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Computational and experimental studies of the IR spectra and structure on violuric acid and its anions

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Dedicated to Acad. Ivan Juchnovski on the occasion of his 80th birthday

The experimental and theoretical IR spectra and structure of violuric acid and its anions have been studied. The triketo tautomer for the molecule and anions are most stable according to the calculations (B3LYP/6-311+G(2df,p). The conversion of molecule into anion causes strong frequency decreases of the three carbonyl stretching bands ν(C=O): computed 153 cm^{-1} (B3LYP/6-311+G(2df,p), measured 138 cm^{-1} and other essential IR changes. The formation of violurate dianion has been assumed to take place in DMSO-d6/CD_3SOCD_2Na solution. The total ν(C=O) decrease, caused by the molecule ⟶ diazanion conversion is: predicted 485 cm^{-1}, measured in DMSO-d_6 483 cm^{-1}.

Key words: violuric acid; IR; DFT; anions

INTRODUCTION

Bayer was the first to prepare violuric acid (2,4,5,6(1H,3H)-pyrimidinetetrone 5-oxime) as early as 1864 [1]. It is well known the very broad applications of violuric acid in analytical chemistry to detect cations of some metals [2-5] (e.g., used as a reagent for cobalt[2], for determination of copper, cobalt, lead, and iron in table salt [5]). Violuric acid behaves as a weak triprotic acid in aqueous solution (pKa_1 =4.35, pKa_2 =9.64, pKa_3 =13.1) [6,7]. The remarkable ability of its anion to form compounds of differing color with metal ions[8], as well as with organic cations [9] has been underlined in the last 20 years. Violuric acid is used and in biological research. It is active as an antihypoxic agent [10]. It can be used to inhibit and/or prevent the growth of many undesirable forms of algae, bacteria and fungi [11]; as mediator in the laccase-catalyzed pesticide degradation [12], *etc.* Its cobalt complexes are active as antiviral and antibacterial agents [13]. Violuric acid is a reversible monoamine oxidase-B inhibitor and may be useful in the treatment of neurodegenerative diseases such as Parkinson's disease [14]. The complex compounds of violuric acid derivatives with Pt(II) showed a activity to human acute myeloid leukemia HL-60 [15].

Different functional groups in violuric acid, such as the –C=O, =N–OH and –N–H groups, provide a large variety of bonding behaviour, so it is use for the construction of coordination and supramolecular compounds (e.g. the complexes of mononuclear Fe (III), cobalt (III) manganese (II) [16,17 and refs. therein]. In these new crystalline arrangements violurate anion appears as monodentate, chelate or ionic form [16].

The spectral study of violuric acid and their anions attract the attention of the researchers in the last two decades. The subject of these studies is the spectra and structures of mono anion with different counter anions in solid state. Oliveira *et al.* studied vibrational spectra of violuric acid and its Na salt in solid state and in aqueous solution in different pH and propose tentative assignment of observed bands [7]. IR and Raman spectra and tautomerism of violuric acid have been studied on the basis of ab initio and DFT calculations [18]. To the best of our knowledge no vibrational spectra in aprotic solvents are published in the literature however it can supply the information about the structure of these species. It is important to know if they exist as solvent separated ions or are kinetically independent ones.

In this study we present and discuss specific comparisons of vibrational and structural data of violuric acid, its anion, dianion, and trianion, based on density functional computations, as well as, on the basis of original and literature experimental data.

