

**A COMPUTATIONAL STUDY ON THE
STRUCTURE OF ALLENE POLYMERS BY USING
QUANTUM CHEMICAL METHODS**

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ABSTRACT

The conformational analysis of 1,3-dicyanodiethynylallene and 1,3-diethynylallene oligomers have been carried out by using quantum mechanical semiempirical AM1 method implemented in G03 and G98.

Although chiral 1,3-diethynylallene unit upon forming intramolecular hydrogen bond is expected to form helical oligomers and polymers that have optically active character, our results indicate that the oligomers of this molecule have lack of helicity. Instead, the conformations observed for 1,3-diethynylallene oligomers are all unfolded zig-zag like chains.

1,3-dicyanodiethynylallene oligomer, a derivative of 1,3-diethynylallene, is also expected to have a helical conformation. In oligomer structures, the results of optimizations show that 1,3-dicyanodiethynylallene has a well defined three-dimensional helical conformation. This helicity is attributed to electrostatic interactions between cyano carbon which has a high negative charge and oppositely charged allene carbons along the helical axis. We observe P-helix rather than M-helix, no the conformers which may lead to M character is encountered.

ÖZET

Sarmal yapıya sahip olduğu öngörülen 1,3-dietinilalin ve 1,3-disiyanodietinilalin oligomerlerin konformasyonel analizi yarı deneysel kuvantum mekanik AM1 metodu ile G03 ve G98 programları kullanılarak yapılmıştır.

Moleküller içi hidrojen bağ yapan kiral 1,3-dietilenalin biriminin optikçe aktifliğe sahip sarmal oligomer ve polimer olması beklenildiği halde, bu çalışma sonucunda 1,3-dietilenalin oligomerinin sarmal yapıda olmadığı belirlendi. Aksine tüm 1,3-dietilenalin oligomerlerinin zincirsel, katlanmamış zigzag yapıda olduğu gözlenmiştir.

Substituentin katlanmaya etkisini incelemek amacıyla 1,3-diethinilalin molekülünün türevi olan 1,3-disiyanodietinilalin oligomerinin yapıları da incelendi. 1,3-disiyanodietinilalinin oligomer yapılarında, düzgün sarmal konformasyona sahip olduğu optimizasyon sonuçlarına göre bulunmuştur. Bu sarmal yapıya, sarmal eksen boyunca yer alan yüksek negatif yüke sahip siyano karbon ve zıt yüklü alin karbonları arasındaki elektrostatik etkileşimlerin neden olarak görülmektedir. Bulunan sarmal oligomerlerde sadece P-heliks gözlemlendi, hiçbir oligomer yapısı M-heliks yönünde bir işaret vermedi.

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CHAPTER 1

INTRODUCTION

Important functions of naturally occurring polymers such as nucleic acids and proteins are owing to their well-defined 3-D structures. This structure, namely α -helix, causes significant stabilization from intramolecular hydrogen bonding between n th peptide unit and $(n+4)$ th one (Masuda et al. 2003). Based on the studies of Pauling in 1951, the α -helix can be formed both in solid state and in solution (Jaycox et al. 1987). Another area taking helicity into account as well as biological supramolecules are the synthetic studies. In this case also intramolecular nonbonding attractive and/or repulsive interactions play an important role in forming molecular strands into helical structures (Masuda et al. 2003, Sisido et al. 1998, Mcgrath et al. 2002, Jaycox et al. 1987, Diederich et al. 2002a, Okamoto et al. 2001, Meijer et al. 2001, Leclerc et al. 2002, Masuda et al. 2002, Lehn et al. 2001).

As right and left-handed helices are not mirror images of each other that means helices are chiral structures, so they have the property of optical activity and can show induced Circular Dichroism curves. Because of optical activity property, π -conjugated helical polymers attract interest due to their potential utilizations in polarized luminescent materials, asymmetric electrodes, nonlinear optics, polarized light emission, asymmetric catalysis, chiral separation, and enantioselective sensing (Luh et al. 2003, Pu 2000, Skotheim 1998, Tang et al. 2002, Meijer et al. 1996). Due to these valuable properties, there are significant studies based on helical conjugated polymers introduced herein.

Although there are many studies showing the syntheses and the conformational analyses of helical polymers bearing chiral units, the following works explain the first syntheses and analyses of them. One of the first structures studied for the proposed helicity was the vinyl polymers. Pino et.al. in 1960, realized the helical structure of vinyl polymers in solution that was isotactic poly(3-methyl-1-pentene). Even though it is believed that chirality induces the helical structure, the single-handed helix of poly(triphenyl methyl methacrylate) was proved to have achiral side chains by the synthetic study of Okamoto and Yuki in 1979. Another important polymer

polyisocyanides having the helical conformation was synthesized by Drent and Nolte in 1974 and helical polyisocyanates with chiral side groups were also synthesized by Goodman in 1970. The chirality effect on the helical structure for this polymer was improved by substitution studies by Green in 1988. The first synthesis of polyacetylene derivatives with chiral groups was achieved: by Ciardelli in 1974; Grubbs in 1991; Yashima and Okamoto in 1994. Yashima and Okamoto carried out their studies with a poly(phenyl-acetylene) derivatives having no chiral group and then they showed the helical structure by adding chiral amine groups to the polymer. Other significant polymers having helical conformation were postulated. First one is polychloral, its conformational analysis and synthesis were achieved in solution by Vogl in 1980 and then other studies followed.

There are also inorganic helical polymers (e.g. polysilane). The conformational analysis and synthesis in solution of it were obtained at the same time by Fujiki and Möller to point out its helical conformation owing to the chiral chains. Solid state structure of polysilane was studied by Matyjaszewski in 1992 (Okamoto et al. 2001).

Theoretical and experimental study have been applied on conformational investigation of poly(N-propargyl-alkyl amides) by means of UV-Vis, CD, IR spectroscopic methods and computational tools. In that study, poly(N-propargyl-alkylamide) was found to have two helically arranged H-bond strands resulting from the rigid structure of conjugated main chain due to the intramolecular H-bond (Masuda et al. 2003). Based on that molecular modeling study by using AM1 semiempirical method elucidates the helical conjugated backbone with two helically H-bond strands.

The chemistry of silylene-spaced conjugated polymers experimentally has been worked out. Silylene –spaced alternating donor-acceptor copolymers form a random coil conformation. In that study, the first optically active silylene-spaced divinylarene copolymer was synthesized by adding chiral groups into these copolymers (Luh et al. 2003).

An interesting study which was related to the determination the structure of chiral binaphthyl group based was optically active polycarbonates. As the oligomers were synthesized, their optical properties leading to helical structure are studied by CD spectra, and this helical structure is also obtained by MM2 calculation in which empirical conformational analysis of a decamer was performed (Sisido et al. 1998).

Another research was carried out to synthesize and characterize chiral substituents bearing conjugated (1,4-(2,3-dialkoxyphenylene)-alt-2,5-furan)s. At the

first attempt, achiral (octyloxy) substituent was synthesized, chiroptical properties cannot be observed, and these results show equal preference for left and right handed helices. To prevent this equal preference which leads to lack of optical activity, chiral poly(1,4-(2,3-di-S)-methyl butoxyphenylene)-alt-2,5-furan was synthesized (Leclerc et al. 2002).

A computational study to analyze conformations and electronic structures of poly(m-phenylene), (PMP), and its derivatives containing vinylene copolymers were investigated and that research elucidated that reason of broken conjugation of PMP was based on the nodal nature of the frontier molecular orbitals (Hoffmann et al. 2001). According to the results of electronic structure determination, the electronic structure depends on the torsional angle between the adjacent phenyl rings. Since the adjacent rotational axes of poly(m-phenylene) were not collinear as in the case of poly(p-phenylene) then, for poly(m-phenylene) a helical conformation resulted.

Conformational analysis of semiflexible substituted polyacetylene was investigated by Masuda et al. Substitution of semiflexible stereoregular cis(poly(propionic esters)) made the polymer backbone rigid which lead to a helical structure having a long persistence length. It was found that extended main chain conjugation caused red shift observation in CD spectra. Polymers with non-branched α -carbons express very intense CD signals whereas, for polymers having α -branched carbons very weak cotton effect of the CD spectrum was observed. So the main chain of polymers with non-branched α -carbons existed in the helical conformation. To investigate the secondary structure of poly(propionic esters) computational tools were also used by means of MM2 and PM3 methods, it was found that the helical conformation was the most stable secondary structure (Masuda et al. 2003).

Synthesis and folding of oligopyridine-dicarboxamides into single helices were studied. The reason of helicity was attributed to the intramolecular hydrogen-bonds between the amide NHs and the pyridine nitrogen in the pyridinecarboxamide groups. In order to elucidate the mechanism of folding of these strands into helix conformational and molecular dynamics studies were performed (Lehn et al. 2001).

Polyisocyanates reflect an interesting type of polymer owing to their dynamic helical conformation and stiff polymer backbone. The helical conformation of polyisocyanates was observed both in solution and in the solid state. Based on quantum mechanical calculations in solution the most stable configuration was trans-gauche conformation. To determine the helical conformation temperature dependent NMR

spectroscopy was used and it revealed that even short ethylisocyanate oligomers form a helical conformation (Zentel et al. 2001).

In order to synthesize N-alkylated poly(p-benzamide)s chain-growth polycondensation methodology was used. According to the circular dichroism (CD) spectra N-alkylated poly(p-benzamide)s display a right-handed helical structure in solution and according to X-ray crystallography, it also forms a helix in the solid state but the backbone in this case was highly flexible. The reason of helicity due to the aromatic amide bonds (Yokozawa et al. 2005).

One of the most celebrated conjugated helical polymer bearing rings is the polythiophene. A wide range of experimental and computational studies introduced to search its conformation.

The first analyses on the structure of polythiophene, polypyrrole and their derivatives were carried out with computational tools and IR spectroscopy. In the computational part of the study, semiempirical MNDO (modified neglect of diatomic overlap) method was used. Firstly, calculations were made on bithiophene and its derivative. The result indicates that bithiophene was planar and anti form was more stable than syn form. For one of the bithiophene derivatives, bi-3-methylthiophene, the calculations indicate that more stable conformation in this case was also anti form. In these bithiophene derivatives nonplanarity has been attributed to the repulsions between methyl group and sulfur atom. The conformational features of polypyrrole and poly(3-methylpyrrole) indicated that more stable conformations were planar zigzag conformations (Kertesz et al. 1989).

In one of the experimental studies chiral monoalkyl and dialkoxy side chains bearing polythiophenes were synthesized and the helical structure was investigated (Tang et al. 2002). In one another includes the iterative synthesis of cross-conjugated oligothiophene (Rajca et al. 2000). There is another interesting research which illustrates the synthesis of poly(thiaheterohelicene) having π -conjugated ladder structure. The CD measurements were made using 1,4-Dioxane, CHCl_3 , 1,2-DCE, 1,2-DCE/EtOH, DMF, DMSO solvents. The result of CD indicated no change in intensity of CD curves. The temperatures used in determining the effects of helicity was between -30 to $+80^\circ\text{C}$ and again CD intensity did not change (Nishide et al. 2005).

Compounds having two sequential π -bonds between three carbon atoms are known as allenes. Their significance is a result of their unusual stereochemistry. The applications of allene compounds include a wide range of industrial area that they can

be used as dyes, drugs, anti-oxidants, and in polymers or copolymers suitable for paints, fibers, elastomers, printable films, and heat or corrosion resistant materials. Analyses in their distinctive stereochemistry show that allenes have the two mutually orthogonal π -bonds with the central carbon atom (sp -hybridized) joined in a straight line to two end carbon atoms (sp^2 -hybridized) in the most stable bonding arrangement. In this arrangement H atoms only one end project below and above the plane containing the whole molecule and the two π -bonds are not coplanar (Taylor 1966). An interesting consequence of this configuration is that allenes with two substituents on the end carbon atoms are chiral.

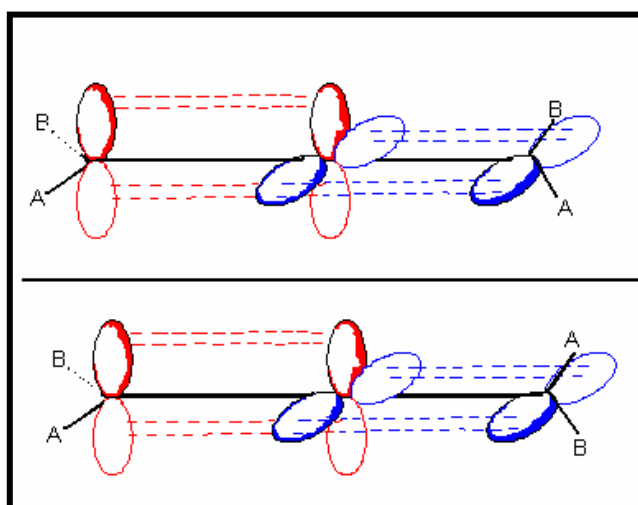


Figure 1.1 Stereochemistry of allene (A > B)

The diagram shows an allene with different substituents (A and B) on each of the terminal (sp^2) carbon atoms the top one indicating S configuration and below one R configuration so they are an enantiomeric pair indicating their chiral character (WEB_1 2005). Having chiral property, polymer of allene is optically active so that it exhibits many distinctive properties, and owing to its conjugated structure, it may show circular dichroic properties and be applicable to electrode for asymmetric synthesis (WEB_2 2005).

Due to the chirality of allene molecule the polymers of allene have the potential to be in a helical conformation.

One of the allene molecules attracting interest is 1,3- diethyleneallene which has a main chain with π -electron delocalization by addition of substrates and owing to its

chiral structure, it was proposed to be induced in a helical conformation. Provided that it has helical structure and conjugated backbone, this molecule exhibits very interesting properties like materials having circularly polarized electroluminescence and dopants for cholesteric liquid. Owing to this different structure furthermore different properties leading to fascinating applications. Synthesis of this structure is the aim of the researchers. Even if earlier works to synthesize it failed because of the possible [2+2] cycloaddition reactions even at room temperature or below. After the efforts aimed at the synthesis of 1,3- diethynylallene shows that [2+2] cycloaddition of this molecule may be prevented by attaching bulky groups, and by not increasing π - electron delocalization. Provided that, both cases applied to prevent [2+2] cycloaddition, then 1,3- diethynylallenes dimer was obtained which is an indication for the formation of oligomers and polymers with the proposed helix (Diederich et al. 2002a, Diederich et al. 2002b, Schaefer et al. 1994, François Diederich 1999). It can be well examined in a research which was carried out to synthesize dimer of 1,3- diphenylene allene and the results exhibit the cycloaddition. In order to illustrate the helical structure of 1,3- diethynylallene polymer dodecamer of this molecule was presented which was produced by computer (AM1 method) (Günther et al. 2000).

