Experimental and Theoretical Evidence for HS_4[†]

Giulia de Petris,*[‡] Antonella Cartoni,[‡] Romano Cipollini,[‡] Marzio Rosi,[§] and Anna Troiani[‡]

Dipartimento di Chimica e Tecnologie del Farmaco, Università "La Sapienza", Piazzale Aldo Moro, 5-00185 Rome, Italy, Dipartimento di Ingegneria Civile ed Ambientale, ISTM-CNR, Università di Perugia, Via Duranti, I-06131, Perugia, Italy

Received: April 21, 2009; Revised Manuscript Received: June 12, 2009

The new radical HS_4 containing three sulfur−sulfur bonds has been detected in the gas phase by mass spectrometric experiments. Structures and energies of HS_4 in the three oxidation states +/0/− have been investigated by ab initio calculations. HS_4 is characterized by the HSSSS open-chain structure, and it is stable toward dissociation into S_2 and HS_2 by 23 kcal mol^{-1}. The first detection of HS_4^-, the conjugate base of the strong acid H_2S_4 is also reported.

Introduction

Small radicals and molecules having S−S bonds are building blocks of organic molecules and potential intermediates of biologic and atmospheric processes. Many species of this kind cannot be prepared by conventional procedures in a typical chemical laboratory, being very reactive or intrinsically unstable. According to a recent recommendation, the thermodynamic and kinetic stability of a species is best described by the extreme concepts of "viable" and "fleeting" molecules. Viable species have half-lives of a day or longer under ambient conditions, whereas fleeting molecules are local minima with barriers that prevent escape from their well.[1] The latter are possibly unknown in the real world, yet they may play key roles in planetary atmospheres and interstellar space, being more viable in space than on Earth.

Among the techniques available to investigate reactive intermediates, mass spectrometry has given a great contribution, proving the existence of exotic, elusive molecules and paving the way to more extensive studies. Within this context, the inventory of discovered sulfur-containing radicals is particularly rich.[2] Here, we report on the existence of HS_4, a new radical containing three sulfur−sulfur bonds. Polysulfur radicals and ions are potentially relevant to sulfur-rich planetary atmospheres, such as the Jovian moon Io, where S_3 and S_4 are suggested to be responsible for the red color of the Pele plume deposits and other volcanic deposits.[3] Small radicals having S−S bonds are also of interest to metabolic pathways that generate the "sulfane sulfur" group, thought to be a finely tuned regulator of sulfur metabolism.[4]

Experimental Methods

All experiments were performed using a modified ZABSpec oa-TOF instrument (VG Micromass) described elsewhere.[5] The CAD (collisionally activated dissociation) spectra of mass-selected ions were recorded at 8 keV, and the CAD/TOF spectra of mass- and energy-selected ions were recorded at 0.8 keV in the TOF (time-of-flight) sector of the instrument. In all CAD experiments, helium was utilized as the target gas in the collision cell; the pressure was chosen to provide 80% transmittance.

The neutralization−reionization (NR) experiments[2] were performed at 8 keV in the pair of cells located after the magnet in the second field-free region of the instrument. In the first cell, the mass-selected cation is reduced by collision with Xe. All ions are removed at the exit of the cell by a pair of high-voltage deflecting electrodes. In the second cell, the beam containing only neutrals is either oxidized by collision with O_2 ($^+NR^+$) or reduced by collision with Xe ($^+NR^-$). No signal was obtained by switching the deflector on in the absence of reionizing gas. The detection of intact neutral species is proved by the presence of a "recovery" peak at the same *m/z* ratio as the original ion. Gas pressures were set to achieve a beam transmittance of 80−90% under near-single collision conditions. All NR spectra were averaged over 100 acquisitions to improve the signal-to-noise ratio. The recovery peak of the $^+NR^+$ spectra was mass-selected and further analyzed in the TOF sector, and the spectrum (NR-CAD) was then compared to that of the precursor ions.

