Density Functional Theory Study of the Isomers of C_6N

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Using large-scale basis sets and the B3LYP hybrid functional, the structures of linear and cyclic isomers of C_6N have been studied. The lowest energy conformer is the linear, nitrogen-terminated structure in the $^2\Pi$ electronic state. Surprisingly, the next lowest-lying isomer is a cyclic structure consisting of a cyclopropane ring and a C_3N chain. The ionization energy, electron affinity, and equilibrium dipole moment for the linear ground state are 9.07 eV, 3.55 eV, and 0.69 D, respectively. Harmonic frequencies were determined for the lowest energy structures. In the linear ground-state clusters, the bonding tends toward cumulenic, rather than polyacetylenic as in the odd-carbon molecules of similar length.

Introduction

Small carbon clusters, including those terminated by heteroatoms, have been of theoretical and experimental interest for many years.[1−7] This focus resulted from astrophysical and materials science developments. Predictions of interstellar clusters with as many as eleven carbon atoms have been reported.[8] There remain unidentified interstellar spectral lines whose origin may be in clusters such as C_nN, C_nS and C_nH or their respective ions.[9] In materials science, new methods of deposition involving clusters and interest in self-assembly and surface-cluster interactions require detailed knowledge of the geometry and electronic structure of a range of carbon containing molecules. Computational studies provide critical information for the evolution of these two important research fields.

We have recently completed surveys of the geometries and electronic structures of C_nS (and its anion and cation)[10] for $n < 17$, as well C_nN and C_nN_2, where $n < 11$, using density functional theory.[11] In the latter, the focus was on the lowest energy conformer and the reported results, whereas covering a range of clusters, included mostly the nitrogen-terminated linear forms. For the C_nN series of clusters, experimental structures[12−14] are available for C_3N and C_5N. Computational results have been published for those clusters[15−17] as well as C_2N and C_7N.[3] There have been few studies of the even carbon C_nN clusters. The $n = 2$ case was cited above. More recently, a very complete study of the C_4N cluster was reported[18] and included thirteen isomers, linear, cyclic and branched, as well as transition states connecting these stable molecules. Cyclic isomers were shown to lie relatively low in energy and to be kinetically stable.

Conceptually, linear C_nN clusters with terminal nitrogen atoms may be thought of as resulting from a mixture of two types of resonance structures. The first involves, beginning with the carbon−nitrogen bond, alternating single and triple bonds, whereas the second structure is cumulenic in nature. For clusters with fewer than six carbon atoms, calculations[11] showed that the odd-carbon clusters are polyacetylenic and the even-carbon clusters tended toward cumulenic bonding, with compressed single bonds and extended triple bonds. For clusters with seven or more carbon atoms, the structural difference between the odd- and even-carbon clusters was progressively lost. The $n = 6$ cluster was the structural transition point. Other researchers[3] have noted that the ground electronic state changes from $^2\Sigma$ to $^2\Pi$ for clusters with seven carbon atoms; however, the ground state of the six-carbon cluster has not been studied. Given the differences between even- and odd-carbon clusters, and the possibility of low-lying cyclic structures versus the general observation that terminal heteroatoms stabilize linear carbon chains, further computational effort, especially for even-numbered carbon clusters, is clearly justified. Here, we present the results of a detailed study of the C_6N clusters, for which no previous data, computational or experimental, has been reported. We have included all linear and many cyclic structures calculated using density functional theory and a range of basis sets.