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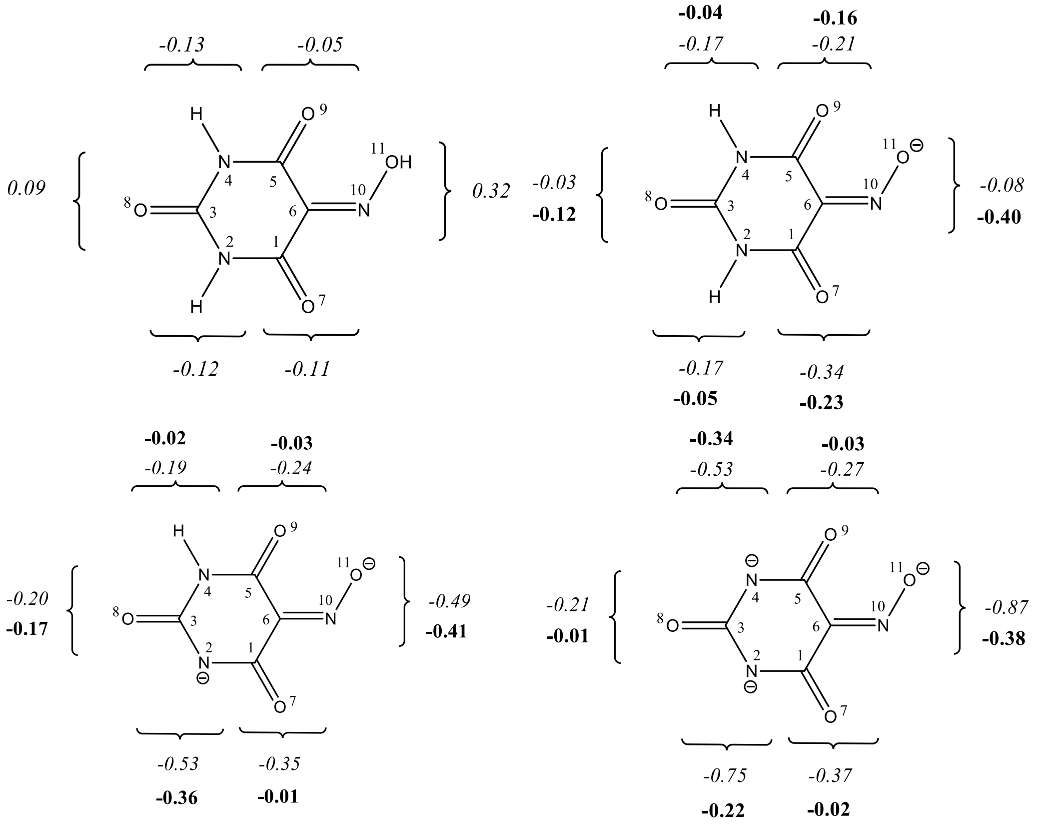
EXPERIMENTAL AND COMPUTATIONS

Violuric acid monohydrate (Sigma-Aldrich, 98%) was used without additional purification. We prepared sodium violurate monohydrate from violuric acid and sodium hydroxide [8]. The violurate anion (counter ion Na^+) was prepared by adding dimethyl sulfoxide (0.10 - 0.15 mol l^{-1} DMSO/DMSO-d_6) solutions of violuric acid to excess of dry sodium methoxide-d_0 and -d_3, and filtration of the reaction mixture by a syringe filter. The violurate dianion (counter ions Na^+) was prepared by adding dimethyl sulfoxide (0.10 - 0.15 mol l^{-1} DMSO/DMSO-d_6) solutions of violuric acid or violurate sodium to DMSO-d_6/D_3CSOCD_2Na solution. IR spectra were measured on Bruker Tensor 27 Fourier transform infrared (FTIR) spectrophotometer in a CaF_2 cell of 0.13 mm path length and in KBr pellets, at a resolution of 1 cm^{-1} and 64 scans. The quantum chemical calculations were performed using the Gaussian 09 package [19]. The geometry optimizations of the structures investigated were done without symmetry restrictions, using density functional theory (DFT). We employed B3LYP hybrid functional, which combines Becke's three-parameter nonlocal exchange with the correlation functional of Lee *et al.* [20,21], adopting 6-311+G(2df,p) basis sets. The stationary points found on the molecular potential energy hypersurfaces were characterized using standard harmonic vibrational analysis. The theoretical vibrational spectra were interpreted by means of potential energy distributions (PEDs) using VEDA 4 program [22]. For a better correspondence between experimental and calculated values, we modified the results using the empirical scaling factors.

