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Electronic Structure of C_5N_2, C_6N_2, and Isoelectronic Molecules

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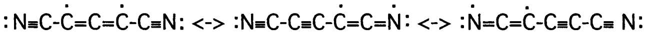
Density functional calculations (B3LYP/cc-pVTZ) have been used to determine the ground-state energies and bonding in C_5N_2 and C_6N_2 and isoelectronic molecules including C_nO, C_nH_2, C_nN^-. and $C_nO_2^{2+}$. In general, the odd numbered carbon clusters have triplet ground states and are more cumulenic, whereas the even clusters are singlets in the ground state and acetylenic in structure. Energies and structures of the lowest excited states of different multiplicity have also been calculated, and CASSCF calculations (CASSCF/cc-pVTZ//B3LYP/cc-pVTZ) were employed to estimate the vertical transition energies between the states. The transitions for the C_5N_2 series are dominated by the $4\pi \rightarrow 5\pi$ excitation and the transition energies lie in a small range, spanning less than 0.5 eV. The separation between spin states is much greater, 2−4 eV, for the C_6N_2 series of clusters. The effect of the heteroatoms on the molecular orbital structure of each series of target molecules is discussed.

Introduction

Carbon clusters are important in basic chemical processes and in interstellar chemistry. In addition, those terminated by heteroatoms have been of special theoretical and experimental interest for many years.[1−7] This focus resulted, in part, from materials science developments. In materials science, new methods of deposition involving clusters and the application of self-assembly techniques and surface-cluster interactions require detailed knowledge of the geometry and electronic structure of a range of carbon containing molecules. Computational studies provide this information that is important for the evolution of the field.

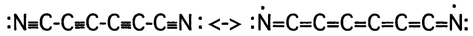
We have recently completed surveys of the geometries and electronic structures of C_nS (and its anion and cation)[8] for $n < 17$, as well C_nN and C_nN_2, where $n < 11$, using density functional theory.[9] In the latter, the focus was on the lowest energy conformer and the reported results, whereas covering a range of clusters included mostly the nitrogen-terminated linear forms. Studies of structural parameters for the C_nN_m series of linear clusters have indicated a fundamental difference in the structure of odd and even carbon heteroclusters, so that the two maybe considered as separate series. Conceptually, linear C_nN_2 clusters with terminal nitrogen atoms may be thought of as resulting from a mixture of resonance structures.

For odd-numbered carbon structures, and C_5N_2 in particular, the blending of the possible resonance forms implies that the observed structure should tend toward a cumulenic form with elongated triple bonds and shortened single bonds.



$$:N\equiv C-\dot{C}=C=\dot{C}-C\equiv N: \text{ <-> } :N\equiv C-C\equiv C-\dot{C}=C=\dot{N}: \text{ <-> } :\dot{N}=C=\dot{C}-C\equiv C-C\equiv N:$$

For even-numbered carbon structures, such as C_6N_2, the geometry results from a hypothetical mixture of a resonance structure involving alternating single and triple bonds and one in which the cluster consists of double bonded atoms; the even clusters are expected to be purely acetylenic.



$$:N\equiv C-C\equiv C-C\equiv C-C\equiv N: \text{ <-> } :\dot{N}=C=C=C=C=C=C=\dot{N}:$$

However, detailed information on the relevant molecular orbitals as well as a context for understanding the physical properties has not been provided. To provide a more detailed understanding of the dicyano-carbon clusters, we have undertaken calculations of related isoelectronic clusters, including ground and low lying excited-state structures and energies and the nature of the molecular orbitals. A combination of density functional theory and CASSCF methods were used to arrive at the relevant data.

Computational Details

The B3LYP functional with Dunning's correlation consistent polarized valence triple-ζ basis set, cc-pVTZ, as implemented in the Gaussian 98 suite[10] of programs was used to determine equilibrium geometries and physical properties in the lowest singlet and triplet electronic states. The complete active space method (CASSCF) available within the same program was used to calculate the vertical energy differences between the ground and excited states, using the same basis set. The HOMO and LUMO in all cases are π-orbitals. Extensive CASSCF calculations, involving 8 or 12 electrons, were completed for selected species as a check on the inclusion of all of the relevant configurations and convergence of the transition energies. Based on these results, a two-electron−five-orbital active space (2,5) is employed for the C_5N_2 analogues and a four-electron−six-orbital active space (4,6) for the C_6N_2 analogues. The added computational cost of the more extensive active space was not justified by the minimal change in transition energies. An additional set of DFT calculations using the augmented basis set that includes diffuse, nonpolarization orbitals, aug-cc-pVTZ, was completed for C_5N_2 and C_5P_2 to provide a comparison point for the accuracy of the unaugmented basis set.

