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Structure and Stability of Small NaC$_n$, NaC$_n^+$, and NaC$_n^-$ Clusters: A Theoretical Study

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NaC$_n$, NaC$_n^+$, and NaC$_n^-$ ($n = 1-8$) open-chain and cyclic clusters have been studied using the B3LYP method. Predictions for several molecular properties that could help in possible experimental characterization, such as equilibrium geometries, electronic energies, dipole moments, and vibrational frequencies, are provided. NaC$_n$ open-chain clusters are predicted to be linear with $^2\Pi$ lowest-lying states, whereas for both cationic and anionic clusters the lowest-lying state alternates between singlet and triplet. Also, cyclic neutral clusters have doublet lowest-lying states. An even−odd alternation in stability is observed for both cationic and anionic cyclic clusters, whereas no parity effect is observed generally for the corresponding neutrals. Ionization potentials and electron affinities of NaC$_n$ cyclic clusters also exhibit a clear even−odd parity effect. It is generally observed that removing an electron destabilizes the cyclic isomer, whereas adding an electron generally increases the stability of the cyclic species. NaC$_2$ and NaC$_3$ are predicted to have cyclic ground states, whereas most anionic clusters up to $n = 8$ prefer also a cyclic arrangement.

Introduction

Small heteroatom-doped carbon clusters containing second-row elements, C$_n$X, have received much attention in recent years. One of the reasons for this interest is that several binary compounds of general formula C$_n$X, especially containing sulfur, silicon, and phosphorus, have been detected in space.[1−8] Since other small binary compounds containing metallic elements could be interesting in astrochemistry, much effort has been devoted to the theoretical prediction of structural properties of such molecules in order to aid in their identification in astronomical sources. This is the case of small metal carbides such as AlC$_3$, MgC$_3$, NaC$_3$, and CaC$_3$, which have recently been the subject of theoretical studies.[9−12]

Because small heteroatom-doped carbon clusters are also the basic structural units of new materials with interesting potential applications, it is also important to have a knowledge of possible systematic trends of their stability and structural properties as a function of the cluster size; that is, in terms of the number of carbon atoms. Several theoretical works studying the properties of heteroatom-doped carbon clusters containing second-row elements have been published recently. Much of the interest has focused on nonmetallic elements, and therefore neutral and charged C$_n$S,[13] C$_n$Si,[14−16] C$_n$P,[17] and C$_n$Cl[18] clusters have been studied. Heteroatom-doped carbon clusters containing metallic elements, such as AlC$_n$[19] or MgC$_n$,[20] have also been studied in past years. Quite recently a systematic analysis of the properties of carbon clusters doped with second-row elements has appeared.[21] Most of these theoretical studies have considered only the linear (or in general open-chain) isomers of the clusters. However, systematic studies of cyclic isomers (considering their relative stability compared with the linear ones) have been carried out for MgC$_n$/MgC$_n^+$/MgC$_n^-$ compounds.[22] The interest in cyclic clusters is not merely academic, since cyclic ground states are found for many of these compounds.

The aim of the present work is to provide a theoretical study of the NaC$_n$, NaC$_n^+$, and NaC$_n^-$ ($n = 1-8$) open-chain and cyclic clusters. It is hoped that the reported equilibrium geometries, as well as other spectroscopic data, could help in their experimental detection. The systematic behavior of their properties, as functions of the size of the cluster, will also be discussed.

Computational Methods

We have employed the same theoretical approach as was used in our previous studies on second-row heteroatom-doped carbon clusters,[18−20,22] and therefore the density functional theory (DFT) formalism has been used in our theoretical calculations. We have employed the B3LYP exchange-correlation functional,[23,24] which has been shown by other authors to be well adapted to medium-sized impurity-containing carbon clusters.[25] This consists of the Lee−Yang−Parr[26] correlation functional in conjunction with a hybrid exchange functional first proposed by Becke.[27] The latter is a linear combination of local density approximation, Becke's gradient correction,[28] and the Hartree−Fock exchange energy based on Kohn−Sham[29] orbitals. In these calculations we used both the triple split-valence d-polarized 6-311G(d) basis set[30] and the 6-311+G(d) basis set, which also includes diffuse functions. The same level of theory has been employed by Li and Tang[21] in their general study of C$_n$X clusters.

An analysis of the harmonic vibrational frequencies was carried out for all structures. This allows an estimate of the zero-point vibrational energy (ZPVE) correction for each structure, as well as to assess the nature of the stationary points and therefore characterize if they are true minima on the respective potential surface.

All calculations reported in this work were carried out with the Gaussian 98 program package.[31]

Results and Discussion

NaC$_n$ Open-Chain Clusters. NaC$_n$ linear isomers have already been considered in a very interesting previous general work on C$_n$X compounds,[21] reporting their electronic ground state as well as the systematic behavior as a function of the cluster size of some properties, such as stabilities, ionization

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TABLE 1: Electronic Energies, $\langle S^2\rangle$ Values, Vibrational Frequencies, Binding Energies (for the ground states), Dipole Moments, Rotational Constants, and Relative Energies for Linear NaC_n Clusters with the B3LYP/6-311G(d) (first line) and B3LYP/6-311+G(d) (second line) Methods

isomer	state	$-E$ (a.u.)	$\langle S^2\rangle$	vibrational frequencies (cm^{-1})	binding energies (eV)	μ (D)	rotational constants (GHz)	ΔE (kcal mol^{-1})
NaC	$^2\Pi$	200.172727	0.9071	326		4.50	10.599	22.36
		200.175446	0.8694	333		5.35	10.675	22.63
	$^4\Sigma^-$	200.208584	3.7529	421	1.77	6.89	12.724	0.00
		200.211693	3.7531	415	1.81	7.48	12.625	0.00
NaC_2	$^2\Pi$	238.339004	0.7522	110/248/373/1767	9.11	3.57	4.657	0.00
		238.343398	0.7522	132/263/368/1760	9.15	3.61	4.621	0.00
	$^4\Pi$	238.223386	3.7534	13i/6i/8/1692		0.08	0.912	71.42
		238.224849	3.7541	4/14/28/1689		0.01	0.608	73.23
NaC_3	$^2\Pi$	276.433090	0.7663	73/99/338/344/421/1235/1849	15.47	12.29	2.350	0.00
		276.437851	0.7664	73/100/335/342/422/1233/1846	15.49	12.76	2.336	0.00
	$^4\Sigma^-$	276.371279	3.8124	96(2)/356/454(2)/1280/1644		8.91	2.385	38.82
		276.374638	3.8119	92(2)/348/443(2)/1275/1644		9.25	2.371	39.65
NaC_4	$^2\Pi$	314.537125	0.7618	73/75/211/257/321/528/588/965/1818/2116	22.06	14.25	1.365	0.00
		314.542179	0.7618	71/74/222/255/312/510/563/963/1816/2117	22.06	14.70	1.359	0.00
	$^4\Pi$	314.434865	3.7781	76/97/213/284/319/400/528/908/1206/2065		13.49	1.327	62.95
		314.439943	3.7786	74/105/216/282/311/390/505/909/1203/2072		14.16	1.322	62.96
NaC_5	$^2\Pi$	352.623758	0.7766	58/62/175/180/305/361/393/641/765/813/1488/1929/1978	28.20	15.69	0.866	0.00
		352.629094	0.7765	57/62/172/179/298/357/386/597/732/811/1488/1924/1975	28.17	16.18	0.864	0.00
	$^4\Sigma^-$	352.563264	3.8559	62(2)/190(2)/314/400(2)/651(2)/820/1541/1726/1928		10.68	0.872	37.66
		352.566859	3.8547	62(2)/187(2)/307/396(2)/625(2)/818/1537/1729/1924		10.95	0.870	38.79
NaC_6	$^2\Pi$	390.721434	0.7687	51(2)/138/146/265/287/291/485/524/694/900/919/1241/1886/2058/2164	34.59	17.42	0.584	0.00
		390.727018	0.7685	51(2)/140/146/269/284/285/474/512/693/849/863/1240/1883/2056/2166	34.54	17.91	0.583	0.00
	$^4\Pi$	390.642893	3.7960	32i/51/69/140/269/286/292/356/491/685/769/877/1169/1531/1781/2119		17.08	0.577	47.55
		390.648502	3.7962	30/51/68/140/268/284/285/323/479/683/700/815/1171/1531/1778/2123		17.67	0.576	47.51
NaC_7	$^2\Pi$	428.807792	0.7863	43(2)/114/115/222/226/281/375/390/563/614/652/1103/1120/1190/1603/1864/2018/2098	40.71	18.73	0.413	0.00
		428.813584	0.7861	42/43/113/114/221/222/276/367/378/536/612/630/1102/1057/1126/1604/1862/2016/2096	40.63	19.26	0.412	0.00
	$^4\Sigma^-$	428.750868	3.8971	44(2)/116(2)/236(2)/287/347(2)/557(2)/616/1107/1120(2)/1640/1667/1988/2016		12.47	0.414	35.04
		428.754895	3.8956	44(2)/115(2)/232(2)/283/324(2)/538(2)/614/1076(2)/1105/1643/1663/1985/2015		12.71	0.414	36.18
NaC_8	$^2\Pi$	466.903058	0.7751	36/37/93/95/180/193/271/298/307/471/501/548/721/730/978/1387/1428/1429/1898/2055/2105/2180	47.01	20.33	0.302	0.00
		466.909086	0.7749	36/37/93/94/181/191/267/294/298/448/480/544/667/668/977/1308/1321/1386/1889/2052/2107/2178	46.92	20.88	0.302	0.00
	$^4\Pi$	466.839938	3.8114	34/36/81/94/150/184/271/299/326/368/480/544/632/711/960/1354/1386/1392/1623/1812/1928/2105		20.25	0.300	37.94
		466.845985	3.8112	33/36/73/94/136/183/267/292/307/322/457/542/580/653/959/1240/1271/1387/1622/1811/1927/2109		20.84	0.300	37.84

potentials, or electron affinities. Therefore, we should present only the information that may serve to complement such information and to guide experimental work on these compounds, reporting their molecular properties for the lowest-lying states of each multiplicity (doublet and quartet for the neutral species). Only a brief discussion of the more relevant structural characteristics of these compounds will be presented.

