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Empirical and computational studies on newly synthesis cyclohexylammonium perchlorate

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Highlights

- The novel compound (C₆H₁₄N)ClO₄ has been elaborated by slow evaporation.
- Optimized geometry and UV-Vis spectrum were computed using DFT method
- Vibration modes of the compound were identified by IR analysis.
- The intermolecular interactions were analyzed by HS, AIM and RDG.
- Dipole moment, polarizability and hyperpolarizability values were computed.

Abstract

Cyclohexylammonium perchlorate (C₆H₁₄N)ClO₄ have been achieved from the mixture of perchloric acid with an ethanol solution containing cyclohexylamine by slow evaporation technique. The structure of this compound has been determined by single crystal X-ray diffraction method. This compound crystallizes in monoclinic P2₁/c space group with the lattice parameters $a = 11.1501(19) \text{ \AA}$, $b = 8.4987(15) \text{ \AA}$, $c = 9.9517(16) \text{ \AA}$, $\beta = 104.166(6)^\circ$, $Z = 4$ and $V = 914.4(3) \text{ \AA}^3$. The FT-IR was used to identify the different vibrational assignments present in the compound. The optical properties were analyzed by UV-Vis spectral analysis. The intermolecular interactions in the crystal structure were examined via topological Atom-in-Molecules (AIM), **Natural Bond Orbital (NBO)** and Hirshfeld surface (HS) analyses. Reduced density gradient (RDG) was used to study non-covalent interactions. HOMO-LUMO orbital energies were studied by using DFT calculations at B3LYP/6-311++G(d,p) level of theory.

Keywords

Single crystal X-diffraction analysis; IR spectrum; UV-Vis spectroscopy Hirshfeld surface; **NMR, NBO**

1. Introduction

Hybrid materials have attracted a great of attention because they bring together the properties of organic and inorganic molecules. This combination of these two materials can also lead to completely new properties.

For several years numerous research works have been devoted to the preparation of hybrid organic-inorganic materials [1]. This new area of research particularly interesting in materials science covering many fields of applications: biology [2-3], optics, electrical conductivity, photochemistry [4-5], medicine [6-7], and photo catalysis [8].

In particular hybrid compounds based on perchlorates have been studied because of interesting physical properties that they present as the ferroelectricity [9] and nonlinear optics [10]. They are characterized by their extreme solubility as well as the high degree of their ionic character.

Perchlorates are salts of perchloric acid, the latter are characterized by the presence of the perchlorate ion ClO_4^- , consisting of a chlorine atom surrounded by four oxygen atoms as a regular tetrahedron. The perchlorate anions are linked to each other through strong intrapolyanionic bonds. They are mainly found in salts like ammonium perchlorates NH_4ClO_4 , potassium KClO_4 , magnesium MgClO_4 , or sodium NaClO_4 . This inorganic compound found in the air, in the soil and in water. They have been detected in drinking water in communities around the United States [11] as well as in a variety of food products such as lettuce and wheat [12-13]. They have also been reported in urine [14], breast milk [15] and blood serum in the United States [16].

Perchlorates are widely used as oxidants in energy materials such as propellants and explosives. In addition, perchlorate is a chemical used in the military, aerospace and industries to produce rocket fuel, fires fireworks and for the manufacture of paint.

In this work we report our investigations on a new perchlorate hybrid $(\text{C}_6\text{H}_{14}\text{N})\text{ClO}_4$ which was identified by single crystal X-ray diffraction. Within this context chemical preparation, structural study, Hirshfeld analysis and infrared spectroscopy are discussed. In addition theoretical calculation was used to simulate and interpret the infrared and UV-visible spectra and revealed with the experimental values.

The electronic properties are determined from HOMO-LUMO orbital analyses. In addition the topological properties AIM and thermodynamical properties are also discussed.

2. Experimental details

2.1. Synthesis and crystallization

Stoichiometric solution of perchloric acid (0.1 g, 1 mmol, purity 96%, Aldrich) is added dropwise to a solution of cyclohexylamine (0.1 g, 1 mmol, purity 99%, Aldrich) dissolved in ethanol. The mixture is left under stirring at room temperature for 30 minutes.

Two weeks later single crystals of $(C_6H_{14}N)ClO_4$ are formed into fine colorless needles. The crystals can be stable for months under normal conditions of temperature and humidity.

Schematically the reaction can be written as follow:



Elemental analysis, calc. (found): C, 36.07% (36.12); H, 7.01% (7.08); N, 7.01% (6.98). Melting point temperature = 513 K.

2.2. Investigation techniques

2.2.1. X-ray data collection

The intensity data were collected by means of a D8 VENTURE Bruker-AXS diffractometer equipped with Multilayer monochromator and $MoK\alpha$ radiation ($\lambda = 0.71073$ Å) at 150 K. Absorption corrections were performed using the multi-scan technique using the SADABS program [17]. The total number of measured reflections was 8245 among which 2083 were independent and 1511 had the intensity $I > 2\sigma(I)$.

The structure was solved by direct methods using SHELXS-97, which revealed the position of all non-hydrogen atoms, and then refined with full-matrix least-square methods based on F^2 (SHELXL-97) [18] included in the WINGX program [19].

A final refinement on F^2 converged at $R(F^2) = 0.053$ and $wR(F^2) = 0.143$. A summary of the crystallographic data and the structure refinements are given in **Table 1**.

Supporting data (CIF files) have been deposited in the Cambridge Crystallographic Data centre as supplementary materials N° CCDC 1998687. Copies of the data can be obtained, free of charge via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; or by email to deposit@ccdc.cam.ac.uk.

2.2.2. Physical measurements

IR spectrum was recorded at room temperature in the frequency range $4000\text{--}400\text{ cm}^{-1}$ with a Perkin-Elmer FT-IR 1000 spectrometer using the technique of pellets with KBr as a dispersant.

Solid state UV-Vis spectrum was registered with a Perkin-Elmer Lambda 35 spectrophotometer in the range of 200-800 nm.

The ^{13}C NMR experimental spectrum was recorded by employing BRUKER 400 MHz NMR spectrometer in DMSO solvent using tetramethylsilane (TMS) as the reference material.

2.3. Computational details

The molecular geometry optimization has been performed with the Gaussian 09 software package [20] and the GaussView molecular visualization program [21] by using the Density functional theory (DFT) with the Becke-three-parameter hybrid exchange functional combined with the Lee-Yang-Parr correlation functional (B3LYP) [22-23] levels, the 6-311++G(d,p) basis set was used for all. Many theoretical calculations shows that for molecules that exhibits inter or intra-molecular interactions, the B3LYP-D3 functional corrected for dispersion is most preferred [24]. That's why in this paper, we have regard to correction of the Grimme at D3 [25].