To evaluate isobaric contributions, high-resolution CI (chemical ionization) mass spectra were recorded at a resolution of 12 000 fwhm (full width at half-maximum) at the first detector. A possible contribution to the HS_4^+ precursor ion (*m/z* 129) is the $^{33}SS_3^+$ isotopomer (*m/z* 129) of the molecular ion S_4^+ (*m/z* 128). S_4^+ was minimized by H_2 chemical ionization of elemental sulfur (see next paragraph). Under these conditions, high-resolution CI spectra showed that the $^{33}SS_3^+$ contribution was ≤0.5% of the precursor ion, whereas measurements of I/I^+ neutralization efficiency set the contribution to the recovery peak at ≤0.3%. Any contamination by isotopomers of S_4^+ was conclusively eliminated by producing the $H^{34}S_4^+$ ion by elemental ^{34}S in H_2/CI.

The chemicals were research-grade products used as received, with the following stated purity: elemental sulfur, S (Aldrich, 99.998 mol %); elemental sulfur, ^{34}S (Isotec, 99.5% ^{34}S atoms). All other chemicals were research-grade products with a stated purity in excess of 99.95 mol %. Elemental sulfur was directly introduced into the ion source through a heated probe at 450 K.

Computational Methods

The investigation of the potential energy surfaces of HS_4^+, HS_4, and HS_4^- was performed by B3LYP[6] calculations. The basis set employed was the aug-cc-pVTZ[7] augmented with a

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[†] Part of the "Vincenzo Aquilanti Festschrift".

* Corresponding author. E-mail: giulia.depetris@uniroma1.it.

[‡] Università "La Sapienza".

[§] Università di Perugia.

10.1021/jp9036556

tight d function for sulfur (exponent 2.457),[8] to take properly into account core polarization effects.[9] The basis set is denoted aug-cc-pV(T+*d*)Z.[10] The nature of the stationary points was established by analysis of the vibrational frequencies computed at the same level of calculation. The assignment of the saddle points was performed using intrinsic reaction coordinate (IRC) calculations.[11] The energies of all stationary points were refined by performing CCSD(T)[12] calculations using the same aug-cc-pV(T+*d*)Z basis set. Both the B3LYP and the CCSD(T) energies were corrected to 298.15 K by adding zero point energies and thermal corrections computed at the B3LYP level of theory. For selected systems, geometry optimizations were performed at the B3LYP level using the 6-311++G(3*df*,3*pd*) basis sets;[13] at the MP2 level[14] with the aug-cc-pV(T+*d*)Z basis set; at the CASSCF level[15] with the aug-cc-pV(T+*d*)Z basis set considering as active space the 3p orbitals on sulfur and the 1s orbital on hydrogen (this means 13 orbitals with 17 electrons for the HS_4 system); at the BP86 level[16] with the aug-cc-pV(T+*d*)Z basis set. All calculations were performed using Gaussian 03,[17] whereas the analysis of the vibrational frequencies was performed using Molekel.[18]

Results and Discussion

There is a consensus of evidence that the most stable structure of S_4 is the singlet cis C_{2v}.[19] Among the less stable species, the three-membered branched ring C_s[19b] and trans-planar C_{2h}[19d] were attributed to the red adsorbing species identified by infrared spectroscopy in solid argon. The C_s and C_{2h} isomers were calculated to be higher in energy than the global minimum by 12−14 and 10 kcal mol^{-1}, respectively.[19a,d] Interestingly, a comparable energy difference can be found in the protonated forms: the cis HS_4^+ isomer is the most stable one; the branched ring and trans isomers are higher in energy by ~13 and 6 kcal mol^{-1}, respectively;[19c,e] As a result, the proton affinities of the S_4 isomers are expected to be very close.

Mass spectrometric experiments aimed at revealing HS_4 require the preparation of HS_4^+ under the constraint that no isobaric contamination is superimposed on the precursor ion. The most viable route to HS_4^+ is the protonation of S_4. Mixtures of sulfur clusters S_n ($n = 2-12$) with variable compositions can be obtained in the gas phase by heating elemental sulfur or by decomposition of metal sulfides.[20] Similar pressure and temperature conditions generally ensure workable fractions of both S_3 and S_4 in the sulfur vapor.[2j,20d] Although S_4 has a higher proton affinity than S_3,[2j,19e] the HS_4^+ ion (*m*/*z* 129) is invariably accompanied by significant amounts of the molecular ion S_4^+ (*m*/*z* 128) possibly formed also by ion−molecule reactions. To eliminate the contribution of the $^{33}SS_3^+$ isotopomer (*m*/*z* 129) to the HS_4^+ precursor ion, the following protonation reactions were carried out by chemical ionization of elemental sulfur and either H_2O or H_2:

