Ab Initio Calculation of Molecular Properties of Cyanopolyynes, $H—(C≡C)_n—CN$

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Results of ab initio SCF calculations on cyanopolyynes, $H—(C≡C)_n—CN$ with n up to 7 are reported. Calculated rotational constants and one-electron properties are compared with the available experimental values. The effects of the C≡C chain length on the physical properties are discussed.

1. Introduction

In a very recent communication, Bell et al. [1] reported the observation of $HC_{11}N$ (cyano-deca-penta-yne) in the microwave spectrum of the interstellar space. The $HC_{11}N$ species represents the largest and heaviest extraterrestial molecule ever detected outside the earth's atmosphere.

Previously, lower members of cyanopolyynes also have been detected partly from the chemical preparation of these compounds in the laboratory or partly from the interstellar space; HC_3N [2–4], HC_5N [5–7], HC_7N [8, 9] and HC_9N [10, 11].

With respect to the effect of chain lengthening on the individual bond lengths in linear conjugated systems, cyanopolyynes are also of interest for theoretical study. There are a few ab initio SCF studies reported previously for the $H-(C\equiv C)_n-CN$ species. Moffat [12] and Figeys et al. [13] have studied cyanoacetylene (HC_3N) cyanodiacetylene (HC_5N) and Haese and Woods [14] reported calculations on HC_3N and its isomers or protonated forms. Recently, Boyd et al. [15] carried out a systematic ab initio study on geometries, energies and polarities of the $H-(C\equiv C)_n-CN$ species with n up to 5.

In the present study, we consider cyanopolyynes up to $H-(C\equiv C)_7-CN$ and report results of ab initio SCF calculations on the moments of inertia, rotational constants and various one-electron properties of these species. The calculated values are compared with available experimental ones.

2. Calculation

Ab initio SCF calculations have been carried out using the STO-3G [16], 3-21G [17] and 6-31G** [18] basis sets. Except for $HC_{13}N$ and $HC_{15}N$, the geometrical parameters reported by Boyd et al. [15] have been employed and for $HC_{13}N$ and $HC_{15}N$ the STO-3G basis set was used for geometry optimization. The geometry optimization and one-electron properties have been calculated employing the MONSTERGAUSS program [19]. A list of basis sets used for $H-(C=C)_n-CN$ calculations are summarized in Table 1.

3. Results and Discussion

The effect of the employed basis sets on the C−C and C≡C bond lengths in $H-(C=C)_n-CN$ ($n=1$ to 5) has been extensively discussed by Boyd et al. [15]. It is observed that the STO-3G basis set yields the C≡N bond lengths which agree very

Table 1. List of basis sets used for $H-(C\equiv C)_n-CN$ calculations.

n	STO-3G	3-21G	6-31G**
0	x	x	x
1	x	x	x
2	x	x	
3	x	x	
4	x		
5	x		
6	x		
7	x		

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well with experiment and that the calculated C − C and C ≡ C bonds are about 0.04 and 0.03 Å too long and too short, respectively. From the results obtained for the geometry optimization of $HC_{13}N$ and $HC_{15}N$, which were not considered in previous studies, it is confirmed that the C ≡ N, the adjacent C − C and C ≡ C bonds reach limiting values of 1.160, 1.403 and 1.183 Å, respectively, and at the other end the C − C, C ≡ C and C − H bonds have the asymptotic limits of 1.402, 1.176 and 1.067 Å, respectively as the n value is getting larger.

