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Dipole Bound Excited States of Polycyclic Aromatic Hydrocarbons containing Nitrogen and their Relation to the Interstellar Medium

Mallory L. Theis
Georgia Southern University

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Dipole Bound Excited States of Polycyclic Aromatic Hydrocarbons containing Nitrogen and their Relation to the Interstellar Medium

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By

Mallory Theis

Under the mentorship of Dr. Fortenberry

ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are the most abundant type of molecule present in the interstellar medium (ISM). It has been hypothesized that nitrogen replacement within a ring is likely for PAHs present in the ISM. Additionally, electrons, protons, and hydrogen atoms are readily added to or removed from PAHs creating a truly diverse set of chemistries in various interstellar regions. The presence of a nitrogen within a PAH (called a PANH herein) that is additionally dehydrogenated leads to a neutral radical with a large dipole moment. It has recently been shown through the use of high-level quantum chemical computations for small molecules that the corresponding closed-shell anions support electronically excited states within a dipole- bound formalism as a result of the interaction between the loosely bound excited electron and the dipole moment of the neutral radical. We are extending this methodology to larger molecules, PANHs in this case. If a dipole-bound excited state of a PANH anion exists, it could possess unique features that could shed light on various unresolved interstellar spectra potentially including even the diffuse interstellar bands.

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Dr. Ryan C. Fortenberry

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Introduction

The range of varying chemical species in outer space is most easily approximated as infinite. Scientists are able to make accurate assumptions about the development of the universe, and more specifically our world, by analyzing the chemical makeup of the interstellar medium (ISM). In order to shed light upon the possible composition of the cosmos, this study is attempting to analyze specific spectroscopic features of the ISM in order to determine their carriers. This will add to the knowledge of what makes up the universe.

Astronomical Spectroscopy

Spectroscopy uses a chemical's distinct interactions with electromagnetic radiation to detect the compound, much like a fingerprint. Photons are directed at the respective analyte and cause either electronic, vibrational, or rotational (or with some combination) changes in quantized energy levels.[1] The energy associated with these changes, or transitions as they are called, between energy levels varies for every chemical species. In processes such as electronic absorption, the energy or wavelength required to excite an electron into a higher energy state can be measured. In other processes, such as emission and photoluminescence, the electron goes through a relaxation process to a lower energy state, which releases energy in the form of a new photon.[1] The energy seen as either absorption or emission corresponds to a specific, unique wavelength for each molecule. In the readout of a spectrophotometer, peaks are observable at the wavelengths associated with the energy released or absorbed by the analyte. A peak's width can

identify the numerous lower-energy (vibrational, rotational, rovibronic) transitions of the electrons in a molecule. The given peak can be thought of as the summation of all the energetic transitions that take place.[2] Therefore, the placement and spread of peaks uniquely describes the chemical that is analyzed.

Due to the ability of spectroscopy to properly identify a large number of compounds and elements, it is an ideal method of observation in astronomy, where classification of certain molecules informs observers about the physical conditions of a given extraterrestrial region. Spectroscopy is also a tool for astronomers to use in the determination of the specific chemical species and their relative abundances present in the universe beyond our planet. Spectroscopy allows scientists to accurately analyze the composition of the universe without the necessity of tangibly acquiring samples, and to observe minute amounts of chemical species in diffuse regions due to the high level of sensitivity associated with modern instrumentation.[3]

There are some important characteristics which influence the analysis of chemicals in space. Spectroscopy is known for reproducibility. However in space, the chemicals analyzed often seem to have fluctuating wavelengths of energy. At first glance, this appears as though the energy levels of molecules in space are shifting. Thus, spectroscopy is not a viable method of analysis. However, it is not the species that are changing, but rather the distance they are away from the spectrograph that is changing. The universe exists in a constant state of expansion. This causes bodies of stellar matter to move in relation to the Earth, which causes the photons of light released by the spectrophotometer to be stretched. This stretching of the waves leads to a shift in wavelength towards the IR, which is known as red shifting. Blue shifting is the

phenomenon that describes particle waves that are shortened in transit when on object, like the Andromeda galaxy is approaching the observer. These shifts coupled together are known as the Doppler Effect.[4]

Astronomical spectroscopy is used to determine the composition of stars, as well as the interstellar medium. It can identify many physical properties of stellar compounds and the stars themselves that scientists are not able to observe simply using telescopic methods. Of particular interest is a set of absorption bands known as the diffuse interstellar bands (DIBs), which have baffled scientists for nearly a century.[6]

Diffuse Interstellar Bands

The DIBs are a set of absorption bands found within nearly every sight line of the ISM.[6] They were first discovered by Mary Lea Heger of the University of California's Lick Observatory in 1918. Heger observed two interesting absorption peaks that were much broader than what would be expected for atomic spectra. Additionally, the features did not fluctuate in wavelength, as would be expected due to the Doppler Effect, whereas other peaks did shift as the observed rotating binary star moved towards and away from the Earth.[5] The diffuseness of the bands is indicative of a molecular spectrum as opposed to an atomic spectrum. As discussed previously, the spread of a peak represents all possible energy transitions of a chemical. Atomic spectra are normally very sharp peaks, representing one transition (electronic), whereas a spectrum of a molecule would show many more transitions.[5] As the size of the molecule increases, so does the width of the peak.

Due to these bands' characteristic of being independent of the Doppler effect, it was determined by Paul Merrill in 1938 that the chemical species causing these bands were present in the ISM as opposed to the circumstellar regions originally observed.[7] The ISM has, on average, a very low density of matter, and the matter that is present is in the form of either gas (99%) or interstellar dust (1%). This distribution is due to the highly radiative environment of this region.[2,8] It has been determined that the temperature and density across this region of space varies greatly. Within the ISM there are vast areas of essentially empty space, as well as clusters of matter known as diffuse clouds, which have higher densities of matter.[2] Attention has been turned to analyzing these clouds in order to gain understanding of the mysterious bands, where the molecular densities generate greater signal.

Today, there have been over 300 DIBs observed, ranging from the ultraviolet to IR regions of the electromagnetic spectrum. However the identities of these bands evades scientists.[5,8,9,10,11] Unlike many known chemical species, the spectral features of these bands are not reproducible in laboratory or other experimental settings.[10] It has also been proposed that the actual absorption features of the DIBs may be skewed due to a misinterpretation of what is being analyzed in the line of sight.[11] As a photon travels through space, it will not stop until it is fully absorbed by some form of matter. The photon does not discriminate against where this matter is present. This leads to possible Doppler splitting as a result of more than one stellar cloud being present in the line of sight of the spectrometer.[11] The widening of some bands could be the result of different absorption points within the interstellar medium, causing a fluctuation in wavelengths of returning photons.

Another concern of the DIBs is their interaction with other forms of absorption. These forms include continuous extinction, polarization, and absorption by neutral gasses and absorption by small molecular species.[11] Continuous absorption spectroscopy does not sort absorption information based on what chemical species it was absorbed. It is up to the observer to make observations, connections, and inferences about what causes the absorption. Because there is so little known about the DIBs identities, this low selectivity in absorption could be a large reason why they are still unknown.

