J. Phys. Chem. A **2003,** *107,* 2974−2980

Stable Compounds of the Lightest Noble Gases: A Computational Investigation of RNBeNg (Ng = He, Ne, Ar)

Paola Antoniotti

Dipartimento di Chimica Generale ed Organica Applicata, Università degli Studi di Torino,
C.so M. D' Azeglio, 48, 10125 Torino, Italy

Nicoletta Bronzolino and Felice Grandinetti*

Dipartimento di Scienze Ambientali and Istituto Nazionale di Fisica della Materia (INFM), Unità di Viterbo,
Università della Tuscia, L.go dell' Università, s.n.c., 01100 Viterbo, Italy

Received: December 18, 2002; In Final Form: February 28, 2003

The structure and stability of as yet unreported compounds with the general formula RNBeNg (Ng = He, Ne, Ar) have been theoretically investigated at various ab initio and B3LYP density functional (DFT) levels of theory. Exemplary species include the parent HNBeNg and saturated and unsatured compounds such as HONBeNg, FNBeNg, X−CH_2−NBeNg, X−C(O)−NBeNg (X = H, OH, F), and C_6H_5−NBeNg. The thermochemical stability of these molecules, invariably characterized as true energy minima on the singlet potential energy surface, depends on two factors, namely, the energy of dissociation ΔE into singlet RNBe and Ng and the energy difference between the singlet and triplet states of RNBe. The values of ΔE are essentially independent of the nature of the substituent R and are around 6.5 kcal mol^{-1} for Ng = He, 8.5 kcal mol^{-1} for Ng = Ne, and 11.0 kcal mol^{-1} for Ng = Ar. In addition, for most of the investigated RNBeNg compounds, we have found that the singlet state of RNBe is more stable than the triplet state or for RNBe, with a triplet ground state, that the singlet−triplet gap is lower than the ΔE value given above. Therefore, our calculations support the prediction that this class of thermochemically stable RNBeNg compounds could actually be very large.

I. Introduction

Since pioneering work by Bartlett in 1962,[1] numerous compounds of krypton, xenon, and radon have been prepared and structurally characterized.[2−4] However, only a few stable compounds containing argon, including, for example, ArBeO,[5] ArAgX,[6] ArCuX,[7] (X = F, Cl, Br), ArAuCl,[8] HArF,[9] and CUOAr,[10] have been experimentally observed in low-temperature matrices, and no stable compounds containing helium and neon have been reported to date. This is in line with the results of the theoretical predictions that have outlined, over the years, only rare examples of suitable candidates for the preparation of compounds of the lightest noble gases.[11−13] In particular, Frenking, Cremer, and co-workers have reported[11] that the diatomic BeO in its singlet ground state $^1\Sigma^+$ fixes the lightest noble gases with the formation of OBeNg complexes (Ng = He, Ne, Ar, Kr, Xe), which are thermodynamically stable with respect to dissociation into BeO and Ng. The OBe−Ng bond energies were calculated to range from about 3 kcal mol^{-1} for Ng = He to about 13 kcal mol^{-1} for Ng = Xe. More recently, as part of our continuing interest in the chemistry of gaseous fluorinated cations,[14−22] we have theoretically found[23] that, in its singlet ground state $^1\Sigma^+$, the BeF^+ cation, which is isoelectronic with BeO but positively charged, fixes helium, neon, and argon with the formation of thermochemically stable $FBeNg^+$ adducts, whose enthalpies of dissociation (at 298.15 K) into BeF^+ and Ng are computed at the Gaussian-3 level of theory[24] to be as large as 10.6 kcal mol^{-1} for Ng = He, 16.0 kcal mol^{-1} for Ng = Ne, and 34.5 kcal mol^{-1} for Ng = Ar. As a further contribution to the study of stable compounds of the lightest noble gases, we report here computational evidence for a new large class of species strictly related to OBeNg and $FBeNg^+$. These compounds have the general formula RNBeNg (Ng = He, Ne, Ar) and arise from the ligation of the noble gas Ng with a singlet beryllium imide RNBe. The results of our calculations, performed at various ab initio and density functional (DFT) levels of theory, indicate that the monovalent residue R may actually be very different in nature and size, ranging from the parent H atom to more complex aliphatic, carbonylic, and aromatic groups. Our theoretical findings could stimulate future experimental work aimed at the observation and characterization of these novel stable compounds of the lightest noble gases.