All the calculations have converged to an optimized geometry that corresponds to the lowest energy. Positive vibrational frequencies obtained confirming the stability of the optimized geometries.

The vibrational assignments were performed considering the potential energy distribution components (PED) $\geq 10\%$ using the VEDA4 package. The GaussView molecular visualization program [26] was used to verify the assignments of the bands.

To examine the contacts in the crystal, Hirshfeld surfaces mapped with d_{norm} and their associated 2D fingerprint offered in this paper were plotted using Crystal Explorer version 3.1 software [27] imported on a CIF file. The topological properties at the BCPs were determined with the Multiwfn program [28] while the reduced density gradient of the title molecule are graphed by Multiwfn and plotted by the VMD program [29].

Also, the analysis of the structure was examined using ^{13}C NMR spectroscopic techniques DFT/gauge-including atomic orbitals (GIAO) methods [30].

3. Results and discussion

3.1. X-ray diffraction and geometry optimization

The title compound crystallizes in the monoclinic system, space group $P2_1/c$ and four formula units in unit cell with the lattice constants of $a = 11.1501(19) \text{ \AA}$, $b = 8.4987(15) \text{ \AA}$, $c = 9.9517(16) \text{ \AA}$ and $\beta = 104.166(6)^\circ$. The asymmetric unit of the synthesized compound is formed by a monoprotonated cationic entity which is cyclohexylammonium ($\text{C}_6\text{H}_{11}\text{NH}_3^+$) and an anionic entity which is the perchlorate ion (ClO_4^-). The optimized geometry of the title compound was performed using Gaussian program [20] and their interface Gauss view [21] is given in Fig.1. The minima energy structure is found with ground state energy calculated to be -28626.3759 eV . The junction between the cations and anions is provided by hydrogen bonds of type N-H ... O and C-H ... O. The organic entity presents a disorder which is manifested by the thermal agitation of all the atoms of hydrogen, nitrogen and carbon. The

structure is characterized by a succession of cationic and anionic layers along the axis \vec{a} which extends in $x = 1/2$ (Fig. 2a) which are linked to a further by additional hydrogen bonds, therefore forming the three dimensional infinite network. The projection of such a layer is given in (Fig.2b). The protonation on the N site of the cation is confirmed from the elongated C-N bond distance ($d_{N-C} = 1.493 \text{ \AA}$) (**Table 2**) are similar to those observed in other compounds with the same amine [31-34]. In addition the C-C bond lengths experimental are between 1.427 and 1.546 \AA . We notice that there is not a big difference between the experimental and theoretical bond lengths: in gas the C-C bond lengths vary from 1.5272-1.5365, in solution C-C vary from 1.527 \AA -1.536 \AA (without dispersion) and 1.526 \AA -1.535 \AA (with dispersion). Cyclohexanammium which is formed by a cyclohexyl group adopts a chair conformation with an ammonium group in equatorial position with bond angles C-C-C vary from 109.441° - 116.233° and N-C-C vary from 112.349° - 114.105° . By comparison between the theoretical and experimental binding angles there is a slight difference. This is due to the fact that the theoretical calculations have been carried out on isolated molecule in gaseous phase whereas the experimental results correspond to molecules in solid state. In addition it is noted that the lengths of the experimental C-H bond are shorter than the theoretical bond lengths. The examination of the perchlorate anion shows that the group ClO_4 is formed by a regular arrangement of oxygen atoms with a chlorine atom which presents a slight displacement of the center of gravity of the tetrahedron $\delta = 0.018 \text{ \AA}$.

In this context the calculated average values of distortion Cl-O, O-O distance indices and O-Cl-O angles in the ClO_4 tetrahedra according to the Baur method [35] are: $\text{ID}(\text{ClO}) = 0.0062$; $\text{ID}(\text{OO}) = 0.0038$ and $\text{ID}(\text{OCIO}) = 0.0057$, show a strong distortion of Cl-O distances compared to O-O. However these values are comparable with the corresponding values observed for molecules containing the perchlorate anion [36-38].

The packing for $(\text{C}_6\text{H}_{14}\text{N})\text{ClO}_4$ are established by hydrogen bonding (**Table 3**) of types N-H...O and C-H...O. It's worth noting that N-H...O hydrogen bonds are bi and trifurcated with donor-acceptor distances varying between 2.922(14) and 3.32 (3) \AA . Whereas, C-H...O interactions are non-bifurcated with donor-acceptor distances ranging from 3.183 (6) to 3.325 (6) \AA .

3.2. Hirshfeld surface analysis

The Hirshfeld surface (HS) analysis of the asymmetric unit provides insight into the presence of hydrogen bonds and intermolecular interactions in crystal packing [39]. The three-dimensional Hirshfeld surfaces as well as the two-dimensional fingerprints of the asymmetrical unit $(\text{C}_6\text{H}_{14}\text{N})\text{ClO}_4$ were calculated using the Crystal Explorer program [27]

based on the results of X-ray studies in CIF format. The Hirshfeld surfaces mapped over d_{norm} is illustrated in Fig.3. The surfaces are shown as transparent to allow visualization of the orientation and conformation of the functional groups in the crystal.

The interaction between the hydrogen atoms carried by the nitrogen atoms of the organic group and the oxygen atoms of the inorganic group as well as the hydrogen atoms of the organic groups linking the oxygen atoms of the perchlorate group (**Table 3**) can be seen on the surface of Hirshfeld as bright red areas in Fig.3. The light red spots are due to the C–H...O and N–H...O interactions (see **Table 3**). These red spots have the shortest intermolecular contacts. The white spots correspond to the type H ... H interaction and the blue spots illustrate the longest contacts in the structure.

More the Fig.4 illustrates the two-dimensional fingerprint of the totality contacts contributing to the surface Hirshfeld represented in d_{norm} mode where the O...H/H...O interactions have the largest contributions on the Hirshfeld surface 53.4% and appears by two symmetrical wings with $d_e + d_i \sim 2 \text{ \AA}$. These data are characteristic of hydrogen bonds N–H...O and C–H...O. The H ... H contacts comprise 44.2% of the total area Hirshfeld surface. They are characterized by two extremities which point to the origin and which correspond to $d_e + d_i \sim 2 \text{ \AA}$. The O ... O contacts are also visible on the HS and this contact of around 2.8 \AA . This graphic is characterized by two wings and which correspond to $d_e + d_i \sim 3.2 \text{ \AA}$. We find that the contacts O ... H / H ... O and H ... H are considered to be close contacts with a sum of $d_e + d_i$ less than or equal to the sum of the van der Waals radii of the atoms involved (H: 1.09 \AA , O: 1.52 \AA). The intermolecular interactions were additionally evaluated by using the enrichment ratio, ER. The enrichment ratio ER_{XY} of a pair of chemical elements (X, Y) is defined as the ratio between the proportion of actual contacts in the crystal and the theoretical proportion of random contacts [40].