Although there have been pitfalls associated with the determination of DIBs, many scientist still search for their respective carriers.[9-15] Many different species that have been studied as possible carriers include: dust particles, silicates, and free molecules. However, much attention has recently turned to organic compounds that are found in space.[11-15] Organic compounds provide a range of possibilities, both large and small, and readily bind with other atoms which could lead to greater variance in DIB carrier possibilities. Specifically, large molecules like polycyclic aromatic hydrocarbons (PAH) have always been of particular interest is the determination of the chemical carriers of these bands due to their numerous degrees of freedom where energy can be stored.

Polycyclic Aromatic Hydrocarbons

PAHs are large carbon molecules where the carbon atoms are arranged in six member ring systems, resembling the shape of honeycomb.[24] These molecules are highly stable due to the arrangement of electrons around the molecule. For each carbon atom, three of the four valence electrons participate in σ-bonds with either other carbon atoms, or hydrogen atoms. The final valence electron can be found within a p-orbital, located

either above or below the plane of the molecule, where it participates in π-bonding with other electrons of this nature.[24] This delocalization of the final electron causes the electron density to be evenly dispersed across the entire molecule, which gives rise to high levels of aromaticity, or stability, found within this class of molecules. As the class becomes more concentric, aromaticity is increased. The larger, more centrally condensed molecules are considered to be supraromatics. [24]

PAHs can absorb UV radiation and emit radiation in the IR region of the electromagnetic spectrum.[11,13] As with any molecule, when a PAH absorbs UV radiation, it will only absorb discrete amounts of energy based on excitation of an electron into a specific electronic energy level. Once excited, the electron releases energy in the form of IR emission as it relaxes back to a lower energy state. Due to the various processes of transitional relaxations available to these molecules, it would be expected to see large smears as bands, as opposed to sharper peaks.[12] This aspect makes this class of molecules a definite contender in the determination of DIB carriers.

One of the first types of polycyclic aromatic hydrocarbons that was theorized to be a band carrier was a PAH with 60 carbon atoms known as fullerene. This is also commonly called a "buckyball." Although this molecule has been positively identified in space, it has not been confirmed as a DIB carrier. Buckyballs also have different characteristics than typical PAHs, such as an atypical sphere shape instead of a flat confirmation.[13] Their confirmed existence in space opens the door for other PAHs to be observed as well.

The presence of these molecules within the ISM has been theorized to be in high abundance. Within the ISM, large diffuse cloud formations can be found. These dense clouds are the ideal environment for the formation of PAHs, and are where the greatest focus of PAH observation is being aimed today. However, the larger a PAH becomes, the lower the probability that it will be detected in the ISM. The larger molecules are not as readily created, and this leads to a lower unique abundance in the ISM. Even so, PAHs, as a class, are the most common molecular type found.

Although large PAHs (C >25) have been considered as carriers, smaller PAHs are also worth considering. Small PAHs have the advantage of having a higher probability of detection in space, but the number of energetic transitions decreases as that size of the molecule decreases. The fewer transitions could lead to less diffuse absorption banding. Even though the diffuseness of a given band decreases with the reduction in size, the energetic transitions available to the molecule could still cause spreading of the bands. Carbon atoms do not bond exclusively with other carbons and hydrogens, which also provides the possibility of oxygenated or nitrogenated PAH species. Carbon only has four valence electrons, which allows an atom to have a wide variety of bonding options. Most commonly, the element binds, covalently, with other nonmetal species, such as hydrogen, nitrogen, and oxygen.

Along with closed-shell neutral PAHs, derivatives of these molecules that are ionized or radicals are becoming of particular interest. With the abundant amount of radiation in the ISM, there is the possibility that a molecule may gain or lose an electron.[11,13,14] There has been much investigation into the possibility of a PAH cation as a carrier of a DIB or the related unidentified infrared bands.[11,13] Cations are molecules

that have a positive charge due to the loss of an electron. The radiative pressure within the ISM has the capability of exciting an electron past the electron binding energy. If this were to occur, the electron would be lost by the molecular system to the environment causing a positive charge to form. Cationic and even hydrogenated, where a proton is added, PAHs should absorb at the visible level, instead at the near IR. However, their electrons are more tightly bound, once no conclusive data thus far suggests, that these are DIB carriers.[13]

Negative PAHs, or PAH anions have been proposed as DIB carriers as well.[14] Anions differ from cations in that they possess an additional electron, instead of fewer electrons. Addition of an electron to a closed shell neutral molecule is seen as highly unlikely due to the repulsive interactions between the added electron and electrons already present within the molecule. The additional electron would have to excite below the binding limit, which is energetically unfavorable, due to the ground state shells of the PAH being already filled. Closed-shell anions and their related open-shell neutral radicals are seen as a possible solution to this issue.[15] These compounds are believed to absorb in the near-IR range, which is still within the range of DIB absorption. PAH neutral radicals containing nitrogen are of particular interest within this study. This new class of PANHs has been little studied and may yet possess novel excitation properties of relevance to even the elusive DIBs.

Dipole Bound States

A Rydberg state has an electron excited into a very diffuse energy level and acts like a hydrogen atom with the entire molecule functioning as the proton. This electron is spatially distant from the actual molecule in order to avoid repulsion by other electrons

within the molecule. When it is far enough away, the molecular orbital surrounding the molecule acts as an *s*-type orbital, which is shaped like a sphere. The loosely bound electron is considered to be in a very diffuse energy state. This state exists at the continuum, where there are infinitely many energy states that exist right below the electron disassociation energy.[17]

In a dipole-bound excited state of an anion, the corresponding neutral radical has a separation of charge which creates a dipole. The positive end of the dipole attracts an electron. However due to repulsion by the electrons already present within the molecule, the electron being attracted by the system remains at a far distance from the molecule. At a far enough distance, the molecular charge is seen as diffused across the entire molecule. This behavior acts as a Rydberg atom. It has been determined that the necessary dipole moment required for an anion to sustain a dipole bound state is 1.625 D. [16,17,19] In practice it more appropriate to measure molecules that have a dipole moment of at least 2.5 D.[18] A second dipole-bound state requires at least a 9.0 D dipole moment.

It has recently been shown that some anions may possess an additional excited state besides the lone dipole-bound state. Most electronically excited states exist within the valence cloud and are not diffuse like Rydberg or dipole-bound states. In a valence state the electron is pulled closer to the molecule and actually fills the open shell.[19] The resulting molecular orbitals are not spherical around the entire molecule, but follow the pattern of standard, valence MOs around the atoms that are closest to the electronic interaction. These states can be differentiated from the dipole-bound states computationally by a steady prediction of the absorption energy as more diffuse basis sets

are employed, whereas dipole-bound states show a reduction in the absorption energy as more diffuse basis sets are employed. [19]

When the binding of electrons occurs, an anion can be produced. PAHs containing nitrogen (PANHs) are common in the creation of PAHs in laboratory conditions under the right circumstances, and should be in the ISM, as well. However, nitrogen only has five valence electrons. When participating in bonding with carbon, the final pair of nitrogen electrons left in an orbital by themselves. Hence, one less hydrogen is present in the new PANH. The subsequent chemistry and physics of a PANH is similar to its PAH counterpart, but additional charge separation is present creating an ideal circumstance for dipole-bound states to exist. The optical features of PANH anions are largely a mystery. It is believed that many of these molecules in space are frozen within ice particles. This could cause the absorption features of PANHs to be skewed. However, by analyzing these molecules computationally, more can be determined about the molecules.

