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Synthesis and Characterization of Ethylidynearsine

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Abstract: Ethynylarsine (**2a**) is synthesized by reaction of arsenic trichloride with ethynyltributylstannane followed by a chemoselective reduction of the formed ethynyldichloroarsine (**1a**). The base-induced rearrangement of compound **2a** on a solid base in VGSR conditions leads to ethylidynearsine (**3a**) characterized by ^1H and ^{13}C NMR and by microwave spectroscopy. The rotational spectrum of **3a** is recorded in the frequency range 90–470 GHz. Rotational and centrifugal distortion constants are determined and the quadrupole hyperfine structure is analyzed. The structure of $CH_3C{\equiv}As$ has been estimated from the rotational constants of eight different isotopic species and from *ab initio* calculations. Compound **3a** exhibits a low stability at 0 °C in deuteriochloroform ($\tau_{1/2}$ ca. 1 h) or in the gaseous phase at a pressure of 10 Pa ($\tau_{1/2}$ ca. 30 min).

Introduction

Although numerous phosphaalkynes have been described in the literature,[1] few experimental results have been reported on the corresponding arsenic derivatives, the arsaalkynes. Only the kinetically stabilized 2-(2,4,6-tri-*tert*-butylphenyl)-1-arsaethyne has been isolated until now.[2] The chemical trapping of *tert*-butylarsaalkyne (t-BuC≡As) has recently been described, but all the attempts to spectroscopically characterize this derivative have failed.[3] This is not very surprising since compounds containing an $-As{=}C<$ bond such as arsinines[4] and arsaalkenes[5] are less stable than the corresponding phosphorus derivatives. In a previous paper, some of us have reported the base-induced rearrangement of ethynylphosphines into the corresponding phosphaalkynes.[6] We now report the chemoselective reduction of ethynyldichloroarsine (**1a**) into the corresponding ethynylarsine (**2a**) and the base-induced rearrangement of **2a** into ethylidynearsine (**3a**). Spectroscopic characterization of arsaalkyne **3a** was performed by low-temperature ^1H and ^{13}C NMR and by microwave spectroscopy.

Experimental Section

Caution: Arsines are potentially highly toxic molecules. All reactions and handling should be carried out in a well-ventilated hood.

Materials. Arsenic trichloride (Strem), dibutyl ether, and decahydronaphthalene (Janssen) and acetylene ($H^{12}C{\equiv}^{12}CH$ (Alphagaz) and $H^{13}C{\equiv}^{13}CH$ (Euriso-Top, CEA)) were used without further purification. Tributylethynylstannane (**4a**),[7] ethynylenebis(triethylstannane), ethynylenebis(tributylstannane),[7] tributylstannane,[8] and tributylstannane-*d*[9] were prepared as previously reported.

General. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-300P spectrometer. The spectra of the parent compounds are fully described; the chemical shifts of the isotopic species are almost identical with those of the corresponding parent compound and only the J_{CD} and J_{CC} coupling constants are given. IR spectra were obtained using a Perkin-Elmer 1420 spectrometer and HRMS (high resolution mass spectrometry) experiments were performed on a Varian MAT 311 instrument. Special equipment was used for recording the IR spectrum of **2a** in the gas phase: a small Pyrex tube (l = 10 cm, i.d. = 3 cm) equipped with a stopcock and sealed at each extremity with a KBr window was filled with pure ethynylarsine to a pressure of 100 hPa. To record the mass spectrum, ethynylarsine (**2a**) was directly introduced from a cell into the ionization chamber of the spectrometer.

Triethyl(ethynyl-*d*)stannane (4b). The procedure of Bogoradovski *et al.* has been modified.[10] A mixture of 50 mmol of ethynylenebis(triethylstannane)[7] and 55 mmol of 1-butanethiol-*d* (prepared by addition of D_2O on acetyl chloride followed by bubbling of the formed DCl in an etheral solution of 1-butanethiol, sodium salt) was stirred for 3 h at 80 °C. By distillation, compound **4b** was isolated in a 62% yield: bp$_{0.1}$ 66 °C ($^1J_{CD}$ = 35.5 Hz (t)).

Tributyl(ethynyl-*$^{13}C_2$*)stannane (4c). This compound was prepared by the reported procedure[7] from acetylene-*$^{13}C_2$* ($^1J_{CC}$ = 117.4 Hz (d)).

Tributyl(ethynyl-*$^{13}C_2$,d*)stannane (4d). This compound was prepared by the procedure given above for **4b** from (ethynylene-*$^{13}C_2$*)bis(tributylstannane) and 1-butanethiol-*d*.

Ethynylarsinous Dichloride (1a). In a 25-mL two-necked round-bottomed flask equipped with a nitrogen gas inlet was introduced arsenic trichloride (2.0 g, 11 mmol). The reagent was frozen to −40 °C and the ethynyltributylstannane (3.2 g, 10 mmol) was added. The solution was then vigorously stirred and allowed to warm to room temperature over 10 min. Distillation of the volatile compounds gave a mixture containing ethynylarsinous dichloride (**1a**) (yield (crude product): 75%) in the presence of impurities, diethynylarsinous chloride (7%) [^1H NMR (300 MHz, $CDCl_3$) δ 3.14 (s, $H{\equiv}$); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 82.0 (d, $^2J_{CH}$ = 44.3 Hz, $\equiv C-As$), 97.1 (d, $^1J_{CH}$ = 250.2 Hz, $\equiv CH$)], triethynylarsine[11] (18%), and arsenic chloride (20%). Purification of arsine **1a** by trap-to-trap distillation led to a significant loss of product. Therefore, the crude mixture was used in the following step without further purification. Crude **1a** must be kept at low temperature (−20 °C): ^1H NMR (300 MHz, $CDCl_3$) δ 3.43 (s, $H{\equiv}$); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 87.9 (d, $^2J_{CH}$ = 43.2 Hz, $\equiv C-As$), 99.9 (d, $^1J_{CH}$ = 251.5 Hz, $\equiv CH$).

(Ethynyl-*d*)arsinous Dichloride (1b). This compound was prepared by the procedure given above from (triethylethynyl-*d*)stannane (**4b**) ($^1J_{CD}$ = 19.3 Hz (t)).

