The Microwave Spectrum of Ethyl Isocyanate

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The microwave spectrum of ethyl isocyanate, CH_3CH_2NCO, has been obtained in the frequency region from 8.5 to 35.5 GHz. The spectrum idantified is attributed to the *cis* conformation, in which the methyl group eclipses the isocyanato group. The rotational constants in the ground vibrational state obtained are $A=14110\pm3$, $B=3067.91\pm0.02$, and $C=2605.01\pm0.02$ MHz. The dipole moment (μ_a) for this rotamer is 2.81 ± 0.02 D. Four sets of vibrational satellites were observed and assigned to the transitions in the first, second, third, and fourth excited states of the C–N torsional vibration.

We have previously reported the microwave spectrum of the *cis*-rotational isomer of ethyl isothiocyanate,[1] CH_3CH_2NCS, as an example of the rotational isomerism about single carbon-heteroatom bonds in mono-substituted ethanes. Kniseley *et al.* have studied the structure of ethyl isocyanate using infrared spectroscopy. They reported that the rotational isomerism about the C–N bond for alkyl isocyanate was not possible on the basis of these observation that, in the solid-state spectrum, the absorption band assigned to the NCO asymmetric stretching vibration decreased sharply in intensity and usually exhibited a poorly defined band envelope.

It is interesting to determine the conformation of the ethyl isocyanate molecule and compare the result with that for ethyl isothiocyanate.[1] In this paper, the microwave spectrum of ethyl isocyanate in the *cis*-conformation will be reported and the structure and the dipole moment will be discussed.

Experimental

The sample of ethyl isocyanate was obtained commercially (from the Tokyo Kasei Co.) and was purified by distillation *in vacuo*. The rotational spectrum was measured over the frequency range from 8.5 to 35.5 GHz with a conventional 100-kHz sinusoidal- and square-wave Stark modulation spectrometer. The wave-guide cell was cooled with Dry Ice in order to enhance the intensity of the absorption lines. The transition frequencies were measured with a Hewlett-Packard Model 5245 L frequency counter.

Results and Discussion

Microwave Spectrum and Assignment of the Vibrational Ground State. The observed spectrum was quite dense in appearance, consisting of a large number of absorption lines. This feature may be ascribed to the various rotational isomers and their vibrationally-excited states. Four rotational isomers may be considered for ethyl isocyanate, as for ethyl isothiocyanate, namely, the *cis*, *gauche*, *skew*, and *trans* forms, as is shown in Fig. 1. The moments of inertia calculated from the assumed structure, indicated that all the isomers are nearly prolate symmetric tops (the value of Ray's asymmetric parameter lie in the range from −0.995 to −0.920). A large a-component of the dipole moment can be expected for these isomers because the –N=C=O bond, with a large moment, lies close to the a-axis. Consequently, strong a-type R-branch transitions with $K_{-1}=0$ and 1 are to be expected. In the vicinity of the $K_{-1}=0$ line, absorption lines for K_{-1} equal to or larger than two should appear, and a large Stark effect should be observed.

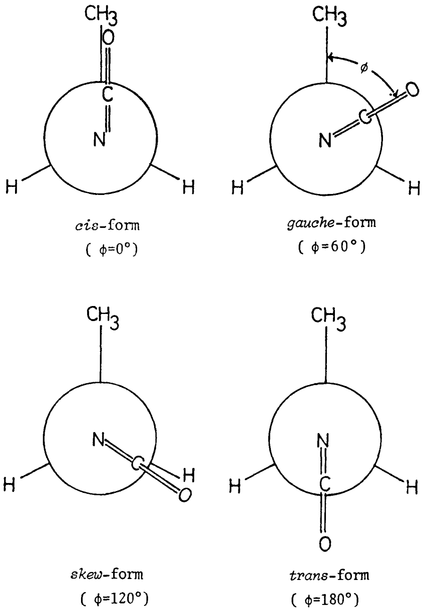

Fig. 1. Model of rotational isomers of ethyl isocyanate. ϕ: dihedral angle.