Computational Details

Geometry optimizations of the neutral radicals and their corresponding anions of the different constitutional isomers of quinoline are computed using the Guassian09[40] program with the B3LYP functional and 6-31G** basis set.[42] Analysis of the relative energies and dipole moments of the different conformations of quinoline and isoquoinoline derivatives use the same methodology. All isomers whose dipole moments are greater than 2.0 D are possible dipole-bound producing anions. These B3LYP/6-31+G** optimized geometries are used in the computation of the vertical excitation energies. These computations are done by collaborators at the University of Leiden.

The reference wave function of the open-shell neutral radicals employs spin-unrestricted Hartree-Fock (UHF)[25], whereas the closed shell anions used reference wave functions involving spin-restricted Hartree-Fock (RHF).[26,27] Excited states of the different confirmations use equation of motion coupled cluster theory at the singles and doubles level (EOM-CCSD).[33-35] The cc-pVDZ, aug-cc-pVDZ, d-aug-cc-pVDZ, and t-aug-cc-pVDZ basis sets provide the varying energy differences in the vertical excitations necessary to classify states as dipole-bound.[38] Computations of the excited energy states employ the PSI4 suite of computational chemistry programs.[42]

Results and Discussion

There are fourteen isomers associated with the dehydrogenated quinoline and isoquinoline species. The parent non-dehydrogenated molecules are planar with a high level of aromaticity. However with the introduction of a nitrogen atom into the ring system, the symmetry of these formerly D_{2h} structures lowers to C_s. From this point, a hydrogen atom is removed so that the open-shell neutral radical can be formed. The removal of a hydrogen
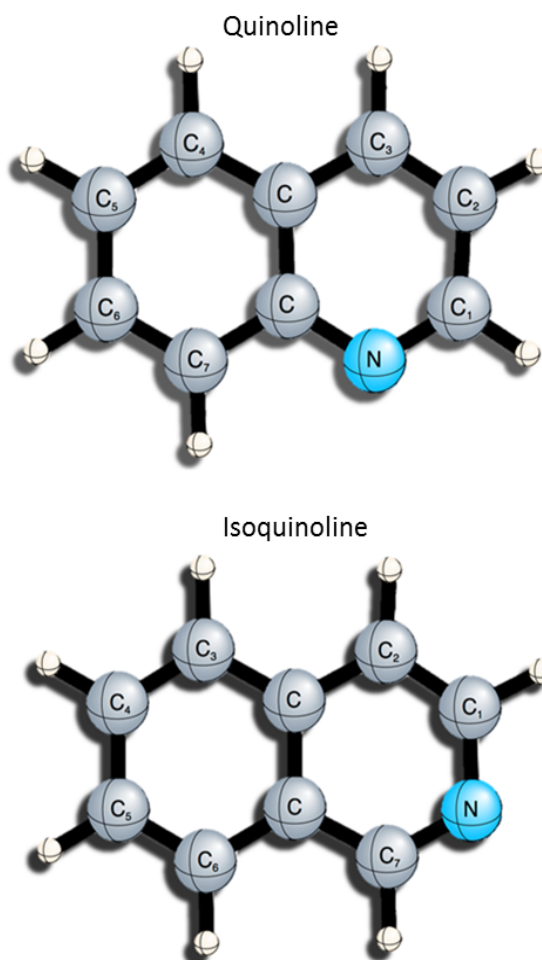

Figure 1. Molecular structures and atom numbering of quinoline (top) and isoquinoline (bottom).

atom will form a new, unique isomer. Thus, since there are two nitrogen positions and seven hydrogens for both the quinolone and isoquinoline species, the total number of isomers is fourteen.

The convention for naming is based first upon the placement of the nitrogen within the molecule. The symbol "N1" denotes the placement of the nitrogen to form quinoline, whereas "N2" represents the formation of isoquinoline as given in Fig. 1. The nomenclature then identifies each isomer based upon the associated carbon for the hydrogen that has been removed from the system to form the neutral radical. For example, a hydrogen removed from the second carbon of quinoline is called the "N1H2" isomer.

Relative Energies and Dipole Moments

Table 1. Relative energies and dipole moments of the fourteen dehydrogenated quinoline and isoquinoline structures.

Name	Anionic Relative Energies (eV)	Radical Relative Energies (eV)	Dipole Moment (D)
N1H3	0.000	0.213	1.20
N1H2	0.133	0.272	2.01
N2H6	0.151	0.322	2.99
N2H3	0.171	0.324	2.33
N2H2	0.176	0.316	2.76
N1H4	0.182	0.235	1.24
N2H4	0.221	0.304	1.73
N2H5	0.254	0.315	2.25
N1H5	0.327	0.262	1.78
N1H6	0.351	0.249	2.76
N2H7	0.436	0.000	3.19
N1H1	0.478	6.685	3.02
N1H7	0.480	0.339	3.08
N2H1	0.622	0.123	3.47

The geometry optimization of the fourteen isomers determine the relative energies and the dipole moments for each of the isomers. The relative energy for both the anionic and radical species is determined by taking the difference between the most stable isomer, denoted by the lowest energy and the energy of each successive isomer. The most stable isomer of the anionic isomers is N1H3, and the most stable of the radical isomers is N2H7, as shown in Table 1. This shows that

the most stable isomer of one form does not necessarily equate to the most stable isomer of the other form. Although N1H3 is the lowest energy isomer of the anions, its dipole moment is below 2.0 D, which means the lowest energy anionic isomer which could sustain a dipole-bound state is N1H2. There also exists a high relative-energy isomer for the radical species, the N1H1 isomer, at about 20 times higher in energy than the relative energies of the other radical anions.

The dipole moments of the fourteen isomers are computed, and it can be seen that ten of the fourteen isomers possess a dipole moment of greater than 2.0 D. The dipole moments range between 1.20 D and 3.47 D, with no isomer reaching the threshold of sustaining a second dipole-bound state, which would require a dipole moment of >9.0 D. The isomer with the lowest dipole moment (1.20 D) is N1H3, which is, again, the lowest energy isomer of the anionic species. However, no correlation was determined to exist between relative radical energy and the magnitude of the dipole moment.

Table 2. Relative energies, dipole moments and relative distances between the nitrogen atom and the dehydrogenated carbon atom for the fourteen isomers of quinoline and isoquinoline