II. Computational Details

The quantum chemical calculations have been performed using Unix versions of the Gaussian 98[25] and MOLPRO 2000.1[26] sets of programs installed on a Alphaserver 1200 and a DS20E Compaq machine. The standard internal 6-311G(d,p) and 6-311++G(2df,2p) basis sets were employed. The geometry optimizations of BeNH and HNBeHe performed at the complete active space SCF (CASSCF) level of theory[27] were based on analytical gradients and used the full-valence active spaces of 8 electrons in 9 molecular orbitals for BeNH and 10 electrons in 10 molecular orbitals for HNBeHe. The single-point calculations performed at the multireference CI (MR-CI) level of theory[28] used these CASSCF reference wave functions and

---

* To whom correspondence should be addressed. E-mail: fgrandi@unitus.it.

10.1021/jp027760b CCC: $25.00

TABLE 1: Equilibrium Bond Distances (Å), Harmonic Vibrational Frequencies, and Energies for the Dissociation of HNBeNg Molecules ($C_{\infty v}$) into BeNH ($^1\Sigma^+$) and Ng (ΔE)

method/basis set[a]	Be−Ng	Be−N	N−H	ν (cm^{-1})[b]	ΔE (kcal mol^{-1})[c]
			Ng = He		
CCSD(T)/B1	1.497	1.364	1.003		4.1(4.9)
CCSD(T)/B2	1.496	1.363	0.999		4.4(4.9)[d]
B3LYP/B1	1.481	1.349	1.000	205.3(0.4), 581.5(0.5), 598.4(45.2), 1630.2(38.3), 3778.7(60.3)	5.6(6.3)
B3LYP/B2	1.480	1.349	0.998		5.8(5.9)[e]
CASSCF/B1	1.534	1.364	1.008		7.0(7.3)[d]
MR-CI/B1[f]					4.0(4.7)[d]
			Ng = Ne		
CCSD(T)/B1	1.813	1.361	1.002		2.7(6.8)[e]
CCSD(T)/B2	1.794	1.362	0.999		2.9(5.8)[e]
B3LYP/B1	1.806	1.348	1.000	146.2(11.7), 275.2(1.2), 571.4(32.7), 1626.6(68.4), 3782.3(59.8)	4.6(8.1)[e]
B3LYP/B2	1.805	1.348	0.998		3.8(4.7)[e]
			Ng = Ar		
CCSD(T)/B1	2.048	1.365	1.003		8.7(13.3)[e]
CCSD(T)/B2	2.065	1.366	0.999		10.5(12.7)[e]
B3LYP/B1	2.093	1.352	1.000	155.8(6.1), 262.3(3.0), 572.3(43.0), 1612.5(123.3), 3780.9(60.1)	8.8(9.5)[e]
B3LYP/B2	2.071	1.353	0.998		10.6(10.9)[e]

[a] B1 = 6-311G(d,p), and B2 = 6-311++G(2df,2p). [b] IR intensities (km mol^{-1}) are in parentheses. [c] Values in parentheses do not include the BSSE. [d] ZPE at the CCSD(T)/B1 level of theory. [e] ZPE at the B3LYP/B1 level of theory. [f] At the CASSCF/B1 optimized geometry.

included the contributions of single and double excitations as well as the Davidson correction for quadruple excitations.[29] The geometry optimizations and vibrational frequency calculations performed at the coupled cluster level of theory,[30,31] including the contributions from single and double substitutions and an estimate of connected triples (CCSD(T)), were based on numerical differentiation and do not include the effect from inner-shell correlation. For the triplet states, we used the spin-restricted coupled cluster theory as implemented in MOLPRO. The geometry optimizations and vibrational frequency calculations performed at the B3LYP level of theory[32−34] were based on analytical gradients and second derivatives. The basis set superposition error (BSSE) was included by using the full counterpoise method.[35]

Chemical bonding analysis was based on the theory of atoms in molecules (AIM) using the implementation in Gaussian 98 due to Cioslowski and co-workers.[36−40] In particular, we have calculated the MP2(full)/6-311G(d,p) charge density ρ and the Laplacian of the charge density $\nabla^2\rho$ at the bond critical points (bcp), which are intended to be the points on the attractor interaction lines where $\nabla\rho = 0$.