The $J=3\leftarrow2$ transitions with $K_{-1}=2$ were first observed with a low Stark voltage, and next a $K_{-1}=0$ line in the vicinity of the $K_{-1}=2$ line was observed with a high Stark voltage. The transitions of $3_{13}\leftarrow2_{12}$, $3_{03}\leftarrow2_{02}$, and $3_{12}\leftarrow2_{11}$ were identified from their characteristic Stark behavior. The frequencies of the observed transitions in the ground vibrational state are listed in Table 1.

With the preliminary values of the rotational constants fitted to the low-J transition frequencies, the high-J transition frequencies were predicted by the rigid-rotor approximation. As the values of J and K_{-1} increased, the difference between the observed and calculated transition frequencies was found to become larger, in particular for the lines with K_{-1} values larger than one, as in the case of ethyl isothiocyanate. This deviation is probably attributable to the centrifugal distortion effect. Therefore, the observed transition frequencies given in Table 1 were fitted to the equation of the rotational energy, with correction for the first-order centrifugal

Table 1. Rotational transitions of the ethyl isocyanate in the ground state (MHz)

Transition	ν_{obsd}	$\nu_{\text{obsd}}-\nu_{\text{calcd}}$
$2_{12}\leftarrow 1_{11}$	10882.03	−0.03
$2_{02}\leftarrow 1_{01}$	11329.78	0.07
$2_{11}\leftarrow 1_{10}$	11805.85	−0.21
$3_{13}\leftarrow 2_{12}$	16313.97	−0.13
$3_{03}\leftarrow 2_{02}$	16958.99	0.07
$3_{22}\leftarrow 2_{21}$	17016.49	−0.06
$3_{21}\leftarrow 2_{20}$	17072.87	−0.36
$3_{12}\leftarrow 2_{11}$	17700.03	0.20
$4_{14}\leftarrow 3_{13}$	21735.52	−0.21
$4_{04}\leftarrow 3_{03}$	22545.76	−0.12
$4_{23}\leftarrow 3_{22}$	22677.20	0.01
$4_{32}\leftarrow 3_{31}$	22717.28	−0.12
$4_{31}\leftarrow 3_{30}$	22719.03	−0.01
$4_{22}\leftarrow 3_{21}$	22818.37	0.03
$4_{13}\leftarrow 3_{12}$	23582.47	−0.37
$5_{15}\leftarrow 4_{14}$	27144.07	−0.03
$5_{05}\leftarrow 4_{04}$	28078.99	−0.13
$5_{24}\leftarrow 4_{23}$	28327.93	−0.09
$5_{42}\leftarrow 4_{41}$	28395.99	0.20
$5_{41}\leftarrow 4_{40}$		0.17
$5_{33}\leftarrow 4_{32}$	28407.85	0.36
$5_{32}\leftarrow 4_{31}$	28412.84	−0.37
$5_{23}\leftarrow 4_{22}$	28608.04	0.17
$5_{14}\leftarrow 4_{13}$	29448.49	0.11
$6_{16}\leftarrow 5_{15}$	32537.13	0.27
$6_{06}\leftarrow 5_{05}$	33546.14	0.19
$6_{25}\leftarrow 5_{24}$	33966.30	−0.25
$6_{52}\leftarrow 5_{51}$	34075.60	−0.12
$6_{51}\leftarrow 5_{50}$		−0.12
$6_{43}\leftarrow 5_{42}$	34084.34	0.14
$6_{42}\leftarrow 5_{41}$		−0.02
$6_{34}\leftarrow 5_{33}$	34103.56	0.23
$6_{33}\leftarrow 5_{32}$	34118.36	−0.18
$6_{24}\leftarrow 5_{23}$	34448.91	−0.03
$6_{15}\leftarrow 5_{14}$	35293.30	−0.35

distortion effect.

The rotational and centrifugal distortion constants, as obtained by the least-squares method, are given in Table 2. The observed and calculated transition frequencies are in good agreement, as is shown in Table 1. The centrifugal distortion effect of ethyl isocyanate was similar in magnitude to that of ethyl isothiocyanate.[1)]

Conformation of the Molecule. If the molecule studied in this work has a plane of symmetry, *viz.*, a *cis* or *trans* conformation, four hydrogen atoms are located out of this plane. For this instance, the following relation is valid if the molecule is a rigid rotor:

$$8m_{\text{H}}c_{\text{H}}^2 = I_{\text{a}} + I_{\text{b}} - I_{\text{c}}$$

where m_{H} is the mass of one hydrogen atom and c_{H} is its distance from the plane of symmetry. Using the assumed structural parameters given in Table 3, the value of $8m_{\text{H}}c_{\text{H}}^2$ for the two forms, *cis* and *trans*, was calculated to be 6.344 amu Å^2. This is in good agreement with the value determined experimentally. This result suggests that the conformation of the molecule for which the transitions are assigned is a form having a plane of symmetry, namely, the *cis* or *trans* form. Moreover, comparing the rotational constants determined experimentally with those calculated from the assumed structures, as are shown in Table 4, the preferred conformation is clearly the *cis* form shown in Fig. 2.