Computational Details

All calculations were carried out using the GAUSSIAN 98 package of programs.[19] Structures were fully optimized, in the absence of symmetry constraints, using UHF and B3LYP levels of theory. Double- and triple-ζ basis sets, including 6-311G**, cc-pVDZ, cc-pVTZ, and aug-cc-pVTZ, were employed in this study. Final structures, dipole moments and energies for linear and low-lying cyclic clusters were obtained using the largest basis set, i.e., at the B3LYP/aug-cc-pVTZ level of theory. We have shown in previous work that the B3LYP/cc-pVTZ level of calculation produces good agreement with available experimental results for bond lengths; to within ∼0.005 Å for carbon−nitrogen clusters.[10,11] A more rigorous comparison is presented in the discussion section of this report. Frequencies were calculated from structures fully optimized with the smaller 6-311G** basis set. Transition states were located using the QST2 method with the PM3 formalism. The reactant/product channels connected by the transition were verified by intrinsic reaction coordinate (IRC) calculations.

Results

In this work, we continue with the DFT approach of our earlier studies, but also examine the accuracy of the 6-311G** basis set and, for the select group of lowest energy structures, include diffuse functions by using the more extensive aug-cc-pVTZ basis set. The lowest energy isomer is the linear, nitrogen-terminated chain, which lies approximately 1.2 eV below the isonitrile isomer. The symmetric C−C−C−N−C−C−C isomer

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TABLE 1: Absolute Energies at Various Levels of Theory in Hartrees[a]

structure	ROHF/6-311G**	UHF/6-311G**	B3LYP/cc-pVDZ	B3LYP/6-311G**	B3LYP/aug-cc-pVTZ
CCCCCCN	−281.421 155	−281.483 252	−283.116 948	−283.166 243	−283.198 503 (0.00)
CCCCCNC	−281.399 741	−281.427 604	−283.077 847	−283.126 162	−283.159 283 (1.07)
CCCNCCC	−281.328 336	−281.351 822	−283.028 937	−283.076 852	−283.110 005 (2.41)
CCCCNCC	−281.281 661	−281.339 789	−282.973 131	−283.061 263	−283.094 353 (2.84)
structure	designation		B3LYP/cc-pVDZ	B3LYP/6-311G**	B3LYP/aug-cc-pVTZ
c-(CCC)-CCCN	I		−283.094 602	−283.143 316	−283.176 739 (0.59)
c-(CCC)-CCNC	II		−283.056 005	−283.104 079	−283.138 388 (1.64)
bicyc-CCCCCCN	III		−283.020 414	−283.061 287	−283.094 792 (2.83)
c-CCCCCCN	IV		−282.986 213	−283.034 265	−283.067 442 (3.57)

[a] Relative energies in eV are shown in parentheses for the highest level calculation.

TABLE 2: Bond Lengths for All Linear Clusters (at the B3LYP/aug-cc-pVTZ and *B3LYP/cc-pVDZ* levels of theory)

cluster	bond lengths, Å
C−C−C−C−C−C−N	1.3018, 1.2680, 1.3054, 1.2347, 1.3456, 1.1632
	1.3158, 1.2806, 1.3161, 1.2479, 1.3548, 1.1754
C−C−C−C−C−N−C	1.2995, 1.2695, 1.3048, 1.2331, 1.2792, 1.1901
	1.3138, 1.2817, 1.3155, 1.2460, 1.2869, 1.2036
C−C−C−C−N−C−C	1.2934, 1.2801, 1.2783, 1.2057, 1.2398, 1.2883
	1.3062, 1.3001, 1.2819, 1.2188, 1.2667, 1.2373
C−C−C−N−C−C−C	1.2893, 1.2751, 1.2225, 1.2225, 1.2751, 1.2893
	1.3040, 1.2868, 1.2311, 1.2311, 1.2868, 1.3040

TABLE 3: Bond Lengths, Ionization Energies and Electron Affinities (B3LYP/aug-cc-pVTZ level of theory) for the Lowest Energy Cluster

cluster ion	total energy, au	IE and EA, eV
C−C−C−C−C−C−N$^+$	−282.865026	(vertical) 9.09
C−C−C−C−C−C−N$^+$ ($^1\Sigma$)	−282.865846	(adiabatic) 9.07
C−C−C−C−C−C−N$^-$	−283.325679	(vertical) 3.47
C−C−C−C−C−C−N$^-$ ($^3\Sigma$)	−283.328670	(adiabatic) 3.55
C−C−C−C−C−C−N	−283.198503	
C−C−C−C−C−C−N$^+$		
C−C−C−C−C−C−N$^-$		