III. Results and Discussion

III. A. Structure and Stability of BeNH and HNBeNg (Ng = He, Ne, Ar). The prototype members of the presently investigated class of compounds are the adducts between the beryllium imide BeNH and helium, neon, and argon.

The beryllium imide has been observed in low-temperature matrices via the thermal decomposition of $Be(NH_2)_2$.[41,42] Subsequent theoretical calculations[43,44] revealed that the electronic ground state of this linear molecule is the singlet $^1\Sigma^+$, which is more stable than the first excited triplet state $^3\Pi$ by 9.4 kcal mol^{-1} at the MP4/6-31+G(2df,p) level of theory[44] and 1.6 kcal mol^{-1} at the SDCI + DC level of theory with a triple-ζ-quality basis set.[43] In addition, it was found that, in the $^3\Pi$ state, BeNH has a flat bending motion, thus suggesting a quasi-linear or weakly linear conformation of triplet BeNH.[43] On the basis of these findings, in the present study we decided to investigate the three electronic states of the lowest energy of BeNH, namely, the linear $^1\Sigma^+$ and $^3\Pi$ and the nonlinear $^3A''$, using the CASSCF, the MR-CI, and the CCSD(T) levels of theory. The results of our calculations confirmed that the singlet $^1\Sigma^+$ is the electronic ground state of BeNH, which is more stable than the nonlinear $^3A''$ by 5.4 kcal mol^{-1} at both the MR-CI/6-311++G(2df,2p)//CASSCF/6-311G(d,p) and the CCSD(T)/6-311++G(2df,2p) levels of theory. (At both computational levels, the zero-point energy contribution, ZPE, has been included by using the CCSD(T)/6-311G(d,p) harmonic frequencies.) In addition, at the same computational levels, the $^3A''$ was more stable than the linear $^3\Pi$ by only 0.2−0.3 kcal mol^{-1}. At the B3LYP/6-311++G(2df,2p) level of theory, the predicted triplet state of lowest energy, $^3\Pi$, is again less stable than the singlet $^1\Sigma^+$ by 5.1 kcal mol^{-1}. (The ZPE has been included by using the B3LYP/6-311G(d,p) harmonic frequencies.)

As already pointed out in previous theoretical investigations,[11,23] in their singlet ground state $^1\Sigma^+$, diatomics BeO and BeF^+ fix helium, neon, and argon with the formation of thermochemically stable OBeNg and $FBeNg^+$ adducts (Ng = He, Ne, Ar). It was therefore conceivable that, in its singlet ground state $^1\Sigma^+$, the strictly related BeNH could fix the lightest noble gases with the formation of thermochemically stable HNBeNg adducts (Ng = He, Ne, Ar). As a matter of fact, all of the linear HNBeNg compounds ($C_{\infty v}$ symmetry) were characterized, at any computational level, as true energy minima on the singlet potential energy surface. Their relevant structural and stability data are collected in Table 1.

The geometry of HNBeHe was first optimized at the CCSD(T) level of theory, and, irrespective of the employed basis set, the T1 diagnostic was within the threshold of 0.02,[45] thus suggesting that this adduct is reasonably well described by a single electronic configuration. This has been confirmed by the results of CASSCF/6-311G(d,p) calculations, which showed that the wave function of HNBeHe is by far dominated by the ground-state electronic configuration. From Table 1, the Be−He bond distance of HNBeHe, computed as 1.534 Å at the CASSCF/6-311G(d,p) level of theory, becomes 1.497 Å at the CCSD(T)/6-311G(d,p) level of theory and 1.496 Å at the CCSD(T)/6-311++G(2df,2p) level of theory. As to the HNBeNe and

HNBeAr adducts, as already noted for HNBeHe, at the CCSD(T) level of theory the T1 diagnostic of both of these species was less than the 0.02 threshold value. From Table 1, except for the Be−Ng distance, computed to be about 1.805 Å for Ng = Ne and 2.050 Å for Ng = Ar, the calculated structural parameters of HNBeNe and HNBeAr are quite similar to those of HNBeHe. In addition, we note the satisfying agreement between the CCSD(T) and the B3LYP computed geometries.

