Theoretical Study of the Structure and Properties of Polyynes and Monocyano- and Dicyanopolyynes: Predictions for Long Chain Compounds

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Geometrical parameters and harmonic vibration frequencies of polyynes $HC_{2n}H$ ($n = 1-8$), cyanopolyynes $HC_{2n-1}N$ ($n = 1-7$), and dicyanopolyynes $NC_{2n}N$ ($n = 1-8$) have been calculated with various density functionals using the Dunning triple-ζ basis set. For selected data, we propose extrapolation formulas for longer molecules of the series. Bond lengths and electron localization function analysis indicate that a marked bond alternation persists in molecules as long as $HC_{30}H$. The evolution along the series of some vibration frequencies and their accuracy for the identification of long molecules in extraterrestrial systems are also discussed.

Introduction

Except for their first members, polyynes $H(C{\equiv}C)_nH$, monocyanopolyynes $NC(C{\equiv}C)_nH$, and dicyanopolyynes $NC(C{\equiv}C)_nCN$ are highly reactive under usual terrestrial conditions and thus can be obtained only in drastic experimental circumstances such as low-temperature matrixes.[1] Nevertheless, monocyano compounds have been detected since the 70s,[2−5] in interstellar clouds thanks to their microwave emission because of a permanent dipole moment. The other two series are “microwave silent” but should also be present, because the derived radicals C_xH and C_xN[6−9] have been detected. The atmosphere of Titan, mainly composed with H, N, and C elements, and which is believed quite similar to the early terrestrial one, contains polyynes already characterized. Indeed, the 80th Voyager 1 and 2 flybys, exploring this satellite of Saturn, have provided ultraviolet and infrared spectral data. The InfraRed Interferometer Spectrometer (IRIS) data have shown evidence for the presence of butadiyne (diacetylene, C_4H_2) and cyanoacetylene (HC_3N).[10−12] Photochemically reactive in the UV range, these compounds constitute precursors to the visible-absorbing haze materials present in Titan and many of the outer planets atmospheres (ref 13 and references therein). Dicyanoacetylene (C_4N_2) has also been detected but in condensed phase.[14] Numerous of Voyager detections have been confirmed in the 90s by ISO (Infrared Space Observatory).[15] Recently, this observatory has provided the first detection of butadiyne (diacetylene, C_4H_2) and hexatriyne (triacetylene, C_6H_2) outside the solar system, in circumstellar envelope.[16]

Our knowledge of Titan’s chemical composition and particularly polyynes and monocyano- and dicyanopolyynes abundances will be improved in 2005 thanks to the composite infrared spectrometer (CIRS) aboard the Cassini mission. Other space instruments are under development to open new observing windows in the far IR at high resolution. This might allow the identification of polyynes and monocyano- and dicyanopolyynes and produce new insights on their dissemination in extraterrestrial environments. To derive large scientific profits from the past and the forthcoming observational data, an important effort in laboratory work has been undertaken. For example, on the basis of theoretical models as well as laboratory simulations of Titan’s atmosphere, one can expect the formation of polyynes, monocyano- and dicyanopolyynes.[17,18] In parallel, laboratory measurements have been performed to determine IR absorption coefficients of products identified in simulation experiments such as HC_3N, C_6H_2, C_4H_2, and C_4N_2.[19−22] Unfortunately, the spectroscopic characteristics of longer chain compounds are not easy to obtain in the laboratory. Because of their high reactivity, they are difficult to synthesize. In addition, polyynes and monocyano- and dicyanopolyynes, especially as long linear molecules and as electric conductors, are of intrinsic interest. We will present here the results for geometrical parameters, rotational constants, dipole moments, and vibration frequencies of the following molecules: $H(C{\equiv}C)_nH$ ($n = 1-8$), series **1**, $NC(C{\equiv}C)_nH$ ($n = 1-6$), series **2**, and $NC(C{\equiv}C)_nCN$ ($n = 1-7$), series **3**. For some selected data, we will propose extrapolation formulas allowing predictions for larger n values. This way our aim is to select physical properties suitable for the experimental characterization of long chain polyynes.

Calculation Methods

The Gaussian 98 series of programs[23] has been used throughout this work. Full geometry optimizations and frequency calculations were performed at various DFT levels with the Dunning TZ basis set (4s, 3p, 2d, 1f for heavy atoms and 3s, 2p, 1d for hydrogens).[24] After exploratory calculations using B3LYP,[25,26] SVWN,[27,28] B3PW91,[25,29] and BP86[30,31] functionals on species for which experimental data are available, it has been found that better geometrical parameters are obtained when

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TABLE 1: Bond Lengths (Å) in C_yH_2 (B3LYP/CC-pVTZ) with Experimental Values Given in Italics

y	2 (ref 49)	4 (ref 50)	6	8	10	12	14	16	18	30
C−H	1.062	1.061	1.061	1.061	1.061	1.062	1.062	1.062	1.062	1.062
	1.059	*1.062*								
C≡C	1.196	1.204	1.207	1.208	1.208	1.208	1.208	1.208	1.208	1.209
	1.209	*1.206*								
C−C		1.364	1.355	1.352	1.351	1.350	1.350	1.349	1.349	1.349
		1.380								
C≡C			1.215	1.219	1.220	1.221	1.221	1.221	1.221	1.222
C−C				1.343	1.340	1.338	1.337	1.336	1.336	1.336
C≡C					1.223	1.225	1.226	1.226	1.226	1.227
C−C						1.335	1.333	1.332	1.332	1.331
C≡C							1.227	1.228	1.228	1.229
C−C								1.331	1.330	1.328
C≡C									1.229	1.230
C−C										1.327
C≡C										1.231
C−C										1.326
C≡C										1.231
C−C										1.326
C≡C										1.231

TABLE 2: Bond Lengths (Å) in HC_yN (B3LYP/CC-pVTZ) with Experimental Values Given in Italics

y	1 (ref 51)	3 (ref 51)	5 (ref 51)	7	9	11	13
C−H	1.065	1.062	1.062	1.062	1.062	1.062	1.062
		1.058	*1.056*				
C≡C		1.201	1.205	1.207	1.208	1.208	1.208
		1.205	*1.2087*				
C−C		1.368	1.360	1.358	1.357	1.349	1.349
		1.378	*1.3623*				
C≡C			1.212	1.215	1.217	1.220	1.221
			1.2223				
C−C			1.355	1.351	1.350	1.338	1.337
			1.3636				
C≡C				1.217	1.219	1.224	1.225
C−C				1.344	1.341	1.335	1.333
C≡C					1.222	1.223	1.226
C−C					1.339	1.339	1.333
C≡C						1.217	1.224
C−C						1.357	1.338
C≡C							1.218
C−C							1.356
C≡N	1.146	1.155	1.158	1.159	1.159	1.159	1.159
		1.159	*1.1606*				

