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Ab initio and DFT calculations of the structure and vibrational spectra of trigonelline

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Abstract

The geometries, frequencies and infrared intensities of the vibrational bands of trigonelline its monohydrate and dimer have been computed by the MP2 and B3LYP approaches using the cc-pVDZ and 6-31G(d,p) basis sets. The computed geometry of the pyridine ring is slightly affected by hydration and dimerization, and satisfactorily agrees with the X-ray data. In contrast, the geometry of the COO group changes significantly on hydration and dimerization. All the measured IR bands were assigned in terms of the calculated vibrational modes. Most computed bands are predicted to lie at higher wavenumbers than the experimental bands. R.M.S. deviation between the experimental and the calculated harmonic frequencies is 69 cm^{-1} for all of the bands, and 46 cm^{-1} for all bands except those corresponding to ν(OH), δ(OH) and ν(CH). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Trigonelline; Geometry; Vibrational spectra; MP2 and DFT calculations

1. Introduction

Trigonelline, *N*-methyl-3-carboxy-pyridine, is a natural betaine isolated from various plants, seeds and the western rock lobster [1–5]. Trigonelline crystallizes as monohydrate and its structure was determined by X-ray diffraction [5].

In this paper, the geometry and vibrational spectra of trigonelline monohydrate (TRGWI–TRGWIII), anhydrous trigonelline (TRG), and its dimer (TRGDIM) have been computed by the MP2 and B3LYP approaches using the cc-pVDZ and 6-31G(d,p) basis sets.

2. Experimental

2.1. Synthesis

Trigonelline hydroiodide. A solution of nicotinic acid (15 g) in methanol (70 cm^3) and methyl iodide (26 g) was heated at 70 °C in a sealed tube for 40 h. Yellow crystals were filtered off and washed with small amount of acetone. The filtrate was evaporated to dryness under reduced pressure and the solid residue was washed with acetone. Both fractions of the crystals were combined and recrystallized from methanol, total yield 63%, m.p. 235 °C (Ref. [1] 218 °C).

Trigonelline monohydrate. Trigonelline hydroiodide (10 g) was dissolved in water (20 cm^3) in a small canonical flask, propylene oxide (2.6 g) was added slowly; the flask was closed with a cork and left for 3

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Table 1
Local-symmetry coordinates of trigonelline and its monohydrate (atom numbering as in Fig. 1)