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(Ethynyl-$^{13}C_2$)arsinous Dichloride (1c). This compound was prepared by the procedure given above from (tributylethynyl-$^{13}C_2$)stannane (**4c**) ($^1J_{CC}$ = 146.2 Hz (d)).

(Deuterioethynyl-$^{13}C_2$,*d*)arsinous Dichloride (1d). This compound was prepared by the procedure given above from (ethynyl-$^{13}C_2$,*d*)tributylstannane (**4d**).

Ethynylarsine (2a). In a 50-mL two-necked flask were introduced Bu_3SnH[12] (8.7 g, 30 mmol) and decahydronaphthalene (10 mL). The flask was fitted on a vacuum line equipped with a stopcock, a cold trap, and a cold finger.[13] In an other flask, a solution of crude arsine **1a** (8.0 mmol) in decahydronaphthalene (5 mL) was degassed and slowly transferred through a flex-needle onto the reducing mixture. To limit oligomerization, ethynylarsine was distilled off in vacuo from the reaction mixture during the course of the addition of **1a**. High boiling impurities were selectively trapped in the cold trap (–95 °C) and ethynylarsine (**2a**) was condensed with a cosolvent on the cold finger (–196 °C). After disconnection from the vacuum line, the apparatus was filled with dry nitrogen and the cold finger was allowed to warm to room temperature. Thus, compound **2a** was collected in a Schlenk flask or in a NMR tube and was kept at low temperature (-40 °C) (similar results were obtained using an excess of Bu_3SnH in absence of solvent or using $AlHCl_2$[13] diluted in ethoxyethyl ether as reducing agent): 0.28 g, 34%; ^1H NMR (300 MHz, $CDCl_3$, –30 °C) δ 2.37 (t, $^4J_{HH}$ = 2.8 Hz, H—C≡), 3.40 (d, $^4J_{HH}$ = 2.8 Hz, H_2As); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 71.5 (dt, $^2J_{CH}$ = 45.6 Hz, $^2J_{CH}$ = 6.6 Hz, ≡C—As), 92.6 (dt, $^1J_{CH}$ = 245.3 Hz, $^3J_{CH}$ = 3.8 Hz, ≡C—H); IR (gaseous phase, 100 hPa, cm^{-1}) $\nu_{\equiv CH}$ 3318, $\nu_{C\equiv C}$ 2180, ν_{As-H} 2118; HRMS calcd for C_2H_3As 101.9451, obsd 101.945; MS, *m/z* (rel intensity) 103 (4), 102 (100), 101 (64), 100 (26), 99 (10), 76 (14), 75 (35); CAD 101, 100; CAD-MIKE 101, 100, 87, 75, 27.

(Ethynyl-*d*)arsine (2b). This compound was prepared by the procedure given above from (ethynyl-*d*)arsinous dichloride (**1b**) using tributylstannane as reducing agent ($^1J_{CD}$ = 32.1 Hz (t), $^2J_{CD}$ = 7.1 Hz (t)).

Ethynylarsine-d_2 (2c). This compound was prepared by the procedure given above from ethynylarsinous dichloride (**1a**) and tributylstannane-*d*.

(Ethynyl-*d*)arsine-d_2 (2d). This compound was prepared by the procedure given above from (ethynyl-*d*)arsinous dichloride (**1b**) and tributylstannane-*d* as reducing agent.

(Ethynyl-$^{13}C_2$)arsine (2e). This compound was prepared by the procedure given above from (ethynyl-$^{13}C_2$)arsinous dichloride (**1c**) ($^1J_{CC}$ = 147.2 Hz (d)).

(Ethynyl-$^{13}C_2$,*d*)arsine-d_2 (2f). This compound was prepared by the procedure given above from (ethynyl-*d*)arsinous dichloride (**1d**) and tributylstannane-*d*.

Ethylidynearsine (3a). The reaction was performed under VGSR conditions.[14] Powdered and dried sodium carbonate (15 g) was introduced into a VGSR reactor (*l* = 30 cm, i.d. = 3.5 cm Pyrex tube) and then horizontally distributed between two pads of glass wool 20 cm distant from each other. This reactor was fitted onto a vacuum line equipped with a cold trap and a cold finger. Ethynylarsine (**2a**) (0.51 g, 5.0 mmol) diluted in dibutyl ether (30 mL) and cooled at –70 °C was fitted on the vacuum line. Pure ethynylarsine (**2a**) was slowly vaporized *in vacuo* through the reactor heated to 80 °C. Ethylidynearsine (**3a**) and a cosolvent were condensed on the cold finger (–196 °C). After disconnection from the vacuum line, the apparatus was filled with dry nitrogen and the cold finger was allowed to warm to room temperature. Thus, compound **3a** was collected in a Schlenk flask or in a NMR tube and was kept at low temperature (–60 °C) (0.15 g, 29%): ^1H NMR (300 MHz, $CDCl_3$, –30 °C) δ 2.09 (s, CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, –30 °C) δ 24.2 (q, $^1J_{CH}$ = 132.0 Hz, CH_3), 196.4 (q, $^2J_{CH}$ = 12.5 Hz, C≡As).

Ethylidynearsine-*d* (3b). This compound was prepared by the procedure given above from (ethynyl-*d*)arsine (**2b**) ($^1J_{CD}$ = 19.6 Hz (t)).

Ethylidynearsine-d_2 (3c). This compound was prepared by the procedure given above from ethynylarsine (**2c**).

Ethylidynearsine-d_3 (3d). This compound was prepared by the procedure given above from (ethynyl-*d*)arsine-d_2 (**2d**).

Ethylidynearsine-$^{13}C_2$ (3e). This compound was prepared by the procedure given above from (ethynyl-$^{13}C_2$)arsine (**2e**) ($^1J_{CC}$ = 41.3 Hz (d)).

Ethylidynearsine-$^{13}C_2$,d_3 (3f). This compound was prepared by the procedure given above from (ethynyl-$^{13}C_2$,*d*)arsine-d_2 (**2f**).

