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Density Functional Theory Study of the Electronic State, Geometry, and Harmonic Frequencies for Linear C_nP_2 Clusters: A Comparison with C_nN_2

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Linear C_nN_2 and C_nP_2 clusters, in the lowest energy singlet and triplet states, were studied using the B3LYP/6-311G** theoretical method for $n = 5-10$ and the B3LYP/aug-cc-pVTZ method for $n = 5-8$. Harmonic frequencies are also reported. Clusters with odd numbers of carbon atoms have lower lying triplet ground states, while those with even numbers of carbons are singlets. The energies of the acetylenic singlet ground states are approximately 2.5 eV below those of the lowest triplet state, while the triplet ground states tend to be more cumulenic and are preferred by 0.6−0.8 eV. A comparison of the properties of the di-heteroatom terminated clusters, on the basis of the atomic properties of nitrogen and phosphorus, is presented. Some important differences in molecular properties are highlighted.

1. Introduction

Clusters of carbon with one or two heteroatoms have become the focus of much recent research interest[1−7] after the discovery of such species in the interstellar medium and in the atmosphere of some planets.[8−12] Such species also appear during the arc-driven evaporation of graphite in the presence of a donor compound that provides the heteroatoms.[13] Monocyano and isocyano compounds are readily detected because of their permanent dipole moment. One may expect also that dicyano terminated species will be produced both as a result of the recombination of two monocyano radicals and the higher stability of the closed shell species. A classical example is the very stable NCCN. The higher homologues are much more reactive and are generally produced in low-temperature matrixes.[14] Since these clusters possess an even number of electrons, the ground state of C_nN_2 could be either singlet or triplet, requiring any computational study to include the lowest states of each multiplicity. A series of other related molecules have either been observed or predicted by ab initio calculations. Although the molecular structure is similar, the varying terminating atoms in these clusters lead to variations in the molecular properties. Even within a specific series of clusters, these physical property variations will be observed. For example, recently published results hint of differences in molecular properties with changing parity of the carbon chain in C_nH_2.[15]

One might expect that the presence of phosphorus and nitrogen in the same group of the periodic table would infer that the C_nN_2 and C_nP_2 clusters have similar physical properties. However, there are significant differences in the properties of nitrogen and phosphorus and these may result in differences in the corresponding clusters. In fact, it has been reported that stronger similarities, with respect to physical properties, exist between carbon and phosphorus than between carbon and silicon or phosphorus and nitrogen.[16] Unlike nitrogen, phosphorus may take a coordination number of six and has a much larger covalent radius, 1.10 Å, as compared to nitrogen, 0.70 Å. The electronegativity of phosphorus is 2.2 on the Pauling scale.[17] This should be compared with that of carbon, 2.5, and nitrogen, 3.0. Finally, the ionization energy of phosphorus is significantly lower than that of nitrogen: 1012 kJ mole^{-1} compared with 1402 kJ mole^{-1}. In terms of the electronic structure of the heteroatom-containing molecules, a comparison of imine (CH_2NH) and phosphaethylene (CH_2PH) indicates that the HOMO of the former is the lone pair, while that of the latter corresponds to the π-bond.[16,18] It has also been shown[16] that phosphaalkynes (R−C≡P) and nitriles (R−C≡N) differ in bond polarity because of the electronegativity difference noted above. The ionization energy of the phosphaalkynes is reported in the same work to be much lower than that of the nitriles. The C≡P bond length is very short, typically between 1.5 and 1.6 Å. Finally, the chemistry of the phosphaalkynes is similar[16] to that of alkynes.

The only reported work on diphosphaalkynes has focused on the smallest member of the series, PCCP, the phosphorus analogue of the well-studied NCCN.[19−21] The calculated geometry of the ground and lowest excited states as well as the predicted photoelectron spectra were consistent[19] with the physical property information provided above and were, therefore, different from the related data available for the nitrogen analogue. The existence of the PCCP molecule was later confirmed by a neutralization−reionization mass spectrometric investigation,[20] but this experiment could not, by its nature, provide any structural information. A later, computational study considered all of the possible PCCP isomers and concluded that the lowest conformer was the linear form terminated by phosphorus atoms.[21]

With this background, we have explored the clusters of intermediate-sized carbon chain length, from 5 to 10 atoms, with the goal of comparing the structures and properties of the nitrogen- and phosphorus-terminated clusters. We report here the results of the density functional theory calculations for geometry, electronic structure, and physical properties and compare the results for the two series of clusters.