Symmetry coordinate[a]	Description
$S_{1} = r\mathrm{N_{1}{-}C_{2}}$	ν CN
$S_{2} = r\mathrm{N_{1}{-}C_{6}}$	ν CN
$S_{3} = r\mathrm{N_{1}{-}C_{11}}$	ν CN
$S_{4} = r\mathrm{C_{2}{-}C_{3}}$	ν CC
$S_{5} = r\mathrm{C_{3}{-}C_{4}}$	ν CC
$S_{6} = r\mathrm{C_{4}{-}C_{5}}$	ν CC
$S_{7} = r\mathrm{C_{5}{-}C_{6}}$	ν CC
$S_{8} = r\mathrm{C_{3}{-}C_{15}}$	ν CC
$S_{9} = r\mathrm{C_{15}{-}O_{16}} + r\mathrm{C_{15}{-}O_{17}}$	ν CO
$S_{10} = r\mathrm{C_{15}{-}O_{16}} - r\mathrm{C_{15}{-}O_{17}}$	ν CO
$S_{11} = r\mathrm{C_{2}{-}H_{7}}$	ν CH
$S_{12} = r\mathrm{C_{4}{-}H_{8}}$	ν CH
$S_{13} = r\mathrm{C_{5}{-}H_{9}}$	ν CH
$S_{14} = r\mathrm{C_{6}{-}H_{10}}$	ν CH
$S_{15} = r\mathrm{C_{11}{-}H_{12}} + r\mathrm{C_{11}{-}H_{13}} + r\mathrm{C_{11}{-}H_{14}}$	ν_{s} $\mathrm{CH_{3}}$
$S_{16} = 2r\mathrm{C_{11}{-}H_{12}} - r\mathrm{C_{11}{-}H_{13}} - r\mathrm{C_{11}{-}H_{14}}$	ν_{as} $\mathrm{CH_{3}}$
$S_{17} = r\mathrm{C_{11}{-}H_{13}} - r\mathrm{C_{11}{-}H_{16}}$	ν_{as} $\mathrm{CH_{3}}$
$S_{18} = \beta\mathrm{C_{6}{-}N_{1}{-}C_{2}} - \beta\mathrm{N_{1}{-}C_{2}{-}C_{3}} + \beta\mathrm{C_{2}{-}C_{3}{-}C_{4}} - \beta\mathrm{C_{3}{-}C_{4}{-}C_{5}} + \beta\mathrm{C_{4}{-}C_{5}{-}C_{6}} - \beta\mathrm{C_{5}{-}C_{6}{-}N_{1}}$	Ring 1
$S_{19} = 2\beta\mathrm{C_{6}{-}N_{1}{-}C_{2}} - \beta\mathrm{N_{1}{-}C_{2}{-}C_{3}} - \beta\mathrm{C_{2}{-}C_{3}{-}C_{4}} + 2\beta\mathrm{C_{3}{-}C_{4}{-}C_{5}} - \beta\mathrm{C_{4}{-}C_{5}{-}C_{6}} - \beta\mathrm{C_{5}{-}C_{6}{-}N_{1}}$	Ring 2
$S_{20} = \beta\mathrm{N_{1}{-}C_{2}{-}C_{3}} + \beta\mathrm{C_{2}{-}C_{3}{-}C_{4}} + \beta\mathrm{C_{4}{-}C_{5}{-}C_{6}} - \beta\mathrm{C_{5}{-}C_{6}{-}N_{1}}$	Ring 3
$S_{21} = \beta\mathrm{N_{1}{-}C_{11}{-}H_{12}} + \beta\mathrm{N_{1}{-}C_{11}{-}H_{13}} + \beta\mathrm{N_{1}{-}C_{11}{-}H_{14}} - \beta\mathrm{H_{12}{-}C_{11}{-}H_{13}} - \beta\mathrm{H_{13}{-}C_{11}{-}H_{14}}$ $-\beta\mathrm{H_{12}{-}C_{11}{-}H_{14}}$	δ_{s} $\mathrm{CH_{3}}$
$S_{22} = 2\beta\mathrm{H_{12}{-}C_{11}{-}H_{13}} - \beta\mathrm{H_{13}{-}C_{11}{-}H_{14}} - \beta\mathrm{H_{12}{-}C_{11}{-}H_{14}}$	δ_{as} $\mathrm{CH_{3}}$
$S_{23} = 2\beta\mathrm{N_{1}{-}C_{11}{-}H_{12}} - \beta\mathrm{N_{1}{-}C_{11}{-}H_{13}} - \beta\mathrm{N_{1}{-}C_{11}{-}H_{14}}$	$\mathrm{CH_{3}}$ wag
$S_{24} = \beta\mathrm{H_{13}{-}C_{11}{-}H_{14}} - \beta\mathrm{H_{12}{-}C_{11}{-}H_{14}}$	δ_{as} $\mathrm{CH_{3}}$
$S_{25} = \beta\mathrm{N_{1}{-}C_{11}{-}H_{13}} - \beta\mathrm{N_{1}{-}C_{11}{-}H_{14}}$	$\mathrm{CH_{3}}$ wag
$S_{26} = \tau\mathrm{C_{6}{-}N_{1}{-}C_{2}{-}C_{3}} - \tau\mathrm{N_{1}{-}C_{2}{-}C_{3}{-}C_{4}} + \tau\mathrm{C_{2}{-}C_{3}{-}C_{4}{-}C_{5}} - \tau\mathrm{C_{3}{-}C_{4}{-}C_{5}{-}C_{6}}$ $+\tau\mathrm{C_{4}{-}C_{5}{-}C_{6}N_{1}} - \tau\mathrm{C_{5}{-}C_{6}{-}N_{1}{-}C_{2}}$	τ ring 1
$S_{27} = \tau\mathrm{C_{6}{-}N_{1}{-}C_{2}{-}C_{3}} - \tau\mathrm{C_{2}{-}C_{3}{-}C_{4}{-}C_{5}} + \tau\mathrm{C_{3}{-}C_{4}{-}C_{5}{-}C_{6}} - \tau\mathrm{C_{5}{-}C_{6}{-}N_{1}{-}C_{2}}$	τ ring 2
$S_{28} = -\tau\mathrm{C_{6}{-}N_{1}{-}C_{2}{-}C_{3}} - \tau\mathrm{N_{1}{-}C_{2}{-}C_{3}{-}C_{4}} + 2\tau\mathrm{C_{2}{-}C_{3}{-}C_{4}{-}C_{5}} - \tau\mathrm{C_{3}{-}C_{4}{-}C_{5}{-}C_{6}}$ $-\tau\mathrm{C_{4}{-}C_{5}{-}C_{6}N_{1}} + 2\tau\mathrm{C_{5}{-}C_{6}{-}N_{1}{-}C_{2}}$	τ ring 3
$S_{29} = \beta\mathrm{C_{3}{-}C_{15}{-}O_{16}} + \beta\mathrm{C_{3}{-}C_{15}{-}O_{17}}$	δ_{s} $\mathrm{CO_{2}}$
$S_{30} = \beta\mathrm{C_{3}{-}C_{15}{-}O_{16}} - \beta\mathrm{C_{3}{-}C_{15}{-}O_{17}}$	δ_{as} $\mathrm{CO_{2}}$
$S_{31} = \tau\mathrm{C_{2}{-}N_{1}{-}C_{11}{-}H_{12}} + \tau\mathrm{C_{2}{-}N_{1}{-}C_{11}{-}H_{13}}$ $+\tau\mathrm{C_{2}{-}N_{1}{-}C_{11}{-}H_{14}} + \tau\mathrm{C_{6}{-}N_{1}{-}C_{11}{-}H_{12}} + \tau\mathrm{C_{6}{-}N_{1}{-}C_{11}{-}H_{13}} + \tau\mathrm{C_{6}{-}N_{1}{-}C_{11}{-}H_{14}}$	τ Me-ring
$S_{32} = \tau\mathrm{C_{2}{-}C_{3}{-}C_{15}{-}O_{16}} + \tau\mathrm{C_{2}{-}C_{3}{-}C_{15}{-}O_{17}}$	τ $\mathrm{CO_{2}}$
$S_{33} = \tau\mathrm{C_{2}{-}C_{3}{-}C_{15}{-}O_{16}} - \tau\mathrm{C_{2}{-}C_{3}{-}C_{15}{-}O_{17}}$	τ $\mathrm{CO_{2}}$
$S_{34} = \beta\mathrm{H_{7}{-}C_{2}{-}N_{1}}$	β CH
$S_{35} = \beta\mathrm{H_{8}{-}C_{4}{-}C_{3}}$	β CH
$S_{36} = \beta\mathrm{H_{9}{-}C_{5}{-}C_{4}}$	β CH
$S_{37} = \beta\mathrm{H_{10}{-}C_{6}{-}C_{5}}$	β CH
$S_{38} = \beta\mathrm{C_{11}{-}N_{1}{-}C_{2}}$	β CN
$S_{39} = \beta\mathrm{C_{15}{-}C_{3}{-}C_{2}}$	β CC
$S_{40} = \gamma\mathrm{H_{7}{-}C_{2}{-}N_{1}{-}C_{3}}$	γ CH
$S_{41} = \gamma\mathrm{H_{8}{-}C_{4}{-}C_{3}{-}C_{5}}$	γ CH
$S_{42} = \gamma\mathrm{H_{9}{-}C_{5}{-}C_{4}{-}C_{6}}$	γ CH
$S_{43} = \gamma\mathrm{H_{10}{-}C_{6}{-}N_{1}{-}C_{5}}$	γ CH
$S_{44} = \gamma\mathrm{C_{11}{-}N_{1}{-}C_{2}{-}C_{6}}$	γ CN
$S_{45} = \tau\mathrm{C_{11}{-}N_{1}{-}C_{2}{-}C_{3}}$	τ CC

