White Phosphorus Is Air-Stable Within a Self-Assembled Tetrahedral Capsule

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batic sweep width, there was some loss of intensity due to diffusion (Fig. 4B). These losses could be reduced with the scheme of Fig. 1E, as shown in Fig. 4C for a total of six adiabatic pulses of 6-ms duration (instead of two otherwise identical pulses of 18 ms each, as in Fig. 4B). The linewidth in Fig. 4C is about 70 Hz. Increasing the gradient strength further to 11 G/cm (~140 ppm or ~84 kHz) led to the spectrum in Fig. 4D. In this case, the signal amplitude suffers not only from diffusion losses, but also from the limited rf amplitude (25 kHz) of the initial $\pi/2$ pulse. In stronger gradients, one should use a large number of short inversion pulses that cover a very broad bandwidth with the desired phase profile. In addition, the (possibly frequency-swept) $\pi/2$ pulses should excite the full bandwidth uniformly, bearing in mind that a linear dependence of the phase with respect to offset is allowed.

References and Notes

1. G. Eidmann, R. Savelsberg, P. Blumler, B. Blümich, *J. Magn. Reson. A* **122**, 104 (1996).
2. B. Blümich, J. Perlo, F. Casanova, *Prog. Nucl. Magn. Reson. Spectrosc.* **52**, 197 (2008).
3. Y.-Y. Lin et al., *Phys. Rev. Lett.* **85**, 3732 (2000).
4. B. Shapira, K. Shetty, W. W. Brey, Z. Gan, L. Frydman, *Chem. Phys. Lett.* **442**, 478 (2007).
5. I. J. Cox et al., *J. Magn. Reson.* **70**, 163 (1986).
6. C. E. Mountford, S. Doran, C. L. Lean, P. Russell, *Chem. Rev.* **104**, 3677 (2004).
7. E. L. Hahn, *Phys. Rev.* **80**, 580 (1950).
8. H. Y. Carr, E. M. Purcell, *Phys. Rev.* **94**, 630 (1954).
9. E. L. Hahn, D. E. Maxwell, *Phys. Rev.* **88**, 1070 (1952).
10. R. L. Vold, S. O. Chan, *J. Chem. Phys.* **53**, 449 (1970).
11. R. Freeman, H. D. W. Hill, *J. Chem. Phys.* **54**, 301 (1971).
12. C. A. Meriles, D. Sakellariou, H. Heise, A. J. Moulé, A. Pines, *Science* **293**, 82 (2001).
13. V. Demas et al., *Concepts Magn. Reson. B* **29B**, 137 (2006).
14. J. Perlo et al., *Science* **308**, 1279 (2005); published online 7 April 2005 (10.1126/science.1108944).
15. B. Shapira, L. Frydman, *J. Am. Chem. Soc.* **126**, 7184 (2004).
16. B. Shapira, L. Frydman, *J. Magn. Reson.* **182**, 12 (2006).
17. A. Wokaun, R. R. Ernst, *Chem. Phys. Lett.* **52**, 407 (1977).
18. K. Nagayama, K. Wüthrich, R. R. Ernst, *Biochem. Biophys. Res. Commun.* **90**, 305 (1979).
19. L. Frydman, T. Scherf, A. Lupulescu, *Proc. Natl. Acad. Sci. U.S.A.* **99**, 15858 (2002).
20. P. Pelupessy, *J. Am. Chem. Soc.* **125**, 12345 (2003).
21. P. Giraudeau, S. Akoka, *J. Magn. Reson.* **186**, 352 (2007).
22. L. Frydman, A. Lupulescu, T. Scherf, *J. Am. Chem. Soc.* **125**, 9204 (2003).
23. S. Vathyam, S. Lee, W. S. Warren, *Science* **272**, 92 (1996).
24. G. Galiana, R. T. Branca, W. S. Warren, *J. Am. Chem. Soc.* **127**, 17574 (2005).
25. P. Giraudeau, S. Akoka, *J. Magn. Reson.* **195**, 9 (2008).
26. P. J. McDonald, *Prog. Nucl. Magn. Reson. Spectrosc.* **30**, 69 (1997).
27. P. Pelupessy, L. Duma, G. Bodenhausen, *J. Magn. Reson.* **194**, 169 (2008).
28. E. Kupce, R. Freeman, *J. Magn. Reson. A* **115**, 273 (1995).
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White Phosphorus Is Air-Stable Within a Self-Assembled Tetrahedral Capsule