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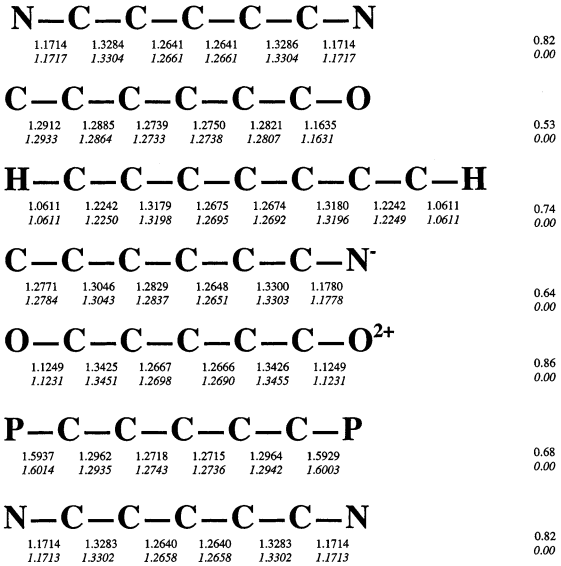


Figure 1. Bond lengths and relative energies for singlet/*triplet* C_5N_2 and isoelectronic species using the B3LYP/ cc-pVTZ theoretical method. The last two entries show calculated structures at the B3LYP/ aug-cc-pVTZ level of theory.

Results and Discussion

There have been experimental and computational studies on selected molecules from among the members of this class of dinitrogen clusters, although the theoretical level of the calculations and the objective of those calculations were not always directly relevant to the present study. Among the dicyanopolyynes, the C_2N_2 isomers have been examined both experimentally[11] and computationally.[11,12] C_4N_2 clusters have been detected in astrophysical studies,[13,14] observed in the laboratory,[15] and studied computationally.[16−18] C_5N_2 conformers have been studied both experimentally[19] and computationally,[20,21] whereas C_6N_2 conformers have been explored in recent computational and experimental studies.[22] Here, we compare the geometry, MO structure, and transition energy for C_5N_2, C_6N_2, and isoelectronic series of clusters. The specific isoelectronic molecules of interest here have not received much attention. Calculated structures for the C_nO clusters, including C_6O and C_7O, have been reported,[23,24] but no structures exist for the remaining C_5N_2- or C_nN_2-like clusters.

Geometries. We have previously shown that the computational technique used here underestimates the carbon−nitrogen triple bond by 0.0055 Å and the carbon−carbon singlet bond by 0.0060 Å. The details on these estimates may be found in the literature.[9,25] The B3LYP/cc-pVTZ optimized bond lengths of C_5N_2, C_6O, C_6N^-, HC_7H, and $C_5O_2^{2+}$ are shown in Figure 1, along with those of C_5P_2 for comparison. The relative energies of both the ground-state triplet and the lowest singlet state are also presented in the figure for each cluster. The analogous data are presented in Figure 2 for C_6N_2 and its isoelectronic molecules.

For the odd carbon cluster, C_5N_2, a calculation with a smaller basis set reported bond lengths of 1.182, 1.335, and 1.274 Å, beginning with the carbon−nitrogen triple bond.[20] The authors also report that the ground-state triplet lies 0.30 eV below the lowest singlet state. A later report, using a more extensive basis set reports an energy difference of 0.82 eV.[21] The bond lengths in Figure 1 indicate that cumulenic bonding is dominant in these clusters. In the dicyano cluster, the carbon−nitrogen bonds are slightly elongated from those typical of a triple bond, whereas the carbon−carbon bonds have slight deviations from the standard value of a —C═C— bond length. The energy difference between the relaxed geometries is identical to that reported earlier.[21] The cumulenic effect is more clearly shown in the structures for C_6N^- and C_6O, where no carbon−carbon triple bond is indicated at all. Previous calculations,[24] with a slightly smaller basis set, reported bond lengths in C_6O as 1.1794, 1.2889, 1.2854, 1.2833, 1.2980, and 1.3098 Å, in good agreement with the current work. No acetylenic bonding trends are detected until we reach a significantly longer carbon chain, HC_7H, but the effect is small.