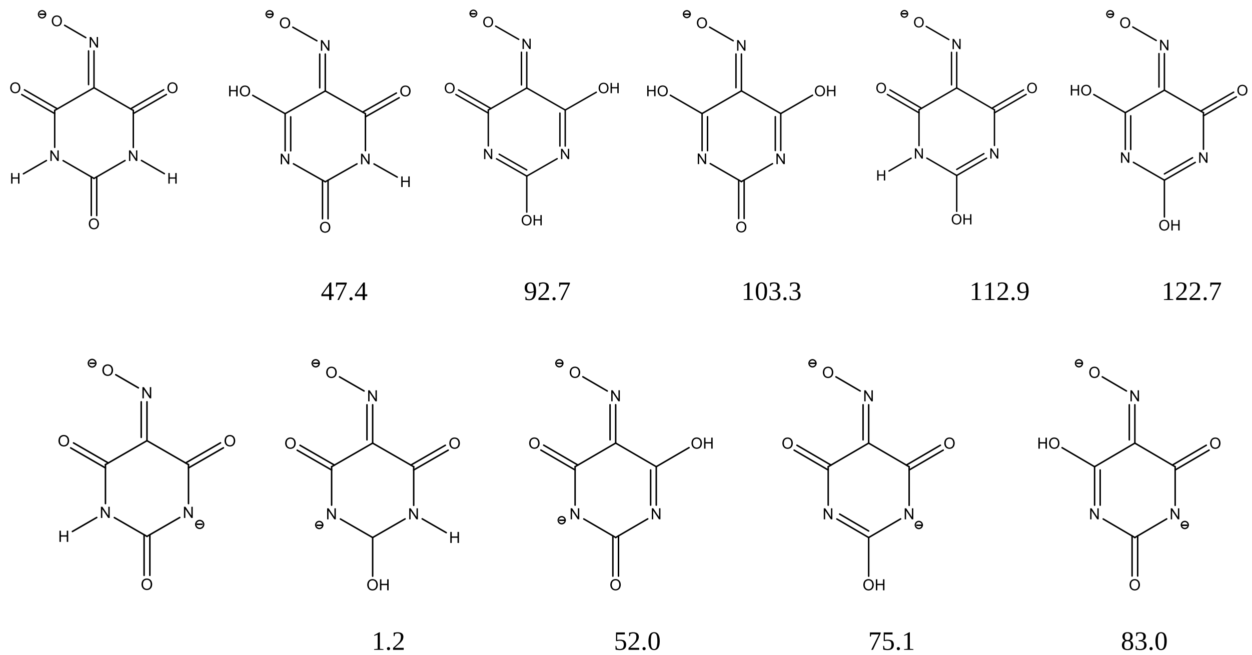
RESULTS AND DISCUSSION

Energy analysis

The violuric acid can exist as 10 different tautomers. The most stable among the molecular tautomers is the triketo form shown in Scheme 1. The same form is supported by single crystal X-ray data [23]. The relative stability of tautomers in the gas phase computed by us is in agreement with the previously computed results at the B3LYP/6-31G* level [18]. The six possible tautomers for anion and five ones for the dianion together with the values of relative energy are shown on Scheme 2. In both anions the triketo form is predicted as the most stable. The largest energy difference between the anionic tautomers studied is 102.7 kJ mol^{-1}; for the dianionic tautomers it is smaller, 52.0 kJ mol^{-1}.



Scheme 1. B3LYP 6-311+G(2df,p) structure of the most stable tautomers of violuric acid, its anion, dianion, and trianion. The net charges of fragments (in italics) and charge changes (in bold) are given in the formulae.



Scheme 2. The possible tautomers of violuric acid anion and violuric acid dianion and the relative energies with respect to the most stable isomer (ΔE in kJ mol^{-1}).

The energy difference E_1^D = E_{anion} – $E_{molecule}$ between the most stable forms of anion and molecule can be used as an approximate measure of pKa of a given compound in polar aprotic solvents [24]. The B3LYP value E_1^D of studied species of 1354.3 kJ mol^{-1} corresponds to a moderately weak acid; its experimental pKa_1 is 4.35 (solvent water). For comparison, the E_1^D energy is lower than E_1^D acetanilide (1489.06 kJ mol^{-1} [25]) and a little higher than E_1^D of acesulfame (1324.31 kJ mol^{-1} [26]).

