New Group 2 Chemistry: A Multiple Barium-Nitrogen Bond in the CsNBa Molecule

Gagliardi, Laura

How to cite

GAGLIARDI, Laura. New Group 2 Chemistry: A Multiple Barium-Nitrogen Bond in the CsNBa Molecule. In: Journal of the American Chemical Society, 2002, vol. 124, n° 29, p. 8757–8761. doi: 10.1021/ja0260216

This publication URL: https://archive-ouverte.unige.ch/unige:3523

Publication DOI: 10.1021/ja0260216

J|A|C|S
ARTICLES

New Group 2 Chemistry: A Multiple Barium−Nitrogen Bond in the CsNBa Molecule

Laura Gagliardi*

Contribution from the Dipartimento di Chimica G. Ciamician, University of Bologna,
Viale F. Selmi 2, I-40126 Bologna, Italy

Received February 25, 2002

Abstract: The existence of a series of triatomic molecules with the general formula MNM′, where M is an alkaline metal (K, Rb, Cs), and M′ is an alkaline earth metal (Ca, Sr, Ba), has been predicted by quantum chemical methods. Among these, the CsNBa molecule shows a feature not found before, the presence of a multiple bond between barium and nitrogen. As a consequence of this novel bonding situation, the molecule is linear. The same holds for all Ba triatomics, MNBa, independent of the nature of the alkali M atom, and for all Sr compounds, MNSr. The presence of a multiple bond makes CsNBa, and other related Ba and Sr molecules, particularly stable and appealing experimentally. The systems with the alkaline earth metal M′ = Ca, on the other hand, turned out to be bent. Calculations have also been performed on the negative ions BaN^- and CaN^-, which form a well-defined entity in the MNM′ systems (M′ = Ba, Ca). The results show that the two ions have a different electronic structure in the ground state, which is one reason for the different properties of the MNM′ systems and explains why the molecules containing the BaN^- moiety are linear, while those containing CaN^- are bent.

Introduction

Quantum chemical calculations suggest that a series of triatomic molecules with the general formula MNM′, where M is an alkaline metal (K, Rb, Cs), and M′ is an alkaline earth metal (Ca, Sr, Ba), are stable as single molecules in the gas phase. Among the possible MNM′ species, with M = K, Rb, Cs, and M′ = Ca, Sr, Ba, the combinations where M and M′ belong to the same row, KNCa, RbNSr, CsNBa, and some crossed combinations such as KNSr and KNBa were considered. All of the systems explored were found to be stable in their singlet ground state. However, despite the common nature of the group 2 atoms, they have different characteristics. The M′ = Ca compounds have strongly polarized bonds resembling the ionic structure $M^+N^{3-}Ca^{2+}$. This makes them rather standard and of limited interest. The CsNBa molecule, as well as the other M′ = Ba, and Sr present, however, a different bonding situation. A multiple bond occurs between Ba (Sr) and N, while the Cs (and other M) atom does not participate in the bonding. The system can be viewed as being formed by the ion pair Cs^+ and BaN^-, where the bonding in the negative ion has a larger covalent character than that in CaN^- (see below). To our knowledge, these systems have never been investigated before, either in the gas phase or in the solid state. Among the barium−nitrogen compounds, solid barium nitride Ba_3N_2, barium azide $Ba(N_3)_2$[1] (and refs therein), and BaN_2[2] are known. Among the strontium−nitrogen compounds, the number of systems is relatively small: Sr_3N_2, Sr_8N_5, and SrN have been reported;[1] the subnitride Sr_2N[3] and the azide $Sr(N_3)_2$[4] have been structurally characterized. In a recent work by Auffermann et al.,[5] SrN and SrN_2 have been synthesized and structurally characterized (see also ref 6 and refs therein).

Given the different characteristics between the triatomics with M′ = Ca and M′ = Ba (Sr), and because all of the MNM′ systems are formed by the ion pair M^+ and $M'N^-$, the $M'N^-$ with M′ = Ca, Ba were also investigated. The results show that the CaN^- and BaN^- ions have a different electronic structure in the ground state, which is one reason for the different properties of the MNM′ systems and explains why the molecules containing the BaN^- moiety are linear, while those containing CaN^- are bent.