2. Computational Details

The calculations reported in this work were all completed with the GAUSSIAN98 suite of programs.[22] Although other

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theoretical methods were used during the study, the primary computational tools involved the B3LYP functional[23] with the 6-311G** basis set and, unless otherwise noted, all reported structural results were obtained via that theoretical method. This theoretical method and the basis sets have been previously tested on a set of comparison molecules of well-known geometry. Calculations using the same theoretical method employed here were reported for HCN and HCCCN and the maximum difference between the experimental and calculated bond lengths was less than 0.008 A.[24−26] All of the structures and energies for the clusters from C_5 to C_8 were also explored using the same functional with the more extensive aug-cc-pVTZ basis set. The latter could not be used for the C_9 and C_{10} clusters because of the significant computational times. No significant improvement was noted for the clusters using the more extensive basis set. It is important to keep in mind that, as shown recently by Schaefer, DFT calculations may in general overestimate the energies for clusters similar to those studied here.[27]

Two geometries were optimized for each cluster: the lowest lying singlet and triplet electronic states. All harmonic frequencies and force constants were obtained with the 6-311G** basis set, after optimizing the structures at the same level of theory. The calculated value for $\langle S^2 \rangle$ was always zero for the singlets and within 10% (pre-annihilation) of the expected value of two for the triplets (and equal to two, post-annihilation), indicating that there was minimal spin contamination in the open shell cases where the wave function is not an eigenvalue of the S^2 operator.

For the calculation of vertical transition energies, the CASSCF[28−33] method was employed. Several active spaces were used. The final calculations were completed for both singlet and triplet configurations, with an active space of six electrons and fourteen spin−orbitals. For all clusters, the major configuration (identical to that optimized by DFT) was at least 80% of the total wave function. However, even though the contributions of the remaining configurations are individually small, the total contribution is significant to the final energy.

3. Results and Discussion

a. Isomers. Calculations, using the B3LYP/6-311G** theoretical method, were completed for the linear isomers of C_5N_2 to $C_{10}N_2$ and C_5P_2 to $C_{10}P_2$, where the heteroatoms terminated both ends of the carbon chain. These structures were demonstrated, after calculations involving other isomeric forms of C_nN_2 and C_nP_2, to have the lowest energies of all of the possible linear isomers. For example, the data indicate that singlet C_6N_2 with terminal nitrogen atoms, the dicyano cluster, lies 1.11 eV below the next lowest energy isomer, which has one cyano and one isocyano group. The cluster with two isocyano groups lies 1.10 eV above the mixed terminal cluster. Similar results are obtained for C_6P_2. Populated orbitals, as expected from the total energy, shift up as the nitrogen or phosphorus atoms are moved away from the terminus of the chain. Molecular orbitals of σ symmetry, essentially the lone pair orbitals, increase in energy and become mixed in with the higher lying π orbitals. Movement of any nitrogen (or phosphorus) atom away from the terminal position results in an increase in the total ground-state energy and a corresponding decrease in the regularity of the single−triple bond length alternation within the chain.[26] For this reason, the calculations in this work were focused on the most stable species, that is, those terminated by the two heteroatoms.

b. Geometries. We first consider the nitrogen clusters. For clusters with an even number of carbon atoms, the ground state is a singlet spin state with alternating triple and single bonds. For example, the singlet state of C_6N_2 has a bond length alternation of 1.160, 1.360, 1.216, 1.347, 1.216, 1.360, and 1.160 Å. The acetylenic nature of this cluster, and by examination of the data in Table 1, all of the even carbon-, nitrogen-terminated clusters is clear. The excited-state triplet C_6N_2 has significantly longer cyano bonds, 1.182 Å, and less obvious bond length alternation in the carbon chain. The cyano groups in the even carbon cluster singlet electronic states have a slightly shorter bond length than those in the comparison standards, HCN and HCCCN. All triplet ground states, that is, the odd carbon clusters in Table 1, have bond orders that are difficult to characterize. However, these clusters are clearly more cumulenic than the even carbon clusters with singlet ground states. As the chain length of the odd carbon clusters increases, the structure tends to more resemble that of the singlet ground states. That is, the structure becomes more acetylenic. The cyano bond lengths in the triplet ground states are in much closer agreement with the reference molecules HCN and HCCCN.