Table 4 shows the enrichment ratios of the main intermolecular interactions for the compound. The O... H/H...O contacts appear with an enrichment ratios larger than unity ($RE_{\text{OH}} = 1.29$) which prove to be favored in the crystal package with the formation of the N–H...O and C–H...O type hydrogen bonds. On the other hand, the H...H contacts appear with an enrichment ratios close to unity ($RE_{\text{OH}} = 0.88$). It's worth noting that O...H/H...O and H...H contacts are most plentiful interactions because hydrogen atoms occupy more than half of the molecular surface (% $S_{\text{H}} = 70.9 \%$).

3.3. Quantum theory of atoms in molecules (QTAIMs) analysis

Atoms-In-Molecule (AIM) analysis is an efficient tool to determine the presence of critical points (CPs). This point is used for the identification of chemical bonds between atoms and

interatomic interaction. The topological parameters proposed by Bader [41] can be calculated in the bond critical point using the Multiwfn program [28] such as the electron density $\rho(r)$, the Laplacian values $\nabla^2\rho(r)$, the ellipticity (ϵ), which makes it possible to evaluate the properties of the bonds in the compound and more particularly the hydrogen bonds. The latter can be classified into three categories according to Rozas et al. [42]:

- Weak hydrogen bonds: $\nabla^2\rho(r_{\text{BCP}}) > 0$ and $H(r_{\text{BCP}}) > 0$
- Moderate hydrogen bonds: $\nabla^2\rho(r_{\text{BCP}}) > 0$ and $H(r_{\text{BCP}}) < 0$
- Strong or very strong hydrogen bonds: $\nabla^2\rho(r_{\text{BCP}}) < 0$ and $H(r_{\text{BCP}}) < 0$

The graphical representation of AIM analysis of the $(\text{C}_6\text{H}_{14}\text{N})\text{ClO}_4$ compound is illustrated in Fig.5 and the calculated topological parameters are assembled in **Table 5**.

The AIM topological analysis reveals that our crystal is stabilized by three hydrogen bonds H...O. The BCP analysis in **Table 5** shows that the three O...H bonds are considered weak with hydrogen bond energies of -4.34; -28.57 and -1.81 kcal/mol. The laplacian of electron density (0.01725, 0.09187, 0.00984) and the energy density (0.00602, 0.02967, 0.00264) confirm the strength of these hydrogen bonds. These values are greater than zero according to the Rozas criterion. In addition, the AIM analysis allows us to detect the presence of cycles in a molecular system through the presence of a new ring critical point “RCP” and NRCP1 and NRCP2 cycles that are formed through the interactions between the organic group and the perchlorate anion via hydrogen bonds as shown in Fig.5.

To conclude we can say that the AIM analysis is used to confirm the H ... H contacts that are already observed by Hirshfeld surface analysis and to detect the presence of cycles in a molecular system.

3.4. Reduced density gradient analysis

The weak interactions play an important role in many of physical, chemical or biological phenomena [43]. They can be used in various applications such as hydrogen storage for renewable energies [44]. Reduced density gradient (RDG) is a very popular and powerful method for analyzing weak interactions such as repulsive interactions, van der Waals interactions and hydrogen bonds using a simple color code. The RDG approach is based on the charge density introduced by Johnson et al. [45] and Contreras-Garcia et al. [46].

Figs. 6a and 6b gives a visualization of non covalent interaction in the molecular space of $(\text{C}_6\text{H}_{14}\text{N})\text{ClO}_4$ molecule by using VMD and Multiwfn programs [29,28], respectively. Fig. 6b illustrates the RDG function versus the electron density ρ multiplied by the sign of the second

eigenvalue λ_2 for $(C_6H_{14}N)ClO_4$ compound. Through a color code we can differentiate between different regions of interactions (show Fig. 6c). This figure highlights regions of color that allows us to describe the type of interaction. When sign $(\lambda_2)\rho$ take a negative value, we have a strong attractive interactions (blue color). Strong repulsive interactions when sign $(\lambda_2)\rho$ have a positive value (red color). The last case, we have van der Waals interactions when sign $(\lambda_2)\rho$ is close to zero (green color).

As clearly seen, the blue spot between the oxygen atom carried by the nitrogen atom and the oxygen atom carried by the perchlorate group indicates the formation of a strong attractive interaction N-H ... O. Moreover the green plates with slight brown located between the hydrogen atoms are attributed to van der Waals interactions and the elliptic red plate located at the center of the cycle is related to repulsive interactions. These results are consistent with that of the AIM analysis.

3.5. Thermodynamic Analysis

The thermodynamic parameters of the title compound are shown in **Table 6**. These thermodynamic parameters were calculated by DFT methods with 6-311++G (d,p) basis set at a constant temperature 298.15 K and pressure $P = 1\text{atm}$.

As can be seen from the table, the value of the dipole moment in solution is greater compared to that of the gas phase. This high value is explained by the high delocalization of a pair of electrons isolated in the perchlorate group where the perchlorate anion has four oxygen atoms.

Moreover, the values of the polarizability α in the solution with and without dispersion are almost equivalent ($\alpha = 155.83876$ a.u and $\alpha = 155.5042$ a.u respectively) and greater than those obtained in the gas phase ($\alpha = 112.22611$ a.u.). A great difference is noted for the hyperpolarizability β values in the solution with and without dispersion ($\beta = 196.82125$ a.u. and $\beta = 146.93182$ a.u., respectively) and in the gas phase ($\beta = 391.90919$ a.u.).

3.6. Frontier molecular orbital analysis

The frontier molecular orbitals are two types: highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The difference between these two orbitals called gap energy is useful to characterize the chemical stability of a molecule. A high gap indicates a high stability of the molecule and therefore low reactivity and vice versa. The HOMO, HOMO-1, LUMO, LUMO+1 orbitals as well as the gap energy calculated in the gas phase are mapped in Fig.7 in which red and green regions represent positive and negative phase, respectively.