Computational Details

To elucidate the electronic structure of the MNM′ compounds in more detail, quantum chemical calculations have been performed using density functional theory, DFT, with the B3LYP exchange-correlation functional. The program Gaussian 98 was employed. Some studies were also made at a higher level of theory: multiconfigurational SCF level, followed by perturbation theory, CASSCF/CASPT2,[7] using the program MOLCAS5.2.[8] The 6-31G* basis set was employed for the nitrogen atom and for M = K, M′ = Ca in the DFT calculations (replaced by the MOLCAS5.2 ANO-L basis in the CASSCF/CASPT2 calculations). For M = Rb, Cs, and M′ = Sr, Ba, the energy-adjusted Stuttgart ECPs

---

* To whom correspondence should be addressed. E-mail: laurag@ciam.unibo.it.

(1) Gregory, D. H. *Coord. Chem. Rev.* **2001**, *215*, 301.
(2) Vajenine, G. V.; Affermann, G.; Prots, Y.; Schnelle, W.; Kremer, R. K.; Simon, A.; Kniep, R. *Inorg. Chem.* **2001**, *40*, 4866.
(3) Brese, N. E.; O'Keeffe, M. *J. Solid State Chem.* **1990**, *87*, 134.
(4) Kirschner, H.; Kelz, G. *Z. Anorg. Allg. Chem.* **1982**, *494*, 203.
(5) Auffermann, G.; Prots, Y.; Kniep, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 547.
(6) Kroke, E. *Angew. Chem., Int. Ed.* **2002**, *41*, 77.
(7) Anderson, K.; Malmqvist, P.-A.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.
(8) MOLCAS, Version 5.2; Lund University, Sweden, 2001.

10.1021/ja0260216 CCC: $22.00 © 2002 American Chemical Society

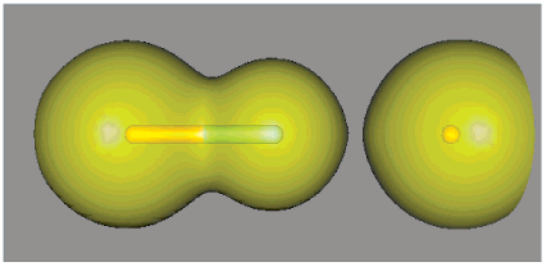

Figure 1. The CASSCF total electronic density in the singlet ground state of CsNBa.

were used in the DFT calculations.[9] The accompanying basis set of the ECPs was used to describe the valence electron density,[10] Rb[7s6p]/(5s4p), Sr[6s6p5d]/(4s4p2d), Cs[7s6p]/(5s4p), Ba[6s6p5d1f]/(4s4p2d1f). Two d and one f functions were added to the Cs valence basis (d exponents 0.133 and 0.404 from Huzinaga,[11] and f exponent 0.6970 was taken from the Ba valence basis set), and two d functions were added to the Rb valence basis (with exponents 0.226 and 0.695[11]). In the CASSCF/CASPT2 calculations, an all-electron relativistic ANO basis from the MOLCAS5.2 library was used for Cs and Ba-[25s21p14d3f2g]/(8s7p5d1f).[12]

The crucial step in a CASSCF/CASPT2 calculation is the choice of the active space. After several tests, it was found appropriate to use an active space formed by six electrons in seven molecular orbitals (6/7). These MOs are the three bonding and three antibonding linear combinations of the 2p atomic orbitals (AOs) with the M′ (Ca, Ba) valence AOs of appropriate symmetry (two σ and four π). The seventh active orbital included has σ symmetry. The lower energy doubly occupied valence MO was found to be largely AO like, and the inclusion of such MO (together with the corresponding antibonding MO) did not seem to affect the results. We will thus present only results generated with the 6/7 active space. In the calculations on BaO and BaC^{2-}, an analogous active space was used.