TABLE 3: Bond Lengths (Å) in C_yH_2 (B3LYP/CC-pVTZ) with Experimental Values Given in Italics

y	2 (ref 52)	4 (ref 53)	6	8	10	12	14	16
C≡N	1.153	1.156	1.158	1.158	1.159	1.159	1.159	1.159
	1.154	*1.161*						
C−C	1.375	1.362	1.359	1.358	1.357	1.357	1.357	1.356
	1.389	*1.367*						
C≡C		1.208	1.213	1.215	1.216	1.217	1.217	1.218
		1.198						
C−C			1.346	1.342	1.340	1.339	1.338	1.338
C≡C				1.220	1.222	1.223	1.224	1.224
C−C					1.336	1.334	1.333	1.332
C≡C						1.225	1.226	1.227
C−C							1.331	1.330
C≡C								1.227

using the B3LYP functional, whereas better vibration frequencies are obtained with BP86 or SVWN. The reliability of the latter functional for calculating frequencies in quite different systems has yet been reported.[32] In addition, MP2 calculations have been performed with the same basis set for a few selected molecules for which experimental results are available: C_4H_2, C_6H_2, HC_3N, HC_5N, and C_2N_2. Because the results of these calculations (supporting information may be requested by e-mail: scemama@lct.jussieu.fr.) are not significantly better than those of DFT, with larger computation times, we only report the latter. The same remark has been done by Molinet et al.[33] when comparing rotational constants of cyanopolyynes obtained by MP2/6-31G* and BP86/6-31G*.

Results and Discussion

Bond Lengths and Bond Order Alternation. *Bond Lengths.* The geometrical parameters, optimized at the B3LYP level are displayed in Tables 1−3 with experimental values. The calculated values generally differ by less than 0.01 Å from the experimental available ones, with a maximum error of 0.012 Å.

The C−H bond length in series **1** and **2** is essentially constant. In polyynes, its value increases from 1.0612 Å for C_4H_2 to 1.0615 Å for $C_{18}H_2$. In monocyanopolyynes, this value decreases from 1.0624 Å for HC_3N to 1.0618 Å for $HC_{13}N$. Using regression functions, the common asymptotic value in both series has been found to be equal to 1.0618 Å.

In the series **2** and **3**, the C≡N bond lengthens from 1.153 Å in NCCN and 1.146 Å in HCN to a common value of 1.159 Å for $C_{14}N_2$ and $HC_{15}N$. This bond is more sensitive to conjugation than C−H and reaches an asymptotic value which has been evaluated to 1.1591 Å.

As expected, in all of the series, the alternation of short bonds and long bonds becomes less and less marked when *n* increases and principally in the central region of molecules. For example, for $n > 4$, the central “single” bond becomes shorter than the ethylene C═C bond (1.3333 Å at the same calculation level).

The problem of bond length alternation has been already raised in the series **1** of polyynes. Previous studies at the extended Hückel level[34] as well as ab initio calculations[35−37] concluded that bond alternation persists in long polyyne chains. A bond alternation index was defined by keeping equal, on one hand, all of the triple bonds and on the other hand all of the single bonds of polyynes of various sizes and then optimizing their geometry under these constraints: the difference between long and short bonds, after extrapolation at infinite, lies from 0.170 to 0.089 Å according to the calculation method.[38,39] Recent periodic MP2 calculations by Poulsen et al.[40] yield values of 0.092 and 0.057 Å with 4-31G and 6-31G** basis sets, respectively. Nevertheless, periodic VASP calculations (the authors acknowledge Pr. Minot and Dr. Markowits for performing this calculation) for infinite carbon linear chains yield equal C−C bonds with an optimized C−C distance of 1.274 Å. If all of the C−C bonds should become equal for n infinite, this convergence appears nevertheless quite slow: in the highest member studied in the series **1**, $C_{18}H_2$, the "triple" bonds remain shorter than 1.23 Å and the "single" bonds longer than 1.33 Å.

To get reasonable geometries of longer chains taking into account the "edge effect", we give extrapolation formulas for the surfaces $d(x,y)$ (d is the length of the bond, x is the index of the bond in the chain, and y is the total number of carbon atoms) obtained as follows. First, the B3LYP/CC-pVTZ lengths of the first, second, and central C≡C bonds have been fitted as functions of y, so as to obtain extrapolated values of these bond lengths in $C_{40}H_2$, which are necessary for correct asymptotic values of the surface. Then, for each polyyne C_yH_2 and $C_{40}H_2$, we fitted the length of the triple bond as a function of x on the following function:

$$d(x) = d_0 + a|x - x_0|^b$$

Each parameter d_0, a, x_0, and b has been fitted as a function of y. We obtain surfaces of equation

$$d(x,y) = d_0(y) + a(y)|x - x_0(y)|$$

The parameters for the lengths of the triple bonds of HC_yH are

$$\left\{\begin{array}{lcl} d_0(y) & = & 1.2289 - 0.06294e^{-0.2318y} \\ a(y) & = & -0.1041e^{-0.3613y} \\ x_0(y) & = & 0.5 + 0.25y \\ b(y) & = & 1.7 + 0.1y \end{array}\right\}$$

Thus, as an end result we get

$$d(x, y) = 1.2289 - 0.06294e^{-0.2318y} - 0.1041e^{-0.3613y}|x - 0.5 + 0.25y|^{1.7+0.1y} \quad (1)$$

The same method has been applied for single bonds. The parameters for the lengths of the single bonds of HC_yH are

$$\left\{\begin{array}{lcl} d_0(y) & = & 1.3290 - 0.1096e^{-0.2401y} \\ a(y) & = & -0.2169e^{-0.3634y} \\ x_0(y) & = & 0.25y \\ b(y) & = & 1.6 + 0.098y \end{array}\right\}$$

$$d'(x,y) = 1.3290 + 0.1096e^{-0.2401y} + 0.2169e^{-0.3634y}|x - 0.25y|^{1.6+0.098y} \quad (2)$$

One can remark that the asymptotic values of the lengths of the triple and the single bonds respectively 1.229 and 1.329 lead to a bond length alternation of 0.1 Å. Thus, DFT does not seem to underestimate the bond length alternation in polyyne series as it was stated for polyenes.[41]