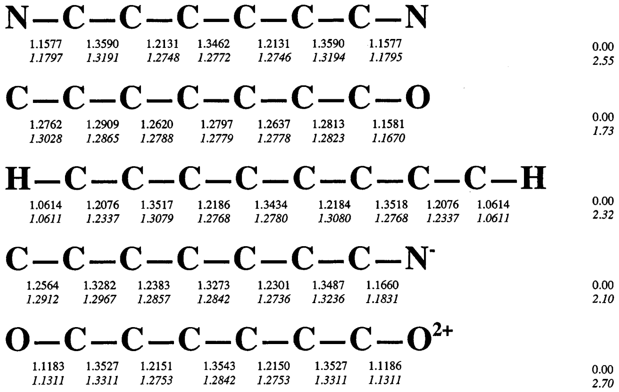


Figure 2. Bond lengths and relative energies for singlet/*triplet* C_6N_2 and isoelectronic species using the B3LYP/ cc-pVTZ theoretical method.

More data exists for the even carbon cluster, C_6N_2, because the geometry is more amenable to computational techniques. Calculations with the same theoretical method used in this study have been reported for both the C_6N_2 and C_8H_2 clusters.[26] The relative energies of the ground singlet and excited triplet states were not included in that previous report. Earlier calculations with smaller basis sets report bond lengths in C_7O as generally cumulenic: 1.287, 1.297, 1.271, 1.286, 1.272, 1.286, and 1.169 Å for the ground singlet state (CCSD/aug.cc-pVDZ//B3LYP/6-31G*)[27] and 1.2942, 1.3000, 1.2747, 1.2883, 1.2764, 1.2884, and 1.1753 Å (BLYP/6-311G**).[24] Our results are in good agreement with these reports. No geometry for the lowest triplet state has been reported. Finally, the most recent study[28] of the C_7N^- ground state using the B3LYP/6-311G* (B3LYP/aug-cc-pVTZ) method reported bond lengths of 1.262 (1.256), 1.330 (1.330), 1.242 (1.238), 1.328 (1.328), 1.233 (1.230), 1.350 (1.349), and 1.169 Å (1.166 Å). The bond lengths in Figure 2 indicate that polyacetylenic bonding is dominant in these clusters. The polyacetylenic bonding effect is least obvious in the structure for C_7O, where there is clearly an alternation in bond lengths, however, the difference is slight.

The results in the lower half of Figure 1 indicate that the inclusion of diffuse functions, the aug-ccpVTZ basis set, has no effect at all on the calculated parameters for C_5N_2; the bond lengths and the relative energies of the two electronic states are unchanged. At least for the symmetric C_nN_2 clusters, this added computational effort is not worthwhile. C_5P_2 and C_5N_2 are not isoelectronic; however, they are analogous clusters. The calculated structural parameters reflect this similarity in the cumulenic bonding. Note that the terminal C−P bond is short in comparison to both a C−P single bond (CH_3P: 1.86 Å) and a C═P double bond (CH_2P: 1.67 Å).[29] The best description for the bond in this cluster is as a strong double bond.

Molecular Orbitals. By definition, all of the C_5N_2-like species have a $^3\Sigma$ ground state and the same electronic configuration, $8\sigma^2\ 9\sigma^2 ... 15\sigma^2\ 1\pi^4\ 2\pi^4\ 3\pi^4\ 4\pi^2$; however, the energy ordering of these orbitals differs among the isoelectronic

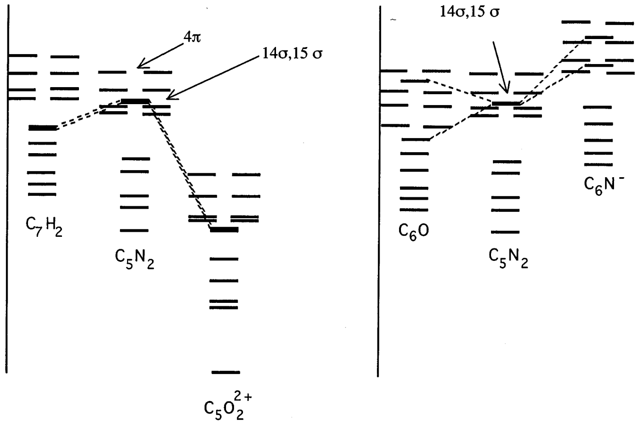


Figure 3. Occupied molecular orbitals for isoelectronic species, compared with those of C_5N_2.