(*continued on next page*)

Table 1 (*continued*)

Symmetry coordinate[a]	Description
Monohydrate	
$S_{46} = r\mathrm{O}_{16.}-\mathrm{H}_{18}$	ν OH
$S_{47} = r\mathrm{O}_{16}\cdots\mathrm{O}_{19}$	ν(OHO)
$S_{48} = \beta\mathrm{C}_{15}-\mathrm{O}_{16}-\mathrm{H}_{18}$	β OH
$S_{49} = \beta\mathrm{O}_{16}-\mathrm{H}_{18}-\mathrm{O}_{19}$	β OH
$S_{50} = \gamma\mathrm{H}_{18}-\mathrm{O}_{16}-\mathrm{C}_{15}-\mathrm{O}_{17}$	γ(OHO)
$S_{51} = \gamma\mathrm{O}_{19}-\mathrm{H}_{18}-\mathrm{O}_{16}-\mathrm{C}_{15}$	δ(OHO)
$S_{52} = r\mathrm{O}_{19}-\mathrm{H}_{20}$	ν(OH)
$S_{53} = \beta\mathrm{H}_{18}-\mathrm{O}_{19}-\mathrm{H}_{20}$	γ OH
$S_{54} = \gamma\mathrm{O}_{16}-\mathrm{H}_{18}-\mathrm{O}_{19}-\mathrm{H}_{20}$	γ OH

[a] Definitions are made in terms of standard valence coordinates: r_{ij} is the bond length between atoms i and j; β_{ijk} is the valence angle between atoms i, j and k, with j the central atom; γ_{ijkl} is the out-of-plane angle between the i–j bond and the plane defined by the j, k, and l atoms; τ_{ijkl} is the torsional (dihedral) angle between the planes defined by the i,j,k and j,k,l atoms.

days. To remove iodopropanols, the reaction solution was extracted six times with equal volumes of diethyl ether, then evaporated under reduced pressure to dryness and the residue was recrystallized from methanol and white crystals were filtered off, m.p. 218 °C (Ref. [5] 215–217 °C (dec.), Ref. [6] 230–233 °C); δ_{H} 8.88 (s, C_2H), 8.61 (1H, m, C_6H), 8.58 (1H, m, C_4H), 7.83 (1H, dd, C_5H, J 6.2, 7.9), 4.20 (3H, s, N–CH_3); δ_{C} 168.5 (COO), 146.8 (C_6), 146.7 (C_2), 145.6 (C_4), 137.8 (C_3), 128.5 (C_5), 49.1 (CH_3).

Anhydrous trigonelline was obtained by dehydration of monohydrate in vacuum at 110 °C over P_2O_5 for 5 h. The anhydrous trigonelline is very hygroscopic and converts into the monohydrate when it is left in open vessel overnight.

2.2. Spectra

FT-IR spectra were recorded on a Bruker IFS 113v spectrometer at a 2 cm^{-1} resolution in Nujol and Fluorolube mulls. Raman spectra were recorded on a Magna 760 Nicolet operating at the 1064 nm exciting line of an Nd:YAG laser.

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 VT spectrometer operating at 300.07 and 75.46 MHz for proton and carbon-13, respectively. The ^{1}H and ^{13}C chemical shifts were measured in D_2O solution relative to internal dioxane and were recalculated relative to TMS by adding 3.55 and 67.40 ppm, respectively. Chemical shifts were confirmed by COSY, HETCOR and NEODIF experiments.

2.3. Calculations

The calculations have been performed using the GAUSSIAN 98 package [7] at the MP2 [8] and B3LYP [9,10] levels of theory with the basis sets of double-zeta quality cc-pVDZ [11] and 6-31G(d,p) [12]. The vibrational IR spectra (the harmonic wavenumbers and absolute intensities) were calculated only for the most stable structures.

The harmonic force fields, determined initially in the cartesian coordinates, were transformed to the force fields in the internal local-symmetry coordinates. The local-symmetry coordinates, defined in terms of the internal valence coordinates following the IUPAC recommendation [13,14] are given in Table 1. In this way, the redundant internal coordinates were removed. The force fields determined in this way were used to calculate the harmonic wavenumbers and vibrational potential energy distribution (PED) among the normal coordinates. PED is defined as recommended by Keresztury and Jalsovszky [15] and calculated with the program PACK [16,17].

