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Synthesis, thermodynamic and spectroscopic study of violurate salt

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ABSTRACT

The organic salts are a broad class of ionic chemicals with a variety of properties. Scientists have an interest in violurate salts because of their bright color and crystal structure. In this study, 4-chloroanilinium violurate salt was synthesized and identification using infrared spectroscopy, 13C NMR spectroscopy and Electrospray ionization (ESI). Density functional theory (DFT) calculations have been performed using B3LYP/6-31++G**, and CAM-B3LYP/6-31++G** levels of theory. Practically, chloroanilinium ion $(M+H)^+$ has a relative abundance of 100% in ESI+, indicating its excellent stability. The protonation formula for violuric acid $(VA+H)^+$ shows instability, despite the observation of a low abundance of the $(VA+3H)^{3+}$ ion. DFT calculations demonstrate the exothermic nature of the salt formation reaction. The calculated enthalpy change is -26.861kJ in the B3LYP/6-31++G** level of theory and -31.82kJ in the CAM-B3LYP/6-31++G** level of theory.

1. Introduction

The organic salts are a wide range of ionic compounds possessing a wide range of characteristics, such as surfactants [1], reagents utilized for the synthesis of other organic compounds [2], lubricants [3], dyes [4], anti-inflammatory [5]. Violuric acid has astounding capacity to form salts with ions of metals and organic amines results in a wide range of colors [6]. A series of brightly colored alkali metal 1,3-dimethylviolurates have been synthesized by Edelmann and coworkers. X-ray crystal structure determination indicates that the compounds exist in the solid state as one- (Li, Na), two- (K, Cs), or three-dimensional (Rb) coordination polymers [7]. A variety of beautifully colored alkali metal 1,3-dimethylviolurates were synthesized by Lorenz and coworkers. The dimensions of synthesized compounds vary, ranging from polymeric networks to monomeric, neutral complex molecules and hydrogen-bonded ions [8]. Koleva and coworkers utilized quantum chemical calculations (MP2/6-31++G** level of theory) to discover the cinchoninium violurate monohydrate's physical characteristics. The absorption peak at about 3,400cm^{-1} in the infrared spectrum generated by quantum chemical calculations has been attributed to the stretching vibration of the hydroxyl group [9]. In the next study, Koleva and coworkers synthesized Ephedrinum violurate dihydrate salt. To determine the physical properties of salt, they used quantum chemical computations MP2 and B3LYP/6-31++G** level of theory. In the solid-state infrared spectrum, they observed that the low-frequency shifting of the υNH stretching vibration by ephedrine in type N–H….O intermolecular interactions is 87 cm-1, which is different from the theoretical value [10].

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At room temperature, violurate salts formation reactions are distinguished by their rapidity. Therefore, it is challenging to determine the rate constant of these reactions experimentally. Given the above rationale, the present study will use the results of the Density Functional Theory (DFT) calculations to determine the rate constant of synthesis for one of the violurate salts. In practice, the study aims to evaluate the stability of positively charged violuric acid ions in a variety of polar solvents generated using the electrospray ionization technique.

2. Materials and Instruments

All of the chemicals were purchased from Sigma-Aldrich and had not undergone any further purification. FTIR spectra utilizing the KBr pressed disk method have been acquired in the 4000-400 cm-1 region accomplished on a Fourier transform infrared spectrophotometer Shimadzu FT-IR 8400S. NMR spectra were acquired at the University of Basrah in Iraq utilizing Bruker 400 MHz for 1H-NMR and 100 MHz for 13C-NMR in the deuterated solvent DMSO-d6. Tetramethylsilane (TMS) was used as the internal reference. Utilizing a positive ion mode and negative ion mode the electrospray ionization (ESI) method were used for acquiring the mass spectra for compound H19 using the Waters Alliance 2695 HPLC-Micro mass quattro micro API mass spectrometer. A mixture of 0.1% formic acid and ethanol was used as the mobile phase in ESI+ ,and a mixture of 0.1% NH_4OH and acetonitrile was used as the mobile phase in ESI-.

