

Structure Conformation, Vibrational Properties, NLO Activity, HOMO-LUMO and Thermodynamic Parameters of Dinicotinic Acid Using Experimental and Theoretical Approach

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Received: 30.03.2021; Revised: 15.05.2021; Accepted: 20.05.2021; Published: 8.08.2021

Abstract: In the present study, the Dinicotinic acid was characterized by FTIR and FT-Raman spectra in the range of 4000-450 and 4000-50 cm^{-1} . The most stable molecular structure and optimized geometrical parameters are calculated using DFT studies. Normal Co-ordinate Analysis (NCA) was studied out by solving Inverse Vibrational Problem using 74-valence force field calculations using overlay least square technique. It reproduces into 35 fundamental frequencies with an rms error of 9.28 cm^{-1} in the zero-order calculations. Based on PED, vibrational modes are assigned for this molecule. The energy of HOMO & LUMO, NLO parameters, and thermodynamic parameters were computed.

Keywords: 35PDICA; FT-IR; FT-Raman; DFT; NLO properties; HOMO-LUMO.

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1.Introduction

Pyridine carboxylic acids are the most important compounds for human beings and are implicated in several biochemical processes. We investigated the structural conformation and molecular vibrational properties of Dinicotinic acid using their experimental IR and Raman spectra; and applied to NCA using DFT of Dinicotinic acid and solving IVP. In our previous paper [1], we have reported the experimental and computational study of some pyridine dicarboxylic acid.

As the same procedure, now we investigated the structure and vibrational properties of dinicotinic (3,5-pyridine di-carboxylic) acid. Dinicotinic acid has more significance in coordination chemistry [2, 3]. In medicines, PDA is found in HIV agents [3-5]. Pyridine-dicarboxylic acids have huge applications in the chemical and pharmaceutical fields. Kose *et al.* [6] reported the FT-IR, FT-Raman, and NMR studies of neutral and anion forms for 3,5-pyridine dicarboxylic acid.

The current study intends to have theoretical computations of FT-IR, FT-Raman, and vibrational characteristics using DFT (Density Functional Theory) and NCA (Normal Coordinate Analysis) approach. It is also designed to have the theoretical calculation of

optimized geometrical parameters, HOMO-LUMO, NLO, and thermodynamic parameters for a chosen molecule using density functional theory (DFT).

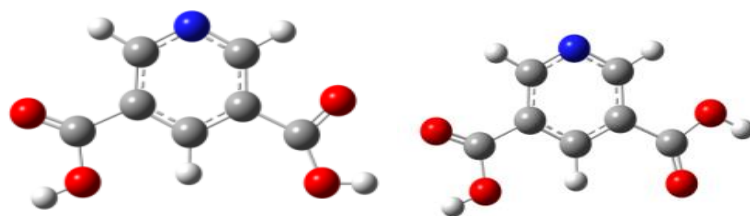
2. Material and Methods

The title molecule was purchased from Sigma Aldrich Chemical Company without further purification for the spectral measurement. The FTIR spectrum of dinicotinic acid has been recorded in the region 4000-450 cm^{-1} by Perkin Elmer FT-IR spectrum instrument, and FT-Raman spectra of the chosen molecule have been recorded from the range 4000-50 cm^{-1} .

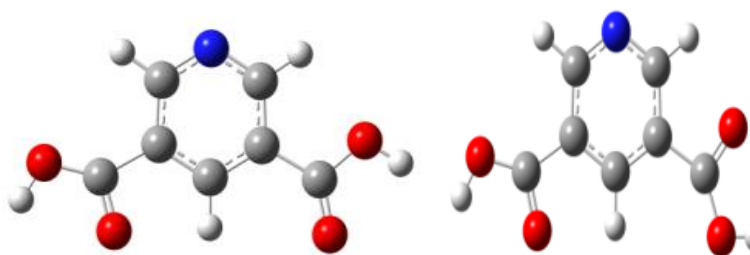
2.1. Computational procedure.