In general, the geometries of the C_nP_2 clusters appear to be less acetylenic for all species. The geometries are shown in Table 2. A bond length alternation does still exist for the even carbon clusters in the singlet state, but the triplet−singlet alternation is less distinctive than that in the nitrogen analogues. For example, the bond lengths for the C_6P_2 singlet state are 1.565, 1.336, 1.233, 1.330, 1.233, 1.336, and 1.565 Å. As with the nitrogen analogues, the carbon−phosphorus bond always appears to be shorter in the singlet state of the even carbon molecules than in the odd-carbon species. The C≡P bond length may be compared to the experimental value in the molecule *t*-BuC≡P, which has been studied by X-ray analysis. That reference bond length is reported to be 1.548 Å,[34] which is approximately 0.02 Å shorter than the bond lengths calculated for the even carbon clusters. As was true for the nitrogen analogues, there are no significant bond length changes as the length of the even carbon chain is increased. The triplet ground states for the odd carbon clusters are more cumulenic than those reported above for the nitrogen analogues. However, the trend toward a more acetylenic structure as the chain length increases is also observed for these clusters. The C≡P bond in the odd carbon clusters is approximately 0.02−0.03 Å longer than that of the reference molecule.

The singlet/triplet alternation of ground states as the number of carbon atoms increases is readily understood from a consideration of the molecular orbitals. The highest occupied orbitals are π-type. All of the odd carbon species have a $^3\Sigma$ ground state and a valence electronic configuration of the type, $1\sigma^2\ 2\sigma^2\ ...n\sigma^2\ 1\pi^4\ 2\pi^4\ 3\pi^4...m\pi^2$. The triplet spin state results from Hund's Rule. The electronic configuration of the even carbon clusters is $1\sigma^2\ 2\sigma^2\ ...(n+2)\sigma^2\ 1\pi^4\ 2\pi^4\ 3\pi^4...m\pi^{\ 4}$ and the ground state is $^1\Sigma$. The additional six electrons, present by increasing the number of carbon atoms by one in moving up from the odd cluster, occupy two additional core σ-orbitals and complete the occupation of the highest π-orbital.

c. Energies. The relative energies from optimized geometries of all of the heteroatom-terminated clusters are shown in Tables 1 and 2. The $^3\Sigma$ ground state of C_5N_2, calculated at the B3LYP/6-311G** level, lies 0.83 eV lower than the $^1\Sigma$ state. With increasing length of the carbon chain, the triplet−singlet energy difference decreases, to 0.71 eV for C_7N_2 and 0.64 eV for C_9N_2. The separation between the energies of the optimized singlet and triplet states for clusters with even numbers of carbon atoms is much greater. The singlet states for C_6N_2, C_8N_2 and $C_{10}N_2$ are situated 2.54 eV, 2.15 eV, and 1.88 eV below the triplets.

TABLE 1: Bond Lengths, Adiabatic, and Vertical Energy Differences Calculated as $E_T - E_S$, in eV, for Singlet and Triplet Electronic States of Linear C_nN_2 Clusters at the B3LYP/ 6-311G and B3LYP/aug-cc-pVTZ (in Parentheses) Levels of Theory**