Microwave Spectroscopy. Rotational spectra in the frequency range 90–200 GHz were measured with a computer controlled millimeterwave spectrometer using superheterodyne detection.[15] This spectrometer uses klystrons or Gunn diodes followed by Schottky diodes as multiplier or mixer for the source oscillator as well as for the local oscillator. The signal was averaged and filtered and the line frequencies were calculated by a Macintosh II computer using the LabView software. The lines between 200 and 470 GHz were measured with a source-modulated spectrometer using either phase-stabilized submillimeter BWOs (range 340–470 GHz) or harmonics of a Gunn diode as sources and a He-cooled InSb bolometer as detector. This spectrometer uses the same signal processing system as the superheterodyne spectrometer. A Schlenk flask containing a mixture of ethynylarsine in dibutyl ether at –40 °C was adapted at an extremity of a Pyrex tube (*l* = 8 cm, i.d. = 2 cm) containing solid sodium carbonate and heated to 80 °C. The other extremity of the tube was directly connected to the absorption cell.

Quantum Mechanical Methods. *Ab initio* calculations were performed with the GAUSSIAN 92[16] series of programs. The chemically inert, core electrons were replaced by an effective core potential where relativistic effects are incorporated. For that purpose the LANL1DZ basis set[17] was employed. Electron correlation effects were included at the MP2 level.

Ethylidynearsine was pumped over sodium carbonate heated to 80 °C, and the resultant products were directly introduced in the cell. We did not attempt to purify ethylidynearsine because of its great instability. All spectra were measured at room temperature. The lifetime of the species in the closed cell was more than 30 min. The accuracy of the measurements was better than 50 kHz.

Results

Few studies have been devoted to functional ethynylarsines[18] and no primary or secondary ethynylarsine has been described up to now. We have prepared ethynylarsinous dichloride (**1a**) by condensation of ethynyltributylstannane onto arsenic trichloride. After distillation, arsine **1a** is obtained in the presence of arsenic trichloride, diethynylarsinous chloride, and triethynylarsine.[11] Purification by trap-to-trap distillation leads to a significant loss of product. The reduction of the crude mixture using tributylstannane (Bu_3SnH)[12] in decahydronaphthalene leads after purification by trap-to-trap distillation to ethynylarsine (**2a**) in pure form (yield 34%). The structure is assigned on the basis of IR, HRMS, and low-temperature (–30 °C) NMR spectra. The ^1H NMR spectrum of **2a** shows a triplet at δ 2.37 and a doublet at δ 3.40 ($^4J_{HH}$ = 2.8 Hz); these two signals are assigned to ≡C—*H* and As—H_2, respectively. The ^{13}C NMR spectrum shows two signals at δ 71.5 for As—*C*≡ and δ 92.6 for ≡*C*—H with coupling constants $^2J_{CH}$ = 45.6 Hz and $^1J_{CH}$ = 245.3 Hz, respectively, which are characteristic of acetylenic derivatives. The ^{13}C–^{13}C coupling constant of 147.2 Hz has been determined from the NMR spectra of the compound **2e** and is consistent with

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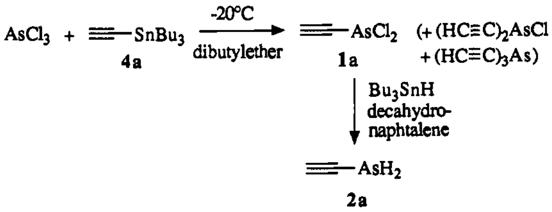
Table 1. Measured Ground-State Rotational Frequencies (MHz) of $CH_3C{\equiv}As$

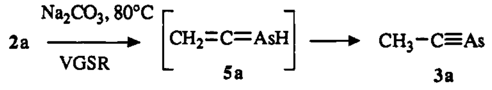
J	K	F_{exp}	e – c[a]	J	K	F_{exp}	e – c[a]	J	K	F_{exp}	e – c[a]
13	3	98 419.347	–0.006	21	2	154 654.476	–0.005	61	7	435 214.083	0.017
13	9	98 343.062	0.063	21	3	154 646.124	–0.021	61	8	435 144.812	–0.054
13	10	98 322.995	0.102	21	4	154 634.507	0.029	61	9	435 066.480	–0.020
13	11	98 300.811	0.120	21	5	154 619.589	0.106	61	10	434 979.002	0.013
13	12	98 276.541	0.141	21	7	154 579.539	0.012	61	11	434 882.349	–0.010
20	0	147 632.954	0.023	21	8	154 554.570	–0.007	65	0	463 464.823	0.008
20	1	147 631.325	–0.014	21	9	154 526.289	–0.033	65	1	463 459.909	0.006
20	2	147 626.553	–0.010	21	10	154 494.744	–0.026	65	2	463 445.172	0.004
20	3	147 618.629	0.025	21	11	154 459.913	–0.016	65	3	463 420.621	0.006
20	4	147 607.445	–0.020	21	12	154 421.795	–0.014	65	4	463 386.254	0.003
20	5	147 593.158	0.009	21	15	154 287.873	–0.017	65	5	463 342.089	0.004
20	6	147 575.672	0.013	61	0	435 440.455	–0.007	65	6	463 288.139	0.009
20	7	147 554.993	–0.009	61	1	435 435.831	–0.006	65	7	463 224.404	0.002
20	8	147 531.210	0.029	61	2	435 421.956	–0.005	65	8	463 150.914	–0.004
20	9	147 504.214	0.009	61	3	435 398.838	–0.002	65	9	463 067.681	–0.020
20	10	147 474.078	–0.003	61	4	435 366.480	0.001	65	10	462 974.749	–0.024
21	0	154 661.125	–0.026	61	5	435 324.894	0.006	65	11	462 872.219	0.058
21	1	154 659.453	–0.030	61	6	435 274.086	0.007				

[a] Calculated with the parameters of Table 2.

Scheme 1



Scheme 2



the reported data of alkynes.[19] In the IR spectrum of **2a**, values at 3318 cm^{-1} and 2180 cm^{-1} are typical of $\nu_{\equiv CH}$ and $\nu_{C\equiv C}$ stretching, respectively. The ν_{As-H} absorption is observed at 2118 cm^{-1}. The mass spectrum confirms the presence of the molecular ion corresponding to the C_2H_3As structure (calculated 101.9451, observed 101.945). The half-life of **2a** (3% in $CDCl_3$) is of about 30 min at room temperature; a brown material is slowly formed under these conditions (Scheme 1).