Table 3. Structural parameters[a)]

Distances	Angles
C–H: 1.091 Å[b)]	∠HCH: 108.8°[b)]
C_α–C_β: 1.520 Å[b)]	∠H$C_\beta C_\alpha$: 109.6°[b)]
C_α–N: 1.461 Å	∠$C_\beta C_\alpha$H: 112.0°[b)]
N=C: 1.207 Å[b)]	∠$C_\beta C_\alpha$N: 109.14°
C=O: 1.171 Å[b)]	∠C_αNC: 142.11°
	∠N=C=O: 180°[b)]

a) The carbon atoms at the α- and β-positions are denoted as C_α and C_β respectively. The structural parameters are taken from the mono-substituted ethanes, CH_3CH_2X,[1)] for the ethyl group and from the methyl isocyanate for the isocyanato group.

b) Assumed parameters fixed for structural analysis. Three other were also determined.

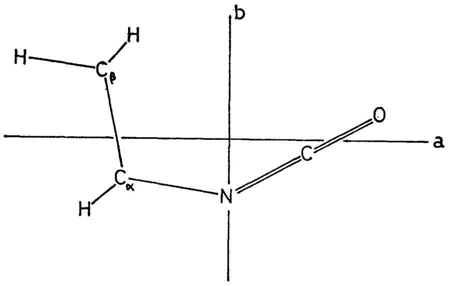

Fig. 2. Conformation of the *cis*-ethyl isocyanate.

Table 2. Rotational and centrifugal distortion constants and moments of inertia[a)] for ethyl isocyanate

	$v=0$	$v_t=1$	$v_t=2$	$v_t=3$	$v_t=4$
A(MHz)	14110±3	14657±20	15215±25	15919±56	16853±110
B(MHz)	3067.01±0.02	2982.36±0.09	2922.95±0.08	2861.01±0.12	2792.80±0.17
C(MHz)	2605.01±0.02	2578.47±0.09	2556.90±0.08	2533.53±0.14	2505.87±0.13
D_J(kHz)	4.17±0.22	5.69±1.04	7.15±0.99	9.38±1.44	11.48±1.73
D_{JK}(kHz)	−39.1±0.5	−69.3±2.9	−95.0±2.8	−145.5±6.2	−428.4±5.1
I_a(amu Å^2)	35.816±0.009	34.480±0.049	33.215±0.056	31.745±0.111	29.987±0.178
I_b(amu Å^2)	164.778±0.001	169.455±0.005	172.899±0.005	176.642±0.007	180.956±0.011
I_c(amu Å^2)	194.001±0.002	195.998±0.007	197.651±0.006	199.475±0.011	201.676±0.010
ΔI(amu Å^2)[b)]	6.593±0.012	7.937±0.061	8.463±0.067	8.912±0.129	9.267±0.199

a) Conversion factor=505376 MHz amu Å^2. b) $\Delta I=I_a+I_b-I_c$.

TABLE 4. OBSERVED AND PREDICTED ROTATIONAL CONSTANTS

	Obsd	Calcd			
		cis	*gauche*	*skew*	*trans*
A(MHz)	14110.25	14111.78	16091.99	24577.12	34937.53
B(MHz)	3067.01	3068.93	2796.52	2376.32	2242.26
C(MHz)	2605.01	2603.11	2499.49	2292.55	2164.28
κ	−0.919689	−0.919049	−0.956295	−0.992481	−0.995241
Δ(amu Å^2)a)	−6.592	−6.344	−9.929	−12.791	−6.344
ϕ(°)b)		0	60	120	180

a) $\Delta = I_c - I_b - I_a$. b) ϕ: dihedral angle about the C–N bond; see Fig. 1.