The energy difference between the dianion and anion E_2^D = $E_{dianion}$ – E_{anion} of 1811.033 is essentially higher, and can be compared with the corresponding energy of paracetamol (1880.2 kJ mol^{-1} [27]). The energy difference E_3^D = $E_{trianion}$ – $E_{dianion}$ is larger (2281.16 kJ mol^{-1}). Experimental pKa data in water for the violuric acid dianion and trianion are 9.6 and 13.1, respectively [6,7]. However, we found in the literature neither theoretical, nor experimental data for violuric acid and its anion in DMSO.

The experimental pKa values depend strongly on the solvent, counter ion, nature of both the Brønsted acid and its conjugate base (e.g., carbanion or azanion, with localized or delocalized charge), concentration, temperature [28].

Infrared analysis

Let us consider consecutively the IR data for the species studied, which will make it possible to specify the spectral changes, caused by the conversion of the violuric acid molecule into corresponding anions.

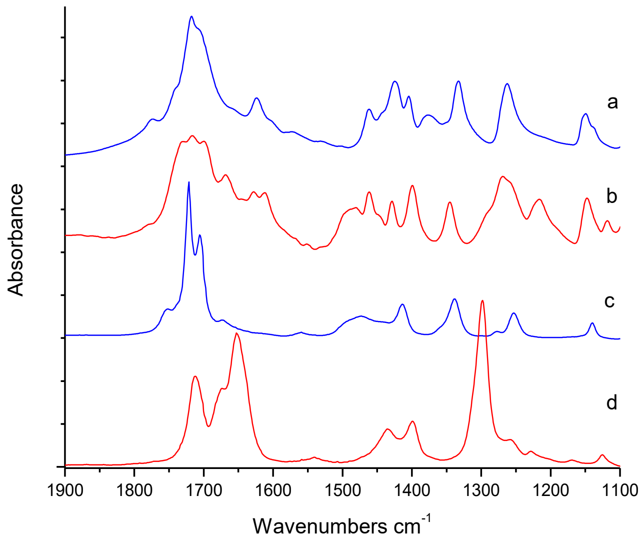


Fig. 2. IR spectra: of violuric acid in KBr (**a**); sodium salt of violuric acid in KBr (**b**); violuric acid in DMSO-d_6 (**c**), anion of violuric acid (counter ion Na^+) in DMSO-d_6 (**d**).

The spectrum of violuric acid in solid phase is rather complicated. The conversion of the neutral molecule into anion makes it more difficult. In order to eliminate strong intermolecular interactions in the molecule of violuric acid the experimental spectra were measured in polar aprotic solvent DMSO. It is known that in this solvent the ions exist as free species and there are no anion/counter ion interactions [29]. The influence of the counterions on the frequencies is neglectful. This makes it possible to compare, in this work, the experimental infrared data for the anions with the theoretical data. The numerical values of the experimental vibrational frequencies in DMSO-d$_6$ and band intensities are listed with the theoretical ones in Table 1.

Table 1. Theoretical (B3LYP/6-311+G(2df,p) and experimental (solvent DMSO-d6) vibrational frequencies (cm^{-1}) and IR integrated intensities (A in km.mol^{-1}) of violuric acid and its anion.