Similarly, the following extrapolated parameters have been obtained in the dicyano series **3** for triple bonds:

$$d(x,y) = 1.2281 - 0.1112e^{-0.2947y} - 0.1159e^{-0.3614y}|x - 0.25y|^{1.6+0.1y} \quad (3)$$

and for single bonds

$$d'(x,y) = 1.3295 + 0.1442e^{-0.3071y} + 0.2685e^{-0.4301y}|x - 0.5 + 0.25y|^{2.0+0.115y} \quad (4)$$

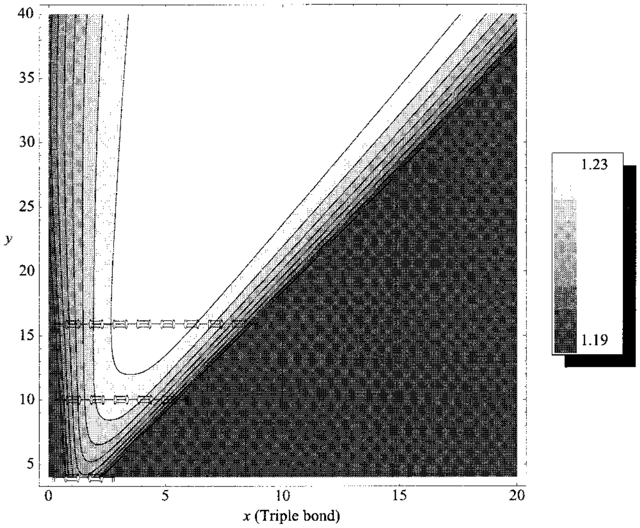

Figure 1. Lengths of the xth C≡C bonds in C_yH_2 (Å), extrapolated from B3LYP/CC-pVTZ calculations using formula 1.

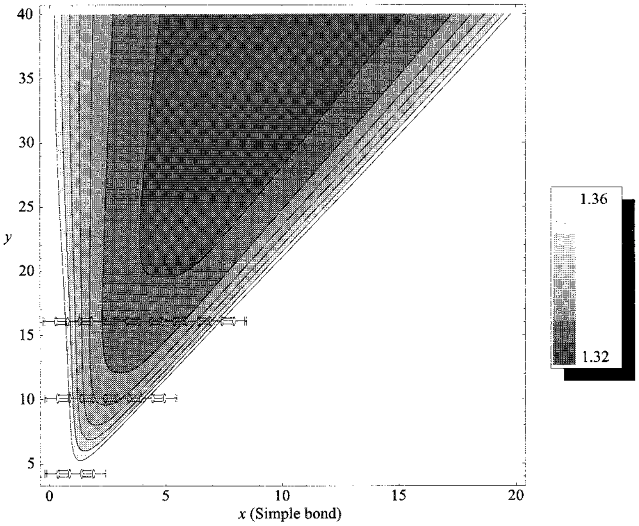

Figure 2. Lengths of the xth C−C bonds in C_yH_2 (Å), extrapolated from B3LYP/CC-pVTZ calculations using formula 2.

These results are graphically summarized in the 2D projections 1 and 2, in which the label x of the bond is on the X axis and the length y of the molecule is on the Y axis. Each area refers to a value r such that a bond length d in this area is $r < d < r + 0.005$. For instance, in the $C_{40}H_2$ polyyne, the three triple bonds at each end of the molecule have lengths ranging from 1.19 to 1.23 Å, whereas the 14 central ones have lengths ranging from more than 1.230 to less than 1.235 Å.

ELF Study of the Bonds. The alternation of qualitatively different bonds is evidenced by Becke and Edgecombe's[42] electron localization function (ELF) analysis. Let us recall that this function, a measure of the "degree of pairing of electrons", can vary from 0 to 1. It is 0.5 for a homogeneous electron gas: a value greater than 0.5 thus indicates electrons more paired than in the electron gas. The ELF has been calculated for $C_{30}H_2$ using the ToPMoD program[43] from the SCF/6-31G** wave function. In Figures 3 and 4 are displayed the ELF contours for a 0.85 value of this function for C_2H_6, C_2H_4, C_2H_2, and $C_{30}H_2$ (limited to one end and the central part of this molecule). A topological analysis of ELF allows a space partitioning into "basins", playing different roles, around "attractors". The various C−C bonding basins have a characteristic shape according to

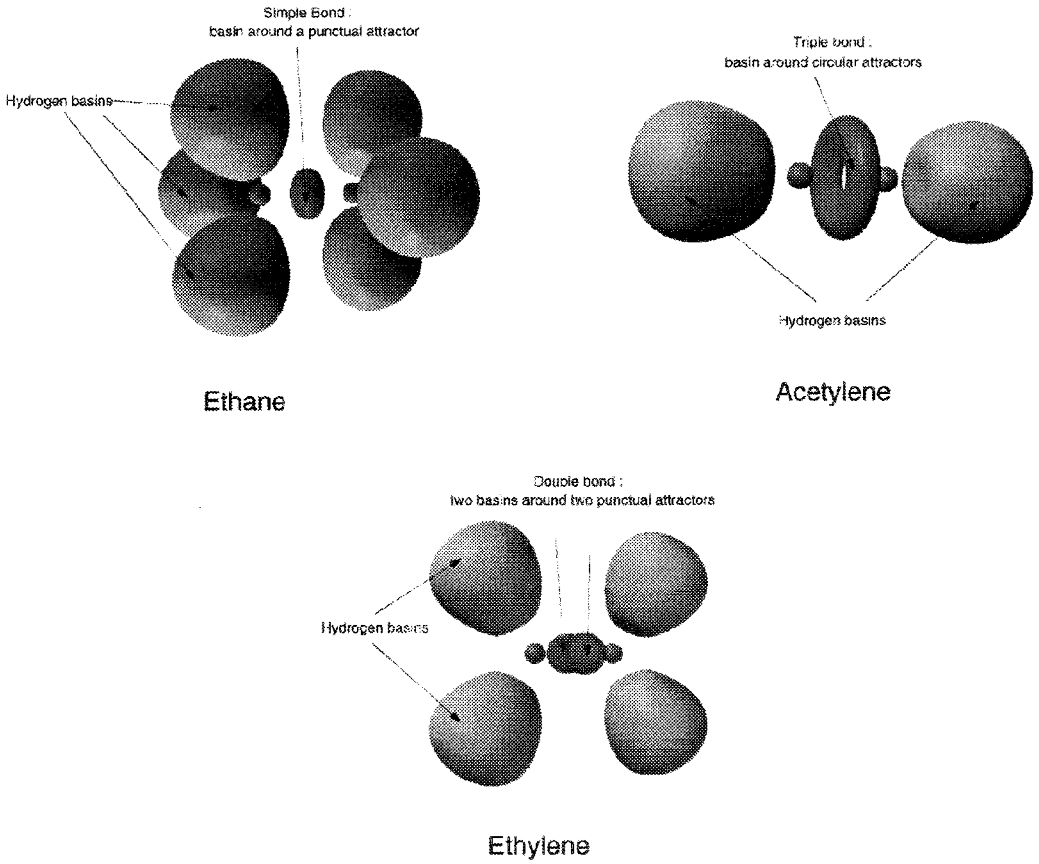

Figure 3. Ethane, ethylene, and acetylene, ELF = 0.85.

