Structure and Stability of AlC_2N Isomers: A Comparative ab Initio and DFT Study

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Received: January 23, 2001; In Final Form: May 1, 2001

A theoretical study of the different AlC_2N isomers has been carried out. The global minimum is predicted to be a linear AlCCN isomer, whereas the previously predicted ground state, a three-membered ring isomer, lies much higher in energy (more than 25 kcal/mol at the more reliable levels of theory). We have found four other structures lying lower in energy than the three-membered ring, two of them being rhombic structures. The preferred atomic arrangement for linear geometries, as in the case of its analogue BC_2N system, is AlCCN. However, contrary to what is observed for BC_2N, the global minimum is a $^3\Sigma$ state. Predictions for the vibrational frequencies, rotational constant, and dipole moment, as well as for the atomization energy and dissociation into Al + CCN, have been made for the global minimum. On the basis of these results we may conclude that the ground state of AlC_2N is relatively stable and therefore it might be of interest for experimentalists.

Introduction

The study of mixed B−C−N compounds has known an increased interest in recent years, due to their different structural forms, some of them being of relevance in new materials science. For example, depending on the experimental conditions, graphitic-sheet-like structures, nanotubes, as well as other structures can be synthesized.[1,2] Even though several proportions of carbon in BCN compounds are possible, the most usual is BC_2N. The properties of BC_2N materials are intermediate between those of carbon and BN. Theoretical calculations[3−5] predict that BN is a wide-band semiconductor, whereas BC_2N is a medium-gap semiconductor[6] with potential interesting applications. In BC_2N nanotubes the predicted most stable structure corresponds to a boron−nitrogen network with carbon bonds forming a connected helix,[7] suggesting that they may serve as nanocoils. These structures have been theoretically studied by different groups,[8−14] confirming that the most likely arrangement tries to maximize the number of B−N and C−C bonds. Furthermore, one of the most interesting features of BC_2N is that, due to the anisotropic geometry of a BC_2N sheet, chiral structures prevail. Different types of semiconductors, n- or p-type, could be obtained by small deviations from stoichiometry,[7] and these materials might have important applications in nanotechnology.

The interest of these materials led to Kar et al.[15] to perform a very detailed and complete high-level ab initio study of the basic building block, the BC_2N molecule. The most stable structure is predicted to be linear BCCN ($^3\Pi$ electronic state), and in general triplet states are preferred over singlet ones for the different BC_2N isomers. There are several linear species lying close in energy to the predicted global minimum, particularly the $^3\Sigma$ and $^3\Pi$ electronic states of the CBCN isomer, that lie about 6 and 10 kcal/mol, respectively, above BCCN. On the other hand the lowest-lying cyclic isomer is a rhombic structure which is predicted to lie more than 28 kcal/mol higher in energy than linear BCCN.

Given the general interest on aluminum-doped carbon clusters, quite recently Zheng et al.[16] reported a theoretical study of the aluminum analogue of BC_2N, that is the AlC_2N system. The main conclusion of their study is that the predicted global minimum is a closed-shell cyclic form with a C_2N ring and the aluminum atom in an exocyclic position bonded to a carbon atom. Other linear structures, as well as another cyclic structure with a AlC_2 ring, were found to lie much higher in energy, namely more than 60 kcal/mol. This result is in contrast with the conclusions of the study by Kar et al.[15] on the analogue BC_2N system, where a linear triplet state is predicted to be global minimum. Basically there are two main limitations in the work by Zheng et al.:[16] (i) only closed-shell singlet states were considered for the different possible isomers; (ii) only cyclic structures containing three-membered rings were studied, whereas for the BC_2N system the lowest-lying cyclic state is a rhombic structure. Therefore we decided to reinvestigate the AlC_2N system in both the singlet and triplet surfaces.