Bondlengths (S: Singlet; T: Triplet)												ΔE_{ad}	ΔE_{vert}
N—C—C—C—C—C—N													
S	1.1742	1.3297	1.2666	1.2666	1.3296	1.1742						-0.83	-0.83
S	(1.1714	1.3283	1.2640	1.2640	1.3283	1.1714)							
T	1.1743	1.3315	1.2685	1.2685	1.3322	1.1743						(-0.81)	
T	(1.1713	1.3302	1.2658	1.2658	1.3302	1.1713)							
N—C—C—C—C—C—C—N													
S	1.1604	1.3598	1.2157	1.3474	1.2157	1.3598	1.1604					2.54	3.03
S	(1.1574	1.3593	1.2127	1.3464	1.2127	1.3593	1.1574)						
T	1.1822	1.3209	1.2770	1.2794	1.2770	1.3209	1.1822					(2.55)	
T	(1.1793	1.3193	1.2743	1.2771	1.2743	1.3193	1.1793)						
N—C—C—C—C—C—C—C—N													
S	1.1695	1.3398	1.2491	1.2897	1.2899	1.2487	1.3397	1.1693				-0.71	-0.71
S	(1.1667	1.3384	1.2463	1.2877	1.2878	1.2463	1.3384	1.1667)					
T	1.1696	1.3409	1.2506	1.2918	1.2920	1.2504	1.3410	1.1696				(-0.70)	
T	(1.1667	1.3399	1.2476	1.2896	1.2897	1.2475	1.3399	1.1667)					
N—C—C—C—C—C—C—C—C—N													
S	1.1610	1.3586	1.2179	1.3428	1.2220	1.3428	1.2179	1.3586	1.1610			2.15	2.83
S	(1.1581	1.3579	1.2150	1.3416	1.2190	1.3416	1.2150	1.3579	1.1581)				
T	1.1749	1.3318	1.2618	1.2846	1.2836	1.2846	1.2618	1.3318	1.1749			(2.15)	
T	(1.1721	1.3305	1.2590	1.2824	1.2812	1.2824	1.2590	1.3305	1.1721)				
N—C—C—C—C—C—C—C—C—C—N													
S	1.1669	1.3451	1.2398	1.3038	1.2704	1.2704	1.3038	1.2398	1.3451	1.1670		-0.64	-0.65
T	1.1670	1.3461	1.2408	1.3053	1.2721	1.2721	1.3053	1.2408	1.3461	1.1670			
N—C—C—C—C—C—C—C—C—C—C—N													
S	1.1612	1.3582	1.2190	1.3407	1.2246	1.3374	1.2245	1.3408	1.2191	1.3582	1.1612	1.88	2.52
T	1.1709	1.3388	1.2508	1.2939	1.2779	1.2774	1.2779	1.2940	1.2508	1.3389	1.1709		

In general, the adiabatic triplet−singlet energy separation decreases as the carbon chain length increases. This is true for both odd and even carbon chains. However, the small energy separation for the odd carbon clusters means that the trend may indicate a change in the nature of the electronic ground state for a sufficiently large cluster size.

The trends observed for the nitrogen-terminated clusters are also present for the C_nP_2 series. The adiabatic energy differences between the electronic states for C_5P_2, C_7P_2, and C_9P_2 are 0.68 eV, 0.62 eV, and 0.580 eV at the B3LYP/6-311G** level of theory. These values are comparable to those of their respective nitrogen analogues. C_6P_2, C_8P_2, and $C_{10}P_2$ have singlet states lying 1.41 eV, 1.52 eV, and 1.24 eV below the triplets; these values are significantly smaller than those for the corresponding nitrogen clusters. Interestingly, the singlet−triplet energy difference for C_8P_2 is greater than that for C_6P_2, while all other such energy differences tend to decrease with increasing carbon chain.

To more accurately calculate vertical energy differences, CASSCF calculations using the 6-311G** basis set were applied. The active space ranged from (2,6) up to (6,14). In general, with increasing size of the active space, the energies of the triplet states for the odd clusters decrease faster than those of the singlet states and the energy difference becomes essentially constant at the largest active space employed. The C_7P_2 cluster was the single exception. For this molecule only, an additional calculation with an (8,16) active space was required before the triplet state was located below the singlet. In the larger active space, no one additional configuration was a major contributor to the overall wave function; however, while small, the nonzero contribution of each configuration was clearly significant.

The CASSCF results are presented in Table 3. For the nitrogen clusters, the data show a preference for triplet electronic states by 0.16−0.45 eV among the species with an odd number of atoms. However, unlike the results in which the geometry of the two electronic states are separately optimized, there is no trend with increasing chain length. The singlet states for the even carbon-, nitrogen-terminated clusters were 2.5−4.3 eV below the triplets. All of these latter energy differences are significantly greater than those calculated for the adiabatic transitions by means of the B3LYP functional. However, they are consistent with the vertical energy differences calculated by the DFT method. The one obvious deviation of the CASSCF data from the DFT results is that even though the ΔE_{vert} values for the latter are larger for the vertical case, the DFT values are