We have searched for open-chain isomers on both the doublet and quartet NaC_n potential surfaces. We have collected in Table 1 some of the most interesting properties, such as harmonic vibrational frequencies, rotational constants, dipole moments, binding (fragmentation) energies, and absolute and relative energies, for the lowest-lying open-chain NaC_n species. In all cases, linear geometries were found. Only the quartet state for NaC_6 shows an imaginary frequency at the B3LYP/6-311G(d) level, but at the B3LYP/6-311+G(d) level it is shown to be a true minimum. For all NaC_n clusters, the lowest-lying doublet state is $^2\Pi$ (corresponding to an electronic configuration ... $\pi^4\sigma^2\pi^1$ for n-odd clusters, and ... $\pi^4\sigma^2\pi^3$ for n-even clusters). The lowest-lying quartet state is $^4\Sigma^-$ for n odd and $^4\Pi$ for n even. As can be seen in Table 1, for $^2\Pi$ and $^4\Pi$ electronic states the B3LYP method (as well as single-reference based methods such as HF or MP2) provides nondegenerate π vibrational frequencies.

Only in the case of the doublet state for the first member of the series, NaC, does the $\langle S^2\rangle$ value deviate significantly from that corresponding to the pure spin value. Therefore, spin contamination does not seem in general to be a problem for studying NaC_n open-shell states with the B3LYP method.

Our results for the predicted ground states are basically in agreement with those of Li and Tang,[21] except for NaC_2, since these authors report a $^2\Sigma^+$ ground state, although with two imaginary frequencies. Since we are interested in predicting properties for structures that could be eventually characterized by experimental studies, we have preferred to propose the $^2\Pi$ state as the ground state, since this is a true minimum on the potential surface. Another minor difference is that Li and Tang[21] report an imaginary frequency for the $^2\Pi$ state of NaC_6, but in our calculations with both basis sets we obtained only real frequencies for this species.

It is readily seen in Table 1 that all NaC_n clusters have $^2\Pi$ ground states (with quartet states lying in general quite high in

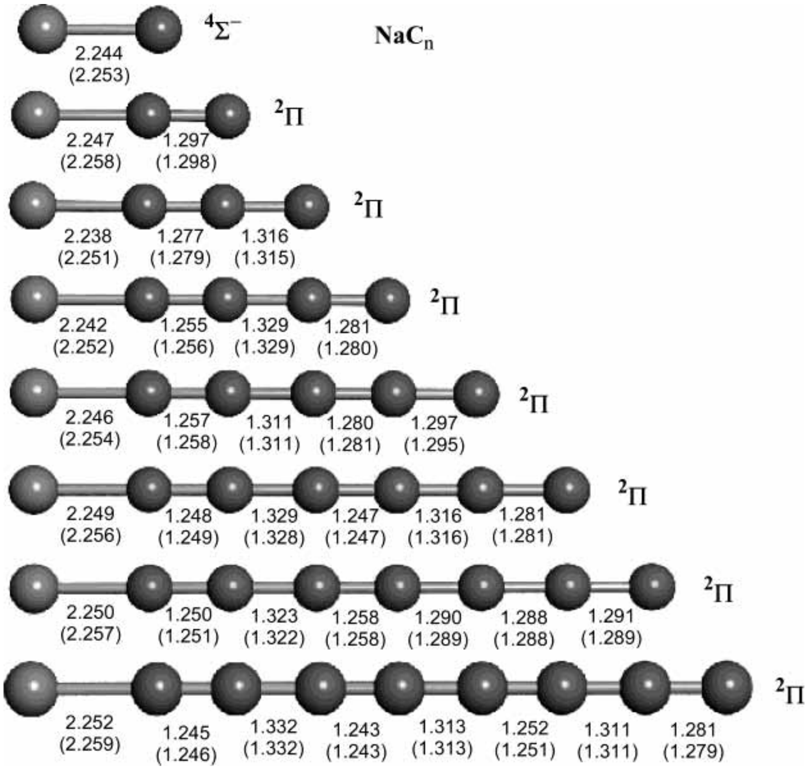

Figure 1. Equilibrium geometries of open-chain NaC_n ($n = 1-8$) clusters at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) (in parentheses) levels of theory. Distances are given in angstroms and angles in degrees.

energy), with the only exception being the first member of the series, NaC, which has a $^4\Sigma^-$ ground state. Previous theoretical studies[32,33] on NaC also agree in that the ground state is $^4\Sigma^-$, with a $^2\Pi$ state lying about 27 kcal/mol higher in energy. This energy difference between the ground state and the first excited state is in reasonable agreement with our own prediction (22 kcal/mol). The predicted bond distance for NaC in our calculations (2.253 Å) is also in reasonable agreement with the bond length obtained in the multireference computations of Kalcher and Sax (2.266 Å).[33]

The optimized geometries at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) levels of theory for the most stable structures are shown in Figure 1. It can be seen that the inclusion of diffuse functions in the basis set has only a minor effect on the geometrical parameters of the neutral clusters, affecting only slightly to the Na−C bond distance. The relative energies and binding energies computed with both basis sets are also quite close, and therefore it can be concluded that diffuse functions are not essential for the description of neutral NaC_n species.

As can be seen in Figure 1 the Na−C bond distance is rather similar for all NaC_n clusters. The C−C bond distances are within the range 1.24−1.33 Å, typical of cumulene structures with moderately strong double bonds which can be formulated as

$$\mathrm{Na}-\dot{\mathrm{C}}(=\mathrm{C})_{n-2}=\mathrm{C}:$$

Nevertheless, the clear alternation in C−C distances suggests that, as in the cases of open-chain AlC_n[19] and MgC_n,[20] there is a substantial contribution of polyacetylenic valence-bond structures with alternating triple and single C−C bonds, which can be illustrated as

$$\mathrm{Na}-\mathrm{C}(\equiv\mathrm{C})_{(n-1)/2}-\dot{\mathrm{C}}: \quad n \text{ odd}$$

$$\mathrm{Na}-\mathrm{C}(\equiv\mathrm{C})_{(n/2)-1}-\dot{\mathrm{C}}=\mathrm{C}: \quad n \text{ even}$$

This overall picture is compatible with the population analysis, which shows that the unpaired electron is mainly distributed among C_1 and the terminal carbon atom (n odd), or among C_1 and C $_{n-1}$ carbon atoms (n even). The population analysis also shows that the Na−C bond has a high ionic character, because there is a substantial charge transfer from Na to C, although this is in part compensated by a certain degree of p_C-p_{Na} back-donation. This delocalization of the unpaired π electron toward the sodium atom undoubtedly contributes to the linearity of these species.

As a consequence of the large ionic character of the Na−C bond, very large dipole moments are found for the ground states of NaC_n clusters, and this might help in their possible experimental detection.

Given the high ionic character of NaC_n clusters, the linear species can be related to the C_n^- structures, since essentially an electron is transferred from sodium to the C_n moiety. In fact C_n^- linear structures are found to have $^2\Pi$ ground states,[34,35] at least for values of n relevant to the present work, with the only exception being NaC_2, which has a $^2\Sigma_g^+$ ground state. Therefore, good agreement with the ground states of linear NaC_n structures is found, except for NaC_2, since we have found a $^2\Pi$ ground state for this species. As mentioned earlier, the corresponding $^2\Sigma^+$ state was found to lie slightly lower in energy than the $^2\Pi$, but it has two imaginary frequencies. When we tried to optimize the geometry following the normal mode associated to the degenerate π imaginary frequencies, we reached a cyclic structure (reported below). Therefore, according to our results, the $^2\Sigma^+$ state does not represent a true minimum on the NaC_2 potential surface, and consequently we have chosen the $^2\Pi$ state as the candidate for the ground state of linear NaC_2.

In Figure 2 we have represented the rotational constants for NaC_n clusters and their cationic and anionic derivatives as a function of the number of carbon atoms. Obviously, the rotational constants regularly decrease as the size of the molecule

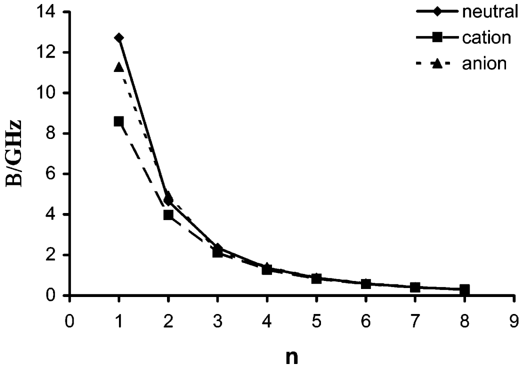

Figure 2. Rotational constants (GHz) for the linear NaC_n, NaC_n^+, and NaC_n^- clusters vs the number of carbon atoms.

increases. It is also observed that for larger clusters the rotational constants are very similar, and even are very close for the neutral and charged species. Of course this is somewhat artificially enhanced in Figure 2 because the scale is not the best one for the larger clusters. However, this clearly reflects the fact that the substitution by a heteroatom (or if the molecule is charged or not) has only a very small effect on the rotational constant.

To the best of our knowledge there is only one experimental study reporting the rotational spectrum of NaC.[36] The rotational constant obtained from this spectrum is 12.86313 GHz, which is in reasonable agreement with our theoretical value (as well as the bond distance derived form the rotational constant, namely 2.232 Å).

NaC_n^+ Open-Chain Clusters. The optimized geometries for the lowest-lying states of open-chain NaC_n^+ clusters are shown in Figure 3, whereas their corresponding properties are given in Table 2. The dipole moments are computed taking the center of mass as the origin, and this applies to all charged species reported in this work.