A study in synthesis of 1,3-bis (4-bromo phenyl)-1,3- diphenylpropadiene as the target molecule was worked out owing to the significance of conjugated polymers with allene moieties in the main chain. As the synthesis of molecule was achieved in good yield its characterization is made by ^{13}C NMR,UV-VIS spectra to prove the success of synthesis (Shirakawa et al. 2002).

Due to the chiral main chains and being highly reactive, allenes are one of the most interesting molecules in synthesis. Although many studies exist in synthesis of allenes, there is no study showing successful synthesis of allenes. In order to have an idea about the interaction between the π -electrons of aromatic rings and allene bridges, ring strain and CD measurements should be carried out. The first synthesis of one of the allenophanes, [3₄] allenophane 1, 3, 10, 12, 19, 21, 28, 30-octamethyl[3.3.3]paracyclophan-1, 2, 10, 11, 19, 20,28, 29- octaene was worked out which has four diastereomers (Krause et al. 1999).

The synthesis and separation of chiral unsaturated tetrameric anthracenophanes macrocycles based on the 1,3-diethynylallene unit was carried out. The compounds are the first allene-alkyne macrocycles containing no aromatic rings in the backbone. Based

on semiempirical AM1 calculations the conformations did not prefer to form in all P oligomers (Diederich et al. 2005).

Monomeric and dimeric silyl protected cyanoethynlethenes (CEEs) and N,N-dimethylanilino substituted CEEs were synthesized. The significance of these molecules (CEEs) is due to their strong electron accepting character. In order to decrease band gap, since higher conjugated molecules have lower HOMO level, so larger band gap, acetylenes were added between donor and acceptor groups. Based on electrochemistry measurements, the average electron acceptor strength was found to increase when cyano groups were attached which was also calculated with B3LYP method with 6-31G** basis set. An anodic shift which increases the acceptor strength was observed when conjugated length was increased. The increase occurred as a result of dimer formation (Diederich et al. 2005) CEEs were significant in the way they have cyano groups which are the side groups also in 1,3-dicyanodiethynyleneallene molecule.

Having well documented the applications, stereochemical features, syntheses and analyses methods of conjugated helical polymers, in particular polymers bearing allene units, now we present our object in this research. Our aim was to carry out a conformational analysis in order to investigate the proposed helicity in 1,3-diethynylallene and 1,3-dicyanodiethynylallene oligomers by utilization of semiempirical AM1 quantum chemical method and a statistical method (principal coordinate analysis). The substituent effect on the helix structure has been examined by attaching cyano instead of hydrogens. Cyanide is known to be a strongest electron acceptor.

CHAPTER 2

METHODS

2.1. Computational Chemistry Tools

Many aspects of molecular structure and dynamics can be modeled using classical methods in the form of molecular mechanics and dynamics. The classical force field is based on empirical results, averaged over a large number of molecules. Because of this extensive averaging, the results can be good for standard systems, but there are many important questions in chemistry that can not at all be addressed by means of this empirical approach. If one wants to know more than just structure or other properties that are derived only from the potential energy surface, in particular properties that depend directly on the electron density distribution, one has to resort to a more fundamental and general approach: quantum chemistry. The same holds for all non-standard cases for which molecular mechanics is simply not applicable. In quantum chemistry, the system is described by a wavefunction which can be found by solving the Schrödinger equation (WEB_3 2005).

$$H\Psi = E\Psi \quad (2.1)$$

This equation relates the stationary states of the system and their energies to the Hamiltonian operator, which can be viewed as the recipe for obtaining the energy associated with a wavefunction describing the positions of the nuclei and electrons in the system. The modeling applications themselves encompass a wide variety of different theoretical methods of which three are most commonly employed as they are introduced in the following Figure 2.1 (WEB_3 2005).

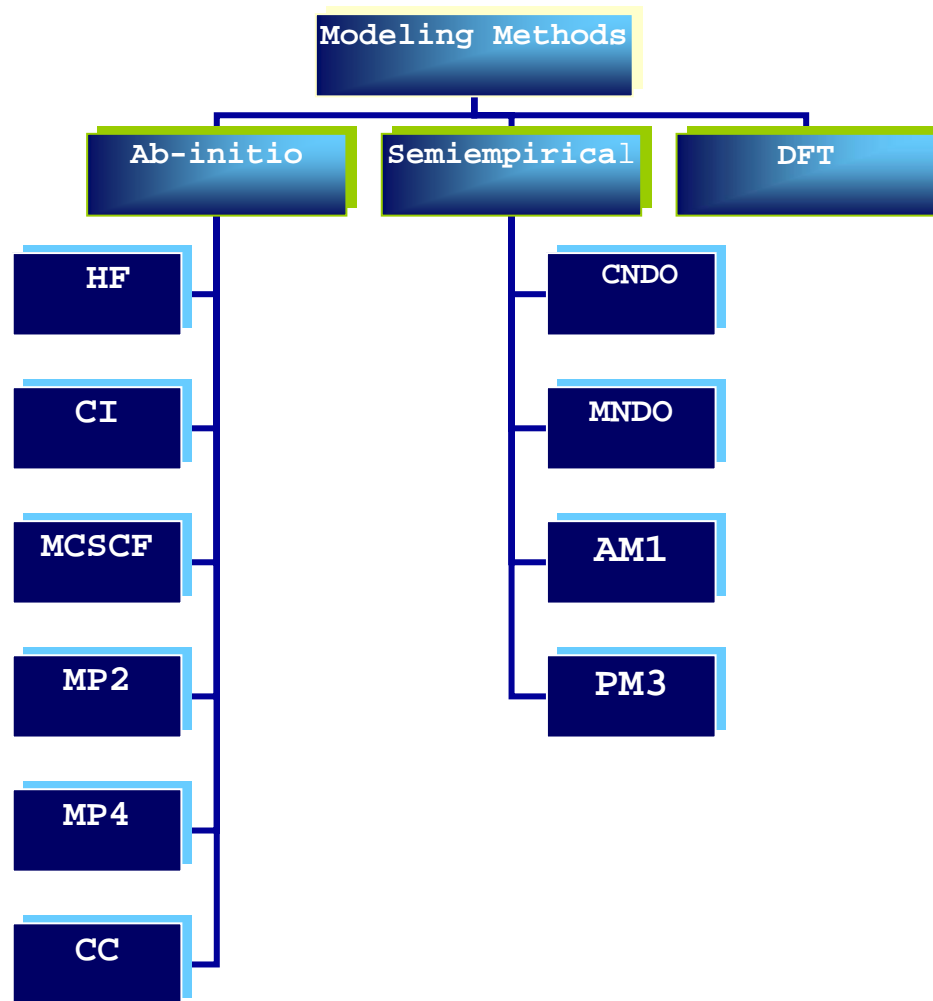


Figure 2.1. Quantum chemical methods

Ab Initio Quantum Method

HF : Hatree-Fock

CI : Configuration Interaction

MCSCF :Multi Configuration Self Consistent Field

MP2 :Moller Plesset perturbation MP4 :Moller Plesset perturbation

CC:Coupled Cluster

DFT : Density Functional Theory

Semiempirical methods

CNDO :Complete Neglect of Differential Overlap

MNDO : Modified Neglect of Differential Overlap

AM1 : Austin Model 1

PM3 :the third parametrization of MNDO

Semiempirical molecular orbital theories use experimental parameters to determine the two electron integrals involved in solving Schrödinger equation,

$$E=2\sum H_{ii} + \sum \sum (2J_{ij}-K_{ij}) \quad (2.2)$$

where, H_{ii} represents one electron integral, J_{ij} represents two electron integral (Coulomb integral), and K_{ij} two electron integral (exchange integral) (Hilger 1998).

2.1.1. Ab Initio Quantum Method

The name ab initio implies non-empirical solution of the time-independent Schrödinger equation, or solutions based on genuine theory. However besides the Born-Oppenheimer approximation, relativistic effects are ignored, and the concept of molecular orbitals (or wave functions) is introduced.

In ab initio methods, molecular orbitals are approximated by a linear combination of atomic orbitals. These are defined for a certain basis set, often Gaussian functions. The coefficients describing this linear combination are calculated by a variational principle that is by minimizing the electronic energy of the molecular system for a given set of chosen orbitals.

This energy (known as Hartree-Fock energy) and the associated coefficients are calculated iteratively by the Self Consistent Field (SCF) procedure with positions of the nuclei fixed. This calculation is expensive for large systems –as computations of many integrals involved- and makes ab initio methods computationally demanding.

In practice, the basis set for the molecular wave functions is represented in computer programs by stored sets of exponents and coefficients. The associated calculated integrals are then used to formulate the Hamiltonian matrix on the basis of the interactions between the wave functions of the pairs of atoms (off-diagonal elements) and each atom with itself (diagonal elements) via some potential that varies

from method to method. An initial guess of the molecular orbitals is then obtained, and the Schrödinger equation is solved explicitly for a minimum state of electronic energy.

The quality of molecular orbitals used, and hence the accuracy of the calculated molecular properties depends on the number of atomic orbitals and quality of the basis set. The electronic energy often ignores correlation between the motions of the electrons, but inclusion of some correlation effects can improve the quality of the ab initio results (Schlick 2002).

Ab initio calculations are limited to tens of atoms and best performed using a supercomputer. They can be applied to organics, organo-metallics, and molecular fragments (e.g. catalytic components of an enzyme). The modeling environments are vacuum or implicit solvent environments. This method can be used to study ground, transition and excited states. There are specific implementation of this method including GAMESS and GAUSSIAN (Dewar et al. 2002).

2.1.2. Density Functional Theory (DFT)

DFT can be formulated as a variant of ab initio methods where exchange/correlation functionals are used to represent electron correlation energy. DFT methods are based on the use of the electron density function as a basic descriptor of the electronic system. The electronic wave function is represented by a single ground state wave function in which the electron density is represented as the sum of the squares of the orbital densities. DFT schemes differ by their treatment of exchange/correlation energy, but in general this class of method offers a good combination of accuracy and computational requirements especially for large systems (Schlick 2002).

2.1.3. Semiempirical Quantum Method

In semiempirical methods, the matrix elements associated with the wavefunction interactions are not explicitly calculated via integrals but are instead constructed from a set of predetermined parameters. These parameters define the forms and energies of the atomic orbitals so as to yield reasonable agreement with experimental data. Thus, most integrals are neglected in semiempirical methods, and empirical parameters are used as compensation. Although good parametrization is a challenging task in these approaches, and parameters are not automatically transferable from system to system, semiempirical methods retain the flavor of quantum approaches (solution of the Schrödinger equation) and are less memory intensive than ab initio methods. As in ab initio methods, the quality of the results depends critically on the quality of the approximations made (Schlick 2002).

Semiempirical calculations are limited to hundreds of atoms. They can be applied to organics, organo-metallics, and molecular fragments (e.g. peptide, nucleotide, saccaride). This method can be used to study ground, transition and excited states. There are specific implementation of this method including AMPAC, MOPAC, ZINDO and GAUSSIAN (Dewar et al. 2002).

In AM1 method for these two electron integrals empirical parameters are used. Due to the report for the initial four elements, AM1(Dewar et al. 1985).

parametrizations for B , F , Al , Si , P , S , Cl , Zn , Ge , Br , I and Hg have been reported, because AM1 calculations are so fast and the model is reasonably robust over a large range of chemical functionality, AM1 is included in many molecular modeling packages and results of AM1 calculations continue to be reported in the chemical literature for a wide variety of applications . However, they have a drawback, they can produce extremely inaccurate results when applied to classes of molecules not included in the parametrization set (WEB_4 2005, Pascunelli 1998).

2.2. Computational Aspects

2.2.1. Oligomer Growth

For the ground electronic state calculations, the geometries of allene oligomers are carried out with semiempirical AM1 method implemented in Gaussian-98 and Gaussian-03 molecular modeling program packages .

The oligomer growth can be made in the following way. The oligomer growth can be created by replacing hydrogen of the one of the acetylene moiety, that means there are two possible growth sides. These possibilities (Figure 2.1) depend on the stereochemistry of allene molecule since it has two mutually orthogonal π -bonds with the central C-atom joined in a straight line to the two ends allene carbon atoms. Then the substituents attached to these C atoms also become perpendicular.

To observe oligomer growth, two methods are combined namely, molecular modeling and statistical methods. First part of the methodology includes the geometry optimization which was the only procedure carried out in order to observe oligomer growth until the number of oligomer is large. All of the possible conformations are taken into consideration.

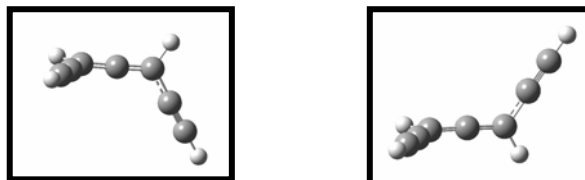


Figure 2.2. $+90^{\circ}$ dihedral and -90° dihedral angle having allene molecules which are used to construct next oligomer

In the first possibility $+90^{\circ}$ dihedral angle between the substituents at the same side and the allene moiety is taken into account. The second probability -90° of this dihedral angle is taken for the first step of this conformational analysis, namely computing the geometrical features of monomer, and hence by using this method two possible arrangements of monomer unit is found. Accounting these facts the overall possibilities becomes four.

Dimer can be constructed by attaching another monomer unit to the two optimized structures of monomers individually (Figure 2.2).

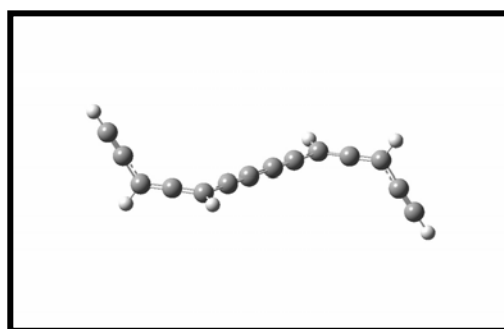


Figure 2.3 Optimized structure of dimer

The possibilities include, attaching a monomer unit having a $+90^{\circ}$ dihedral angle to the beginning of the previous optimized monomer unit and -90° dihedral angle having monomer unit is attached to the same side. Other possibility arise from the same principle the $+90^{\circ}$ and -90° dihedral angle having monomer units are attached to the other acetylene group. And hence in constructing an oligomer unit, there appear four different probabilities to carry out. As the oligomer unit increases to trimer, tetramer, pentamer, and also considering the fact that every possible conformation resulting from the previous oligomer unit is used (except from the structures having the same geometrical conformations and the same energies), the work become hard to handle since each optimized geometry leading to four others. This result is concluded when 48 structures are obtained at the end of the analysis of pentamer. The 48 geometrical conformations mean that, there would be maximum $4 \times 48 = 192$ number of structures in the analysis of hexamer, and for heptamer this will grow too. So that at this number of oligomer unit, another treatment besides this computational method is required. In order to visualize the difficulty of the optimization with a huge number of structures is seen in the table showing all possibilities (Table 2.1).

