

An ab initio study of electric properties of linear $(\text{HCN})_N$ and $(\text{HNC})_N$ aggregates in gas phase



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ABSTRACT

We have accurately estimated the dipole moment (μ), the static linear polarizability $\bar{\alpha}$ and first hyperpolarizability (β_{tot} and β_{HRS}) per unit of long linear chains of HCN and HNC molecules, using the MP2/6-311++G(2d,2p) approach. It is found for both isomers that the intermolecular interactions have a substantial impact on the first hyperpolarizability, in comparison with the corresponding monomer results. For the infinite HCN [HNC] chains, the extrapolated values for μ , $\bar{\alpha}$, β_{tot} and β_{HRS} per unit are estimated in 1.655 [2.145], 16.96 [19.42], 76.6 [134.9] and 32.4 [54.6] a.u., respectively.

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1. Introduction

Molecular assembly through hydrogen bonding has been an issue of perennial discussion in the scientific literature because of its interest in fields ranging from astrophysics to biology [1–4]. Recently, this process of molecular association into stable aggregates has received a great deal of attention in the assembly of extended surface architecture of single molecule units [5,6]. Among plenty of molecules capable to form hydrogen bonded aggregates with well-defined composition and structure, hydrogen cyanide (HCN) meets a special place, since it has been discussed as a possible precursor to amino acids and nucleic acids [7]. Indeed, chemical investigations under prebiotic conditions have led to the discovery of new routes to organic molecules derived from HCN oligomers [8]. For this reason, long linear HCN chains are of special interest for the understanding of more complex mechanisms of molecular association. Aside from HCN, its tautomeric form, i.e., hydrogen isocyanide (HNC), is a simple zwitterion with ability to form linear chains [9]. Interestingly, these chain structures from both molecules exhibit enormous stability with large dipole moments [10,11]. As a consequence of these properties, HCN tends to form highly anisotropic hydrogen-bonded molecular crystals, developing an electric polarization when subjected to a uniform temperature change [12]. In principle, many properties of these pyroelectric molecular crystals may be discussed in terms of finite linear chains considered individually. However, this is still an interesting open problem to be treated [13].

From the quantum chemical point of view, understanding how the microscopic properties of molecular aggregates change at large

extension is a grand challenge. In particular, the convergence of some molecular properties with the size of the system is only expected for largely extended configurations of molecules. In this sense, HCN and HNC offer both simple and exciting chemical models that allow a refined study by employing high-level quantum chemical calculations. For example, the multiple-body effects on HCN chains, investigated by employing many-body perturbation/coupled cluster theories [14], have demonstrated that the co-operative effects in these linear molecular aggregates are dominated by electrostatic interactions. Among the electric properties, the dipole moment has been the property most deeply investigated with the increase of the HCN or HNC chains [10,11,14–17]. But previous studies on the other electric properties such as the dipole polarizability and first hyperpolarizability of these linear chains are scarce in the literature. Indeed, Adrian-Scotto and Vasilescu [18] carried out a DFT study on the linear clusters of HCN and reported significant cooperative effects on the linear polarizability. More recently, Góra et al. [19] have reported extrapolated CCSD(T) values for these electric properties of linear chains of HCN, based on the interaction energy decomposition scheme. Their results have shown that the co-operative effects are particularly important for the first hyperpolarizability. However, an analysis of how the electric properties are affected by the structural isomerization of HCN has not yet been previously investigated.