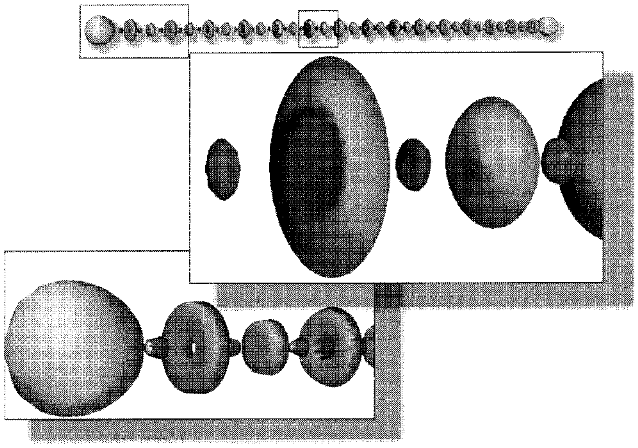

Figure 4. ELF contour (0.85) in $C_{30}H_2$: overall view (upper part); zooms of the middle and of the edge of the molecule (lower parts).

the bond type. We observe[44] (1) in ethane, a single basin around a punctual attractor, (2) in ethylene, two basins around two punctual attractors, symmetrical with respect to the molecular plane, and (3) in acetylene, a single toric basin around three degenerate circular attractors.

It appears on the conjugated $C_{30}H_2$ molecule as a marked alternation of punctual attractors with a basin population of 2.2−2.3 electrons, a characteristic of single bonds, and of circular attractors with a basin population of 5.0−5.45 electrons (because of an artifact arising from the size of the grid used in the computation, the total population of the triple bond basins are slightly underestimated; thus, the sum of the populations of one single bond and one triple bond is inferior to the expected value of 8), a characteristic of triple bonds, though the length of the central triple bond $C_{15}{\equiv}C_{16}$, 1.229 Å, only differs by 0.1 Å from that of its "single" neighbor $C_{14}{-}C_{15}$, 1.329 Å.

Dipole Moments and Rotational Constants in the $HC_{2n-1}N$ (2) Series. In Table 4, we report calculated dipole moments and rotational constants (at BP86, SVWN, B3LYP, and MP2 levels) and available experimental values in the $HC_{2n-1}N$ series. Though it has been recently pointed out[45] that DFT is not the best approach to estimate dipole moments of push−pull conjugated systems (the authors acknowledge one referee for having raised this point), one can remark that B3LYP results are in good agreement with the experimental ones. Calculated dipole moments are nevertheless overestimated, more and more along the series. As a matter of fact, the error increases from 3% in HC_3N to 6% in HC_9N. At any rate, DFT results appear of a higher quality than MP2 ones, as displayed in Table 4.

Calculated values μ_c exhibit a quasilinear variation, but a more careful fit leads to the following development as a function of y, number of carbon atoms, according to the calculation method:

$$\mu_c(y) = 2.4607 + 18.6213(1 - e^{-0.02426y}) \quad \text{(BP86)} \quad (5)$$

$$\mu_c(y) = 2.5142 + 9.5001(1 - e^{-0.04941y}) \quad \text{(B3LYP)} \quad (6)$$

Rotational constants in the series **1** and **2** are available as supporting information.

Vibration Frequencies. The harmonic vibration frequencies were calculated at BP86, SVWN, and B3LYP levels with the CC-pVTZ basis set. In Tables 5−7, we report calculated results using the BP86 functional which generally yields a better fit. The intensities must be considered with some caution. It has been reported[46] that DFT calculations do not allow a strict comparability with experimental results, and they are thus given as landmarks. We only can expect indicative trends along the

TABLE 4: Dipole Moments (Debye) and Rotational Constants (GHz) of $HC_{2n-1}N$

	dipole moments (Debye)					rotational constants (GHz)				
	BP86	SVWN	B3LYP	MP2	exp. (ref 5)	BP86	SVWN	B3LYP	MP2	exp. (ref 5)
HCN	2.909	2.971	2.980	3.261		44.0454	44.5574	44.9722	43.6526	
HC_3N	3.762	3.829	3.821	4.182	3.72	4.5366	4.6031	4.5944	4.1821	4.5491
HC_5N	4.592	4.677	4.578	4.946	4.53	1.3289	1.3484	1.3434	1.3196	1.3313
HC_7N	5.371	5.477	5.267		5.0	0.5633	0.5714	0.5690		0.5640
HC_9N	6.112	6.239	5.980		5.6	0.2902	0.2944	0.2931		0.2905
$HC_{11}N$	6.819		6.489			0.1689		0.1706		0.1693
$HC_{13}N$	7.499	7.654	7.005			0.1069		0.1079		

TABLE 5: Harmonic Wavenumbers of $C_{2n}H_2$ (cm^{-1}), BP86/CC-pVTZ[a]