TABLE 2: Bond Lengths, Adiabatic, and Vertical Energy Differences Calculated as $E_T - E_S$, in eV, for Singlet and Triplet Electronic States of Linear C_nP_2 Clusters at the B3LYP/ 6-311G and B3LYP/aug-cc-pVTZ (in Parentheses) Levels of Theory**

Bondlengths (S: Singlet; T: Triplet)	**ΔE_{ad}**	**ΔE_{vert}**
P—C—C—C—C—C—P		
S 1.5950 1.2994 1.2736 1.2733 1.2996 1.5940	-0.68	-0.68
S (1.5937 1.2962 1.2718 1.2715 1.2964 1.5929)		
T 1.6022 1.2970 1.2761 1.2753 1.2978 1.6006	(-0.67)	
T (1.6014 1.2935 1.2743 1.2736 1.2942 1.6003)		
P—C—C—C—C—C—C—P		
S 1.5650 1.3364 1.2325 1.3298 1.2325 1.3364 1.5650	1.41	2.04
S (1.5635 1.3336 1.2306 1.3280 1.2306 1.3336 1.5635)		
T 1.6155 1.2862 1.2837 1.2726 1.2837 1.2862 1.6155	(1.36)	
T (1.6154 1.2826 1.2820 1.2699 1.2820 1.2826 1.6154)		
P—C—C—C—C—C—C—C—P		
S 1.5873 1.3069 1.2646 1.2831 1.2819 1.2657 1.3063 1.5881	-0.62	-0.63
S (1.5869 1.3036 1.2633 1.2803 1.2803 1.2633 1.3036 1.5869)		
T 1.5945 1.3037 1.2682 1.2830 1.2821 1.2690 1.3029 1.5954	(-0.62)	
T (1.5942 1.2999 1.2668 1.2806 1.2798 1.2676 1.2992 1.5949)		
P—C—C—C—C—C—C—C—C—P		
S 1.5650 1.3360 1.2329 1.3293 1.2323 1.3293 1.2329 1.3360 1.5650	1.52	1.73
S (1.5634 1.3333 1.2308 1.3277 1.2299 1.3277 1.2308 1.3333 1.5634)		
T 1.6050 1.2942 1.2764 1.2771 1.2811 1.2771 1.2764 1.2942 1.6050	(1.48)	
T (1.6052 1.2904 1.2747 1.2749 1.2788 1.2949 1.2747 1.2904 1.6052)		
P—C—C—C—C—C—C—C—C—C—P		
S 1.5835 1.3116 1.2589 1.2900 1.2737 1.2734 1.2903 1.2588 1.3119 1.5832	-0.58	-0.58
T 1.5901 1.3077 1.2634 1.2885 1.2755 1.2751 1.2889 1.2631 1.3081 1.5898		
P—C—C—C—C—C—C—C—C—C—C—P		
S 1.5653 1.3357 1.2331 1.3289 1.2326 1.3289 1.2326 1.3289 1.2331 1.3357 1.5653	1.24	1.66
T 1.5996 1.2982 1.2719 1.2797 1.2800 1.2748 1.2800 1.2798 1.2719 1.2983 1.5995		

TABLE 3: CASSCF(6,14) Energies for C_nN_2 and C_nP_2 Clusters, Calculated with the 6-311G Basis Set[a]**

cluster	singlet, a.u.	triplet, a.u.	ΔE (vertical), eV
C_5N_2	−298.1919	−298.1978	−0.16
C_6N_2	−336.1285	−335.9671	4.39
C_7N_2	−373.8844	**−373.9011**	−0.45
C_8N_2	−411.8024	−411.6668	3.69
C_9N_2	−449.5843	−449.5968	−0.34
$C_{10}N_2$	−487.5111	−487.3847	3.44
C_5P_2	−870.7198	−870.7240	−0.12
C_6P_2	−908.6250	−908.5305	2.57
C_7P_2[b]	−946.4118	−946.4104	0.22
C_8P_2	−984.3043	−984.2005	2.57
C_9P_2	−1022.0890	−1022.0931	−0.11
$C_{10}P_2$	−1060.0046	−1059.9083	2.62

[a] The ground-state geometries were previously optimized at the B3LYP/6-311G** level of theory. [b] C_7P_2 at (8,16): singlet −964.4539 au; triplet −964.4616 au.