Ethyl isocyanate, as one of the rotational isomers, is in the *cis* conformation in the gas phase. This result is consistent with the case of ethyl isothiocyanate,1) for which the spectrum identified is attributed to the *cis* conformation.

Three structural parameters, ($r_{C_\alpha-N}$, $\angle C_\beta C_\alpha N$, and $\angle C\alpha NC$), of the ethyl isocyanate were obtained from the observed rotational constants, fixing the remaining parameters to the values assumed. The results thus obtained are given in Table 3.

Comparing the CNC angle obtained (142°) here for CH_3CH_2NCO with that (151°) obtained for CH_3CH_2NCS1) in the previous work, a large increase in the angle (about 9°) is seen on the replacement of O by S. Similar trends are evident for the cases of the HNC angle of HNCO3) (128°) and HNCS4) (135°), and the CNC angle of CH_3NCO5) (140°) and CH_3NCS5) (147.5°).

The dense spectrum suggests the presence of other rotamers in appreciable concentrations. An attempt

TABLE 5. ROTATIONAL TRANSITIONS OF THE ETHYL ISOCYANATE IN THE TORSIONAL-EXCITED STATE (MHz)

Transition	$v_t=1$		$v_t=2$		$v_t=3$		$v_t=4$	
	ν_{obsd}	Δa)	ν_{obsd}	Δa)	ν_{obsd}	Δa)	ν_{obsd}	Δa)
$2_{12}\leftarrow 1_{11}$	10717.74	0.04	10593.65	−0.10	10461.92	0.01	10311.08	−0.67
$2_{02}\leftarrow 1_{01}$	11111.12	−0.04			10781.82b)	−0.89	10592.92	0.29
$2_{11}\leftarrow 1_{10}$	11525.60	−0.17	11326.06	−0.01			10887.73b)	2.12
$3_{13}\leftarrow 2_{12}$	16069.69	−0.42	15885.10	−0.21	15688.06	−0.47	15463.81	−0.44
$3_{03}\leftarrow 2_{02}$	16640.77	0.02	16406.58	−0.02	16158.87	0.54	15877.61	0.21
$3_{22}\leftarrow 2_{21}$	16683.81	0.25	16441.57b)	0.50	16186.95b)	0.81	15905.90b)	0.84
$3_{21}\leftarrow 2_{20}$	16724.11b)	−0.60	16472.96	−0.30	16210.49	0.04	15922.36	−0.06
$3_{12}\leftarrow 2_{11}$	17282.05b)	−0.61	16983.88b)	0.53	16671.60b)	0.70	16326.50b)	1.51
$4_{14}\leftarrow 3_{13}$	21414.18	−0.36	21170.08	−0.38	20909.17b)	−0.88	20612.06	−0.68
$4_{04}\leftarrow 3_{03}$	22139.30	−0.01	21837.25	−0.04	21514.88	−0.24	21148.44	0.01
$4_{23}\leftarrow 3_{22}$	22236.19	0.07	21914.48	0.11	21576.16	0.42	21202.93b)	0.85
$4_{22}\leftarrow 3_{21}$	22338.56	−0.11	21994.46	−0.20	21635.99	−0.42	21245.24	−0.20
$4_{13}\leftarrow 3_{12}$	23029.79b)	0.64	22634.29	0.28	22219.90	0.35	21762.61b)	2.40
$5_{15}\leftarrow 4_{14}$	26748.88	−0.05	26447.08	−0.35	26124.79	−0.16	25755.92	0.07
$5_{05}\leftarrow 4_{04}$	27597.32	−0.07	27235.84	0.01	26846.78	−0.31	26400.98	−0.08
$5_{24}\leftarrow 4_{23}$	27781.27	0.04	27381.68	0.07	26960.09	−0.28	26581.19	−0.40
$5_{42}\leftarrow 4_{41}$	27835.46	0.14	27428.49	−0.31	27004.85	0.01	26565.18	−0.63
$5_{41}\leftarrow 4_{40}$		0.13		−0.32		0.02		−0.63
$5_{33}\leftarrow 4_{32}$	27842.20b)	0.92						
$5_{32}\leftarrow 4_{31}$	27884.07b)	−0.67						
$5_{23}\leftarrow 4_{22}$	27985.23	0.07	27541.47	0.01	27081.52	0.18	26581.19	−0.40
$5_{14}\leftarrow 4_{13}$	28764.98	0.01	28275.56	0.18	27760.88	0.01	27191.40b)	1.62
$6_{16}\leftarrow 5_{15}$	32071.86	0.49	31715.34b)	0.77	31332.74b)	0.91	30893.68	0.79
$6_{06}\leftarrow 5_{05}$	33006.90	−0.01	32595.20	−0.17	32148.90	0.17	31630.97	−0.32
$6_{25}\leftarrow 5_{24}$	33317.01	−0.11	32841.24	−0.05	32338.95	0.11	31782.86	−0.27
$6_{52}\leftarrow 5_{51}$	33406.53	−0.12	32921.65	0.05				
$6_{51}\leftarrow 5_{50}$		−0.12		0.05				
$6_{43}\leftarrow 5_{42}$	33408.31	0.09	32918.75	0.19	32407.75	−0.06		
$6_{42}\leftarrow 5_{41}$		−0.17		0.19		−0.02		
$6_{34}\leftarrow 5_{33}$	33420.30	0.58	32924.70	0.25	32406.87	0.51		
$6_{33}\leftarrow 5_{32}$	33428.89	0.01	32930.45	−0.19	32410.19	−0.15	31853.70	0.30
$6_{24}\leftarrow 5_{23}$	33670.10	−0.13	33118.75	−0.07	32549.29	0.01	31932.23b)	−1.69
$6_{15}\leftarrow 5_{14}$	34484.95b)	−0.64	33904.21	−0.48	33292.10b)	−0.64	32611.98b)	−1.64