Results and Discussion

In the following, we shall use CsNBa as an example and discuss in some detail the results of the CASSCF MO analysis. Results for BaN^-, BaO, BaC^{2-}, and CaN^- will also be presented.

The MNM′ Triatomic Systems. Three bonding orbitals are present in CsNBa. They are essentially one σ Ba−N bond involving the Ba 6s, 6p, and 5d atomic orbitals and N 2p, and two Ba−N π bonds involving the Ba 6p, 5d and N 2p atomic orbitals. The presence of a multiple bond gives cylindrical symmetry to the system, explaining why the Cs atom stays linear with respect to the NBa moiety. In contrast, the lighter systems, for example, KNCa, are found to be bent. This will be discussed further below. Is there then a triple bond between Ba and N in CsNBa? Not quite; the lowest triplet state of CsNBa lies only 5 kcal/mol higher in energy than the singlet ground state and corresponds to an excitation from the σ bonding orbital to another σ orbital, mainly localized on barium. While the two π bonds are present both in the singlet and in the triplet states, the σ bond is not maintained in the triplet state. The total electronic density of CsNBa (Figure 1) in the ground state indicates a pronounced bond between barium and nitrogen.

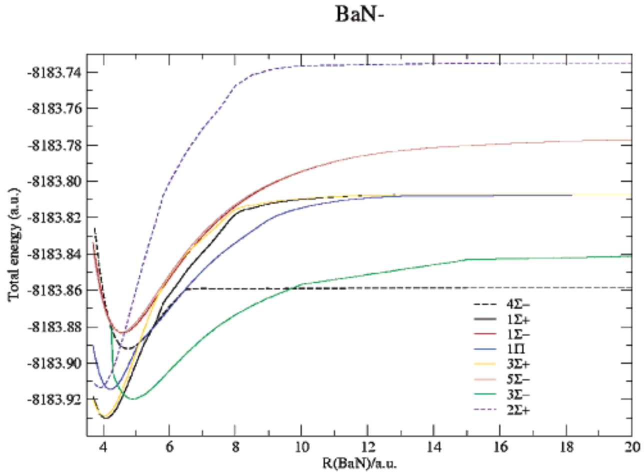

Figure 2. Potential energy curves for BaN^- and BaN as a function of the Ba−N distance (au) (CASSCF/CASPT2). Black solid $^1\Sigma^+$. Yellow $^3\Sigma^+$. Green $^3\Sigma^-$. Blue $^1\Pi$. Red $^1\Sigma^-$. Brown $^5\Sigma^-$. Black dashed $^4\Sigma^-$ (BaN neutral). Indigo dashed $^2\Sigma^+$ (BaN neutral).

Table 1. Bond Lengths (Å), Angles (deg), and Dipole Moment (debye) for the MNM′ Molecules

MNM′	R(M–N)	R(N–M′)	∠MNM′	dipole
KNCa[a]	2.502	2.188	122.27	4.26
KNCa[b]	2.625	2.234	128.05	4.15
KNSr[a]	2.433	2.048	180.00	2.48
RbNSr[a]	2.525	2.047	180.00	2.87
KNBa[a]	2.461	2.066	180.00	0.65
CsNBa[a]	2.567	2.086	180.00	1.10
CsNBa[b]	2.599	2.047	180.00	1.00

[a] DFT/B3LYP. [b] CASSCF/CASPT2.