Table 2.1. Number of all possible isomers in oligomers

Number of monomer units	Allene (expected)
Dimer	4
trimer	16
tetramer	64
pentamer	256
hexamer	1024
heptamer	4096
octamer	16384
nanomer	65536
decamer	262144
undecamer	4194304

2.2.2. Statistical Method (Principal Coordinate Analysis)

The principal coordinate (PCoor) analysis is used to reduce number of dimensions in a system to lower manageable number giving the most information about a system. By utilizing this knowledge, the method can be used to differentiate between structures of clusters or polymers, in our study by means of internuclear distances in each conformer is used in the PcoorA. PCoor analysis is developed based on earlier method which is principal component analysis (PCA). Principal component analysis uses a correlation matrix formed from comparisons between the variables that distinguish the individuals of a set, in our study this is a set of coordinates that differentiate among structures. A sample matrix, X , is considered, with dimensions $n \times p$, which has p variables and n observables or individuals. PCA uses the $p \times p$ matrix $(X^T X)$, as a starting (correlation) matrix and determines the most changing variables among all p members. Besides, PCoorA uses the $n \times n$ matrix, $(X X^T)$ as its starting matrix to find which groups of observable have the same features. If the number of variables is larger than the number of observables, it is better to use the PCoor technique due to obtaining eigenvalues easier.

The first step of the method is constructing the similarity or dissimilarity matrix, the distance matrix between pairs of observables. We have n different conformations (observables) with each conformation defined by p variables, usually coordinates of each atom in the system and equal to three times the number of atoms, N .

The distance matrix defined as

$$d_{ij} = \sum_{r=1}^p (X_{ir} - X_{jr})^2 \quad (2.3)$$

i and j are the conformation indices, r is the coordinate index, and d_{ij} is the measure of dissimilarity between the i th and j th conformations. Different X matrices is set up based on pair distances between two atoms $p=N(N-1)/2$;

After the distance matrix is prepared, these following steps are applied

- 1) Defining the matrix \mathbf{A} whose elements are $-d_{ij}/2$;
- 2) Obtaining the \mathbf{B} matrix (the centralized form of \mathbf{A}),

$$b_{ij} = a_{ij} - a_{i.} - a_{.j} + a_{..} \quad (2.4)$$

a_i is the average of the elements of the i th row of the **A** matrix, a_j is the average of the elements of the j th column of the **A** matrix, and $a_{..}$ is the average of all elements of the **A** matrix;

3) Diagonalizing the **B** matrix and finding its eigenvalues. Eigenvectors are scaled to find the sum of squares of elements of each eigenvector equal to the corresponding eigenvalue. The eigenvalues of **B** are the new dimensions and its eigenvectors are the coordinates corresponding to those eigenvalues. The largest eigenvalue represents the maximum variance of the original set of variables and carries the most information about the system (Berry et al. 1999.).

In our study, the set of locally stable conformations has been obtained by computational analysis with semiempirical AM1 method and after the pentamer oligomers are reached the method of PCoor is used to decrease the number of structures obtained from the results of AM1 semiempirical calculations for the next generation of oligomer. Below table showing the reduced number of oligomer by this method.

Table 2.2. Number of isomers in oligomers

Number of monomer units	Allene (expected)	1,3-dicyanodiethynyl allene (Reduced)	1,3-diethynylallene (Reduced)
dimer	4	2	2
trimer	16	3	3
tetramer	64	17	5
pentamer	256	58	12
hexamer	1024	70	13
heptamer	4096	55	30
octamer	16384	14	56
nanomer	65536	9	
decamer	262144	8	
undecamer	1048576	7	

CHAPTER 3

RESULTS AND DISCUSSION

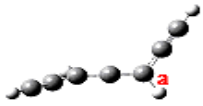


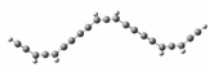


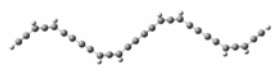
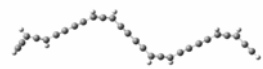
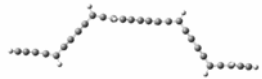

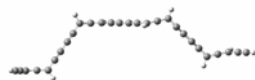


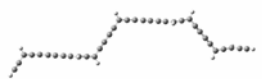
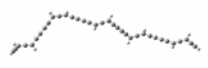

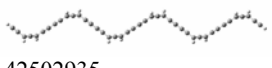
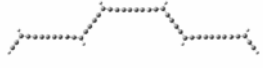
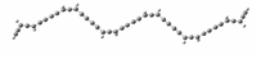
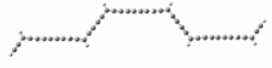
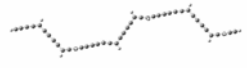
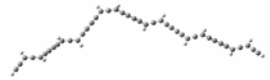
In order to find ground state energies of 1,3-diethynylallene, Molecule **1**, and 1,3-dicyanodiethynylallene, Molecule **2**, semiempirical AM1 method implemented in Gaussian-98 and Gaussian-03 molecular modeling program packages are utilized. Since these molecules are organic we preferred semiempirical AM1 method which gives very good results for this kind of molecules [38].

The results of geometry optimizations are given in Table 3.1. for **1** and in Table 3.2 for **2** are given. The oligomer conformers are given according to increasing energies.

In both molecules, the monomer structures have about $+90^{\circ}$ and -90° dihedral angle between the side groups and allene moiety. In molecule **1**, the dihedral angle is 92° and in the molecule **2** it is 89° . It indicates that they have very close dihedral angles. The small difference can be attributed to the effect of cyano groups in molecule **2**. When the bond distances are compared, they have approximately the same values as seen in Tables 3.7 and 3.8.

In dimer of **1** and **2**, there is not a remarkable difference between these two molecules, and when the structures of isomers in each molecule are examined, they only differ in the positions of the side chains, the same dihedral angles (as it is indicated in the monomer structures) again show the similar trend. It is 92° for molecule **1** and 89° for molecule **2**.

Table 3.1. The different conformers for 1,3-diethynyllallene oligomers

Oligomer	Isomers in Each Oligomer and Their Energies (au)		
Monomer	 0.24289139		
Dimer	 0.47921311	 0.47921911	
Trimer	 0.71565392	 0.71566286	 0.71567213
Tetramer	 0.95210946	 0.95211784	 0.95212273
	 0.952126	 0.95213161	
Pentamer	 1.18856883	 1.18857704	 1.18858126
	 1.18859001	 1.1885945	
Hexamer	 1.42502935	 1.42504104	 1.42504556
	 1.42504878	 1.42505314	 1.42505409

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Table 3.1. (cont.)


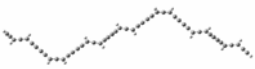

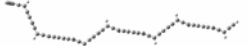


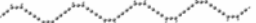





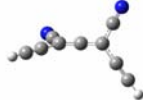
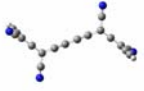
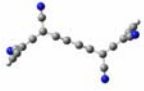
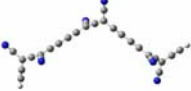


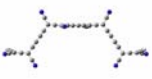
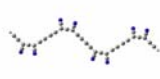
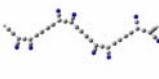







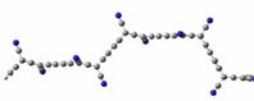
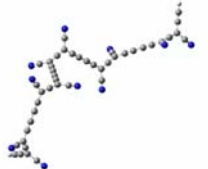

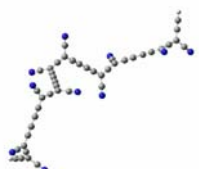
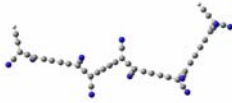
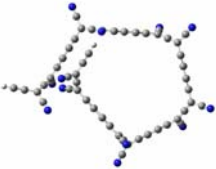
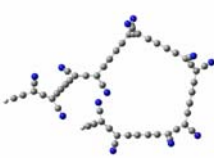




Heptamer			
	1.66149031	1.6615	1.66150179
			
	1.66150233	1.66152188	1.66152961
Octamer			
	1.89795143	1.89795948	1.89796268
			
	1.89797203	1.89797494	1.89798255

Table 3.2. The different conformers for 1,3-dicyanodiethynylallene oligomers (monomer-heptamer)

Oligomer	Isomers in Each Oligomer and Their Energies (au)		
Monomer			
	0.35828079		
Dimer			
	0.713762	0.713762	
Trimer			
	1.069687	1.069697	1.069757




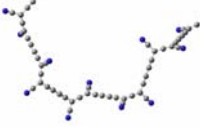
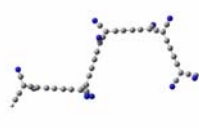
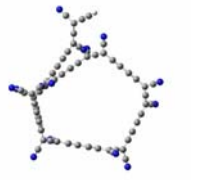

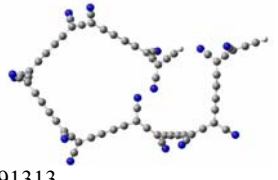

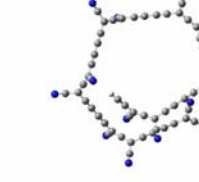

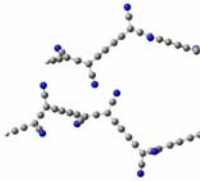


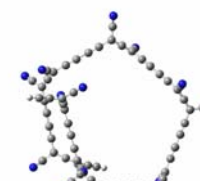
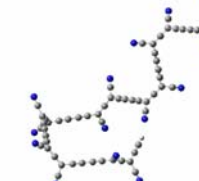
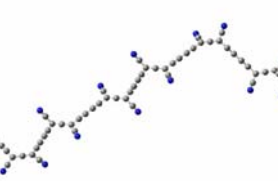
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Table 3.2. (cont.)

Tetramer	 1.425685	 1.425686	 1.425691
	 1.425735	 1.425736	
Pentamer	 1.7797	 1.780037	 1.780153
	 1.780563	 1.781696	 1.781696
	 1.781754	 1.781767	 1.781776
	 1.781851		
Hexamer	 2.13557	 2.135621	 2.135927
	 2.135942	 2.136079	 2.136086

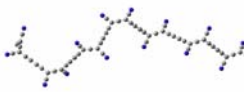
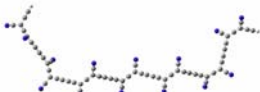

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Table 3.2. (cont.)

	 2.13614	 2.136183	 2.136458
	 2.137772	 2.137896	
Heptamer	 2.49091984 Imaginary frequency=0	 2.491311 Imaginary frequency=1	 2.491313 Imaginary frequency=2
	 2.491354 Imaginary frequency=1	 2.491361 Imaginary frequency=1	 2.491394 Imaginary frequency=1
	 2.491427 Imaginary frequency=1	 2.49147 Imaginary frequency=2	 2.491655 Imaginary frequency=1
	 2.491716 Imaginary frequency=1	 2.49255 Imaginary frequency=3	 2.493727 Imaginary frequency=5

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Table 3.2. (cont.)

		
2.49378 Imaginary frequency=6	2.493795 Imaginary frequency=6	2.493804 Imaginary frequency=6

Trimer isomers in each molecule express another pattern. For **2**, the first and the second conformers demonstrate similar geometries, they only differ in the positions of the side groups at terminals but the third one has a twisted structure in one end which shows that the structure may have a potential to give a complete turn for the next generations. Another interesting pattern observed is the most stable conformer obtained in molecule **2** is the second most stable conformer in molecule **1**.

In the tetramer structures, the discrepancy begins to form between these two oligomers having different monomer unit. The first isomers have two dimensional wavy geometry, the third one displays a wide semicircle-like geometry and the remaining structures do not give a distinguishing property. The tetramer of **2** has mainly two isomers showing a narrower semicircle than **1** and the others have a structure with the same geometrical repeating unit. In tetramer **1** the conformer with semicircle structure is the most favorable one however the tetramer **2** has a zigzag shape.

As the size of oligomer increases the conformation of **1** does not exhibit the sign of helicity though some of them have a wide semicircle. Generally, a 2-D conformation is observed in pentamer. On the other hand, the first turn which is a sign of helicity is observed for the first four conformers of **2**, whereas the other isomers show twisted and planar structures (all the conformers in the Table 3.2 for pentamer, hexamer, heptamer selected according to the results obtained from principal coordinate analysis which will be discussed in the next section).


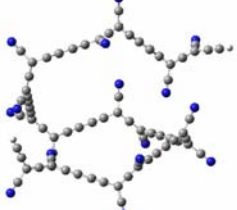
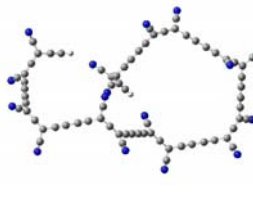
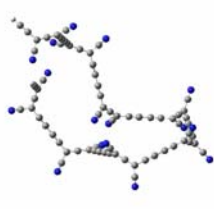



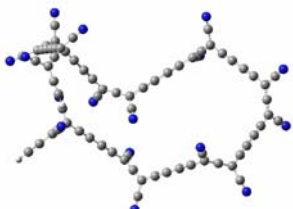
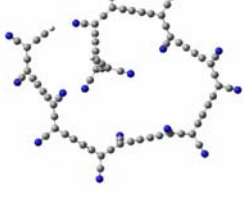
In the hexamer structures, again there is no obvious difference, and no turn is observed for **1**. In contrast, **2** expresses well-defined different turns. Almost closed turns for low energy conformers and a wide semi-turn for high energies are observed

The frequency calculations are performed for heptamer through undecamer in order to question whether the optimized geometry is a true minimum. If all frequencies came as positive numbers then the result of the optimization is a true minimum if some of them are negative the point has a saddle nature. For example if there is one negative frequency, which means there is a maximum in one direction although all the other directions indicate minimum. Unfortunately all of the configurations in **1** and some in **2**

have at least one negative frequency except monomer. **1** has mainly two dimensional planar, V-shaped and ladder like geometries in heptamer. However The first two lowest energy structures of **2** have a well-defined complete turn. For the intermediate ones, some of them have uncomplete turns some of them have again completed circles. The semi- and completely unfolded configurations are seen in the high energy region.

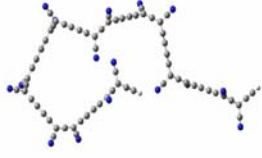

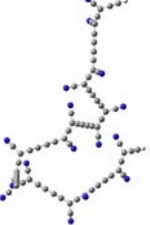

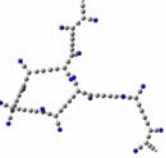
In octamer, **1** shows a 2-D chain in the most stable structure Table 3.3, as well as in the others. Since we have not seen any sign of helicity including octamer, we stop the computations on **1**.