Bond lengths, Å
1.3191, 1.2507, 1.3155, 1.2269, 1.3468, 1.1620
1.2768, 1.3050, 1.2823, 1.2647, 1.3297, 1.1785

lies approximately the same energy above the isonitrile form. The ground-state molecular orbital configuration for the lowest energy isomer is (core)^{14} $(8\sigma)^2$ $(9\sigma)^2$ $(10\sigma)^2$ $(11\sigma)^2$ $(12\sigma)^2$ $(13\sigma)^2$ $(1\pi)^4$ $(14\sigma)^2$ $(2\pi)^4$ $(3\pi)^4$ $(15\sigma)^2$ (4π) and the ground electronic state is $^2\Pi$,_as was observed for the C_4N cluster.[18]

The ground electronic state of all of the linear isomers is $^2\Pi$ and the calculated energies are shown in Table 1. The $\langle S^2 \rangle$ value for all neutral, ground-state structures reported in this study, linear or cyclic, was 0.75, as expected for a doublet electronic state. Table 2 presents the bond lengths for the linear isomers. Results from lower level calculations are also included. As the position of the heteroatom is moved toward the center of the molecule, the resulting cluster becomes increasingly more cumulenic and the energy increases. An estimate of the errors in the calculated geometries may be made in the now standard manner. We have calculated the equilibrium geometries for HCN and NCCCH, for which experimental structures are well-known. Calculations with the cc-pVDZ basis set, for these clusters, overestimate the −C≡N− bond lengths by 0.0056 Å, the −C≡C− bond lengths by 0.0084 Å and give essentially exact agreement for −C−C− bond lengths. Calculations using the 6-311G** and aug-cc-pVTZ basis sets underestimate these bond lengths for the same molecules. In the case of the augmented basis set, the errors are 0.0064, 0.0052, and 0.0080 Å, respectively. These differences are consistent in magnitude with those reported for CCSD(T) calculations involving other, odd-carbon C−N clusters using large basis sets. The bond lengths provided in Table 2 are not corrected for these estimated errors.

DFT is known as a "ground state theory", because there is no practical computational scheme to extract excited-state information from the ground-state density.[20] Recent work has been directed toward the prediction of excitation energies. Time-dependent DFT is especially promising, but practical applications at the moment are only available for closed shell systems. The only pragmatic approach to excited states using DFT is to set up the corresponding Kohn−Sham determinants and calculate the energy differences between them. This is the approach we have taken with the implicit assumption, of uncertain validity, that the excited state may be written as a single determinant. The energy difference between the lowest such excited state and the ground state for the lowest energy isomer has been obtained. The excitation energy, to the (core)^{14} $(8\sigma)^2$ $(9\sigma)^2$ $(10\sigma)^2$ $(11\sigma)^2$ $(12\sigma)^2$ $(13\sigma)^2$ $(1\pi)^4$ $(14\sigma)^2$ $(2\pi)^4$ $(3\pi)^4$ (15σ) (16σ) (4π)**,** $^2\Pi$ state is 1.71 and 1.73 eV at the B3LYP/6-311G** and B3LYP/aug-cc-pVTZ levels of theory, respectively. This excitation energy is greater than the value of 0.062 eV (500 cm^{-1}) reported for the C_5N cluster using the CCSD(T)/cc-pVTZ level of theory;[17] however, our earlier work has indicated that the odd- and even-carbon series of clusters do not necessarily fit the same trend, the nature of the lowest excited electronic state is not the same in the two cases and we have made a significant assumption in arriving at our estimate.