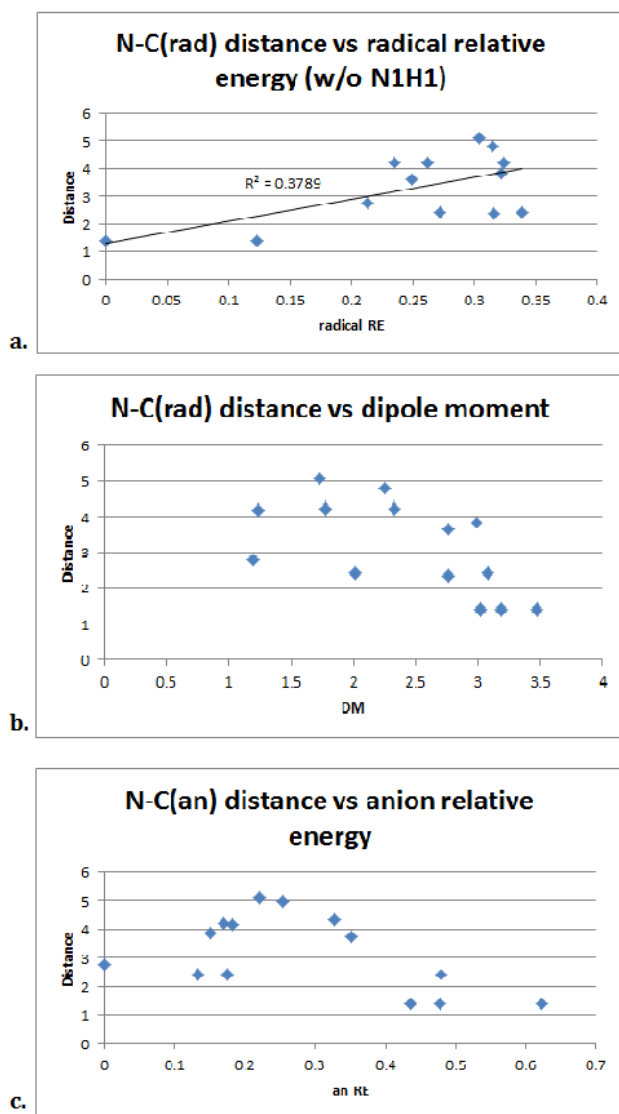| Name	Radical Relative Energies (eV)	Dipole Moment (D)	Distance b/t N and Carbon radical(radical)	Anionic Relative Energies (eV)	Distance b/t N and Carbon radical(anion)
N1H3	0.213	1.2	2.764	0	2.764
N1H2	0.272	2.01	2.411	0.133	2.411
N2H6	0.322	2.99	3.844	0.151	3.858
N2H3	0.324	2.33	4.228	0.171	4.214
N2H2	0.316	2.76	2.366	0.176	2.412
N1H4	0.235	1.24	4.202	0.182	4.175
N2H4	0.304	1.73	5.085	0.221	5.085
N2H5	0.315	2.25	4.799	0.254	4.958
N1H5	0.262	1.78	4.215	0.327	4.330
N1H6	0.249	2.76	3.616	0.351	3.743
N2H7	0	3.19	1.396	0.436	1.396
N1H1	6.685	3.02	1.413	0.478	1.413
N1H7	0.339	3.08	2.418	0.48	2.416
N2H1	0.123	3.47	1.392	0.622	1.392

Figure 2. {a.} Distance between nitrogen atom and dehydrogenated carbon atom versus radical relative energy (with the removal of N1H1 outlier). {b.} Distance between nitrogen atom and dehydrogenated carbon anion versus the dipole moment{c} Distance between nitrogen atom and dehydrogenated carbon anion versus the anionic relative energy.

The relative distances between the nitrogen atom and the dehydrogenated carbon atom were analyzed for the radical (N-C•) and anionic (N-C^{-1}) forms of each isomer. As described in Table 2, these values are compared to the relative radical and anionic energies, as well as the dipole moments for the isomers. There appears to be a loose linear correlation between the N-C• distance and the radical relative energy, shown in Fig. 2. This would imply that an increase in distance between the radical carbon and the nitrogen of quinoline or isoquinoline could lead to greater instability of the molecule. Also, the N-C^{-1} distance versus anionic relative energy as well as the N-C• distance versus dipole moment data produced distributions which resemble Gaussian/normal distributions.

By analyzing the relative energies and dipole moments of the fourteen isomers, it is possible to make inferences of possible experimental methods for the construction of PANH open-shell radicals and their corresponding closed-shell anions.

To date, there have not been any studies conducted on dipole-bound excited state anions of PANHs, only cationic PAHs. However, by having a measure of the approximate energy, as well as corresponding dipole moments of these different isomers allows for determination of the most experimentally relevant isomer. A basic experiment would consist of the formation of the radical and the anion in two separate steps. Therefore, it is necessary to analyze both relative energies for each isomer. The relative energy of the radical stage of an isomer is reflective of the initial creation of the molecule. The lower the relative energy of the radical, the lower the likelihood there is that the intended radical intermediate will degrade or unintentionally react. Whereas a low anionic relative energy is important with consideration for the analysis of these molecules; for a lower anionic relative energy correlates to a higher stability of the final dipole-bound anion. In terms of astronomical spectroscopy, a more stable anion will have a higher detection possibility due to its higher retention tie in the ISM. Henceforth, it will be necessary to look at isomers with low relative radical energy, as well as, a low anionic energy, such as N1H2, when considering future experimental methods.

Vertical Excitation Energies

Table 3. Vertical excitation energies of the ten quinoline and isoquinoline isomers with a dipole moment greater than 2.0 D.

	pVDZ	apVDZ	dapVDZ	tapVDZ	OS
N2H1	5.223	2.249	1.737	1.637	0.0019
N1H7	5.193	2.497	1.912	1.735	1.4824
N1H1	5.041	2.342	1.73	1.542	0.1151
N2H7	5.193	2.241	1.72	1.618	0.1803
N2H6	4.313	2.65	2.182	2.091	0.0379
N2H2	4.278	2.661	2.134	2.019	1.3474
N1H6	5.388	2.661	2.035	1.843	0.0064
N2H5	5.58	2.556	2.176	1.11	0.055
N2H3	5.59	2.615	2.246	1.19691	0.2544
N1H2	5.651	2.938	2.259	1.224	0.0639

The vertical excitation energies of the ten isomers with a dipole moment greater than 2.0 D are given in Table 3. A vertical excitation computes the excitation of

the excitement of an electron from the ground state to some point in the excited state, whereas an adiabatic excitation allows for the vibrational relaxation of the electron to the ground vibrational state of the excited state through the transformation of the geometry Vertical excitation is used as opposed to adiabatic excitation, due to the size of the molecules. Because quinoline and isoquinoline are larger molecules, it was necessary to fix the geometry in order to limit the computational cost. The employment of increasing spatial extent of the basis set makes it possible to better characterize the space in which the bound electron can be found. This leads to a decrease in energy as the basis set is increased. All ten anion isomers analyzed show a decrease in energy as the basis set is increased, which is significant at first, but begins to taper off at the larger basis sets. This indicates that all ten isomers will have a dipole bound excited state. Because most of the isomers experienced a less than 1 eV drop in energy going from the d-aug-cc-pVDZ to the t-aug-cc-pVDZ level, it is approximated that the energy of each isomer computed at the t-aug-cc-pVDZ is a proper approximation for the excitation energy of each isomer.
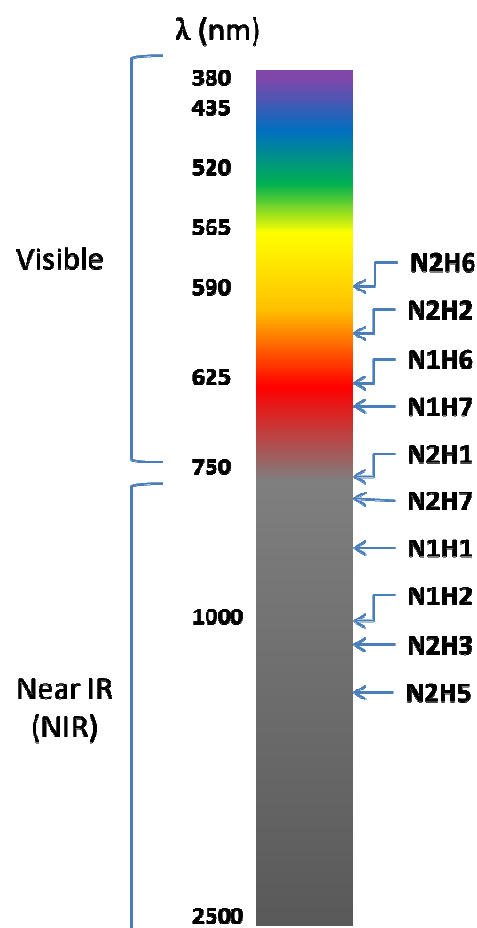

Figure 3. Relative wavelengths of the ten quinoline and isoquinoline species in the visible and near IR region of the electromagnetic spectrum

The excitation energies of the ten isomers show unique transitions which correspond to

distinct wavelengths of the electromagnetic spectrum. DIBs range from the UV to the IR

regions of the electromagnetic spectrum. However, it has been determined experimentally

that PAHs that have been ionized normally exhibit longer wavelengths falling within the

IR region.[18] The wavelengths range from the visible range to the near IR, as seen in Fig.