a) $\Delta = \nu_{obsd} - \nu_{calcd}$. b) Not included in the least-squares fitting.

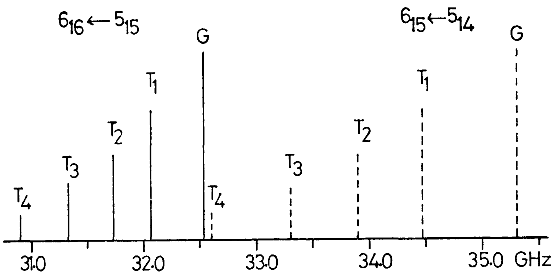

Fig. 3. Typical satellite pattern of $J=6\leftarrow5$ transitions of *cis*-ethyl isocyanate: dotted lines are $6_{15}\leftarrow5_{14}$ transition.

was made to find the transitions due to *skew* or *trans* forms. Measurements were carefully made near the transition frequencies predicted by the rotational constants of the models of the *skew* and *trans* forms calculated with the structural parameters in Table 3. However, no transition could be assigned which might be ascribed to the *skew* or *trans* form.

Vibrationally-excited State. Four sets of the spectrum due to the vibrationally-excited states were found. The satellite lines have essentially the same Stark effect behavior and the same K_{-1} series pattern as those of the ground state. Figure 3 illustrates same typical satellite patterns of $6_{16}\leftarrow5_{15}$ and $6_{15}\leftarrow5_{14}$ transitions. The vibrationally-excited states lines were assigned as is shown in Table 5. The effective rotational constants of the four excited vibrational states were obtained in a manner similar to that used for the ground state. These results are also given in Table 2.

From the relative intensities of the satellite lines with respect to the ground-state line, the vibrational frequency of 150±50 cm^{-1} for $v_t=1$ was obtained. Referring to Kniseley's assignment of this molecule and to the study of ethyl isothiocyanate, the observed vibrational frequencies (100, 144, and 224 cm^{-1}) were assigned to the C–N torsion, CNC bending, and C–C torsion modes respectively, as is shown in Table 6. Because the value of $\Delta' I (I_c-I_b-I_a+8m_{H}c_{H}^{2})$ obtained for $v_t=1$ has a negative value,[6] the vibrational satellite corresponding to 150 cm^{-1} can be ascribed to the excited state of the C–N torsion mode.

Table 6. Far-infrared spectra (cm^{-1})

CH_3CH_2NCS	CH_3CH_2NCO	Assignment
70(w)	100(w)	C–N torsion
130(s)	144(s)	CNC bending
225(w)	224(w)	C–C torsion
380(s)	395(s)	CCN bending (in-plane)[a]
450(m)	595(m)	NCX bending (out-of-plane)[a]
540(s)	608(s)	NCX bending (in-plane)[a]

Abbreviations: s, strong; m, medium; w, weak.
a) Ref. 2.