2.1.1. Geometry optimization.

The first task is to calculate the most stable conformer for the Pyridine-3,5-dicarboxylic acid (35PDICA). For this, all calculations were done with the Gaussian-09 software package [7]. All the vibrations of 35PDICA were calculated by using B3LYP [8, 9] methods. This molecule gives 8 (eight) conformers for 35PDICA, as depicted in Figure-1. Among all the conformers, Figure-1(d) has minimum global energy for the title molecule. The optimized structure along with energy $E = -625.6009$ Hartree is depicted in Figure-1. The optimized structural parameters of the title molecule are presented in Table 1. In the present study, the bond length between the pyridine ring and the two acid groups is 1.487 and 1.404 Å. The average bond distance of C-N (N1-C2 and C6-N1) is computed as 1.334 Å for the title compound.



(a) C₁ Conformer ($E_1 = -625.5368$ Hartree) (b) C₂ Conformer ($E_2 = -625.5692$ Hartree)



(c) C₃ Conformer ($E_3 = -625.5692$ Hartree) (d) C₄ Conformer ($E_4 = -625.6004$ Hartree)

Figure 1. Optimized structure along with energy ($E = -625.6074$ Hartree) of 35PDICA.

Table 1. Bond length, bond angle, and torsional angles of 35PDICA.

Bond length	Value (Å)	Bond angle	Value(in degree)	Torsional angle	Value(in degree)
N ₁ -C ₂	1.334	N ₁ -C ₂ -C ₃	123.03	N ₁ -C ₂ -C ₃ -C ₄	0.0
C ₂ -C ₃	1.404	C ₂ -C ₃ -C ₄	117.68	C ₂ -C ₃ -C ₄ -C ₅	0.0
C ₃ -C ₄	1.397	C ₂ -C ₃ -C ₄	119.46	C ₂ -C ₃ -C ₄ -C ₆	0.0
C ₄ -C ₅	1.386	C ₄ -C ₅ -C ₆	118.19	C ₆ -N ₁ -C ₂ -C ₇	173.87

Bond length	Value (Å)	Bond angle	Value(in degree)	Torsional angle	Value(in degree)
C ₃ -C ₆	1.392	N ₁ -C ₂ -C ₇	113.31	N ₁ -C ₂ -C ₃ -C ₈	-180.0
C ₆ -N ₁	1.334	C ₂ -C ₃ -C ₈	125.01	C ₂ -C ₃ -C ₄ -H ₉	180.0
C ₂ -C ₇	1.513	C ₃ -C ₄ -H ₉	118.74	C ₃ -C ₄ -C ₅ -H ₁₀	180.0
C ₃ -C ₈	1.491	C ₄ -C ₅ -H ₁₀	121.21	C ₄ -C ₅ -C ₆ -H ₁₁	180.0
C ₄ -H ₉	1.083	C ₅ -C ₆ -H ₁₁	120.78	N ₁ -C ₂ -C ₇ -O ₁₂	-104.56
C ₅ -H ₁₀	1.082	C ₂ -C ₇ -O ₁₂	123.45	N ₁ -C ₂ -C ₇ -O ₁₃	72.25
C ₆ -H ₁₁	1.085	C ₂ -C ₇ -O ₁₃	112.10	C ₂ -C ₇ -O ₁₃ -H ₁₄	-176.43
C ₇ -O ₁₂	1.202	C ₇ -O ₁₃ -H ₁₄	107.36	C ₂ -C ₃ -C ₈ -O ₁₅	-162.57
C ₇ -O ₁₃	1.343	C ₃ -C ₈ -O ₁₅	124.05	C ₂ -C ₃ -C ₈ -O ₁₆	19.14
O ₁₃ -H ₁₄	0.969	C ₃ -C ₈ -O ₁₆	112.95	C ₃ -C ₈ -O ₁₆ -H ₁₇	-180.00
C ₈ -O ₁₅	1.207	C ₈ -O ₁₆ -H ₁₇	107.61		
C ₈ -O ₁₆	1.349				
O ₁₆ -H ₁₇	0.968				