Table 2. DFT/B3LYP Harmonic Frequencies (cm^{-1}) and Their IR Intensities (km mol^{-1}) in Parentheses for the MNM′ Species ((a) Singly Degenerate Modes; (e) Doubly Degenerate Modes)

MNM′	ν bend	ν sym. stretch	ν asym. stretch
KNCa	94.75(a)	300.32(a)	581.19(a)
	[21.1]	[15.3]	[108.3]
KNSr	48.49(e)	208.77(a)	644.16(a)
	[52.5]	[3.2]	[24.3]
RbNSr	54.85(e)	161.21(a)	638.40(a)
	[49.2]	[3.1]	[19.7]
KNBa	87.29(e)	190.85(a)	674.04(e)
	[83.3]	[0.47]	[66.10]
CsNBa	94.64(e)	130.79(a)	630.18(a)
	[58.2]	[5.5]	[89.0]

The dissociation of CsNBa, as a function of the Cs−N distance, was investigated at the CASSCF/CASPT2 level of theory. While around the equilibrium, CsNBa is essentially formed by two ionic moieties Cs^+ and BaN^-, it dissociates to neutral Cs and BaN. A crossing between the ionic and neutral curves occurs at a Cs−N bond distance of ca. 4 Å. The energy difference between CsNBa and the ionic dissociation products, Cs^+ and BaN^-, is 116 kcal/mol, while the energy difference with respect to the neutral products, Cs and BaN, is only 21 kcal/mol. The crossing distance between the ionic and neutral curves could also be estimated by using the Herschbach harpooning mechanism,[13] and this gives a value in the range of 3.5−4.0 Å.

Equilibrium geometries and harmonic frequencies were computed for all of the triatomic MNM′ species. In Table 1,

---

(9) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 1233.

(10) Institut fur Theoretische Chemie, Universitat Stuttgart. *ECP and Corresponding Valence Basis Sets;* http://www.theochem.uni-stuttgart.de/.

(11) Huzinaga, S. *Gaussian Basis Sets for Molecular Calculations, Physical Sciences Data 1*; Elsevier: Amsterdam, 1991, 1995.

(12) Roos, B. O., to be published.

(13) Herschbach, D. R. *Adv. Chem. Phys.* **1966**, *10*, 319.

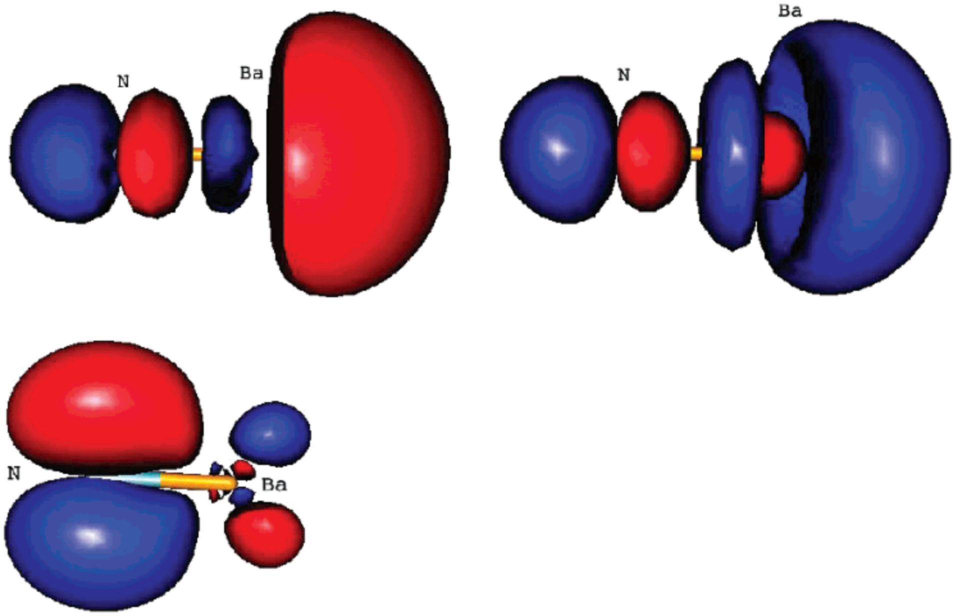

Figure 3. The two σ, and one component of the π MOs of BaN^- with occupation nos. 1.27, 0.72, 1.94, respectively (isosurface = 0.02).

the bond distances and bond angles are reported, together with the total dipole moments. The Ba−N and Sr−N bond distances are always shorter than the Ca−N bond distances, despite the larger atomic radii of the heavier elements, again indicating a different bonding mechanism. The Ca species are bent, while the Sr and Ba molecules are linear, independent of the M atom. The energy barrier from the bent to the linear form is, however, small. It was computed to be ca. 2−3 kcal/mol for all of them, with the inclusion of zero point energy correction. The Ca species have the largest dipole moments, indicating a large polarization, while the Ba species have the smallest dipole moment of all of the studied molecules.