	Theoretical data			Experimental data[a]	
No	$\nu_{\text{theor.}}$[a]	A[b]	Approximate description[c]	$\nu_{\text{exp.}}$	A[c]
			Violuric acid molecule		
1.	3644	186.9	99ν(OH)	3500	w
2.	3475	78.5	93 ν(NH)	3445	
3.	3471	100.5	94 ν(NH)		
4.	1753	65.9	36 ν(C^{12}O^{2}), 31ν(C^{11}O^{1}), 12ν(C^{13}O^{3})	1753	m
5.	1737	853.9	37ν(C^{12}O^{2}), 29ν(C^{11}O^{1})	1722	s
6.	1711	479.2	61ν(C^{13}O^{3}), 20ν(C^{11}O^{1})	1706	s
7.	1586	51.6	64 ν(C-NO), 16δ(NOH)	1560	vw
8.	1405	188.2	42 ν(CN), 20δ(NOH)	1413	m
9.	1378	257.0	42 ν(CN),28 ν(CC)	1360	sh
10.	1371	116.0	48 δ(NOH), 12δ(CNH)	1344	sh
11.	1352	36.0	66 δ(CNH),14δ(OCN)	1339	m
12.	1274	168.6	59 ν(CN),12 ν(CC)	1277	w
13.	1185	102.2	37 ν(CN), 33 ν(CC)		
14.	1105	120.3	25 ν(ON), 17 ν(CN), 16 δ(NCC)	1140	w
15.	1035	247.8	53 ν(ON),17 ν(CN)		
16.	989	1.1	36 ν(CN), 16 δ(CNH)		
			Violuric acid anion		
1.	3535	40.6	100 ν(NH)		
2.	3561	35.4	100 ν(NH)		
3.	1713	566.1	69 ν(C^{5}O^{12})	1716	s
4.	1681	368.7	37 ν(C^{1}O^{11}), 33ν(C^{6}O^{19}) s	1676	s
5.	1654	1050.2	37 ν(C^{1}O^{11}), 33ν(C^{6}O^{19}) as	1655	vs
6.	1443	34.2	76 ν(ON)	1444	sh
7.	1431	139.2	42 ν(CN),20δ(O^{12}CN)	1435	m
8.	1357	53.0	55(CNH), 23 ν(C^{5}O^{12})	1396	m
9.	1327	20.6	78δ(CNH)	1343	w
10.	1306	961.3	34 ν(C-NO),10 ν(N-O)	1299	vs
11.	1236	97.8	59 ν(CN)	1255	w
12.	1135	16.2	37 ν(CN), 33 ν(CC)	1128	w
13.	1050	16.7	25 ν(ON), 17 ν(CN), 16 δ(NCC)		
14.	1010	11.8	53 ν(ON),17 ν(CN)		

[a]Scaled infrared frequencies by 0.969.[b]Vibrational modes: ν, stretching; δ, bending; perscripts: s – symmetrical, s – asymetrical. The numbers before the mode symbols indicate % contribution (10 or more) of a given mode to the corresponding normal vibration, according to the potential energy distribution [c]Relative intensities: vw, very weak; w, weak; m, moderate; s, strong; vs, very strong; sh, shoulder.

The agreement between the calculated frequencies and the experimental data is very good. The mean absolute deviation between experimental and theoretical frequencies is 8 cm^{-1} for the molecule and 11 cm^{-1} for the anion.

According to our calculations the strong band at 3644 cm^{-1} is assigned to ν(O-H) while the bands at 3475 and 3471 cm^{-1} are attributed to ν(N-H). The experimental observed bands are lower than calculated ones because of the formation of hydrogen bonds mainly with solvent. Of course, the three carbonyl bands are the strongest and the most interesting in the IR spectra of violuric acid. According to our computations, however, all the ν(C=O) coordinates are strongly coupled with each other, and the approximate descriptions of the corresponding bands are given in Table 1. The band predicted at 1586 cm^{-1} and measured at 1560 cm^{-1} belongs to ν(C=N). The bands between 1426-1260 cm^{-1} are connected mainly to ν_{ring}(C-N) and ν_{ring}(C-C). The middle strong band measured at 1140 cm^{-1} is assigned to ν(O-N) is strongly coupled vibration with ν(CN) and δ(NCC).

The strongest IR spectral changes, caused by the molecule →anion conversion, take place in the 1800–1770 cm^{-1} region (Table 1 and Fig.2). The following bands have been measured in this region of the IR spectrum of violuric acid: 1710, 1676 and 1655 cm^{-1}. The highly frequency band at 1710 cm^{-1}is attributed to ν(C^3=O^8). The two lower bands are assigned to the asymmetric and symmetric to ν(C^1=O^7) and to ν(C^5=O^9). So, the total ν(CO) decrease, caused molecule →anion conversion is: predicted 153 cm^{-1}, measured 138 cm^{-1}.