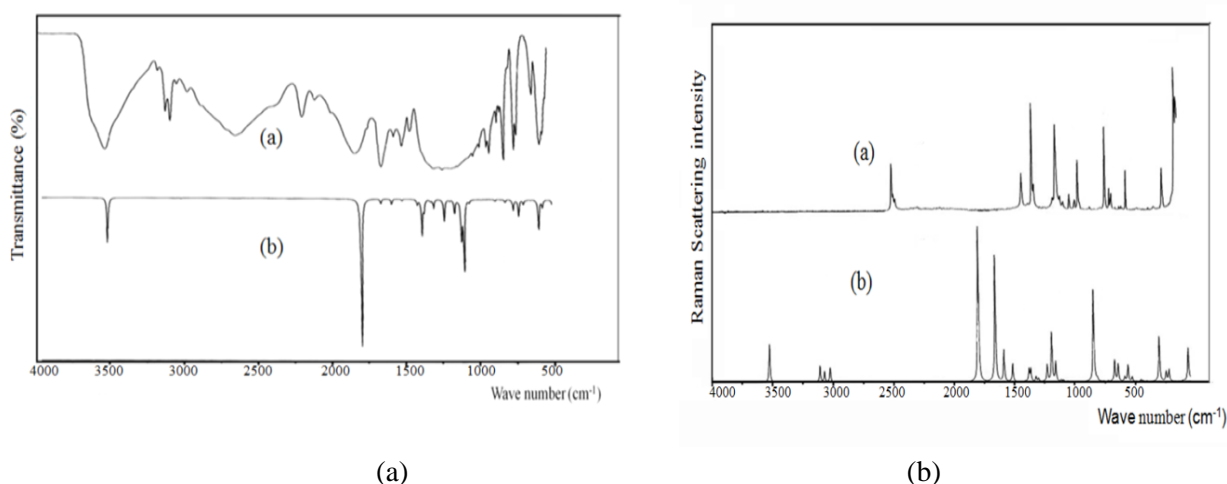


Figure 2. (a) Experimental and simulated FTIR of 35PDICA; (b) experimental and simulated FT-Raman spectrum of 35PDICA.

Based on DFT computations, optimized Dinicotinic (3,5-pyridine di-carboxylic) acid has C₁ point group symmetry and has 17 atoms with 45 fundamental frequencies. Out of this, thirty-one fundamentals frequencies are in-plane vibrations, and fourteen frequencies are in out-of-plane. All the vibrations of C₁ symmetry are active in both IR and Raman.

A detailed description of vibrational modes discussed in our earlier work [1]. Figure 2 represents the calculated and observed FT-IR and FT-Raman spectrum of Dinicotinic acid; all the modes of a given molecule are in Table-2.

2.1.2. Solving inverse vibrational problem (IVP).

Normal coordinate analysis was accepted to solve IVP employing Wilson’s GF-matrix method. The geometrical parameters (Table-2) of dinicotinic acid (35PDICA) is calculated by using DFT computations. Thus valence force field was preferred for solving IVP using NCA for all the fundamental vibrations of pyridine-3,5-dicarboxylic acid under investigation. A zero-order NCA of all the fundamental vibrations of 35PDICA was made by IVP [1]. The first set of seventy-four force constants was transferred and thirty-five observed frequencies using Dinicotinic acid with an rms error of 9.28 cm⁻¹. The experimental and theoretically calculated frequencies by Inverse Vibrational Problem (IVP) method & DFT method are tabulated in Table-2.

3. Results and Discussion

3.1. Vibrational assignments.

The vibrational assignments were made by using quantum chemical calculations (DFT) as well as solving the inverse vibrational problem (NCA). Experimental and theoretically (NCA and DFT) calculated frequencies of 35PDICA are shown in Table 2, along with vibrational assignments. The vibrational frequencies are assigned based on PED and eigenvector; obtained based on the computations [10] and based on the suggestions made by Varsanyi for 1,3,5-tri light (35PDICA) substituted benzenes [11], respectively. It is observed that from Table-2, the theoretically calculated frequencies are obtained by using the normal coordinate analysis method are evidence with experimental and DFT values. PED shown in Table-2 is obtained from the results of NCA method.