The HNBeHe adduct is stable with respect to the dissociation

$$\mathrm{HNBeHe} \rightarrow \mathrm{BeNH}\ (^1\Sigma^+) + \mathrm{He} \qquad (1)$$

whose energy change at 0 K is computed to be 4.9 kcal mol^{-1} at the CCSD(T)/6-311++G(2df,2p) level of theory, 4.7 kcal mol^{-1} at the MR-CI/6-311G(d,p)//CASSCF/6-311G(d,p) level of theory, and 5.9 kcal mol^{-1} at the B3LYP/6-311++G(2df,2p) level of theory. The corresponding values obtained, including the correction for the BSSE, are 4.4, 4.0, and 5.8 kcal mol^{-1}, respectively. Since the triplet state of BeNH is less stable than the singlet, the HNBeHe adduct can be stated to be thermochemically stable with respect to the dissociation into BeNH and He. As to the relative stability of the HNBeNg adducts (Ng = He, Ne, Ar), the polarizability of helium, neon, and argon increases in the order He < Ne < Ar,[46] and one expects the energies of dissociation ΔE of HNBeNg into BeNH ($^1\Sigma^+$) and Ng to follow the same trend, namely, HNBeHe < HNBeNe < HNBeAr. As a matter of fact (from Table 1, at any computational level if not corrected for the BSSE), the computed values of ΔE follow this expected trend. The only exceptions are the B3LYP/6-311++G(2df,2p) results, which predict that HNBeNe is slightly less stable than HNBeHe. However, if one includes the BSSE correction, the values of ΔE of HNBeAr are invariably larger than those of HNBeHe and HNBeNe but the stability of HNBeNe drastically decreases, and irrespective of the employed computational level, this species is predicted to be less stable than the helium-containing analogue. It is interesting that quite similar results have been obtained for the computed stabilities of the OBeNg adducts, which were found to increase in the unexpected order OBeNe < OBeHe < OBeAr when the BSSE correction was included.[11b] As already noted in this previous study, these anomalous trends could be partially affected by the inadequacy of the counterpoise method to correct for the BSSE, and the differences in the ΔE values of HNBeHe and HNBeNe are not large enough to support a safe conclusion of which of these two compounds is actually more stable.

As found for the previously investigated OBeNg,[11] the HNBeNg adducts cannot be viewed as chemically bound compounds. Rather, they must be perceived as strongly bound van der Waals complexes arising from the electrostatic interaction between the HNBe Lewis acid and the Ng atom. This conclusion comes from the results of the MP2(full)/6-311G(d,p) AIM calculations, which rule out any covalent character in the Be−Ng bonding of HNBeNg and indicate that the closed shell of the Ng atom is basically preserved. Thus, the Laplacian of the electron density $\nabla^2\rho$ at the bond critical points located on the attractor interaction lines corresponding to the Be−Ng bond of HNBeNg was found to be positive and was computed to be as large as +0.346e/au^5 for Ng = He, +0.224e/au^5 for Ng = Ne, and +0.222e/au^5 for Ng = Ar. In addition, the total charges (in electronic units) of the Ng atoms were computed to be as low as −0.036 for Ng = He, −0.027 for Ng = Ne, and −0.009 for Ng = Ar. We have also found that, irrespective of Ng, the total charge on the beryllium atom was as large as ca. +1.55e. This finding provides a reasonable explanation for the stable attachment of Ng to HNBe if one assumes that, because of the small radius of the beryllium atom, any approaching Ng experiences an electric field large enough to allow its fixation into a relatively deep potential energy well. The electrostatic character of the HNBeNg complexes is also consistent with their vibrational patterns, which include, in particular, the N−Be−Ng bendings at 205.3 (Ng = He), 146.2 (Ng = Ne), and 155.8 cm^{-1} (Ng = Ar) and the rather low Be−Ng stretchings at 581.5 (Ng = He), 275.2 (Ng = Ne), and 262.3 cm^{-1} (Ng = Ar).