3. Synthesis

3.1. Preparation of violuric acid (VA) [11]

Begin by dissolving 6.4 g, equivalent to 50 mmol, of barbituric acid and 4 g, equivalent to 100 mmol, of sodium hydroxide in 36 mL of water. Following that, incorporate 3.8 mmol of sodium nitrite, weighing 55 g, into the mixture. Proceed by cooling the mixture to a temperature of 10 degrees Celsius, and subsequently introduce 18 mL of acetic acid, equivalent to 300 mmol, and 50 g of ice. Keep the reaction mixture for an hour at 25 °C, after which the solution begins to turn pink and the acid gradually precipitates, taking care to stir the solution with a glass rod. The precipitated acid was separated by filtration and washed with 25 mL of hydrochloric acid (30%). After drying, a cream-colored solid with a melting point of 146 °C was obtained.

3.2 Synthesis of violuric acid salt

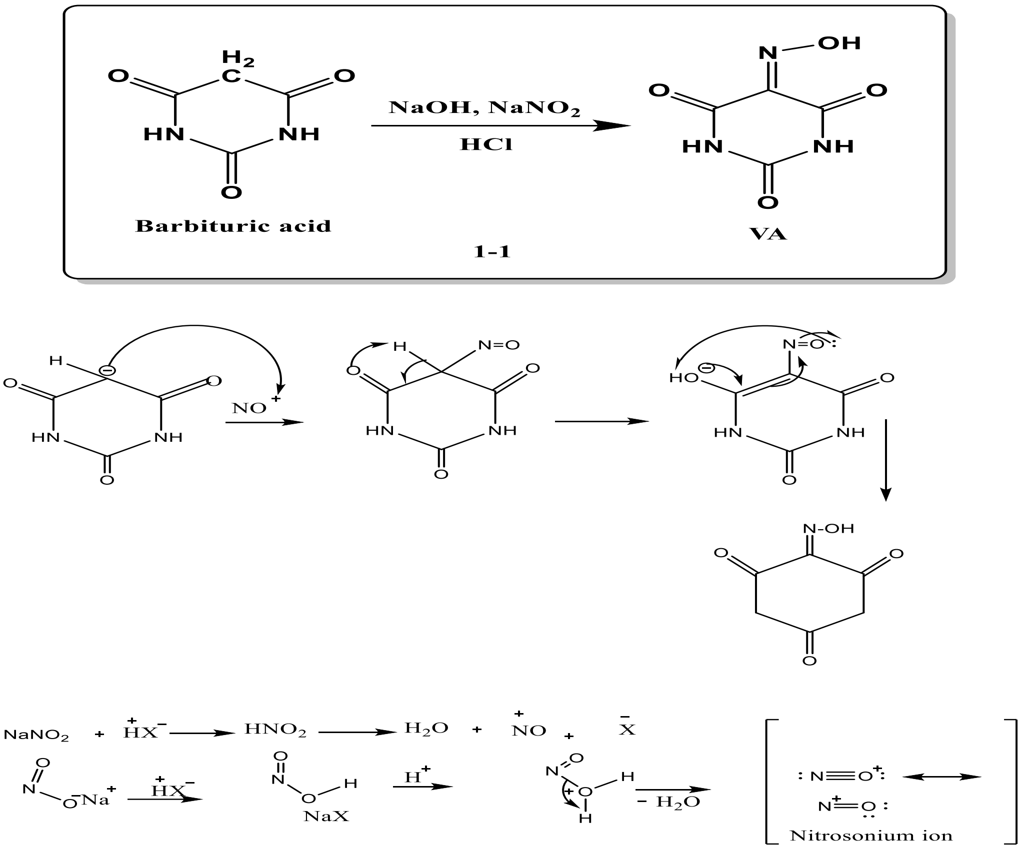
In a 100 mL Erlenmeyer flask, 1 mmol of 4-chloroaniline was dissolved in 10 mL of ethanol. In another flask dissolved 0.06 g of violuric acid in 10 mL of ethanol. When it dissolves completely, add the second solution to the first solution. We notice the color change. The mixture is left to settle and the final product of the violuric salts precipitates.