Only in the case of triplet NaC_2^+ is a nonlinear structure found with the smallest basis set, but with the 6-311+G(d) basis set this state is also shown to be linear. Therefore, it seems safe to predict that all these cationic clusters are linear. The first two members of the series, NaC^+ and NaC_2^+, have $^3\Pi$ ground states, whereas for the rest of the clusters the ground state is alternatively $^1\Sigma$ (corresponding to an electronic configuration ... $\pi^4\sigma^2$) or $^3\Sigma^-$ (corresponding to ... $\pi^4\sigma^2\pi^2$, and therefore preferred over the $^1\Delta$ state). This agrees exactly with the previous predictions of Li and Tang[21] on linear NaC_n^+ clusters.

Again the high ionic character of the NaC_n^+ species allows a comparison with the C_n structures. In both cases *n*-odd clusters ($n = 3, 5, 7$) have $^1\Sigma^+$ ground states, whereas *n*-even clusters ($n = 4, 6, 8$) all possess $^3\Sigma^-$ ground states. The only discrepancy between the NaC_2 and C_n series occurs again for $n = 2$, since for C_2[33] a $^1\Sigma_g^+$ ground state is found whereas the singlet state of NaC_2 lies much higher in energy (about 34 kcal/mol) than the proposed $^3\Pi$ ground state.

The positive charge, as expected, is mainly located at the sodium atom, which has atomic charges around +0.92e for all compounds. As a consequence, the Na−C bond is considerably weakened in all NaC_n^+ clusters with respect to their neutral counterparts (and this is clearly reflected in the much longer Na−C bond distances found for NaC_n^+ clusters), since now the bonding is essentially of a dative nature from carbon to sodium. For example, the first member of the series can be represented by the following valence-bond picture:

$$\overset{+}{\mathrm{Na}} \leftarrow : \overset{\bullet}{\underset{\bullet}{\mathrm{C}}}$$

The ability of carbon to donate part of its electronic density toward the sodium atom is higher for the larger clusters, and therefore the Na−C bond distance is shortened as the number of carbon atoms increases.

NaC_n^- Open-Chain Clusters. The geometrical parameters for the lowest-lying states of NaC_n^- anions are shown in Figure

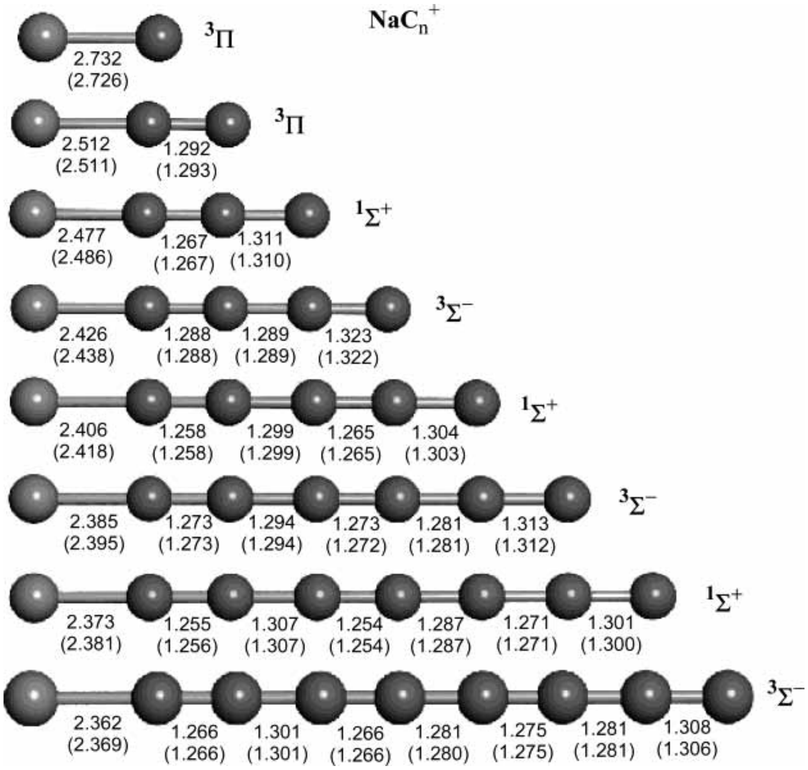

Figure 3. Equilibrium geometries of open-chain NaC_n^+ ($n = 1-8$) clusters at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) (in parentheses) levels of theory. Distances are given in angstroms and angles in degrees.

TABLE 2: Electronic Energies, ⟨S²⟩ Values, Vibrational Frequencies, Binding Energies (for the ground states), Dipole Moments, Rotational Constants, and Relative Energies for Linear NaC_n^+ Clusters with the B3LYP/6-311G(d) (first line) and B3LYP/6-311+G(d) (second line) Methods

isomer	state	$-E$ (a.u.)	$\langle S^2 \rangle$	vibrational frequencies (cm^{-1})	binding energies (eV)	μ (D)	rotational constants (GHz)	ΔE (kcal mol^{-1})
NaC^+	$^1\Sigma^+$	199.904931		237		3.21	8.682	31.59
		199.905344		239		3.20	8.749	31.58
	$^3\Pi$	199.955148	2.0027	182	0.31	3.51	8.590	0.00
		199.955536	2.0029	183	0.28	3.49	8.627	0.00
NaC_2^+	$^1\Sigma^+$	237.990890		115/433(2)/1908		6.10	3.533	34.55
		237.991670		117/437(2)/1904		6.07	3.550	34.52
	$^3A'$	238.044251	2.0083	173/212/1755	6.53	3.09	3.976	0.00
	$^3\Pi$	238.145089	2.0085	46/185/214/1753	6.20	4.82	3.977	0.00
NaC_3^+	$^1\Sigma^+$	276.191848		79(2)/217/261(2)/1250/2178	14.33	8.04	2.123	0.00
		276.193356		82(2)/216/254(2)/1249/2176	14.26	8.13	2.114	0.00
	$^3\Pi$	276.122948	2.0601	110/118/240/350/416/1283/1867		5.29	2.176	43.32
		276.124048	2.0601	110/120/238/341/409/1281/1866		5.33	2.168	43.57
NaC_4^+	$^1\Delta$	314.225196		72/82/186/224/236/463/537/954/1633/2138		9.99	1.268	18.49
		314.227181		72/79/187/219/237/432/504/953/1631/2135		10.13	1.263	18.46
	$^3\Sigma^-$	314.254400	2.0340	75(2)/183(2)/225/481(2)/957/1621/2120	19.82	9.90	1.271	0.00
		314.256344	2.0341	75(2)/187(2)/220/448(2)/957/1621/2121	19.74	10.04	1.266	0.00
NaC_5^+	$^1\Sigma^+$	352.381593		63(2)/159(2)/228/339(2)/746(2)/813/1503/2078/2273	27.04	11.28	0.834	0.00
		352.383805		62(2)/156(2)/221/324(2)/663(2)/812/1502/2076/2271	26.90	11.44	0.831	0.00
	$^3\Pi$	352.320014	2.0987	67/68/195/206/241/380/385/642/751/818/1558/1942/2020		7.59	0.841	38.30
		352.321573	2.0987	66/67/188/203/234/365/372/549/670/817/1556/1942/2018		7.64	0.839	38.70
NaC_6^+	$^1\Delta$	390.427912		50/55/125/146/228/253/271/464/490/689/872/969/1248/1767/2061/2174		13.27	0.566	14.15
		390.430557		50/54/124/142/220/248/262/431/463/687/709/828/1247/1766/2060/2175		13.46	0.565	14.13
	$^3\Sigma^-$	390.450090	2.0545	52(2)/129(2)/229/251(2)/462(2)/690/896(2)/1246/1758/2028/2162	32.65	13.05	0.567	0.00
		390.452689	2.0544	52(2)/129(2)/222/246(2)/433(2)/688/734(2)/1245/1757/2028/2164	32.54	13.24	0.566	0.00
NaC_7^+	$^1\Sigma^+$	428.566585		44(2)/111(2)/205(2)/222/365(2)/607/635(2)/1123/1232(2)/1607/2032/2226/2252	39.52	14.12	0.406	0.00
		428.569466		44(2)/109(2)/202(2)/223/344(2)/594(2)/606/1047(2)/1122/1607/2030/2225/2251	39.39	14.32	0.406	0.00
	$^3\Pi$	428.511040	2.1288	46/47/121/122/237/239/245/369/387/572/635/607/1123/1181/1244/1671/1864/2046/2110		9.82	0.407	34.29
		428.513141	2.1287	45/46/118/120/231(2)/240/351/367/518/584/606/11003/1068/1122/1669/1864/2045/2110		9.86	0.407	34.76
NaC_8^+	$^1\Delta$	466.621477		37/39/90/97/161/187/227/292/296/463/472/538/692/778/989/1410/1475/1545/1807/2059/2111/2167		16.28	0.298	11.75
		466.624742		36/38/90/95/164/184/221/280/281/427/444/536/604/689/988/1228/1287/1410/1806/2059/2113/2168		16.51	0.298	11.75
	$^3\Sigma^-$	466.639642	2.0727	38(2)/94(2)/172(2)/228/289(2)/455(2)/538/703(2)/988/1408/1477(2)/1793/2033/2083/2159	45.28	15.90	0.298	0.00
		466.642864	2.0723	37(2)/92(2)/170(2)/223/278(2)/423(2)/537/609(2)/988/1408/1218(2)/1793/2034/2085/2160	45.13	16.12	0.298	0.00

4, whereas their corresponding properties are given in Table 3. In this case we have not tabulated the results obtained with the 6-311G(d) basis set, since for most properties basis sets without diffuse functions are not very reliable. In fact, even though inclusion of diffuse functions has only a minor effect on the geometrical parameters and vibrational frequencies of NaC_3^- clusters, it has a significant influence on dipole moments, with variations up to nearly 2D between 6-311G(d) and 6-311+G(d) values. The effect of diffuse functions on relative energies is also relatively high, especially in some cases where differences of more than 5 kcal/mol ($n = 4$) are found.