The C−C−C−C−C−C−N ionization energy and electron affinity were calculated at the highest level of theory. The results for the ion bond lengths and (vertical and adiabatic) energy differences are shown in Table 3. The differences between the adiabatic and vertical parameters are quite small, reflective of the fact that the geometry in both the neutral and ionic states is linear. In comparison to the neutral cluster, the cation becomes more polyacetylenic and the anion, more cumulenic. In the former, the nominal triple bonds are shortened and the single bonds lengthened, whereas the opposite effect is observed in the anion. The changes in bond lengths are small for the cation, but dramatically larger for the anion. The effective change in geometry for the anion should be very evident in any photoelectron spectroscopy studies. The calculated harmonic frequencies for the ions are shown in Table 4.

The harmonic frequencies and IR intensities for all of the neutral, linear clusters are also contained in Table 4, along with the dipole moments. The clusters may be uniquely identified by their spectra. The most intense IR bands, at approximately 2000 cm^{-1}, result from compression or extension of alternate bonds. The B3LYP technique often results in overestimates of the frequencies, especially for high-frequency vibrations such as the stretching modes at 2000 cm^{-1}. To provide guidance on the accuracy of the values reported in Table 4, we have calculated the frequencies for the analogous C_3S cluster, for which experimental values[21] are known, $v_1 = 2046.2$ cm^{-1}, $v_2 = 1533.2$ cm^{-1} and $v_3 = 725.6$ cm^{-1}. Our calculated frequencies

TABLE 4: Frequencies, cm^{-1} *(IR intensities)* and Dipole Moments, D, for the Linear Clusters and Cluster Ions at the B3LYP/6-311G Level of Theory**

C−C−C−C−C−C−N	C−C−C−C−C−N−C	C−C−C−C−N−C−C	C−C−C−N−C−C−C	C−C−C−C−C−C−N$^+$	C−C−C−C−C−C−N$^-$
80 *(10)*	81 *(9)*	80 *(15)*	69 *(12)*	73 *(4)*	84 *(12)*
80 *(10)*	82 *(9)*	80 *(15)*	69 *(12)*	74 *(4)*	84. *(12)*
183 *(1)*	172 *(0)*	172 *(0)*	161 *(0)*	157 *(0.2)*	196 *(10*
184 *(0)*	182 *(1)*	180 *(0)*	180 *(0)*	159 *(0)*	197 *(3)*
329 *(5)*	283 *(4)*	272 *(5)*	223 *(7)*	300 *(3)*	402 *(5)*
352 *(2)*	340 *(1)*	324 *(1)*	274 *(3)*	300 *(4)*	406 *(4)*
458 *(2)*	358 *(0)*	369 *(1)*	343 *(0)*	530 *(2)*	517 *(4)*
553 *(4)*	398 *(0)*	409 *(0)*	361 *(0)*	530 *(2)*	517 *(4)*
557 *(2)*	491 *(1)*	488 *(0)*	521 *(0)*	561 *(21)*	558 *(4)*
558 *(2)*	573 *(2)*	549 *(1)*	534 *(16)*	684 *(4)*	624 *(2)*
722 *(1)*	601 *(6)*	599 *(0)*	608 *(0)*	684 *(4)*	624 *(4)*
1068 *(9)*	1111 *(7)*	1103 *(70)*	1065 *(20)*	1072 *(51)*	1067 *(10)*
1559 *(120)*	1578 *(90)*	1559 *(0)*	1609 *(0)*	1545 *(164)*	1613 *(20)*
1962 *(730)*	1910 *(975)*	1858 *(3300)*	1849 *(1500)*	2149 *(615)*	1870 *(23)*
2097 *(8)*	2069 *(2)*	2086 *(371)*	1974 *(2)*	2273 *(2345)*	1981 *(200)*
2249 *(65)*	2141 *(1)*	2134 *(20)*	2165 (23)	2317 *(730)*	2123 *(544)*
0.69D	2.31D	0.03D	0.00D	2.62D	3.11D

