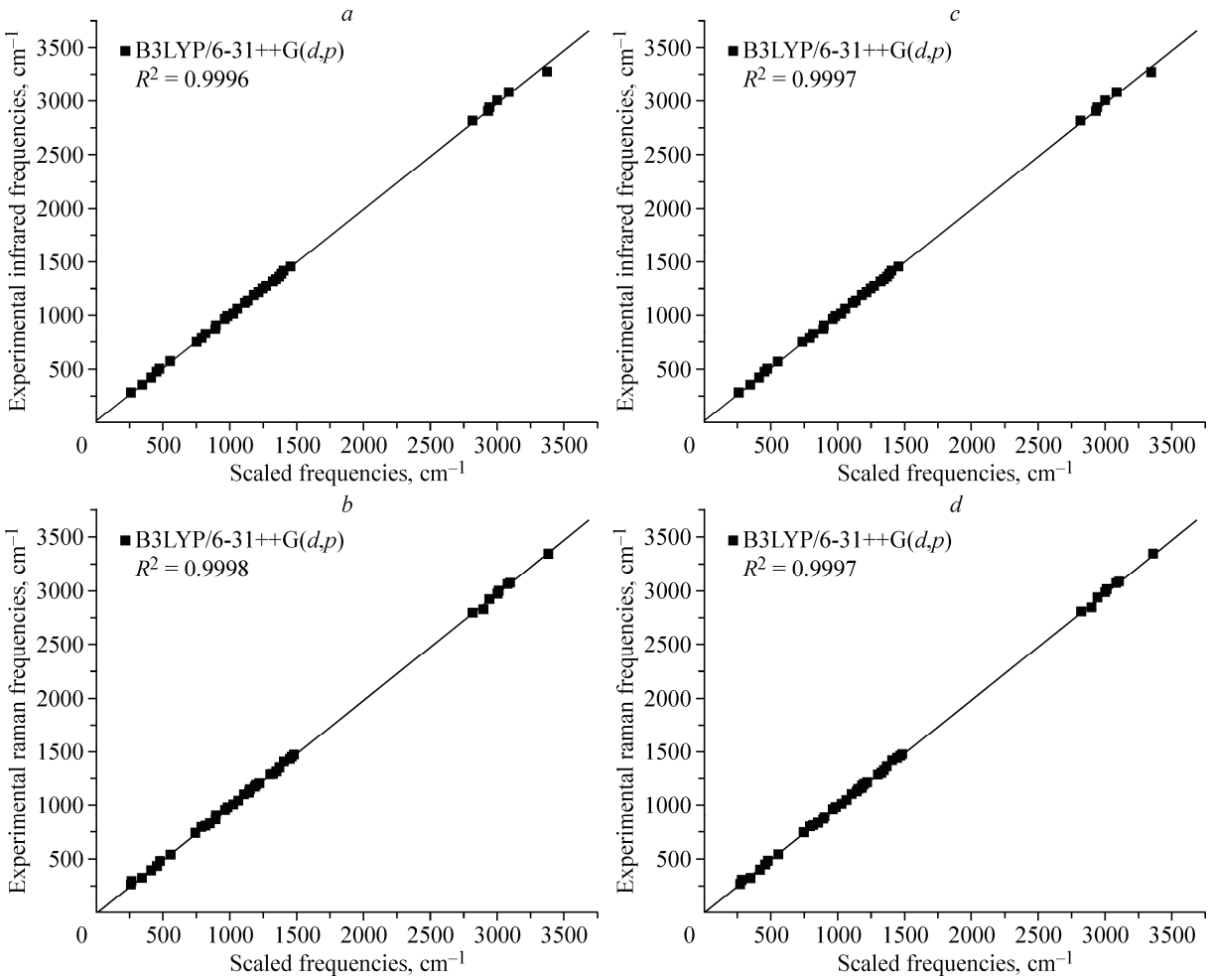


*Fig. 4*. Correlation graphics between the experimental and scaled calculated frequencies for 1cppp

$$I_i = f(\nu_0 - \nu_i)^4 S_i / \nu_i[1 - \exp(-hc\nu_i / kT)],$$

where $\nu_0$ is the laser exciting wavenumbers in cm$^{-1}$, $\nu_i$ is the vibrational wavenumbers of the ith normal mode, $S_i$ is the Raman scattering activity of the normal mode $\nu_i$, and $f$ is a suitably chosen common normalization factor for all peak intensities, $10^{-14}$. $h$, $k$, $c$ and $T$ are the Planck and Boltzmann constants, speed of light, and temperature in Kelvin respectively [ 15, 27 ].