3. Results and discussion

3.1. Molecular parameters

The labelling of atoms in TRG·H_2O is given in Fig. 1. Some of the possible structures of trigonelline monohydrate (TRGWXR, TRGWI–TRGWIII) are

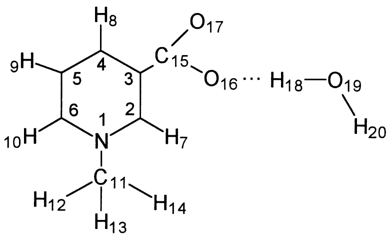

Fig. 1. Atom numbering for trigonelline monohydrate.

shown in Fig. 2. The calculated structural parameters, total energies and dipole moments are collected in Table 2, together with the X-ray results [5]. The computed geometry of pyridine ring is only slightly affected by attaching the water molecule and by dimerization, and it satisfactorily agrees with the X-ray data. In contrast, the calculated geometry of the COO group changes significantly on hydration and dimerization.

In crystal, the hydrogen atoms of water molecule bridge to successive O(17) atoms of trigonellines (TRGWXR, Fig. 2) separated by the z translation; O(17)···H(A)OH $(1-x, 2-y, 1-z)$ being 2.06(5) and O(17)···H(B)OH $(1-x, 2-y, 2-z)$ being 1.99(4) Å [5]. In the calculated structures (TRGWI–TRGWIII) the water molecule forms one or two hydrogen bonds with one trigonelline molecule. In the gas phase, the most stable is TRGWI. The water molecule forms hydrogen bond to the O(16) atom and the oxygen atom of the water molecule interacts electrostatically with the positively charged nitrogen atom; the $N^{+}(1)\cdots O(19)$ distance being 3.940 Å and is remarkably shorter than in TRGWII and TRGWIII.

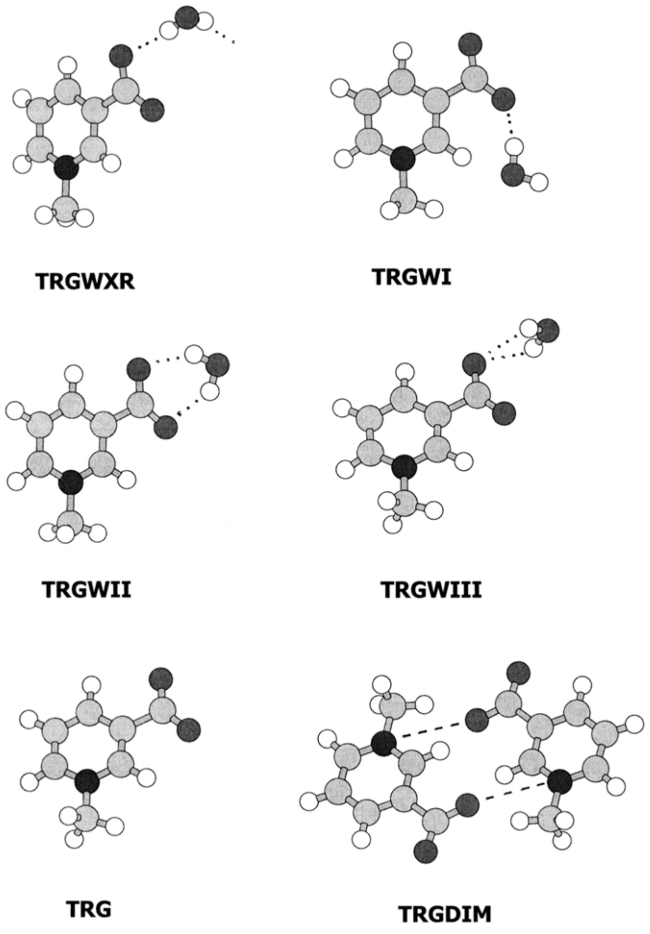

Fig. 2. Structures of trigonelline monohydrate, anhydrous trigonelline and its dimer.

Table 2
Energies, dipole moments and structural parameters for trigonelline monohydrates, anhydrous and dimer