In the present study we report the dipole moment, linear polarizability and first hyperpolarizability of linear chains of hydrogen cyanide and of hydrogen isocyanide, using the second-order Møller-Plesset perturbation theory (MP2) method [20]. This method has been proven to be very efficient for calculating the nonlinear properties of molecules [21–24] as well as polymers [25–29]. We have estimated the extrapolated values of electric properties per unit using the finite oligomer approach. The co-operative

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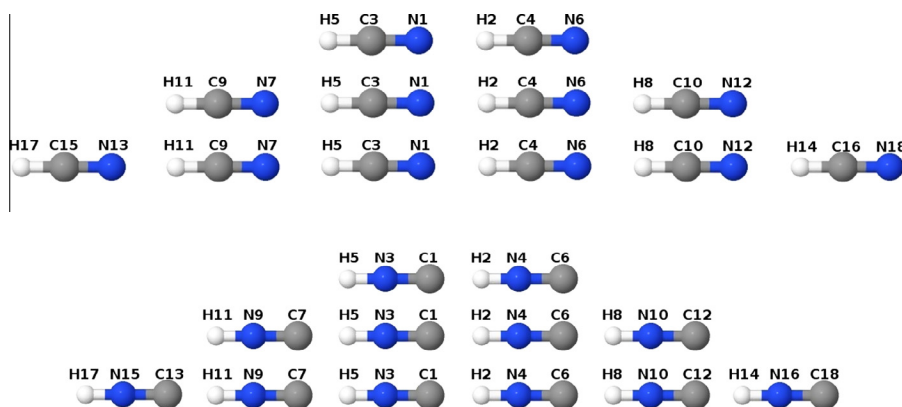


Figure 1. Schematic representation of the HCN and HNC chains with the backbone atom numbering.

effects arising from the molecular association were comparatively investigated for the structural and electric properties of both systems.

2. Computational details

Initially, the ground state geometry of the chains represented by the series $(\text{HCN})_N$ and $(\text{HNC})_N$ (for $N = 1-10$) were fully optimized at the MP2 level using the 6-311++G(2d,2p) basis set. The geometry optimization calculations were carried out using the GAUSSIAN 09 electronic structure package [30]. To confirm the stability of these linear structures we have analyzed the harmonic vibrational frequencies that were found to be positive. Sánchez et al. [17] have reported a DFT and MP2 study on the interaction energy of linear chains of hydrogen isocyanide and hydrogen cyanide, with the former being more stable than the latter. Structures of studied linear chains in this letter are displayed in Figure 1.

In the presence of a static uniform electric field (\vec{F}), the electronic energy (E) can be written as

$$E = E_0 - \mu_i F_i - \frac{1}{2!} \alpha_{ij} F_{ij}^2 - \frac{1}{3!} \beta_{ijk} F_{ijk}^3 - \dots \quad (1)$$

where E_0 is the energy of the molecule in the absence of the external electric field and μ_i , α_{ij} , and β_{ijk} are, respectively, the components of the dipole moment, linear polarizability, and first hyperpolarizability. The components of μ_i and α_{ij} were analytically determined with the MP2 method and the components of β_{ijk} were calculated at the same level by numerical differentiation of the analytical polarizabilities in relation to the electric field, as implemented in GAUSSIAN 09 program [30]. The 6-311++G(2d,2p) basis set has also been employed in the calculations of electric properties. The choice of this basis set represents a good compromise between computational cost and accuracy, although the results could undoubtedly be improved by using a more extended basis set [31].

Here, we have reported the average linear polarizability $\bar{\alpha}$ and the total intrinsic first hyperpolarizability β_{tot} which are defined as

$$\bar{\alpha} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \quad (2)$$

and

$$\beta_{\text{tot}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (3)$$

where

$$\beta_i = \frac{1}{3} \sum_j (\beta_{jij} + \beta_{jji} + \beta_{jji}) \quad (4)$$

For both studied chains, the longitudinal components of the electric responses constitute the dominant terms only for the dipole moment and first hyperpolarizability. Additionally, we have reported the quantity sampled in the hyper-Rayleigh scattering intensity for the plane polarized incident light, which is given by

$$\beta_{\text{HRS}} = \sqrt{\langle \beta_{\text{ZZZ}}^2 \rangle + \langle \beta_{\text{ZXX}}^2 \rangle} \quad (5)$$

and the associated depolarization ratio defined as

$$\text{DR} = \frac{\langle \beta_{\text{ZZZ}}^2 \rangle}{\langle \beta_{\text{ZXX}}^2 \rangle} \quad (6)$$

where $\langle \beta_{\text{ZZZ}}^2 \rangle$ and $\langle \beta_{\text{ZXX}}^2 \rangle$ are the orientationally averaged hyperpolarizabilities, whose the expressions are given in Ref. [24].