Table 3.3. Different conformers for 1,3-dicyanodi ethynylallene oligomers (octamer)

Octamer	Isomers in Each Octamer and Their Energies(au)		
	 <p data-bbox="400 1055 628 1111">2.846497 Imaginary frequency=0</p>	 <p data-bbox="718 1055 946 1111">2.846725 Imaginary frequency=1</p>	 <p data-bbox="1078 1055 1307 1111">2.846957 Imaginary frequency=0</p>
	 <p data-bbox="400 1395 628 1451">2.846993 Imaginary frequency=2</p>	 <p data-bbox="718 1395 946 1451">2.8470682 Imaginary frequency=2</p>	 <p data-bbox="1078 1395 1307 1451">2.847202 Imaginary frequency=0</p>
	 <p data-bbox="400 1731 628 1787">2.84729 Imaginary frequency=3</p>	 <p data-bbox="718 1731 946 1787">2.847391 Imaginary frequency=1</p>	 <p data-bbox="1078 1731 1307 1787">2.847477 Imaginary frequency=0</p>

(cont. on the next page)

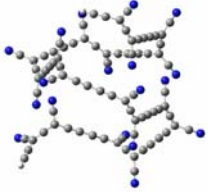
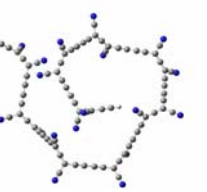
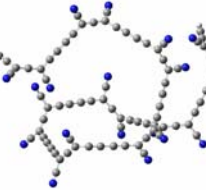
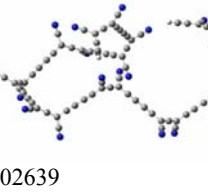
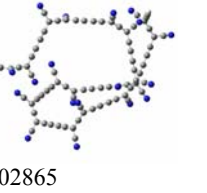
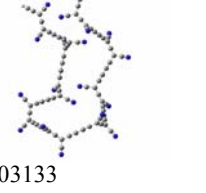
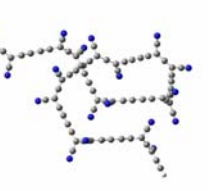
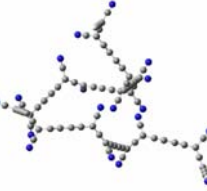
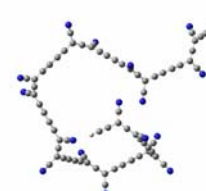
Table 3.3. (cont.)

 2.847494 Imaginary frequency=3	 2.84768 Imaginary frequency=1	 2.848188 Imaginary frequency=4
 2.848576 Imaginary frequency=4	 2.848839 Imaginary frequency=5	

14 structures were selected among 220 isomers in octamer for **2** (see Table 3.3). These 14 geometries are different structures each represents a group that have similar conformations. The most stable oligomer has one and a half turn. The second turn is beginning to form as already a half turn is growing. The second most stable conformer also has one and a half cycle but the shape of the half turn is different than in the first one. The third structure illustrates another geometry. After the first turn is formed the second turn is beginning to form behind the first turn, their ends are not pointing opposite directions, and they are at the same directions. The fourth three dimensional structure shows an interesting geometry, the turn does not form completely and two ends are pointing up. A possible complete turn may form after adding monomer units and for the following oligomer units a second turn is expected. A well-defined turn is observed for the fifth structure, two ends tend to go in opposite directions. Growing this isomer will result in another turn. The sixth conformer has a circle and one end going through upward. The seventh conformer does not complete a turn, both ends are growing in the same direction to upwards. Another unusual conformation is obtained for eight geometrical structures, there is not a full turn seen, instead with all the monomer units a big circle is resulted. The ninth oligomer has a turn and after this turn there is a twist in the structure which tends to go straight. The tenth structure after making a turn grows upward then makes a twist. The eleventh structure is also display similar geometry but in this case the part adjacent to the turn goes upward. For twelfth conformer both ends after a turn grow in the same direction but one is pointing up and one is pointing down. The same pattern is observed for the last structure, but in this case

at the beginning the end groups do not lie in the same plane they tend to go through opposite directions.

Table 3.4. The different conformers for 1,3-dicyanodi ethynylallene oligomers (nanomer)


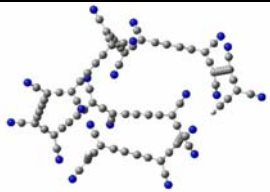

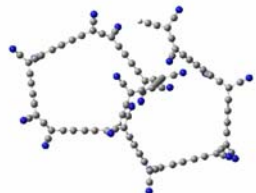
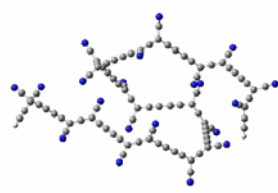
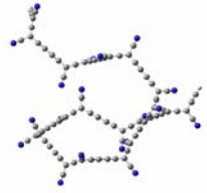
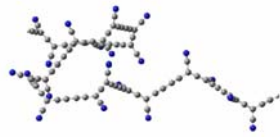
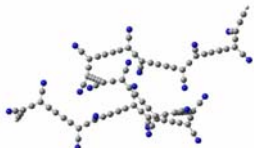
Nanomer	Isomers in Each Nanomer and Their Energies(au)		
	 <p data-bbox="438 788 670 840">3.2021345 Imaginary frequency=0</p>	 <p data-bbox="758 788 989 840">3.2022 Imaginary frequency=0</p>	 <p data-bbox="1077 788 1308 840">3.202637 Imaginary frequency=0</p>
	 <p data-bbox="438 1055 670 1106">3.202639 Imaginary frequency=3</p>	 <p data-bbox="758 1055 989 1106">3.202865 Imaginary frequency=0</p>	 <p data-bbox="1077 1055 1308 1106">3.203133 Imaginary frequency=1</p>
	 <p data-bbox="438 1373 670 1424">3.203262 Imaginary frequency=2</p>	 <p data-bbox="758 1373 989 1424">203526 Imaginary frequency=3</p>	 <p data-bbox="1077 1373 1308 1424">3.203697 Imaginary frequency=3</p>

For nanomer conformers 9 structures are chosen among 52 isomers. Table 3.4 shows the optimized geometries of selected 8 isomers in nanomer. The energies of structures are ranging from 3.2022 to 3.203697 a.u. they are close to each other. The most stable isomer has a turn in its structure and the second turn is beginning to form. An interesting geometry is seen in the second structure after forming a turn, one end makes a circle which is perpendicular to the turn and the other end tends to grow in the same direction. The third geometry has two turns laying side by side the shape of it resembles the number 8. In order to form a helical structure one of the turns must be above the other one, this might be possible as the chain grows. In the fourth conformer after forming a turn both ends grow in the same direction but one of them is above the

turn and forms a small turn. In fifth isomer a symmetrical growing in two ends is seen. Both ends go toward up but there is no circular shape in two ends.

In sixth geometry, ends go in opposite sides one is pointing up and the other one is pointing down, in the seventh isomer the same trend is seen the two ends point different directions. The last isomer on the other hand shows another feature in its structure, it forms a turn then forms another turn lying above the other one and goes straight.

Table 3.5. Different conformers obtained for 1,3-dicyanodi ethynylallene oligomers (decamer)

Decamer	Isomers in Each Decamer and Their Energies(au)		
	 3.55703527 Imaginary frequency=0	 3.5576039 Imaginary frequency=1	 3.5581282 Imaginary frequency=1
	 3.5581332 Imaginary frequency=1	 3.5590607 Imaginary frequency=1	 3.5591297 Imaginary frequency=2
	 3.5592321 Imaginary frequency=2	 3.5594922 Imaginary frequency=2	

Different geometries obtained for decamer oligomer are given in Table 3.5. Although these conformers represent different features, they all have a turn in their structures. The difference is due to the shape of the second turn. Generally, they form a turn then the geometry of the potential second turn differs. The first is a well-ordered foldamer and has no imaginary frequencies, it is a plausible true minimum. It has a P-character in terms of stereochemistry. A nearly full well-defined second turn is observed in the fourth structure whereas the second turn is not lying above the first one instead it

is lying adjacent to the first turn so it cannot be said that the structure has a helical structure.

Table 3.6 Different conformers obtained for 1,3-dicyanodi ethynylallene oligomers (undecamer)

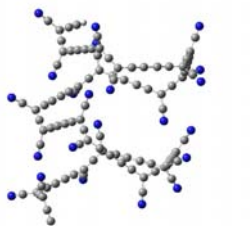


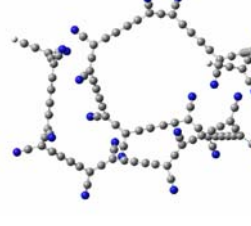

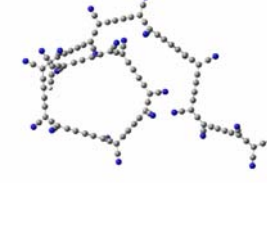
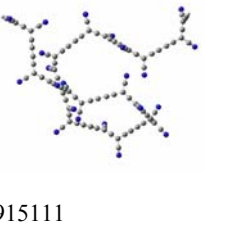
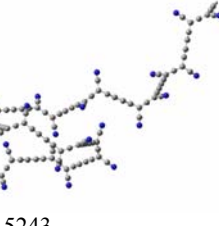
Undecamer	Isomers in Each Undecamer and Their Energies(au)		
	 <p data-bbox="448 837 679 891">3.91298793 Imaginary frequency=0</p>	 <p data-bbox="783 837 1015 891">3.912104 Imaginary frequency=0</p>	 <p data-bbox="1145 837 1377 891">3.913622 Imaginary frequency=1</p>
	 <p data-bbox="448 1155 679 1209">3.914114 Imaginary frequency=3</p>	 <p data-bbox="783 1167 1015 1220">3.91412 Imaginary frequency=1</p>	 <p data-bbox="1145 1167 1377 1220">3.914186 Imaginary frequency=1</p>
	 <p data-bbox="448 1447 679 1500">3.915111 Imaginary frequency=5</p>	 <p data-bbox="783 1458 1015 1512">3.915243 Imaginary frequency=4</p>	

Table 3.6. illustrates different undecamer geometries obtained. The most stable conformer forms a well-ordered helical structure. An different structure is observed for the second conformer, it has a box-like structure, and the two ends are in side by side. It contains three circles one following the other but they do not form in the way a helical structure forms. The third geometry has two circles lying in the same plane and it grows from the centre of two circles. The fourth conformer forms a turn then two terminals grow in the same direction one form another turn nearly perpendicular to the first turn and the other turn goes straight. The fifth geometry has a turn and the second tend to

form but it is relatively larger. For the last three structures there is not any distinctive property leading to prove the helicity, there is a circle and the difference occurs because of the terminal groups. As it is given in the table imaginary frequency is zero for the first and second conformer means that the local minimum is obtained in these structures. They both have no imaginary frequency, which means that they are true minimum. The helical conformation is the most favorable one, also from thermodynamic point of view.

The computations the further oligomers will take time, which will be the subject of another project.

Principle coordinate analysis is applied to 1,3-dicyanodiethynylallene oligomers after pentamer. The graphs are drawn energy vs. eigenvector values. The eigenvector values are obtained from the results of principle coordinate analysis. Figure 3.1 illustrates the graph for pentamer oligomers. In the graph most of the clusters lie in the energy values between 1.7815-1.782 a.u.. There are eight clusters between these energy values. The general pattern observed in these clusters is that most of the conformers do not have a turn, they have twisted structures instead. The other clusters in this graph are more stable than clusters lying above. These clusters indicating conformers have turns in their structures. The circles in the graph show the clusters and within each cluster isomers representing the groups are chosen.

Figure 3.2 is the graph for hexamer oligomer, in the graph as the number of isomers in this oligomer unit increase, the clusters approach to each other so selecting an isomer representing the cluster becomes hard. In order to select a structure, the isomers in each cluster are examined and then one isomer representing the cluster is chosen. There is also a gap as it is observed in the pentamer graph. The low energy structures in the graph have turns in their geometries.

In the graph showing heptamer conformers (Figure 3.3), the clusters are not identifiable. The principle coordinate analysis does not work well in this case. In order to select isomers representing a cluster, each cluster is investigated and different geometries are taken to form next generation of oligomers.

The number of selected isomers in octamer is decreased. The reason for decreasing the structures is because of the structure in clusters with higher energies has similar geometries. After electing these conformers 13 isomers are taken as the structures representing clusters in order to be used for the generation of nanomers. In this oligomer the graph (Figure 3.4) does not illustrate well clustered structures so in this oligomer unit, all of the geometries are examined in order to find the different structures. At this point we also use our inspection to generate additional inputs (starting geometries) which may give helical outputs.

