



# Hydrogen bond cooperativity effects in cyclic and ladder cyanamide oligomers using density functional theory method



Bhagwat Kharat<sup>a</sup>, Vinayak Deshmukh<sup>b</sup>, Ajay Chaudhari<sup>c,\*</sup>

<sup>a</sup> Department of Physics, L.B.S. Sr. College, Partur, Maharashtra, India

<sup>b</sup> Department of Physics, Shri Siddheshwar College, Majalgaon, Maharashtra, India

<sup>c</sup> Department of Physics, The Institute of Science, Fort, Mumbai 400032, India

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## ABSTRACT

The hydrogen bond cooperativity effects in cyclic and ladder oligomers of cyanamide are studied using density functional theory (DFT) method. Among different levels of theory used here, the geometrical parameters for cyanamide monomer at B3LYP/aug-cc-pvdz level are in excellent agreement with the experimental determinations. Cyclic oligomers are found to be more stable than the ladder, and the hydrogen bonds in the former are stronger than those in the latter. The hydrogen bond cooperativity effects are discussed in terms of the strength of hydrogen bonds, energy per hydrogen bond, excess energy, inter- and intra-molecular distances and vibrational frequencies. The positive and negative hydrogen bond cooperativity effects are found for the cyclic and ladder oligomers, respectively. We also report hyperpolarizabilities for these oligomers.

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## 1. Introduction

For the past two decades there have been several investigations on oligomers due to their various applications in scientific field. Several oligomers have been studied both theoretically and experimentally [1–14]. The properties of oligomers saturated after some number of monomeric units in oligomers help to predict the properties of polymers. The study of hydrogen bonded oligomers helps to understand the cooperativity of hydrogen bonds in these oligomers. In hydrogen bonded oligomers of  $n$  molecules, molecules may hold together strongly or weakly compared to the dimer depending upon their various bonding possibilities. It can be investigated using various indicators such as strength of a hydrogen bond, bonding energy per hydrogen bond, and inter- and intra-molecular distances. Several organic oligomers have also been studied for their possible applications as nonlinear optical (NLO) materials. It includes polythiophenes, polyacetylene, polydiacetylene, formaldehyde oligomers, poly-oxazolones, macromolecules consisting of fluorine and tetraphenyl diamminobiphenyl, and  $\pi$ -conjugated oligomers [15–40]. Organic molecules and their oligomers with high NLO properties are important for the development of photonic devices, which utilize photon instead of electrons in the transmission of information. They are the promising candidates in this regard due to their high NLO properties in particular the first ( $\beta$ ) and second ( $\gamma$ ) hyperpolarizabilities. The first and second hyperpolarizabilities are the origin of the macroscopic second and third order non-linear optical

responses of organic molecules [41–44]. Theoretical methods such as quantum chemical methods play an important role for studying the cooperativity effects, predicting the NLO properties of a material and predicting its suitability for photonic applications.

Cyanamide, which contains both, nucleophilic and electrophilic sites, is widely used for the production of several organic compounds. The molecule features a nitrile group attached to the amino group. It can act as a hydrogen bond donor as well as an acceptor. Tyler and Sheridan [45] have fully characterized the microwave spectra of cyanamide. Kapellos and Mavridis [46] have obtained the structural parameters of cyanamide using *ab initio* methods. Wagner and Wagner [47] have studied the vibrational spectra and structure of cyanamide and deuterio-cyanamide. Vibrational spectra and the inversion phenomenon in cyanamide have been studied by Fletcher and Brown [48]. The pyramidal structure about the amino nitrogen of cyanamide has been confirmed experimentally by microwave and high resolution Fourier Transform Infrared spectroscopy as well as theoretically [49–54]. Recently photo dissociation dynamics of cyanamide at 193 and 212 nm was reported [55,56]. Since cyanamide has amino and nitro groups, it will be interesting to study hydrogen bond cooperativity effects of cyanamide oligomers and their NLO properties.

The aim of this article is to study cyclic and ladder type cyanamide oligomers using density functional theory (DFT) method. We have also obtained vibrational frequencies of these oligomers. Special attention has been paid on hydrogen bond cooperativity effects and NLO properties of cyanamide oligomers. We have used here energy based equations for obtaining hyperpolarizabilities using the finite-field method [24,32–35,57]. Effect of basis sets and electron correlation methods on NLO properties is also studied.