The band ν(O-N) is shifted from 1140 to 1444 cm^{-1} because the bond order increase nearly double. In the spectrum of anion appears very strong band at 1300cm^{-1}, according the calculations very strong mixed between ν(C=N), ν(O=N) and ν_{ring}(C-N).

According to our computations, the IR spectrum of the violuric acid dianion should show three bands, corresponding to strongly coupled vibrations of the three carbonyl groups at 1603 cm^{-1}, 1586 cm^{-1} and 1530 cm^{-1}. We tried to prepare dianion (counter ions 2Na$^+$) by adding dimsil sodium to a DMSO-d_6 solution of violuric acid. The IR spectrum of the solution after metalation showed three bands in the above region: 1600, 1560 and 1533 cm^{-1}. If we assume that these bands really correspond to ν(CO) of the dianion, we can calculate the total ν(CO) decrease, caused by the anion → dianion conversion: predicted 332 cm^{-1}, measured 345 cm^{-1}. Respectively, the total ν(CO) decrease, caused by the molecule → dianion conversion would be: predicted 485 cm^{-1}, measured 483 cm^{-1}.

The IR spectrum of trianion of violuric acid was calculated theoretically by B3LYP/6-311G(2df,p). The ν(C=O) bands are predicted at 1510, 1445 and 1410 cm^{-1}, but experimental metalation cannot succeed. Probably in this basic medium violuric acid can undergo some decomposition as cited by [6].

Structural analysis

According to X-ray diffraction the plane of the acetamide group is oriented at 40.4° with respect to the benzene ring, whereas the plane of the carboxylic acid group is essentially coplanar with the benzene ring [21]. According to the calculations in the most stable conformers of the isolated molecule these groups are planar. The same groups in the isolated oxyanion and dianion have been predicted to be again planar. The theoretical and experimental bond lengths and angles in the 4-acetamidobenzoic acid and its oxyanion and dianion are listed in Table 4. The most significant changes caused by the conversion from molecule to anion take place both at the anionic center and next to it, with agrees the data for other anions [25-27,30,31] They are strong shortening of the N_{10}-O_{11} with 0.11 Å and strong lengthening of the C_6-N_{10} with 0.09 Å and shortening of C_1-C_6 and C_5-C_6 with 0.05 Å and 0.04 Å respectively. The second deprotonation from anion to dianion as can see in Table 2 causes bond shortenings at the azanionic center N_2 and bond lengthenings next to it. The bonds lengths change both at and next to the azanionic center N_4, caused by the dianion →trianion conversion are is qualitatively similar to the azanionic center N_2. The net electric charges (q_i) of fragments of the species studied are shown in Scheme 1. The charge changes q_i(anion) - q_i(molecule), q_i(dianion) - q_i(anion), q_i (trianion) - q_i (dianion) can also be seen in Scheme 1. The charge changes are usually quite informative to show the distribution of the new charges over the corresponding anions [25-27,30,31]. For the conversions studied the change charges, accompanying the conversion molecule →anion→dianion→trianion are also quite informative, to shown that the first oxanionic charge is delocalized over whole anion. That is in agreement with observed deep color of monoanion in the UV-vis spectra - due of strongly conjugated system. The second and third charges are also delocalized over the dianion and trianion forms.

Table 2. Theoretical (B3LYP/6-311++G**) and experimental bond lengths R (Å) and bond angles A (°) the vialuric acid molecule and its anion, dianion, trianion.