Computational Methods

To compare our results with the previous study of Zheng et al.[16] we have employed similar theoretical methods. Consequently, the geometries of the different AlC_2N species have been obtained employing two different methods. First we have applied the second-order MØller−Plesset theory with the 6-311G(d) basis set,[17] including all electrons in the calculations, which is usually denoted MP2(full)/6-311G(d). The only difference with the calculations by Zheng et al. is that they used the so-called frozen-core approximation, that is inner electrons are not taken into account for computing correlation energies. Second we have employed the density functional theory (DFT), selecting the B3LYP exchange-correlation functional[18] with the 6-311G(d) basis set, that is exactly the same procedure used by Zheng et al.[16] In addition we should mention that DFT calculations have proved useful as a complement to experimental studies in other related small aluminum systems.[19,20]

Harmonic vibrational frequencies have been computed on each optimized structure at its corresponding level of theory.

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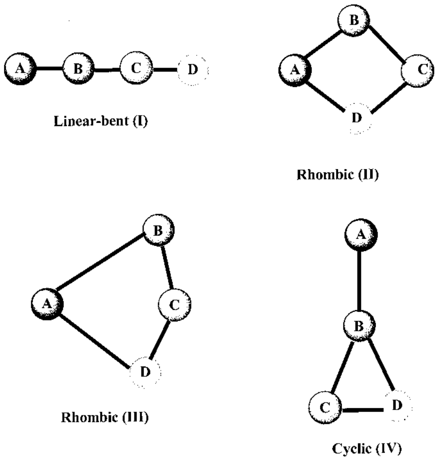

Figure 1. Schematic representation of the different structural forms of AlC_2N considered in this work.

This not only serves to estimate the zero-point vibrational energy (ZPVE) correction, but also allows to assess the nature of stationary points in order to verify that they correspond to true minima on the potential surface.

Zheng et al.[16] computed relative energies for the different AlC_2N species employing their MP2/6-311G(d) and B3LYP/6-311G(d) values. To compute more accurate relative energies we have employed two different higher-level theoretical methods. In first place we have applied the so-called G2 method,[21] where the geometries are obtained at the MP2 level and the electronic energy is computed, making additivity assumptions, effectively at the QCISD(T)/6-311+G(3df,2p) level. QCISD(T) stands for a quadratic configuration interaction calculation with single and double substitutions followed by a perturbative treatment of triple substitutions. Since we are dealing with open-shell states and spin-contamination may affect the convergence of the MP series, approximate projected MP values were employed also to compute electronic energies. These results will be denoted as G2(P). In addition we have carried out single-point calculations with the CCSD(T) method[22] (coupled-cluster single and double excitation model augmented with a noniterative triple excitation correction) with the cc-pVTZ basis set of Dunning[23,24] on the B3LYP geometries.

All calculations in this work were carried out with the Gaussian 98 program package.[25]

Results and Discussion

We will employ a similar notation to that used by Kar et al.[15] in their study of BC_2N isomers with a few variations. The different structural forms of AlC_2N are schematically represented in Figure 1. All open-chain structures, linear and bent, are included in category I, and all possible combinations of atomic arrangements have been considered. Bearing in mind the results for several binary carbon clusters of the type C_3X (where X is a second-row atom, such as C_3Al,[26] C_3Si,[27] C_3Si^+[28], or C_3P[29]), two different rhombic species, II and III, have been considered. Structure II can be viewed as an atom A bonded to the side of a cyclic BCD unit, whereas structure III is formally derived from the side interaction of atom A with a quasi-linear BCD unit. Finally cyclic structures with a three-membered ring and an exocyclic atom were also considered and they are denoted, following Kar et al.,[15] as AB(CD).

The relative energies, calculated at different levels of theory and incorporating ZPVE corrections, of the different structural forms of AlC_2N are summarized in Table 1, whereas their energy ordering at the G2(P) level is represented in Figure 2. Given the number of open-chain structures found in the course of our work, in Figure 2 we have represented in separate columns the results for the singlet and triplet states of the open-chain structures. Several other cyclic species were searched for, such as triplet states for structures II and III with a AlCCN arrangement (C_s symmetry), or structures of type IV with an exocyclic carbon or nitrogen atom (which should be denoted as NC(AlC) or CN(AlC), for example)). However in all cases they collapsed to the corresponding linear structures upon optimization at both MP2 and B3LYP levels. Most of the AlC_2N structures correspond to true minima on the potential surface (all their vibrational frequencies are real), with the only exceptions of the cyclic species III—AlCNC($^3B_1$) and IV—AlN(CC)($^1A_1$), where one imaginary frequency was found. In both cases we followed the associated normal mode and performed optimizations in C_s symmetry, and finally we reached the open-chain structure I—AlCNC or the rhombic II—AlCCN isomer, respectively.