TABLE 4: CCSD(T) Energies and Energy Differences ($E_T - E_S$), in a.u., Calculated with the 6-311G Basis Set at the B3LYP Optimized Geometry**

cluster	energy, a.u.	ΔE (adiabatic), eV
S NC−CCC−CN	−299.1033	−0.84
T NC−CCC−CN	−299.1342	
S NC−CCCC−CN	−337.1801	3.09
T NC−CCCC−CN	−337.0668	
S NC−CCCCC−CN	−375.0796	−0.68
T NC−CCCCC−CN	−375.1046	
S NC−CCCCCC−CN	−413.1452	2.80
T NC−CCCCCC−CN	−413.0424	

still smaller than those calculated using the CASSCF method. For comparison with the adiabatic energy differences obtained via DFT, additional single-point energy calculations at the CCSD(T)/ 6-311G** level were completed for the C_nN_2 clusters with $n = 5-8$. As expected, the new absolute energies were higher than those obtained with the B3LYP functional, but the relative differences between singlets and triplets remain essentially unchanged, indicating that the relative energy differences we have computed actually reflect the true differences. These results are shown in Table 4.

The data for the phosphorus-terminated clusters are quite interesting. For the even carbon clusters, the vertical energy differences are approximately double the adiabatic differences. However, this difference is constant for the three clusters in the table. The energy differences for the C_5P_2 and C_9P_2 clusters are identical, while as noted above, the ordering for the C_7P_2 cluster for the “standard” active space used in this calculation is reversed; the triplet is higher in energy than the singlet state. The ordering returns to that found by DFT when the active space is further increased. There appears to be state mixing occurring and that mixing is only properly treated when a larger number of configurations are included in the CASSCF calculation.

TABLE 5: IR Frequencies of C_nN_2 and C_nP_2 Clusters, Optimized at the B3LYP/6-311G Level of Theory**[a]

C_5N_2		C_5P_2		C_6N_2		C_6P_2		C_7N_2		C_7P_2		C_8N_2		C_8P_2		C_9N_2		C_9P_2		$C_{10}N_2$		$C_{10}P_2$	
78	Π/6	60	Π/0	65	Π/5	48	Π/0	51	Π/4	39	Π/0	42	Π/4	32	Π/0	34	Π/3	26	Π/0	29	Π/2	23	Π/0
78		60		65		48		51		39		42		32		34		26		29		23	
189	Π/0	176	Π/0	172	Π/0	142	Π/0	131	Π/0	112	Π/0	112	Π/0	93	Π/0	92	Π/0	77	Π/0	80	Π/0	66	Π/0
189		176		172		142		131		112		112		93		92		77		80		66	
431	Π/7	353	Π/5	310	Π/6	274	Π/4	236	Π/5	222	Π/2	210	Π/6	185	Π/2	171	Π/5	153	Π/1	151	Π/5	133	Π/1
431		354		310		274		236		222		210		185		172		154		153		133	
500	Π/0	395	Σ/0	476	Σ/0	361	Σ/0	413	Π/0	334	Σ/0	316	Π/0	290	Π/0	265	Π/0	252	Π/0	241	Π/0	219	Π/0
500		495	Π/0	485	Π/0	43 7	Π/0	413		368	Π/0	316		290		266		253		241		220	
546	Σ/0	495		485		437		434	Σ/0	368		387	Σ/0	307	Π/0	360	Σ/0	290	Σ/0	325	Σ/0	270	Σ/0
585	Π/3	694	Π/0	565	Π/0	545	Π/4	506	Π/7	493	Π/3	459	Π/2	420	Π/4	433	Π/5	377	Π/5	352	Π/4	319	Π/4
586		695		565		545		506		493		459		420		434		378		353		320	
1058	Σ/2	730	Σ/21	566	Π/5	547	Π/0	596	Π/0	634	Σ/25	521	Π/0	497	Π/0	507	Π/0	487	Π/0	489	Π/0	451	Π/0
1706	Σ/0	1209	Σ/0	566		547		596		643	Π/0	521		497		507		488		490		451	
1723	Σ/28	1315	Σ/80	927	Σ/0	728	Σ/0	844	Σ/2	643		566	Π/5	549	Π/3	589	Π/4	561	Σ/25	560	Π/5	531	Σ/10
2101	Σ/0	1821	Σ/0	1337	Σ/0	1133	Σ/0	887	Π/2	965	Π/3	566		549		589		615	Π/3	560		555	Π/3
2132	Σ/0	1908	Σ/0	2184	Σ/0	1574	Σ/160	888		965		574	Π/0	560	Π/0	702	Σ/3	618		641	Σ/1	556	
				2286	Σ/0	1705	Σ/0	1236	Σ/0	994	Σ/0	574		560		784	Π/0	834	Π/1	672	Π/0	679	Π/0
				23 27	Σ/0	2151	Σ/0	1605	Σ/15	1131	Σ/12 3	758	Σ/1	612	Π/9	784		838		673		680	
				2367	Σ/47	2177	Σ/79	1760	Σ/0	1536	Σ/6	1109	Σ/0	936	Σ/0	1034	Σ/0	850	Σ/0	922	Π/2	802	Σ/0
								2061	Σ/0	1613	Σ/0	1418	Σ/0	1277	Σ/54	1271	Π/2	1026	Σ/246	924		932	Π/1
								2162	Σ/1	1958	Σ/25	2160	Σ/0	1601	Σ/0	1272		1328	Σ/154	944	Σ/0	933	
								2189	Σ/27	2030	Σ/0	2251	Σ/0	1707	Σ/212	1342	Σ/0	1432	Σ/5	1226	Σ/0	108 8	Σ/31
												2254	Σ/0	2078	Σ/0	1517	Σ/0	1480	Σ/3	1457	Σ/4	1358	Σ/0
												2337	Σ/0	2183	Σ/0	1782	Σ/0	1480	Σ/3	1468	Σ/0	1585	Σ/4
												2353	Σ/124	2220	Σ/80	2074	Σ/4	1720	Σ/20	1478	Σ/2	1592	Σ/0
																2077	Σ/1	1840	Σ/4	2140	Σ/0	1633	Σ/288
																2212	Σ/5	2039	Σ/0	2212	Σ/1	1702	Σ/2
																2230	Σ/72	2082	Σ/5	222 8	Σ/1	2025	Σ/0
																				2285	Σ/21	2120	Σ/103
																				2332	Σ/230	2226	Σ/17
																				2347	Σ/6	2234	Σ/16