4. Computational calculations

The preliminary computations were a fully geometrical optimizing utilizing the functional B3LYP (Becke's 3 parameter functional combined with Lee, Yang, and Parr's correlation functional) [12-13], and CAM-B3LYP(Coulomb-attenuating method-B3LYP)[14] for the gas phase structures of the molecule under study at 6-31++G(d,p) basis sets. Then, in order to make sure that there were no imaginary frequencies (stationary points behaving as minima), the frequencies of vibration were computed using a harmonic oscillator.

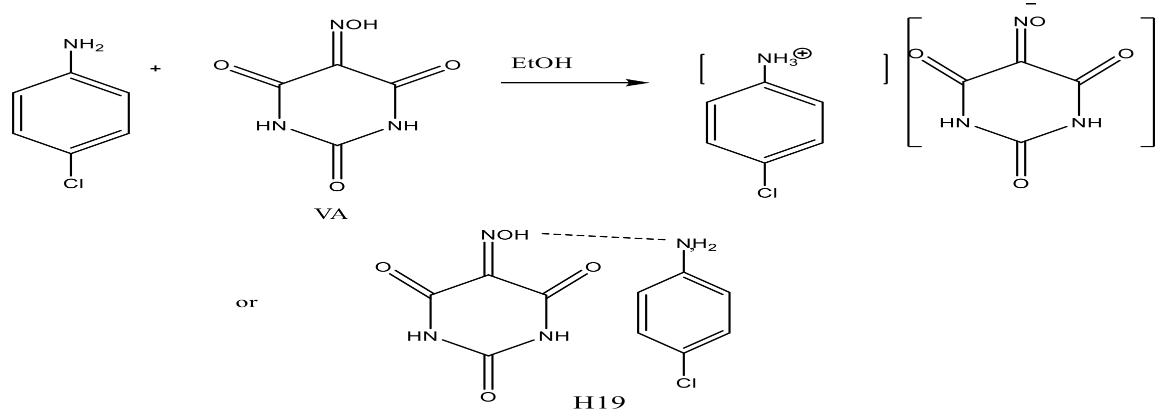
5. Results and discussion

Violuric Acid (VA) was prepared by reacting barbituric acid with sodium hydroxide, then cooled to 10 °C, then adding acetic acid. The reaction mixture was kept for an hour at 25 °C. The reaction began by turning pink, then gradually precipitated. After filtration, the acid that had precipitated was isolated and subsequently rinsed using diluted hydrochloric acid. The resulting solid should be dried in order to obtain a cream-colored substance as shown in the equation 1-1 and Scheme 1-1.



Scheme 1-1

voliurate salt was prepared by reacting 4-chloroaniline with violuric acid using ethanol as a solvent as shown in equation 1-2:



1-2

5.1. Infrared spectrum of H19

Infrared spectra of H19 can be seen in Fig. 1. It is characterized by the presence of bands at 3381 and 3473 cm^{-1}, which are assigned to the vibration of the N-H group, as well as the appearance of a band at 2999 cm^{-1}, which is ascribed to the amplitude vibration of an aromatic C-H group, and the appearance of a weak band at 2578 cm^{-1}, which is attributed to the amplitude vibration of the aliphatic C-H group.The appearance of a weak band at 1726, 1678 and 1620 cm^{-1} is assigned to the stretching vibration of the carbonyl group. Also, the appearance of a band at 1579 cm^{-1} is ascribed to the oxime group NOH, and the appearance of a band at 1492 and 1417 cm^{-1} is assigned to the stretching vibration of the C=C group, and the appearance of a weak band at 1396 cm^{-1} is attributed to the amplitude vibration of the C=N group, as well as the appearance of a beam at 1444 cm^{-1} is attributed to the bending vibration of the N-H amide group, and the appearance of a weak band at 1276 cm^{-1} is attributed to the amplitude vibration of the C-N group, and the appearance of a weak band at 1134 cm^{-1} is ascribed to the amplitude vibration of the C-C group, and the appearance of a broad band in the region 3200 - 2500 cm^{-1} is assigned to the vibration stretching of the OH group.