	X-ray (TRGWXR)	MP2/cc-pVDZ			B3LYP/6-31G** (TRG)	MP2/cc-pVDZ (TRG)	B3LYP/6-31G** (TRGDIM)	MP2/ccpVDZ (TRGDIM)
		TRGWI	TRGWII	TRGWIII				
E (a.u.)		−551.019626	−551.015366	−551.007625	−476.129125	−474.764158	−952.319755	−949.595399
$E_{\mathrm{rel.}}$ (kcal/mol)		0	2.7	7.5				
ΔE (kcal/mol)		-16.8^{a}	-14.1^{a}	-9.3^{a}			-38.6^{b}	-42.1^{b}
μ (Debye)		11.9	17.5	16.9	13.8	15.0	0.3	0.002
N(1)–C(2)	1.343(5)	1.357	1.356	1.356	1.354	1.357	1.355	1.358
N(1)–C(6)	1.354(5)	1.361	1.362	1.362	1.361	1.363	1.358	1.360
N(1)–C(11)	1.480(5)	1.477	1.477	1.476	1.476	1.476	1.486	1.485
C(2)–C(3)	1.380(4)	1.401	1.398	1.398	1.386	1.398	1.393	1.402
C(3)–C(4)	1.380(5)	1.403	1.402	1.402	1.393	1.403	1.393	1.402
C(4)–C(5)	1.383(6)	1.404	1.404	1.405	1.401	1.405	1.399	1.403
C(5)–C(6)	1.366(5)	1.395	1.396	1.396	1.381	1.396	1.380	1.395
C(3)–C(15)	1.528(5)	1.571	1.562	1.569	1.565	1.578	1.549	1.556
C(15)–O(16)	1.253(4)	1.259	1.255	1.247	1.250	1.251	1.264	1.268
C(15)–O(17)	1.235(4)	1.242	1.250	1.253	1.243	1.246	1.239	1.241
C(2)–N(1)–C(6)	120.4(3)	121.8	121.3	121.2	120.6	121.2	121.1	121.7
C(2)–N(1)–C(11)	120.5(3)	118.9	120.0	120.1	120.4	120.1	119.7	119.1
C(6)–N(1)–C(11)	119.1(3)	119.2	118.7	118.7	119.0	118.7	119.1	119.2
N(1)–C(2)–C(3)	121.7(3)	120.8	121.1	121.2	121.4	121.2	120.6	120.3
N(1)–C(6)–C(5)	120.3(4)	119.6	119.9	119.9	120.3	119.9	120.6	120.1
C(2)–C(3)–C(4)	117.9(3)	118.3	118.6	118.5	118.4	118.4	118.7	118.9
C(2)–C(3)–C(15)	119.2(3)	120.7	118.5	118.3	118.6	118.5	120.9	120.4
C(4)–C(3)–C(15)	123.0(3)	120.1	122.8	123.2	123.0	123.0	120.4	120.7
C(3)–C(4)–C(5)	120.3(3)	119.9	119.5	119.5	119.8	119.6	120.0	119.6
C(4)–C(5)–C(6)	119.6(4)	119.6	119.7	119.7	119.4	119.6	119.1	119.4
C(3)–C(15)–O(16)	116.8(3)	114.1	112.8	113.1	112.6	112.3	114.1	113.3
C(3)–C(15)–O(17)	115.6(3)	113.2	113.3	112.6	113.3	112.7	115.1	115.0
O(16)–C(15)–O(17)	127.6	132.7	133.9	134.3	134.2	135.0	130.8	131.7
C(11)–N(1)–C(2)–C(3)	−179.6	180.0	180.0	180.0	179.9	180.0	179.9	−179.5
C(2)–C(3)–C(15)–O(16)	−166.6	0	0.0	0.0	−0.0	0	1.1	−0.5
C(2)–C(3)–C(15)–O(17)	13.3	180.0	180.0	180.0	180.0	180.0	−178.9	179.4
N(1)···O(16)	4.722	4.159	4.074	4.077	4.063	4.078	4.136^{c}, 3.443^{d}	4.126^{c}, 3.417^{d}
N(1)···O(17)	4.114	4.753	4.751	4.751	4.740	4.756	4.745^{c}, 5.503^{d}	4.759^{c}, 5.464^{d}
N(1)···O(19)	7.260	3.940	6.896	7.344				
O(16)···H(18)		1.740	2.084	–				

(*continued on next page*)

Table 2 (*continued*)

	X-ray (TRGWXR)	MP2/cc-pVDZ			B3LYP/6-31G** (TRG)	MP2/cc-pVDZ (TRG)	B3LYP/6-31G** (TRGDIM)	MP2/ccpVDZ (TRGDIM)
		TRGWI	TRGWII	TRGWIII				
O(17)· · ·H(20)			2.137	2.363				
O(16)· · ·O(19)		2.705	2.930	–				
O(17)· · ·O(19)			2.958	2.894				
O(16)·H(18)–O(19)		164.4	144.6	–				
O(17)·H(20)–O(19)			141.6	114.0				
C(15)–O(16)–H(18)–O(19)		0.0	0.0	–				
C(15)–O(17)–H(20)–O(19)			−0.0	96.5				
O(16)–H(18)–O(19)–H(20)		−180.0	0.0	–				
O(17)–H(18)–O(19)–H(20)			0.0	0.0				

[a] Interaction energy between trigonelline and water, calculated with $E(H_2O) = -76.228666$ a.u.

[b] Energy of dimerization.

[c] Intramolecular.

[d] Intermolecular.

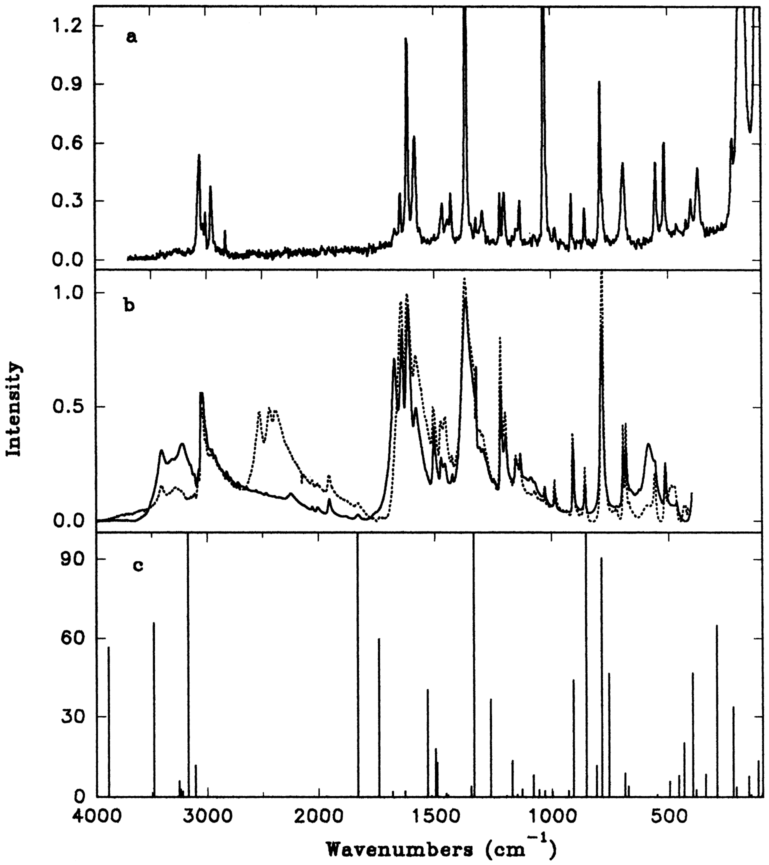

Fig. 3. Comparison of the experimental and calculated spectra of TRG·H_2O: (a) the Raman spectrum in the solid state; (b) IR spectrum in Nujol and Fluorolube emulsion; TRG·D_2O dotted line; (c) the IR spectrum predicted at the MP2/cc-pVDZ level of theory.