The extended hydrogen-bonded chain properties have been obtained by extrapolating the finite oligomer values. The values of μ , $\bar{\alpha}$, β_{tot} and β_{HRS} per unit were calculated using an alternative definition based on the difference between the properties of two consecutive chains [32]. Thus, the value of a molecular property P ($P = \mu, \bar{\alpha}, \beta_{\text{tot}}$ or β_{HRS}) per unit has been determined by $\Delta P(N) = [P(N) - P(N-1)]$.

3. Results and discussion

Table 1 presents a comparison between the $r(\text{N-H})$ [$r(\text{C-H})$] intermolecular bond distances of the linear $(\text{HCN})_N$ [$(\text{HNC})_N$] chains for $N = 1-10$ optimized at the MP2/6-311++G(2d,2p) level. As previously reported for the linear HCN chains [33], the most significant changes due to cooperative effects are observed for the intermolecular bond lengths at the central segment of both studied isomers. Figure 2 shows the chain length dependence of $r(\text{N-H})$ and $r(\text{C-H})$ in the middle of the linear chains. One can see that the values of $r(\text{N-H})$ and $r(\text{C-H})$ decrease with increasing cluster size and properly converge toward the corresponding infinite chain values. The results for $r(\text{N-H})$ and $r(\text{C-H})$ of the decamers of HCN and HNC (although in both cases the expected convergence limit have not been yet reached) are of 2.066 and 1.852 Å, respectively. These findings are in concordance with the MP2/cc-pVTZ results of 2.123 and 1.942 Å (hexamer), reported in Ref. [9]. In comparison with the corresponding dimer result for the hydrogen cyanide, the reduction of $r(\text{N-H})$ is of 0.14 Å. A equivalent asymptotic value

Table 1

Intermolecular bond distances (Å) of linear clusters of HCN and HNC obtained at the MP2 level with the 6-311++G(2d,2p) basis set (see also Figure 1). N is the number of units.

N	$(\text{HCN})_N$		$(\text{HNC})_N$			
	$r(\text{N7-H5})$	$r(\text{N1-H2})$	$r(\text{N6-H8})$	$r(\text{C7-H5})$	$r(\text{C1-H2})$	$r(\text{C6-H8})$
2		2.2066		2.0536		
4	2.1429	2.1103	2.1517	1.9633	1.9252	1.9839
6	2.0904	2.0820	2.0922	1.8916	1.8826	1.8996
8	2.0740	2.0712	2.0747	1.8657	1.8616	1.8682
10	2.0674	2.0663	2.0677	1.8535	1.8516	1.8546

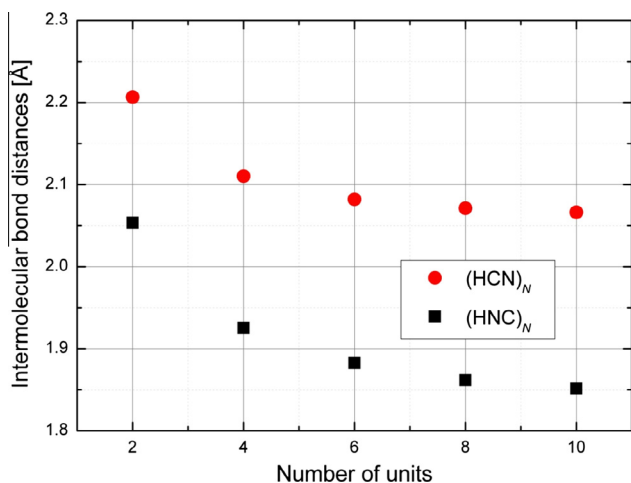


Figure 2. Chain length dependence of the intermolecular bond distances [$r(\text{N}-\text{H})$] [$r(\text{C}-\text{H})$] at the central segment of the HCN [HNC] chains.