	Π_g	Π_u	Σ_g	Σ_u
C_2H_2	*612.8*/594.0	*730.3* /734.5(95.2)	*1974.3* /2008.3	*3281.9* /3340.9(83.6)
ref 49			*3372.8*/3440.8	
C_4H_2	*483* /508.0	*220*/231.2(6.9)	*872*/905.3	*2022*/2040.0(4.3)
ref 54	*628* /607.7	*626*/606.6(89.9)	*2189*/2205.8	*3334*/3393.7(182.6)
			3332/3392.3	
C_6H_2	*258*/265.1	*105*/108.4(4.0)	*625*/628.8	*1115*/1197.0(4.4)
ref 55	*491*/509.3	*443*/466.0(0.5)	*2019*/2027.1	*2125*/2146.9(8.1)
	625/589.2	*625*/590.4(90.7)	*2201*/2214.5	*3313*/3391.2(269.3)
			3328/3391.7	
C_8H_2	163.1	62.2(2.3)	481.4	932.7(8.0)
	438.2	283.9(2.9)	1337.9	2018.2(7.9)
	510.1	492.2(0.0)	2099.0	2205.4(5.4)
	585.9	585.4(91.2)	2167.6	3389.5(359.7)
			3390.9	
$C_{10}H_2$	107.5	40.1(1.5)	389.8	762.2(10.7)
	294.0	198.9(3.0)	1110.5	1421.1(3.3)
	471.0	421.4(0.8)	2006.1	2079.8(13.9)
	499.5	497.0(0.2)	2100.8	2207.4(2.4)
	582.8	583.2(90.0)	2175.9	3389.6(457.3)
			3390.3	
$C_{12}H_2$	75.9	28.0(1.0)	327.5	643.7(12.9)
	223.4	143.8(2.4)	946.0	1225.5(6.5)
	409.8	301.1(1.6)	1474.1	1998.0(8.8)
	482.9	456.8(0.3)	2037.4	2139.2(11.6)
	498.1	498.5(0.2)	2071.1	2186.0(0.1)
	582.0	581.9(89.3)	2200.6	3389.2(559.0)
			3389.8	
$C_{14}H_2$	56.4	20.7(0.7)	282.3	556.9(14.6)
	171.8	108.1(1.9)	822.2	1073.8(9.4)
	305.8	241.0(2.1)	1306.0	1511.2(2.4)
	444.1	401.3(0.6)	1983.5	2045.9(17.0)
	487.0	472.8(0.1)	2001.8	2151.3(0.6)
	499.1	499.6(0.2)	2117.5	2182.1(6.3)
	581.9	582.1(89.4)	2201.1	3388.6(665.9)
			3389.2	
$C_{16}H_2$	43.5	15.9(0.6)	248.1	490.5(16.0)
	134.9	83.9(1.4)	726.7	953.2(11.9)
	254.2	193.3(1.9)	1167.9	1364.7(5.3)
	394.9	309.6(1.0)	1538.4	1980.6(7.8)
	462.2	434.0(0.4)	1950.6	2090.4(13.2)
	488.2	480.7(0.0)	2036.6	2124.3(3.4)
	499.5	499.9(0.2)	2157.4	2195.1(4.7)
	581.7	581.7(90.0)	2190.3	3388.4(777.3)
			3388.9	

[a] Intensities are mentioned in parentheses (km/mol), and experimental values are mentioned in italics.

series, for a given type of vibration. Harmonic SVWN and B3LYP frequencies are available as supporting information. We will briefly discuss some of these results, limited to IR allowed vibrations. For vibration frequencies of a peculiar interest, we propose regression formulas, allowing predictions for longer molecules, in the form

$$\omega(y) = \omega_\infty + a e^{-by} + c e^{-dy} \tag{7}$$

where y is the number of carbon atoms.

C−H Stretching Vibrations. In the series **1** of polyynes (Table 5), two C−H stretching modes are observed, one symmetrical Σ_g IR forbidden and one Σ_u IR allowed. The coupling between both C−H vibrators is weak in C_4H_2 (3392.3 and 3393.7 cm^{-1}) and, with frequencies only differing by less than 1 cm^{-1}, appears negligible in the higher terms.

In the monocyano series **3** (Table 6), one stretching C−H mode is present, whose calculated frequency remains constant at 3386 cm^{-1} from HC_5N to $HC_{11}N$.

A salient point in the allowed stretching C−H modes, as well in the series **1** as in series **3**, is an increase (nearly linear) in their intensity as the molecule lengthens. As an example, this intensity in $C_{16}H_2$ is almost 10 times that of C_2H_2. The extrapolation formulas of Table 8 can be established.

TABLE 6: Harmonic Wavenumbers of $HC_{2n-1}N$ (cm^{-1}), BP86/CC-pVTZ^{a}

	Π		Σ	
HCN[52]	*713.46*/723.7(38.0)		*2096.7*/2115.1(0.1)	*3311.47*/3363.7(50.9)
HC_3N	*222*/232.5(0.1)	*663*/649.8(42.1)	*864*/889.7(0.0)	*2274*/2273.2(15.7)
refs 56−59	*499*/522.3(3.1)		*2079*/2093.5(0.1)	*3327*/3387.4(84.9)
HC_5N	108.5(0.2)	520.4(1.8)	619.7(0.0)	2196.8(0.3)
ref 60	268.8(6.5)	620.8(42.9)	1189.3(1.0)	*2256*/2251.5(67.3)
	484.9(0.5)		2063.0(0.3)	3386.5(123.3)
HC_7N	62.0(0.1)	502.7(1.1)	476.1(0.0)	2146.4(17.6)
	162.7(5.5)	515.3(1.4)	924.4(3.1)	2185.1(96.2)
	285.3(0.0)	607.2(42.9)	1333.8(0.4)	2240.3(44.9)
	452.1(1.8)		2042.9(0.0)	3386.2(166.0)
HC_9N	40.1(0.1)	482.3(1.0)	386.4(0.0)	2111.9(61.5)
	107.5(3.9)	505.7(1.4)	755.8(5.1)	2124.6(161.8)
	198.2(0.1)	511.9(1.2)	1104.1(0.7)	2198.6(0.6)
	295.5(2.7)	599.7(43.6)	1417.4(0.5)	2233.4(64.4)
	432.1(0.0)		2025.6(0.7)	3386.1(212.0)
$HC_{11}N$	27.9(0.1)	464.8(0.1)	325.2(0.1)	2059.6(308.2)
	75.9(2.8)	492.0(0.6)	639.2(6.9)	2095.1(38.8)
	143.4(0.1)	506.1(1.4)	940.0(0.6)	2169.2(12.0)
	222.8(3.4)	510.2(1.1)	1221.6(1.5)	2195.6(28.4)
	302.3(0.0)	596.5(43.6)	1471.8(0.4)	2227.9(85.4)
	418.2(1.1)		2012.4(0.4)	3386.6(269.4)
$HC_{13}N$	20.6(0.0)	451.2(0.8)	280.6(0.1)	2012.5(376.0)
	56.3(2.1)	479.4(0.2)	553.4(8.5)	2071.3(17.2)
	107.8(0.1)	495.9(0.5)	817.3(0.8)	2143.3(4.7)
	170.9(3.1)	506.1(1.4)	1069.0(3.0)	2165.6(63.3)
	240.4(0.0)	509.4(1.1)	1303.1(0.9)	2195.6(0.0)
	307.1(1.5)	593.8(43.9)	1509.4(0.4)	2224.8(123.0)
	408.4(0.0)		1997.5(87.0)	3386.2(314.7)

[a] Intensities are mentioned in parentheses (km/mol), and experimental values are mentioned in italics.