Structure TRGWII has the water molecule bonded to both oxygen atoms (O(16) and O(17)) and its energy is larger by 2.7 kcal/mol. In TRGWIII, the water molecule is engaged in bifurcated hydrogen bond to the O(17) atom; both O(17)···H(OH) distances are 2.363 Å. The dimer (TRGDIM, Fig. 2) is stabilized by an electrostatic interaction between the oppositely charged nitrogen and oxygen atoms. The dimerization energy are −38.6 (B3LYP) and −42.1 kcal/mol (MP2) (Table 2).

3.2. The experimental spectra

TRG·H_2O is soluble in water and alcohols and insoluble in aprotic organic solvents and its vapour pressure is very low. Therefore, the IR and Raman spectra were measured in the solid state and are shown in Fig. 3. The broad absorption with maxima at 3414 and 3233 cm^{-1} in the IR spectrum (Fig. 3b) arise from the stretching vibration of the crystalline water. On deuteration the bands are shifted to 2526 and 2434 cm^{-1}, respectively. In the Raman spectra, intensity of the O–H stretching frequency is weak and in TRG·H_2O this absorption band is absent (Fig. 3a). In the crystal, two TRG molecules are bridged by a water molecule forming two (A, B) hydrogen bonds with the COO groups (see earlier). This explains the observed absorption shape in the 3400–3150 cm^{-1} region (Fig. 2b). Another interesting feature is the lack of a typical strong band near 1600 cm^{-1}, which is normally attributed to the antisymmetric COO stretching mode and its frequency increases very markedly with the electron-withdrawing effect of substituent [18]. Four bands in this region are due to

Table 3
Observed and calculated (MP2/cc-pVDZ) vibrational frequencies, infrared intensities and potential energy distribution (PED) for trigonelline monohydrate and anhydrous

$TRG{\cdot}H_2O$				$TRG{\cdot}D_2O$			TRG		
Raman (ν_{obs})	FTIR			FTIR			FTIR		
	ν_{obs}	ν_{cal}	PED[a]	ν_{obs}	ν_{cal}	PED[a]	ν_{obs}	ν_{cal}	PED[a]
	3414	3891 (56.4)	S_{52} 99	2526	2832	S_{52} 98			
	3233	3483 (65.7)	S_{47} 99	2434	2527	S_{47} 99			
		3268 (0.1)	S_{14} 71 S_{13} 26		3268	S_{14} 71 S_{13} 26		3268 (0.9)	S_{14} 73 S_{13} 21
		3255 (6.0)	S_{12} 50 S_{13} 30 S_{14} 20		3255	S_{12} 50 S_{13} 30 S_{14} 20		3253 (6.1)	S_{12} 44 S_{13} 37 S_{14} 17
		3244 (2.8)	S_{12} 46 S_{13} 41		3244	S_{12} 46 S_{13} 41		3242 (2.5)	S_{12} 53 S_{13} 40
3071	3057	3242 (2.8)	S_{16} 90		3242	S_{16} 90	3054	3248 (1.3)	S_{16} 93
3028		3226 (2.0)	S_{17} 96		3226	S_{17} 96		2327 (1.3)	S_{17} 100
3003	3040	3175 (188)	S_{11} 97		3179	S_{11} 97	3021	3262 (16.1)	S_{11} 92
2959		3111 (11.8)	S_{15} 99		3111	S_{15} 99	2995	3116 (11.0)	S_{15} 99
1645	1640	1831 (397)	S_{10} 96	1642	1830	S_{10} 96	1650	1851 (299)	S_{10} 97
1668	1673	1741 (59.7)	S_{53} 84	1294?	1268	S_{53} 76			
1615	1614	1683 (2.0)	S_4 23 S_7 20 S_{19} 11 S_{34} 10	1616	1683	S_4 23 S_7 20 S_{19} 11 S_{34} 10	1621	1680 (3.7)	S_4 25 S_7 19 S_5 14 S_{19} 11
1583	1580	1630 (2.1)	S_6 29 S_5 28 S_1 11	1581	1630	S_6 29 S_5 28 S_1 11	1584	1625 (1.3)	S_6 30 S_5 26 S_1 12
	1506	1533 (40.2)	S_{34} 29 S_7 19 S_{36} 12	1506	1533	S_{34} 29 S_7 19 S_{36} 12		1526 (8.0)	S_7 23 S_4 22 S_2 14 S_1 14
		1517 (0.4)	S_{24} 23 S_2 15 S_4 12 S_{23} 10 S_7 10 S_1 10		1517	S_{24} 23 S_2 15 S_4 12 S_{23} 10 S_7 10 S_1 10		1507 (44.3)	S_{24} 34 S_{22} 11 S_{23} 10
	1473	1498 (17.8)	S_{24} 29 S_{22} 15 S_{37} 14		1498	S_{24} 29 S_{22} 15 S_{37} 14	1487	1495 (3.53)	S_{37} 22 S_{36} 17 S_6 11 S_{21} 10
1461	1457	1492 (12.8)	S_{22} 66	1458	1492	S_{22} 66		1488 (12.7)	S_{22} 67 S_{24} 23 S_{25} 10
1429	1425	1453 (1.3)	S_{24} 35 S_1 22 S_2 12		1453	S_{24} 35 S_1 22 S_2 13		1449 (5.6)	S_{24} 24 S_2 17 S_1 15
		1446 (0.7)	S_{21} 86		1446	S_{21} 87		1443 (0.7)	S_{21} 90
1319	1321	1347 (4.0)	S_{34} 41 S_{35} 21 S_{36} 16	1322	1347	S_{34} 41 S_{35} 21 S_{36} 16	1309	1289 (23.3)	S_{37} 21 S_{34} 18 S_{35} 16