The calculated moments of inertia and rotational constants are summarized in Table 2 and compared them with available experimental values. It is shown that the calculated rotational constants obtained from the STO-3G basis set underestimate the experimental values by only about 0.7% in all cases, while those from the split-valence (3-21G) or the split-valence plus polarization function (6-31G**) basis set appreciably overestimate the experimental values. The 3-21G basis set shortens all bond lengths except the C ≡ C bond and the 6-31G** basis set shortens the C ≡ C and C ≡ N bonds and lengthens the C − C and C − H bonds. For HC_3N, two previous ab initio calculations employing the double-zeta (DZ) basis set gave better agreement with experiment. The calculated values of rotational constants amounted to 4539 MHz [21] and 4556 MHz [14] which agree excellently with the experimental value of 4549 MHz [20]. The cancellation of bond length errors in the C − C and C ≡ C bonds introduces only a small error in the rotational constants. A systematic underestimation of experimental values obtained by the STO-3G basis set calculation up to $HC_{11}N$ may thus be useful to serve as a guidance for experimental detections of the higher homologues, $HC_{13}N$ and $HC_{15}N$ in the future. It should be mentioned that Oka [22] employed a simple extrapolation scheme assuming the structural parameters and calculated the rotational constant of $HC_{11}N$ to be 169.0629 MHz which is in excellent agreement with the most recent experimental value 169.27 MHz of this molecule [1].

Table 2. Moments of inertia and rotational constants of $H{-}(C{\equiv}C)_n{-}CN$.

		I_b[a]	B[b]
HC_3N	STO-3G	111.6985	4524.4656
	3-21G	108.8238	4643.9858
	6-31G**	109.9234	4597.5295
	Expt[c]		4549.0583
HC_5N	STO-3G	382.0552	1322.7828
	3-21G	373.6548	1352.5210
	Expt[d]		1331.3313
HC_7N	STO-3G	902.1925	560.1643
	3-21G	884.0074	571.6875
	Expt[e]		564.0007
HC_9N	STO-3G	1751.8751	288.4772
	Expt[f]		290.5184
$HC_{11}N$	STO-3G	3011.0950	167.8379
	Expt[g]		169.27
$HC_{13}N$[h]	STO-3G	4759.1026	106.1914
$HC_{15}N$[i]	STO-3G	19267.5012	26.2295

[a] Amu Å^2 units. [b] MHz units. [c] Ref. [20].
[d] Ref. [5]. [e] Ref. [8]. [f] Ref. [10].
[g] Ref. [1]. [h] SCF energy: −540.11512 a.u.
[i] SCF energy: −614.85628 a.u.

Several molecular properties have been calculated with the STO-3G, 3-21G and 6-31G** basis sets including the dipole moment, second moment, quadrupole moment, potential, electric field and electric field gradient at nuclei. These are summarized in Table 3 for HC_3N, HC_5N and HC_7N and compared with the calculated values for HCN. Since calculated values from the STO-3G basis set are considered as too crude for quantitative purpose they are omitted. It is perhaps worthwhile only to mention that the calculated dipole moment values from the STO-3G basis set are about 30% smaller than those from the 3-21G basis set or experimental ones in all cases and that the calculated electric field gradients at nitrogen are about one thirds of the 3-21G values. A systematic analysis of the basis set effect on the calculated molecular properties will be reported separately for HCN [23].

First of all, it may be confirmed that the calculated properties from the 3-21G basis set are in general in good agreement with experiment. For example, the calculated dipole moments of 3.042, 3.874, 4.474 Debye for HCN, HC_3N and HC_5N, respectively agree fairly well with experimental values of 2.99 [3], 3.6 [5] and 4.33 [3]. The calculated dipole moments from the 6-31G** basis set for HCN and HC_3N are shown to overestimate the corresponding experimental values. The dipole and second moments are shown to increase in magnitude from HCN to HC_7N monotonically. While the potential at H increases, those at C and N are found to decrease as n becomes larger. It is also of interest that the quadrupole moment decreases in magnitude from HC_3N to HC_7N. The electric field

Table 3. One-electron properties of $H-(C\equiv C)_n-CN$ calculated by the 3-21G and 6-31G** basis sets[a].