The high intensity of this absorption mode in long molecules may be related to the conduction properties of polyynes:[47] C−H stretching induces a change in the net charge of these atoms which is propagated far away in the chain, which results in a large variation of the molecule dipole moment. A model calculation was performed at the BP86/6-31G** level on HC_7N indicating that the stretching of 0.1 Å of the H−C bond (the other parameters being frozen) yields the following Mulliken charge variations:

$$\begin{bmatrix} \mathrm{H} & \mathrm{C(1)} & \mathrm{C(2)} & \mathrm{C(3)} & \mathrm{C(4)} & \mathrm{C(5)} & \mathrm{C(6)} & \mathrm{C(7)} & \mathrm{N} \\ -0.04 & 0.04 & 0.04 & -0.01 & -0.04 & -0.03 & 0.04 & 0.01 & -0.01 \end{bmatrix}$$

and a total variation of the dipole moment of −0.17 D.

We remark that the slope of the intensity as a function of the number of carbon atoms in unsubstituted polyynes (motion of two hydrogens) is about twice these in cyanopolyynes (motion of one hydrogen).

C−H Deformation Vibrations. The polyynes of series **1** exhibit two bending C≡C−H modes of Π_u and Π_g symmetries. The Π_u mode is of a peculiar interest for the experimentalists, because it is easily observed in the emission spectrum of planetary atmospheres.[10−15] This vibration exhibits a quite constant absorption intensity (within about 1%) along the series, and its frequency decreases as the length of the chain increases (Figure 5), from 734 cm^{-1} in C_2H_2 to 581.7 cm^{-1} in $C_{16}H_2$ (BP86) toward an asymptotic limit which has been found at 581.6 (BP86), 595.9 (SVWN), and 651.6 (B3LYP). This result is not surprising: this vibration essentially involves the motion of H atoms at each end of the molecule perpendicularly to the chain and is thus almost independent of its length, except for the first terms. We can remark that the frequencies of both Π_u and Π_g modes of the C−H bending are equal for C_8H_2 and for longer chains, indicating that their coupling is negligible. A question is now, what resolution is needed to characterize with this mode two consecutive terms in the series? We can see that the frequencies in $C_{14}H_2$ and $C_{16}H_2$ differ by ca. 0.5 cm^{-1} at the BP86 level. The corresponding extrapolation formula (Table 9) predicts that the $C_{16}H_2$ value is only 0.1 cm^{-1} above the asymptote and thus that this vibration mode cannot be used to characterize easily higher terms than $C_{16}H_2$. In fact, from the available experimental values, it appears that an asymptotic value of 617.0 cm^{-1} could be reached more rapidly.[48]

In series **3** of monocyano compounds, only one C≡C−H bending mode is present, of Π symmetry and IR allowed. Its intensity is about half that of the series **1**, in agreement with the fact that the dipole moment variation during the motion of one hydrogen atom should be half that observed by the motion of two hydrogen atoms. The vibration frequency follows the same trend as the previous one (Figure 6), decreasing from 723 cm^{-1} in HCN to 594 cm^{-1} in $HC_{13}N$ (BP86) and from 729 cm^{-1} in HCN to 614 cm^{-1} in HC_9N (SVWN), toward respective limits of 591.2 and 609.0 cm^{-1}. The convergence of these values toward their limit appears nevertheless slower that in the series **1**, because a difference of ca. 3 cm^{-1} is observed between C_{11} and C_{13} molecules (vs ca. 0.5 cm^{-1} between the molecules having the same number of heavy atoms $C_{12}H_2$ and $C_{14}H_2$). Regression coefficients are given in Table 10.

C≡N Vibrations. When C≡N vibrations are dealt with, the situation is quite different from the C−H ones, because the associated simple vibrators (C≡N stretching and C−C≡N bending) have frequencies similar to the corresponding carbon vibrators of the skeleton and thus are strongly coupled with them.

In series **2** of monocyanopolyynes (Table 6), the stretching C≡N vibration appears as rather intense bands at 2273 cm^{-1} in HC_3N and 2251 cm^{-1} in HC_5N, but is split by coupling into several bands of noticeable intensity in the other terms: three for HC_7N and HC_9N, five for $HC_{11}N$, and six for $HC_{13}N$.

Because of higher symmetry, the situation is clearer in series **3** of dicyanopolyynes (Table 7). From C_4N_2 to $C_{10}N_2$, only one

TABLE 7: Harmonic Wavenumbers of $C_{2n}N_2$ (cm^{-1}), BP86/CC-pVTZ[a]

	Π_g	Π_u	Σ_g	Σ_u
C_2N_2	*507*/533.2	*233.1*/242.1(18.8)	*854.2*/866.6	*2157.8*/2165.6(0.4)
ref 52			*2329.9*/2323.4	
C_4N_2	*263*/275.6	*107*/110.1(9.2)	*640*/609.1	*1154*/1176.7(0.0)
ref 61	*504*/526.4	*471*/494.2(6.1)	*2224*/2119.5	*2267*/2242.1(4.9)
			2333/2275.5	
C_6N_2	*156*/163.3	*62*/62.5(5.3)	470.1	913.8(0.5)
ref 62	463.7	*276*/290.2(5.4)	*1288*/1325.6	2086.3(0.0)
	519.3	508.9(5.0)	2190.2	*2266*/2259.9(37.5)
			2235/2206.0	
C_8N_2	107.9	40.2(3.4)	382.6	748.3(1.6)
	299.4	198.9(5.7)	1095.8	1411.8(0.1)
	490.2	441.1(2.3)	2059.8	2153.5(1.5)
	515.2	509.8(4.5)	2139.0	2243.9(102.3)
			2228.1	
$C_{10}N_2$	75.8	27.9(2.4)	322.6	633.7(2.8)
	222.7	143.3(4.7)	933.3	1215.3(0.0)
	426.1	305.4(2.5)	1469.6	2039.1(0.0)
	494.8	472.5(2.0)	2079.0	2193.6(1.0)
			2126.0	2216.5(207.3)
			2239.0	
$C_{12}N_2$	56.2	20.5(1.8)	278.7	549.5(3.9)
	170.8	107.7(3.8)	811.7	1063.3(0.2)
	309.7	240.4(3.4)	1298.4	1507.9(0.0)
	457.7	414.8(1.2)	2019.3	2102.0(2.5)
	495.9	485.2(1.5)	2027.0	2176.0(231.6)
	507.4	507.6(4.4)	2168.6	2221.5(119.4)
			2232.0	
$C_{14}N_2$	43.3	15.8(1.4)	245.3	484.8(4.9)
	134.2	83.6(3.0)	718.3	943.7(0.6)
	253.7	192.3(3.5)	1159.6	1359.1(0.0)
	406.6	313.4(1.5)	1536.0	2006.2(0.1)
	473.4	446.2(1.2)	1976.6	2138.1(326.5)
	495.6	490.3(1.2)	2082.5	2147.2(42.1)
	507.1	507.2(4.4)	2192.9	2227.3(172.4)
			2219.7	
$C_{16}N_2$	34.4	12.5(1.2)	219.1	433.7(5.8)
	107.8	66.7(2.4)	643.8	848.1(1.2)
	209.3	156.2(3.1)	1045.1	1232.6(0.0)
	316.0	263.9(2.2)	1405.3	1557.4(0.0)
	436.8	400.2(0.7)	1933.1	2064.7(7.4)
	481.2	463.7(1.1)	1993.4	2104.8(499.8)
	495.4	492.8(0.9)	2125.6	2175.2(1.1)
			2186.1	2224.8(264.9)
			2219.2	