The energy values of HOMO, LUMO, LUMO+1, HOMO-1 were calculated from the TD-DFT method associate B3LYP/6-311++G (d,p) are: $E_{\text{HOMO}} = -7.640$ eV; $E_{\text{LUMO}} = -1.210$ eV; $E_{\text{LUMO}+1} = -0.610$ eV; $E_{\text{HOMO}-1} = -7.673$ eV, corresponding to HOMO-LUMO gap of 6.429 eV and HOMO-1-LUMO+1 gap of 7.063 eV. Moreover the E_{HOMO} and E_{LUMO} values are easily used to calculate the chemical hardness ($\eta = \frac{I-A}{2}$), the global softness ($S = \frac{1}{2\eta}$), the electron affinity ($I = -E_{\text{HOMO}}$) and the ionization potential ($A = -E_{\text{LUMO}}$). Also, the values of electronegativity can be determined according to the definition of Mulliken [47] ($\chi = \frac{I+A}{2}$), the global chemical potential ($\mu = -\frac{I+A}{2}$) and the global electrophilicity introduced by Parr et al. [48] ($\omega = \frac{\mu^2}{\eta}$). **Table 7** regroups all the calculated values of chemical reactivity descriptors. From the above values, we can see that the value of the gap energy is high then means a high kinetic stability and a low chemical reactivity. Comparing the gap energy in gas phase and in solution, we observed that ($\Delta E_{\text{Gas}} < \Delta E_{\text{solution}}$). In addition, the values of the chemical potential (μ) are negative which implies that our molecule is quite stable. From the previously results we can deduce that our compound in solution is more stable than in the gas phase. Also the smaller value of global hardness η means that the compound has a high polarizability. Finally we notice that the electrophilicity index has decreased $\omega_{\text{gas}} < \omega_{\text{solution}}$ this is used to evaluate the lowering of energy due to maximal electron flow between donors and acceptors.

3.7. Electronic properties

The experimental electronic absorption spectrum of title compound has been measured in DMSO solvents at room temperature while the theoretical spectrum was determined by using B3LYP/6-311++G(d,p) level of theory in the same solvent. Experimental and theoretical spectra are shown in Figs.8a and 8b. The two spectra exhibit two peaks of different intensity and wavelengths. Experimentally, the broad and intense band observed at 340 nm can be attributed to the $n-\pi^*$ transition of the anion perchlorate while the less intense peak located at 260 nm is assigned to a charge transfer transition. Theoretically, the spectrum has two intense bands also at 380 nm which corresponds to $n-\pi^*$ and at 270 nm which corresponds to a charge transfer transition. The optical band gap energy is determined by the Tauc method [49] by plotting $(\alpha h\nu)^2$ versus $h\nu$ as shown in Fig. 8c. Gap energy (E_g) can be calculated by extrapolating the linear part and is found to be 6.23eV. This value reveals that the crystal is a typical of dielectric material [50]. This result confirms that the experimental result is in good agreement with the theoretical calculation ($E_g = 6.429$ eV).

3.8. Vibrational analysis

FT-IR spectroscopy is a widely used technique for measuring and identifying the vibrational frequencies of atomic groups of compounds. The FTIR spectrum of $C_6H_{14}N(ClO_4)$ was measured between 4000 and 400 cm^{-1} and compared to the theoretical spectrum by using the density functional theory (DFT) method associated with the B3LYP/6-311++G (d,p) basis set on the optimized geometries of the compound with ClO_4 group in monodentate coordination mode. The calculated and experimental infrared spectra are shown in Fig.9a and b respectively. This figure shows a good correlation between the theoretical and experimental spectra with a small difference which may be due to the fact that the experimental spectrum is measured in the crystalline phase although the theoretical spectrum is measured in the gas phase. The experimental and the calculated infrared wavenumber are provided in **Table 8**. Based on the bibliographic study [33, 36, 51-54], the different modes of vibration of the perchlorate anion as well as the organic cation have been assigned to all the bands appeared in the IR spectrum.

3.8.1. ClO_4^- vibrations analysis

In the Free State, the ClO_4 group adopts a regular tetrahedral structure with tetrahedral symmetry (T_d), having nine degrees of freedom of vibration distributed between four normal vibration modes: $\Gamma = A_1 + E + 2F_2$.

These normal modes of vibration are: symmetric stretching ν_1 (A_1), symmetric deformation ν_2 (E), asymmetrical stretching ν_3 (F_2) and asymmetrical deformation ν_4 (F_2). All the modes are Raman active, whereas only ν_3 and ν_4 are active in the IR [55] and are expected to occur at 928, 459, 1119 and 625 cm^{-1} , respectively [56,57]. Here, The ν_3 (F_2) stretching vibration appears as one intense band at 1079 cm^{-1} , whereas the calculated frequency of this vibration is 929 cm^{-1} . The band observed at 624 cm^{-1} is assigned to ν_4 (F_2) asymmetric bending. The theoretical frequency of ν_4 (F_2) mode was found at 538 cm^{-1} . The band due to symmetric stretching ν_1 (A_1) is obtained at 923 cm^{-1} and calculated at 890 cm^{-1} . The symmetric bending is observed at 453 cm^{-1} . The DFT calculations give this mode at 394 cm^{-1} .

3.8.2. $C_6H_{11}NH_3^+$ vibrations

The N–H stretching vibration is located in the region 3457-3132 cm^{-1} and 3345-3142 cm^{-1} in B3LYP methods, respectively, shows good accord with literature studies [58] as well as recorded spectrum.

The band observed at 1590 cm^{-1} is assigned to the asymmetric bending mode of N–H and which corresponds to a theoretical value 1592 cm^{-1} . The symmetric bending modes of N–

H assigned to the band of medium intensity at 1581 cm^{-1} and which corresponds to a theoretically predicted value at 1580 cm^{-1} .

The asymmetric and symmetric stretching vibrations of CH_2 are observed at 2952 and 2859 cm^{-1} respectively. Whereas, these vibrations are calculated at $\nu_{\text{as}} = 2960\text{ cm}^{-1}$ and $\nu_{\text{s}} = 2882\text{ cm}^{-1}$. The band observed at 1447 cm^{-1} is assigned to the symmetric bending mode δ_{s} and is predicted at 1448 cm^{-1} in DFT method.

The bands at 923 cm^{-1} are attributed to the C—C stretching modes and calculated at 884 cm^{-1} . Also the band observed at 1079 cm^{-1} is attributed to the stretching vibration of the group C-N and predicted by DFT calculation at 939 cm^{-1} . Besides, the band situated at 453 cm^{-1} corresponds to the C-C-C bending vibrations. This mode it is theoretically calculated at 450 cm^{-1} by DFT method.