In Table 2, the harmonic frequencies with IR intensities are reported. These data will be appealing to experimentalists who wish to prepare these molecules and study them, with spectroscopic methods, such as vibrational matrix isolation techniques, laser-induced fluorescence, and photoelectron spectroscopy.[14,15] Possible ways of making CsNBa are reacting cesium with heated barium nitride (i.e., Ba_3N_2) in a nitrogen atmosphere, and dissolving barium in molten cesium in an oxygen free environment and passing nitrogen through the melt.

The M′N⁻ Anions. Given the different characteristics between the triatomics with M′ = Ca and M′ = Ba (Sr), and because the $M'N^-$ anion forms a well-defined moiety in the MNM′ triatomics, the $M'N^-$ with M′ = Ca and Ba were also investigated. CASSCF/CASPT2 show that BaN^- is a stable entity with a bond distance of 2.17 Å. The neutral BaN system has a positive electron affinity of ca. 11 kcal/mol. The dissociation curves for several electronic states of BaN^- and BaN were also computed at the CASSCF/CASPT2 level. The results are presented in Figure 2. The potential energy curve of the ground state of BaN, $^2\Sigma^+$, is reported, together with the curve of the $^4\Sigma^-$ state of BaN, which dissociates to the neutral atoms in their ground state and crosses the $^1\Sigma^+$ curve of BaN^- at $R(Ba-N) \approx 5.5$ au. The dissociation products of BaN^- will thus be the neutral atoms plus an electron. The energy difference between BaN^- at equilibrium and the neutral atoms in their ground states is 45 kcal/mol.

The CASSCF wave function of the ground state of BaN^- at equilibrium is highly biradical with two configurations of almost equal weight, one with the bonding and one with the antibonding σ orbital doubly occupied. This gives an unusual character to the electronic structure: a π double bond and two odd σ electrons, one on Ba and one on N^-. The biradical nature also explains the low excitation energy to the $^3\Sigma^+$ state. The Mulliken charges are +0.3 on Ba and −1.3 on N. The valence electronic configuration of BaN^- can thus be summarized as $(\sigma)^{1.27}(\sigma^*)^{0.72}(\pi)^{3.88}(\pi^*)^{0.12}$.

The anion BaN^- is isoelectronic to the neutral molecule BaO, which has been studied in the gas phase by Dyke et al.[14] CASSCF/CASPT2 calculations on BaO gave a bond distance of 2.00 Å and a dissociation energy of ca. 110 kcal/mol to Ba and O atoms in their ground state. The $^3\Sigma^+$ state is bound (R_{eq} = 2.19 Å) and lies 37 kcal/mol higher in energy than the $^1\Sigma^+$ ground state. The bonding in BaO is qualitatively different than that in BaN^-. The wave function analysis shows that BaO is a closed-shell system with Mulliken partial charges of −1.1 on O and +1.1 on Ba. The negative charge is thus localized on O, and the bonding has more ionic character. The active space used in the CASSCF calculations for both BaN^- and BaO is formed by the σ and two π bonding molecular orbitals, MOs, and the corresponding antibonding MOs. The MO occupation is clearly different in the two cases. In BaO, both the bonding σ and the two π MOs have an occupation close to two (1.96), and the corresponding antibonding MOs are almost empty. In BaN^-, on the other hand, the two π MOs have an occupation close to two (1.94), while the σ bonding MO is only singly occupied (1.27), and the σ antibonding is also singly occupied (0.72). The active orbitals used in the CASSCF calculations for BaN^- and BaO with an occupation number significantly different from zero are reported in Figures 3 and 4 (generated with the same isosurface = 0.5). The π MOs are similar in the two cases. The σ MO of BaO is analogous to one of the two singly occupied

---

(14) Dyke, J. M.; Feher, M.; Morris, A. *J. Chem. Phys.* **1987**, *91*, 4476.
(15) Cai, M. F.; Carter, C. C.; Miller, T. A.; Bondybey, V. E. *J. Chem. Phys.* **1986**, *95*, 161.