for this cluster are 2104, 1567, and 739 cm^{-1}, respectively, using the 6-311G** basis set. As expected, the discrepancy increases with increasing frequency, so that for the most intense stretching mode, an error of 58 cm^{-1} is observed. We expect, therefore, that the values reported here have uncertainties of similar magnitude. The dipole moments for the lowest energy linear isomers, C−C−C−C−C−C−N and C−C−C−C−C−N−C are sufficiently large so as to indicate that the C_6N clusters would be detected in laboratory experiments or in the interstellar medium.

Recent computational work has shown that cyclic forms of the C_4N cluster lie close in energy to the linear ground state.[18] These clusters have a cyclopropane ring with a −C≡N or −N≡C substituent. An analogous cyclic structure, *c*-(C−C−C)-C−C−C−C−H has been predicted to lie near the energy of the linear ground state for the C_7H cluster, which is isoelectronic with C_6N.[4] To test the possibility of low-lying cyclic structures for these clusters, we have optimized a number of cyclic geometries, most in the absence of symmetry constraints, except constraints necessary to ensure a specific general geometry. We have explored three-, four-, five-, and seven-membered monocyclic rings as well as a range of bicyclic systems, all at lower levels of theory. Most of these structures have energies significantly higher than the linear isomers and we have restricted our most detailed calculations to the lowest energy isomers. The four lowest energy cyclic structures are shown in Figure 1 and the calculated energies are presented in Table 1; these lowest energy cyclic isomers were studied at the B3LYP/aug-cc-pVTZ level of theory to allow comparison with the linear forms. Structures **I** and **II** are analogous to the lowest energy cyclic structures reported for C_4N and C_7H. Moreover, at least thermodynamically, these isomers are potentially important forms of the cluster, since structure **I** is the second lowest energy form and lies only 0.6 eV above the C−C−C−C−C−C−N isomer. The energy of the second cyclic isomer, **II**, is 1.2ev above the first and only 0.6 eV greater than the linear isonitrile form. It is, then, the fourth lowest energy isomer.

The harmonic frequencies, dipole moments and predicted IR intensities for cyclic clusters are presented in Table 5. For structures **I** and **II**, the largest IR intensities are predicted for twisting motions about the carbon adjacent to the −C≡N− bond (∼500 cm^{-1}) and for compression/extension of the bonds in the carbon chain (∼2200 cm^{-1}). For the bicyclic structure, **III**, the largest IR intensity is expected to occur for a motion that elongates the bicyclic bridging bond (1770 cm^{-1}). We expect uncertainties in these frequencies to be similar in magnitude, 50 cm^{-1}, as those reported in Table 4. The dipole moments for the three-membered ring structures are comparable to those of the linear isomers, indicating that the cyclic isomers could be detected, if indeed they are formed in the laboratory or in the interstellar region.

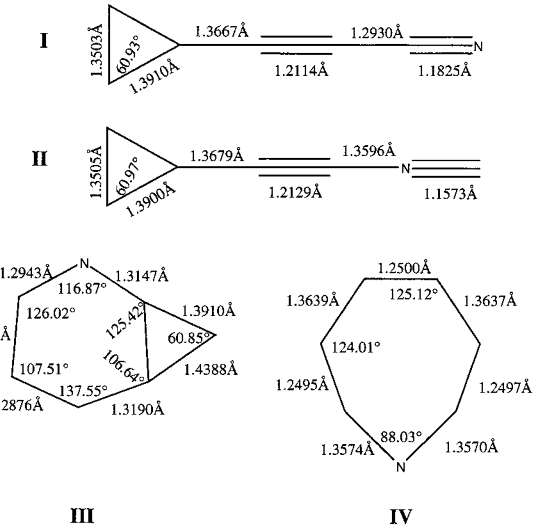

Figure 1. Geometry of optimized cyclic isomers at the B3LYP/aug-cc-pVTZ (**I** and **II**) and B3LYP/6-311G** (**III** and **IV**) levels of theory.