3. The four isomers that fall within the visible range are N2H6, N2H2, N1H6 and N1H7.

The N2H2 and N1H6 isomers are in the orange range and the N1H6 and N1H7 isomers

are within the red range. The other six isomers are found in the near IR region of the

electromagnetic spectrum. They appear in the following order according to increasing

wavelength: N2H1, N2H7, N1H1, N1H2, N2H3, and N2H5. The wavelengths of the

isomers produced through computation follow with the trend of falling farther to the right

of the DIB range.

The oscillator strength for each isomer is a byproduct of the excited state

computation. The oscillator strength is a measure of the absorption probability of an

excitation. It is proportional to the wave function of both the ground state isomer and the

wave function of the excited state isomer ($f \propto <\psi_n | \mu | \psi_m>$). If the wave functions

for the ground and excited states of a molecule are similar, there will be more overlap in

their Moors potential. This leads to a higher chance that an excitation of an electron from

the ground state into the excited state, which is indicated by a high oscillator strength.

There are two anions with notably high oscillator strengths, as can be seen in Table 3.

These are N2H2 and N1H7. The oscillator strengths for these isomers are, on average,

twenty times greater than that of any other isomer. This reflects the occurrence of a very

strong transition in both cases. The large transition is indicative of a large absorption

potential, which is analyzed through spectroscopy through the examination of peak

height. A high oscillator strength becomes significant when there is a large amount of thermal energy allotted a molecule.

<u>Relative Abundances</u>

Table 4. Relative abundances of the ten quinoline and isoquinolie isomers in different temperature environments

	tapVDZ (eV)	10 K Abs	100 K Abs	500 K Abs	1000 K Abs	5000 K Abs	10 scale to N1H2	100 scale to N1H2	500 sale to N2H2	1000 scale to N2H2	5000 scale to N2H2
N2H1	1.637	6.8E-250	4.31E-28	2.24E-08	6.52E-06	0.000611	1.067E-248	6.74E-27	4.47E-08	7.94E-06	0.00050044
N1H7	1.735	2E-175	4.82E-18	0.000471	0.026434	0.662529	3.055E-174	7.54E-17	0.000941	0.032182	0.5428713
N1H1	1.542	1.5E-175	4.72E-19	3.83E-05	0.002101	0.051681	2.416E-174	7.38E-18	7.66E-05	0.002557	0.04234701
N2H7	1.618	3.6E-154	9.67E-17	0.000159	0.005357	0.089245	5.561E-153	1.51E-15	0.000318	0.006522	0.07312692
N2H6	2.091	3.21E-11	0.004693	0.024958	0.030756	0.036349	5.0296E-10	0.073448	0.049842	0.037443	0.02978436
N2H2	2.019	4.32E-22	0.009551	0.500735	0.821396	1.220416	6.7544E-21	0.14947	1	1	1
N1H6	1.843	8.7E-113	6.6E-14	4.06E-05	0.00051	0.003859	1.36E-111	1.03E-12	8.11E-05	0.000621	0.00316182
N2H5	1.11	5.74E-63	4.39E-08	0.003317	0.013507	0.041534	8.9849E-62	6.87E-07	0.006624	0.016444	0.03403238
N2H3	1.19691	1.8E-20	0.003093	0.105316	0.163684	0.232924	2.8109E-19	0.048406	0.210322	0.199275	0.19085654
N1H2	1.224	0.0639	0.0639	0.0639	0.0639	0.0639	1	1	0.127612	0.077794	0.05235922

The relative abundance of the ten quinoline and isoquinoline isomers are analyzed for different temperature environments in space. The lower temperatures (10 K and 100 K) are scaled to the isomer N1H2, which has the greatest abundance at these temperatures, whereas the higher temperatures (500 K, 1000K, and 5000 K) were scaled to N2H2 for the same reason. It can be seen that in the lower temperatures, there is near zero abundance for all isomers except N1H2. This isomer is also the lowest anionic energy isomer with a large dipole, which implies that at lower astronomical temperatures, like those that are found in the diffuse interstellar medium, only the lowest energy isomer will prevail. However, as the energy (or temperature) is increased, the spectra become more complicated.

With an increase in temperature, the relative abundances for different isomers begin to grow, specifically N2H2. At a temperature of 163 K, the relative abundance of N2H2 equals that of N1H2. If the temperature is increased past this point, the relative abundance of N2H2 surpasses that of the lowest energy isomer. The N2H2 isomer has a high

oscillator strength, which is what allows the intensity to increase so rapidly when introduced to larger amounts of thermal energy. This is also seen for N1H7, which has the highest oscillator strength and becomes the second most abundant isomer at higher temperature, such as 5000 K. At lower temperatures where there is little radiative energy, the spectra are dependent on stability. However, at higher temperatures (above 163 K) the appearance of isomeric species in spectra is more dependent upon the specific oscillator strength of an isomer. Also, it can be concluded that an increase in temperature will lead to the formation of more isomers which can be detected.

The analysis of relative abundances for different temperature profiles in various interstellar environments of quinoline and isoquinoline allows for the investigation of the characteristics of this class of molecules in the ISM. It has already been stated that the lower temperatures are representative of diffuse interstellar regions, but there has not yet been discussion of the environments with warmer temperatures. The cosmic region in which the spectra goes from being dominated by the most energetically favored isomer to the isomer with the greatest oscillator strength is within the Cold Neutral Medium of the ISM. The regions which contain the highest analyzed temperature is the Warm Neutral Medium or circumstellar envelopes where temperatures can reach and even exceed 5000 K. It is within these regions where the oscillator strength of an isomer has a greater effect on relative abundance. The distribution of this class of molecules across different regions of space allows for the comparison of absorption spectra for a particular isomer, which may be linked to the DIBs.