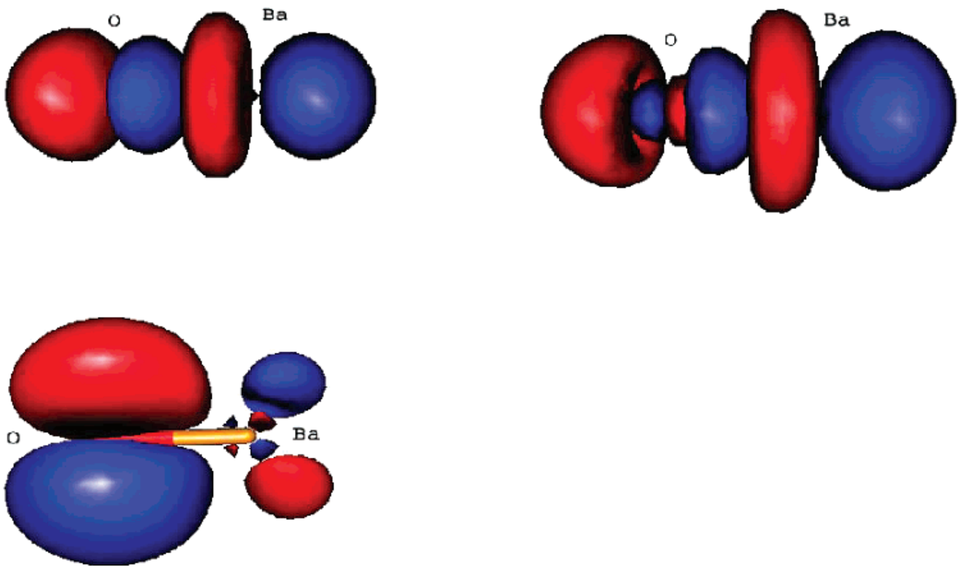

Figure 4. The two σ, and one component of the π MOs of BaO with occupation nos. 1.96, 0.04, 1.96, respectively (isosurface = 0.02).

σ MOs in BaN^-. The second singly occupied (0.72) σ MO in BaN^- has instead an occupation of almost zero (<0.002) in BaO.

The isoelectronic BaC^{2-} anion presents a weak bond (R_{eq} = 2.5 Å) in its triplet ground state. However, the dissociation products Ba^- and C^- lie lower in energy than the bound system. It can thus be considered as a metastable species. The isoelectronic series BaC^{2-}, BaN^-, BaO gives some insight into the differences in the bonding. BaN^-, with its unique biradical nature, falls between a metastable weakly bounded species, BaC^{2-}, and a stable closed-shell ionic species, BaO. The dissociation energy of BaN^- is slightly less than one-half of the value of BaO. The different nature of the electronic structure and bonding capability of these systems is reflected in their relative stability, along the BaX (X = C, N, O) series.

The BaN^- anion was also compared to the analogous CaN^- anion, in view of the difference between the triatomics containing the BaN^- and CaN^- moieties. Unlike BaN^-, CaN^- has a $^3\Sigma^-$ ground state (R_{eq} = 2.38 Å), with a wave function corresponding to two doubly occupied σ orbitals, one mainly located on Ca and one on N, and two singly occupied π orbitals, essentially corresponding to N p atomic orbitals. The electronic configuration of CaN^- is thus $\sigma^2(\text{Ca sp})\sigma^2(\text{N p}_z)\pi^1(\text{N p}_x)\pi^1(\text{N p}_y)$. The different electronic ground state of BaN^- and CaN^- explains why the CaN^- triatomics are bent, while the BaN^- triatomics are linear. The dissociation curves for several electronic states of CaN^- were computed at the CASSCF/CASPT2 level (Figure 5), together with two electronic states of neutral CaN. The ground state of CaN is $^4\Sigma^-$. This is almost degenerate with the $^2\Pi$ state of neutral CaN (Figure 5). The $^4\Sigma^-$ state of neutral CaN dissociates to neutral atoms in their ground states and crosses the $^3\Sigma^-$ curve of CaN^- at R(Ca−N) ≈ 9 au, at which distance the ion will lose the extra electron and dissociate into the neutral atoms. The energy difference between CaN^- at equilibrium and the neutral atoms in their ground states is 33 kcal/mol.