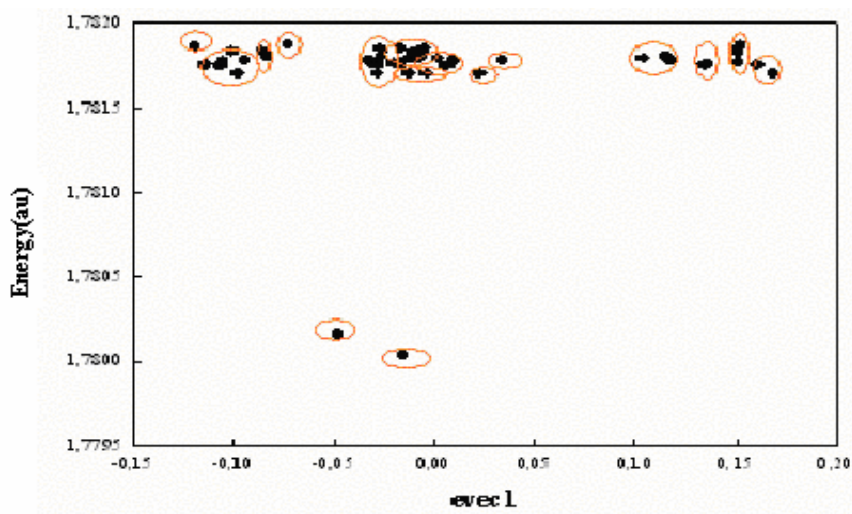


Figure 3.1. Results of PCoordAn for pentamer

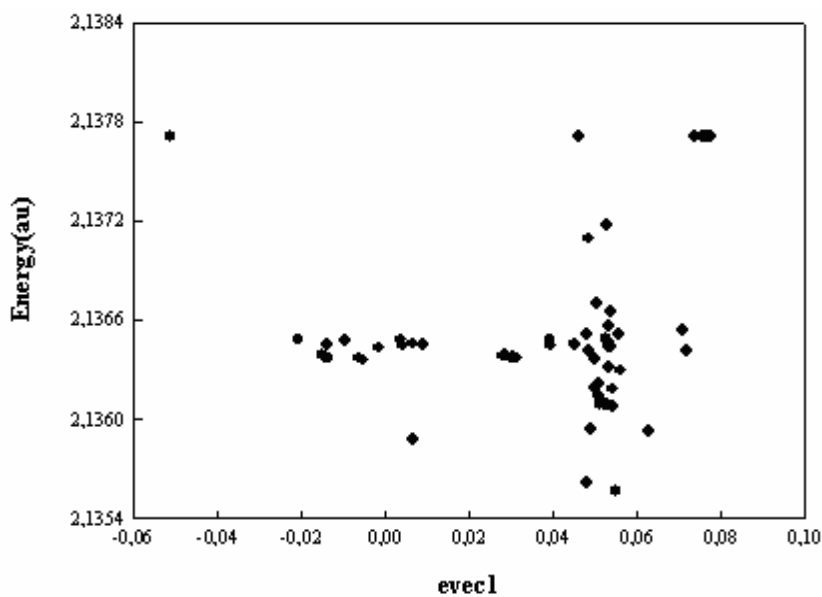


Figure 3.2. Results of PCoordAn for hexamer

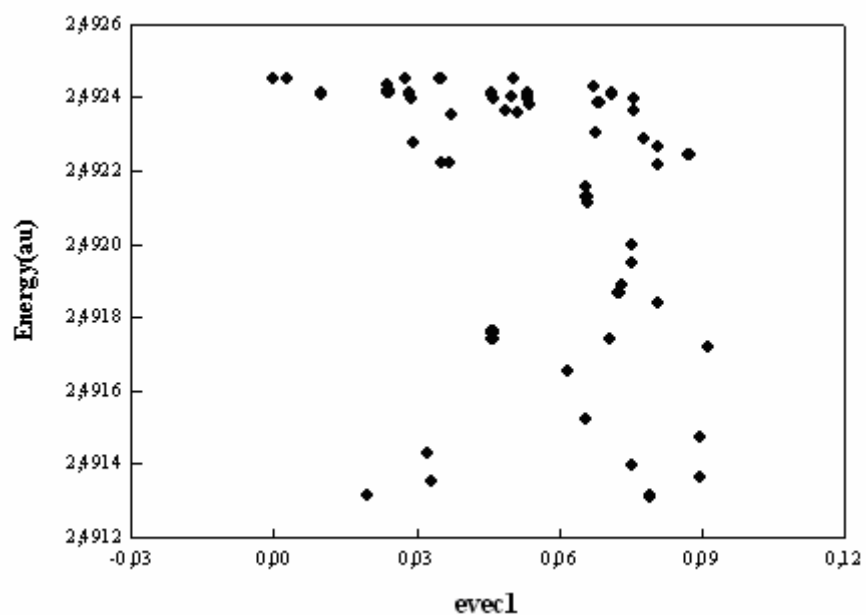


Figure 3.3. Results of PCoorAn for heptamer

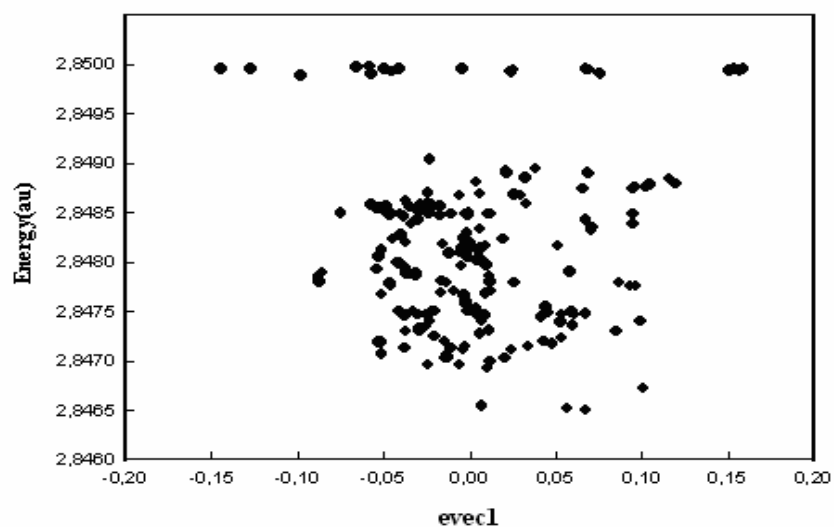


Figure 3.4. Results of PCoorAn for octamer

The graphs of energy versus conformer number belong to 1,3-dicyanodiethynylallene oligomers are prepared to see how the values varies and close to each other (Figures 3.5-3.14). For trimer (Figure 3.6) there are three points, first two indicate similar geometries the last one has another geometry as it can be clearly seen in Table 3.2. For tetramer graph (Figure 3.7), in the lower part of the graph there is a group

of structures which are separated from the other groups and the energy values relatively different than the other groups.

The other group of structures follows an increasing order in energy. In pentamer (Figure 3.18) most of the structures lie in a straight line between 1.7815 to 1.782 energy values however, there are a few geometries depart from this linear group having turn in their structures which are grouped between the energy values of 1.7800 and 1.7805 au. The similar pattern is observed in hexamer (Figure 3.9) less stable isomers lay in a straight line having so close energies but there are three groups of 3-D structures having closer energies in magnitude. In heptamer graph (Figure 3.10), the energies of structures begin to have different values. There are three groups obtained in this graph. The first small group contains the most stable conformers all of which possess circular geometry. The energies of structure until 2.493 forms another group then a break occurs and after the second group, a small group of structures are observed. In this group of structures twisted geometries are observed. Most of the points showing conformers have closer energy values approximately, 2.494 au. In octamer graph (Figure 3.11), similar features are seen in the shape of the plot. An increasing pattern is seen in energy values, in the lowest energy values a small group of conformers is seen then there is a small break and another group of conformers is observed having an energy value of approximately 2.85 a.u. In the graph showing nanomer structures (Figure 3.12), the number of structures is less compared to heptamer or octamer since after heptamer, conformers having lower energies are preferred. The reason for choosing lower energy valued conformers is because after forming a turn at pentamer, the most stable oligomers have circular geometries and this trend is the reason of decreasing number of structures after heptamer. Although this is the way that is used in octamer the graph resembles to the graphs of hexamer and octamer. The difference in the graph is that there are more breaking points of different energies. For decamer the graph (Figure 3.13) illustrates different pattern, there are more clusters observed. The reason for clustering can be attributed to the selecting conformers having similar geometries. Figure 3.14 is for undecamer structures which have different geometries and divided into 3 groups in this Figure.

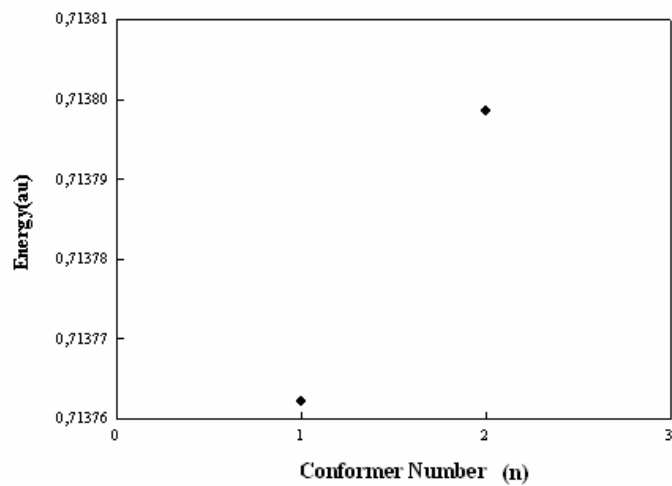


Figure 3.5 Graph of energy vs. conformer number 1,3-dicyanodiethynylallene (dimer)

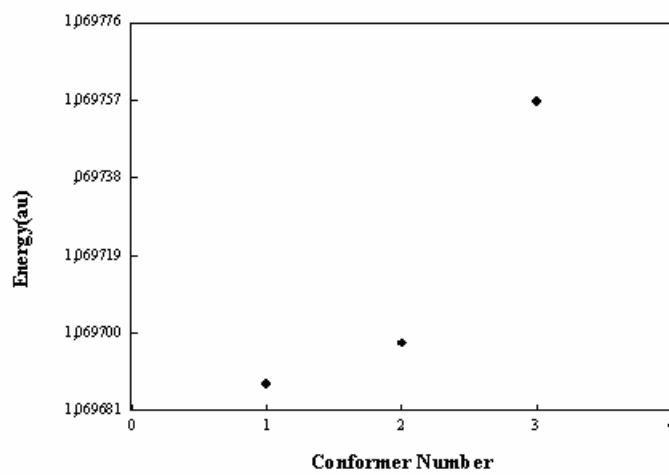


Figure 3.6 Graph of energy vs. conformer number 1,3-dicyanodiethynylallene (trimer)

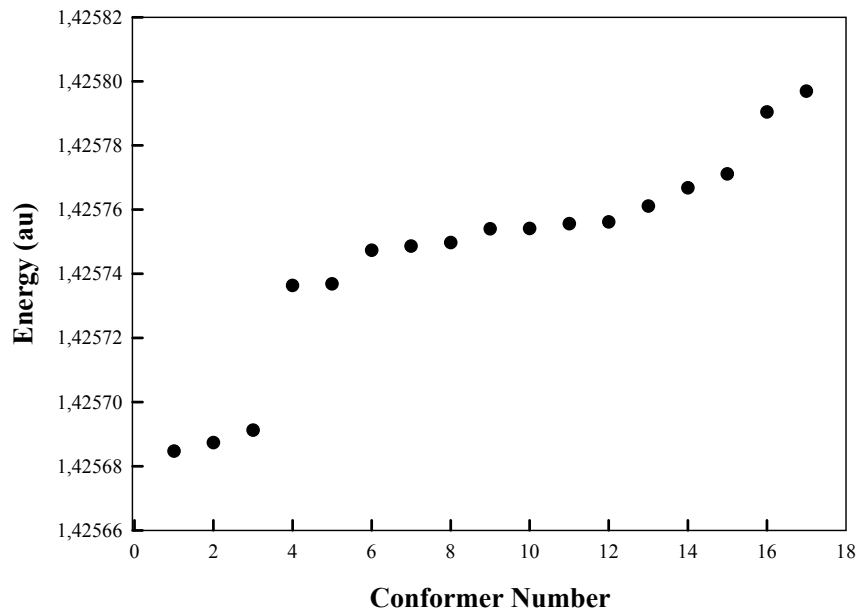


Figure 3.7. Graph of energy vs. conformer number 1,3-dicyanodiethynylallene (tetramer)

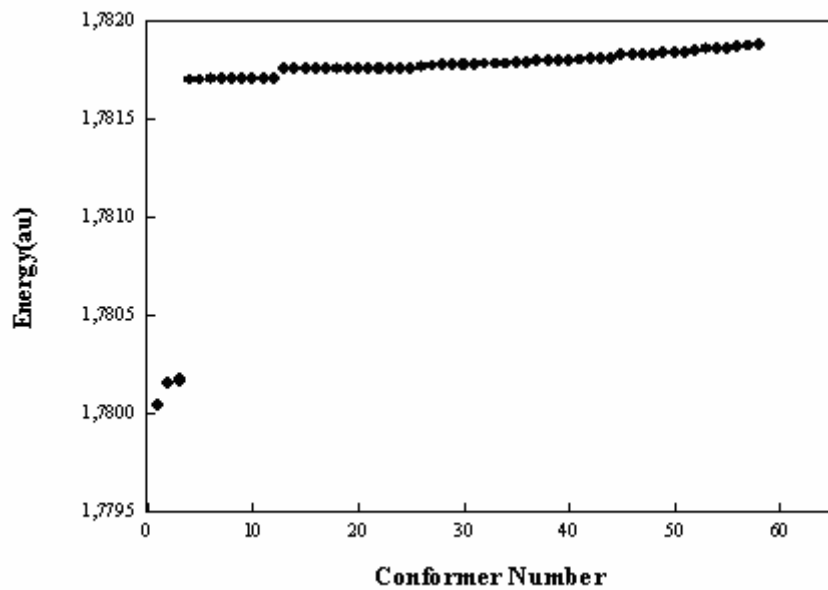


Figure 3.8. Graph of energy vs. conformer number 1,3-dicyanodiethynylallene (pentamer)

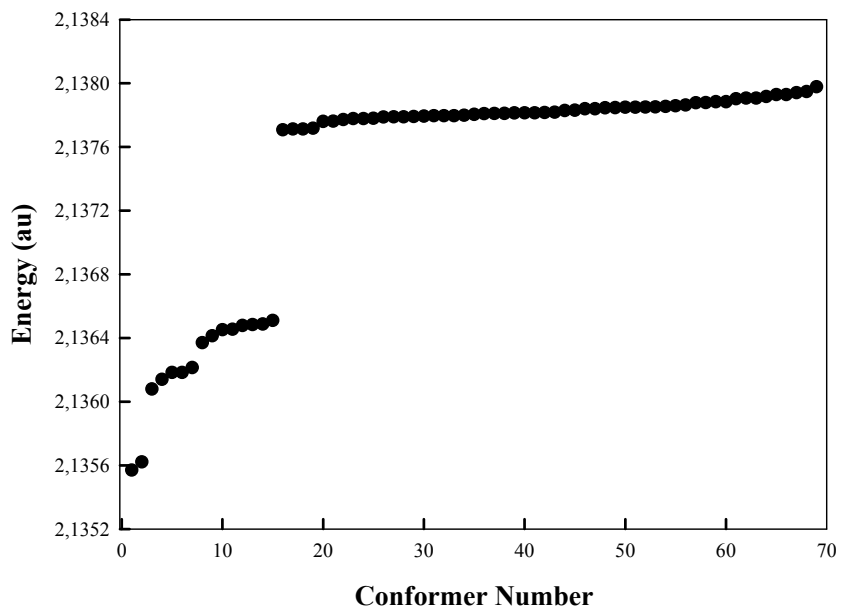


Figure 3.9. Graph of energy vs. conformer number 1,3-dicyanodiethynylallene (hexamer)

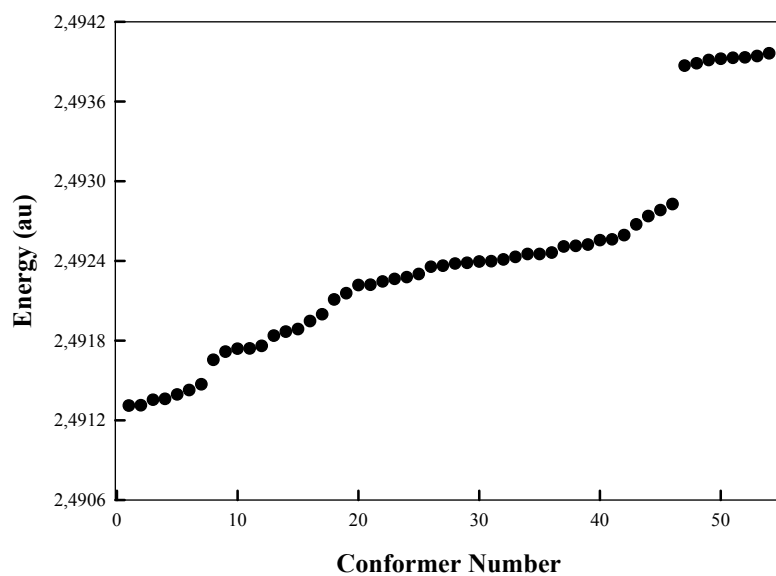


Figure 3.10. Graph of energy vs. conformer number 1,3-dicyanodiethynylallene (heptamer)