3.1.1. Carbon-Carbon (CC) and Carbon-Nitrogen (CN) stretching vibrations.

The modes 1, 8a, 8b, 14, 19a, and 19b are known as CC/CN stretching vibrations in pyridine and its derivatives. For the Dinicotinic acid, the modes 8a and 8b are found at 1600 cm^{-1} . The higher frequency has PED to the extent of 50% from C-C stretching character, and the remaining PED comes from C-C $_{\alpha}$ mode 7b and ring vibrations in Dinicotinic acid. Hence, the absorptions near 1610 cm^{-1} are assigned to C-N of 8a, and bands near 1591 cm^{-1} are coming to C-C mode 8b in P35DICA. CC vibration has PED extent of 36% combined with C-C $_{\alpha}$, whereas the CC mode to the extent of 58% mixes with CH in-plane bending vibration. Hence, 1537 cm^{-1} is ascribed to mode 19a, and the absorptions around 1466 cm^{-1} are assigned to mode 19b in pyridine-3,5-dicarboxylic acid, respectively The C-C and C-N vibrations are concurrences with P. Koczon *et al.* [12], and C-C vibrations are in good agreement with N. L. John *et al.* [13].

3.1.2. Kekule (mode 14) and CH in-plane bending vibrations.

C-H in-plane bending vibrations appears around 1000-1300 cm^{-1} [14-17]. As per density functional theory and the inverse vibrational problem, it is observed at 1266 and 1215 cm^{-1} in Dinicotinic acid and strong mixing with modes 14 and 3. Kekule and CH in-plane are presented in Table 2.

Table 2. Detailed vibrational assignments of experimental and theoretical frequencies of Dinicotinic acid.

Modes**	Obs. freq.		Cal. freq. (cm^{-1})			Vibrational assignment
	IR	Ra	DFT		NCA	
			Uns.	Sc.		
$\nu(\text{CH})_2$	3090	3084	3187	3087	3095	2(100)
$\nu(\text{CH})_{20a}$	-	-	3140	3061	3067	20a(99)
$\nu(\text{CH})_{20b}$	2909	-	3008	2910	2918	20b(98)
$\nu(\text{CC}_{\alpha})_{7b}$	-	1034	1059	1037	1031	7b(40)+19a(24)+6a(12)
$\nu(\text{CC}_{\alpha})_{13}$	-	1305	1357	1312	1310	13(43)+19b(12)+ $\nu(\text{C}_{\alpha}-\text{O})$ (10)
$\nu(\text{CN})_1$	801	800	824	802	809	1(71)+12(20)
$\nu(\text{CC})_{8a}$	1610	1607	1630	1609	1616	8a(50)+12(19)+7b(12)
$\nu(\text{CN})_{8b}$	-	-	1587	1580	1591	8b(41)+18b(28)+14(17)
$\nu(\text{CC})_{14}$	1266	1266	1281	1271	1267	14(65)+3(34)
$\nu(\text{CC})_{19a}$	-	-	1548	1530	1537	19a(36)+18b(24)+7b(17)
$\nu(\text{CC})_{19b}$	1466	1461	1497	1468	1464	19b(58)+18b(30)
$\beta(\text{CH})_3$	1215	-	1254	1218	1220	3(41)+14(28)
$\beta(\text{CH})_{18a}$	1055	-	1074	1056	1048	18a(37)+19a(24)
$\beta(\text{CH})_{18b}$	1162	1149	1181	1167	1150	19b(48)+18b(30)
$\beta(\text{CC}_{\alpha})_{9a}$	-	201	180	197	206	9a(74)+ $\tau\tau(\text{C}_{\alpha}-\text{O})$ (12)