TABLE 1: Relative Energies (kcal/mol) of the AlC_2N Species at Different Levels of Theory, Including ZPVE Corrections, and $\langle S^2 \rangle$ Expectation Values for the Reference HF/6-311(G) Wavefunction Employed in MP2 Calculations

	B3LYP	MP2(full)	CCSD(T)	G2	G2(P)	$\langle S^2 \rangle$
			Structures I			
AlCCN($^3\Sigma$)	0.0	0.0	0.0	0.0	0.0	2.268
AlCCN($^3\Pi$)	27.9	22.3	28.4	27.8	32.2	2.119
AlCCN($^1A'-^1\Delta$)	23.4	12.5	22.8	20.3	27.7	
AlCCN($^1\Sigma$)	94.3	58.7	82.6	74.3	81.7	
AlCNC($^3\Sigma$)	20.1	14.5	21.0	20.7	23.6	2.158
AlCNC($^3\Pi$)	55.1	38.7	54.9	52.1	57.7	2.064
AlCNC($^1A'-^1\Delta$)	41.3	30.7	40.9	37.4	44.8	
AlCNC($^1\Sigma$)	121.6	96.4	111.2	101.3	108.7	
AlNCC($^3\Sigma$)	13.3	4.7	14.7	14.5	19.3	2.090
AlNCC($^3\Pi$)	55.1	55.8	68.7	65.2	70.3	2.090
AlNCC($^1A'-^1\Delta$)	34.6	22.1	31.3	28.2	35.6	
AlNCC($^1\Sigma$)	125.2	96.0	90.8	73.3	80.7	
CAlCN($^3A''$)	54.0	32.2	46.2	48.7	53.3	2.859
CAlNC($^3A''$)	51.9	33.9	44.0	46.1	50.7	2.859
NAlCC($^3\Sigma$)	90.2	76.3	87.0	86.1	92.2	2.031
			Structures II			
AlCNC($^1A_1$)	27.5	0.7	18.6	15.7	23.1	
AlCNC($^3B_1$)	64.5	38.5	57.0	55.5	61.7	2.059
AlCCN($^1A'$)	30.8	4.9	22.2	17.8	25.2	
			Structures III			
AlCNC($^1A_1$)	46.3	28.6	40.1	36.9	44.3	
AlCNC($^3B_1$)[a]	42.4	34.8	39.3	39.2	40.0	2.248
AlCCN($^1A'$)	35.1	16.1	28.6	25.8	33.2	
			Structures IV			
AlC(NC)($^1A'$)	28.5	5.2	21.8	18.5	25.9	
AlC(NC)($^3A''$)	54.3	50.7	52.1	51.3	55.3	2.205
AlN(CC)($^1A_1$)[a]	40.5	19.4	33.1	30.0	37.4	
AlN(CC)($^3B_1$)	86.3	76.2	84.1	91.3	98.5	2.007
NAl(CC)($^1A_1$)	118.2	100.7	106.1	102.3	109.7	
NAl(CC)($^3A_2$)	75.4	52.4	66.7	65.8	72.3	2.016

[a] Species with one imaginary vibrational frequency.

In Table 1 we have also included in the case of triplet states the $\langle S^2 \rangle$ expectation values of the HF/6-311G(d) reference wave function employed in the MP2 calculations. In most cases these values are within 10% of the exact value, with a few exceptions such as AlCCN($^3\Sigma$) and AlCNC($^3B_1$), with values above 2.2, and two pathological cases where very high $\langle S^2 \rangle$ values are observed, CAlCN($^3A''$) and CAlNC($^3A''$). In all these cases the DFT calculations should be more reliable than the MP2 ones. Spin contamination for DFT calculations is virtually negligible in all cases and therefore $\langle S^2 \rangle$ values for B3LYP are not reported in Table 1.