Our calculations suggest that the thermochemically stable HNBeNg adducts (Ng = He, Ne, Ar) are probably novel conceivable candidates for the preparation of compounds of the lightest noble gases, including helium. Since the precursor BeNH in its singlet ground state $^1\Sigma^+$ can be produced from the pyrolysis of beryllium amide $Be(NH_2)_2$,[41,42] the experimental preparation of these species appears to be a viable possibility. In addition, the stability of the HNBeNg molecules is not only of interest per se but also has attractive implications related to the conceivable existence of a large class of stable or metastable compounds of the lightest noble gases. This concept can be generally stated as follows. The beryllium imide BeNH is just a special case of substituted beryllium imides RNBe that can be combined with a noble gas Ng to form RNBeNg molecules that exist as energy minima on the singlet potential energy surface. The loss of Ng from these RNBeNg molecules, with the formation of singlet RNBe, is an endothermic process. However, an RNBeNg can be stated to be thermochemically stable only if the singlet state of RNBe is more stable than the triplet or if the triplet state is more stable than the singlet but the singlet−triplet gap is smaller than the endothermicity of the spin-allowed loss of Ng from singlet RNBeNg. However, if the stability of the triplet state of RNBe with respect to the stability of the singlet exceeds the endothermicity of the spin-allowed loss of Ng from singlet RNBeNg, then the latter species may still be metastable because of the conceivable occurrence of an energy barrier that separates the singlet RNBeNg and the thermochemically favored dissociation products RNBe (triplet state) and Ng. Since the residue R of RNBeNg can in principle be very different in nature and size, the variety of conceivably stable or metastable compounds in this class may actually be very large. To better disclose this fascinating possibility, we have focused on a number of model RNBeNg compounds (Ng = He, Ne, Ar) including HONBeNg and FNBeNg, the saturated $X-CH_2-NBeNg$, the unsaturated X−C(O)−NBeNg (X = H, OH, F), and the aromatic $C_6H_5-NBeNg$. The results of these calculations will be discussed in the forthcoming paragraphs.

III. B. Structure and Stability of RNBeNg (R = CH_3, OH, F; Ng = He, Ne, Ar). We have first focused on RNBeNg complexes containing prototype substituents of different character, ranging from the electron-releasing CH_3 to the more electronegative OH and F. The geometries of these complexes, invariably characterized as true energy minima on the B3LYP/6-311G(d,p) potential energy surface, have also been optimized at the CCSD(T)/6-311G(d,p) level of theory, and the more relevant parameters, together with the energy change at 0 K of the reaction

$$\mathrm{RNBeNg} \rightarrow \mathrm{RNBe} + \mathrm{Ng} \qquad (2)$$

are collected in Table 2.

We first note that, irrespective of the substituent R, the Be−Ng bond distances of the various RNBeNg complexes computed at the CCSD(T)/6-311G(d,p) and B3LYP/6-311G(d,p) levels of theory are quite similar and are around 1.48 Å for the species containing helium, 1.8 Å for the species containing neon, and 2.0 Å for the species containing argon. These values are also

TABLE 2: Bond Distances (Å), Harmonic Vibrational Frequencies, and Energies for the Dissociation of RNBeNg Molecules into Singlet RNBe and Ng (Δ*E*)