\* Corresponding author.

E-mail address: [ajaychau5@yahoo.com](mailto:ajaychau5@yahoo.com) (A. Chaudhari).

## 2. Computational details

We first optimized the geometries of cyanamide monomer using different methods and aug-cc-pvdz basis sets. Our calculations have been made using MP2 and DFT with different exchange and correlation functionals viz. BLYP, B3LYP, B3PW91, PBE and PBE0. We compared the geometrical parameters from all the methods with the experimental values and found that there is an agreement between the theory at B3LYP/aug-cc-pvdz level and the experiment. We then optimized the geometries of cyclic and ladder cyanamide oligomers viz. dimer, trimer, tetramer and pentamer at the same level of theory. We have optimized the oligomers at MP2/aug-cc-pvdz level also and found that the structures at B3LYP/aug-cc-pvdz level are lower in energy than those at MP2/aug-cc-pvdz level. Vibrational frequencies of cyanamide oligomers are also obtained at this level of theory to confirm the minimum energy structures. The first and second hyperpolarizability components are obtained by using the finite field method using the following equations:

$$\beta = \{-E(2Fz) + E(-2Fz) + 2[E(Fz) - E(-Fz)]\} / 4(Fz)^3$$

$$\gamma = \{E(3Fz) - 12E(2Fz) + 39E(Fz) - 50E(0) + 39E(-Fz) - 12E(-2Fz) + E(-3Fz)\} / 36(Fz)^4.$$

Here  $E(Fz)$  indicates the total energy in presence of the field ( $F$ ) applied in the  $Z$ -direction.  $E(Fz)$  can be obtained using quantum chemical methods by optimizing the geometry in presence of the field with field strength  $F$ .

We have applied many-body analysis techniques to study various interactions in cyanamide oligomers [58–64]. The total energy is corrected for the Basis Set Superposition Error (BSSE) as suggested by Valiron and Mayer [65]. All the calculations are performed using Gaussian suit of program [66].

## 3. Results and discussion

The structural parameters of cyclic and ladder type cyanamide oligomers at B3LYP/aug-cc-pvdz level along with available experimental values [45,52] are presented in Table 1. The optimized structures of cyclic and ladder cyanamide oligomers are shown in Figs. 1 and 2 respectively. The calculated dipole moment (4.6 D) for the monomer at this level is also in good agreement with the available experimental value of (4.32 D).

For the monomer, the N–H, C–N and C≡N bond lengths are 1.014, 1.347 and 1.165 Å and the corresponding experimental values are 1.001, 1.345 and 1.160 Å, respectively. The angles  $\angle H-N-H$ ,  $\angle C-N-H$  and  $\angle N-C-N$  for the monomer are 113.1°, 115.0° and 177.0° respectively and the corresponding angles reported experimentally are 113.3°, 115.6° and 180.0°. The dipole moments of ladder cyanamide dimer and tetramer are zero due to the centrosymmetry of molecules. The dipole moments for the cyclic trimer and pentamer are negligible as compared to the monomer and tetramer.

From Table 1, the C–N bond length gets shortened for the oligomers than the monomer whereas the C≡N bond length little elongated. The hydrogen bonds in cyanamide oligomers are also listed in Table 1. In the dimer, there is only ladder type alignment whereas in trimer to pentamer, there is ladder as well as cyclic arrangement of cyanamide molecules. In cyclic trimer, tetramer and pentamer, there are three, four and five hydrogen bonds, respectively. The hydrogen bonds have been defined here by geometrical criteria. In ladder dimer, trimer, tetramer and pentamer, there are two, four, six, and eight hydrogen bonds, respectively. For the cyclic structures, the hydrogen bonds in trimer, tetramer and pentamer are in a range of 1.883–1.889, 1.846–1.848 and 1.833–1.838 Å, respectively. The hydrogen bonds in ladder trimer, tetramer and pentamer are in a range of 2.290–2.293, 2.278–2.344 and 2.474–2.346 Å, respectively. Comparing hydrogen bonds in cyclic

**Table 1**

Structural parameters for cyanamide oligomers at B3LYP/aug-cc-pvdz level of theory along with experimental values for the monomer. The bond lengths are in Å and the angles in degrees.