According to this attribution, a good analogy is observed between the theoretical and experimental spectra with a small difference which may be due to the fact that the experimental spectrum is measured in the crystalline phase although the theoretical spectrum is measured in the gas phase.

3.9. Nuclear magnetic resonance studies

The ^{13}C NMR spectral analysis is the most important analytical technique used to confirm the chemical structure of $(\text{C}_6\text{H}_{14}\text{N})\text{ClO}_4$ crystal. The ^{13}C NMR experimental spectrum is shown in Fig.10 which is quite similar to other spectra found in compounds involving the same organic group [59].

The chemical shift calculations of the compound was made by GIAO [30] method using 6-311+ G(2d,p) basis set and reported in ppm relative to TMS. The theoretical ^{13}C NMR chemical shifts of ^{13}C have been compared with the experimental data as shown in **Table 9**.

Fig. 10 and **Table 9** show that theoretically there are six carbon rays, while experimentally there are only four rays. This can be explained by the presence of carbon atoms having the same chemical shifts which are the pairs (C2, C6) and (C3, C5). The DMSO solvent shifts are observed between 39 to 41 ppm in Fig.10. The signal at the chemical shift value of 24.15 ppm is attributed to the two carbons (C3 and C5) in the form of $-\text{CH}_2$ groups of the $(\text{C}_6\text{H}_{14}\text{N})\text{ClO}_4$ while the calculated shifts were identified from 29.9266 to 29.9303 ppm. The NMR signals at 24.99 ppm correspond to the C4 whereas the computed chemical shift value is 29.2161 ppm. The single signal at 30.83 ppm was due to 2 carbon atoms (C2 and C6) with same chemical environment are in good agreement with the measured values (35.8008 and 35.7989 ppm).

The carbon C1 takes experimentally the value 49.79 ppm and the value 62.9622 ppm theoretically.

3.10. NBO analysis

NBO method provides valuable information of conjugative interaction, hyper-conjugative interaction, intra and inter-molecular hydrogen bonding in a compound [60]. The second-order Fock matrix was carried out to evaluate the donor–acceptor interactions in the NBO analysis [61]. For each donor NBO (i) and acceptor NBO (j), the donor acceptor stabilization energy $E^{(2)}$ associated with $i \rightarrow j$ delocalization is estimated as:

$$E^{(2)} = q_i \frac{F^2(i, j)}{\epsilon_i - \epsilon_j}$$

Where q_i is the donor orbital occupancy, ϵ_i and ϵ_j are diagonal elements and $F(i, j)$ is the off diagonal NBO Fock matrix element. The results of NBO analysis using B3LYP method have been reported in **Table 10**. The value associated with $E^{(2)}$ reflects the extent of conjugation present in the system. The delocalization of electron density between occupied and unoccupied orbitals results in the stabilization of donor-acceptor interactions.

The intermolecular interaction is formed by oxygen lone electron pairs LP(O24) and $\sigma^*(N1-H4)$ anti-bonding orbitals which is characterized by a stabilizing energy that equals to 6.96 kcal.mol⁻¹. This result confirm the existence of hydrogen bonds N–H...O which are already observed by other analysis such as X-ray diffraction, Hirshfeld surface, AIM and RDG at the level of the compound structure.

4. Conclusion

In summary, the (C₆H₁₄N)ClO₄ compound was synthesized and characterized by both experimental and computational methods such as single crystal X-ray diffraction, Elemental analysis, Hirshfeld surface analysis, DFT, ¹³C NMR, FT-IR and UV-visible spectroscopies.

X-ray analysis revealed that the structure crystallizes in the Monoclinic with space group P2₁/c. The studied compound presents a disorder in the organic entity which is manifested by the thermal agitation of all the hydrogen, nitrogen and carbon atoms. The crystal packing is stabilized by hydrogen bonding network and also by van der Waals interactions.

AIM approach suggests a good stability of title compound. The analysis of the Hirshfeld surface derived fingerprint plots is used to identify and examine the different types of intermolecular contacts.

Theoretical calculation was used to simulate and interpret the infrared and UV-visible spectra. The electronic properties are determined from HOMO, LUMO and gap energy (E_g) orbital analyzes. In addition, the ^{13}C NMR spectrum confirms the results revealed by X-ray diffraction.

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Fig. 1. ORTEP of $C_6H_{14}N(ClO_4)$ with atoms-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are represented as small spheres (a) and Optimized molecular structure using DFT/B3LYP method and 6-311++G (d, p) basis set (b).

Fig. 2. Projection along the \vec{b} axis of atomic arrangement of $C_6H_{14}N(ClO_4)$ (a) Projection along the \vec{a} axis of atomic arrangement of $C_6H_{14}N(ClO_4)$ (b). The organic cations are represented by the atoms which have the greatest occupation for the clarity of the figure.

Fig. 3. Hirshfeld surfaces mapped with d_{norm} (a) (dotted lines “red” represent hydrogen bonds).

Fig. 4. Fingerprint plots of the different intercontacts and percentage of various intermolecular contacts contributed to the Hirshfeld surface in the $(\text{C}_6\text{H}_{14}\text{N})\text{ClO}_4$ compound.

Fig. 5. Graphical representation of the AIM analysis of $(\text{C}_6\text{H}_{14}\text{N})\text{ClO}_4$: Red and Yellow dots indicate the position of the bond and ring critical points, respectively.

Fig. 6. Representation of different types of interactions in the monomer (a). Graph of the reduced density gradient vs. $\text{sign}(\lambda_2)\rho$ for $(\text{C}_6\text{H}_{14}\text{N})\text{ClO}_4$.(b). Color code for different regions of interactions (c).

Fig. 7. The frontier molecular orbitals of $(\text{C}_6\text{H}_{14}\text{N})\text{ClO}_4$ with TD-DFT(B3LYP)6-311++G(d,p) method.

Fig. 8. Experimental (a) and theoretical (b) **UV-visible spectrum** of $(\text{C}_6\text{H}_{14}\text{N})\text{ClO}_4$. Optical band gap spectrum of $\text{C}_6\text{H}_{14}\text{N}(\text{ClO}_4)$ obtained via Tauc model (c).

Fig. 9. The experimental and theoretical infrared spectra for $(\text{C}_6\text{H}_{14}\text{N})\text{ClO}_4$.

Fig. 10. Experimental ^{13}C NMR spectrum of $(\text{C}_6\text{H}_{14}\text{N})\text{ClO}_4$.

Table 1. Crystal data and experimental parameters used for the intensity data collection strategy and final results of the structure determination.