(*continued on next page*)

Table 3 (*continued*)

TRG·H_2O				TRG·D_2O			TRG		
Raman (ν_{obs})	FTIR			FTIR			FTIR		
	ν_{obs}	ν_{cal}	PED[a]	ν_{obs}	ν_{cal}	PED[a]	ν_{obs}	ν_{cal}	PED[a]
									S_3 12 S_{36} 10
1364	1367	1334 (238)	S_9 85 S_{29} 10	1370	1334	S_9 84 S_{29} 10	1377 1361	1308 (203)	S_9 84
1219	1217	1262 (36.6)	S_3 36 S_{37} 20 S_{18} 13 S_2 12 S_1 10	1217	1261	S_3 34 S_{37} 17 S_{18} 13 S_2 10	1218	1239 (24.3)	S_3 26 S_{18} 19 S_{34} 17
1201	1196	1194 (0.4)	S_{37} 21 S_7 15 S_{35} 13	1197	1194	S_{37} 22 S_7 15 S_{35} 12 S_{36} 10		1189 (1.0)	S_{36} 27 S_{37} 26 S_7 20
	1153	1170 (13.5)	S_{36} 28 S_{23} 16 S_5 10	1153	1168	S_{36} 26 S_{23} 16 S_5 10	1176	1145 (0.1)	S_{25} 86
		1150 (0.9)	S_{25} 81		1150	S_{25} 81		1125 (17.2)	S_{23} 45 S_{35} 18 S_{34} 12
1134	1134	1128 (2.8)	S_{23} 34 S_{35} 15 S_{36} 14 S_6 14	1134	1128	S_{23} 34 S_{35} 15 S_{36} 15 S_6 14	1114	1115 (28.4)	S_{34} 28 S_{36} 18 S_6 15 S_8 10
	1089	1080 (8.0)	S_{35} 29 S_{23} 21 S_6 12	1073	1080	S_{35} 29 S_{23} 21 S_6 12	1080	1073 (12.1)	S_{35} 27 S_{23} 25
1030	1030	1055 (2.7)	S_{40} 88 S_{41} 13	1032	1053	S_{40} 87 S_{41} 14	1028	1008 (0.0)	S_{41} 75 S_{42} 35
		1032 (2.3)	S_{18} 45		1031	S_{18} 45		1033 (2.7)	S_{18} 48 S_6 11 S_7 10
981	987	999 (2.0)	S_{41} 59 S_{42} 43 S_{40} 12	987	998	S_{41} 58 S_{42} 43 S_{40} 14		941 (0.9)	S_{42} 43 S_{40} 40 S_{43} 24
913	909	929 (2.2)	S_{42} 39 S_{43} 39 S_{41} 24	909	927	S_{42} 39 S_{43} 39 S_{41} 24	906	910 (9.5)	S_{40} 58 S_{41}17 S_{43} 14
857	857	909 (44.0)	S_3 29 S_8 20 S_{19} 15	857	909	S_3 29 S_8 20 S_{19} 15	843	898 (28.0)	S_3 29 S_8 18 S_{19} 17 S_{18} 10
	585	854 (319)	S_{49} 65 S_{54} 15	487	620	S_{49} 67 S_{54} 15			
		810 (11.6)	S_{43} 54 S_{33} 22 S_{42} 11		810	S_{43} 54 S_{33} 23 S_{42} 10		805 (14.2)	S_{43} 59 S_{33} 21 S_{42} 10
789	784	787 (90.4)	S_{29} 59	782	787	S_{29} 60	781 768	777 (95.6)	S_{29} 66 S_{20} 10

(*continued on next page*)

Table 3 (*continued*)

TRG·H_2O				TRG·D_2O			TRG		
Raman (ν_{obs})	FTIR			FTIR			FTIR		
	ν_{obs}	ν_{cal}	PED[a]	ν_{obs}	ν_{cal}	PED[a]	ν_{obs}	ν_{cal}	PED[a]
691	694	756 (46.5)	S_{33} 49 S_{43} 13 S_{42} 13	693	756	S_{33} 49 S_{43} 14 S_{42} 13		751 (37.1)	S_{33} 52 S_{43} 12 S_{42} 12 S_{41} 10
	681	689 (8.8)	S_{20} 66 S_{29} 15	680	691	S_{20} 65 S_{29} 14	688 678	686 (7.5)	S_{20} 68 S_{29} 16
553	557	675 (4.0)	S_{26} 104	558	675	S_{26} 103	553	670 (1.9)	S_{26} 107
		552 (0.9)	S_{19} 45 S_{30} 21		552	S_{19} 46 S_{30} 21		548 (0.2)	S_{19} 48 S_{30} 20 S_3 10
516	514	498 (5.8)	S_{30} 31 S_{19} 21 S_{39} 14	515	496	S_{30} 32 S_{19} 20 S_{39} 14	510	494 (5.4)	S_{30} 40 S_{19} 17 S_{39} 14
	466	459 (7.9)	S_{27} 38 S_{44} 36 S_{26} 12		459	S_{44} 36 S_{27} 35 S_{26} 11 S_{28} 11		456 (4.24)	S_{27} 36 S_{44} 36 S_{28} 13 S_{26} 11
		436 (20.1)	S_{28} 55 S_{51} 50 S_{32} 14 S_{49} 10	428	303	S_{51} 116 S_{49} 26 S_{53} 10			
399		400 (46.6)	S_{51} 74 S_{28} 28 S_{49} 14 S_{27} 10		425	S_{28} 79 S_{27} 16 S_{32} 13		414 (0.0)	S_{28} 85 S_{27} 19
372		385 (2.7)	S_{38} 47 S_{30} 25		385	S_{38} 47 S_{30} 25 S_8 10		381 (0.7)	S_{38} 54 S_{30} 17
		344 (8.4)	S_8 42 S_{38} 13 S_{19} 10		344	S_8 41 S_{38} 14 S_{19} 10		330 (6.0)	S_8 48 S_{38} 11 S_{19} 11 S_{18} 10
		296 (64.7)	S_{54} 121 S_{50} 20		211	S_{54} 84 S_{50} 19 S_{46} 18 S_{27} 12			
224		227 (33.6)	S_{46} 71 S_{39} 14		226	S_{54} 39 S_{46} 31			
172		213 (3.7)	S_{27} 44 S_{44} 40		212	S_{27} 35 S_{44} 32 S_{46} 11		213 (2.1)	S_{44} 42 S_{27} 39 S_{28} 10
		160 (7.6)	S_{48} 64 S_{45} 37 S_{51} 10		157	S_{48} 66 S_{45} 35 S_{51} 13			
		150 (0.7)	S_{39} 28 S_{45} 27 S_{46} 19 S_{48} 16		148	S_{45} 28 S_{39} 24 S_{46} 21 S_{48} 15		143 (2.3)	S_{45} 90
114		119 (13.4)	S_{39} 28		117	S_{39} 29		171 (4.2)	S_{39} 70