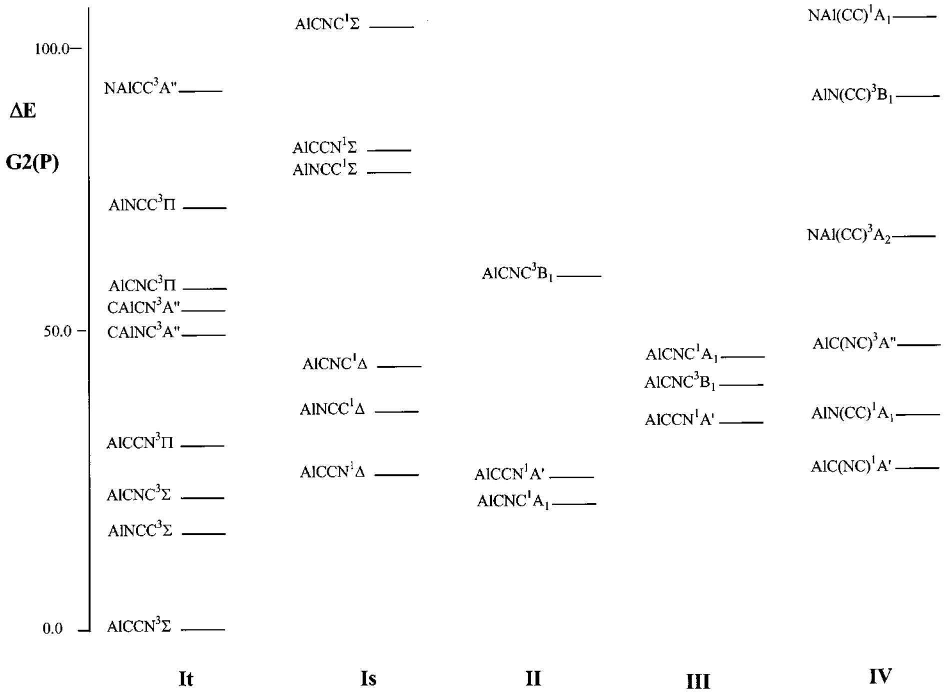

Figure 2. G2(P) energy diagram (in kcal/mol) for AlC_2N. Is and It stand for the singlet and triplet, respectively, states of structures I (see Figure 1).

Concerning the performance of the different theoretical methods employed in the present study we should mention that all of them provide virtually the same relative energy ordering, with the only exception of the MP2 level which deviates considerably from the predictions of other methods for several isomers. Taking the G2(P) results as the most reliable ones, since the possible effect of spin-contamination is somewhat alleviated in this method, it is worth mentioning the relatively good performance of B3LYP, which in most cases (with very few exceptions, such as the high-lying linear $^1\Sigma$ states) gives relative energies closer to the G2(P) ones than both CCSD(T) and G2 methods, that are much more computational demanding. In fact there is little choice between CCSD(T) and G2 results, since both provide very close relative energies. This is interesting because the results in Table 1 suggest that for larger systems of this kind a DFT method, such as B3LYP, could be a reasonable choice, even better than other more expensive traditional ab initio methods.

The most important result from Table 1 is that a linear AlCCN isomer ($^3\Sigma$ state) is predicted to be the global minimum. This is in contradiction with the work by Zheng et al.,[16] where the cyclic Al(NC) isomer ($^1A_1$ state) was suggested as the most stable AlC_2N species. This cyclic state is shown to lie about 25.9 kcal/mol (G2(P)) or 28.5 (B3LYP, the same method employed by Zheng et al.[16]) above the triplet linear isomer. In fact according to our results there are four other isomers which should be also more stable than cyclic Al(NC): AlNCC($^3\Sigma$), which is predicted to lie about 19.3 kcal/mol above the global minimum at the G2(P) level; II—AlCNC($^1A_1$), 23.1 kcal/mol; AlCNC($^3\Sigma$), 23.6 kcal/mol; and II—AlCCN($^1A'$), 25.2 kcal/mol. Therefore there are also two ring isomers that seem to be more stable than the ground state predicted by Zheng et al.[16] However it is not surprising that these authors failed to predict the correct global minimum, because they only searched for singlet states (whereas the analogue BC_2N system has a triplet ground state[15]), and did not consider rhombic species (that are found to be quite stable for other related systems, such as C_3Al[24]).