n	0	1	2	3
Dipole moment[b]				
	3.042	3.874	4.474	4.910
	(3.204)	(4.085)		
Second moment[c]				
$\langle x^2\rangle = \langle y^2\rangle$	-8.5862	-17.0376	-25.4800	-33.9060
	(-8.5934)	(-16.7508)		
$\langle z^2\rangle$	-7.2867	-15.4027	-24.0478	-33.0159
	(-6.8193)	(-15.0074)		
Quadrupole moment[d]				
$Q_{xx} = Q_{yy}$	-0.6498	-0.8175	-0.7161	-0.4450
	(-0.8871)	(-0.8717)		
Q_{zz}	1.2996	1.6349	1.4323	0.8900
	(1.7741)	(1.7434)		
Potential[e]				
$\langle 1/r\rangle$ (C)	-14.5874	-14.5648	-14.5604	-14.5581
	(-14.6890)	(-14.6652)		
$\langle 1/r\rangle$ (N)	-18.2223	-18.2141	-18.2103	-18.2081
	(-18.3329)	(-18.3260)		
$\langle 1/r\rangle$ (H)	-0.9566	-0.9720	-0.9768	-0.9801
	(-0.9686)	(-0.9887)		
Electric field[f]				
E_z (C)	0.0501	0.0112	0.0089	0.0093
	(0.0255)	(-0.0338)		
E_z (N)	-0.2158	-0.2183	-0.2183	-0.2183
	(-0.0790)	(-0.0827)		
E_z (H)	0.0819	0.0817	0.0810	0.0808
	(0.0106)	(0.0098)		
Electric field gradient[g]				
q_{zz} (C)	0.2678	0.1918	0.1803	0.1761
	(0.3443)	(0.2606)		
q_{zz} (N)	0.9742	0.9064	0.9042	0.9060
	(0.9953)	(0.9441)		
q_{zz} (H)	-0.3846	-0.3878	-0.3892	-0.3897
	(-0.3497)	(-0.3582)		

[a] The z-axis is the molecular axis. The C atom refers to the nitrile carbon.
[b] Debye units.
[c] Atomic units. Calculated at center of mass.
[d] Atomic units. Calculated at center of mass.
[f] Atomic units.
[e] Atomic units.
[g] Atomic units.

gradient at proton remains almost constant as the chain length increases. On the other hand, the electric field gradient at the nitrile C atom is found to decrease markedly from HCN to HC_7N. The electric field gradient at N in HCN differs considerably from the rest of the systems, but it remains almost constant among HC_3N, HC_5N and HC_7N. The quadrupole coupling constants at nitrogen are calculated, employing $Q(^{14}N) = 1.56 \times 10^{-26}$ cm^2 [24], as 3.33 MHz with the 3-21G basis set and as 3.47 MHz with the 6-31G** basis set for HC_3N, HC_5N and HC_7N, and the corresponding values at ^2H amount to 253 kHz (3-21G) and 230 kHz (6-31G**), respectively.

The total atomic charges obtained by using the Mulliken population analysis yielded, also as observed by Boyd et al., unrealistic values for the central C atom for HC_5N and HC_7N (e. g. the net charges of the central C atom is calculated as -1.08 e for HC_7N), if the split-valence basis set such as the 3-21G basis set was employed. This might be due to the biased delocalization of the diffuse orbital in the split-valence set in describing the σ-orbital. We propose therefore to use the calculated magnetic shielding or the $\langle 1/r \rangle$ values as an alternative measure to the total charges obtained from the Mulliken population analysis. Table 4 summarizes the magnetic shielding and the $\langle 1/r \rangle$ values for N, H and C_n atoms in $H-(C\equiv C)_n-CN$ ($n =$ 0, 1, 2, 3) calculated from the 3-21G basis set. It is found that these values on the central C atoms do not differ appreciably from the rest of the C atoms, in contrast to the atomic charges defined by Mulliken population analysis.