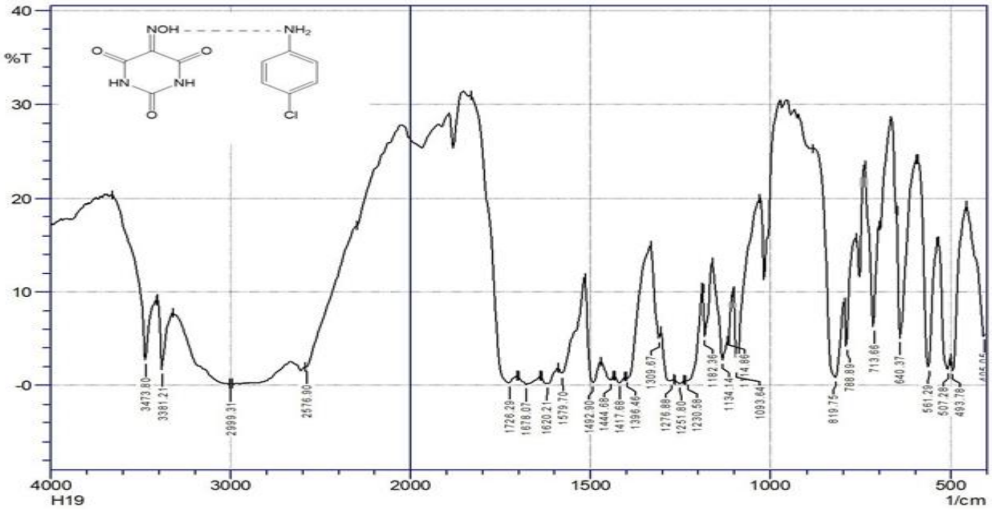


Fig. 1. Infrared spectra of H19

5.2. ^{1}HNMR spectrum of compound H19

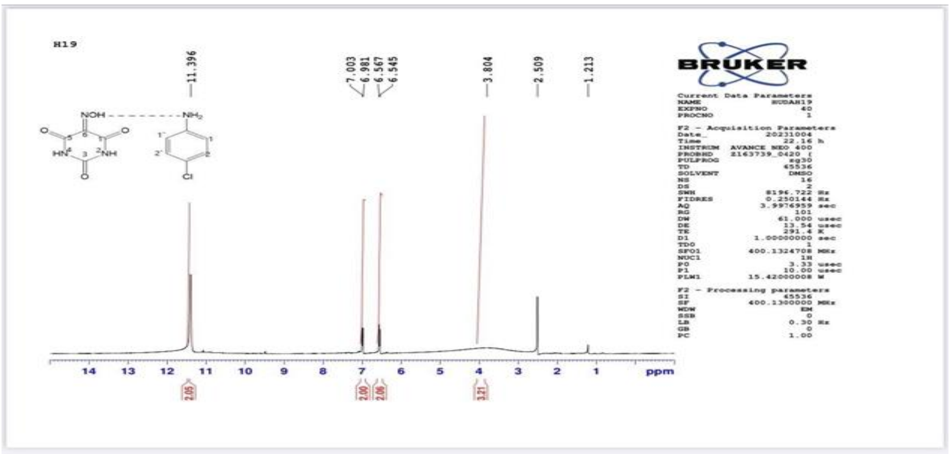
The ^{1}HNMR spectra of H19 is presented in Fig. 2. The spectrum was characterized by the presence of the following signals.