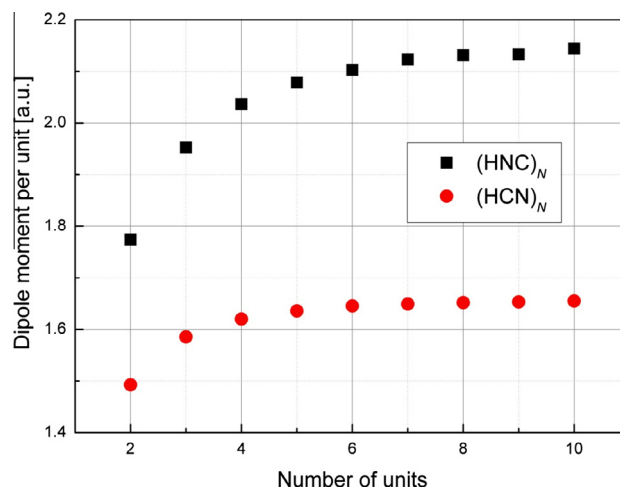


Figure 3. Evolution of dipole moment per unit of the HCN and HNC chains.

obtained at the HF/6-31 + G(d) level has been reported in Ref. [7]. For the hydrogen isocyanide, the corresponding reduction of $r(\text{C}-\text{H})$ is larger and given by 0.20 Å. Furthermore, the intermolecular interactions lead to slight lengthening of the $r(\text{HC})$ [$r(\text{HN})$] bond lengths of the HCN [HNC] chains but almost no affect the $r(\text{CN})$ [$r(\text{NC})$] bond lengths. At the central segment of the HCN [HNC] chains, the predicted increases of the $r(\text{HC})$ [$r(\text{HN})$] bond length in going from the dimer to the decamer is of 0.08 [0.03] Å (results not shown in table).

Table 2 presents the MP2/6-311++G(2d,2p) results for the electric properties of the studied linear chains. For comparison, our results for the dipole moment of 3.02, 6.81 and 10.85 D obtained for the monomer, dimer and trimer of HCN, respectively, are in good concordance with the corresponding experimental results of 2.99 [34], 6.55 [35] and 10.6 D [36] (1 D = 0.3934 a.u.) and with the CCSD(T) values of 3.01, 6.77 and 10.77 D [19] (the former was obtained with aug-cc-pVQZ and the last two with aug-cc-pVTZ basis sets). Figure 3 presents the evolution of $\Delta\mu$ (dipole moment per unit) as the chain length is increased for both isomers. The results show that the values of $\Delta\mu$ increase rapidly with chain length for small chains and tend for converged values of infinite chains. A typical shape has been observed in polysilaacetylene chains [PSA, $-(\text{CH}=\text{SiH})_N-$] [37]. The converged results for $\Delta\mu$ of 1.655 and 2.145 a.u. for the infinite chains of HCN and HNC (found between heptamer and decamer) respectively, are enhanced by factors of 40% and 66%, as compared with the corresponding monomer results. This emphasizes the zwitterionic character of HNC. Otherwise, the dipole moment of HCN [HNC] decamer is 3.89

[6.86] a.u. greater than that obtained from an additive model based on the monomer dipole moment. MP2/6-311++G(2p,2d) results for the CHELPG atomic charges are listed in Table 3. From this table, we realize that at the central region the charge of each atom tends to a constant value. The net charge of the central moiety tends to vanish, whereas its dipole moment converges to a non-vanishing value. Furthermore, there is an accumulation of charge with opposite sign in the ends of the chains that tends to constant values, providing another contribution to the dipole moment per unit. The results also show a considerable effect due to the isomeric change on the dipole moment. For example, the $\mu^{\text{HNC}}/\mu^{\text{HCN}}$ ratio varies between 1.09 and 1.25. A larger value of the dipole moment of HNC chains in relation to the HCN can be understood from a larger charge accumulation at the ends. For infinite chains, it is noted that $\Delta\mu^{\text{HNC}}$ is 30% larger than $\Delta\mu^{\text{HCN}}$.