According to our results n-odd compounds have triplet ground states, whereas n-even clusters have singlet ground states. Our results are in agreement with those of Li and Tang.[21] We find that the ground state of NaC_3^- deviates slightly from linearity (the corresponding linear $^3\Pi$ state has an imaginary frequency, as shown also in the calculations by Li and Tang[21]). In the case of NaC_4^-, the B3LYP/6-311+G(d) level shows an imaginary degenerate π frequency, and optimization in C_s symmetry leads to the NaC_4^- cyclic isomer. However, as pointed out also by Li and Tang,[21] a true minimum with all its frequencies real is obtained with the 6-311G(d) basis set.

Singlet states are favored for n-even clusters, as a consequence of the ... $\pi^4\sigma^2\pi^4$ electronic configuration obtained upon addition of an electron to the neutral compound. The lowest-lying triplet state (corresponding to $\pi^4\sigma^2\pi^3\sigma^1$ electronic configuration) lies always more than 14 kcal/mol higher in energy than the singlet state. In the case of n-odd clusters the ground state is always a triplet (although the energy gap between the lowest-lying singlet and triplet states is clearly reduced as the number of carbon atoms increases), but there is a competition between $^3\Sigma^-$ (...$\pi^4\sigma^2\pi^1\pi^1$ electronic configuration) and $^3\Pi$ (...$\pi^4\sigma^2\pi^1\sigma^1$) states. $^3\Sigma^-$ ground states are found for $n = 1$ and $n = 7$, whereas $n = 3$ and $n = 5$ have $^3\Pi$ ground states (the $^3A''$ state obtained for NaC_3^- derives from a $^3\Pi$ state with an imaginary frequency).

In the case of NaC_n^- clusters, comparison can be established with the C_n^{2-} species, given the high ionic character of the former. A relatively good correlation is found again between the ground states in both cases, since singlet ($^1\Sigma_g^+$) states are

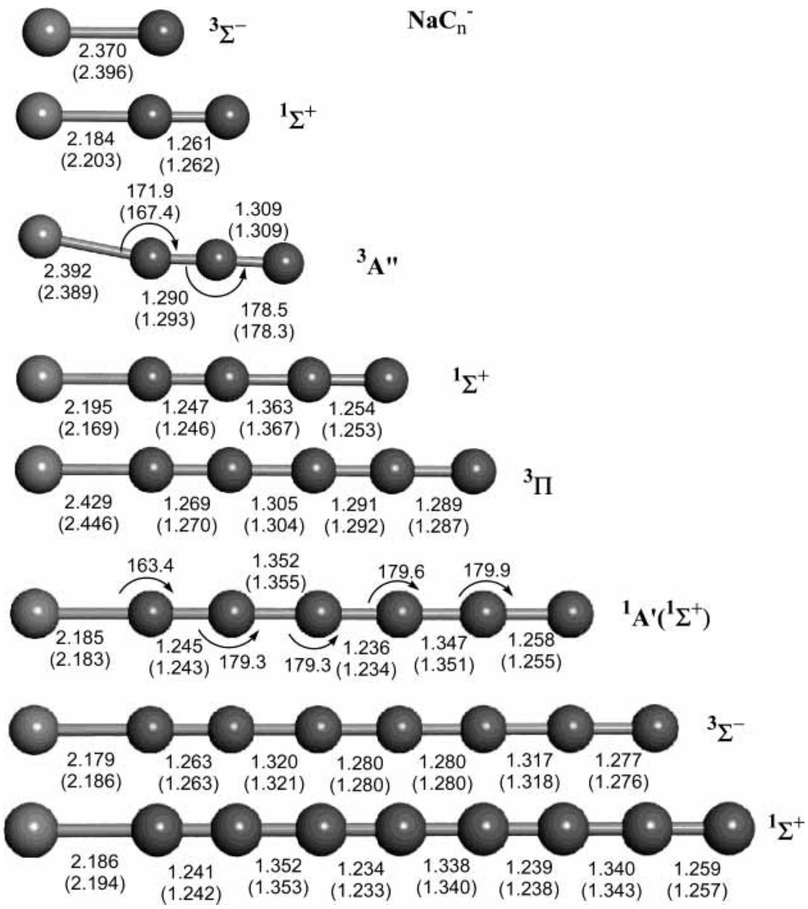

Figure 4. Equilibrium geometries of open-chain NaC$_n^-$ ($n = 1-8$) clusters at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) (in parentheses) levels of theory. Distances are given in angstroms and angles in degrees.

TABLE 3: Electronic Energies, $\langle S^2\rangle$ Values, Vibrational Frequencies, Binding Energies (for the ground states), Dipole Moments, Rotational Constants, and Relative Energies for Linear NaC$_n^-$ Clusters with the B3LYP/6-311+G(d) Method

isomer	state	$-E$ (a.u.)	$\langle S^2\rangle$	vibrational frequencies (cm^{-1})	binding energies (eV)	μ (D)	rotational constants (GHz)	ΔE (kcal mol^{-1})
NaC	$^1\Delta$	200.174982		464		2.70	11.167	42.71
	$^3\Sigma^-$	200.242979	2.8532	319	2.09	1.46	11.172	0.00
NaC$_2^-$	$^1\Sigma^+$	238.405922		74(2)/383/1866	10.28	10.68	4.866	0.00
	$^3\Pi$	238.380191	2.0023	134/231/270/1744		2.21	4.207	16.12
NaC$_3^-$	$^1\Delta$	276.437533		115/166/347/374/534/1231/1818		8.04	2.355	28.39
	$^3A''$	276.481442	2.0192	81/231/319/376/1213/1782	16.12	1.05	870.911/2.209/2.203	0.00
NaC$_4^-$	$^1\Sigma^+$	314.613325		139i(2)/196(2)/353/507(2)/938/1937/2100	23.42	18.30	1.395	0.00
	$^3\Pi$	314.590029	2.0110	66/69/217/248/263/501/544/945/1797/2119		2.42	1.272	14.66
NaC$_5^-$	$^1\Delta$	352.652539		64/69/197/215/321/379/455/640/753/804/1489/1885/1920		14.31	0.870	17.45
	$^3\Pi$	352.679963	2.0280	54/60/169/185/203/353/389/507/660/792/1485/1898/1943	29.00	2.80	0.817	0.00
NaC$_6^-$	$^1\Sigma^+$	390.815782		31(2)/130(2)/285(2)/315/526(2)/686/875(2)/1200/1955/2096	36.36	22.57	0.588	0.00
	$^3\Pi$	390.780588	2.0169	43/44/133/136/194/272/279/455/484/672/709/728/1230/1873/2043/2185		3.14	0.227	21.13
NaC$_7^-$	$^1A'$	428.869784		23/82/90/165/211/310/322/400/441/478/541/576/677/1078/1601/1811/1983/2052		11.10	12.447/0.485/0.466	4.52
	$^3\Sigma^-$	428.879270	2.0835	44(2)/125(2)/243(2)/302/412(2)/580(2)/614/1062(2)/1079/1604/1685/1932/1979	41.85	23.05	0.4236	0.00
NaC$_8^-$	$^1\Sigma^+$	447.011252		32(2)/88(2)/190(2)/277/303(2)/504(2)/546/690(2)/953/1317(2)/1340/1973/2054/2191/2207	49.14	26.60	0.303	0.00
	$^3A'$	466.966805	2.0207	33/67/84/170/173/200/274/294/408/436/463/467/514/713/735/967/1384/1871/2020/2082/2136		1.40	200.732/0.296/0.295	24.59

found for n-even C$_n$ clusters, whereas triplet ($^3\Sigma_g^-$) states are predicted for n-odd C$_n$ species.[32]

Concerning the geometrical parameters, it can be seen in Figure 4 that the Na−C bond distances are slightly shortened compared with their neutral counterparts for n-even clusters with $^1\Sigma^+$ ground states. This effect might be ascribed to the enhanced possibility of π-donation toward sodium (the π system is fully occupied) in these clusters. On the other hand, in the case of n-odd clusters in general a lengthening of the Na−C distance is found, especially for those systems with $^3\Pi$ ground states.

TABLE 4: Electronic Energies, $\langle S^2\rangle$ Values, Vibrational Frequencies, Binding Energies (for the ground states), Dipole Moments, Rotational Constants, and Relative Energies for Cyclic NaC_n Clusters with the B3LYP/6-311G(d) (first line) and B3LYP/6-311+G(d) (second line) Methods