There are also considerations for experimental analysis which need to be made. For astronomical spectroscopy it is important that the molecule being analyzed is in great enough

abundance that it is able to be detected. Because the space in which analysis is occurring is so large, and the size of the molecules is so small, in order for a detector to sense it, it is necessary to have a significant amount of the molecule being analyzed. This would suggest that the projected spectroscopic results for the region for which we are concerned (ISM), would show a spectrum for the most abundant isomer within this temperature range, which is N1H2. However, this is not to say that other isomers in this region of space would be unfeasible. There are many other factors which influence formation of molecules in space, so it is not impossible for other isomers to form, only highly unlikely.
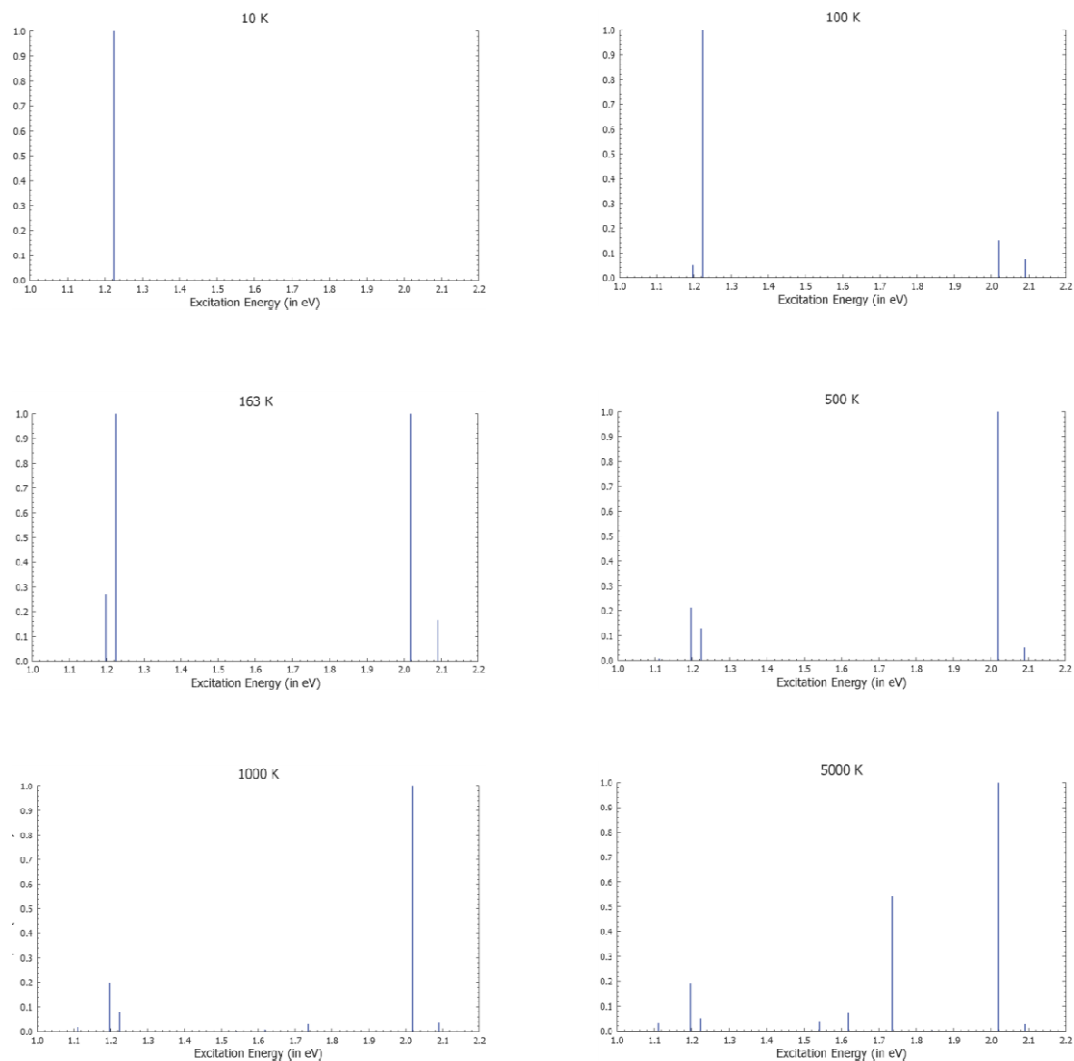

Figure 4. Relative abundance spectra for the ten isomers at different astronomical temperatures.

Conclusions

Of the 14 total dehydrogenated quinoline and isoquinoline derivative radicals, 10 possess dipole moments greater than 2.0 D. The lowest energy isomer, N1H3, has a dipole moment of only 1.2 D precluding a dipole-bound state in the anion. N1H2 is the lowest energy isomer with a conceivable dipole-bound state. The 10 remaining anions should possess lone dipole-bound singlet excited states. Even though the relative stabilities are close, each isomer excites at unique and distinguishable wavelengths with unique intensities. Different astronomical environments will display unique absorption spectra for this family of anions due to difference in ambient temperature. The diffuse interstellar medium will only absorb for the most stable anion, but at temperatures above ~160K, the spectra become more complicated.

References

1. Allamandola, L. J.; Tielens, G. G. M.; Barker, J. R. Interstellar polycyclic aromatic hydrocarbons - The infrared emission bands, the excitation/emission mechanism, and the astrophysical implications. *Astrophysical Journal, Supplement Series; (USA)* **1989**, 733.

2. Bakes, E. L. O.; Tielens, A. G. G. M.; Bauschlicher, C. W. Theoretical Modeling of Infrared Emission from Neutral and Charged Polycyclic Aromatic Hydrocarbons. i. *Astrophys. J.* **2001**, *556*, 501-514.

3. Bauschlicher, C. W.; Jr.; Peeters, E.; Allamandola, L. J. The Infrared Spectra of Very Large Irregular Polycyclic Aromatic Hydrocarbons (PAHs): Observational Probes of Astronomical PAH Geometry, Size and Charge. **2009**.

4. Cook, D. J.; Saykally, R. J. Simulated infrared emission spectra of highly excited polyatomic molecules: a detailed model of the PAH-UIR hypothesis. *Astrophys. J.* **1998***, 493 Pt 1*, 793-802.

5. Crawford, M. K.; Tielens, A. G. G. M.; Allamandola, L. J. Ionized polycyclic aromatic hydrocarbons and the diffuse interstellar bands. *Astrophys. J. , Lett. Ed. ; (United States)* **1985**, L45.

6. Escure, C.; Leininger, T.; Lepetit, B. Ab initio study of valence and Rydberg states of CH3Br. *J. Chem. Phys.* **2009***, 130*, 244306.

7. Fortenberry, R. C.; Crawford, T. D. Singlet Excited States of Silicon-Containing Anions Relevant to Interstellar Chemistry. *JOURNAL OF PHYSICAL CHEMISTRY A* **2011***, 115*, 8119-8124.

8. Fortenberry, R. C. Theoretical Electronic and Rovibrational Studies for Anions of Interest to the DIBs. **2013**.

9. Fortenberry, R. C. Singlet excited states of anions with higher main group elements. *Mol. Phys.* **2013***, 111*, 3265-3275.

10. Fortenberry, R. C.; Crawford, T. D. Theoretical prediction of new dipole-bound singlet states for anions of interstellar interest. *J. Chem. Phys.* **2011***, 134*, 154304.

11. Grein, F. The ClO4 radical: a theoretical study on ground and excited states. *Mol. Phys.* **2009***, 107*, 2005-2013.

12. Hammer, N. I.; Hinde, R. J.; Compton, R. N.; Diri, K.; Jordan, K. D.; Radisic, D.; Stokes, S. T.; Bowen, K. H. Dipole-bound anions of highly polar molecules: Ethylene carbonate and vinylene carbonate. *J. Chem. Phys.* **2004***, 120*, 685-690.