Arsaalkyne **3a** is obtained in a 29% yield by rearrangement of **2a** on solid sodium carbonate heated to 80 °C (VGSR conditions).[14] A plausible mechanism for the rearrangement **2a** → **3a** involves the arsaallene parent compound **5a** as intermediate (Scheme 2); however all attempts to characterize this species by low-temperature NMR analysis were unsuccessful. The mild conditions needed for this rearrangement can be explained by a high As–H acidity of the ethynylarsine (**2a**) due to the presence of an adjacent carbon–carbon triple bond. A similar effect has already been observed with oxygen, nitrogen, and phosphorus derivatives.[6] The ^1H NMR spectrum of ethylidynearsine (**3a**) shows a singlet at δ 2.09 assigned to the protons of the methyl group. The two signals at δ 24.2 ($^1J_{CH}$ = 132.0 Hz) and 196.4 ($^2J_{CH}$ = 12.5 Hz) observed in the ^{13}C NMR spectrum are assigned to CH_3 and $C{\equiv}As$, respectively. The latter value is consistent with the corresponding chemical shift reported for the aryl derivative ($\delta_{C\equiv As}$ 191 ppm).[2] The $^1J_{CC}$ coupling constant of 41.3 Hz observed on the spectrum of **3e** is smaller than the values reported for nitriles.[20] The half-life of **3a** in $CDCl_3$ is 1 h at 0 °C and arsaalkyne **3a** undergoes decomposition under these conditions with formation of brown, arsenic-containing compounds.

Microwave Spectroscopy. Rotational and Centrifugal Distortion Constants. *Ab initio* calculations have been recently reported for the $R{-}C{\equiv}As$ species with R = H[21a] and R = H, F, CH_3, and C_6H_5.[21b] This last calculation was performed with the MOLPRO program at a level of valence electron CEPA (Coupled Electron Pair Approximation). It gives an approximate value of the dipole moment $\mu(CH_3{-}C{\equiv}As)$ = 1.15 D and two interatomic distances r(C–C) = 1.464 Å and r(C–As) = 1.656 Å (the geometry of the CH_3 group has been kept fixed at an old experimental structure of methyl cyanide: r(C–H) = 1.103 Å and ∠(HCC) = 109.5°).[22]

An approximate value of the B rotational constant is first calculated using the *ab initio* structure.[21a] Rough values of the centrifugal distortion constants D_J and D_{JK} are also obtained by scaling the corresponding constants of methyl cyanide.[23] The assignment of the rotational transitions is relatively straightforward because $CH_3C{\equiv}As$ exhibits a typical prolate symmetric top spectrum with a well-resolved K structure. Furthermore the high K transitions show a characteristic nuclear quadrupole hyperfine structure due to the ^{75}As nucleus ($I = {}^3/_2$). The hypothetical unperturbed frequency of the split lines is first calculated as the intensity-weighted mean of the multiplet frequencies.[24] The frequencies are listed in Table 1.

The frequency of a rotational transition $J + 1, K \leftarrow J, K$ in the ground vibrational state may be written as[25]

$$\nu = 2B(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2 + H_J(J+1)^3[(J+2)^3 - J^3] + 4H_{JK}(J+1)^3K^2 + 2H_{KJ}(J+1)K^4 \quad (1)$$

A linear least-squares method is used to fit the unsplit experimental frequencies to the parameters of the above equation. The derived parameters are listed in Table 2, together with their standard deviation and their correlation coefficients.

Quadrupole Coupling Constant. The hyperfine structure is separately analyzed using the first-order perturbation theory. The resulting first-order formula for the quadrupole energy is[25]

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Table 2. Ground-State Molecular Constants for $CH_3C{\equiv}As$[a]

parameter	value	correlation matrix				
B (MHz)	3515.51730(21)	1.000				
D_J (kHz)	0.507371(25)	0.945	1.000			
D_{JK} (kHz)	37.9888(48)	0.671	0.551	1.000		
H_{JK} (Hz)	0.08904(39)	0.702	0.706	0.849	1.000	
H_{KJ} (Hz)	0.887(22)	0.400	0.256	0.854	0.513	1.000
no. of lines: 53						

[a] The errors shown in parentheses are standard errors and are in units of the last digit.

$$E_Q(J,K,F) = \mathrm{eqQ}[(3K^2/J(J+1)) - 1]Y(I,J,F) \qquad (2)$$

where eqQ is the quadrupole coupling constant and $Y(I,J,F)$ the Casimir function. The hyperfine splittings listed in Table 3 are fit to the above formula by using a linear least-squares fit. The derived quadrupole coupling constant is eqQ(^{75}As) = −155.41(45) MHz.

(1) Excited Vibrational State. One strong vibrational satellite series extending to the high-frequency side was readily assigned. It obviously belongs to a degenerate vibration $\nu_t = 1$ which is very likely the C—C≡As bending mode (by analogy with CH_3CN and CH_3CP). The measured transitions are given in Table 4. The molecular parameters have been derived using the perturbation formulation of Amat, Nielsen, and Tarrago:[26]

$$\begin{aligned} \nu = {} & 2B^*(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)(kl-1)^2 + \\ & 2H_{KJ}(J+1)K^4 + 2\rho^*(J+1)(kl-1) \\ & \pm [q_0(J+1) - 2q_1(J+1)^3] \text{ if } kl = 1 \\ & + \frac{q_0^2(J+1)^3}{4(kl-1)(A-B-A\zeta)} \text{ if } kl \neq 1 \end{aligned} \qquad (3)$$