	Molecule			Anion		Dianion		Trianion	
	Exp.^{a}	Calc.	Δ^b	Calc.	Δ^c	Calc.	Δ^d	Calc.	Δ^e
Bond lengths									
R(C^1,N^2)	1.372	1.389	0.017	1.419	0.03	1.378	-0.041	1.353	-0.025
R(N^2,C^3)	1.362	1.384	0.022	1.370	-0.014	1.331	-0.039	1.379	0.048
R(C^3,N^4)	1.379	1.386	0.007	1.368	-0.018	1.412	0.044	1.376	-0.036
R(N^4,C^5)	1.361	1.391	0.03	1.425	0.034	1.390	-0.035	1.357	-0.033
R(C^5,C^6)	1.499	1.491	-0.008	1.450	-0.041	1.456	0.006	1.508	0.052
R(C^6,C^1)	1.506	1.504	-0.002	1.452	-0.052	1.504	0.052	1.511	0.007
R(C^1,O^7)	1.176	1.205	0.029	1.223	0.018	1.242	0.019	1.266	0.024
R(C^3,O^8)	1.225	1.207	-0.018	1.226	0.019	1.254	0.028	1.276	0.022
R(C^5,O^9)	1.212	1.206	-0.006	1.221	0.015	1.239	0.018	1.261	0.022
R(C^6,N^{10})	1.275	1.284	0.009	1.374	0.09	1.350	-0.024	1.333	-0.017
R(N^{10},O^{11})	1.328	1.348	0.02	1.240	-0.108	1.268	0.028	1.299	0.031
Bond angles									
A(C^1,N^2,C^3)	125.9	128.2	2.3	127.9	-0.3	121.5	-6.4	120.8	-0.7
A(N^2,C^3,N^4)	116.1	114.6	-1.5	113.4	-1.2	118.8	5.4	123.9	5.1
A(C^3,N^4,C^5)	128.0	128.5	0.5	128.1	-0.4	127.6	-0.5	121.2	-6.4
A(,N^4,C^5 C^6)	114.4	114.0	-0.4	114.8	0.8	113.1	-1.7	118.3	5.2
A(C^5,C^6,C^1)	119.2	120.4	1.2	120.6	0.2	118.9	-1.7	116.9	-2
A(N^2,C^1,O^7)	119.5	120.9	1.4	116.6	-4.3	119.2	2.6	120.0	0.8
A(N^2,C^3,O^8)	124.0	122.8	-1.2	123.2	0.4	125.7	2.5	118.0	-7.7
A(N^4,C^5,O^9)	121.1	120.7	-0.4	116.4	-4.3	117.7	1.3	120.2	2.5
A(C^5,C^6,N^{10})	125.7	126.2	0.5	125.3	-0.9	125.2	-0.1	128.3	3.1
A(C^6,N^{10},O^{11})	117.9	116.5	-1.4	119.0	2.5	120.5	1.5	123.1	2.6

[a]See Ref. [23]. [b]Algebraic deviations between experimental and theoretical values. [c]Algebraic deviations between theoretical values of the anion and molecule [d]Algebraic deviations between theoretical values of the dianion and anion. [c]Algebraic deviations between theoretical values of the trianion and dianion. For atom numbering see Scheme 1.

CONCLUSION

We report in this work good theoretical descriptions of the IR and structural changes, caused by the conversion of violuric acid into anion and dianion. We found that B3LYP/6-311+G(2df,p) computation are able to predict well the IR changes, which accompany the violuric acid molecule into anion and dianion conversion. So, we can suppose that the combined experimental/DFT approach applied in this work can be used also in cases of other molecules, anions and dianions, which structures cannot be experimental measured.

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ТЕОРЕТИЧНО И ЕКСПЕРИМЕНТАЛНО ИЗСЛЕДВАНЕ НА ИЧ СПЕКТРИ И СТРУКТУРАТА НА ВИОЛУРОВАТА КИСЕЛИНА И НЕЙНИТЕ АНИОНИ

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(Резюме)

Изследвани са експерименталните и теоретичните ИЧ спектри и структурата на виолуровата киселина и нейните аниони. На базата на квантовохимични пресмятания на ниво B3LYP/6-311+G(2df,p) е установено, че трикето тавтомера е най-стабилен и при молекулата и при изследваните аниони. Превръщането на молекулата в моноанион води до силно честотно понижение и на трите валентни карбонилни трептения: пресметнати 153 cm^{-1}, измерени 138 cm^{-1} и други значителни промени във вибрационния спектър. Виолуратния дианион е получен в разтвор на ДМСО-d_6 в присъствие на димсил-натрий. Сумарното ν(C=O) понижение причинено от превръщането на молекулата в дианион е пресказано 485 cm^{-1} и измерено 483 cm^{-1}.