[a] Only ground-state frequencies are shown: singlet states for even numbered carbon chains and triplet states for odd carbon chains. Mode symmetry/IR intensity are also provided.

d. Physical Properties. The calculated harmonic frequencies and intensities, shown in Table 5, reveal a common pattern for all clusters in the electronic ground state. The symmetry of the clusters results in several doubly degenerate vibrations, particularly for low frequency, bending motions. Also, as might be expected for the high symmetry in these clusters, the few infrared active transitions are predicted to have small intensities. For odd carbon clusters, the lowest energy bending vibrations, flexing into a v-shaped configuration, would be observed, but the intensity of such transitions is predicted to be very small. For example, the 78 cm^{-1} and 431 cm^{-1} Π-bending modes in the C_5N_2 cluster and the 353 cm^{-1} Π-bending mode in C_5P_2 have minimal intensities. There are corresponding bending modes at similar energies for all of the clusters. The higher energy (1723 cm^{-1} C_5N_2 and 1315 cm^{-1} in C_5P_2) asymmetric Σ-stretching motion is predicted to have a more significant infrared intensity. Again, this more intense vibrational mode is also present for the other odd carbon clusters. Similar results are observed for the even carbon clusters. In general, the phosphorus clusters exhibit two, rather than one, Σ-asymmetric stretching modes with significant intensity. The longest molecules are, in all likelihood, "floppy". That is, the geometry is not strictly linear, but slightly bent and the cluster is fluxional. Evidence of this structural difference is presented by the increase in the number of IR active modes with significant intensity as the carbon chains grow to 9 or 10 atoms.

As expected on the basis of the relative electronegativities, the termini of the two cluster classes have different properties. The nitrogen-terminated clusters are actually cyano-terminated, if one considered the Mulliken charge distribution. Both the terminal nitrogen and the adjacent carbon atom have a negative charge (approximately $-0.15e$ and $-0.18e$, respectively), while the remaining carbon atoms are positively charged. The cyano group is intact, much as is observed in simple organic substitution reactions. On the other hand, the lower electronegativity of the phosphorus atom is reflected in the Mulliken charge distribution in the C_nP_2 clusters. The terminal phosphorus atoms are positively charged (typically $0.40e$) and all of the carbon atoms are negatively charged, with the adjacent carbon having the greatest charge ($-0.27e$ for even carbon chains and $-0.12e$ for odd carbon chains).