$$H_3O^+ + {}^{34}S \rightarrow H^{34}S_4^+ + H_2O \qquad (1)$$

$$H_3^+ + S_4(S_n) \rightarrow HS_4^+ + H_2\ (+S_{n-4}) \qquad (2)$$

The former gives the $H^{34}S_4^+$ precursor ion (*m*/*z* 137), which is not affected by isotopomers of S_4^+. The latter is an exothermic protonation that also promotes dissociation of higher HS_n^+ ions, formed with excess energy, and significantly increases the HS_4^+ signal with respect to S_4^+.

TABLE 1: Enthalpy Changes and Barrier Heights (kcal mol^{-1}, 298 K) Computed at the B3LYP/aug-cc-pV(T+*d*)Z and CCSD(T)/aug-cc-pV(T+*d*)Z Levels of Theory for Selected Dissociation and Isomerization Processes of HS_4^+, HS_4, and HS_4^-

	Δ*H*		barrier height	
	B3LYP	CCSD(T)	B3LYP	CCSD(T)
1$^+$ → $H^+ + S_4$	188.2	187.9		
1$^+$ → $S_2^+ + HS_2$	49.1	52.2		
1$^+$ → **2**$^+$	3.0	5.0	15.5	16.7
2$^+$ → **3**$^+$	10.8	6.9	26.4	23.9
1 → S_2 ($^3\Sigma_g^-$) + HS_2	19.1	23.1		
3 → S_3 + HS	9.3	9.5		
1 → **3**	28.1	27.4	45.3	44.0
1 → **2**	0.4	1.1	*a*	*a*
1$^-$ → $S_2^- + HS_2$	36.3	41.4		
3$^-$ → S_3^- + HS	25.6	29.5		
1$^-$ → **2**$^-$	0.7	1.1	8.9	7.4
1$^-$ → **3**$^-$	8.4	7.9	22.7	25.8

[a] See text.

The possible presence in the sulfur vapor of S_4 isomers of comparable proton affinity prevents the assumption that the HS_4^+ beam contains a pure population of protonated singlet cis S_4. In addition, the proton affinities of S_4 (187.9 kcal mol^{-1}, Table 1), H_2O (165.0 kcal mol^{-1}),[21] and H_2 (100.9 kcal mol^{-1})[21] make both reactions 1 and 2 quite exothermic, which could promote isomerization processes. This notwithstanding, it will be shown that the neutralization of the most stable cis HS_4^+ ion is the process that most plausibly accounts for the observed result.

The HS_4^+ and $H^{34}S_4^+$ ions formed by reactions 1 and 2 were structurally probed by CAD mass spectrometry. The same spectra were obtained irrespective of the reaction of formation (Figure 1A, B). Importantly, the CAD spectrum recorded in the TOF sector of the instrument (Figure 1C) is a useful reference to compare the HS_4^+ ions submitted to neutralization and those obtained upon reionization of HS_4. The neutralization and reionization processes are, indeed, vertical processes occurring in the femtosecond time scale; thus, the precursor ion, the neutral, and the reionized ion have the same structure unless isomerization processes occur at some stage of the entire process.

When the HS_4^+ and $H^{34}S_4^+$ ions undergo vertical charge transfer, the $^+NR^+$ spectra show recovery peaks at *m*/*z* 129 and