Modes**	Obs. freq.		Cal. freq. (cm ⁻¹)			Vibrational assignment
	IR	Ra	DFT		NCA	
			Uns.	Sc.		
β(CC _α)15	-	330	341	329	335	18b(51)+ ττ (C _α -O)(33)
β(CCC)6a	476	-	490	469	478	6a(48)+20a(25)+δ(C _α =O)(12)
β(CCC)6b	532	-	545	536	530	6b(61)+7b(18)+19a(14)
β(CCC)12	752	-	781	754	751	12(55)+14(15)+7b(11)
π(CH)5	895	-	870	891	894	5(71)+4(22)
π(CH)11	695	-	674	689	698	11(100)
π(CH)17a	942	-	961	937	947	17a(98)
π(CC _α)10b	-	189	201	187	180	10b(34)+τ(OH)(15)+4(12)
π(CC _α)17b	-	137	140	141	138	17b(49)+4(21)+17a(15)
τ(cccc)4	-	677	681	674	678	5(51)+4(35)
τ(cccc)16a	496	-	501	495	491	τ(C _α =O)(44)+16a(24)+10b(18)
τ(cccc)16b	-	277	301	284	279	16b(68)+17b(21)
ν(C _α =O) ₁	1719	1718	1740	1721	1722	ν(C _α =O)(90)
ν(C _α =O) ₂	1719	1718	1754	1718	1729	ν(C _α =O)'(91)
ν(C _α -O) ₁	1368	-	1345	1371	1369	18b(39)+ν(C _α -O)(24)+19b(20)
ν(C _α -O) ₂	1368	-	1349	1369	1359	18a(32)+ν(C _α -O)'(21)+1(19)
δ(OH) ₁	-	1389	1391	1388	1381	δ(OH)(77)+18a(20)
δ(OH) ₂	-	1389	1390	1384	1382	δ(OH)'(71)+ν(C _α =O)'(14)
ν(OH) ₁	3436	-	3624	3439	3442	ν(OH)(98)
ν(OH) ₂	3436	-	3624	3441	3439	ν(OH)'(99)
δ(C _α =O) ₁	626	-	651	630	634	δ(C _α =O)(41)+ν(C _α -O)(14)
δ(C _α =O) ₂	626	-	652	634	628	δ(C _α =O)'(40)+ν(C _α -O)'(18)
γ(C _α -O) ₁	-	505	497	498	497	γ (C _α -O)(38)+9a(22)+8a(14)
γ(C _α -O) ₂	-	505	498	501	500	γ (C _α -O)'(49)+20a(20)+8b(11)
τ(CC _α) ₁		81	120	92	89	τ(CC _α)(39)+10b(21)+ω(OH)4
τ(CC _α) ₂		110	162	109	111	τ(CC _α ')(81)+16b(12)
ω(OH) ₁			480	471	468	ω(OH)(55)+τ(CC _α)(23)
ω(OH) ₂			459	460	468	ω(OH)'(44)+17a(31)+5(17)
ω(C _α =O) ₁		798	888	864	862	ω(C _α =O)(69)+τ(CC _α)(15)
ω ₂ (C _α =O) ₂		798	891	871	869	ω(C _α =O)'(70)+10b(11)

^a: Mode in Wilson's notation [11].

3.1.3. C-C_α vibrations.

Modes 7b and 20a in dinicotinic acid allocate the two C-C_α (stretching vibrations), whereas the modes 9a and 15 (in-plane bending vibrations). The two out-of-plane bending vibrations are designated as modes 10b and 17a in Dinicotinic acid. The pair of frequencies near 1034R and 1305R are ascribed to C-C_α stretching vibrations in 35PDICA. All the C-C_αvibrations (i/p and o/p) were shown in Table-2.

3.1.4. β(CCC) vibrations.

According to NCA, the 330R and 476 cm⁻¹ are attributed to 6a and 6b vibrational modes, whereas the IR near 752 cm⁻¹ is assigned to mode 12.

3.1.5. Ring torsions τ(cccc) vibrations.

Ring torsions are designated with modes 4, 16a, and 16b in pyridine dicarboxylic acid. The absorption near 695cm⁻¹ is assigned as mode 4, and this mode has 35% PED from ring torsion and mixed with C-H wagging in the present molecule.

The frequency near 469 cm⁻¹ having 68% PED from ring torsion character is attributed mode 16b, whereas the IR absorption near 677R cm⁻¹ with 34% PED from τ(cccc) is assigned mode 16a.

3.1.6. Vibrations of the acid groups.

The Vibrational assignments of carboxylic acid groups are shown in Table 2, and they are good agreements with K. McCan and J. Laane[18] and Kourat *et al.* [19]

3.2. NLO parameters.

Non-linear optical crystals are considered to be useful future material for applications in many fields [20,21]. NLO behavior has been investigated on various organic, inorganic, and organometallic compounds [22]. NLO effect arises due to the interaction of electromagnetic radiation with the material; as a result, the propagation properties like frequency, phase, and amplitude can changes [23, 24]. The present research reveals that the organic NLO materials are designed to develop a relatively low-power laser-driven non-linear optical system [25].

The NLO properties [26-29] of dinicotinic acid have been calculated by the DFT computations of first-order hyperpolarizability, electric dipole moment, and total polarizability, and these are furnished in Table 3.