TABLE 5: Frequencies, cm^{-1} *(IR intensities)* and Dipole Moments, D, for the Cyclic Clusters at the B3LYP/6-311G Level of Theory**

structure I	structure II	structure III	structure IV
89 *(20)*	94 *(15)*	209.82 *(20)*	−415.16
103 *(6)*	105 *(5)*	408.64 *(0)*	−301.66
230 *(30)*	225 *(9)*	484.03 *(2)*	211.17
282 *(0)*	248 *(0)*	512.82 *(8)*	391.45
452 *(345)*	415 *(30)*	521.55 *(0)*	396.17
517 *(55)*	471 *(0)*	638.47 *(4)*	448.41
524 *(6)*	497 *(155)*	677.46 *(0)*	483.58
539 *(0)*	548 *(8)*	734.34 *(2)*	494.02
573 *(3)*	552 *(20)*	839.10 *(45)*	828.02
592 *(0)*	556 *(165)*	1020.34 *(7)*	1005.62
1051 *(8)*	1092 *(25)*	1139.60 *(55)*	1172.48
1312 *(30)*	1331 *(35)*	1362.86 *(20)*	1286.31
1660 *(60)*	1661 *(95)*	1399.76 *(65)*	1825.60
2203 *(30)*	2109 *(150)*	1615.34 *(25)*	1854.19
2326 *(0)*	2272 *(275)*	1770.04 *(190)*	1977.04
0.38D	1.05D	0.60D	0.960D

Discussion

C_6N is isoelectronic with C_7H; both have $^2\Pi$ ground electronic states.[4] These two structures have now been shown to be structurally analogous, as well. For both molecules, the ground electronic state has a linear structure capped by the heteroatom. For C_6N, the next lowest energy structure, lying within approximately 0.6 eV, is a cyclic structure. These cyclopropane-based structures have only been recently reported for the smaller C_4N molecule. The thermodynamic stability and large dipole moment predicted for these cyclic isomers leads one to expect that their observation in the interstellar medium would be quite feasible. They must certainly now become targets of matrix isolation studies.

The cluster anion, C_6N^-, is isoelectronic with C_6O. The latter has been studied computationally[22] and has been observed in matrix isolation studies.[23] There has also been a recent report of a computational study[5] of the smaller C_4O cluster and its anion. The $n = 4$ and $n = 6$ oxides are both triplet ground-state molecules, $^3\Sigma^-$, and are expected to exhibit cumulenic-like bonding. The linear C_6N^- ion is also cumulenic (relative to the corresponding neutral cluster) with a $^3\Sigma^-$ ground state. As was described previously for C_4O, we have observed the dependence of the characterization of the linear anion on basis set and theoretical method. That is, using the B3LYP functional with the 6-311G** basis set, the linear anion is a global minimum. If the basis set is improved to the significantly larger aug-cc-pVTZ set, the harmonic frequencies include an imaginary frequency, 213i, indicating that the linear form is a transition state. We have optimized the nonlinear structure and no angles deviate more than 10° from linearity. Moreover, there are no significant changes in any bond distances. We conclude, as did the authors in the case of C_4O, that the C_6N^- anion is a floppy molecule that is essentially linear and may be treated as such, due to its shallow potential well.

The C_6N^+ cation is isoelectronic with C_7. The latter has been shown computationally[3] to be a linear, $^1\Sigma$ ground state chain with essentially cumulenic bonding. The C_6N^+ cation is agreement with electronic and structural expectations built upon the pure carbon observations.