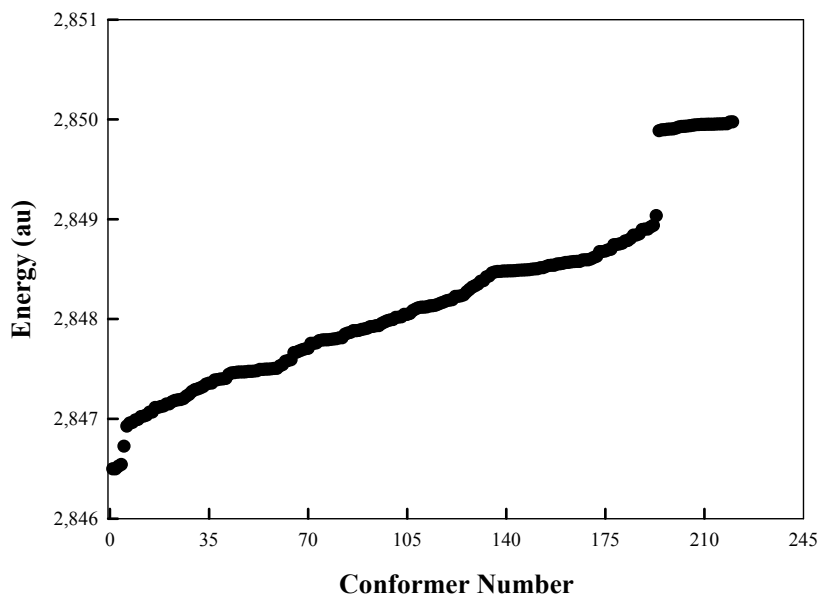


Figure 3.11. Graph of energy vs. conformer number 1,3-dicyanodiethynylallene (octamer)

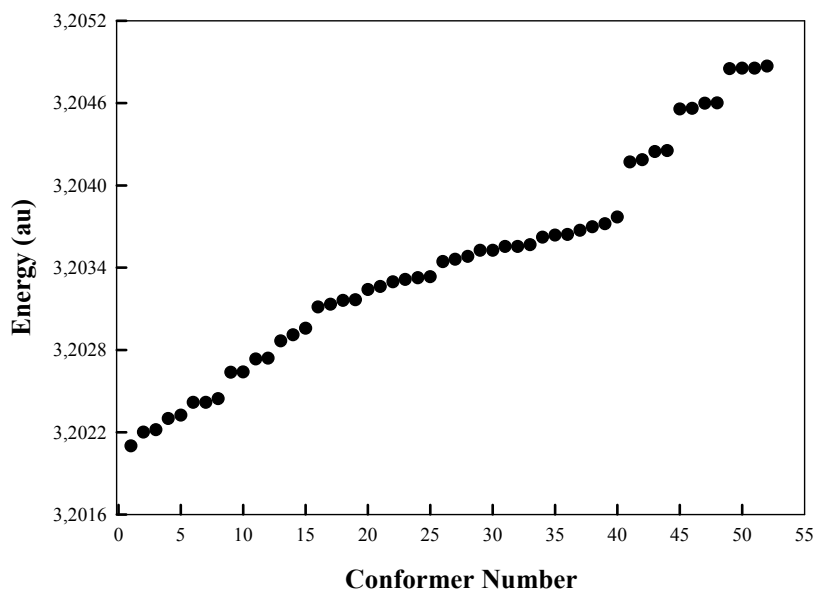


Figure 3.12. Graph of energy vs. conformer number 1,3-dicyanodiethynylallene (nanomer)

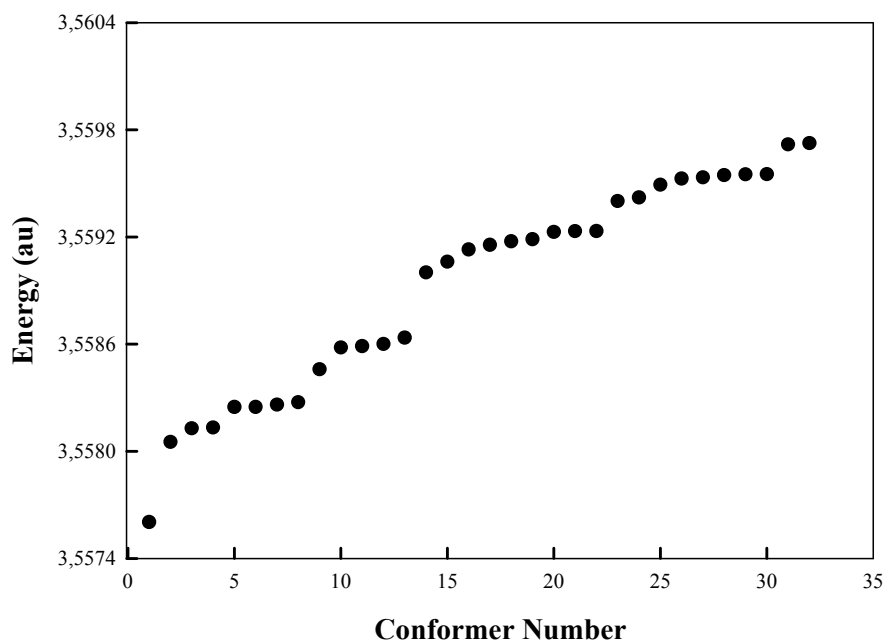


Figure 3.13. Graph of energy vs. conformer number 1,3-dicyanodiethynylallene (decamer)

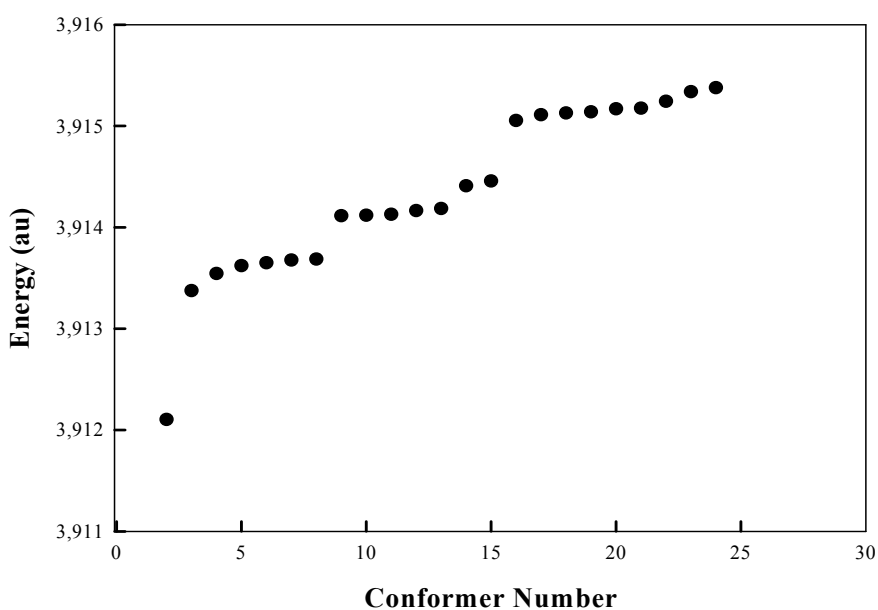


Figure 3.14. Graph of energy vs. conformer number 1,3-dicyanodiethynylallene (undecamer)

The Figures between 3.15.-3.21 are graphs of energy vs. conformers for 1,3-diethynylallene oligomers. When these graphs are compared to graphs of 1,3-

dicyanodiethynylallene oligomer, there are less number of structures. In the graphs of dimer, trimer, and tetramer all values show an increasing trend of closer energies.

In the pentamer the values again tend to grow in an increasing manner but this time there are some structures that they have much closer energy values. For hexamer, heptamer and octamer the graphs exhibit similar pattern except the number of dots indicating the conformers increases as the number of oligomer units increases. In these graphs a breaking point is seen. In each graph the most stable structures and the least stable structures are separated by a breaking point from the other structures.

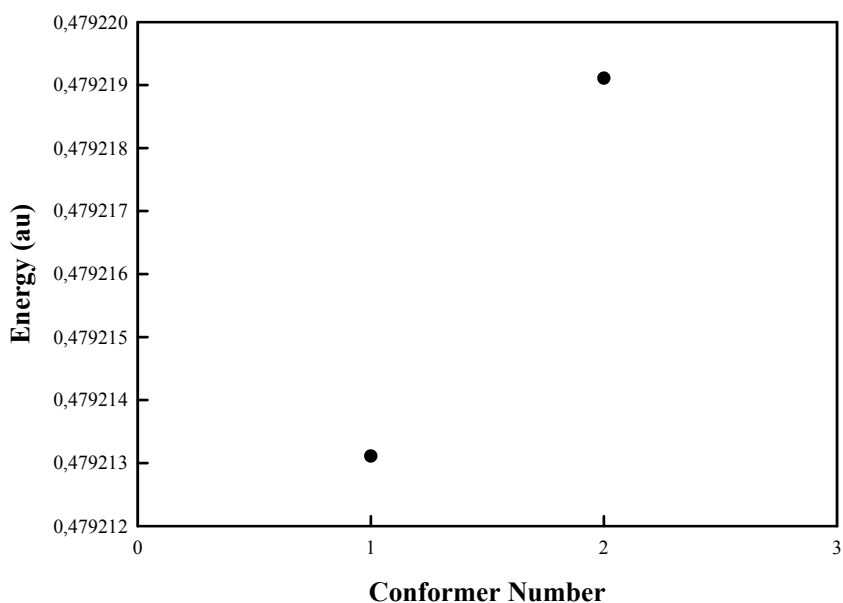


Figure 3.15. Graph of energy vs. conformer number 1,3-diethynylallene (dimer)

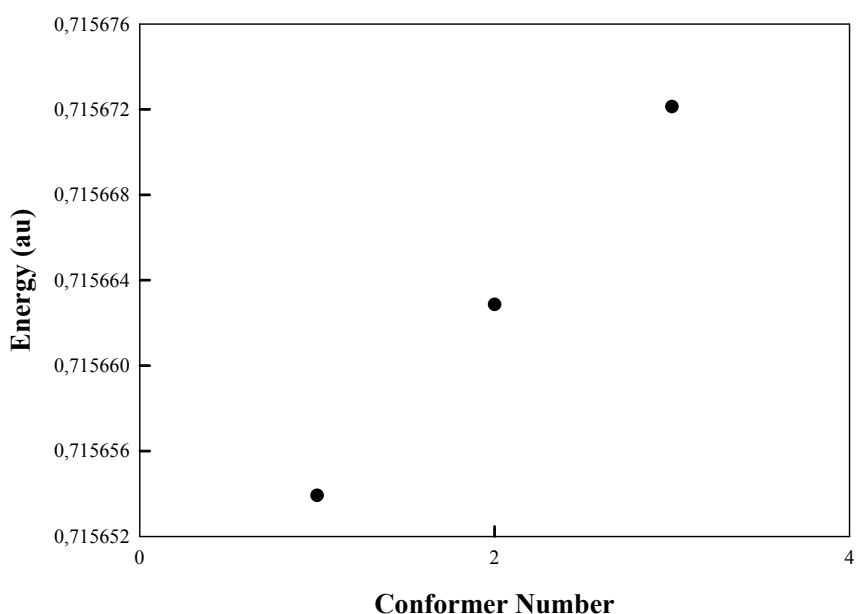


Figure 3.16. Graph of energy vs. conformer number 1,3-diethynylallene (trimer)

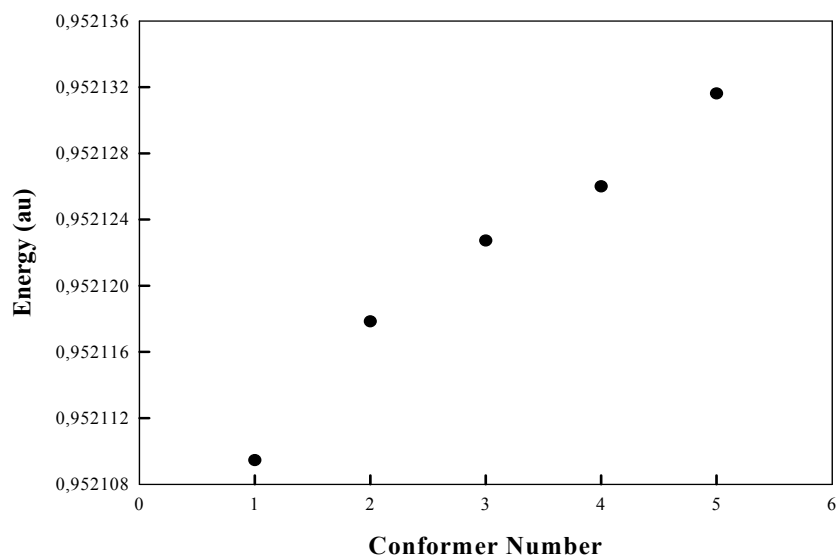


Figure 3.17. Graph of energy vs. conformer number 1,3-diethynylallene (tetramer)

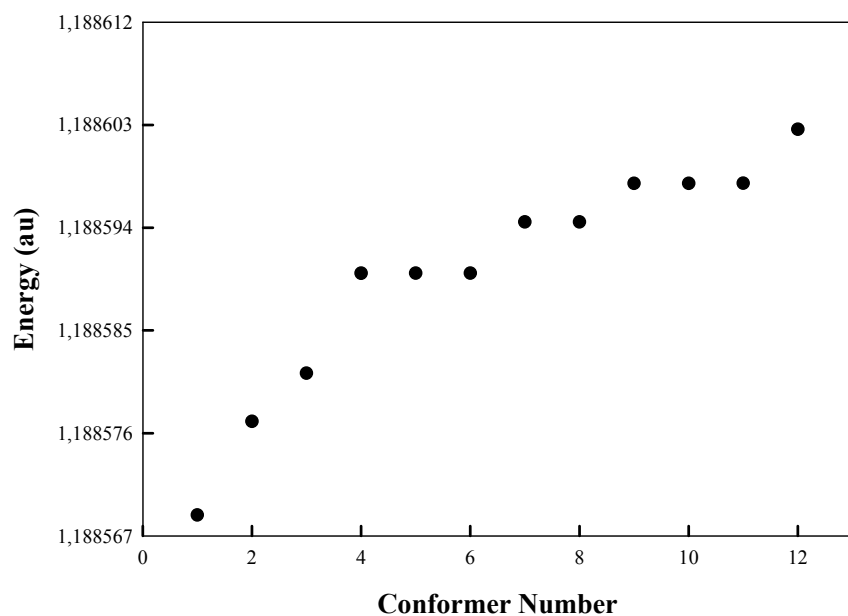


Figure 3.18. Graph of energy vs. conformer number 1,3-diethynylallene (pentamer)