isomer	state	$-E$ (a.u.)	$\langle S^2\rangle$	vibrational frequencies (cm^{-1})	binding energies (eV)	μ (D)	rotational constants (GHz)	ΔE (kcal mol^{-1})
NaC_2	$^2A_1$	238.362421	0.7614	236/372/1826	9.75	7.59	52.632/8.292/7.163	0.00
		238.364539	0.7614	232/368/1823	9.73	7.81	52.611/8.248/7.130	0.00
	$^4A_2$	238.202453	3.7593	336/341/1048		6.08	39.409/8.154/6.756	99.36
		238.204830	3.7602	321/340/1049		6.41	39.517/8.132/6.744	99.20
NaC_3	$^2B_2$	276.434268	0.7674	140/188/302/476/1199/1728	15.52	7.68	12.533/7.069/4.520	0.00
		276.437465	0.7673	135/206/297/472/1198/1732	15.50	7.93	12.527/7.019/4.498	0.00
	$^4A_2$	276.361436	3.8177	61i/300/429/531/1161/1500		8.23	12.282/7.045/4.477	45.54
		276.364515	3.8178	54i/296/428/527/1161/1503		8.41	12.282/7.010/4.463	45.60
NaC_4	$^2A_2$	314.531292	0.7589	89/141/204/323/384/524/949/1751/2075	21.93	7.09	6.682/5.203/2.295	0.00
		314.535009	0.7590	82/154/201/322/393/528/947/1751/2076	21.89	7.29	6.632/5.190/2.911	0.00
	$^4A''$	314.440550	3.7834	160/188/205/296/379/523/990/1330/1788		5.27	6.120/5.751/2.965	56.11
		314.443658	3.7834	156/189/202/295/385/519/989/1328/1787		5.51	6.114/5.715/2.954	62.96
NaC_5	$^2A_1$	352.614555	0.7743	115/127/136/235/256/351/377/526/873/1436/1880/1902	28.01	4.79	6.383/3.005/2.043	0.00
		352.618336	0.7740	102/130/131/235/261/366/376/519/866/1436/1883/1903	27.93	5.02	6.393/2.965/2.026	0.00
	$^4A_2$	352.545275	3.8123	99/109/212/263/364/455/477/580/987/1289/1673/1690		4.35	4.489/4.098/2.142	43.45
		352.548256	3.8117	97/108/208/259/365/450/472/575/987/1287/1674/1691		4.48	4.469/4.092/2.136	43.93
NaC_6	$^2A_1$	390.696138	0.7778	58/81/143/198/239/250/427/448/521/684/811/1254/1843/1981/2119	33.97	2.70	5.606/1.944/1.444	0.00
		390.699837	0.7759	56i/60/126/206/240/243/419/468/508/524/785/1245/1840/1989/2128	33.87	3.22	5.811/1.836/1.395	0.00
	$^4A_2$	390.646560	3.8097	98/109/183/221/253/264/315/494/578/627/912/1183/1496/1792/1873		3.49	3.310/2.848/1.531	30.17
		390.649817	3.8092	96/108/182/223/249/257/322/490/575/619/911/1182/1496/1793/1875		3.62	3.317/2.834/1.528	30.81
NaC_7	$^2A'$	428.778044	0.7934	22/33/62/120/152/168/210/267/336/341/491/508/785/1106/1570/1804/1904/2003	40.07	0.80	4.171/1.471/1.088	0.00
	$^2B_2$	428.783469	0.7864	78i/39/70/180/190/227/270/331/381/382/517/548/614/1081/1575/1826/1955/2072	39.94	5.72	6.021/0.970/0.835	0.00
	$^4A''$	428.728470	3.8309	73/99/124/150/211/244/334/375/413/449/465/580/857/1133/1407/1717/1816/1886		2.29	2.869/1.854/1.126	31.76
		428.731922	3.8301	71/99/124/153/206/240/337/384/410/447/474/580/856/1132/1403/1718/1815/1888		2.41	2.855/1.851/1.123	32.46
NaC_8	$^2B_2$	466.865439	0.7711	66/69/96/152/182/190/221/245/277/358/392/406/439/463/807/1049/1398/1888/1979/2065/2089	46.18	0.92	1.973/1.472/0.843	0.00
		466.869224	0.7706	66/24/97/154/180/172/227/238/273/349/379/410/450/462/808/1049/1398/1885/1976/2063/2087	46.01	1.12	1.945/1.475/0.839	0.00
	$^4B_1$	466.824195	3.8161	63/70/103/150/205/244/255/286/323/388/400/546/548/568/815/1038/1323/1516/1811/1859/2080		1.82	1.911/1.498/0.840	25.46
		466.828114	3.8157	61/70/103/152/203/240/258/283/318/355/404/544/551/566/815/1037/1322/1515/1811/1860/2078		2.04	1.891/1.502/0.837	25.51

Our results can be used to compute the incremental binding energies for the NaC_n, NaC_n^+, and NaC_n^- open-chain clusters, as well as the ionization potentials and electron affinities for the NaC_n clusters. However, we will not discuss them in detail because the recent paper by Li and Tang[21] has addressed the parity alternation effects on these properties for C_nX clusters, including those containing sodium. Therefore, we will focus on the cyclic clusters.

NaC_n Cyclic Clusters. The main properties of the NaC_n cyclic clusters are collected in Table 4. In most cases the reported structures have all their frequencies real, thus confirming that they are true minima on the respective potential surface. Only for the quartet lowest-lying state of NaC_3 ($^4A_2$) is an imaginary frequency found. Our attempts to obtain a true minimum for this structure in C_s symmetry, following the normal mode associated to the imaginary frequency, led to the linear NaCCC structure ($^4\Sigma$). In the case of the doublet states of NaC_6 and NaC_7, we obtained an imaginary frequency with the 6-311+G(d) basis set, whereas the 6-311G(d) basis set provided all real frequencies. Therefore, this seems to be related possibly to a problem of the 6-311+G(d) basis set which becomes over complete due to the large overlap between the diffuse functions, as has been argued by Li and Tang[21] for other C_nX species.

It can be readily seen in Table 4 that all NaC_n cyclic clusters have doublet ground states, whose geometrical parameters are shown in Figure 5. The lowest-lying quartet states lie much higher in energy in all cases and therefore, even though the energy difference is reduced as the number of carbon atoms increases, there seems to be no doubt that the ground state is a doublet for all species. An inspection of Figure 5 reveals that all C−C bond distances are within the range 1.24−1.33 Å and therefore are not rather different than the C−C distances observed for the linear NaC_n structures. On the other hand, the Na−C distances are in general much longer for the cyclic structures, mainly as a consequence of the difficulty of sodium to bond to two different atoms. In fact, for those species where the Na−C distance is relatively close to those values found for the linear isomers, namely NaC_2 and NaC_3, the bonding is essentially between the sodium atom and the π system of the C_n unit, giving rise to a T-shape structure. This is, for example, clearly illustrated in NaC_3, where the sodium atom is closer to the center carbon than to the end carbon atoms of the C_3 unit.

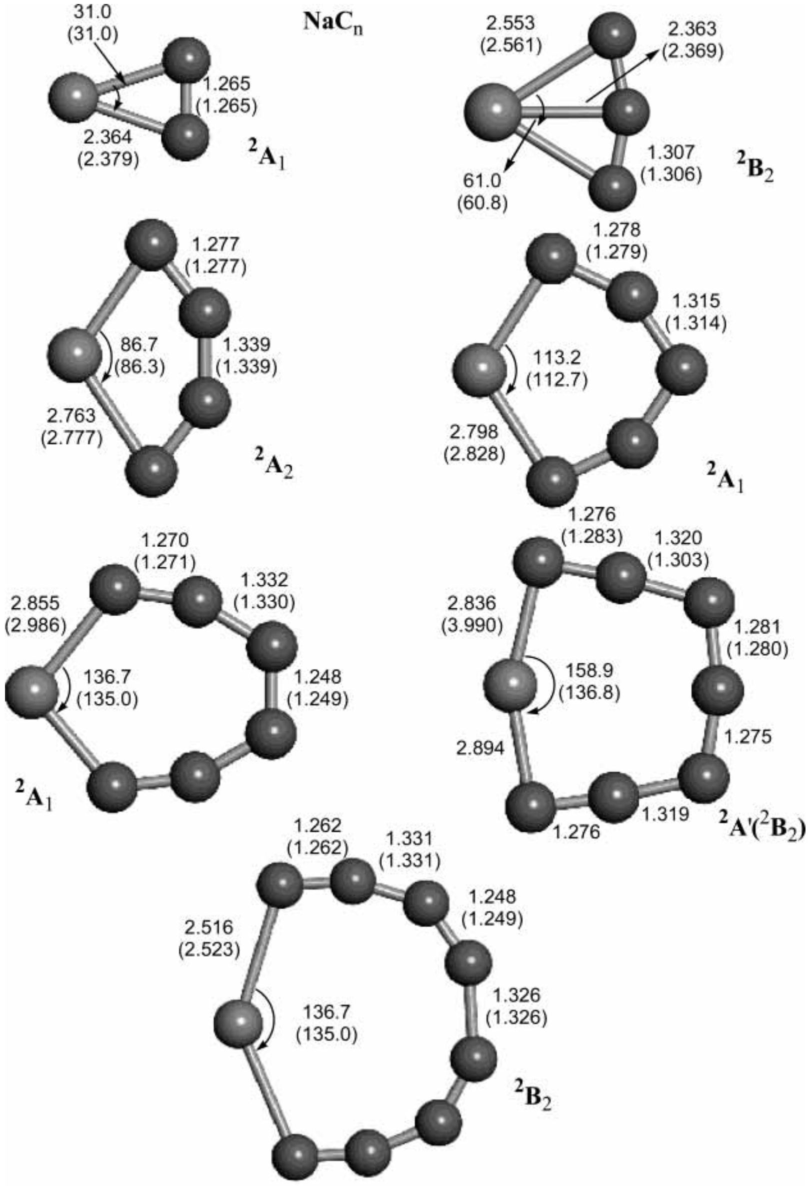

Figure 5. Equilibrium geometries of cyclic NaC_n ($n = 1-8$) clusters at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) (in parentheses) levels of theory. Distances are given in angstroms and angles in degrees.

To the best of our knowledge, no general study of NaC_n cyclic clusters can be found in the literature, and only theoretical studies for NaC_2[37−39] and NaC_3[11] have been carried out. In addition, there is an experimental (ESR) study of NaC_2.[40] The experimental information is compatible with a highly ionic species with a cyclic arrangement. Our prediction of a $^2A_1$ ground state is in agreement with previous theoretical studies. In fact, the MP2 geometry obtained for the ground state in the work by Bruna and Grein[39] (d(C−C) = 1.278 Å; d(C−Na) = 2.392 Å) is in very good agreement with the geometrical parameters shown in Figure 5.