1- The appearance of a single signal due to proton integration at a displacement of 3.804 ppm, attributed to a proton of the NH_3 group.

2- The appearance of a double signal due to proton integration at a displacement of 6.567 ppm, attributed to a proton of the aromatic C-H group.

3- The appearance of a double signal due to proton integration at a displacement of 7.003 ppm, attributed to a proton of the aromatic C-H group.

4- The appearance of a single signal due to proton integration at the displacement of 11.396 ppm, attributed to the protonation of the N-H amide group.



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PROCNO                  1

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Time                22.16 h
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PULPROG              zg30
TD                  65536
SOLVENT              DMSO
NS                     16
DS                      2
SWH              8196.722 Hz
FIDRES           0.250144 Hz
AQ              3.9976959 sec
RG                    101
DW                 61.000 usec
DE                  13.54 usec
TE                  291.4 K
D1             1.00000000 sec
TD0                     1
SFO1          400.1324708 MHz
NUC1                   1H
P0                   3.33 usec
P1                  10.00 usec
PLW1          15.42000008 W

F2 - Processing parameters
SI                  65536
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

Fig.2. ^{1}HNMR spectra of H19

5.3. ^{13}CNMR spectrum of compound H19

The ^{13}CNMR spectrum of H19 is displayed in Fig. 3. It showed a signal at 115.73 ppm that belongs to the resonance of the C-H group. The spectrum also showed a second signal that goes back to the resonance of the C-Cl group at the displacement of 120.92 ppm, and also an indication of the resonance of the C-C atoms at the displacement of 137.07 ppm. The spectrum also showed a signal of the resonance of the C-N group at the displacement is 140.08 ppm, and the spectrum showed a signal belonging to the C=O group at the displacement 150.31 ppm. The spectrum also showed a resonance signal belonging to the C=O group at the displacement 155.22 ppm, and the spectrum also showed a signal belonging to the C=O group at the displacement 160.09 ppm.

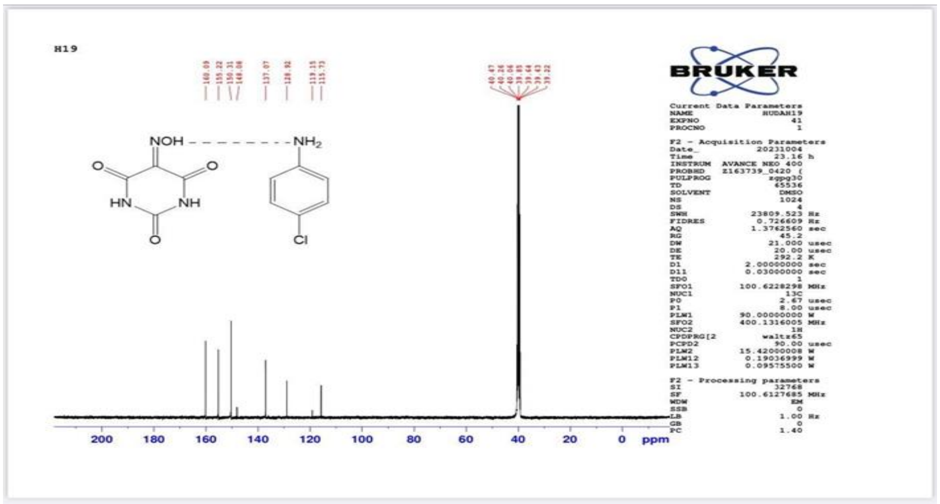

Fig. 3. 13CNMR spectrum of compound H19

5.4. Mass Spectrometry

Mass Spectrometry (MS): Mass spectrometry helps in establishing the molecular mass and fragmentation pattern of violuric salt. It offers insights into the molecular formula and structural fragments present in the compound.