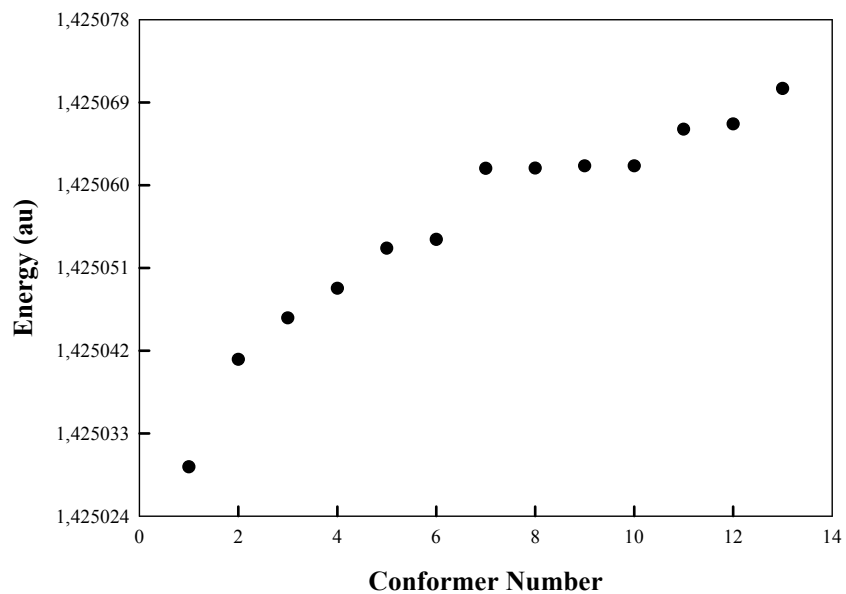


Figure 3.19. Graph of energy vs. conformer number 1,3-diethynylallene (hexamer)

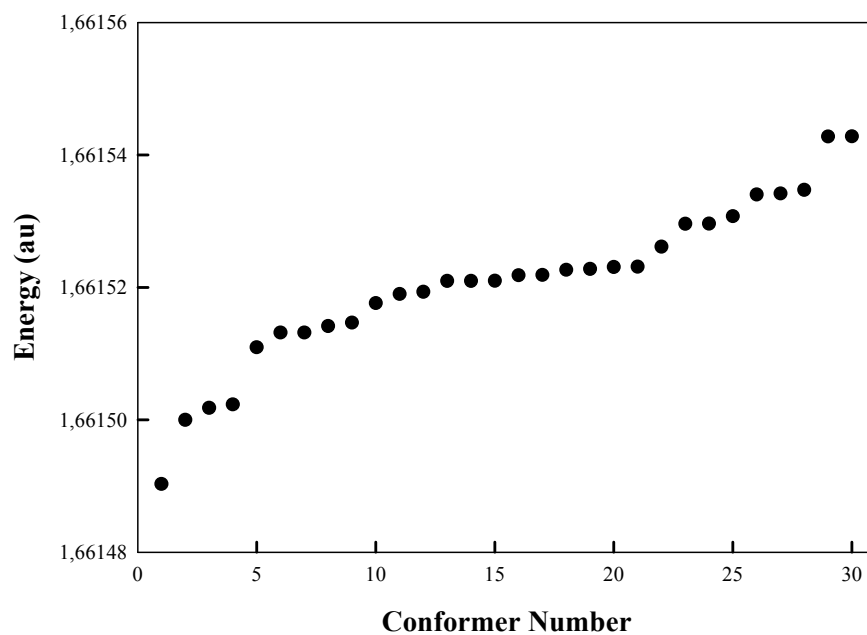


Figure 3.20. Graph of energy vs. conformer number 1,3-diethynylallene (heptamer)

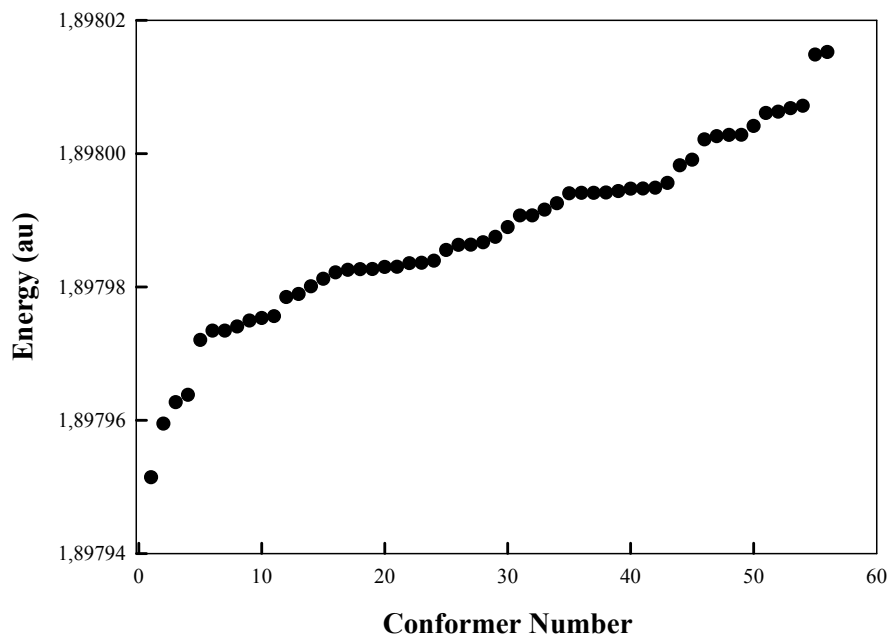


Figure 3.21. Graph of energy vs. conformer number 1,3-diethynylallene (octamer)

The first turn is observed at pentamer and the shape of it is like a pentagon. The edge of this pentagon is measured and it is found to have a value of 13.84 \AA (h in the below figure), and each edge length(l) is 8.30 \AA long. The dihedral angles are as indicated in the following graph as a, 87.89° b, 90.55° c, 89.20° d, 87.87° e, -87.09° .

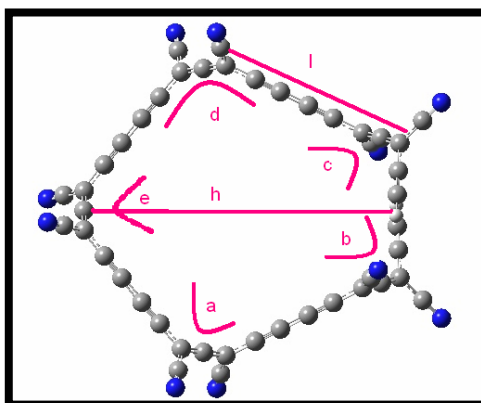


Figure 3.22. The most stable conformation at pentamer (1)

The following figure shows the 15-mer structure. The a and b lengths, which are distances between two turns, are found to be 6.76 \AA and 6.75 \AA , respectively. As the effect of cyano groups is important the distances of neighboring cyanos located in between layers are measured, the largest value is 7.78285 \AA and the lowest value is 3.09756 \AA .

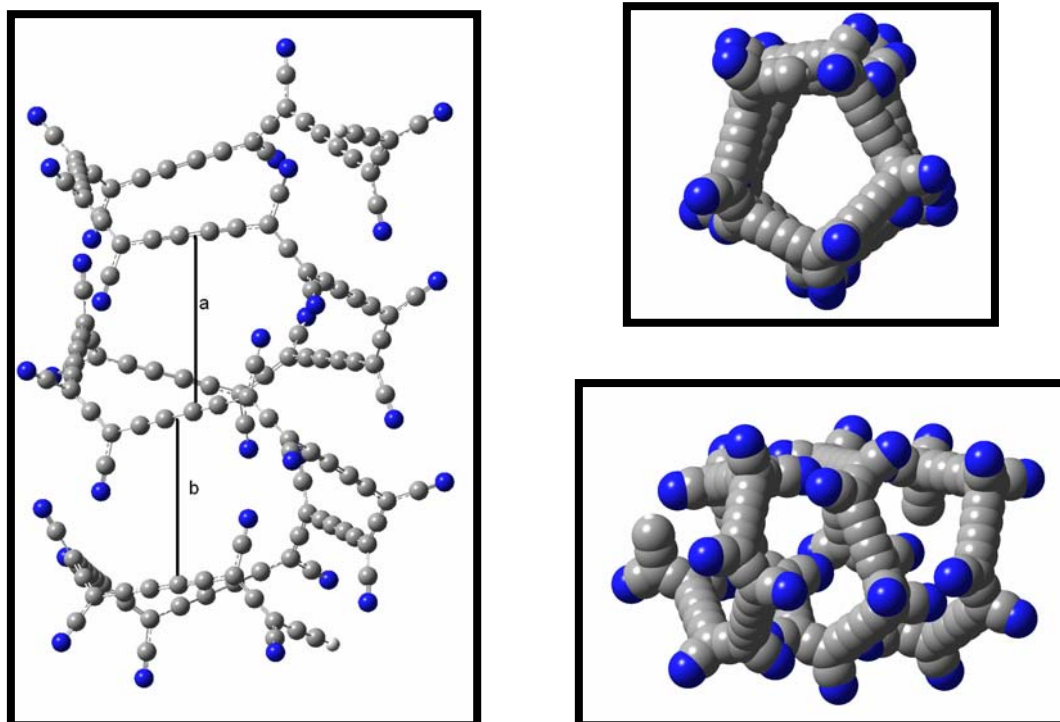


Figure 3.23. The helical conformation at 15-mer with different views (top, sides)

Figure 3.24 shows the Mulliken charges with a color scale from green (most positive) to red (most negative) of undecamer structure. In the figure hydrogen's at each terminals and end carbons of each allene molecule have positive charges (green) the largest positive value is 0.247 C which belongs to the hydrogen atom at one of the terminals, positive charge having carbon atoms have slightly lower values than hydrogen atoms. Lightest red color (most negative charge) is observed for carbon atoms at the end side next to allene carbon, the largest negative value is -0.179 C. Darker red colors indicate lower negative values, nitrile carbons and the carbons adjacent to the end allene carbons represent this type. The values for darker red color charges are approximately 0.10 Debye and nitrile carbons have larger negative values in this group. There is another color (black) which represents atoms having nearly zero charge. Nitrogens and carbons joining two acetylenes are nearly neutral.

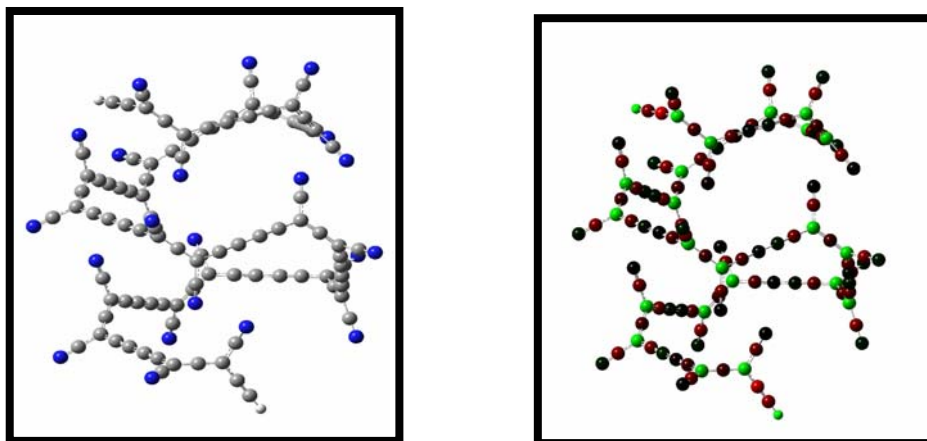


Figure 3.24. Charges of undecamer structure of **2**, charges illustrated by colors, green for positive, red for negative, and dark colors for neutral charges.

In order to see the effects of oligomerization in bond lengths bond distances are measured and the results are given in Table 3.7 for **2** and 3.8 for **1** the corresponding bonds are illustrated in Figures 3.24 and 3.25 for **2** and **1**, respectively. As it is clear in the figures, electron delocalization is seen throughout the backbone with double, triple and one and a half bond orders. The indicated bond distances are showing these bonds. We observed alternating bonds in the acetylenic part. In **1** and **2** the bond distances for each indicated bond remains the same which shows the oligomerization, the growth of the molecule, does not affect the bond lengths. However, there are small unremarkable differences between the magnitudes of bond lengths in **1** and **2** which furthermore indicate that cyano groups do not have very big effects on the bond lengths.