The case of NaC_3 deserves some attention. In a previous study[11] we predicted that the ground state would be a linear NaCCC isomer. Nevertheless, a rhombic structure ($^2A_1$ electronic state, which corresponds to a truly four-membered ring with peripheral Na−C bonding and no transannular Na−C bonding) and a T-shape isomer ($^2A_2$ electronic state) should lie quite close in energy, namely just about 1.5 and 1.7 kcal/mol respectively higher in energy than the linear structure, according to our calculations. In our reexamination of the NaC_3 potential surface we have found another electronic state ($^2B_2$) for the T-shape isomer, depicted in Figure 5, which lies lower in energy. In fact, according to our calculations it should be the best candidate to the NaC_3 ground state, since all levels of theory predict that it lies even lower in energy than the linear isomer. Its relative energy at different levels of theory including ZPVE corrections, in kcal/mol, with respect to the linear structure is as follows: −1.2 (B3LYP/6-311G(d)); −0.2 (B3LYP/6-311+G(d)); −3.9 (CCSD(T)/6-311G(2df); −3.4 (G2). In any case it seems that, given the small energy difference between these species, both T-shape and linear isomers (and perhaps even the four-membered ring) could be accessible to experimental detection.

To discuss the relative stability of NaC_n cyclic clusters we will employ the concept of incremental binding energy[41] that has been shown by Pascoli and Lavendy[17] to be useful for the study of other heteroatom-doped carbon clusters. In our case the incremental binding energy is defined as the change in energy associated to the process:

$$NaC_n \rightarrow NaC_{n-1} + C$$

and can be computed from the values shown in Table 4 as the

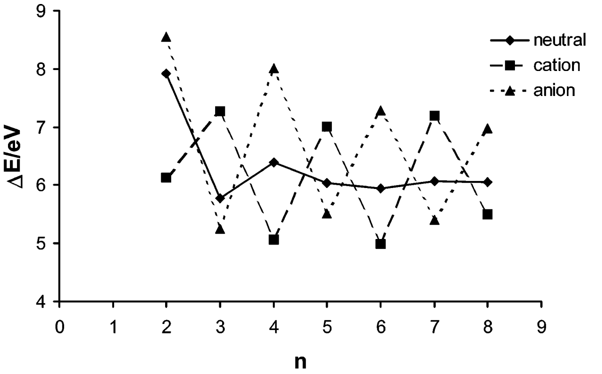

Figure 6. Incremental binding energies (eV) for the NaC_n, NaC_n^+, and NaC_n^- cyclic clusters vs the number of carbon atoms.

consecutive binding energy differences between adjacent NaC_n and NaC_{n-1} clusters. The results for the incremental binding energies are shown in Figure 6. As can be seen in Figure 6, for the smaller clusters there is an even−odd alternation in stability, with *n*-even clusters being more stable than *n*-odd ones, a behavior which is very similar to that found for the linear NaC_n clusters.[21] Nevertheless, this situation changes from $n = 5$, and the incremental binding energies vary only slightly when the number of carbon atoms increases. In fact, although taking rather similar values for *n*-even and *n*-odd clusters it seems that *n*-odd species are even slightly more stable than *n*-even ones.

NaC_n^+ Cyclic Clusters. The molecular properties of NaC_n^+ cyclic clusters are given in Table 5, whereas the geometrical parameters for the respective lowest-lying species are shown in Figure 7. For many of the cationic species (especially the first members of the series), we found imaginary frequencies, mainly associated to normal modes that led to the breaking of the ring. Our attempts to obtain true minima led to the corresponding open-chain isomers. Therefore, it seems that in some cases (for example NaC_4^+ and NaC_5^+) no stable cyclic structures could be reached, and for other clusters (for example NaC_3^+ or NaC_6^+) only cyclic structures corresponding to high (triplet) multiplicity and low stability can be found.

It is generally observed that the lowest-lying states are triplets for small clusters, whereas most of the larger compounds prefer singlet states. The exception is NaC_8^+, which has a triplet ground state although the lowest-lying singlet state is placed just 6 kcal/mol higher in energy. The most relevant characteristic of the optimized geometries shown in Figure 7 is the large Na−C distance found in all cases. From NaC_2^+ up to NaC_6^+ it is generally observed that there is a side interaction of the sodium atom (more properly a sodium cation, since its atomic charge is very close to +1e in all cases) with a quasilinear C_n unit. In

TABLE 5: Electronic Energies, $\langle S^2 \rangle$ Values, Vibrational Frequencies, Binding Energies (for the Ground States), Dipole Moments, Rotational Constants, and Relative Energies for Cyclic NaC_n^+ Clusters with the B3LYP/6-311G(d) (First Line) and B3LYP/6-311+G(d) (Second Line) Methods

isomer	state	$-E$ (a.u)	$\langle S^2 \rangle$	vibrational frequencies (cm^{-1})	binding energies (eV)	μ (D)	rotational constants (GHz)	ΔE (kcal mol^{-1})
NaC_2^+	$^1A_1$	238.009640		148/196/1790		4.28	52.807/6.197/5.546	20.31
		238.010101		150/197/1789		4.25	52.804/6.221/5.565	20.40
	$^3B_1$	238.041285	2.0114	71i/177/1642	6.47	4.85	48.685/5.840/5.215	0.00
		238.041892	2.0117	67i/177/1642	6.41	4.82	48.686/5.860/5.230	0.00
NaC_3^+	$^1A_1$	276.170218		133i/138/176/185/1568/1906	13.76	5.57	18.944/4.230/3.458	0.00
		276.171246		134i/136/174/178/1565/1908	13.68	5.57	18.844/4.234/3.457	0.00
	$^3A_1$	276.082240	2.0132	160/173/203/780/1379/1545		5.04	34.086/4.054/3.623	55.59
		276.093216	2.0134	158/172/203/781/1371/1545		5.02	34.124/4.058/3.627	55.62
NaC_4^+	$^1A_1$	314.194006		86i/101/111/199/222/448/924/1562/2102		7.13	4.945/4.336/2.310	14.59
		314.195689		88i/107/111/199/234/456/924/1562/2104		7.17	4.944/4.293/2.298	14.57
	$^3B_1$	314.217593	2.0438	109i/84/167/176/350/414/981/1590/2056	18.85	6.44	5.297/4.096/2.310	0.00
		314.219155	2.0427	108i/75/164/177/352/408/976/1589/2061	18.76	6.59	5.262/4.014/2.277	0.00
NaC_5^+	$^1A_1$	352.336321		33i/6/111/120/218/224/565/565/801/1489/2034/2254	25.85	19.00	2.576/0.947/0.692	0.00
		352.340025		34i/10/113/122/222/228/558/564/801/1489/2035/2254	25.77	18.96	2.578/0.947/0.692	0.00
	$^3B_2$	352.269963	2.0241	55i/106/127/142/267/309/402/552/1009/1312/1702/1748		4.94	4.091/3.263/1.815	40.62
		352.271425	2.0240	60i/105/127/139/268/309/399/550/1009/1311/1705/1749		4.94	4.087/3.258/1.813	42.01
NaC_6^+	$^1A_1$	390.381098		64i/76/81/132/154/219/303/406/419/585/662/1207/1709/2032/2168	30.88	8.34	3.804/1.445/1.047	0.00
		390.384061		62i/76/86/129/158/221/299/397/406/563/662/1207/1709/2032/2169	30.74	8.44	3.727/1.445/1.041	0.00
	$^3B_2$	390.326353	2.0534	103/104/111/174/179/201/213/481/609/905/1057/1235/1373/1812/1917		4.86	3.195/2.298/1.337	34.81
		390.328132	2.0534	102/100/111/183/175/196/213/479/605/905/1052/1234/1373/1813/1918		4.88	3.189/2.298/1.335	35.59
NaC_7^+	$^1A_1$	428.511101		86/110/135/183/199/210/260/274/509/520/523/529/985/1208/1718/1881/2047/2107	38.12	4.47	2.465/1.787/1.036	0.00
		428.513113		86/110/134/183/195/212/258/276/509/517/523/529/984/1206/1717/1879/2045/2107	37.93	4.47	2.467/1.785/1.036	0.00
	$^3A'$	428.455295	2.0260	85/88/108/118/165/171/247/290/374/397/489/568/908/1167/1439/1726/1822/1913		4.03	2.190/1.906/1.019	33.00
		428.457232	2.0261	85/88/109/114/164/173/249/294/369/395/486/568/908/1166/1436/1729/1823/1915		4.05	2.193/1.900/1.018	33.06
NaC_8^+	$^1A_1$	466.563545		84/100/133/165/172/176/229/257/352/352/391/416/492/522/868/1134/1508/1806/1961/2033/2060		3.34	1.634/1.504/0.783	6.54
		466.565803		84/102/132/167/172/173/233/256/332/349/391/415/488/519/867/1132/1507/1804/1960/2032/2060		3.31	1.632/1.503/0.782	6.49
	$^3A''$	466.572963	2.0533	74/100/103/144/163/168/241/263/271/373/374/423/446/471/854/1096/1458/1773/1930/2009/2035	43.65	3.48	1.645/1.478/0.779	0.00
		466.575196	2.0527	74/102/104/141/162/169/240/263/275/373/374/415/448/472/852/1095/1457/1771/1927/2008/2033	43.43	3.50	1.650/1.473/0.778	0.00