Temperature	150 K
Empirical formula	$\text{C}_6\text{H}_{14}\text{N}(\text{ClO}_4)$
Formula weight (g mol^{-1})	199.63
Crystal system	monoclinic
Space group	$P2_1/c$
a	11.1501 (19) Å
b	8.4987 (15) Å
c	9.9517 (16) Å
β	104.166 °
Z	4
V	914.4(3) Å ³
F(000)	424
$\mu(\text{Mo K}\alpha)$	0.40 mm^{-1}

Index ranges	$-14 \leq h \leq 14, -9 \leq k \leq 11, -12 \leq l \leq 12$
Reflections collected	8245
Independent reflections	2083
Reflections with $I > 2\sigma(I)$	1511
R_{int}	0.043
Absorption correction: multi-scan	$T_{\text{min}} = 0.830, T_{\text{max}} = 0.914$
Refined parameters	103
$R[F^2 > 2\sigma(F^2)]$	0.053
$wR(F^2)$	0.143
Goodness of fit	1.05
$\Delta\rho_{\text{max}} = 0.49 \text{ e } \text{\AA}^{-3}$	$\Delta\rho_{\text{min}} = -0.56 \text{ e } \text{\AA}^{-3}$

Table 2. Optimized and experimental bond lengths and bond angles (\AA , $^\circ$) parameters of $\text{C}_6\text{H}_{14}\text{N}(\text{ClO}_4)$.

		Theoretically calculated		Experimental
	Gas	In solution (without dispersion)	In solution (with dispersion)	
		Bond lengths (\AA)		
$\text{Cl}_{22}\text{-O}_{23}$	1.4881	1.494	1.495	1.433(2)
$\text{Cl}_{22}\text{-O}_{24}$	1.5282	1.506	1.509	1.4485(19)
$\text{Cl}_{22}\text{-O}_{25}$	1.5255	1.494	1.495	1.433(2)
$\text{Cl}_{22}\text{-O}_{26}$	1.4664	1.494	1.493	1.414(2)
$\text{N}_1\text{-C}_5$	1.5093	1.511	1.51	1.493(9)
$\text{C}_5\text{-C}_7$	1.5273	1.528	1.527	1.427(6)
$\text{C}_7\text{-C}_{10}$	1.5365	1.536	1.535	1.500(6)
$\text{C}_{10}\text{-C}_{13}$	1.5353	1.534	1.534	1.545(7)
$\text{C}_{13}\text{-C}_{16}$	1.5354	1.534	1.534	1.535(7)
$\text{C}_{16}\text{-C}_{19}$	1.5365	1.536	1.535	1.485(7)

C₁₉-C₅	1.5272	1.527	1.526	1.474(7)
N₁-H₂	1.019	1.024	1.024	0.91
C₅-H₆	1.0929	1.092	1.024	0.99
C₇-H₈	1.0993	1.097	1.097	0.99
		Bond angles (°)		
O₂₃-Cl₂₂-O₂₄	108.524	108.9755	109.1184	108.70(12)
O₂₃-Cl₂₂-O₂₅	108.6111	109.8100	109.8428	109.08(15)
O₂₃-Cl₂₂-O₂₆	112.4173	109.7181	109.9126	110.87(16)
O₂₄-Cl₂₂-O₂₅	106.3431	109.2208	108.9705	108.91(13)
O₂₅-Cl₂₂-O₂₆	110.2759	109.2696	108.9190	110.40(14)
O₂₅-Cl₂₂-O₂₆	110.4592	109.8274	110.0520	108.85(15)
N₁-C₅-C₇	109.9902	109.4259	109.3941	114.1(7)
N₁-C₅-C₁₉	110.0908	109.4655	109.6913	112.4(7)
C₇-C₅-C₁₉	112.5681	112.4545	112.2501	120.5(5)
C₅-C₇-C₁₀	109.9607	110.4073	110.1612	115.9(7)
C₇-C₁₀-C₁₃	111.41	111.5654	111.3913	116.7(7)
C₁₀-C₁₃-C₁₆	111.3136	111.3718	111.1711	109.9(7)
C₁₃-C₁₆-C₁₉	111.4202	111.5013	111.4362	113.7(5)
C₅-C₁₉-C₁₆	109.9663	110.4580	110.2288	114.8(5)
H₂-N₁-H₃	111.8565	107.8070	107.9521	109.5
H₂-N₁-C₅	112.6605	110.5131	110.5511	109.5
N₁-C₅-H₆	104.473	105.2314	105.3428	102.2
H₈-C₇-C₉	107.6133	109.9704	110.1228	108.3

Table 3. Hydrogen-bond geometry (Å, °)

D—H...A	D—H (Å)	H...A (Å)	D...A (Å)	D—H...A(°)
N1—H1A...O1 ⁱ	0.91	2.31	3.065 (17)	141
N1—H1A...O3 ⁱⁱ	0.91	2.62	3.165 (17)	119
N1—H1B...O2 ⁱ	0.91	2.34	2.983 (14)	128
N1—H1B...O4 ⁱⁱⁱ	0.91	2.41	3.123 (17)	136
N1—H1B...O3 ⁱⁱ	0.91	2.50	3.229 (14)	137
N1—H1C...O2	0.91	2.02	2.922 (14)	169
N1—H1C...O3	0.91	2.62	3.302 (17)	132
N1B—H1B1...O2	0.91	2.21	2.93 (2)	136
N1B—H1B1...O3 ⁱⁱ	0.91	2.47	3.15 (3)	132
N1B—H1B2...O2 ⁱ	0.91	2.11	2.99 (2)	161
N1B—H1B2...O1 ⁱ	0.91	2.34	3.05 (3)	135
N1B—H1B3...O4 ⁱⁱⁱ	0.91	2.48	3.14 (3)	130
N1B—H1B3...O3 ⁱⁱⁱ	0.91	2.63	3.25 (2)	126
N1B—H1B3...O3	0.91	2.64	3.32 (3)	131
C2—H2A...O3 ⁱⁱ	0.99	2.45	3.325 (6)	146
C2—H2B...O1 ^{iv}	0.99	2.36	3.183 (6)	140
C6—H6A...O4 ⁱⁱⁱ	0.99	2.49	3.263 (8)	135

Symmetry codes: (i) $-x+1, y+1/2, -z+1/2$; (ii) $x, -y+1/2, z-1/2$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1, -y, -z+1$.

Table 4. Enrichment ratio of different inter-contact and percentage of each atom on the surface Hirshfeld in (C₆H₁₄N)ClO₄.

Enrichment	H	O
H	0.88	1.29
O		0.28
% Surface	70.9	29.1

Table 5. Topological parameters (distance, electron density, Laplacien, Potential energy density, interaction energy, ellipticity and eta index) of the (C₆H₁₄N)ClO₄ compound.