The evolution of the average linear polarizability per unit for both isomers as function of N is depicted in Figure 4. One can see that $\Delta\bar{\alpha}$ presents a similar shape observed for $\Delta\mu$, also presented by other polymer chains: it quickly increases for the smaller chains due to the increase of electron mobility and converges towards the polymeric value. For the larger HCN and HNC chains the $\Delta\bar{\alpha}$ values are 12% and 15% larger than the corresponding monomer results (see Table 2), showing that the impact of the intermolecular interactions is smaller than those obtained for $\Delta\mu$. It is found, for the studied isomers, $\bar{\alpha}^{\text{HNC}}/\bar{\alpha}^{\text{HCN}}$ ratios between 1.12 and 1.14, what indicates that the effect of the isomeric change is moderated and almost independent of the chain length. For infinite chains, $\Delta\bar{\alpha}^{\text{HNC}}$ is 15% larger than $\Delta\bar{\alpha}^{\text{HCN}}$. The converged results (19.42 and 16.96 a.u.) are found between heptamer and decamer. These ratios also

Table 2

MP2/6-311++G(2d,2p) results for the dipole moment, linear polarizability, first hyperpolarizability, and hyper-Rayleigh depolarization ratio of linear HCN and HNC chains. All results are in a.u. and N is the number of units.

N	(HCN) $_N$							(HNC) $_N$						
	μ	α_L	$\bar{\alpha}$	β_L	β_{tot}	β_{HRS}	DR	μ	α_L	$\bar{\alpha}$	β_L	β_{tot}	β_{HRS}	DR
1	1.189	21.91	15.14	5.58	3.14	2.14	2.2	1.291	23.45	16.88	33.13	58.33	21.32	8.9
2	2.681	48.48	31.38	46.42	41.25	18.40	4.0	3.065	53.40	35.02	114.04	156.18	57.89	8.2
3	4.267	76.50	48.00	106.11	97.98	42.58	4.3	5.017	85.81	53.76	219.04	271.87	102.95	7.3
4	5.887	105.11	64.79	175.22	164.16	70.67	4.4	7.053	119.35	72.81	335.16	396.01	152.24	6.7
5	7.523	133.98	81.65	249.04	235.11	100.73	4.5	9.132	153.47	92.01	457.37	525.12	203.93	6.4
6	9.169	163.01	98.56	325.39	308.61	131.83	4.5	11.235	187.91	111.30	582.84	656.90	265.93	6.2
7	10.818	192.10	115.49	403.05	383.47	163.49	4.6	13.358	222.59	130.66	709.96	789.84	310.56	6.1
8	12.470	221.24	132.43	481.53	459.16	195.49	4.6	15.490	257.38	150.04	838.31	923.88	364.70	6.0
9	14.123	250.40	149.38	560.49	535.40	227.70	4.6	17.622	292.21	169.44	967.69	1058.98	419.31	5.9
10	15.778	279.59	166.34	639.83	611.99	260.07	4.6	19.767	327.16	188.86	1097.18	1193.90	473.90	5.8

Table 3
MP2/6-311++G(2d,2p) results for CHELPG partial atomic charges (in e) at the terminal and central segments of linear chains of HCN and HNC (see also Figure 1). N is the number of units.