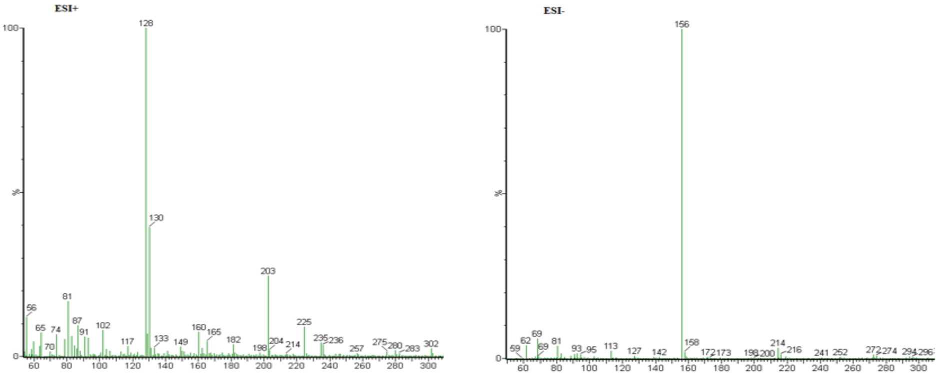

Fig. 4. ESI positive mode and negative mode spectrum of compound H19

Fig. 4 shows the ESI spectra of H19.The protonated 4-chloroaniline molecule is observable in ESI positive mode spectra of H19 at m/z 128 $(M+H)^+$, while the prominent peak seen at m/z 156 $[M - H]^{-1}$ in the ESI negative-ion mode spectra of H19 has been attributed to the violurate ion.

The influence of the solvent on the ions stability from the compound H19 ionization spectrum of Electrospray ionization (ESI +) has been examined. The high polar as acetonitrile solvent (dielectric constant = 36.64) and methanol solvent (dielectric constant = 33) were used to measure the mass spectra [15]. A number of solvents from solvent blending were used as well to correspond with the volumetric ratios listed in Table 1, and the dielectric constant of the solvent mixtures produced was determined using equation 1 [16].

$\varepsilon mix = \varphi MeOH * \varepsilon MeOH + \varphi ACN * \varepsilon ACN$ --------1

εmix ; dielectric constant of mixture
εMeOH: dielectric constant of methanol
εACN: dielectric constant of acetonitrile
φMeOH : Volume fraction of methanol
φACN: Volume fraction of acetonitrile

The volume fraction of solvents by equation 2 [17]

$\phi j= \phi i/\sum \phi i$ -------2

The results of the experiment demonstrated that the 4-chloroanilnium ion's molecular weight was given by the ion $[M + H]^+$, it has a high relative abundance (100%) in all solvents used in the experiment. The stability of the ion $[M+3H]^{3+}$, which forms when three protons are added to the molecules 4-chloroaniline[18], and violuric acid, rises as the solvent polarity increases. It have highest abundance in acetonitrile solvent because solvents with an dielectric constant increase the stability of multi-charge ions resulting from the Electrospray ionization technique and as a result of the increased abundance of ions generated in the gas state [19]

Table 1 Relative abundance of 4-chloroanilinium $(M+H)1^{+,}$ and $(M+H)\ 3^+$ ions , and violuric acid protonated ion $(VA+3H)3^+$ in different polar solvents

	Solevent				
ion	**25%MeOH (ε:35.73)**	**50%MeOH (ε:34.82)**	**75%MeOH (ε:33.91)**	**100%MeOH (ε:33)**	**100%ACN (ε:36.64)**
127.57+H p-Chloro	100%	100%	100%	100%	100%
127.57+3H p-Chloro	38%	46%	42%	39%	68%
157.08+3H VA	<1	<1	8%	8%	12%

5.5. DFT Calculations

The density functional theory (DFT) has been adopted widely to compute a wide range of molecular characteristics such as total energy, dipole moment, energy of molecular orbital, and chemical shifts [20,21]. In this study dft calculations were used to obtain thermodynamic functions values, dipole moment(μ), polarizability (α), and hyperpolarizability(β).