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The air-sensitive nature of white phosphorus underlies its destructive effect as a munition: Tetrahedral P$_4$ molecules readily react with atmospheric dioxygen, leading this form of the element to spontaneously combust upon exposure to air. Here, we show that hydrophobic P$_4$ molecules are rendered air-stable and water-soluble within the hydrophobic hollows of self-assembled tetrahedral container molecules, which form in water from simple organic subcomponents and iron(II) ions. This stabilization is not achieved through hermetic exclusion of O$_2$ but rather by constriction of individual P$_4$ molecules; the addition of oxygen atoms to P$_4$ would result in the formation of oxidized species too large for their containers. The phosphorus can be released in controlled fashion without disrupting the cage by adding the competing guest benzene.

Microenvironment alters behavior in chemical systems; encapsulation within the inner phase (*1–3*) of a molecular container can accelerate a reaction (*4–7*), change a reaction's course (*7–11*), perturb equilibria (*11–13*), or prevent the oligomerization of a reactive species such as a cyclotrisiloxane (*14*) or cyclobutadiene (*15*). The lifetimes of such fleeting molecules as hemiaminals (*16*), benzyne (*17*), and cycloheptatriene (*18*) may also be extended long enough to permit spectroscopic observation. Here, we show how encapsulation can render molecules of white phosphorus (P$_4$) air-stable through a constrictive mechanism.

The P-P bonds of tetrahedral P$_4$ (white phosphorus) are weak (200 kJ mol^{-1}) (*19*), leading to a low activation barrier to oxidation, and the P-O bonds of combustion products are strong (330 to 650 kJ mol^{-1}) (*19*), releasing substantial energy during their formation. P$_4$ is thus violently pyrophoric; its slow chemiluminescent combustion when O$_2$ is limited ["phosphorescence," the meaning of which has since changed (*20*)] defined the element's essence for the first chemists.

We have described the preparation of tetrahedral cage **1** in aqueous solution from the subcomponents shown in Fig. 1 (*21*). When an aqueous solution of **1** was left in contact with solid white phosphorus, uptake of P$_4$ converted **1** into the host-guest complex P$_4 \subset$**1** (Fig. 1) (*22*). Vapor diffusion of acetone into an aqueous solution yielded crystalline P$_4 \subset$**1** in 91% yield.

Incorporation of P$_4$ into **1** was marked by changes in the ^{1}H nuclear magnetic resonance (NMR) chemical shifts of **1** (fig. S1) and by the appearance of a single resonance in the ^{31}P NMR spectrum at –510 parts per million (ppm). Single crystals of sufficient quality for x-ray diffraction were grown by vapor diffusion of 1,4-dioxane into an aqueous solution of P$_4 \subset$**1**. Its x-ray crystal structure is shown in Fig. 2.

The quality and resolution of the diffraction data, although limited, allow for unambiguous assignment of the cage's conformation and the placement of the guest within the cage, where it is disordered between two orientations (only one of

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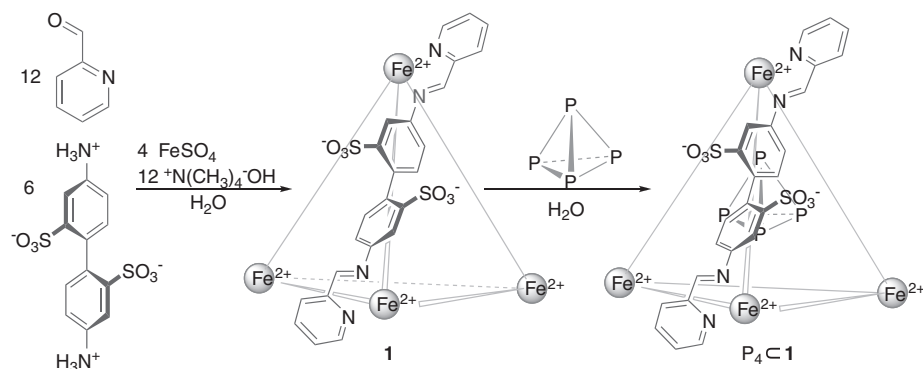
Fig. 1. Synthesis of tetrahedral cage **1** and subsequent incorporation of P$_4$.

which is shown in Fig. 2) (*22*) and stabilized through van der Waals interactions with the hydrophobic phenylene groups lining the cage's interior (*23, 24*). Apart from crystalline white phosphorus (*25*), previous structures of intact P_4 tetrahedra have involved tight coordination to a transition-metal fragment (*26–28*).