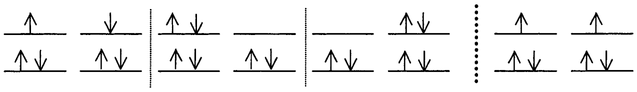
species. The relative orbital energies are shown in Figure 3. In general, the highest occupied orbtials are π-type. However, the similarity is only qualitative. In particular, there are significant variations in the energies of the highest σ orbtials, both with respect to the relative ordering and to the energy spacing between orbitals. Compared to a pure carbon chain, it is expected that the C_5N_2 orbital energies would be stabilized by mixing in orbitals from the heteroatoms and by the symmetry of the cluster. The extent of this stabilization, because of the two terminal heteroatoms, is clear from Figure 1. In C_5N_2, the 14σ and 15σ orbitals are essentially degenerate and are energetically intermediate with respect to the set of four π orbitals. In both C_6O and C_6N^-, this degeneracy is removed. For C_5N_2, the two high-lying σ orbitals are equally stabilized by mixing carbon and nitrogen atomic orbitals to construct the molecular orbitals. In C_6O, the two σ levels split with one increasing and one decreasing in energy. In C_6N^-, both orbitals increase in energy but by different amounts, also removing the degeneracy. In both cases the removal of the degeneracy results from the availability of only a single heteroatom to interact with the carbon chain and the fact that the two σ orbitals are no longer symmetry forbidden from a second-order interaction. The 14σ in C_6O includes a contribution from the oxygen atomic orbitals, whereas the 15σ is purely a function of carbon atomic orbitals. This distinction is not present in C_6N^- where there are nitrogen atomic orbital contributions to both 14σ and 15σ but to a very different extent. There are also significant changes in the energy spacings of the MOs for these two species; the splitting in C_6O is much greater, presumably because of the greater electronegativity of the heteroatom. The negative charge is somewhat delocalized in C_6N^-, and this effect also contributes to an increase in orbital energies relative to C_6O. For both HC_7H and $C_5O_2^{2+}$, the two σ orbitals remain essentially degenerate because of the symmetry but are substantially lowered in energy relative to C_5N_2. For C_7H_2, the addition of a hydrogen 1s component to the MO is more efficient than the mixing of higher order components in $C_5O_2^{2+}$, and the shift in energy for the C_7H_2 σ orbitals, relative to the π orbitals, is greater. The presence of two oxygen heteroatoms, as compared with two hydrogen or nitrogen atoms, along with the charge on the terminal atoms significantly lowers all of the orbital energies in comparison to C_5N_2. The analysis of the MOs indicates that C_5N_2 and its isoelectronic species will have similar excitations and similar transition energies. The latter are expected to be relatively small.

The electronic configuration of the C_6N_2-like species is $8\sigma^2$ $9\sigma^2 ... 17\sigma^2$ $1\pi^4$ $2\pi^4$ $3\pi^4$ $4\pi^4$, and the ground state is $^1\Sigma$. Again, the energy ordering of these orbitals differs among the isoelectronic species. However, the energy ordering and the changes observed in moving through the different isoelectronic species are identical to those just described for the C_5N_2-like species and shown in Figure 3. The additional six electrons, due to the added carbon atom, occupy two additional core σ orbitals and complete the occupation of the highest π orbital. The additional π electrons provide a higher π bond order, but the interactions induced by the terminal atoms and the conclusions remain identical to those observed in C_5N_2. For both series of molecules, the LUMO is a set of π orbitals.