(*continued on next page*)

Table 3 (*continued*)

TRG·H_2O				TRG·D_2O			TRG		
Raman (ν_{obs})	FTIR			FTIR			FTIR		
	ν_{obs}	ν_{cal}	PED[a]	ν_{obs}	ν_{cal}	PED[a]	ν_{obs}	ν_{cal}	PED[a]
			S_{45} 17			S_{45} 15			S_{30} 14
			S_{30} 11			S_{51} 13			
			S_{51} 11			S_{30} 12			
		101 (1.4)	S_{31} 83		101	S_{31} 83		17 (0.0)	S_{31} 92
			S_{32} 10			S_{32} 10			
		66 (0.3)	S_{32} 61		66	S_{32} 62		72 (0.0)	S_{32} 90
			S_{50} 34			S_{50} 33			S_{27} 17
			S_{27} 10			S_{27} 10			
		43 (2.5)	S_{50} 63		43	S_{50} 61			
			S_{32} 22			S_{32} 21			
			S_{48} 11			S_{48} 10			
R.M.S.		46[b], 69[c]					61[b], 85[c]		

[a] Only contributions greater than 10 are listed.

[b] R.M.S. error for bands (without νOH, δOH, γOH and νCH modes).

[c] R.M.S. error for all bands.

strongly coupled in-plane bending vibrations of the water molecule, COO stretching, and ring stretching frequencies. The band at 1673 cm^{-1} is absent in the spectrum of anhydrous trigonelline and it is shifted to 1455 cm^{-1} when H_2O is replaced by D_2O (Fig. 2b). Thus, this band corresponds to the bending mode of the water molecule. The bands at 1640 and 1367 cm^{-1} are due to the antisymmetric and symmetric COO stretching vibrations, respectively.

3.3. The computed IR spectra and interpretation of the experimental spectrum

For the most stable structure of trigonelline monohydrate, TRGWI, the intramolecular $N(1)^{+}\cdots O(19)$ distance is predicted to be 3.940 Å, which is significantly shorter than that found in the crystal (7.260 Å) [5]. In the crystal, the unit cell contents a pair of TRG molecules together with two water molecules. Thus in the crystal, the charged nitrogen atom interacts electrostatically with the oxygen atoms from the neighbouring COO^{-} groups and the water molecules.

Table 3 lists the calculated harmonic frequencies, intensities, and PEDs for normal modes. A comparison of the calculated and experimental frequencies shows substantial differences, especially for the frequencies assigned to water vibrations. Two factors may be responsible for the discrepancy between the experimental and computed spectra of TRGWI. The first is that the experimental spectrum is for the complex in the crystal, whereas the computed one refers to the isolated complex in the gas phase. For the real crystal structure, both hydrogen atoms of the water molecule are engaged in hydrogen bonds, while only one hydrogen atom in the computed structure. Therefore, the calculated frequencies of the νOH and δOH vibrations are overestimated. The second reason for this discrepancy is the fact that the experimental values are anharmonic frequencies while the calculated values are harmonic frequencies. For the skeletal modes, the difference between the experimental and calculated frequencies are much smaller than those for H_2O. R.M.S. deviation between the experimental and calculated harmonic frequencies are 69 cm^{-1} for all bands and 46 cm^{-1} for all bands except the ν(OH), δ(OH) and ν(CH) ones. The MP2 method reproduces correctly the isotope frequency ratio, νH/νD.

4. Conclusions

The structural parameters, harmonic frequencies and IR intensities of the vibrational bands were calculated at the MP2 and B3LYP levels of theory using cc-pVDZ and 6-31G(d,p) basis sets. The predicted frequencies were compared with the experimental data in the solid state. The computed geometry of the pyridine ring is slightly affected by hydration and dimerization, and satisfactorily agrees with the X-ray data. As expected, the geometry of the COO group changes significantly on hydration and dimerization. A satisfactory reproduction of the experimental frequencies, except that of the modes for the water unit, is obtained. The differences for the νOH and νCH stretches are consistent with the expected anharmonicity of 170–200 cm^{-1} for these modes.

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