Left end unit			Central units						Right end units			
N	q(H)	q(C)	q(N)	q(H)	q(C)	q(N)	q(H)	q(C)	q(N)	q(H)	q(C)	q(N)
$(\text{HNC})_N$												
4	0.205	0.153	-0.303	0.149	0.205	-0.354	0.163	0.180	-0.335	0.096	0.276	-0.437
6	0.202	0.159	-0.307	0.155	0.215	-0.372	0.169	0.194	-0.359	0.099	0.275	-0.440
8	0.204	0.156	-0.305	0.171	0.198	-0.362	0.155	0.218	-0.377	0.096	0.278	-0.442
10	0.201	0.161	-0.310	0.171	0.198	-0.363	0.155	0.221	-0.381	0.091	0.289	-0.449
$(\text{HNC})_N$												
	q(H)	q(N)	q(C)	q(H)	q(N)	q(C)	q(H)	q(N)	q(C)	q(H)	q(N)	q(C)
4	0.413	-0.297	0.077	0.122	-0.061	-0.085	0.242	-0.252	0.068	-0.102	0.309	-0.436
6	0.410	-0.288	0.072	0.187	-0.139	-0.032	0.156	-0.105	-0.067	-0.101	0.314	-0.443
8	0.410	-0.286	0.071	0.169	-0.119	-0.051	0.178	-0.132	-0.041	-0.101	0.314	-0.445
10	0.409	-0.286	0.071	0.169	-0.120	-0.048	0.173	-0.125	-0.049	-0.107	0.323	-0.451

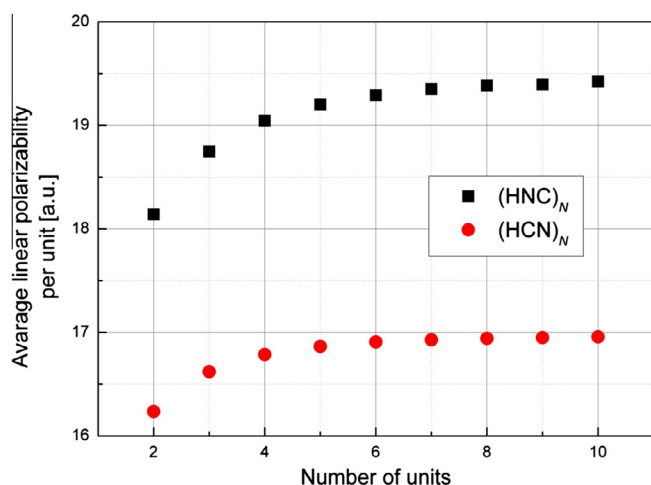


Figure 4. Evolution of static linear polarizability per unit of the HCN and HNC chains.

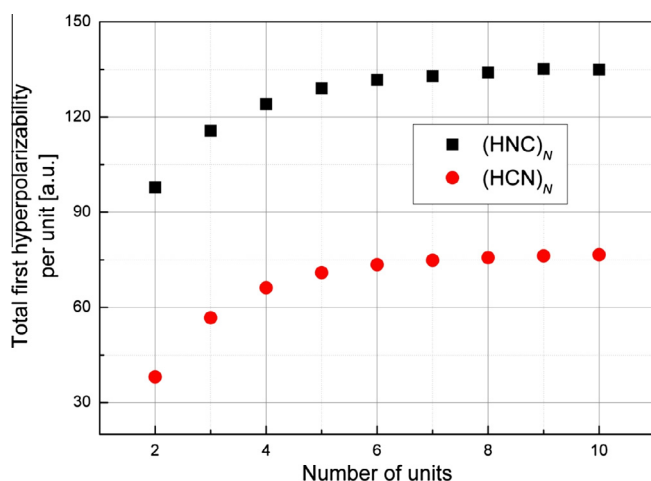


Figure 5. Evolution of static total first hyperpolarizability per unit of the HCN and HNC chains.

suggest that the cooperativity causes an increase of the electron mobility in HNC units slightly larger than in HCN units.