The derived constants are listed in Table 5. An approximate value of the vibrational frequency may be calculated from the experimental *l*-type doubling constant using the semiempirical formula of Grenier-Besson:[27]

$$q = \frac{aB^2}{\omega} \qquad (4)$$

Table 3. Nuclear Quadrupole Hyperfine Splittings of $CH_3C{\equiv}As$

J	K	F_0	F	$\Delta\nu$(exp)[a]	e − c
13	9	29/2	27/2	6.952	0.035
			25/2	6.119	0.023
			23/2	−0.824	−0.004
13	10	29/2	27/2	8.561	0.022
			25/2	7.452	−0.003
			23/2	−1.103	−0.019
13	11	29/2	27/2	10.346	0.014
			25/2	8.940	−0.017
			23/2	−1.735	0.000
13	12	29/2	27/2	12.305	0.009
			25/2	10.581	−0.022
			23/2	−1.684	0.009
20	6	43/2 37/2	41/2 39/2	0.908	−0.001
20	7	43/2 37/2	41/2 39/2	1.236	0.000
20	8	43/2 37/2	41/2 39/2	1.611	−0.003
20	9	43/2 37/2	41/2 39/2	2.034	−0.007
21	7	45/2 39/2	43/2 41/2	1.075	0.000
21	8	45/2 39/2	43/2 41/2	1.405	0.001
21	9	45/2 39/2	43/2 41/2	1.775	−0.001
21	10	45/2 39/2	43/2 41/2	2.180	−0.011
21	11	45/2 39/2	43/2 41/2	2.648	−0.003
21	15	45/2	43/2	4.935	−0.001
			41/2	4.570	0.020
			39/2	−0.346	0.040

[a] Splitting: $\nu(F_0 + 1 \leftarrow F_0) - \nu(F + 1 \leftarrow F)$ in MHz.

The *a* parameter is a complicated function of the force field, but it has been found to vary in a very small range near two. In the present case, it has been estimated from the parameters of the similar molecules CH_3CN[28] and CH_3CP[29] to be 2.3. This gives $\omega_8 = 274$ cm^{-1}. To check this result, we have calculated at the MP2 level the harmonic vibrational frequencies for CH_3CN, CH_3CP, and CH_3CAs. The results are reported in Table 6. They are compared with the best available experimental frequencies, when they exist. There is no large discrepancy between *ab initio* and experimental frequencies. The average percent difference for the calculated frequencies from the experimental harmonic fundamentals are about 5%. The differences may be explained in part by the imperfect anharmonicity correction and in part by the basis set incompleteness. It is interesting to note that the C–H stretch is well predicted and that its frequency decreases from N to As, which is in agreement with the corresponding increase of the C—H bond length.[30]

(2) Molecular Structure. The rotational spectra of seven isotopomers have been measured in order to determine a structure. The rotational frequencies are listed in Tables 7 and 8 and the rotational constants are given in Table 9. Substitution coordinates of the two carbon atoms were calculated using Kraitchman's equations[31,32] and either CH_3CAs or $^{13}CH_3{}^{13}CAs$ as parent species. Both species give almost the same CC distance: 1.4652 and 1.4653 Å. According to the empirical rule of Costain,[33] the error for the substitution coordinate is inversely proportional to the Cartesian coordinate *z*:

$$\sigma(z) = \frac{0.005}{|z|} \qquad (5)$$

where the empirical constant 0.0005 Å^2 was proposed by Van Eijck[34] following a study of many structures. As the smallest Cartesian coordinate is rather large (about 1 Å), the derived r_s(C–C) distance should be fairly accurate: application of eq 5 giving $\sigma(r) = 0.0005$ Å.

As many isotopomers have been investigated, it should be possible to determine the four independent structural parameters [r(C–H), r(C–C), r(C≡As) and ∠(HCC)] by a least-squares fit to the moments of inertia. This gives the effective or r_0 structure which is given in Table 10. The value of r(C–H) is much too large. This is due to two factors: first, the axial rotational constant *A* could not be determined and, therefore, r(C–H) cannot be determined with precision (it is highly correlated with ∠(HCC)). Moreover, in the particular case of a C(sp^3)–H bond, it is well established that the r_0 value is about 0.0056 Å larger than the

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Table 4. Transition Frequencies (MHz) for the Excited State $\nu_8 = 1$ of $CH_3C{\equiv}As$

J	kl	l	F_{exp}	$e - c$[a]	J	kl	l	F_{exp}	$e - c$[a]
20	0	1	148 013.475	−0.012	28	6	1	204 319.554	0.099
20	1	1	148 089.263	−0.023	28	7	1	204 293.970	0.171
20	1	−1	147 943.271	−0.086	31	0	1	225 501.741	0.049
20	−1	−1	148 010.337	0.007	31	1	1	225 620.917	−0.041
20	2	1	148 015.788	−0.043	31	1	−1	225 398.745	−0.015
20	−2	−1	148 003.344	0.032	31	−1	−1	225 498.920	0.029
20	3	1	148 009.192	0.024	31	−3	−1	225 473.528	0.001
20	−3	−1	147 992.998	0.037	31	4	1	225 486.580	−0.035
20	4	1	148 000.122	−0.009	31	−4	−1	225 453.007	−0.027
20	6	1	147 972.570	0.126	31	5	1	225 467.752	−0.033
21	0	1	155 059.639	−0.072	31	−5	−1	225 427.441	0.001
21	1	1	155 139.205	−0.070	31	6	1	225 444.235	0.023
21	1	−1	154 986.223	−0.077	31	−6	−1	225 397.030	−0.049
21	−1	−1	155 056.475	−0.079	31	7	1	225 415.872	0.195
21	2	1	155 062.443	−0.098	42	−1	−1	302 936.988	−0.022
21	−2	−1	155 049.040	0.088	42	1	1	303 104.065	−0.015
21	−3	−1	155 038.250	0.061	42	2	1	302 966.562	0.079
21	4	1	155 045.817	0.022	42	−2	−1	302 924.728	0.038
21	−4	−1	155 023.985	0.077	42	3	1	302 947.088	−0.021
21	5	1	155 033.037	0.062	42	−3	−1	302 904.699	−0.072
21	−5	−1	155 006.359	0.064	42	5	1	302 900.581	−0.125
21	6	1	155 016.975	0.116	42	6	1	302 868.732	−0.167
28	1	1	204 480.039	−0.049	42	7	1	302 830.596	−0.155
28	1	−1	204 278.577	−0.025	42	8	1	302 786.095	−0.098
28	−3	−1	204 346.688	−0.018	42	9	1	302 735.139	0.070
28	4	1	204 357.862	−0.031	42	−9	−1	302 640.931	−0.039
28	−4	−1	204 327.938	0.055	52	1	1	373 487.211	0.013
28	5	1	204 340.926	−0.065	52	−1	−1	373 276.539	0.094
28	−5	−1	204 304.798	0.015	52	3	1	373 299.397	0.116

[a] Calculated with the parameters of Table 5.