TABLE 8: Extrapolation Formulas for the Intensities of the C−H Stretching Harmonic Vibration of Polyynes and Cyanopolyynes (km/mol)

	C_yH_2	HC_yN
BP86	$I(y) = -140.8446 + 60.7488y$	$I(y) = 8.3871 + 23.3329y$
SVWN	$I(y) = -19.3471 + 60.7488y$	$I(y) = 22.8730 + 27.1720y$
B3LYP	$I(y) = 17.5305 + 35.4320y$	$I(y) = 39.503 + 21.7209y$

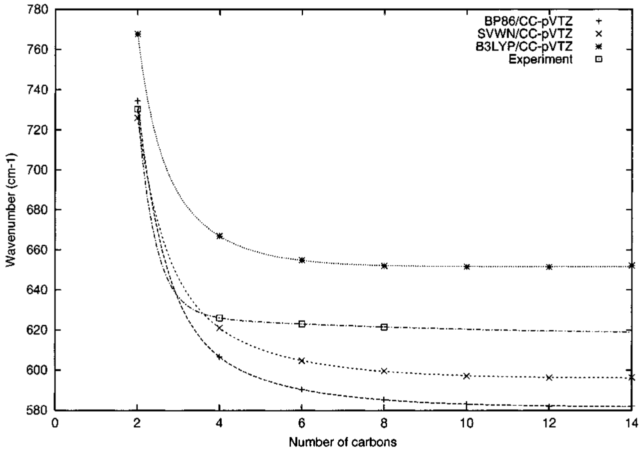

Figure 5. Harmonic wavenumbers of the C≡C−H Π_u bending vibration of $C_{2n}H_2$.

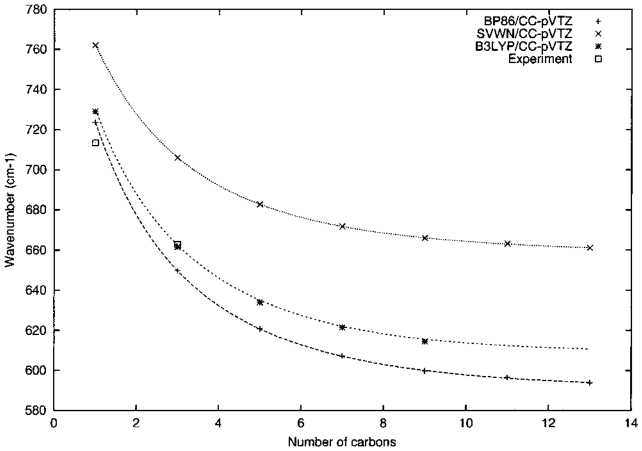

Figure 6. Harmonic wavenumbers of the C≡C−H Π bending vibration of $HC_{2n-1}N$.

high-frequency band appears corresponding to the antisymmetric C≡N stretching mode Σ_u. In the further terms, a stronger coupling with C≡C vibrators yields several high-intensity bands.

In the whole **2** and **3** series, the C−C≡N bending is always strongly coupled with the C−C≡C ones and, thus, is not clearly characterized.

TABLE 9: Regression Coefficients and Exponents in Formula (7) for the C≡C−H Π_u Harmonic Bending Vibration of $C_{2n}H_2$

	ω_∞	a	b	c	d
BP86	5.816×10^{2}	1.079×10^{2}	4.207×10^{-1}	2.271×10^{3}	1.530
SVWN	5.959×10^{2}	1.388×10^{2}	4.613×10^{-1}	1.774×10^{3}	1.583
B3LYP	6.516×10^{2}	3.467×10^{2}	7.860×10^{-1}	6.551×10^{3}	2.500
expt	6.170×10^{2}	1.029×10^{4}	2.304	1.413×10^{1}	1.437×10^{-1}

TABLE 10: Regression Coefficients and Exponents in Formula (7) for the C≡C−H Π Harmonic Bending Vibration of $HC_{2n-1}N$

	ω_∞	a	b	c	d
BP86	5.912×10^{2}	9.749×10^{1}	7.842×10^{-1}	1.175×10^{2}	2.895×10^{-1}
SVWN	6.090×10^{2}	1.394×10^{1}	3.379×10^{-1}	5.835×10^{1}	9.913×10^{-1}
B3LYP	6.587×10^{2}	7.166×10^{1}	2.559×10^{-1}	8.813×10^{1}	6.092×10^{-1}

TABLE 11: Harmonic Wavenumbers of the Low Frequency Π_u Harmonic Bending Vibration of $C_{2n}H_2$ (cm^{-1})

	BP86		SVWN		B3LYP		expt
y	ω (cm^{-1})	I (KM/mol)	ω (cm^{-1})	I (KM/mol)	ω (cm^{-1})	I (KM/mol)	ω (cm^{-1})
4	231.2	6.9	233.2	8.2	239.1	7.5696	220
6	108.4	4.0	108.4	4.0	111.8	4.0659	105
8	62.2	2.3	62.1	2.4	63.9	2.2415	
10	40.1	1.5	40.0	1.6	41.2	1.4093	
12	28.0	1.0	27.9	1.1	28.8	0.9600	
14	10.7	0.7	20.6	0.8	21.2	0.6995	
16	15.9	0.6					