At the STO-3G basis set level, the calculated net charges and overlap populations obtained from Mul-

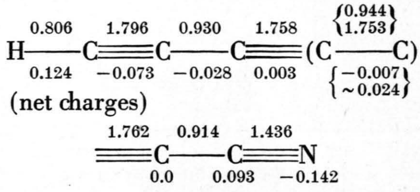
Table 4. Calculated magnetic shielding and $\langle 1/r \rangle$ values of $H-(C\equiv C)_n-CN$ with the 3-21G basis set (a.u.)[a].

n		0	1	2	3
N	xx	− 6.343	− 6.380	− 6.385	− 6.387
	zz	− 5.537	− 5.423	− 5.439	− 5.434
	$\langle 1/r \rangle$	− 18.223	− 18.214	− 18.210	− 18.208
H	xx	− 0.749	− 0.777	− 0.784	− 0.787
	zz	0.542	0.582	0.591	0.594
	$\langle 1/r \rangle$	− 0.956	− 0.972	− 0.977	− 0.980
C_1	xx	− 5.218	− 5.377	− 5.389	− 5.392
	zz	− 4.151	− 3.810	− 3.782	− 3.774
	$\langle 1/r \rangle$	− 14.587	− 14.568	− 14.560	− 14.558
C_2	xx	—	− 5.374	− 5.405	− 5.409
	zz	—	− 3.814	− 3.739	− 3.727
	$\langle 1/r \rangle$	—	− 14.562	− 14.549	− 14.545
C_3	xx	—	− 5.235	− 5.395	− 5.407
	zz	—	− 4.098	− 3.751	− 3.724
	$\langle 1/r \rangle$	—	− 14.570	− 14.542	− 14.538
C_4	xx	—	—	− 5.391	− 5.423
	zz	—	—	− 3.785	− 3.709
	$\langle 1/r \rangle$	—	—	− 14.568	− 14.555
C_5	xx	—	—	− 5.245	− 5.406
	zz	—	—	− 4.085	− 3.735
	$\langle 1/r \rangle$	—	—	− 14.575	− 14.548
C^6	xx	—	—	—	− 5.395
	zz	—	—	—	− 3.780
	$\langle 1/r \rangle$	—	—	—	− 14.570
C_7	xx	—	—	—	− 5.250
	zz	—	—	—	− 4.080
	$\langle 1/r \rangle$	—	—	—	− 14.679

[a] Atomic units, the z-axis is the molecular axis. C_1 refers to the nearest C atom to N.

liken population analysis seem to be reasonable. For $HC_{13}N$ and $HC_{15}N$ the result may be summarized as follows;

(overlap populations)



$$\mathrm{H}\underset{0.124}{\overset{0.806}{-}}\mathrm{C}\underset{-0.073}{\overset{1.796}{\equiv}}\mathrm{C}\underset{-0.028}{\overset{0.930}{-}}\mathrm{C}\underset{0.003}{\overset{1.758}{\equiv}}(\mathrm{C}\underset{\left\{\begin{smallmatrix}-0.007\\ \sim 0.024\end{smallmatrix}\right\}}{\overset{\left\{\begin{smallmatrix}0.944\\ 1.753\end{smallmatrix}\right\}}{-}}\mathrm{C})_n$$

(net charges)

$$\overset{1.762}{\equiv}\underset{0.0}{\mathrm{C}}\overset{0.914}{-}\underset{0.093}{\mathrm{C}}\overset{1.436}{\equiv}\underset{-0.142}{\mathrm{N}}$$

($n = 4$ and 5).

It is observed that the overlap populations of the $C\equiv N$ and $H-C$ bonds in HC_nH for $n = 5$, 7, 9, 13 and 15 remain almost constant with 1.436 e and 0.806 e and that the asymptotic limits of the central $C-C$ and $C\equiv C$ bonds amount to 0.944 e and 1.752 e, respectively. Also the net charges of the individual atom converge very rapidly to their asymptotic limits and the central C atoms have almost neutral charges in contrast to the split-valence basis set results. The increase of the polarity due to the $C-C$ chain length is considered therefore to be modest, which is also supported by the calculated dipole moment values. On the other hand, a recent theoretical study [25] indicates that the carbene isomers of cyanopolyynes, C_nNH become exceedingly polar with increasing chain length.

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