13. Herbig, G. H. The Diffuse Interstellar Bands. *Annual Review of Astronomy & Astrophysics* **1995***, 33*, 19.

14. Kaneda, H.; Onaka, T.; Sakon, I.; Kitayama, T.; Okada, Y.; Suzuki, T. Properties of polycyclic aromatic hydrocarbons in local elliptical galaxies revealed by the Infrared Spectrograph on Spitzer. **2008**.

15. Li, A.; Draine, B. T. Infrared Emission from Interstellar Dust. II. The Diffuse Interstellar Medium. **2000**.

16. Li, A.; Draine, B. T. Infrared Emission from Interstellar Dust. II. The Diffuse Interstellar Medium. **2000**.

17. Mattioda, A. L.; Allamandola, L. J.; Hudgins, D. M. The Ultraviolet to Near-Infrared Optical Properties of Polycyclic Aromatic Hydrocarbons: a Semiempirical Model. *Astrophys. J.* **2005***, 629*, 1183-1187.

18. Mattioda, A. L.; Hudgins, D. M.; Allamandola, L. J. EXPERIMENTAL NEAR-INFRARED SPECTROSCOPY OF POLYCYCLIC AROMATIC HYDROCARBONS BETWEEN 0.7 AND 2.5 mum. *Astrophys. J.* **2005***, 629*, 1188-1210.

19. Page, V. L.; Snow, T. P.; Bierbaum, V. M. Hydrogenation and Charge States of Polycyclic Aromatic Hydrocarbons in Diffuse Clouds. II. Results. *Astrophys. J.* **2003***, 584*, 316.

20. Petrie, S.; Stranger, R.; Duley, W. W. Locally Aromatic Polycyclic Hydrocarbons as Potential Carriers of Infrared Emission Features. *Astrophys. J.* **2003***, 594*, 869-873.

21. Salama, F.; Galazutdinov, G. A.; Krelowski, J.; Biennier, L.; Beletsky, Y.; Song, I. O. Polycyclic Aromatic Hydrocarbons and the Diffuse Interstellar Bands: a Survey. *Astrophys. J.* **2011***, 728*.

22. Sarre, P. J. The diffuse interstellar bands: a dipole–bound state hypothesis. *Monthly Notices of the Royal Astronomical Society* **2000***, 313*, L14.

23. Wakelam, V.; Herbst, E. Polycylcic Aromatic Hydrocarbons (PAH's) in dense cloud chemistry. **2008**.

24. Tielens, A. *The Physics and Chemistry of the Interstellar Medium,* 1st ed.; Cambridge:

25. UniteScheiner, A. C.; Scuseria, G. E.; Rice, J. E.; Lee, T. J.; Schaefer, H. F., III Analytic evaluation of energy gradients for the single and double excitation coupled cluster (CCSD) wave function: Theory and application. *J. Chem. Phys*. 1987, 87, 5361–5373.d Kingdom, **2005**.

26. Gauss, J.; Stanton, J. F.; Bartlett, R. J. Coupled-Cluster Open-Shell Analytical Gradients - Implementation of the Direct-Product Decomposition Approach in Energy Gradient Calculations. *J. Chem. Phys.* **1991**, 95, 2623–2638.

27. Watts, J. D.; Gauss, J.; Bartlett, R. J. Open-Shell Analytic Energy Gradients for the Triple- Excitation Many Body, Coupled-Cluster Methods - MBPT(4), CCSD+T(CCSD), CCSD(T), and QCISD(T). *Chem. Phys.* Lett. **1992**, 200, 1–7.

28. Raghavachari, K.; Trucks., G. W.; Pople, J. A.; Head-Gordon, M. A 5th Order Perturbation Comparison of Electron Correlation Theories. *Chem. Phys. Lett*. 1989, 157, 479–483.

29. Dunning, T. H. Gaussian Basis Sets for Use in Correlated Molecular Calculations. 1: The Atoms Boron through Neon and Hydrogen. *J. Chem. Phys*. 1989, 90, 1007–1023.

30. Peterson, K. A.; Dunning, T. H. Benchmark Calculations with the Correlated Molecular Wave-Functions. 7: Energy and Structure of the HF Dimer. *J. Chem. Phys*. 1995, 102, 2032–2041.

31. Dunning, T. H.; Peterson, K. A.; Wilson, A. K. Gaussian basis sets for use in correlated molecular calculations. X. The atoms aluminum through argon revisited. *J. Chem. Phys*. 2001, 114, 9244–9253.

33 Stanton, J. F.; Bartlett, R. J. The Equation of Motion Coupled- Cluster Method - A Systematic Biorthogonal Approach to Molecular Excitation Energies, Transition- Probabilities, and Excited-State Properties. *J. Chem. Phys*. 1993, 98, 7029–7039.

34 Monkhorst, H. J. Calculation of properties with the coupledcluster method. Int. J. Quantum Chem. Symp. 1977, 11, 421–432.

35 Mukherjee, D.; Mukherjee, P. K. A response-function approach to the direct calculation of the transition-energy in a multiple-cluster expansion formalism. Chem. Phys. 1979, 39, 325–335.

36 Koch, H.; Christiansen, O.; Jørgensen, P.; de Mer_as, A. M. S.; Helgaker, T. The CC3 model: An iterative coupled cluster approach including connected triples. J. Chem. Phys. 1997, 106, 1808–1818.

37 Christiansen, O.; Koch, H.; Jørgensen, P. Response functions in the CC3 iterative triple excitation model. J. Chem. Phys. 1995, 103, 7429–7441.

38 Hald, K.; Jørgensen, P.; Christiansen, O.; Koch, H. Implementation of electronic ground states and singlet and triplet excitation energies in coupled cluster theory with approximate triples corrections. J. Chem. Phys. 2002, 116, 5963–5970.

39 Mach, T. J.; King, R. A.; Crawford, T. D. A Coupled Cluster Benchmark Study of the Electronic Spectrum of the Allyl Radical. J. Phys. Chem. A. 2010, 114, 8852–8857.

40 Fortenberry, R. C.; King, R. A.; Stanton, J. F.; Crawford, T. D. A Benchmark Study of the Vertical Electronic Spectra of the Linear Chain Radicals C2H and C4H. J. Chem. Phys. 2010, 132, 144303

41. Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**

42**.** P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, *J. Phys.Chem.* **98**, 11623 (1994).