TABLE 6: HOMO/LUMO Energies and Koopmans' Theorem Estimate of Vertical Ionization Energies for C_nN_2 and C_nP_2 Clusters, Calculated with the 6-311G Basis Set**

cluster	HOMO, a.u.	LUMO, a.u.	$E_{ionization}$, eV
C_5N_2	−0.2248	−0.1823	6.1
C_6N_2	−0.3123	−0.1363	8.5
C_7N_2	−0.2710	−0.1811	7.4
C_8N_2	−0.2958	−0.1434	8.1
C_9N_2	−0.2616	−0.1801	7.1
$C_{10}N_2$	−0.2840	−0.1481	7.7
C_5P_2	−0.2298	−0.1507	6.3
C_6P_2	−0.2469	−0.1302	6.7
C_7P_2	−0.2273	−0.1533	6.2
C_8P_2	−0.2431	−0.1346	6.6
C_9P_2	−0.2250	−0.1199	6.1
$C_{10}P_2$	−0.2404	−0.1358	6.6

Ionization energies may be estimated via Koopmans' theorem. While this is a severe approximation and is not strictly valid for DFT approaches, it has been shown to provide good estimates, especially for relative ionization energies. The results are shown in Table 6. Our intent here is not to provide high quality values for ionization energies, but rather to use the estimates provided by Koopmans' theorem to allow a comparison to other phosphorus- and nitrogen-terminated organic molecules, in a search for similarities and differences linked to the heteroatom termination. Clearly, the ionization energies for the phosphorus clusters are indeed lower than those for the nitrogen clusters, except for the smallest molecule. While this is consistent with the relative atomic ionization energies, it is not necessarily a reflection of atomic properties since an examination of the molecular orbitals indicates that for all of the clusters studied here, a minimum of the HOMO and the HOMO-1 orbitals are molecular π bonding orbitals. This result for the doubly heteroatom terminated clusters differs from the comparable results for molecules such as CH_2NH and CH_2PH, where the HOMO in the former is a lone pair σ orbital and in the latter is a molecular π orbital. Also, the σ orbitals in the clusters having between seven and eight carbons are nearly degenerate (energy difference of 10−50 meV) with a set of π orbitals involving the heteroatoms.

4. Summary and Conclusions

The linear homologues of C_nN_2 and C_nP_2, $n = 5-10$, with the heteroatoms at both terminal points of the carbon chain, were studied with the B3LYP functional and the 6-311G** basis set. The clusters with odd numbers of carbon atoms have triplet ground states, while the even carbon molecules have singlet ground states. The energy differences between the ground and excited states are 0.6−0.8 eV for the triplet ground states and ~2.5 eV for the singlet ground states. The physical properties of the two heteroatoms are significantly different. Some of these differences are reflected in the calculated molecular properties of the clusters. The ionization energies of the phophaalkynes are lower than those of the nitrogen analogues. The phosphorus atoms in the C_nP_2 clusters have a positive Mulliken charge. By charge considerations, the nitrogen atoms should be considered as a constituent of a cyano group, not as terminal atoms. The cyano group has a negative charge comparable in magnitude to that of the phosphorus atom. On the other hand, both sets of clusters exhibit very short $C\equiv X$ bonds and the MOs for both indicate that the HOMO as well as at least one other orbital directly below the HOMO may be characterized as π bonding and involve the heteroatom. For the nitrogen clusters, this is distinctly different from the mono-nitrogen terminated molecules, reported to have MOs that are essentially lone pair orbitals.[16] This MO similarity predicts that C_nP_2 and C_nN_2 clusters should have similar chemistries. The diphosphaalkynes are reported to have the chemical reactivities of alkynes, leading to the suggestion that C_nN_2 should also be alkynelike. A recent experiment examining the reactive organic chemistry of $C_{10}N_2$ bears out this prediction.[35]

This research is a part of a larger project, calculating periodic properties of C_nX and C_nX_2 clusters with respect of the type of atoms terminating the carbon chain. Current work is focused on the synthesis and theoretical studies of C_nB and C_nB_2 clusters.

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