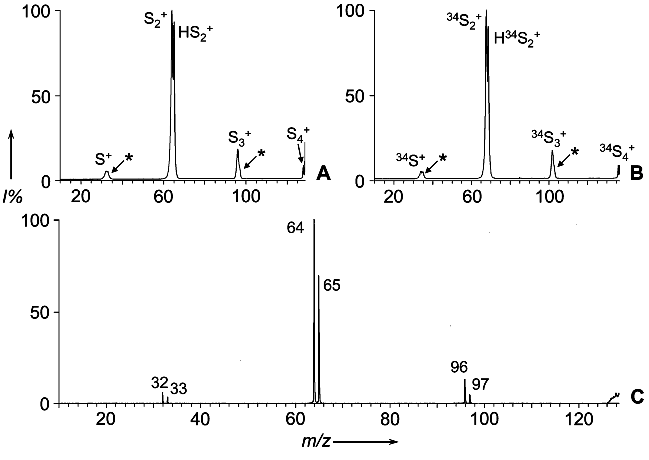

Figure 1. (A) CAD spectrum of HS_4^+ (*m*/*z* 129) from elemental S/H_2 CI. (B) CAD spectrum of $H^{34}S_4^+$ (*m*/*z* 137) from elemental $^{34}S/H_2O$ CI. Stars denote unresolved peaks at *m*/*z* 97 and 103 (HS_3^+, $H^{34}S_3^+$), *m*/*z* 33 and 35 (HS^+, $H^{34}S^+$). (C) CAD/TOF spectrum of HS_4^+ (*m*/*z* 129) from elemental S/H_2 CI.

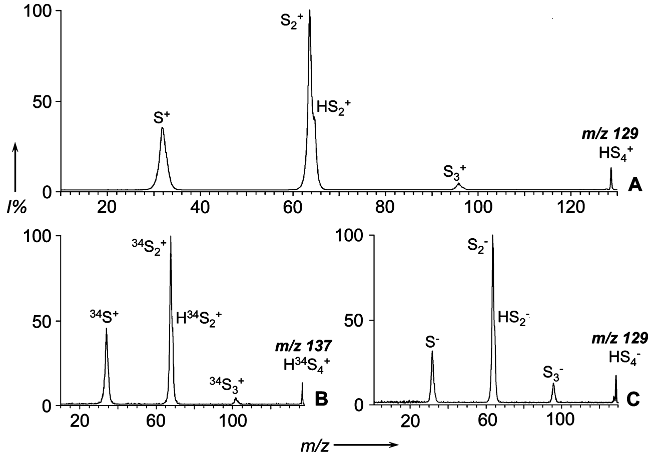

Figure 2. $^+NR^+$ spectra of (A) HS_4^+ and (B) $H^{34}S_4^+$. $^+NR^-$ spectrum of HS_4^+ (C). Note the recovery peaks at *m/z* 129 (HS_4^+, HS_4^-) and 137 ($H^{34}S_4^+$). Peaks corresponding to $HS_3^{+/-}$, $H^{34}S_3^+$, $HS^{+/-}$, and $H^{34}S^+$ are unresolved.

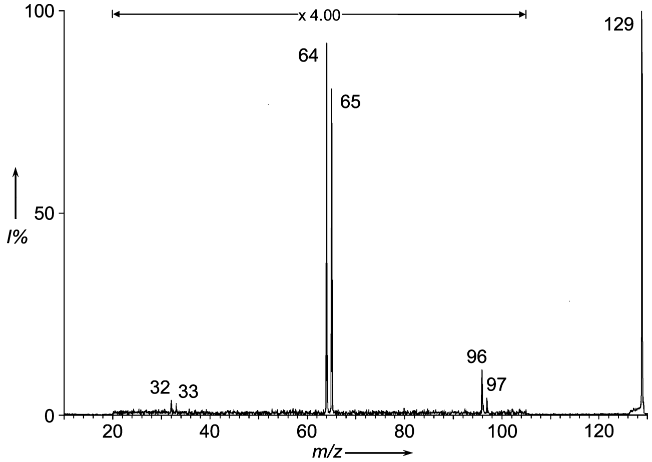

Figure 3. NR-CAD mass spectrum of the HS_4^+ recovery peak from $^+NR^+$.

137 (Figure 2), proving detection of the HS_4 radical. The minimum time the radical survives in the experiment is 0.8 μs. Importantly, Figure 3 reports the NR-CAD spectrum of the HS_4^+ ion obtained from the reionization process, which is superimposable on the CAD spectrum of the HS_4^+ precursor ion (Figure 1C).

Extensive theoretical studies have been made on S_4, particularly because of the importance of tetrasulfur in atmospheric chemistry.[19] Theoretical studies of HS_4^+ are also available,[19c,e] whereas the HS_4 radical is completely unknown, both experimentally and theoretically. We therefore explored the potential energy surface of HS_4. The HS_4^+ cation was also investigated at the same level of calculation to evaluate the Franck−Condon correlation between the neutral and ionic surfaces.