	H ₉ ...O ₂₃	H ₄ ...O ₂₄	H ₆ ...O ₂₅	RCP	NRCP1	NRCP2
Distance (Å)	2.7285	1.8799	3.2006	-	-	-
Density of electrons $\rho(r)$ (a.u.)	0.00602	0.02967	0.00264	0.01843	0.00359	0.00256
Laplacian of electron density $\nabla^2 \rho(r)$ (a.u.)	0.01725	0.09187	0.00984	0.11298	0.01321	0.01007
Potential energy density $V(r)$ (a.u.)	-0.00334	-0.02198	-0.00139	-0.01679	-0.00204	-0.00136
Interaction energy (E_{int}) (kJ.mol ⁻¹)	-4.34	-28.57	-1.81	-	-	-
Ellipticity (ϵ)	0.1470	0.0566	0.7266	-1.2465	-2.1442	-2.0482
Eta index (ζ)	0.1873	0.2466	0.1381	0.2420	0.1572	0.1317

BCP: bond critical point, RCP: ring critical point, NRCP: new ring critical point.

Table 6. Thermodynamic properties of $C_6H_{14}N(ClO_4)$ at B3LYP/6-311++ (d,p) level in gas phase (with dispersion effect) and in solution (with/without dispersion effect) at temperature $T=298.15K$ and pressure $P=1atm$.

	In Gas phase	In solution	
	With dispersion	With dispersion	Without dispersion
E(RB3LYP) (Hartree)	-1052.7978	-1052.8454	-1052.8217
Dipole Moment(Debye)	10.88504	18.20596	19.562398
Polarizability(a.u)	112.22611	155.83876	155.5042
HyperPolarizability(a.u)	391.90919	196.82125	146.93182
Zero-point Energy Correction(Hartree)	0.217645	0.216731	0.21597
E(Thermal)(kcal/mol)	144.531	144.213	143.924
Heat Capacity (Cv) (cal/mol.K)	47.318	48.015	48.376
Entropy (S) (cal/mol.K)	115.618	118.352	123.531

Table 7. Global reactivity descriptors and calculated frontier molecular orbital parameters in gas and in solution phase for (C₆H₁₄N)ClO₄.

Parameters (eV)	TD-DFT		
	In gas phase		In solution
	With dispersion	With dispersion	without dispersion
E_{HOMO}	-7.6406887	-8.3051911	-8.3258718
E_{LUMO}	- 1.210363	- 0.48109753	- 0.46395435
ΔE (HOMO- LUMO)	6.4303259	7.82409357	7.86191745
E_{HOMO-1}	- 7.6738866	- 8.4341731	- 8.4045127
E_{LUMO+1}	- 0.61007957	- 0.064218902	- 0.04571515
ΔE(HOMO-1- LUMO+1)	7.06380703	8.369954198	8.35879755
Electron affinity (I)	7.6406887	8.3051911	8.3258718
Global electrophilicity (ω)	3.045768349	2.4667032417	2.4568129925
Ionization potential (A)	1.210363	0.48109753	0.46395435
Electronegativity (χ)	4.42552585	4.393144315	4.394913075
Global chemical potential (μ)	- 4.42552585	- 4.393144315	- 4.394913075
Global hardness (η)	3.21516285	3.912046785	3.930958725
Global softness (S)	1.607581425	1.9560233925	1.9654793625

Table 8. Experimental and theoretical IR frequencies (cm^{-1}) and their assignments for $(\text{C}_6\text{H}_{14}\text{N})\text{ClO}_4$ in gas phase by using the B3LYP/6-311++G(d,p) Method

Experimental	Theoretical			Vibrational assignments
	Unscaled	Scaled	IR	(% PED)
IR	Unscaled	Scaled	IR	
3457	3492	3345	134.37	νNH (99)
3427	3443	3298	167.74	νNH (95)
3132	3280	3142	742.17	νNH (96)
2952	3090	2960	71.86	νCH (91)
2952	3076	2947	21.5	νCH (84)
2952	3068	2939	97.19	νCH (85)
2952	3065	2937	64.63	νCH (88)
2952	3061	2932	73.91	νCH (87)
2952	3058	2930	90.43	νCH (86)
2859	3018	2891	96.13	νCH (87)
2859	3015	2888	47.27	νCH (90)
2859	3015	2888	17.34	νCH (85)
2859	3011	2884	32.363	νCH (86)
2859	3008	2882	28.77	νCH (87)
1590	1620	1592	63.91	βHNH (78)
1581	1607	1580	45.33	βHNH (85)
1502	1498	1473	98.74	δHNHO (45) βHCH (35)

1447	1487	1462	78.01	δ HNHO (37) β HCH (52)
1447	1479	1454	8.54	β HCH (81)
1447	1478	1453	9.5	β HCH (83)
1447	1473	1448	0.5	β HCH (87)
1447	1471	1446	9.46	β HCH (88)
	1426	1402	42.38	δ HCCC (52)
	1396	1372	4.55	β HCC (64)
	1380	1357	1.17	δ HCCC (58)
	1376	1352	1.71	β HCC (63)
	1374	1351	3.59	β HCC (55)
	1366	1343	0.63	β HCC (72)
	1347	1324	0.58	β HCC (73)
	1308	1286	3.64	β HCC (74)
	1286	1264	3.48	β HCC (71)
	1280	1258	2.6	β HCC(47) δ HCCC(12)
	1244	1223	13.93	β HCC(23) vCC(12) β HCC (12)
	1190	1169	6.94	δ CCCC (44) δ HCCC (15)
	1140	1120	15.53	β HCC (44) vCC (12)
	1101	1082	2.13	β HCC (63) vCC (17)
	1084	1066	3.72	β HCC (17) vCC (56)
1079	1071	1053	5.41	β CCC (29) δ HNHO (13)
1079	1042	1024	11.57	vCC (62)

				vCC(12) β CCC (13)
	1022	1005	31.27	β HNC (11)
	1005	988	27.88	vCC (30) δ HNHO (32)
1079	955	939	16.64	vNC (62)
1079	945	929	612.89	vCIO (88)
923	940	924	409.17	vCIO (62) δ HCCC (13)
923	939	924	245.09	vCIO (33) δ HCCC (24)
923	905	890	627.59	v CIO (83)
923	899	884	18.39	δ HCCC (10) vCC (48)
923	884	869	9.94	δ HCCN (33)
923	853	838	4.74	vCC (76)
923	811	797	23.72	vCIO (94)
				β HCC (16) vCC (12)
	805	791	0.07	δ HCCC (45)
	789	775	0.66	vCC (58) β CCC (18)
				δ HCCN(15)
624	556	547	44.98	γ OOOCl (29) β CCC (11) δ HCCN (11)
624	550	541	35.1	γ OOOCl (41)
624	548	538	49.94	β OClO (79)
624	542	533	69.72	β OClO (84)
453	464	456	14.69	γ NCCC (43)
453	457	450	5.77	β CCC (54)