From the relative intensities and the ΔI values of the remaining sets, $v_t=2$, $v_t=3$, and $v_t=4$, given in Table 2, these sets may be ascribed to the excited states of the C–N torsional vibrations. The variation in the rotational constants (A, B, and C) with the vibrational quantum

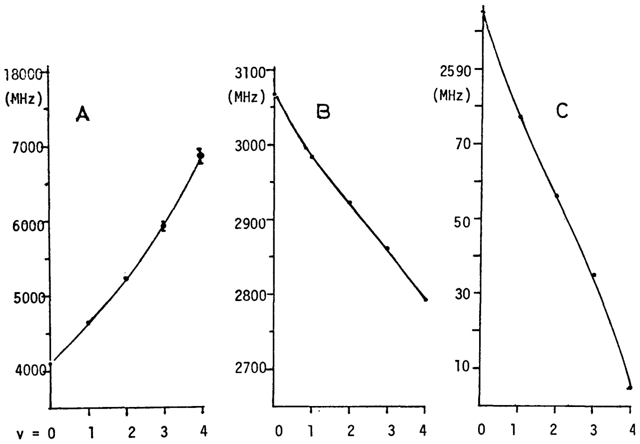

Fig. 4. Variation of rotational constants of *cis*-ethyl isocyanate with the quantum number.

Table 7. Stark coefficients[a] ($\Delta v/E^2$) and dipole moment (D)

Transition	M	$v=0$ obsd	$v=0$ calcd	$v_t=1$ obsd	$v_t=1$ calcd	$v_t=2$ obsd	$v_t=2$ calcd	$v_t=3$ obsd	$v_t=3$ calcd	$v_t=4$ obsd	$v_t=4$ calcd
$3_{03}\leftarrow2_{02}$	0	−0.902	−0.901	−1.15	−1.10	−1.14	−1.04	−1.19	−1.09		
	1	−0.256	−0.256	−0.326	−0.341	−0.259	−0.279	−0.289	−0.306		
	2	1.68	1.68	1.94	1.94	2.10	2.01	2.06	2.05		
$3_{12}\leftarrow2_{11}$	0	−0.240	−0.240								
	1	−3.03	−3.33	−4.64	−4.38	−4.70	−4.91	−5.57	−5.55		
	2			−16.0	−16.6	−18.5	−18.7	−21.1	−21.3		
$4_{04}\leftarrow3_{03}$	0									−0.467	−0.467
	1									−0.297	−0.296
	2									0.226	0.213
$4_{13}\leftarrow3_{12}$	1									−1.07	−0.864
	2									−2.86	−2.72
	3									−5.87	−5.81
μ_a	:	2.81±0.02		2.99±0.04		3.01±0.04		3.02±0.02		3.05±0.05	
μ_b	:	0.03		0.13		0.11		0.03		0.262	
μ_c	:	0 (assumed)		0 (assumed)		0 (assumed)		0 (assumed)		0 (assumed)	

a) [MHz/(V/cm)^2]×10^{-6}.

number of the C–N torsion is non-linear, as is shown in Fig. 4. Therefore, this torsional vibration is rather anharmonic.

Dipole Moment. From the Stark coefficients of the $3_{03}\leftarrow 2_{02}$, and $3_{12}\leftarrow 2_{11}$ transitions for the ground state and the excited states, $v_t=1$, 2, and 3, and the $4_{04}\leftarrow 3_{03}$ and $4_{13}\leftarrow 3_{12}$ for $v_t=4$, the dipole moment of ethyl isocyanate was determined for both the ground and excited vibrational states. From the second-order Stark coefficients determined for the five Stark component lines, the dipole moments shown in Table 7 were obtained. The c-component of the dipole moment was assumed to be zero because of the symmetry, as has been discussed above. The b-component was not determined exactly, since no b-type transitions were observed. The electric-field strength in the absorption cell was calibrated using the $J=1\leftarrow 0$ transition of OCS.[7] The dipole moment (μ_a) for the ground state was determined to be 2.81 ± 0.02 D.

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