The geometries and energy differences between the three HS_4^+ isomers, denoted as **1**$^+$, **2**$^+$, and **3**$^+$ in Figure 4, compare well with data already reported.[19c,e] The most stable species on the neutral surface is the doublet **1** with the hydrogen atom out of the S_4 plane. The neutral surface is flat at energies close to the minimum; that is, the trans isomer **2** is only slightly higher in energy, and the low barrier for the **2** → **1** isomerization disappears with the inclusion of the thermal correction to enthalphy (Table 1). Calculations of **1** and **2** were also performed at different levels of theory: for example, B3LYP/6-311++G(3*df*,3*pd*), BP86/aug-cc-pV(T+*d*)Z, MP2/aug-cc-pV-

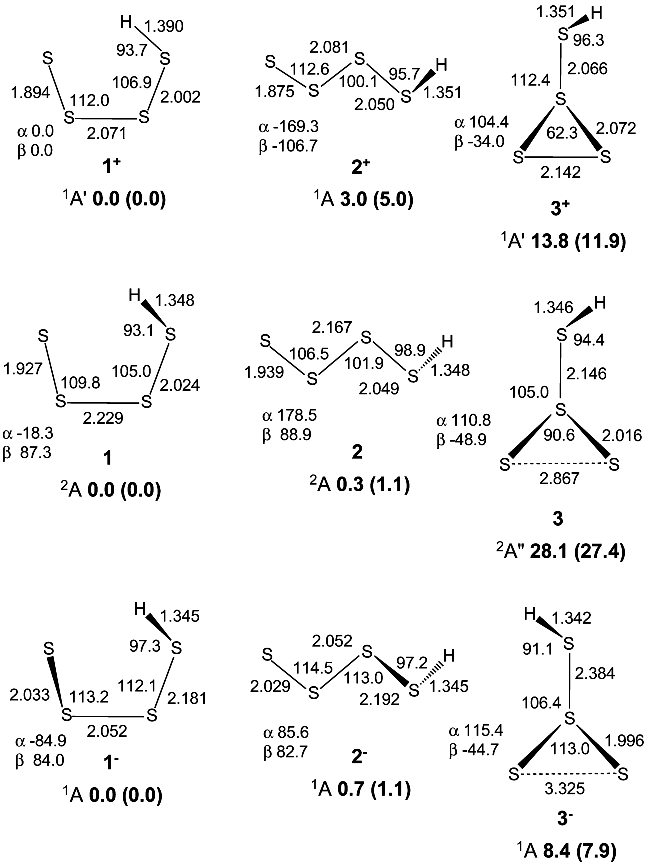

Figure 4. B3LYP-optimized geometries and relative energies (kcal mol^{-1}) at 298.15 K of HS_4^+ (**1**$^+$, **2**$^+$, **3**$^+$), HS_4 (**1**, **2**, **3**), and HS_4^- (**1**$^-$, **2**$^-$, **3**$^-$) species, with CCSD(T) relative energies in parentheses. α and *β* indicate SSSS and SSSH angles, respectively.

(T+d)Z, and CASSCF(17,13)/aug-cc-pV(T+d)Z. At 298 K, species **1** is more stable than species **2** by 0.4, 1.4, 1.7, and 1.9 kcal mol^{-1}, respectively. The barrier for the **1** → **2** isomerization disappears at 298 K at the B3LYP/6-311++G(3*df*,3*pd*) and MP2/aug-cc-pV(T+*d*)Z levels, whereas it is as low as 0.2 kcal mol^{-1} at the BP86/aug-cc-pV(T+*d*)Z level. These calculations, therefore, confirm the CCSD(T)/aug-cc-pV(T+*d*)Z//B3LYP/aug-cc-pV(T+*d*)Z results.

The doublet HS_4 **3** is significantly higher in energy than **1** and **2**. Compared to the branched ring **3**$^+$, **3** has a quite different structure because two sulfur atoms interact at long distance. The different structures of the ion and neutral determine the amount of excitation energy of the neutral formed, which is, indeed, the difference between the adiabatic and vertical recombination energy of the precursor ion. This value and the energetic features of the neutral surface are relevant to evaluate the neutrals' survival in the available time scale.