Within **1**, P_4 became water-soluble and air-stable; ^{1}H NMR spectra of solid samples and aqueous solutions of $P_4 \subset \mathbf{1}$ were unchanged after contact with the atmosphere over 4 months. This behavior contrasts markedly with that of naked P_4, infamous for its pyrophoric nature. Inspection of the crystal structure of $P_4 \subset \mathbf{1}$ reveals a pore of
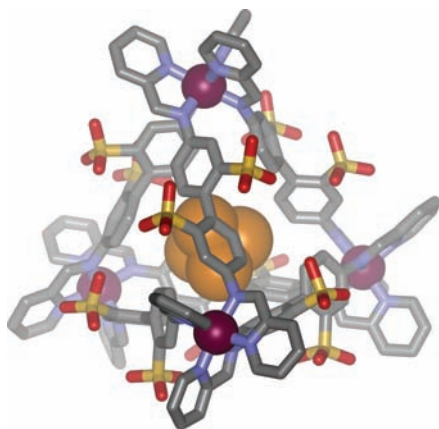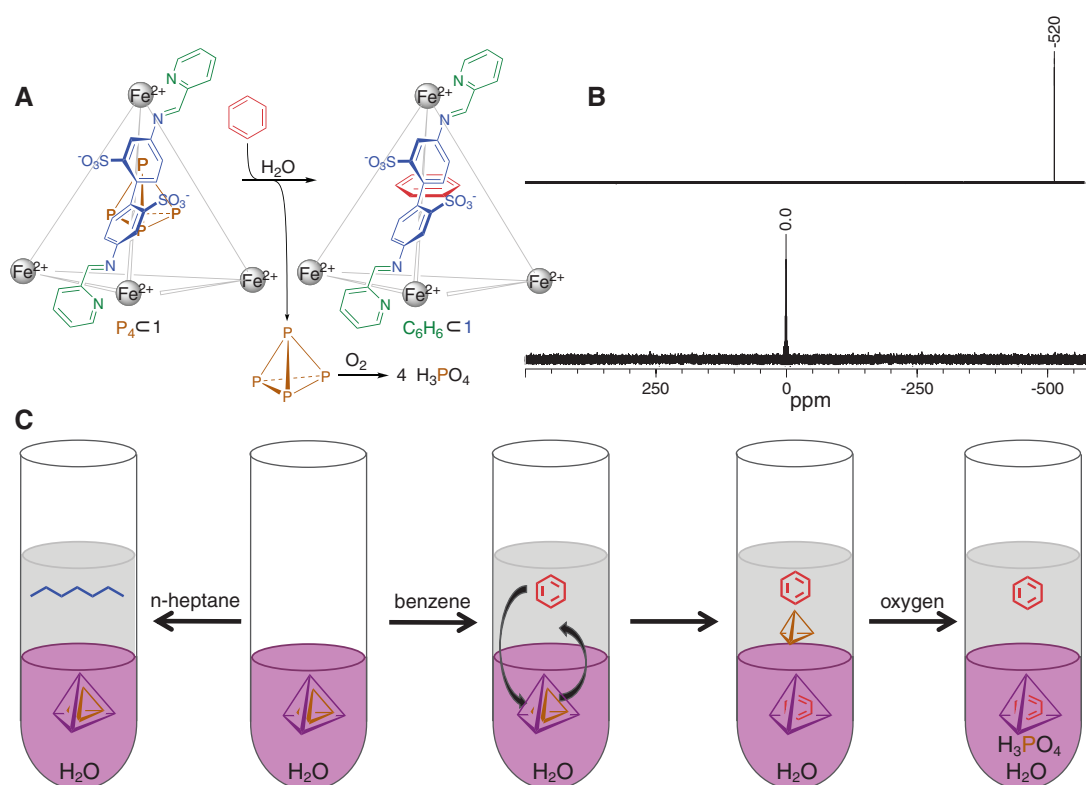
Fig. 2. Crystal structure of $P_4 \subset \mathbf{1}$. Solvent molecules, counterions, and hydrogen atoms are omitted for clarity. Fe, violet; N, blue; C, gray; O, red; S, yellow; P, orange.