453	413	406	4.09	β CCC (55)
453	401	394	1.47	β OCIO (78)
453	394	387	0.02	β OCIO (88)
-	360	354	11.82	δ HNOCI (52) β CCN (21)
-	343	337	5.79	δ CCCC (20) δ HCCC (32)
-	327	321	23.73	δ HNOCI (30) β CCN (39)
-	240	236	0.26	δ HCCC (19) δ CCCC (66)
-	178	175	28.89	δ CCCC(41) ν ON(14)
-	132	130	33.07	ν ON (66)
-	80	79	9.42	β HOCI (76)
-	62	61	11.32	β HNC (37) δ NHOCI (42)
-	48	47	8.39	β CNO (64) δ NOCIO (11)
-	39	38	0.85	δ NOCIO (84)
-	22	22	0.99	δ NHOCI (87)

Table 9. Theoretical and Experimental ^{13}C chemical shift values of $(\text{C}_6\text{H}_{14}\text{N})\text{ClO}_4$.

Atoms	Experimental chemical shift in ppm	Calculated chemical shift in ppm
		TMS B3LYP/6-311 + G (2d,p)GIAO
C1	49.79	62.9622
C2	30.83	35.8008
C3	24.15	29.9266

C4	24.99	29.2161
C5	24.15	29.9303
C6	30.83	35.7989

Table 10. Second order perturbation theory analysis of the Fock matrix in NBO basis of optimized structure of C₆H₁₄N(ClO₄).

Donor NBO(i)	Acceptor NBO(j)	^a E(2) kcal.mol ⁻¹	^b E(j)-E(i) a.u.	^c F(i,j) a.u.
σ (C5-H6)	σ^* (N1-H2)	2.65	1.03	0.047
σ (C5-H6)	σ^* (C7-H8)	3.42	1.08	0.055
σ (C5-H6)	σ^* (C19-H21)	3.27	1.07	0.053
σ (C5-C7)	σ^* (C5-H6)	2.29	1.2	0.047
σ (C5-C7)	σ^* (C5-C19)	2.34	1.11	0.046
σ (C5-C19)	σ^* (C5-C7)	2.33	1.15	0.046
σ (C7-H9)	σ^* (C5-C19)	4.72	0.95	0.06
σ (C7-H9)	σ^* (C10-C13)	3.11	0.91	0.048
σ (C7-C10)	σ^* (N1-C5)	4.93	0.84	0.058
σ (C7-C10)	σ^* (C5-C7)	2.08	1.09	0.043
σ (C10-H11)	σ^* (C5-C7)	2.71	1.01	0.047
σ (C10-H11)	σ^* (C13-C16)	2.23	0.91	0.04
σ (C13-H14)	σ^* (C7-C10)	2.58	0.96	0.044
σ (C13-H14)	σ^* (C16-C19)	2.6	0.96	0.045
σ (C16-H17)	σ^* (C19-H21)	2.37	1.06	0.045
σ (C16-H18)	σ^* (C5-C19)	3.19	0.96	0.049
σ (C16-H18)	σ^* (C10-C13)	2.22	0.92	0.04
σ (C16-C19)	σ^* (N1-C5)	3.86	0.86	0.052
σ (C19-H20)	σ^* (C5-C7)	3.59	1.04	0.055
σ (C19-H20)	σ^* (C13-C16)	3.03	0.94	0.048
σ (C19-H21)	σ^* (C16-H17)	2	1.11	0.042
LP(O24)	σ^* (N1-H4)	2.07	1.36	0.047
LP(O24)	σ^* (N1-H4)	6.96	0.82	0.07
LP(O23)	σ^* (Cl22-O24)	9.57	0.49	0.063
LP(O23)	σ^* (Cl22-O26)	18.3	0.55	0.09
LP(O23)	σ^* (Cl22-O24)	10.61	0.49	0.066
LP(O23)	σ^* (Cl22-O25)	17.88	0.52	0.087
LP(O24)	σ^* (Cl22-O23)	11.75	0.55	0.074
LP(O24)	σ^* (Cl22-O26)	13.59	0.57	0.08
LP(O24)	σ^* (Cl22-O23)	5.4	0.56	0.05
LP(O24)	σ^* (Cl22-O25)	16.42	0.55	0.087
LP(O24)	σ^* (Cl22-O26)	3.63	0.58	0.042

LP(O25)	$\sigma^*(\text{C122-O23})$	6.74	0.54	0.055
LP(O25)	$\sigma^*(\text{C122-O24})$	2.85	0.51	0.035
LP(O25)	$\sigma^*(\text{C122-O26})$	17.98	0.57	0.092
LP(O25)	$\sigma^*(\text{C122-O23})$	11.81	0.55	0.073
LP(O25)	$\sigma^*(\text{C122-O24})$	16.07	0.51	0.083
LP(O26)	$\sigma^*(\text{C122-O23})$	13.9	0.53	0.078
LP(O26)	$\sigma^*(\text{C122-O25})$	17.34	0.53	0.087
LP(O26)	$\sigma^*(\text{C122-O23})$	7.02	0.53	0.055
LP(O26)	$\sigma^*(\text{C122-O24})$	21.95	0.5	0.095
LP(O26)	$\sigma^*(\text{C122-O25})$	3.57	0.53	0.039
$\sigma^*(\text{C122-O23})$	$\sigma^*(\text{C122-O26})$	8.13	0.02	0.025
$\sigma^*(\text{C122-O24})$	$\sigma^*(\text{C122-O23})$	3.79	0.03	0.02
$\sigma^*(\text{C122-O24})$	$\sigma^*(\text{C122-O25})$	6.5	0.03	0.024
$\sigma^*(\text{C122-O24})$	$\sigma^*(\text{C122-O26})$	3.66	0.05	0.026
$\sigma^*(\text{C122-O25})$	$\sigma^*(\text{C122-O26})$	3.65	0.03	0.019

^a E(2) means energy of hyper conjugate interactions ≥ 2 (stabilization energy in kcal.mol⁻¹).

^b Energy difference between donor and acceptor i and j NBO orbitals in a.u.

^c F(i,j) is the Fock matrix element between i and j NBO orbitals in a.u.