TABLE 1: Vertical Transition Energies to the Lowest Excited State

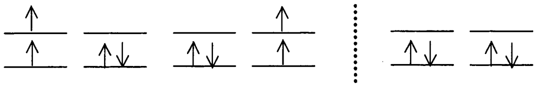
molecule/ion	ΔE, eV	molecule/ion	ΔE, eV
		to the $^1\Sigma$ state	
HC_7H	0.14	NC_5N	0.49
C_6O	0.31	OC_5O^{2+}	0.54
C_6N^-	0.43		
		to the $^3\Sigma$ state	
C_7O	2.01	OC_6O^{2+}	4.27
C_7N^-	3.58	HC_8H	4.72
NC_6N	4.24		

Transition Energies to the Lowest Excited State. Because the transitions involve triplet states and the MOs include relatively close-spaced π orbitals, there is the possibility of error if a single electron configuration is employed in the vertical transition energy calculations. Time-dependent DFT is one possible solution to this problem; however, the method is only defined in the currently available quantum chemistry packages for closed shell systems. The application to open shell systems remains a research topic. An alternative solution is to use a multiconfigurational SCF technique. The most computationally efficient approach is the complete active space method. The $^3\Sigma \rightarrow {}^1\Sigma$ and $^1\Sigma \rightarrow {}^3\Sigma$ vertical transition energies for the two series of clusters, calculated by the multiconfigurational CASSCF method, are shown in Table 1. For the C_5N_2 analogues, energies were obtained at the DFT optimized geometries of the ground states, a CASSCF (2,5)/cc-pVTZ// B3LYP/cc-pVTZ model. The excited states result from configurations in which there are $\pi-\pi$ transitions from the ground-state triplet, and hence, a two-electron−five orbital active space calculation is sufficient to include all important contributions to configuration interaction and obtain the transition energy. This calculation uses 10 electron configurations for triplets and 15 configurations for singlets. Three configurations, involving the 3π and 4π orbitals, dominate the singlet state, and the triplet ground state is described by essentially a single configuration involving the same orbitals.



At this level of calculation, configurations involving the remaining virtual levels do not contribute to any significant extent (<5%, total, for configurations other than those shown above). In the case of the singlet, the configuration with the partially occupied orbitals constitutes approximately 65% of the wave function and the remaining two configurations each contribute approximately 15%. The triplet state is composed of the single configuration shown to the extent of greater than 96%. These observations on the configurations remain valid even if as many as 12 electrons and 12 orbtials are added to the active space. In all cases, the singlet state lies close to the ground state triplet. Moreover, there is little change in geometry upon excitation to the singlet state. All transition energies lie within a small range of approximately 0.5 eV. From the MO point of view, these low transition energies are to be expected, because a spin flip within a π orbtial or to a degenerate π orbital is the only electron displacement required to move to the singlet from the ground state.

For C_6N_2 and its isoelectronic molecules, the excited states also result from configurations in which there are $\pi-\pi$ transitions from the ground state. Here, a four-electron−six orbital active space calculation is required to include all important contributions. This calculation uses 105 electron configurations for both states. Energies were obtained at the DFT optimized geometries of the ground states, a CASSCF (4,6)/cc-pVTZ// B3LYP/cc-pVTZ theoretical model. The closed shell configuration dominates the singlet ground state. This configuration is that one would write for a single determinant representation of the ground electronic state, as shown below. The excited triplet state has two degenerate configurations. The vertical transition energies are significantly greater, 2−4 eV, than those for the five-carbon cluster because in addition to the spin flip, the electron must be promoted to a higher energy orbital. Moreover, the triplet state has a significantly different geometry from the ground state. The values of the transition energies for both series of molecules are consistent with the spacing of the MOs shown in Figure 3. The transition energies shown in Table 1, the vertical excitations, differ from those calculated from the optimized structures as shown in Figures 1 and 2. The latter are adiabatic transition energies between relaxed (optimized) molecules.



Conclusions and Summary

B3LYP/cc-pVTZ density functional calculations have been used to determine the ground-state energies and bonding in C_5N_2 and C_6N_2 and isoelectronic molecules. The odd numbered carbon clusters have triplet ground states and tend to be cumulenic, whereas the even clusters are singlets in the ground state and acetylenic in structure. The transitions between the ground and lowest excited states of different multiplicity are dominated by the $4\pi \rightarrow 5\pi$ excitation and the transition energies for C_5N_2 series lie in a small range near 0.5 eV. The separation between spin states is much greater, 2−4 eV, for the C_6N_2 series of clusters. The presence of the heteroatoms has a direct effect on the ordering of the MOs below the HOMO, but this effect is consistent across the odd and even numbered carbon clusters.

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