Figure 5 shows for both isomers that $\Delta\beta_{tot}$ increases initially with the number of units due to the increase of electron mobility

and saturate for the medium size chains, as noticed for $\Delta\mu$ and $\Delta\bar{\alpha}$ (the same pattern is observed for $\Delta\beta_{HRS}$ and $\Delta\beta_L$). An analogous situation has also been reported for $\Delta\beta_L$ of the polyiminoborane chains [PIB, $-(\text{NH}-\text{BH})_n-$] [38]. For infinite chains of HCN and HNC, the converged results for $\Delta\beta_{tot}$ are 76.6 and 134.9 a.u., respectively, while the corresponding results for $\Delta\beta_{HRS}$ are 32.4 and 54.6 a.u. (see Table 2). In both case, the increments are much large, in comparison with the corresponding monomer results, indicating that the intermolecular interactions have a substantial impact on this NLO property. Considering the monomers, β_{tot}^{HNC} is almost twenty times larger than β_{tot}^{HCN} . For large chains the $\beta_{tot}^{\text{HNC}}/\beta_{tot}^{\text{HCN}}$ ratios converges to approximately 2, indicating clearly that the first hyperpolarizability is particularly affected by the structural isomerization. Differently than is observed for the dipole moment, the cooperativity decreases systematically the influence of the isomeric change for longer chains. For the infinite chains, $\Delta\beta_{tot}^{\text{HNC}}/\Delta\beta_{tot}^{\text{HCN}}$ is around 70% larger than $\Delta\beta_{tot}^{\text{HNC}}/\Delta\beta_{tot}^{\text{HCN}}$. Table 2 also shows results for the calculated depolarization ratio. It can be seen that the cooperative effects affect this property in opposite directions for HCN and HNC chains. For HCN [HNC] the DR value increases [decreases] initially and converges to 4.6 [5.8], which is slightly smaller [larger] than the expected value for ideal one-dimensional systems [24].

It is interesting to compare our findings of linear HCN chains with results of previous studies [18,19]. Based on the BPW91/6-311++G(3d,3p) model, Scotto and Vasilescu [18] reported for μ and $\bar{\alpha}$ of the decamer the values of 16.08 a.u. and 189.85 a.u., respectively. These figures are 2% and 14% greater than those obtained here with the MP2/6-311++G(2d,2p) model. Later, Góra et al. [19] reported results for the longitudinal electric properties of an infinite chain. Based on estimations of monomer and interaction-induced property, the CCSD(T)/aug-cc-pVTZ model predicts for μ , α_L and β_L (per unit) the values of 1.53, 28.6 and 48.9 a.u., respectively. Our MP2/6-311++G(2d,2p) model predicts for these properties values that are greater in 8%, 2% and 62%. The large discrepancy observed for the first hyperpolarizability could be attributed to the interaction energy decomposition scheme that provides for this property results that are underestimated but qualitatively correct [19].

4. Conclusion

We have presented dipole moment and static linear polarizability and first hyperpolarizability of linear hydrogen-bonded chains of HCN and HNC, calculated at the MP2/6311++G(2d,2p) level. Our results show that the effects of the intermolecular interactions increase the magnitude of the studied electric properties of both

isomers in comparison with the corresponding monomer results. It is found for both isomers that the values for $\Delta\mu$, $\Delta\alpha$, $\Delta\beta_{tot}$ and $\Delta\beta_{HRS}$ present a rapid increase with the chain length for small chains and converge toward the values of the polymer chains. The extrapolated values of $\Delta\mu$, $\Delta\alpha$, $\Delta\beta_{tot}$ and $\Delta\beta_{HRS}$ for infinite chains of HCN have been estimated to be 1.655, 16.96, 76.6 and 32.4 a.u.. The corresponding results for HNC chains are 2.145, 19.42, 134.9 and 54.6 a.u.. These results show that the effect of the isomeric change affects the magnitude of all electric properties, particularly the first hyperpolarizability. It turns out that the contribution per unit for the first hyperpolarizability of the large HNC chains is around 70% larger than the corresponding HCN chains.

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