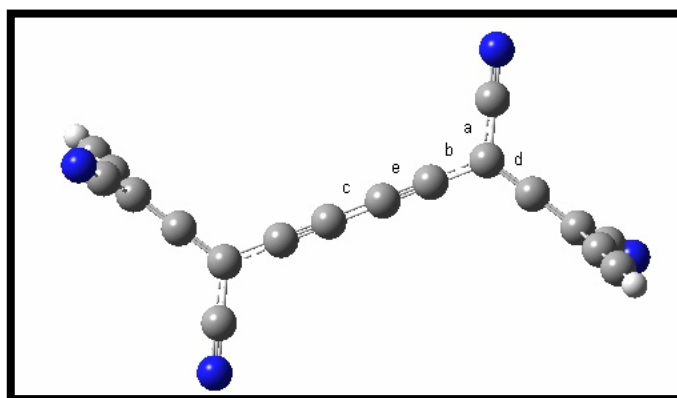


Figure 3.25. Bond distances of **2**

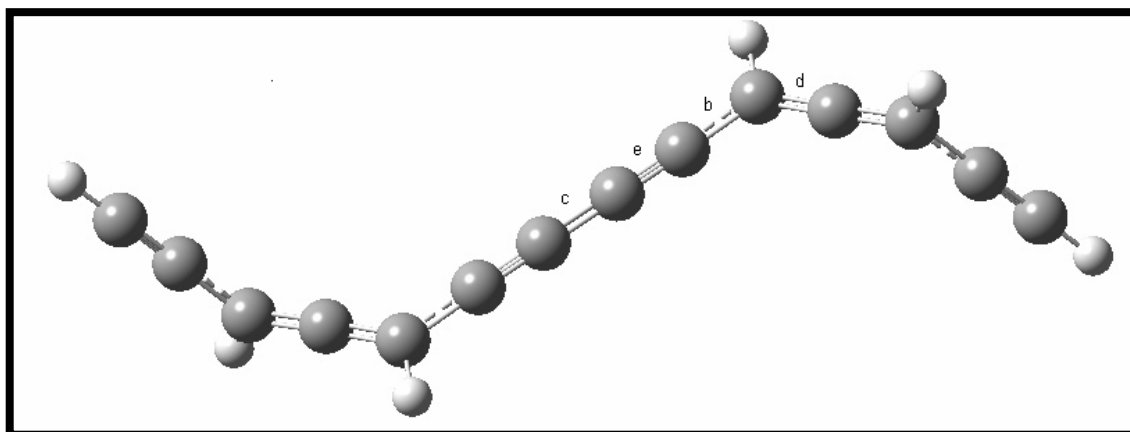


Figure 3.26. Bond distances of **1**

Table 3.7. The values for indicated bond distances for **2**

Molecule 2	a	b	c	d	e
dimer	1.43	1.41	1.35	1.32	1.20
trimer	1.43	1.41	1.35	1.32	1.20
tetramer	1.43	1.41	1.35	1.32	1.20
pentamer	1.43	1.41	1.35	1.32	1.20
hexamer	1.43	1.41	1.35	1.32	1.20
heptamer	1.43	1.41	1.35	1.32	1.20
octamer	1.43	1.41	1.35	1.32	1.20
nanomer	1.43	1.41	1.35	1.32	1.20
decamer	1.43	1.41	1.35	1.32	1.20
undecamer	1.43	1.41	1.35	1.32	1.20

Table 3.8. The values for indicated bond distances for **1**

Molecule 1	b	c	d	e
dimer	1.40	1.35	1.31	1.20
trimer	1.40	1.35	1.31	1.20
tetramer	1.40	1.35	1.31	1.20
pentamer	1.40	1.35	1.31	1.20
hexamer	1.40	1.35	1.31	1.20
heptamer	1.40	1.35	1.31	1.20
octamer	1.40	1.35	1.31	1.20

Another property measured is the dipole moments for **1** and **2** (see Table 3.9). The effect of cyano groups is clearly seen in the monomer unit as the dipole moment values are examined. The value of **2** is so much larger than **1** because of the two electronegative nitrogen atoms at each end in **2**. For **1** the values are almost zero. For **2**, the lowest value is obtained for dimer which is a result of cancellation of the dipole moments of nitrogen atoms at the opposite sides. The dipole moments depend on the position of the cyano groups and the values change as a result of this feature. After the first turn is observed, the dipole moment of the oligomers increases till the next turn, then it drops to near zero and it starts to increase again.

Table 3.9. Dipole moments for **1** and **2** at each oligomer unit for the lowest energy structures

1		2	
Dipole moment (Debye)	Number of Monomer Units	Dipole moment (Debye)	Number of Monomer Units
0.0909	1	3.5675	1
0.0007	2	0.0072	2
0.1574	3	2.7686	3
0.0003	4	3.316	4
0.1616	5	0.6277	5
0.0034	6	1.6091	6
0.1612	7	2.9993	7
0.0033	8	3.8515	8
		5.8711	9
		0.9394	10
		6.8057	11

In Tables 3.10 and 3.11 the charges, homo and lumo surfaces are given for **2** and **1**, respectively. The charges for monomer of **2** have the most positive part at the hydrogens (light green) and relatively less positivity at the terminal allene carbons. The red parts show the negative charge on acetylenic carbons. Monomer **1** has the similar charges, all hydrogens have positive charges and acetylenic carbons again are negatively charged but in this case terminal allene carbons are neutral.

Table 3.10. a) Charges, b) homo surfaces c) lumo surfaces of **2**

# of monomer units	a) charges	b) homo	c)lumo
1			
2			
3			
4			
5			

Table 3.11. a) Charges, b) homo surfaces c) lumo surfaces of **1**

# of monomer units	a) charges	b) homo	c)lumo
1			
2			
3			
4			
5			

When the homo and lumo surfaces are examined (for **1** and **2**, in both cases HOMO has π character LUMO has π^* similar to conjugated molecules. The electron density moved to the alternating bonds from HOMO to LUMO, this is a common property for the conductive conjugated polymers. No substituent effects and no intramolecular charge transfer from the side groups the backbone are seen. **1** and **2** express similar properties till pentamer. The lumo surface is located at the middle (between second and third allenes) of the pentamer in both **1** and **2**. The electron density of homo of **2** is located at two terminal ends which contains first-second and fourth-fifth allenes, but it is only on the one end in **1**.

In order to understand why **2** forms a helix and **1** does not, we did a detailed charge analysis. The charges on the allene carbons and cyano atoms, acetylenic carbons are listed in Table 3.12 and Table 3.13. We used different letter (see Figure 3.26) for the atoms that we compare the charges for the simplicity. The a,c atoms are positive in **2** whereas neutral in **1** for all oligomers. On the other hand b is much more negative in **1** than **2**. The difference in e and f is almost zero in **2**, but -0.054 in **1** at monomer. There is a small change in charge for f and g in monomer, a large variation is observed dimer through pentamer.

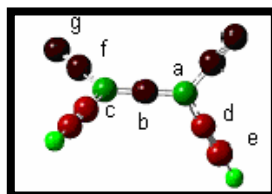


Figure 3. 27. The positions of the indicated bond distances in **2**

Table 3.12. The values of bond distances in Figure 3.26 for **2**

2	a	b	c	d	e	f	g
Monomer	0.171	-0.066	0.171	-0.167	-0.168	-0.061	-0.046
Dimer	0.196	-0.066	0.178	-0.079	0.007	-0.105	0.008
Trimer	0.189	-0.062	0.189	-0.088	0.018	-0.109	0.016
Tetramer	0.191	-0.061	0.187	-0.081	0.012	-0.109	0.017
Pentamer	0.208	-0.067	0.167	-0.080	0.011	-0.089	-0.016

Table 3.13. The values of bond distances in Figure 3.26 for **1**

1	a	b	c	d	e
Monomer	-0.005	-0.116	-0.005	-0.133	-0.187
Dimer	0.001	-0.112	-0.006	-0.080	-0.033
Trimer	-0.001	-0.108	-0.001	-0.085	-0.026
Tetramer	-0.000	-0.107	0.002	-0.081	-0.029
Pentamer	-0.001	-0.106	-0.001	-0.082	-0.028

The charges on the all atoms for 15-mer are shown in the Figure 3.27 in color scale as in before, the most striking observation here is that, the charge on carbon and nitrogen are not same for all cyano. They are changing with cyano location. When the distance between nitrogen and carbon in allene part is in the range of 3.5-5.7 Å, the charges are almost same (around -0.05 C, see the figure both atoms are in red color) if they are far away then the charge on nitrogen is close zero (about -0.02, N atom is in dark color whereas C atom is in red. The cyanos separations are 3.1, 4.4, 4.6 Å when they are positioned next to each other in the adjacent layers.

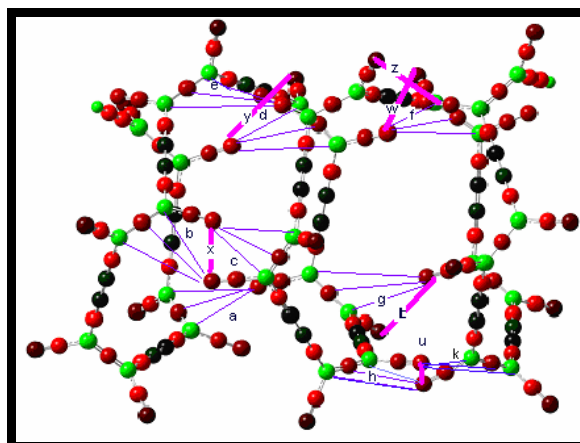


Figure 3.28. 15-mer structure showing the distances in charge surface

Table 3.14. The column a gives the shortest distances from each group between nitrogen and allene carbons and the column B gives the nitrogen nitrogen distances

A	distances (Å)	B	Distances(Å)
a	3.1	x	3.1
b	4.7	y	3.9
c	3.8	t	4.4
d	3.9	u	3.1
e	4.5	w	3.1
f	3.5	z	3.1
g	4.2		
h	4.7		
k	3.8		

The E/n , HOMO LUMO energies and their gap versus n are displayed in the following figures, E/n is almost converged and band gap becomes constant after hexamer of **1** and decamer of **2**. The HOMO-LUMO separations are similar in both type of oligomers, 8.46 eV (**1**) and 8.29 eV (**2**). Based on these, the properties that we observe here for largest oligomer may reflect polymer behavior.

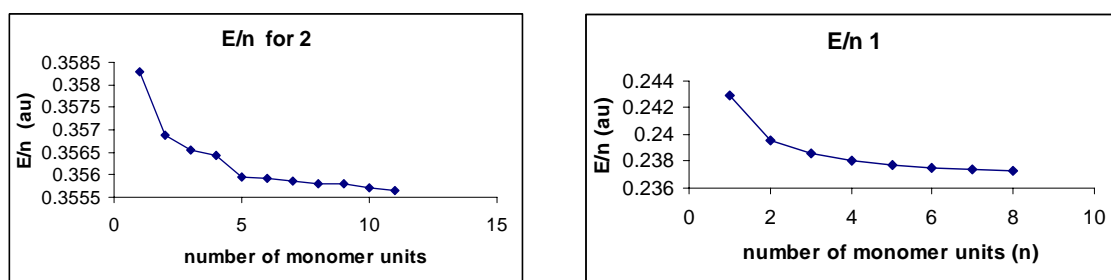


Figure 3.29. Graph of energy/number of monomer vs. number of monomer units for **2** and **1**

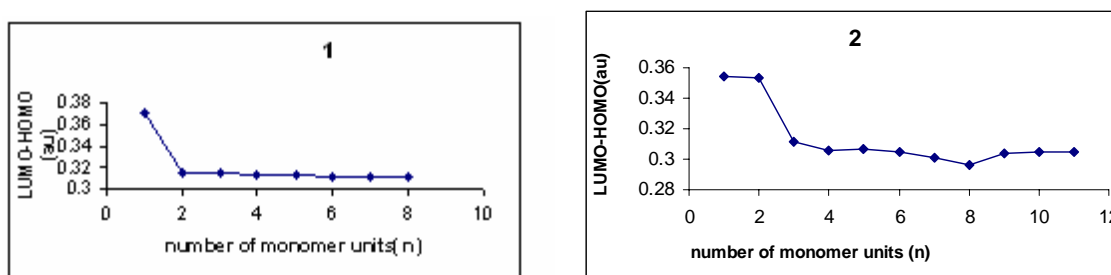


Figure 3.30. Graph of $\Delta LUMO-HOMO$ vs. 1/number of monomer units for **2** and **1**

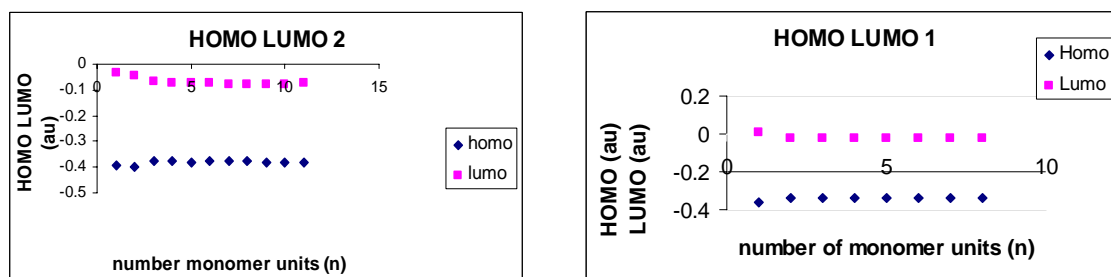


Figure 3.31. Graph of HOMO LUMO vs. number of monomer units for **2** and **1**

Table 3.15. Data for energy, HOMO, LUMO and Δ LUMO-HOMO for molecule 2

# of monomer 2	Energy (au)	HOMO	LUMO	Δ LUMO-HOMO
1	0.358281	-0.39070	-0.03632	0.35438
2	0.713762	-0.39667	-0.04331	0.35336
3	1.069687	-0.37845	-0.06688	0.31157
4	1.425685	-0.37813	-0.07199	0.30614
5	1.77970	-0.38255	-0.07577	0.30678
6	2.135570	-0.37861	-0.07427	0.30434
7	2.490920	-0.37890	-0.07830	0.30060
8	2.846497	-0.37572	-0.07934	0.29638
9	3.202130	-0.38140	-0.07800	0.30349
10	3.557040	-0.38310	-0.07850	0.30468
11	3.912104	-0.38011	-0.07548	0.30463

Table 3.16. Data for energy, HOMO, LUMO and Δ LUMO-HOMO for molecule 1

Number of Monomers (n) 1	Energy (E)	HOMO	LUMO	Δ Lumo-Homo
1	0.242891	-0.36013	0.00958	0.36971
2	0.479213	-0.3348	-0.02087	0.31393
3	0.715654	-0.33649	-0.02271	0.31378
4	0.952109	-0.33724	-0.0247	0.31254
5	1.188569	-0.33746	-0.0253	0.31216
6	1.425029	-0.33756	-0.02584	0.31172
7	1.661490	-0.33761	-0.02620	0.31141
8	1.897951	-0.33764	-0.02645	0.31119

CHAPTER 4

CONCLUSION

The helicity of the 1,3-diethynyllallene(1) and 1,3-dicyanodiethynyllallene(2) oligomers are investigated by performing semi-empirical quantum chemical calculations. The substituents play critical role since the one containing cyano side groups exhibit helical character in contrast to 1. 1 has rod-like wavy chains. The helix contains 5 repeating unit per fold, the shape of each layer of helix is like a pentagon with the radius 7.0 Å and edge 8.3 Å. The interlayer distance is on the order of 7 Å. Since the helix has a loose character, it can be used as a host for doping and interchaleting materials. Among the conformers found from our diggings only P-helix form is encountered, we did not meet any conformers that will give access to the M-helix. One of the future work will be on the stabilities of M and P forms of these helices.

The charges of terminal allene carbons are positive and the central one is near to neutral for 2 while in 1 exterior ones are neutral the interior one is negative. The charges of carbon and nitrogen of cyanos are both negative and almost same in magnitude when they are located close to allene carbon otherwise nitrogen has almost neutral character. The substituent effect implies that the folding of the oligomer is driven by electrostatic interactions between terminal allene carbons and cyano group rather than the π - π interactions of acetylenes in the helical conformation.

The energy values of the conformers that we could find out are very close to each other and most of the conformers have at least one imaginary frequency, that indicates the oligomers are very flexible. They would jump from one state to another one very easily if disturbed externally. The polymer of 2 might be thought as switch materials if they are stable in both P and M helix states and can be synthesized. The monomer and dimer of 1 are synthesized recently, we anticipate that our calculations will lead the experimentalist to design new chiral oligomers with novel interesting properties.

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