Calculations have indicated[4] that one mechanism for formation of both the linear and ring forms of the smaller C_5N cluster would be reaction of a carbon atom with diacetylene, C_4H_2. Given sufficient density of C_5N_2, a similar mechanism should be possible for formation of C_6N, that is, reaction 1

$$C\,(^3P) + C_5N_2 \rightarrow C_6N + N \tag{1}$$

In a molecular beam apparatus, used for gas phase analysis or for cluster deposition, one would expect a reasonable density of the necessary precursor molecules, so detection in the laboratory is entirely feasible. However, because C_5N_2 has not yet been observed in the interstellar medium, reaction 1 may not be a reasonable formation mechanism to pursue for the C_6N species. Other related mechanisms are possible, including those that involve only observed interstellar molecules. For example, reaction 2

$$C_2 + C_4N \rightarrow C_6N \tag{2}$$

or its many analogues, $C_n + C_{6-n}N$, could lead to all of the low energy products, linear and cyclic, predicted for C_6N, depending upon the insertion point of the added carbon atom(s). The reactants have been identified in the interstellar medium.[3,24] We have explored the reaction pathway involving reaction 2 at the PM3 level of theory as proof of the feasibility of this process. The transition state(s) were located and confirmed by IRC calculations. Single point energy calculations at the B3LYP/6-31G* level of theory were performed at the optimized PM3 geometries (B3LYP/6-31G*//PM3 energies). The potential energy for this system is shown in Figure 2. Reaction 2, which involves the C_4N radical, has no reaction barrier. The reaction is energetically downhill, 5.89 eV, to the C−C−C−C−C−C−N product, which represents the absolute minimum for this surface. The linear ground-state cluster is connected, via a bent chain transition state, to the lowest energy cyclic cluster through a reaction barrier of 1.84 eV. The transition state is shown symbolically in Figure 2, along with the vibrational motion that carries the transition state into the product channel, which lies 0.62 eV above the ground-state cluster. The reaction coordinate is the ring closing motion. We expect that analogous mechanisms are plausible for the reactions related to reaction 2.

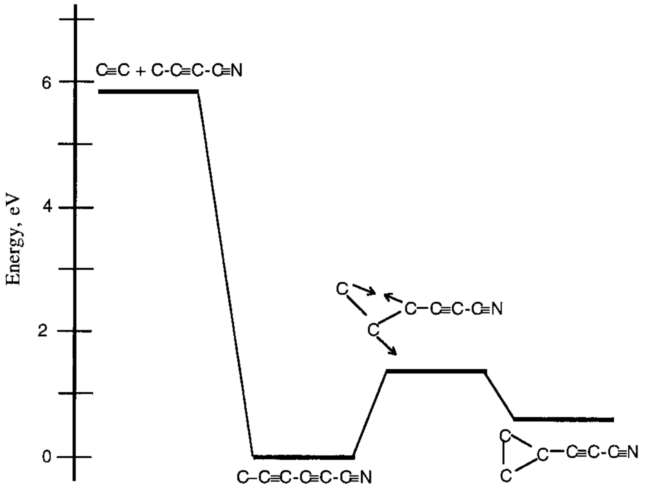

Figure 2. Reaction coordinate profile for Reaction 2 at the B3LYP/6-31G*//PM3 level of theory.

Conclusions

On the basis of density functional calculations using extensive basis sets, we have suggested accurate geometries for a series of isomers of the C_6N cluster. The calculations indicate that, whereas the lowest energy conformer is indeed linear, a very low-lying cyclic structure is thermodynamically stable and should be detectable in laboratory, and perhaps interstellar, spectroscopic measurements. The ionization energy (9.07 eV), electron affinity (3.55 eV) and equilibrium dipole moment (0.69 D) for the linear ground state have been calculated. Large infrared intensities are predicted for harmonic motion involving bond compression and/or twisting about the center of the carbon chain. Comparisons are made with isoelectronic molecules/ions, including C_7H for the neutral cluster, C_6O for the anion and C_7 for the cation and indicate analogous properties for the C_6N clusters.

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