The HOMO and LUMO orbitals are the main orbitals taking part in chemical stability. HOMO describes the ability to donate an electron and LUMO as an electron acceptor. The electronic transition absorption is defined from the ground to the first excited state. In other words, the transitions can be described from HOMO to LUMO. HOMO is located over all carbon and N15 atoms in 1cppp, while LUMO is dominant for the N13 atom. The atomic compositions of the frontier molecular orbital and their orbital energies are shown in Fig. 5.

## CONCLUSIONS

We performed the experimental and theoretical vibrational analysis of 1cppp for the first time. FT-IR and FT-Raman spectra have been recorded in the range 4000—200 cm$^{-1}$. Some important vibrational bands have been discussed and assigned based on the calculated IR intensities and Raman activities. The structural parameters, IR and Raman frequencies, and intensities-activities of the vibrational bands of 1cppp were calculated with density functional theory and the 6-31++G(*d*,*p*) basis set for C1 and $C_s$ conformers. The e-e ($C_s$) conformation was found to be more stable than the other eight

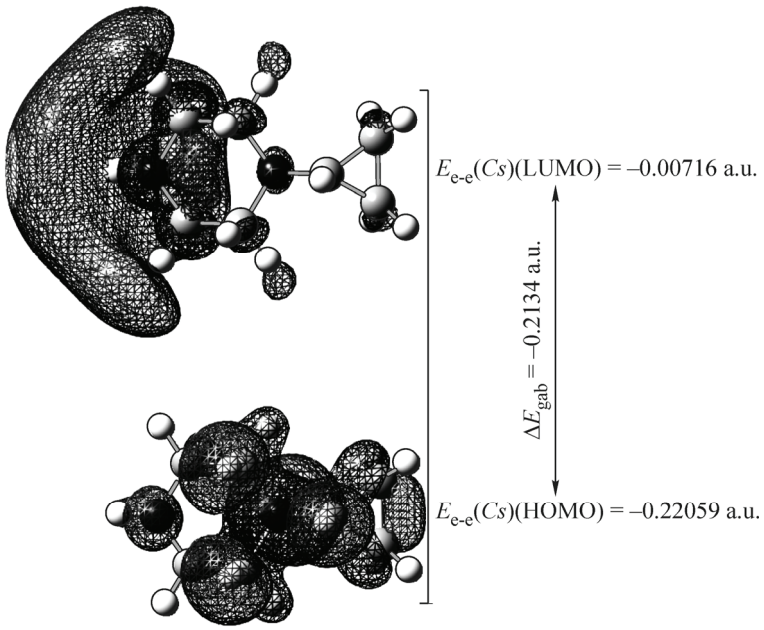


*Fig. 5.* Atomic orbital compositions of the frontier molecular orbital for 1cppp

forms. In order to make a comparison with the experimental wavenumbers, we calculated the root mean square deviation (RMSD) based on the calculation. The following rmsd values were obtained: 21.26 $cm^{-1}$ (IR, 0.955/0.977), 17.19 $cm^{-1}$ (IR, SQM) and 12.97 $cm^{-1}$ (R, 0.955/0.977), 11.81 $cm^{-1}$ (R, SQM). The gas phase energy calculations and the obtained experimental-theoretical rmsd results indicate that it is the most stable conformer of the 1cppp molecule. Any differences observed between the experimental and calculated wavenumbers could be due to the fact that the calculated ones have been obtained for a single molecule in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions and increasing tendendency to unharmonic vibrations in the high wavenumber region. Henceforth, the assignments made at the B3LYP/6-31++G(*d*,*p*) level of theory with only reasonable deviations from the experimental values seem feasible.

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