The main features of the neutral surface are the lowest dissociation limits of **1** and **3** (23.1 and 9.5 kcal mol^{-1}, respectively) and the sizable **1** → **3** isomerization energy (44.0 kcal mol^{-1}) (Table 1, Figure 5). This barrier is due to the partial cleavage of a S−S bond: going from **1** to **3**, the bond between the terminal sulfur atom (S1) and the adjacent atom (S2) is weakened, whereas a new bond is formed between S1 and the sulfur atom S3 adjacent to the SH group. In fact, the S1−S2 bond distance, which is 1.927 Å in **1** and 2.867 Å in **3**, is 2.371 Å in the saddle structure.

Consistent with the structural features illustrated in Figure 4, the excitation energy of **1** vertically formed from **1**$^+$ is 7.1 kcal mol^{-1}. In contrast, that of **3** is 25.7 kcal mol^{-1} due to the

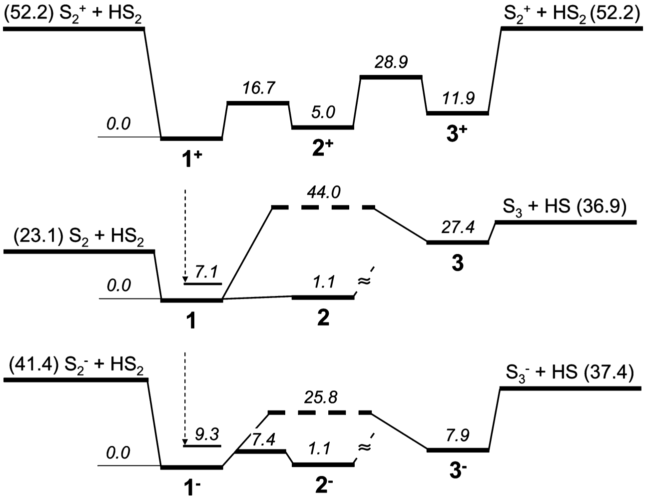

Figure 5. Simplified energy profiles relevant to the $HS_4^{+/0/-}$ species. ($\Delta H°$, kcal mol^{-1}, CCSD(T)). Vertical excitation energies of **1** and **1**$^-$ are shown by arrows.

poor Franck−Condon overlap between **3**$^+$ and **3**. As a consequence, the vertical energy of **3** is far above the dissociation energy, whereas that of **1** is far below its dissociation energy (Figure 5). Moreover, the high barrier to the **1** → **3** isomerization makes unlikely isomerizations of open-chain structures at the neutral stage, which is consistent with the finding that identical CAD spectra are recorded before and after the neutralization process. It can therefore be assessed that the open-chain HSSSS radical is definitely detected in the available time scale.

Confirming evidence is given by an alternative method to detect the HS_4 radical; that is, the vertical reduction to HS_4^-. As shown in Figure 2C, a recovery peak at m/z 129 is detected by $^+NR^-$, which is in keeping with the structures of the radical **1** and the anion **1**$^-$ (Figure 4). The vertical excitation energy of **1**$^-$ is, indeed, 9.3 kcal mol^{-1}, below its dissociation and cyclization energy (Table 1). The experimental detection of HS_4 by reduction to HS_4^- thus proves (i) the existence of a good overlap between the surfaces of the open-chain cation, neutral and anion; (ii) that HS_4 has a sizable electron affinity; and (iii) the existence of the HS_4^- anion. HS_4^- is the conjugate base of the strong acid H_2S_4, a component of the crude sulfane oil.[22] Compared to H_2S ($\Delta G_{acid} = 344.4$ kcal mol^{-1}),[21] the lowest member of the H_2S_n family, tetrasulfane is a stronger acid ($\Delta G_{acid} = 322.5$ kcal mol^{-1}) due to the ability of the HS_4^- anion to carry and distribute the negative charge.[22] This feature also accounts for the electron affinity of HS_4, 2.39 eV (CCSD(T)), higher than any of the known HS_n radicals: HS_3 (2.17 eV)[2j] and HS_2 (1.91 eV).[23]

In conclusion, we have reported the first experimental detection of the sulfur-rich HS_4 radical, which is stable by 23 kcal mol^{-1} toward the dissociation into S_2 and HS_2 and is characterized by a high electron affinity, giving HS_4^- by electron recombination. These results confirm the sulfur's ability to stabilize the bonding in polysulfur species, in line with the structure and properties that are peculiar to elemental sulfur clusters.

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JP9036556