1.0 Å radius in each face of the tetrahedron; although this distance is smaller than the radial cross-section of O_2 (1.4 Å), thermal fluctuations in **1** would be expected to transiently open the cage sufficiently to let O_2 inside, analogously to what presumably occurs during P_4 uptake. We thus attribute encapsulated P_4's remarkable O_2 stability not to the cage's ability to exclude dioxygen but rather to the constriction applied by the confining capsule: The reaction of O_2 with P_4 would generate an intermediate product too large for the cavity of **1**. Modeling suggests that even the insertion of a single oxygen atom into a P-P bond of P_4, or the capping of one P atom of P_4 with an oxygen atom to create a P=O moiety, would require a transition state that could not fit within the hollow of **1** without deformation. This hypothesis is supported by the observation that P_4 within **1** did not react with the single–oxygen atom transfer reagents nitrous oxide or pyridine N-oxide after prolonged exposure (*22*). This constrictive stabilization of a reactive solid thus serves as a counterpoint and complement to the high effective gas pressures that may be observed within molecularly confined spaces (*29*).

Although P_4 appeared to be indefinitely stable within **1**, extracting guest from host through the addition of a competing guest proved to be straightforward. As illustrated in Fig. 3C, the addition of an equal volume of benzene to an aqueous solution of $P_4 \subset \mathbf{1}$ resulted in the quantitative extraction of P_4 from **1** into the benzene layer, as evidenced by the appearance of a ^{31}P NMR peak at –520 ppm with concomitant formation of aqueous $C_6H_6 \subset \mathbf{1}$, as observed by ^{1}H NMR. (Cyclohexane was also

demonstrated to work; see fig. S2.) The essential role played by benzene as a competing guest is highlighted by the outcome of an analogous experiment carried out with *n*-heptane (Fig. 3C), which resulted in no extraction of P_4 from **1**, despite the solubility of P_4 in this solvent. Heptane is a poor guest for **1**, whereas benzene is a good one: Extraction of P_4 thus requires not only the "pull" of a solvent that can extract P_4, but also the "push" of a competing guest that is capable of displacing it.

P_4, once extracted into benzene, regained its air-sensitivity. After exposure to the atmosphere for 24 hours at 323 K, no further evidence was observed by ^{31}P NMR for P_4 in the benzene layer. The aqueous layer, however, showed a new ^{31}P NMR resonance at 0 ppm, attributed to phosphoric acid. Benzene thus mediated the oxidation of P_4, although all phosphorus came from, and ended up in, the aqueous phase.

Only 3.5% phosphorus by mass is contained within $P_4 \subset \mathbf{1}$; however, our capsule is reusable, and the safety benefits of using **1** as a carrier are substantial: **1** could facilitate the handling and use of white phosphorus and could potentially be used directly as a means of cleaning up highly dangerous phosphorus spills. More generally, the method of constrictive encapsulation could find applications in the protection and controlled release of sensitive molecules or alternatively the protection of the environment through the sequestration of hazardous substances. Larger analogs of **1**, whose preparations are currently underway, may serve to stabilize and isolate larger and more complex guest species.

Fig. 3. Extraction of P_4 from **1** by *n*-heptane is not possible, whereas replacing P_4 with another suitable guest (benzene or cyclohexane) results in the facile removal of P_4 into the organic solvent. (**A**) Reaction scheme. (**B**) ^{31}P NMR spectra of P_4 extracted into the benzene layer (top) and phosphoric acid found in the aqueous layer after reaction of P_4 in benzene with oxygen (bottom). (**C**) Schematic representation of the extraction process.