Table 5. Molecular Constants for the Degenerated Excited State $\nu_8 = 1$[a]

parameter	value	correlation matrix							
B^* (MHz)	3524.65307(45)	1.000							
D_J (kHz)	0.51875(12)	0.800	1.000						
D_{JK} (kHz)	38.310(25)	0.579	0.206	1.000					
H_{KJ} (Hz)	2.25(33)	0.525	0.245	0.953	1.000				
ρ^* (kHz)	−18.060(57)	−0.343	−0.112	−0.648	−0.660	1.000			
$q_0^2/(A-B-A\zeta)$(kHz)	0.8200(23)	0.111	0.092	0.157	0.160	−0.426	1.000		
q_0 (MHz)	3.4824(16)	−0.058	−0.156	0.044	0.023	−0.029	−0.007	1.000	
q_1 (Hz)	5.54(49)	−0.078	−0.311	0.132	0.080	−0.085	−0.011	0.848	1.000

[a] The errors shown in parentheses are standard errors and are in units of the last digits.

Table 6. Harmonic Vibrational Frequencies Calculated at the MP2 Level for $CH_3C{\equiv}X$ (with X = N, P, As)[a]

		$CH_3C{\equiv}N$			$CH_3C{\equiv}P$			$CH_3C{\equiv}As$
no.	sym	ω	exptl[b]	% diff	ω	exptl[c]	% diff	ω
1	A_1	3048	3044	−0.1	3016	3019	0.1	3010
2	A_1	2065	2294	11.1	1489	1574	5.7	1452
3	A_1	1475	1418	-3.9	1456	1394	−4.3	1394
4	A_1	894	929	4.0	689	750	8.9	574
5	E	3157	3135	−0.7	3113	3085	−0.9	3107
6	E	1529	1476	-3.5	1515	1466	-3.2	1512
7	E	1108	1062	−4.1	1071	1008	-5.9	1068
8	E	348	365	5.0	266	302	13.6	262

[a] Frequencies ω are in cm^{-1}. [b] Reference 28b. [c] Reference 29b.

r_e value.[35] The C—C and C≡As distances seem to be precisely determined. But, in fact, they are also highly correlated (ρ = −0.998). This is due to the fact that the Arsenic atom has no stable isotope and, therefore, cannot be substituted. To circumvent this problem, it is possible to use the r_s(C–C) value as auxiliary information in the least-squares fit. In this method, called the mixed estimation,[36] the data r(C–C) = 1.465(2) Å is added directly to the data matrix with a weight inversely proportional to the square of its estimated accuracy. In this way, the correlation between r(C—C) and r(C≡As) is significantly reduced and the derived value for r_0(C≡As), 1.660(1) Å, is in very good agreement with that found in the ordinary least-squares fit, 1.661(1) Å. This suggests that this distance is probably accurately determined.

It is not possible to directly compare the experimental results to the *ab initio* calculations because, although the calculated bond angles are generally rather accurate, the bond lengths are computed with errors ranging up to a few hundreds of an angström.[37] But it has been noticed that these errors are largely systematic, provided the basis set is of adequate size. So, the *ab initio* calculations may be used to compare similar bond lengths (as long as the same method and the same basis set are used). Geometries for the CH_3CX molecules (with X = N, P, and As) were fully optimized by the analytical gradient method at the

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Table 7. Transition Frequencies (MHz) for the Observed Symmetric Isotopic Species of $CH_3C{\equiv}As$