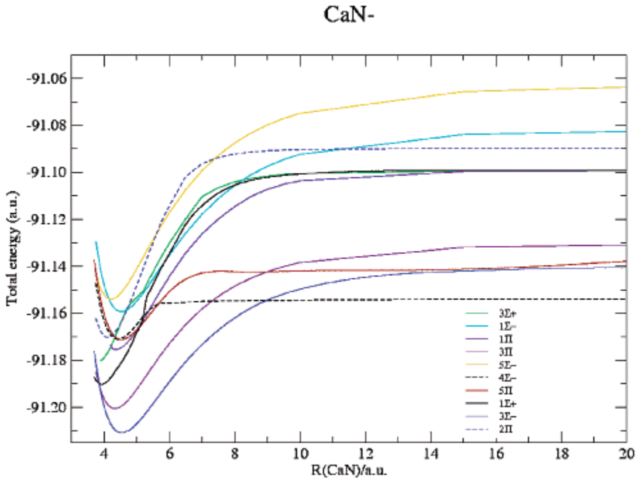

Figure 5. Potential energy curves for CaN^- and CaN as a function of the Ca−N distance (au) (CASSCF/CASPT2). Blue solid $^3\Sigma^-$ ground state. Magenta $^3\Pi$. Green $^3\Sigma^+$. Red $^5\Pi$. Violet $^1\Pi$. Light blue $^1\Sigma^-$. Yellow $^5\Sigma^-$. Black $^1\Sigma^+$. Black dashed $^4\Sigma^-$ (CaN neutral). Blue dashed $^2\Pi$ (CaN neutral).

Not only have BaN^- and CaN^- a different electronic configuration in the ground states, but this is also the case for the corresponding neutral species, BaN and CaN, which have $^2\Sigma^+$ and $^4\Sigma^-$ (or $^2\Pi$) ground states, respectively. This is the reason the triatomics containing the BaN moiety are linear, while those containing the CaN moiety are bent.

Conclusions

The presence of a multiple bond makes CsNBa, and other MNBa and MNSr molecules, particularly appealing. They contain a well-defined BaN^- (SrN^-) moiety, in which Ba (Sr) contributes to the bonding with valence s, p, and d orbitals. BaN^- has been studied together with the isoelectronic BaC^{2-} and BaO. With its biradical nature, BaN^- is between the metastable BaC^{2-} species and the stable closed-shell ionic BaO species. BaN^- has also been compared to the analogous CaN^-, and it has been shown that while BaN^- has a $^1\Sigma^+$ ground state, CaN^- has a $^3\Sigma^-$ ground state. The corresponding neutral species, BaN and CaN, also have different electronic ground states, $^2\Sigma^+$ and $^4\Sigma^-$ (or $^2\Pi$), respectively. This explains why the triatomics containing CaN are bent, while those containing BaN are linear.

Other systems analogous to CsNBa, with this type of multiple bonding, might exist. Applications in solid-state chemistry and nitrogen-doped semiconductors might be possible, and it is therefore appealing to attempt to study these molecules experimentally.

Acknowledgment. Ministero Italiano dell' Istruzione e Universita' supported this work. The author thanks Professor Björn O. Roos and Professor Weston T. Borden for useful discussion of the manuscript.

Supporting Information Available: Table of the total energies for the MNM′ molecules (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0260216