Parameter <sup>a</sup>	Expt. value <sup>a</sup>	Monomer	Dimer	Trimer	Tetramer	Pentamer
<b>Cyclic</b>						
N–H	1.001	1.014	–	1.023	1.023	1.024
C–N	1.345	1.347	–	1.330	1.326	1.325
C≡N	1.160	1.165	–	1.168	1.167	1.167
$\angle H-N-H$	113.3	113.1	–	115.7	116.3	115.9
$\angle C-N-H$	115.6	115.0	–	115.4	116.7	117.0
$\angle N-C-N$	180.0	177.0	–	176.9	177.3	177.3
$\mu$ (Debye)	4.32	4.60	–	0.94	2.96	0.82
<b>Ladder</b>						
N–H	1.001	1.014	1.017	1.017	1.018	1.017
C–N	1.345	1.347	1.338	1.335	1.335	1.333
C≡N	1.160	1.165	1.167	1.168	1.168	1.169
$\angle H-N-H$	113.3	113.1	114.8	115.7	115.9	116.6
$\angle C-N-H$	115.6	115.0	114.3	114.4	114.3	114.6
$\angle N-C-N$	180.0	177.0	176.4	176.9	177.1	177.8
$\mu$ (Debye)	4.32	4.60	0.00	4.36	0.00	4.06
<b>Hydrogen bonds (cyclic)</b>						
5N–10H	–	–	–	1.883	1.847	1.834
9N–11H	–	–	–	1.885	1.846	1.833
15N–2H	–	–	–	1.889	–	–
15N–16H	–	–	–	–	1.848	1.834
20N–1H	–	–	–	–	1.846	–
20N–21H	–	–	–	–	–	1.838
25N–1H	–	–	–	–	–	1.836
<b>Hydrogen bonds (ladder)</b>						
5N–7H	–	–	2.241	2.290	2.278	2.282
9N–1H	–	–	2.241	2.293	2.295	2.291
9N–12H	–	–	–	2.293	2.344	2.346
15N–6H	–	–	–	2.290	2.344	2.340
15N–17H	–	–	–	–	2.295	2.342
20N–11H	–	–	–	–	2.278	2.317
20N–21H	–	–	–	–	–	2.313
25N–16H	–	–	–	–	–	2.274

<sup>a</sup> Ref. [45].

and ladder structures, it can be said that the hydrogen bonds in cyclic structures are stronger than the ladder.

The calculated vibrational frequencies, corresponding mode assignments and IR intensity for the cyclic and ladder oligomers at B3LYP/aug-cc-pvdz level are presented in Tables 2 and 3 respectively, along with available experimental values for cyanamide monomer [48,67]. There is no soft mode for the cyanamide monomer as well as all the oligomers studied here at B3LYP/aug-cc-pvdz level indicating that these structures are quantum mechanically stable at this level of theory. All vibrational frequencies presented here are the unscaled frequencies. The C≡N stretching mode in most of the nitriles is observed within a range of 2325–2125  $\text{cm}^{-1}$  [68]. It is the second intense mode here for cyanamide monomer observed at 2345  $\text{cm}^{-1}$ . The most intense mode for the monomer is the  $\text{NH}_2$  wagging mode appearing at 553  $\text{cm}^{-1}$ . The NCN in plane bending mode is the third intense mode appearing at 480  $\text{cm}^{-1}$ . Apart from these modes, features at 1611, 3535 and 3634  $\text{cm}^{-1}$  are also intense which correspond to the  $\text{NH}_2$  scissoring,  $\text{NH}_2$  symmetric stretching and  $\text{NH}_2$  asymmetric stretching mode respectively. The corresponding experimental modes are observed at 1586, 3420 and 3469  $\text{cm}^{-1}$ . As compared to the C≡N stretching, the C–N stretching mode appearing at 1090  $\text{cm}^{-1}$  is much weaker. Two modes of negligible IR intensity in monomer are the NCN out plane bending and  $\text{NH}_2$  rocking mode appearing at 401 and 1182  $\text{cm}^{-1}$  respectively.

Out of nine fundamental modes, five, six and six modes are blue shifted in cyclic trimer, tetramer and pentamer respectively than the monomer. Four modes in trimer and three in tetramer and pentamer each are red shifted than the corresponding modes in monomer. The highest and lowest blue shifted modes are the  $\text{NH}_2$  wagging and  $\text{NH}_2$  scissoring mode respectively for the cyclic trimer, tetramer and pentamer

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