J	K	F_{exp}	$e-c$[a]
		$^{13}CH_3C{\equiv}As$	
21	0	148472.688	0.001
21	1	148471.150	–0.005
21	2	148466.499	0.014
21	3	148458.782	0.011
21	6	148417.096	0.010
22	0	155219.513	–0.010
22	1	155217.897	–0.008
22	2	155213.092	–0.045
22	3	155204.951	0.027
22	6	155161.415	–0.010
32	0	222671.530	–0.008
32	1	222669.193	0.019
32	2	222662.271	0.011
32	3	222650.715	0.017
32	4	222634.553	0.010
32	5	222613.804	–0.030
32	6	222588.366	–0.001
33	0	229414.861	0.002
33	1	229412.477	0.007
33	2	229405.337	0.010
33	3	229393.446	0.005
33	4	229376.797	–0.001
33	5	229355.372	0.011
33	6	229329.202	0.010
34	0	236157.841	–0.019
34	1	236155.375	–0.001
34	2	236148.056	–0.028
34	3	236135.777	0.009
34	4	236118.637	0.010
34	5	236096.605	0.005
34	6	236069.698	–0.021
45	0	310301.834	0.011
45	1	310298.655	–0.016
45	2	310289.035	–0.012
45	3	310272.980	0.015
		$CH_3{}^{13}C{\equiv}As$	
21	0	153619.267	0.011
21	1	153617.615	0.006
21	2	153612.639	0.009
21	3	153604.378	–0.017
21	6	153559.606	0.001
31	0	223411.709	–0.005
31	1	223409.261	0.038
31	2	223402.094	–0.010
31	3	223390.094	–0.034
31	4	223373.194	0.032
31	5	223351.562	0.019
31	6	223325.121	0.006
32	0	230389.062	–0.027
32	1	230386.535	0.021
32	2	230379.130	–0.012
32	3	230366.703	0.018
32	4	230349.368	–0.002
32	6	230299.813	–0.033
33	0	237366.005	–0.035
33	1	237363.421	–0.005
33	2	237355.750	0.006
33	3	237342.991	–0.004
33	4	237325.107	0.005
33	5	237302.124	0.005
33	6	237274.038	0.001
43	0	307110.957	–0.025
43	1	307107.634	0.005
43	2	307097.746	0.015
43	3	307081.293	0.005
43	4	307058.229	0.020
43	6	306992.407	–0.012
		$^{13}CH_3{}^{13}C{\equiv}As$	
21	0	147558.086	0.018
21	1	147556.542	0.024
21	2	147551.936	0.018
21	3	147544.283	–0.016
21	6	147502.788	0.000
21	7	147482.840	–0.005
21	8	147459.833	–0.006
21	9	147433.779	–0.010
21	5	147519.703	–0.022
21	4	147533.536	–0.028
22	0	154263.353	0.022
22	1	154261.750	0.018
22	2	154256.940	0.006
22	3	154248.921	–0.010
22	6	154205.531	0.025
29	0	201192.491	0.003
29	1	201190.396	0.005
29	2	201184.115	0.008
29	3	201173.645	0.015
29	4	201159.030	–0.014
22	4	154237.672	–0.006
22	5	154223.215	–0.002
22	7	154184.749	–2.809
22	8	154160.612	0.039
22	9	154133.390	0.025
29	5	201140.231	–0.035
29	6	201117.205	–0.002
29	7	201090.023	0.021
29	8	201058.735	–0.007
29	9	201023.267	–0.006
29	12	200892.067	–0.002
33	0	228002.041	0.007
33	1	227999.697	–0.018
33	2	227992.575	–0.004
33	3	227980.725	0.002
33	4	227964.142	0.007
33	6	227916.816	–0.001
45	0	308391.627	–0.014
45	1	308388.421	0.000
45	2	308378.844	0.001
45	3	308362.881	0.009
45	4	308340.584	–0.026
45	5	308311.849	0.007
45	6	308276.783	0.008
46	0	315087.704	–0.017
46	1	315084.443	–0.016
46	2	315074.669	–0.022
46	3	315058.331	0.021
46	6	314970.389	0.029
55	0	375327.515	0.015
55	1	375323.634	0.028
55	2	375312.067	–0.008
55	3	375292.742	–0.019
55	6	375188.383	0.004
55	9	375014.787	–0.007
		$CD_3C{\equiv}As$	
24	0	149447.652	–0.046
24	1	149446.451	–0.038
24	2	149442.873	–0.038
24	3	149436.955	–0.083
24	4	149428.526	–0.003
24	6	149404.644	0.023
24	7	149389.146	0.014
24	8	149371.199	0.067
24	9	149350.939	0.046
24	10	149328.280	0.036
24	11	149303.246	0.014
24	12	149275.840	–0.025
25	0	155423.624	–0.023
25	1	155422.332	0.029
25	2	155418.618	0.022
25	3	155412.431	0.007
32	0	197248.789	0.010
32	1	197247.192	0.033
32	2	197242.490	0.012
32	3	197234.636	–0.006
32	4	197223.603	0.006
32	5	197209.448	–0.009
32	6	197192.162	–0.043
33	0	203222.718	0.038
33	1	203221.101	0.033
33	2	203216.252	0.016
33	3	203208.163	–0.005
33	4	203196.810	–0.007
33	5	203182.186	0.017
33	6	203164.365	–0.006
33	7	203143.369	–0.100
33	8	203119.027	–0.093
33	9	203091.522	–0.171
		$^{13}CD_3{}^{13}C{\equiv}As$	
26	0	155529.649	0.088
26	1	155528.563	–0.038
26	2	155524.908	–0.019
26	3	155518.839	–0.009
26	4	155510.340	0.006
39	0	230367.748	0.017
39	1	230365.973	0.003
39	2	230360.627	–0.018
39	3	230351.671	–0.007
39	4	230339.141	0.000
39	5	230323.039	0.001
39	6	230303.349	0.013
40	0	236122.530	–0.018
40	1	236120.684	–0.005
40	2	236115.189	–0.010
40	3	236106.012	0.002
40	4	236093.187	–0.005
40	5	236076.698	–0.014
40	6	236056.514	0.006
53	0	310901.302	0.007
53	1	310898.896	0.011
53	2	310891.698	0.003
53	3	310879.685	0.006
53	4	310862.874	0.004
53	5	310841.272	–0.012
53	6	310814.842	–0.004
54	0	316650.748	–0.036
54	1	316648.267	0.000
54	2	316640.934	–0.003
54	3	316628.666	0.038
54	6	316562.681	–0.002

[a] Calculated with the parameters of Table 9.

MP2 level with the LANL1DZ basis set (DZ for CH_3CN). Optimized parameters are reported in Table 11. There are three important features of the results to which attention should be drawn. (i) The angle ∠(HCC) slightly increases from X = N to X = As. It is further in good agreement with the experimental structure. (ii) Likewise, the CH distance increases from X = N to X = As. The increase from CH_3CN to CH_3CAs is 0.004 Å and the experimental r_e(C–H) value in CH_3CN is 1.087(2) Å,[38] so the r_e(C–H) distance in CH_3CAs should be approximately 1.091(3) Å. (iii) Likewise, for the C–C distance, the increase from CH_3CN to CH_3CAs is 0.009 Å (in close agreement with the CEPA calculations);[21a] with the r_e(C–C) value in CH_3CN being 1.457(2) Å, which gives for CH_3CAs 1.466(3) Å. This result is in close agreement with the r_s value. This gives further confidence in the accuracy of determined structure.

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Table 8. Transition Frequencies (MHz) in $CH_2DC\equiv As$ and $CHD_2C\equiv As$