Appendix

<u>Appendix A:</u> Bond angles, bond lengths and isomeric structures of specific quinolone and isoquinoline isomers.
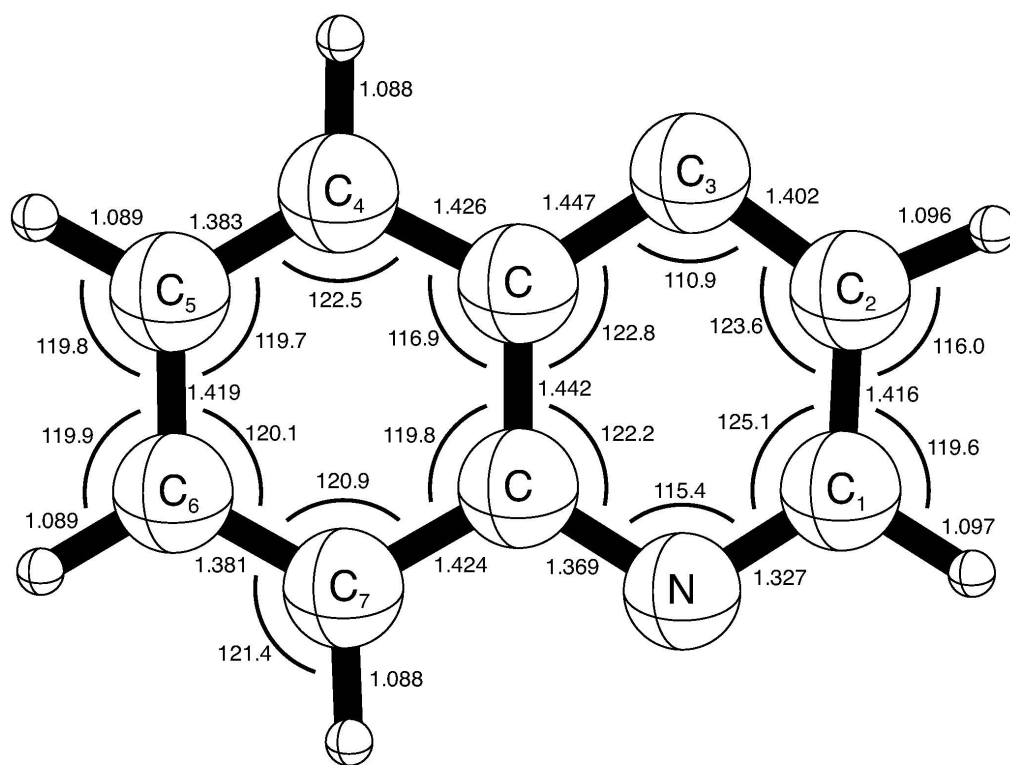

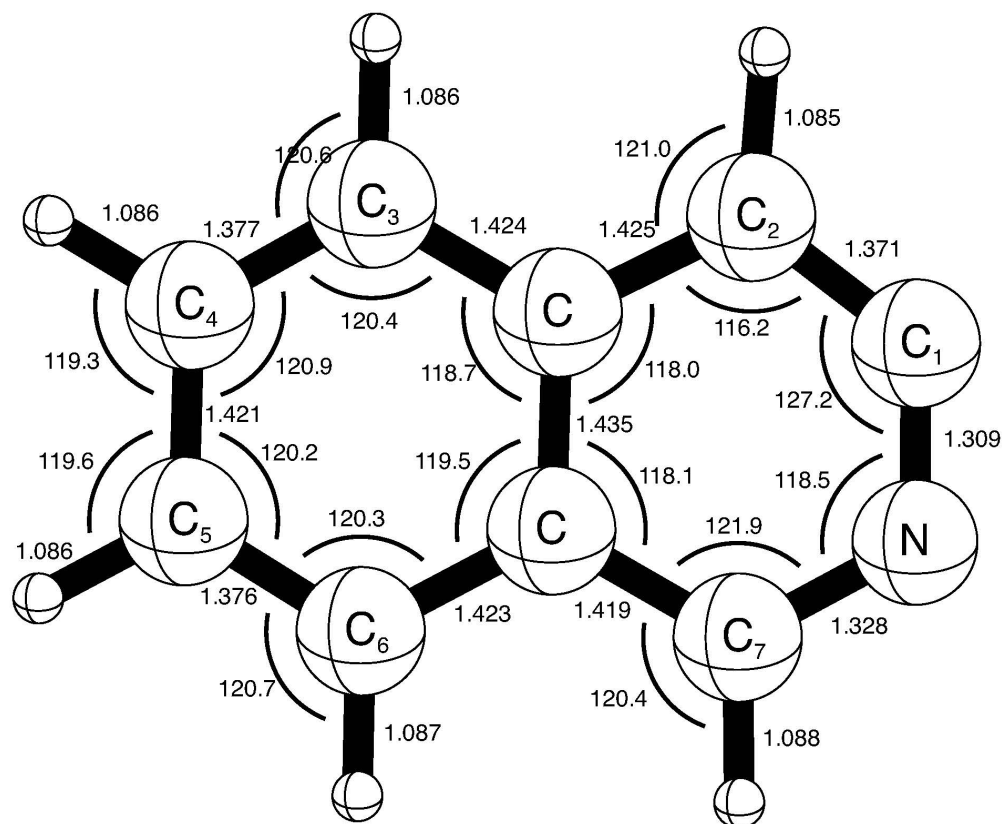**Figure 1A. N1H3 anion geometrical parameters**

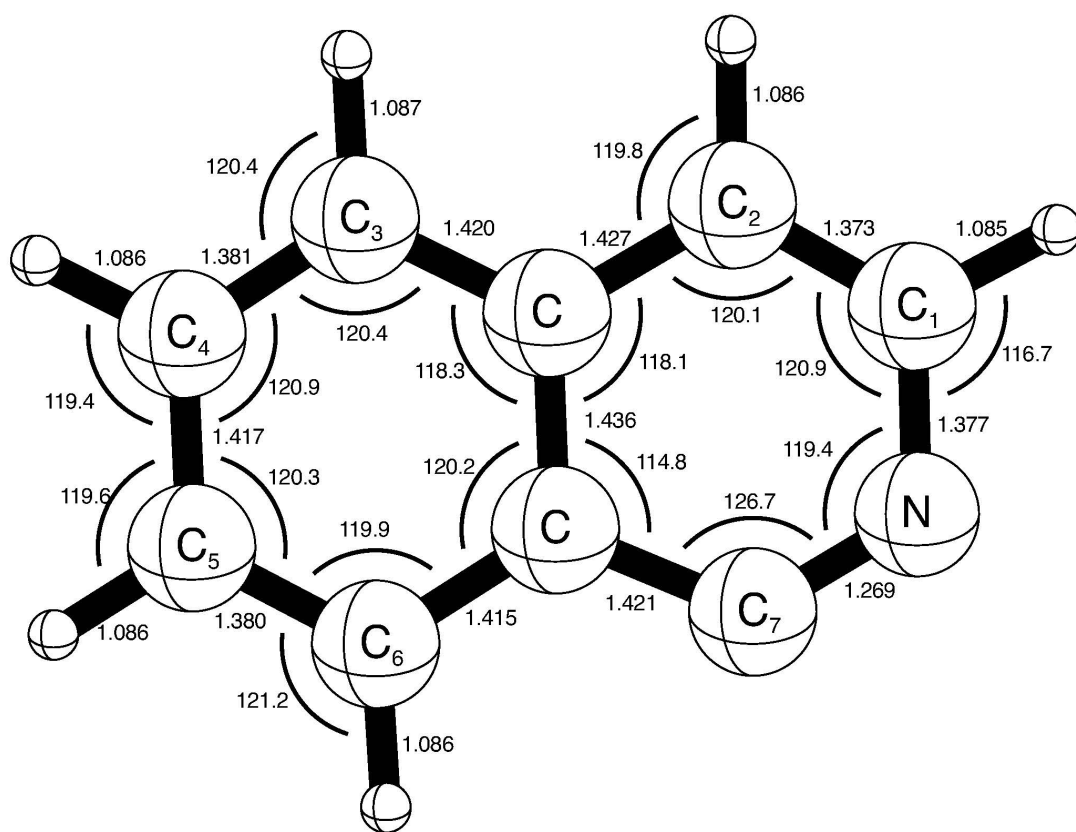**Figure 2A. N1H2 anion geometrical parameters**

Figure 3A. N2H1 radical geometrical parameters

Figure 4A. N2H7 radical geometrical parameters