5.5.1. Thermodynamic Properties

Thermodynamic properties offer valuable information regarding the stability, energy alterations, and characteristics of a compound in various circumstances. Key thermodynamic properties associated with violuric salt encompass its enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG). Through the use of DFT calculations, these properties can be theoretically determined utilizing equations 3-5 from frequency calculations (Table 2).

$\Delta_r H^o\ (298K) = \Sigma[\Delta_f H^o(products)] - \Sigma[\Delta_f H^o(reactants)]$-----3
$\Delta_r S^o = \Sigma[\Delta S^o(products)] - \Sigma[\Delta S^o(reactants)]$-----------------4

$$\Delta_rG^o\ (298K) = \Sigma[\Delta_fG^o\ (products)] - \Sigma[\Delta_fG^o\ (reactants)]\text{-----}5$$

It is noticeable from Table 2 that the salt formation reaction is exothermic because the reaction enthalpy has a negative sign. The salt production reaction has a negative entropy, which suggests that regularity is increasing in the direction of salt formation. The positively free energy change of the reaction that forms salt indicates clear that the process of synthesizing salt is not spontaneous.

5.5.2. Rate of Reaction

The rate constant of the salt formation reaction has been determined utilizing equation 6 [22].

$$\kappa(298K) = (kBT/hCo)*\ e\text{-}\Delta G/RT\text{-----}6$$

kB : Boltzmann constant = 1:380662x 10-23 J/K, co = 1 for the concentration
T : absolute temperature (default is 298.15), κ : rate constant
h : Planck's constant = 6:626176x10-34 J. s, R : gas constant = 0.00831441 kJ/(mol K)

Table 2 . The calculated thermodynamic functions values using DFT calculations, and rate constant for formation reaction of 4-chloroanilinium violurate salt (red color by B3LYP/6-31++G**, and blue color by CAM-B3LYP/6-31++G** level of theory)

Parameter	**VA**	**4-Ch**	**Σreactants**	**products**	**Δp-r**	**Δp-r**
H	-619.295100 a.u	-747.109893 a.u	-1366.40499 a.u	-1366.41520 a.u	-0.01023 a.u	-26.8614 kJ
	-619.05560 a.u	-746.94480 a.u	-1366.00040 a.u	-1366.01522 a.u	-0.01212 a.u	-31.821 kJ
G	-619.340209 a.u	-747.14934 a.u	-1366.48955 a.u	-1366.48620 a.u	0.0033 a.u	8.5643 kJ
	-619.100489 a.u	-747.984102 a.u	-1366.08459 a.u	-1366.08215 a.u	0.0033 a.u	8.5643 kJ
S	94.941 Cal/mol.K	83.034 Cal/mol.K	177.975 Cal/mol.K	149.572 Cal/mol.K	-28.403 Cal/mol.K	-0.1188 kJ/mol.K
	94.473 Cal/mol.K	82.714 Cal/mol.K	177.187 Cal/mol.K	146.556 Cal/mol.K	-30.631 Cal/mol.K	-0.128 kJ/mol.K
Rate Constant ***k***(s^{-1})				1.962E+11 4.736E+11		

The largest rate constant for the formation reaction of the violurate salt under study has been calculated using the CAM-B3LYP functional. The rate constant for this reaction is greater than the rate constant found in literature (3.5×106 s^{-1}) for the reverse reactions of the H-shifts from substituted alkyl peroxy radicals [23].