References and Notes

1. D. J. Cram, *Nature* **356**, 29 (1992).
2. D. M. Vriezema *et al.*, *Chem. Rev.* **105**, 1445 (2005).
3. L. R. MacGillivray, J. L. Atwood, *Angew. Chem. Int. Ed.* **38**, 1018 (1999).
4. J. M. Kang, G. Hilmersson, J. Santamaria, J. Rebek, *J. Am. Chem. Soc.* **120**, 3650 (1998).
5. M. Marty, Z. Clyde-Watson, L. J. Twyman, M. Nakash, J. K. M. Sanders, *Chem. Commun. (Camb.)* 2265 (1998).
6. C. J. Hastings, D. Fiedler, R. G. Bergman, K. N. Raymond, *J. Am. Chem. Soc.* **130**, 10977 (2008).
7. M. Yoshizawa, M. Tamura, M. Fujita, *Science* **312**, 251 (2006).
8. M. Yoshizawa, Y. Takeyama, T. Okano, M. Fujita, *J. Am. Chem. Soc.* **125**, 3243 (2003).
9. D. R. Benson, R. Valentekovich, F. Diederich, *Angew. Chem. Int. Ed. Engl.* **29**, 191 (1990).
10. M. Kuil, T. Soltner, P. van Leeuwen, J. N. H. Reek, *J. Am. Chem. Soc.* **128**, 11344 (2006).
11. M. D. Pluth, R. G. Bergman, K. N. Raymond, *Science* **316**, 85 (2007).
12. V. M. Dong, D. Fiedler, B. Carl, R. G. Bergman, K. N. Raymond, *J. Am. Chem. Soc.* **128**, 14464 (2006).
13. L. Trembleau, J. Rebek, *Science* **301**, 1219 (2003).
14. M. Yoshizawa, T. Kusukawa, M. Fujita, K. Yamaguchi, *J. Am. Chem. Soc.* **122**, 6311 (2000).
15. D. J. Cram, M. E. Tanner, R. Thomas, *Angew. Chem. Int. Ed. Engl.* **30**, 1024 (1991).
16. T. Iwasawa, R. J. Hooley, J. Rebek Jr., *Science* **317**, 493 (2007).
17. R. Warmuth, *Angew. Chem. Int. Ed. Engl.* **36**, 1347 (1997).
18. R. Warmuth, M. A. Marvel, *Angew. Chem. Int. Ed.* **39**, 1117 (2000).
19. F. S. Dainton, *Trans. Faraday Soc.* **43**, 244 (1947).
20. P. R. Lewis, C. Price, *Polymer (Guildf.)* **12**, 258 (1971).
21. P. Mal, D. Schultz, K. Beyeh, K. Rissanen, J. R. Nitschke, *Angew. Chem. Int. Ed.* **47**, 8297 (2008).
22. Materials and methods are available as supporting material on *Science* Online.
23. C. L. D. Gibb, B. C. Gibb, *J. Am. Chem. Soc.* **126**, 11408 (2004).
24. E. Botana, E. Da Silva, J. Benet-Buchholz, P. Ballester, J. de Mendoza, *Angew. Chem. Int. Ed.* **46**, 198 (2007).
25. D. E. C. Corbridge, E. J. Lowe, *Nature* **170**, 629 (1952).
26. A. P. Ginsberg, W. E. Lindsell, K. J. McCullough, C. R. Sprinkle, A. J. Welch, *J. Am. Chem. Soc.* **108**, 403 (1986).
27. M. Peruzzini *et al.*, *Eur. J. Inorg. Chem.* 931 (1999).
28. I. Krossing, L. Van Wullen, *Chem. Eur. J.* **8**, 700 (2002).
29. D. Ajami, J. Julius Rebek, *Angew. Chem. Int. Ed.* **47**, 6059 (2008).
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Trapping Molecules on a Chip

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Magnetic trapping of atoms on chips has recently become straightforward, but analogous trapping of molecules has proved to be challenging. We demonstrated trapping of carbon monoxide molecules above a chip using direct loading from a supersonic beam. Upon arrival above the chip, the molecules are confined in tubular electric field traps ~20 micrometers in diameter, centered 25 micrometers above the chip, that move with the molecular beam at a velocity of several hundred meters per second. An array of these miniaturized moving traps is brought to a standstill over a distance of only a few centimeters. After a certain holding time, the molecules are accelerated off the chip again for detection. This loading and detection methodology is applicable to a wide variety of polar molecules, enabling the creation of a gas-phase molecular laboratory on a chip.