Table 3. First order hyperpolarizability (in 10^{-30} cm⁵/e.s.u), dipole moment and polarizability (in 1.4818×10^{-25} cm³)

Type of component	Value with B3LYP/6-311++G (d,p)	Type of component	Value with B3LYP/6-311++G (d,p)
β_{xxx}	65.14063	μ_x	1.3621
β_{xxy}	280.3822	μ_y	1.0675
β_{xyy}	-37.7120	μ_z	0.0000
β_{yyy}	-90.5951	μ_t	1.7305
β_{xxz}	0.0000	α_{xx}	140.0498
β_{xyz}	0.0000	α_{xy}	0.27949
β_{yyz}	0.0000	α_{yy}	110.5503
β_{xzz}	8.6064	α_{xz}	0.0000
β_{yzz}	-13.2139	α_{yz}	0.0000
β_{zzz}	0.0000	α_{zz}	52.4491
β_t	1.556×10^{-30}	α_t	101.0164
		$\Delta\alpha$	1.3621

The computed dipole moment and first-order hyperpolarizability values for the chosen compound are higher than the urea value and its measure of NLO activity [1, 30-31].

3.3. Frontier molecular orbital studies.

Frontier molecular orbitals's (HOMO and LUMO) are essential parameters in quantum chemistry and play a vital role in the optical and electrical properties [32]. FMO's determine the way the molecule interacts with other species [33]. The energy gap between HOMO and LUMO measure the reactivity and kinetic stability [34, -35] as well as the electrical conductivity [36] and optical polarizability of the molecule [37]. The energy difference between HOMO and LUMO is 0.00866 a.u. This small energy gap indicates the title compound have more reactive. With the help of HOMO and LUMO orbitals, we can compute the global reactivity parameters based on TD-DFT calculations. These parameters can be computed by the Koopman's theorem [38-42]. Parr *et al.* have given the idea that electrophilicity index (ω) is like chemical potential and hardness. Global reactivity descriptors such as chemical softness, hardness, chemical potential, and electrophilicity index values are obtained from Ramesh *et al.* [43]. The computed results of all these parameters are tabulated in Table 4. Currently, HOMO, LUMO energies, and bandgap decide the from intermolecular charge transfer (ICT) [44].

Table 4. Calculated energy values of dinicotinic acid.

Frontier molecular orbital parameter	Value(in a.u)
HOMO energy	-0.20958
LUMO energy	0.21824
Frontier molecular orbital energy gap	0.00866
Ionization energy (I)	0.20200
Electron affinity (A)	0.32404
Global hardness (η)	0.14024
Chemical potential (μ)	-0.35771
Global electrophilicity power (ω)	0.56985

3.4. Thermodynamic parameters and rotational constants.

The computed results of thermodynamic parameters such as SCF energy, vibrational energy (E_{vib}), Specific heat capacity at constant volume (C_v), entropy (S), zero-point energy (E_0), and rotational constants have been performed for title molecule using DFT employing B3LYP method with the basis set of 6-311+G(d,p) and are presented in Table 5. All the present investigations were done in the gas phase, and hence they cannot be used in solution [45-46].

Table 5. Thermodynamic parameters of dinicotinic acid.

Thermodynamic parameter	35PDICA
SCF	-625.62
Vibrational energy (E_{vib})	78.476
C_v	36.907
Entropy (S)	100.533
Zero-point energy (E_0)	73.960
Rotational constants (GHz)	
A	0.09157
B	0.02803
C	0.02146

4. Conclusions

The structural, spectroscopic (FT-IR, FT-Raman) and calculated (DFT & IVP) was performed for the dinicotinic acid molecule. The calculated frequencies of dinicotinic acid using density functional theory better agree with the corresponding observed frequencies. A detailed vibrational analysis of the title molecule is performed using the density functional theory (DFT) method and solving IVP using optimized molecule geometries. The NLO parameters, HOMO, and LUMO energies were performed. The first-order hyperpolarizability (β_{tot}) and dipole moment were also calculated for this molecule. It is found that the values of β_{tot} and μ_t are lower than urea and which shows that the Dinicotinic acid is an excellent NLO behavior.

Funding

This research received no external funding.

Acknowledgments

The authors are thanks to the CSIR, and SAIF, IIT-Madras for spectral measurements

Conflicts of Interest

The authors declare no competing financial interest

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