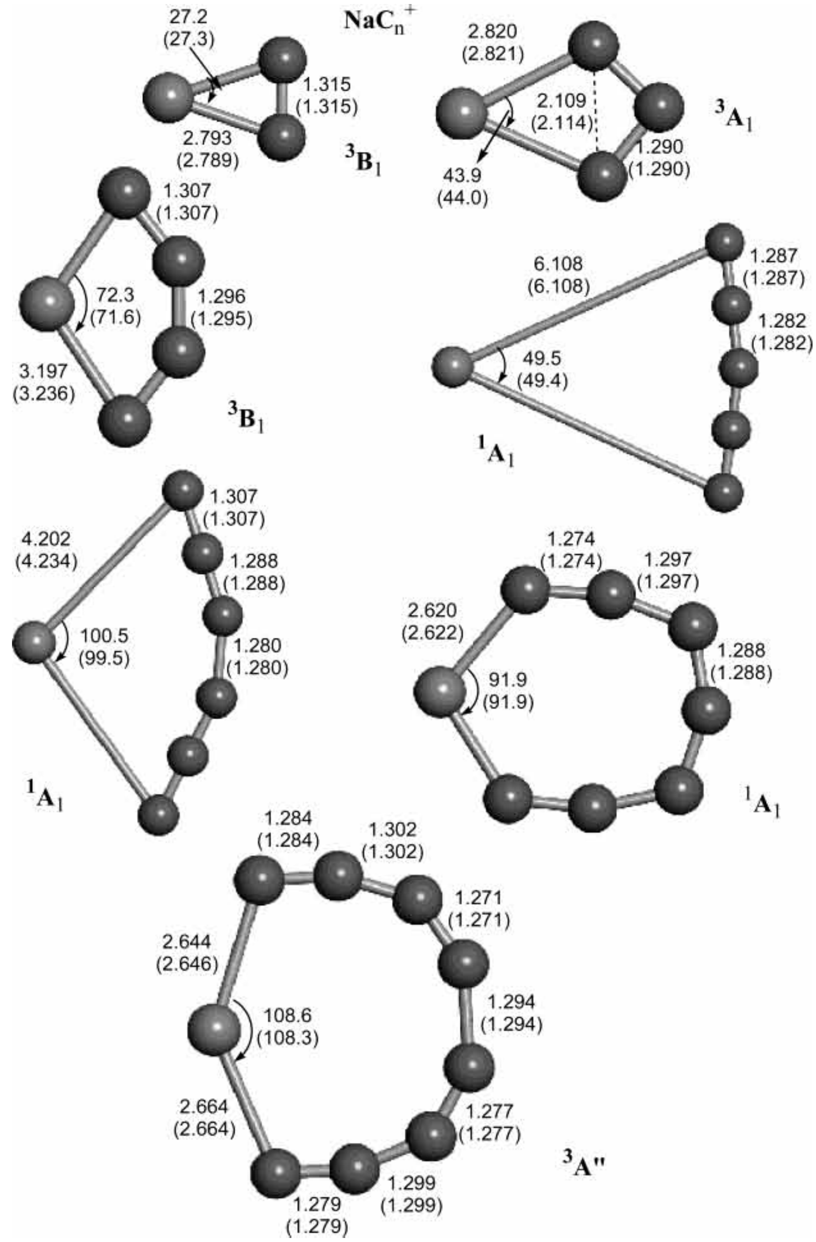

Figure 7. Equilibrium geometries of cyclic NaC_n^+ ($n = 1-8$) clusters at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) (in parentheses) levels of theory. Distances are given in angstroms and angles in degrees.

the cases of NaC_5^+ and NaC_6^+ the situation is rather extreme, since the Na−C distances are very large, 6.1 and 4.2 Å, respectively. In all these cases the interaction is essentially electrostatic. For the larger clusters, NaC_7^+ and NaC_8^+, the sodium atom mainly interacts with the terminal carbon atoms of the C_n unit, and since the size of the molecule allows a ring much less stressed, the cluster adopts a more typical cyclic geometry. It is interesting to note that in these cases the atomic charge at sodium is much lower, about +0.78e in both cases, as a consequence of a certain degree of charge transfer from the carbon unit.

From the incremental binding energies for the NaC_n^+ species shown in Figure 6, it is readily seen that there is a clear even−odd alternation, with n-odd clusters being more stable. Therefore, the cyclic clusters essentially follow the same pattern as their open-chain isomers, since the same behavior has been observed for linear NaC_n^+ clusters.[21] It is also clear from Figure 6 that the variations found for the incremental binding energies for consecutive members in the series are much higher than for the neutral clusters.

NaC_n^- Cyclic Clusters. Finally we have also studied the anionic cyclic clusters. Their main properties, obtained with the 6-311+G(d) basis set, are given in Table 6 and the optimized geometries for the lowest-lying species are shown in Figure 8. In most cases we found true minima with all frequencies real. Only the triplet state of NaC_4^- (which lies clearly higher in energy than the corresponding singlet) has an imaginary frequency. For both singlet and triplet NaC_8^- species we also found an imaginary frequency with the 6-311+G(d) basis set, a problem that quite likely is associated to the inclusion of diffuse functions for the larger clusters, which makes the basis set to be over complete as mentioned before. In fact both states have all their frequencies real at the B3LYP/6-311G(d) level.

Only in the case of NaC_3^- did we find a triplet ground state, whereas all other clusters have singlet ground states. Nevertheless, we should point out that in the case of the rest of n-odd compounds ($n = 5$, 7) the difference in energy between the lowest-lying triplet state and the singlet ground state is rather small, about 2 and 1 kcal/mol, respectively. It is interesting to recall that the n-odd linear neutral clusters have triplet ground

TABLE 6: Electronic Energies, ⟨S^2⟩ Values, Vibrational Frequencies, Binding Energies (for the ground states), Dipole Moments, Rotational Constants, and Relative Energies for Cyclic NaC$_n^-$ Clusters with the B3LYP/6-311G(d) (first line) and B3LYP/6-311+G(d) (second line) Methods

isomer	state	$-E$ (a.u)	⟨S^2⟩	vibrational frequencies (cm^{-1})	binding energies (eV)	μ (D)	rotational constants (GHz)	ΔE (kcal mol^{-1})
NaC$_2^-$	$^1A_1$	238.419209		262/402/1785	10.63	9.35	52.162/8.876/7.585	0.00
	$^3A_1$	238.391841	2.0083	163/263/1831		4.90	52.780/7.166/6.310	16.90
NaC$_3^-$	$^1A_1$	276.451430		200/234/317/667/1031/1451		2.77	35.618/4.718/4.166	13.41
	$^3B_2$	276.472603	2.0159	23/184/240/415/1191/1758	15.89	3.87	12.393/5.597/3.856	0.00
NaC$_4^-$	$^1A_1$	314.631282		162/243/249/389/478/555/897/1890/2045	23.90	8.08	7.756/5.245/3.129	0.00
	$^3A_2$	314.575807	2.0095	57i/129/198/246/405/501/923/1759/2091		3.37	5.012/4.786/2.448	33.87
NaC$_5^-$	$^1A_1$	352.694371		154/187/228/260/315/326/483/649/883/1235/1826/1886	29.40	5.52	6.139/3.393/2.185	0.00
	$^3B_1$	352.690139	2.0598	131/166/179/280/379/429/445/582/845/1374/1639/1790		4.54	7.042/3.072/2.139	2.38
NaC$_6^-$	$^1A_1$	390.825152		106/121/103/256/267/308/421/454/473/523/769/1153/1913/2022/2138	36.68	2.42	6.529/1.879/1.459	0.00
	$^3A''$	390.756407	2.0279	81/123/240/251/251/272/382/505/525/625/855/1085/1606/1826/1828		3.06	4.351/2.528/1.604	42.32
NaC$_7^-$	$^1A'$	428.884842		98/111/157/178/208/242/311/326/431/457/542/623/799/1033/1316/1848/1933/1994	42.10	1.39	3.953/1.639/1.159	0.00
	$^3A''$	428.881214	2.0982	48/93/111/121/190/193/348/349/377/386/453/558/774/1051/1508/1603/1856/1982		0.55	4.529/1.485/1.118	1.26
NaC$_8^-$	$^1A_1$	467.004166		68i/16/79/153/233/191/263/274/375/378/502/494/508/517/632/941/1300/1935/2014/2147/2161	49.07	0.30	4.673/0.827/0.703	0.00
	$^3B_2$	466.944736	2.0254	101i/62/66/142/165/218/219/283/335/350/418/498/545/578/774/988/1287/1625/1858/1883/2028		1.59	2.851/1.290/0.888	36.16

states, suggesting that in a certain sense the stability of *n*-odd triplets is retained upon cyclization.

Concerning the geometrical parameters, it can be seen in Figure 8 that cyclic NaC$_n^-$ clusters have Na−C distances slightly shorter than their neutral counterparts, with the only exception being $n = 8$. This observation suggests that the extra electron slightly strengthens the Na−C bonding, probably as a consequence of an enhanced possibility of charge transfer from the C$_n$ unit toward sodium.

The incremental binding energies for NaC$_n^-$ clusters, shown in Figure 6, exhibit also a similar behavior to that found for the open-chain isomers,[21] with *n*-even clusters being comparatively much more stable than *n*-odd clusters. As in the case of the cationic clusters, NaC$_n^-$ species show variations in the incremental binding energies for consecutive members in the series much higher than their neutral analogues.

The computed energies for cationic and anionic NaC$_n$ cyclic clusters allow to estimate the corresponding ionization potentials (IP) and electron affinities (EA). The IPs and EAs for NaC$_n$ cyclic clusters are shown in Figure 9 (the case of $n = 1$ has also been included for comparison). Since these magnitudes were computed as the energy difference between the charged and neutral species at their respective optimized geometries, values correspond to vertical IP and EA. As can be seen in Figure 9, there is a clear even−odd alternation in the IPs and EAs, *n*-even clusters having higher IP and EA than *n*-odd ones, and this is again the same behavior found for the linear clusters.[21] Whereas the IPs within *n*-even and *n*-odd series remain rather the same, in the case of EAs it seems that there is a substantial increment within each series, suggesting that larger clusters have much higher electron affinities.

The energy differences between cyclic and open-chain isomers for NaC$_n$ clusters and their cationic and anionic derivatives are shown in Figure 10. A negative value indicates that the cyclic isomer is more stable than the open-chain isomer. It can be seen in Figure 10 that neutral NaC$_n$ clusters are predicted to prefer open-chain arrangements, except for the two first members of the series. In the case of NaC$_2$, the ground state is predicted to be cyclic by more than 13 kcal/mol, whereas for NaC$_3$ the cyclic and linear isomers are nearly isoenergetic, although the cyclic one lies slightly lower in energy at the B3LYP level. The prediction for NaC$_2$ is in agreement with the experimental study[40] and with previous theoretical studies,[37−39] since all of them reported a cyclic ground state. On the other hand, all NaC$_n^+$ clusters are predicted to prefer open-chain arrangement, and it seems that no cyclic cationic species could eventually be characterized in experimental studies. However, both neutral and cationic clusters show in fact a similar trend, with energy differences between open-chain and cyclic isomers increasing quasi-monotonically as the number of carbon atoms increases, and in fact the corresponding lines are nearly parallel. The results for NaC$_n^+$ clusters are similar to those obtained for C$_n$ clusters. For example, Hutter et al.[42] found that DFT calculations predict that the lowest-energy form for C$_n$ species with $n < 10$ is the linear chain.