Although the global minimum of both AlC_2N and BC_2N is linear, corresponding to the same arrangement, AlCCN and BCCN, respectively, there are important differences between both systems. In the case of BC_2N the global minimum corresponds to a $^3\Pi$ electronic state,[15] whereas in the case of AlC_2N the lowest-lying state is $^3\Sigma$. This difference can be rationalized in terms of the valence-bond structures describing both states. The $^3\Sigma$ state corresponds to the following electronic configuration:

$$\{\text{core}\}\ 7\sigma^2\ 8\sigma^2\ 9\sigma^2\ 2\pi^4\ 10\sigma^2\ 11\sigma^2\ 3\pi^1\ 3\pi^1$$

and its dominant valence-bond structure can be depicted as follows:

$$:\!\text{Al}{-}\dot{\text{C}}{=}\text{C}{=}\dot{\text{N}}\!: \qquad (1)$$

whereas the $^3\Pi$ state corresponds to the following electronic configuration:

$$\{\text{core}\}\ 7\sigma^2\ 8\sigma^2\ 9\sigma^2\ 2\pi^4\ 10\sigma^2\ 11\sigma^1\ 3\pi^3$$

and the most contributing valence-bond structures (which are compatible with the population analysis) can be represented as

$$\underset{(2a)}{\cdot\text{Al}{=}\dot{\text{C}}{-}\text{C}{\equiv}\dot{\text{N}}\!:} \leftrightarrow \underset{(2b)}{\cdot\text{Al}{=}\text{C}{=}\text{C}{=}\dot{\text{N}}\!:} \qquad (2)$$

It is then clear that the $^3\Pi$ state would be favored in the case of the BC_2N system, because of the higher preference for multiple bonding of boron compared with aluminum.

Several general trends concerning linear isomers can be observed in Figure 1. Triplet structures are clearly preferred over singlet ones, and the energy differences between triplet states and $^1\Sigma$ states are much higher than those found in the case of BC_2N.[15] $^1\Delta$ states are much more stable than the corresponding $^1\Sigma$ states (about 45−55 kcal/mol, depending on the atomic arrangement). The linear structures reported by Zheng et al.[16] correspond to the $^1\Sigma$ states, and therefore these authors predict linear structures quite high in energy. It should be noted that $^1\Delta$ states have an imaginary vibrational frequency (corresponding to a bending mode) at the B3LYP level. Therefore we carried out optimizations in C_s symmetry obtaining the corresponding $^1A'$ bent structures. These bent structures deviate considerably from linearity, with for example a <AlCC bond angle of 144.6° for AlCCN. At the MP2 level all $^1\Delta$ states are true minima since all their vibrational frequencies are real. Nevertheless we have carried out optimizations in C_s symmetry but in all cases linear structures were finally reached. We are aware that the $^1\Delta$ states are not properly described by a monodeterminantal wave function (as employed in the reference HF for the MP2 calculations). However we have reported the MP2 and G2 results for these structures to have an estimate of their relative stabilities at those levels of theory. Nevertheless the energy differences between these states and the AlCCN($^3\Sigma$) structure seem large enough to discard any of these states as a candidate for the AlC_2N global minimum. In addition it should be noted that their relative energies at the G2(P) level are not too far from the corresponding CCSD(T) ones.

Another characteristic which can be observed in Figure 1 is that for all states, with the only exception of $^1\Sigma$ where AlNCC is slightly more stable, the preferred arrangement is AlCCN, with nitrogen in a terminal position where its lone pair may be located outside the chain. In general isomers with a terminating aluminum atom are more stable, a fact that is expected being aluminum a second-row atom. In fact only the $^3A''$ states for CAlNC, CAlCN, and NAlCC are reported in Figure 1 and Table 1, because other states lie even higher in energy.

For all cyclic isomers singlet states are generally preferred over triplet ones. Of the two rhombic isomers, II is more stable for the singlets, whereas III is more stable for triplet AlCNC. Nevertheless III−AlCNC($^3B_1$) is not a true minimum, since it has an imaginary b_2 vibrational frequency at both MP2 and B3LYP levels. In fact, optimizations lowering the C_{2v} symmetry lead to the AlC_2N global minimum, that is to linear AlCCN. It is interesting to note that for isomer II the symmetric arrangement, AlCNC, is more stable, whereas for isomer III the arrangement with C_s symmetry, AlCCN, is preferred. This reflects, as in the case of the linear isomers, the preference for Al−C bonding instead of Al−N bonding, since in structures III Al is mainly bonded to the middle atom of the quasilinear CCN or CNC moiety (see below).