5.5.3. Dipole moment, polarizability, and hyperpolarizability

The molecule dipole moment is one of the most significant numbers in chemistry. It is important to estimate long-range interactions between electrostatics and induction, as well as infrared spectra[24]. An electric dipole forms when the centres of the positive and negative charges in a molecule are separated. Scientists termed this polarity [25]. The first-order response of the dipole moment to external electric fields is explained by its linear polarizability, α [26]. Variations in polarizability cause modifications to linear optical characteristics, such as absorption and refractive indices [27]. The hyperpolarizability (β) of a molecule represents its propensity to form a dipole upon being subjected to an electric field. Therefore, changes in an atom's or molecule's charge distribution carried on by an electromagnetic field can be measured using hyperpolarizability [28]. Hyperpolarizability is an indication of the nonlinear optical response (NLO response) in compounds with an extensive intramolecular charge transfer (ICT)[29]. Nonlinear optical response resulting from quasi-delocalized electrons interacting with applied electric fields, which includes nonlinear variations in absorbance or index of refraction [30]. NLO materials are widely used in optical memory devices, optical switches, processing of signals, image processing, and communication systems [31-33]. Table 3 shows that the calculated values for the dipole moment(μ), polarizability (α), and hyperpolarizability(β). The physical properties of 4-chloroanilinium violurate salt have been compared using Urea Sulfamic acid as a reference material [34]. The dipole moment value of H19 molecule is smaller than that of urea-sulfamic acid. In contrast, the α and β values of the H19 molecule are higher than the values of urea-sulfamic acid. Based on general study results, the chemical under examination (H19) seems to exhibit polarizable characteristics.

Based on Table 3, it can be observed that the polarization values computed by functional B3LYP are significantly greater than those with CAM-B3LYP. The literature suggests that B3LYP functionally exaggerates the β, and that the long-range corrected functional CAM-B3LYP is an acceptable method for computing the β [35].

Table3. The calculated dipole moment(μ), polarizability (α), and hyperpolarizability(β) values using DFT calculations for sulfamic acid-urea and 4-chloroanilinium violurate salt (H19). (red color by B3LYP/6-31++G**, and blue color by CAM-B3LYP/6-31++G** level of theory)

Parameter	H19	Urea-sulphamic
μ(Debye)	4.162	4.888
	4.202	5.085
α(a.u)	179.989	74.861
	173.58	72.174
β(a.u)	143.387	49.73
	91.502	41.206

6. Conclusions

In practice, the relative abundance of chloroanilinium ion $(M+H)^+$ in ESI+ is 100%, demonstrating its high degree of stability. In contrast, the violuric acid protonation formula $(VA+H)^+$ exhibits instability. violurate salt formation reaction is exothermic, as demonstrated by DFT calculations. Hyperpolarizability value suggests that the chemical under investigation (H19) has NLO properties.

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تحضير ودراسة طيفية وثرموديناميكية لملح الفويلوريت

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الملخص

تعتبر الأملاح العضوية فئة واسعة من المواد الكيميائية الأيونية لامتلاكها مجموعة متنوعة من الخصائص. جذبت املاح الفلويلوريت اهتمام العلماء بسبب لونها الزاهي وبنيتها البلورية. تم في هذه الدراسة، تخليق الملح ا 4-كلوروانيلينيوم فيلوريت وشخص باستخدام مطيافية تحت الحمراء ومطيافية الكتلة بالتاين بالرذاذ الكهربائي ومطيافية الرنين النووي المغناطيسي للبروتون والكاربون13. عمليا يكون لأيون 4-كلوروانيلينيوم $(M + H)^+$ في طيف ESI+ وفرة نسبية 100% مما يشير الى استقراريته العالية. صيغة حامض الفويلوريك المبرتنة $(M + H)^+$ لم تلاحظ في طيف ESI+ ما يدل على عدم استقرارية هذا الايون. من جانب اخر تم ملاحظة الايون ذو البرتنة الثلاثية لحامض الفويليوريك $(VA + 3H)^{3+}$ ولكن بوفرة نسبية قليلة. الحسابات النظرية باستخدام نظرية الكثافة الدالية تشير الى الطبيعة الباعثة لتفاعل تكوين الملح قيد الدراسة حيث أعطى مستوى الحساب النظري CAM-B3LYP/6-31 + G * *تغييرًا في الإنثالبي يساوي -31.82kJ بينما أظهر مستوى الحساب النظري B3LYP/6-31 + G * * تغيرًا في الإنثالبي يساوي -26.861kJ

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