The manipulation of atoms above a chip using magnetic fields produced by current-carrying wires is a mature field of research (*1*). This field was inspired by the notion that miniaturization of magnetic field structures enables the creation of large field gradients, i.e., large forces and steep potential wells for atoms. Modern microelectronics technology makes it possible to integrate the multiple tools underlying these experiments onto a compact surface area. Such atom chips have been used to demonstrate rapid Bose-Einstein condensation (*2*) and have found applications in matter-wave interferometry and in inertial and gravitational field sensing (*3*). Likewise, the engineering of miniaturized electric field structures holds great promise for the manipulation of polar molecules above a chip (*4*). The latter might enable, for instance, the implementation of proposed schemes of quantum computation that use polar molecules as qubits (*5*, *6*). Here, we experimentally demonstrate a method for loading and detecting molecules on

a chip, adding to the recent advances in the taming of molecular beams (*7*).

A schematic of the experimental setup with an expanded view of the chip with the array of microelectrodes, all contained in a compact high-vacuum machine, is shown in Fig. 1. The chip consists of a total of 1254 equidistant 10-μm-wide gold electrodes with a 40-μm center-to-center distance deposited onto a glass substrate, forming a structure that is 5 cm long (micro resist technology GmbH). All electrodes extend over a central 4-mm region, whereas outside this region the electrodes extend alternately to the left or right and terminate at three different lengths. Via the square pads and the nickel wires that are connected to every third electrode on either side of the array, six different potentials are applied to the electrodes. These potentials are described by $\pm V_0[1 + \cos(2\pi\nu t + \phi_n)]$, with exclusively positive (or negative) potentials applied to a given side of the array. Within each polarity set, three different phases ϕ_n with a mutual phase difference of $\pm 2\pi/3$ are used. In this way, tubular minima of electric field strength are generated every 120 μm, and these minima move over the chip with a speed given by 120 μm × ν (in MHz) at a constant height of about 25 μm. The diameter of the tubular

electric field minima is about 20 μm, and with $V_0 = 80$ V, their depth is about 4 kV/cm. The two ends of the 4-mm-long tubular minima are closed in the present design by the fringe fields near the ends of the electrodes. A detailed description of the generation of the moving tubular electric field traps above this particular chip is given elsewhere (*4*, *8*); a pictorial representation of the tubular traps above the chip, indicated in blue, is shown in the lower panel of Fig. 1.

The experiments here were performed with CO molecules in the low-field–seeking levels of the metastable $a^3\Pi_1$ ($v' = 0$, $J' = 1$) state. For these molecules, the electric field minima correspond to traps with a depth of about 50 mK when a constant frequency ν is applied. When the frequency ν is changed linearly in time, i.e., when a constant acceleration is applied, the diameter and depth of the traps decrease but three-dimensional confinement is maintained up to an acceleration of about 1.5×10^6 m/s². In the low–electric field region around the long axis of the trap, molecules can be lost due to nonadiabatic transitions to nontrappable degenerate states (*9*). In magnetic traps for atoms on a chip, this hole at the center of the trap is commonly plugged by adding a homogeneous magnetic field. An offset magnetic field could also be added in the present setup. For molecules in electric traps, however, there often exists the unique alternative solution to simply select an isotopologue with a favorable hyperfine level structure such that there is no degeneracy between trappable and nontrappable states in zero electric field (*10*). The most abundant carbon monoxide isotopologue, $^{12}C^{16}O$, has no hyperfine structure, and the low-field–seeking $M\Omega = -1$ level of the $a^3\Pi_1$ ($v' = 0$, $J' = 1$) state is degenerate with the $M = 0$ level in zero electric field, making this species susceptible to nonadiabatic transitions. In $^{13}C^{16}O$, however, the coupling of the nuclear spin of the ^{13}C nucleus with the orbital angular momentum results in a lifting of this degeneracy. As shown in the inset of Fig. 2, the low-field–seeking

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