TABLE 12: Harmonic Wavenumbers of the Π_u Low Frequency Bending Vibrations of $HC_{2n-1}N$ (cm^{-1})

	BP86		SVWN		B3LYP		expt
y	ω (cm^{-1})	I (KM/mol)	ω (cm^{-1})	I (KM/mol)	ω (cm^{-1})	I (KM/mol)	ω (cm^{-1})
3	522.3	3.1	544.4685	6.3709	537.8	6.9	499
5	268.8	6.5	279.3321	7.3129	272.5	7.6	
7	162.7	5.5	168.6663	6.1559	163.0	6.0	
9	107.5	3.9	111.0291	4.1515	107.5	4.2	
11	75.9	2.8	78.2770	2.9580			
13	56.3	2.1	57.9656	2.1879			

TABLE 13: Harmonic Wavenumbers of the Π_u Low Frequency Bending Vibrations of $C_{2n}N_2$ (cm^{-1})

	BP86		SVWN		B3LYP		expt
y	ω (cm^{-1})	I (KM/mol)	ω (cm^{-1})	I (KM/mol)	ω (cm^{-1})	I (KM/mol)	ω (cm^{-1})
2	242.1	18.8	244.9	20.6	253.3537	21.2	233.1
4	110.1	9.2	110.0	9.8	113.8573	10.3	107
6	62.5	5.3	62.2	5.5	64.2963	5.8	62
8	40.2	3.4	39.9	3.6	41.2213	3.7	
10	27.9	2.4	27.8	2.5	28.6607	2.6	
12	20.5	1.8	20.4	1.9	21.0578	1.9	
14	15.8	1.4	15.6	1.5	16.1523	1.5	
16	12.5	1.2	12.4	1.2	12.7692	1.2	

TABLE 14: Regression Coefficients and Exponents in Formula (7) for the Low Frequency Π_u Harmonic Bending Vibration of $C_{2n}H_2$

	ω_∞	a	b	c	d
BP86	7.838	2.926×10^{2}	2.245×10^{-1}	1.884×10^{3}	7.238×10^{-1}
SVWN	9.149	3.331×10^{2}	2.409×10^{-1}	2.116×10^{3}	7.707×10^{-1}
B3LYP	8.516	3.056×10^{2}	2.277×10^{-1}	1.950×10^{3}	7.239×10^{-1}

TABLE 15: Regression Coefficients and Exponents in Formula (7) for the Low Frequency Π Harmonic Bending Vibration of $HC_{2n-1}N$

	ω_∞	a	b	c	d
BP86	2.440×10^{1}	6.752×10^{2}	2.349×10^{-1}	1.614×10^{3}	7.619×10^{-1}
SVWN	3.781×10^{1}	8.916×10^{2}	2.840×10^{-1}	1.864×10^{3}	9.152×10^{-1}
B3LYP	2.579×10^{1}	7.241×10^{2}	2.395×10^{-1}	1.713×10^{3}	7.786×10^{-1}

A remark can be done concerning triple bond C≡C stretching vibrations. A molecule which contains n such bonds exhibits n vibrations in the 2000 cm^{-1} region. If n is even, there are $n/2$ Σ_u IR allowed modes and $n/2$ Σ_g Raman allowed modes. If n is odd, there is a central triple bond, and we observe $(n - 1)/2$ IR allowed modes and $(n + 1)/2$ Raman allowed modes. The same

TABLE 16: Regression Coefficients and Exponents in Formula (7) for the Low Frequency Π_u Harmonic Bending Vibration of $C_{2n}N_2$

	ω_∞	a	b	c	d
BP86	6.950	5.106×10^{2}	7.294×10^{-1}	1.794×10^{2}	2.161×10^{-1}
SVWN	5.684	5.118×10^{2}	6.516×10^{-1}	1.474×10^{2}	1.932×10^{-1}
B3LYP	6.944	5.506×10^{2}	7.296×10^{-1}	1.817×10^{2}	2.140×10^{-1}

remark can be done for C−C vibrators but is of lesser interest, because some of these vibrations can be hardly distinguished from deformation modes.

Low-Frequency Vibrations. It is worthy to note that in the largest of these molecules it appears in deformation modes at very low frequencies, usually associated to molecular motions linking two conformers. The lowest frequency (Π_u in **1** and **3** and Π in **2**) of each molecule, gathered in Tables 11−13 with the corresponding regression coefficients (Tables 14−16), consists of the bending of the whole molecule, with in-phase variation of all the bond angles. This vibration is IR allowed, though its intensity is rather weak and decreases along the series. Three remarks can be done.

1. For the longest molecules studied here, these frequencies drop to less than 20 cm^{-1} (15.9 cm^{-1} for $C_{16}H_2$ and 12.5 cm^{-1} for $C_{16}N_2$) out of the so-called IR region and belong in fact to microwave spectroscopy (millimetric wavelengths), so that we can expect to detect such molecules whatever their permanent dipole moment.

2. Moreover, this frequency converges toward an asymptotic limit more slowly than the other characteristic frequencies previously discussed. For example, it differs by nearly 5 cm^{-1} in $C_{14}H_2$ and $C_{16}H_2$. Because, among other, the anharmonicity is supposed negligible, we can expect, for higher terms, a good agreement of the calculated values with the experimental ones. In so far as they can be measured experimentally, these vibration frequencies appear as the most accurate for the characterization of long polyynes.

3. The lowest of these frequencies has a very small vibrational temperature. It is, for example, 23 K for the 15.9 cm^{-1} vibration of $C_{16}H_2$. As a result, several vibrational levels are strongly populated even at 100 K, in Titan's atmosphere. A possible consequence is that these molecules could have a random structure quite different from linearity, which has to be considered when calculating oscillator strengths of electronic transitions.

Conclusion

On the basis of DFT calculations of polyynes, cyanopolyynes, and dicyanopolyynes having up to 16 carbon atoms, we give geometrical parameters and harmonic vibration frequencies. The spectroscopic IR characterization of the longer of these molecules in a natural environment such as planetary atmospheres or interstellar space appears difficult. In this aim, the most accurate vibration mode is a low frequency bending of the molecule, which has unfortunately a low intensity.

Extrapolation formulas for the calculation of bond lengths taking into account the "edge effect" indicates that a marked bond alternation remains in molecules as large as $C_{40}H_2$.

Reliable geometrical parameters will be used for semiempirical calculations of electronic transition energies (this work is in progress).

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