The geometries of the most stable linear and cyclic isomers of AlC_2N are given in Figure 3. For the sake of comparison with other cyclic structures, we have also included the isomers corresponding to structure III, even if they are less stable than other structures. In general there are not severe discrepancies between the geometrical parameters obtained with the B3LYP and MP2 methods.

It is clearly seen in Figure 3 that the bond lengths for the $^3\Sigma$ and $^3\Pi$ states of linear AlCCN reflect the valence-bond structures discussed above. The Al−C bond distance in AlCCN($^3\Sigma$) is typical of a normal single bond (1.957 Å in trimethylaluminum in the gas phase[30]), whereas in AlCCN($^3\Pi$) is much shorter and can be ascribed to a double bond (which can be estimated around 1.73−1.79 Å from theoretical calculations[31]). On the other hand the C−N bond distance is slightly shorter for the $^3\Pi$ state whereas the C−C bond length is slightly longer, as a consequence of the contribution of structure (2a). It is also clear that the Al−N and Al−C bond distances in AlNCC($^3\Sigma$) and AlCNC($^3\Sigma$), respectively, correspond also to single bonds. (The Al−N single bond distance in other theoretical calculations[32] can be estimated to be around 1.81 Å.)

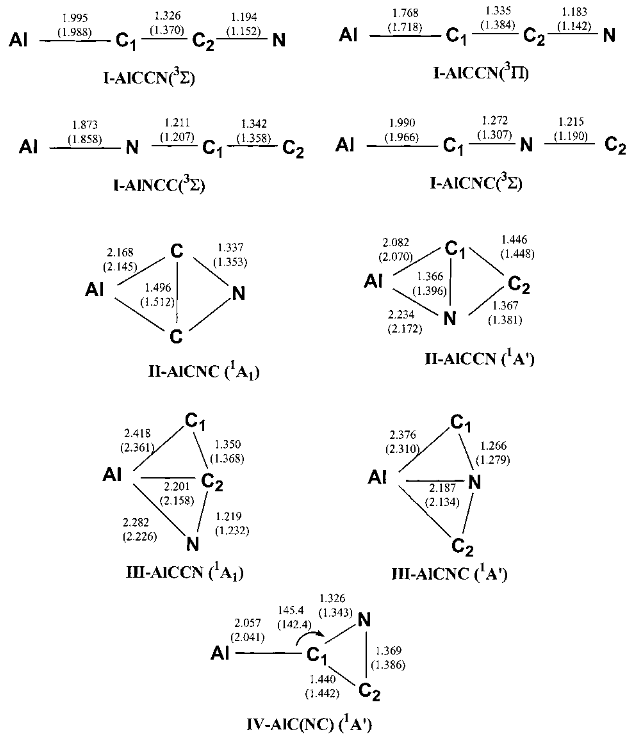

Figure 3. Equilibrium geometries of some of the most stable AlC_2N isomers at the B3LYP/6-311G(d) and MP2(full)/6-311G(d) (in parentheses) levels of theory. Distances are given in angstroms and angles in degrees.

The most interesting feature of the geometries of the rhombic isomers corresponding to structure II concerns the transannular C−C (II−AlCNC) or C_1−N (II−AlCCN) distances. In both cases the transannular distance is short enough to suggest the existence of a bond between both atoms, and therefore these isomers should be best described as bicylic structures rather than as truly four-membered rings. It is also interesting to note that, as in the case of rhombic BC_2N,[15] multicenter bonding is found for structures II. For the other rhombic structures, III−AlCCN and III−AlCNC, whose geometrical parameters are rather different than those of structures II, the most salient feature is the relatively short Al−C_2 and Al−N transannular bonds, in any case much shorter than peripheral bond distances. This fact suggests that the bonding is preferentially located between Al and the central atom of either the CCN or CNC chain, and that therefore they might be better described as T-shape structures rather than as rhombic isomers. Finally our geometrical parameters obtained for the three-membered ring isomer IV−AlC(NC) are obviously quite close to those reported by Zheng et al.,[16] and therefore we will not comment on them further.