A different behavior is found for the NaC$_n^-$ clusters. For the first two members of the series, $n = 2$ and $n = 3$, the stability of the cyclic isomers is somewhat lower than for their neutral analogues, although for NaC$_2^-$ the cyclic isomer is still predicted to be the ground state. The trend is reversed from $n = 4$, since for NaC$_n^-$ ($n = 4−8$) the cyclic isomer is comparatively more stable than in the case of NaC$_n$ clusters, and for all of them the cyclic isomer is always preferred over the open-chain isomer. Nevertheless, for NaC$_8^-$ the energy difference between cyclic and open-chain isomers is just 1.4 kcal/mol, and therefore, given the trend observed in Figure 10, it seems that for larger clusters open-chain isomers could be the preferred ones.

In any case, it seems that small NaC$_n^-$ clusters have a certain tendency to adopt cyclic arrangements, and this behavior is somewhat similar to that found for their isoelectronic series MgC$_n$. Whereas both cationic and anionic small MgC$_n$ species are predicted by DFT calculations to prefer open-chain arrangements, neutral MgC$_n$ clusters are found to prefer mainly cylclic geometries.[22]

Conclusions

A theoretical study using the B3LYP method with the 6-311G(d) and 6-311+G(d) basis sets has been carried out for

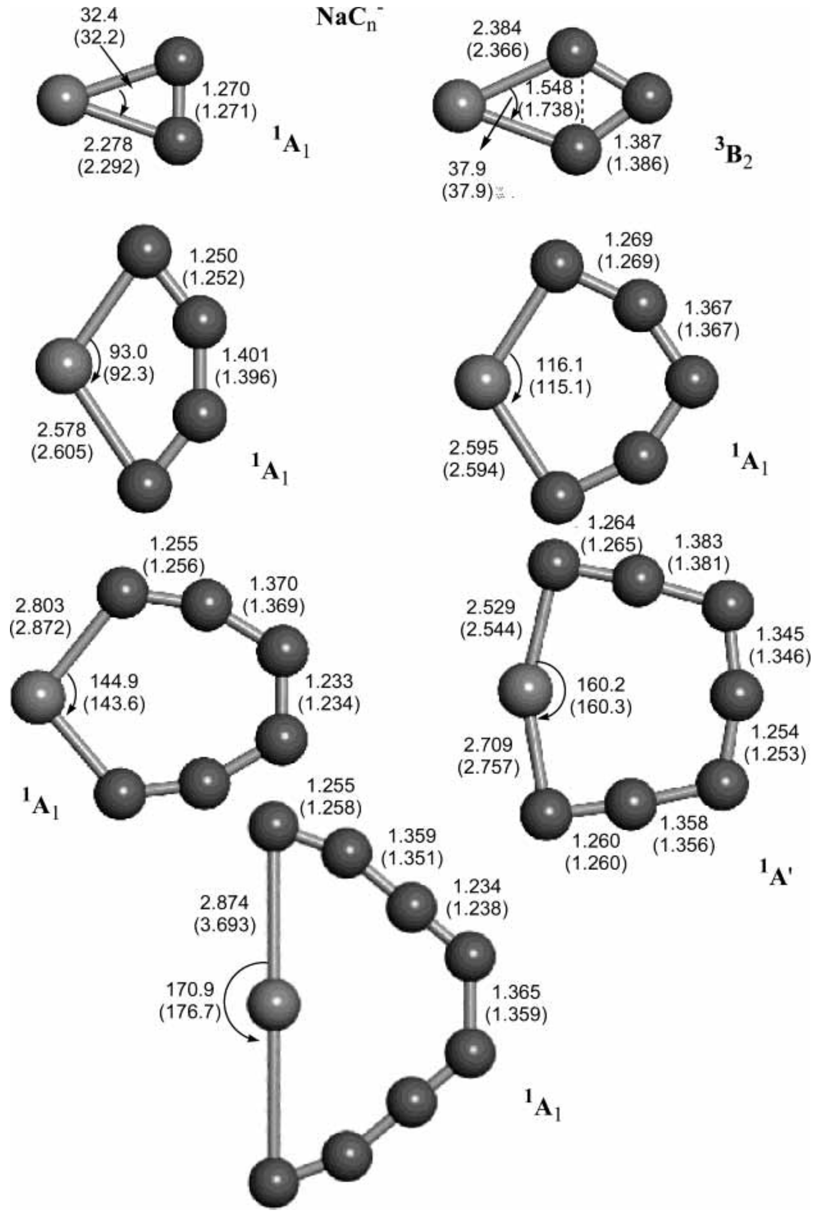

Figure 8. Equilibrium geometries of cyclic NaC$_n^-$ ($n = 1-8$) clusters at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) (in parentheses) levels of theory. Distances are given in angstroms and angles in degrees.

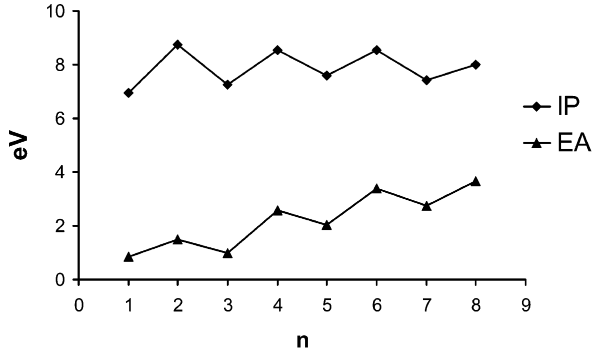

Figure 9. Ionization potentials (IP) and electron affinities (EA), in eV, of cyclic NaC$_n$ clusters vs the number of carbon atoms.

the open-chain and cyclic NaC$_n$ ($n = 1-8$) clusters, as well as their cationic and anionic derivatives. Predictions for their geometrical parameters and other molecular properties that could be useful for an eventual experimental characterization have been provided.

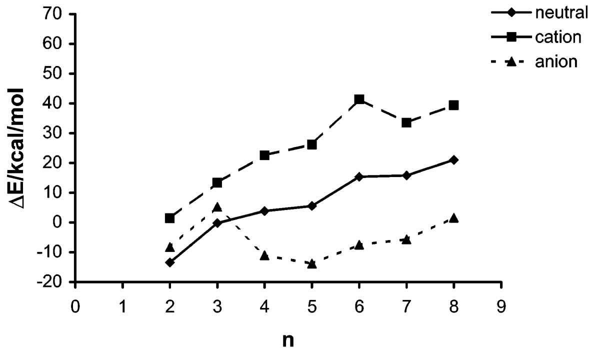

Figure 10. Energy separation (in kcal/mol) between the monocyclic and open-chain structures for the NaC$_n$ clusters as a function of the number of carbon atoms. A negative value indicates that the open-chain isomer is less stable than the corresponding cyclic one.

According to our calculations, open-chain NaC$_n$ clusters are predicted to be linear and to have $^2\Pi$ lowest-lying states. All cationic and most of the anionic clusters are also linear. In the case of NaC$_n^+$ clusters, the ground state is alternatively triplet (n even) or singlet (n odd with the only exception of the first member of the series, NaC$^+$). For anionic clusters, the multiplicity of the ground state also alternates, but opposite to their cationic analogues n-even clusters have singlet ground states, whereas n-odd species have triplet ground states. The rotational constants for all charged and neutral clusters follow similar trends and are quite insensible to the charge of the cluster.

Cyclic neutral clusters have doublet ground states and are generally characterized by long Na−C distances. The smaller clusters should be best described as T-shaped rather than true monocyclic species, since the bonding of sodium takes place essentially with the π system of the C$_n$ moiety. NaC$_n^+$ cyclic clusters are shown to be of low stability, and this is reflected also in the long Na−C distances found for most of them. In fact, many of the cationic cyclic clusters, especially the smaller compounds, are not true minima on the potential surface, and collapse into the linear isomers. On the other hand, anionic clusters have comparatively much shorter Na−C distances and have generally all their frequencies real. Most of the NaC$_n^-$ clusters (except $n = 3$) have singlet ground states.

The stability of cyclic clusters as a function of the size has been discussed in terms of the incremental binding energies. For the neutral clusters there is only even−odd alternation in stability for the first members in the series, whereas from $n = 5$ only slight variations in the incremental binding energy are observed. On the other hand, for both cationic and anionic clusters a clear even−odd alternation is found, although with opposite behavior. In the case of NaC$_n^+$ n-odd clusters are more stable, whereas for NaC$_n^-$ n-even clusters are clearly preferred. Ionization potentials and electron affinities also show a clear parity alternation effect, with n-even clusters having higher IP and EA values.

One of the most interesting results of the present work concerns the competition between linear and cyclic isomers. NaC$_2$ and NaC$_3$ are predicted to prefer a cyclic arrangement, although for the latter the linear isomer is very close in energy (nearly isoenergetic) to the cyclic one. All other neutral clusters are predicted to be linear, and the general trend is to increase the energy difference between linear and cyclic isomers. For all cationic derivatives cyclic isomers are destabilized with respect to their neutral analogues, and in fact all of them are predicted to prefer an open-chain geometry. On the other hand, most of the NaC$_n^-$ clusters studied in this work (with the only exception being NaC$_3^-$) are predicted to have a cyclic ground state. In fact, except the two first members of the series, the cyclic isomer is stabilized for the anion with respect to the neutral counterpart. Therefore, even though sodium is a monovalent element, cyclic structures might be important for sodium-doped carbon clusters, and some of them could be possible experimental targets.

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