J	K_-	K_+	←	J	K_-	K_+	F_{exp}	$e-c^a$
$CH_2DC\equiv As$								
22	1	21		21	1	20	146 163.178	0.080
22	1	22		21	1	21	145 674.788	0.027
22	2	20		21	2	19	145 921.291	0.040
22	3	19		21	3	18	145 911.191	−0.006
22	4	18		21	4	17	145 902.254	−0.022
22	5	17		21	5	16	145 891.056	−0.035
22	6	16		21	6	15	145 877.478	−0.039
22	7	15		21	7	14	145 861.434	−0.084
23	0	23		22	0	22	152 546.217	0.103
23	1	23		22	1	22	152 294.352	0.019
23	1	22		22	1	21	152 804.893	0.059
23	2	21		22	2	20	152 552.613	0.019
23	3	20		22	3	19	152 541.697	−0.005
23	5	19		22	5	18	152 520.599	−0.037
23	6	18		22	6	17	152 506.394	−0.045
23	7	17		22	7	16	152 489.631	−0.078
23	8	16		22	8	15	152 470.385	−0.045
23	9	15		22	9	14	152 448.495	−0.100
29	1	29		28	1	28	192 005.749	0.014
29	1	28		28	1	27	192 649.134	0.014
29	2	27		28	2	26	192 336.336	0.018
29	2	28		28	2	27	192 323.639	0.000
29	4	25		28	4	24	192 307.187	0.007
29	6	23		28	6	22	192 274.316	−0.022
29	7	22		28	7	21	192 253.223	0.016
29	8	21		28	8	20	192 228.901	0.025
29	9	20		28	9	19	192 201.404	0.075
30	0	30		29	0	29	198 947.082	0.000
30	1	29		29	1	28	199 288.670	−0.031
30	1	30		29	1	29	198 623.242	0.053
30	2	28		29	2	27	198 966.155	0.016
30	2	29		29	2	28	198 952.117	0.014
30	3	27		29	3	26	198 947.785	−0.070
30	4	26		29	4	25	198 935.277	−0.014
30	5	25		29	5	24	198 919.860	−0.016
30	7	23		29	7	22	198 879.442	0.027
30	8	22		29	8	21	198 854.301	0.061
30	9	21		29	9	20	198 825.831	0.091
31	0	31		30	0	30	205 574.198	−0.018
31	1	31		30	1	30	205 240.296	0.002
31	1	30		30	1	29	205 927.901	−0.026
31	2	30		30	2	29	205 580.224	0.001
31	2	29		30	2	28	205 595.717	0.009
31	3	28		30	3	27	205 576.100	−0.023
31	4	27		30	4	26	205 563.015	−0.065
31	5	27		30	5	25	205 547.134	0.007
39	1	39		38	1	38	258 163.156	−0.034
$CHD_2C\equiv As$								
24	0	24		23	0	23	150 831.359	0.030
24	1	24		23	1	23	150 567.719	0.025
24	1	23		23	1	22	151 106.543	0.054
24	2	23		23	2	22	150 834.183	−0.019
24	2	22		23	2	21	150 843.498	0.036
24	3	21		23	3	20	150 830.685	−0.049
24	5	20		23	5	19	150 810.173	−0.027
24	6	19		23	6	18	150 796.471	−0.035
24	7	18		23	7	17	150 780.310	−0.084
24	8	17		23	8	16	150 761.751	−0.090
31	1	31		30	1	30	194 461.962	−0.015
31	1	30		30	1	29	195 157.632	0.001
31	2	29		30	2	28	194 826.695	−0.023
31	2	30		30	2	29	194 806.766	0.001
31	3	29		30	3	28	194 804.601	0.063
31	4	28		30	4	27	194 792.257	−0.004
31	6	26		30	6	25	194 759.692	0.075
33	0	33		32	0	32	207 354.155	0.030
33	1	33		32	1	32	207 000.382	0.003
33	1	32		32	1	31	207 740.753	−0.049
33	2	31		32	2	30	207 391.634	−0.032
33	2	32		32	2	31	207 367.600	−0.001
33	3	31		32	3	30	207 366.154	0.117
33	4	29		32	4	28	207 352.850	0.033
33	5	28		32	5	27	207 336.925	−0.014
33	6	27		32	6	26	207 318.037	0.080
33	8	25		32	8	24	207 270.252	0.112
41	0	41		40	0	40	257 566.006	0.000
41	1	41		40	1	40	257 138.992	−0.052
41	1	40		40	1	39	258 058.221	−0.040
41	2	39		40	2	38	257 642.423	−0.008
41	2	40		40	2	39	257 596.321	−0.026
41	3	38		40	3	37	257 599.457	0.027
41	3	39		40	3	38	257 599.054	0.053
41	4	37		40	4	36	257 581.748	0.004

[a] Calculated with the parameters of Table 9.

Table 9. Ground-State Rotational and Centrifugal Distorsion Constants for All Isotopic Species Observed[a]

	$^{13}CH_3C\equiv As$	$CH_3{}^{13}C\equiv As$	$^{13}CH_3{}^{13}C\equiv As$	$CD_3C\equiv As$	$^{13}CD_3{}^{13}C\equiv As$		$CDH_2C\equiv As$	$CD_2HC\equiv As$
B (MHz)	3374.83399(14)	3491.83067(21)	3354.04126(11)	2989.40321(45)	2880.66848(21)	A (MHz)	121600(175)	96538(73)
D_J (kHz)	0.469724(49)	0.499410(76)	0.462786(24)	0.36060(24)	0.334817(42)	B (MHz)	3327.9462(20)	3154.2441(82)
D_{JK} (kHz)	35.1701(84)	37.756(13)	35.0255(44)	23.91(10)	22.510(14)	C (MHz)	3305.7345(16)	3131.7200(82)
H_{JK} (Hz)	0.0791(29)	0.0877(45)	0.07769(64)	0.0356(67)	0.04628(27)	Δ_J (kHz)	0.45654(34)	0.40784(29)
H_{KJ} (Hz)			0.790(31)			Δ_{JK} (kHz)	27.8948(52)	25.6946(84)
						δ_J (kHz)	0.00362(46)	0.00233(33)
						δ_K (kHz)		15(4)

[a] The errors shown in parentheses are standard errors and are in units of the last digits.

Table 10. Experimental r_0 structure of $CH_3C\equiv As$[a]

	normal least-squares	mixed estimation[b]
C≡As	1.661(1)	1.660(1)
C—C	1.463(1)	1.465(2)
C—H	1.106(6)	1.105(7)
∠(CCH)	110.55(20)	110.55(22)

[a] Bond lengths in Å and angles in degrees. The errors shown in parentheses are standard errors and are in units of the last digit. [b] See text.

Table 11. MP2/LANL1DZ *ab Initio* Structures of $CH_3C\equiv X$ (with X = N, P, As)[a]

	r(C–C)	r(C–H)	∠(HCC)
$CH_3C\equiv N$	1.491	1.102	110.04
$CH_3C\equiv P$	1.497	1.105	110.78
$CH_3C\equiv As$	1.500	1.106	110.86

[a] Bond lengths in Å and angles in degrees.

Conclusion

The first simple arsaalkyne **3a** has been prepared by base-induced rearrangement of the corresponding ethynylarsine and spectroscopically characterized. This result clearly points out that the ethynamine–nitrile[39] and the ethynylphosphine–phosphaalkyne[6] rearrangements can be generalized to the arsenic derivatives. This work paves the way to the chemistry of unstabilized arsaalkynes.

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