Compared with BC_2N, there are no essential changes in the geometries upon replacement of boron atom by aluminum for open-chain triplet structures. Nevertheless there are some relatively important modifications for the singlet open-chain structures (the C−C distances are reduced up to 0.07 Å), as well as for cyclic species (with lengthenings of C−C or C−N distances up to 0.05 Å).

To aid in the possible experimental observation of AlC_2N we provide the most important information about the predicted global minimum, I−AlCCN($^3\Sigma$), computed at the B3LYP level (which should more reliable than the MP2/6-311G(d,p) level in this case, since it is virtually unaffected by spin contamination):

Rotational constant: $B = 2.326$ GHz

Vibrational frequencies in cm^{-1} (IR intensities, in kmmol^{-1}, are given in parentheses):

π: 63 (1.53), essentially AlCC bending; 459 (5.56), CCN bending.

σ: 421 (141.91), Al$-$C stretching; 1283 (64.89), C$-$C stretching; 1812 (3.81) C$-$N stretching.

(the assignment of normal modes is given for a qualitative description, since they are coupled to a certain extent).

Dipole moment: 2.975 D.

We may comment on the relative stability of the AlC$_2$N global minimum, and for that purpose we have computed the atomization energies at different levels of theory, with the following results in kcal/mol:

383.4 (B3LYP); 353.2 (MP2); 372.0 (CCSD(T));
381.3 (G2); 387.2 (G2(P))

as well as the dissociation energy for the fragmentation into Al and linear CCN:

91.7 (B3LYP); 89.8 (MP2); 90.0 (CCSD(T));
93.6 (G2); 95.3 (G2(P))

From these results, which are in reasonable agreement at the different levels of theory employed, we may conclude that the stability of AlCCN should be slightly lower but of the same magnitude than that of BCCN,[15] since the atomization energy is somewhat smaller for the former. Furthermore the dissociation energy into Al + CCN computed in the present work is much higher than the former predicted value of 76 kcal/mol.[16] Therefore the thermodynamic stability of AlCCN seems relatively high suggesting that it may be of interest for experimentalists.

Conclusions

A theoretical study of the different AlC$_2$N isomers, in both the singlet and triplet surfaces, has been carried out. The most important conclusion of our work is that the global minimum is a linear AlCCN isomer, whereas the previously predicted global minimum, a three-membered ring isomer, lies much higher in energy (more than 25 kcal/mol at the more reliable levels of theory). In fact our results predict that there are even other four structures lying lower in energy than the previously predicted global minimum, two of them being rhombic structures.

The preferred atomic arrangement, as in the case of its analogue BC$_2$N system, for linear isomers is AlCCN. However, contrary to what is observed for BC$_2$N, the ground state is a $^3\Sigma$ state, a fact which can be rationalized bearing in mind the lower preference to form multiple bonds of Al compared to B. The two most stable cyclic isomers, corresponding to rhombic structures seem to present transannular bonding and therefore are best described as bicyclic structures.

Predictions for different molecular properties (vibrational frequencies, rotational constant, dipole moment) have been made for the global minimum, and its thermodynamic stability for its dissociation into the constituent atoms or into Al + CCN has been computed. On the basis of these results we may conclude that the ground state of AlC$_2$N is relatively stable and therefore it might be an interesting target molecule for experimentalists. In addition, given the similar structure of the global minimum of AlC$_2$N to the corresponding ground state of BC$_2$N, both corresponding to XCCN arrangement (X being Al or B), it is possible that AlC$_2$N could also give rise to similar nanostructures with interesting properties in material science.

Another interesting conclusion from our work is that for the AlC$_2$N system the B3LYP method seems to provide results of the same quality than other more computational expensive methods, and therefore DFT methods could be appropriate to study more complex related systems.

Acknowledgment. This research has been supported by the Ministerio de Educación y Cultura of Spain (DGICYT, Grant PB97-0399-C03-01) and by the Junta de Castilla y León (Grant VA 18/00B).

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