method/basis set	Be−Ng	Be−N	N−R	ν (cm^{-1})[a]	Δ*E* (kcal mol^{-1})[b]
			R = CH_3; Ng = He		
CCSD(T)/6-311G(d,p)	1.493	1.367	1.426		5.5
B3LYP/6-311G(d,p)	1.476	1.353	1.413	152.2(10.0), 308.1(23.2), 556.7(0.3), 1009.1(5.3), 1129.2(3.8), 1449.1(59.9), 1486.3(0.5), 1747.0(50.3), 2944.6(173.3), 2976.8(54.2)	6.7
			R = CH_3; Ng = Ne		
CCSD(T)/6-311G(d,p)	1.818	1.364	1.426		6.9
B3LYP/6-311G(d,p)	1.810	1.351	1.414	95.8(0.0), 245.7(1.7), 294.3(26.8), 992.8(1.0), 1130.5(6.3), 1450.7(67.8), 1487.5(0.1), 1749.6(96.4), 2939.2(187.9), 2969.0(56.2)	8.1
			R = CH_3; Ng = Ar		
CCSD(T)/6-311G(d,p)	2.050	1.368	1.426		13.3
B3LYP/6-311G(d,p)	2.098	1.355	1.413	97.4(0.5), 224.0(3.3), 297.8(24.8), 995.2(0.1), 1130.7(3.9), 1450.0(81.8), 1487.3(0.2), 1735.6(158.5), 2932.7(213.4), 2960.0(64.3)	9.4
			R = OH; Ng = He		
CCSD(T)/6-311G(d,p)	1.482	1.360	1.366		5.9
B3LYP/6-311G(d,p)	1.467	1.346	1.357	121.4(30.3), 156.9(8.7), 320.2(24.3), 357.4(11.1), 566.4(6.0), 990.6(115.0), 1357.0(54.7), 1742.1(16.9), 3745.0(37.1)	7.1
			R = OH; Ng = Ne		
CCSD(T)/6-311G(d,p)	1.819	1.356	1.370		6.9
B3LYP/6-311G(d,p)	1.812	1.344	1.362	73.1(6.1), 101.2(3.2), 244.1(1.3), 309.8(28.1), 335.3(0.5), 959.3(137.7), 1352.6(41.9), 1749.1(3.3), 3753.2(32.3)	8.0
			R = OH; Ng = Ar		
CCSD(T)/6-311G(d,p)	2.047	1.360	1.372		13.6
B3LYP/6-311G(d,p)	2.096	1.348	1.364	79.6(6.8), 100.3(3.3), 222.5(2.3), 304.5(25.3), 334.2(1.2), 956.4(178.6), 1349.6(33.8)	9.6
			R = F; Ng = He		
CCSD(T)/6-311G(d,p)	1.483	1.353	1.343		6.1
B3LYP/6-311G(d,p)	1.470	1.339	1.341	153.5(3.8), 322.2(11.7), 561.1(7.0), 989.1(125.1), 1766.6(13.9)	7.1
			R = F; Ng = Ne		
CCSD(T)/6-311G(d,p)	1.809	1.349	1.347		7.5
B3LYP/6-311G(d,p)	1.802	1.337	1.345	97.8(1.7), 247.6(0.4), 308.4(14.9), 960.5(156.7), 1772.1(1.7)	8.6
			R = F; Ng = Ar		
CCSD(T)/6-311G(d,p)	2.039	1.354	1.349		14.6
B3LYP/6-311G(d,p)	2.084	1.342	1.347	96.8(0.5), 226.3(0.9), 299.0(13.1), 956.3(202.0), 1754.0(0.6)	10.6

[a] IR intensities (km mol^{-1}) are in parentheses. [b] ZPE at the B3LYP/6-311G(d,p) level of theory.

comparable with the Be−Ng distances, reported in Table 1, of the HNBeNg adducts. This minor influence of the substituent R on the structure of the RNBeNg complexes (R = H, CH_3, OH, F) is also reflected in their stability data. Thus, from Tables 1 and 2, at the CCSD(T)/6-311G(d,p) level of theory, the energy change of reaction 2 is computed to be 4.9 kcal mol^{-1} for R = H, 5.5 kcal mol^{-1} for R = CH_3, 5.9 kcal mol^{-1} for R = OH, and 6.1 kcal mol^{-1} for R = F. (The quoted values are not corrected for the BSSE.) The values obtained for the RNBeNe adducts are 6.8 kcal mol^{-1} for R = H, 6.9 kcal mol^{-1} for R = CH_3 and OH, and 7.5 kcal mol^{-1} for R = F; the values obtained for the RNBeAr adducts are 13.3 kcal mol^{-1} for R = H and CH_3, 13.6 kcal mol^{-1} for R = OH, and 14.6 kcal mol^{-1} for R = F. The values obtained at the B3LYP/6-311G(d,p) level of theory are only slightly larger, but the trends are quite similar to those obtained at the CCSD(T)/6-311G(d,p) level of theory. Generally speaking, although it is possible to perceive that the stability of the RNBeNg complexes should slightly increase by increasing the electronegativity of the substituent R, also taking into account the conceivable influence of the BSSE suggested by the results concerning the HNBeNg complexes, the differences in the various computed Δ*E* values are probably too small to support this conclusion definitely.

As already pointed out for HNBeNg, all of the RNBeNg adducts (R = CH_3, OH, F) have been characterized as van der Waals complexes arising from the electrostatic interaction between the RNBe Lewis acid and the Ng atom. Thus, the results of the MP2(full)/6-311G(d,p) AIM calculations indicate that the Laplacian values of the electron density $\nabla^2\rho$ at the bond critical points located on the attractor interaction lines corresponding to the Be−Ng bond of the various RNBeNg compounds are invariably positive and, irrespective of the substituent R, are around +0.36e/au^5 for Ng = He and +0.22e/au^5 for Ng = Ne and Ar. In addition, the total charges on the Ng atoms

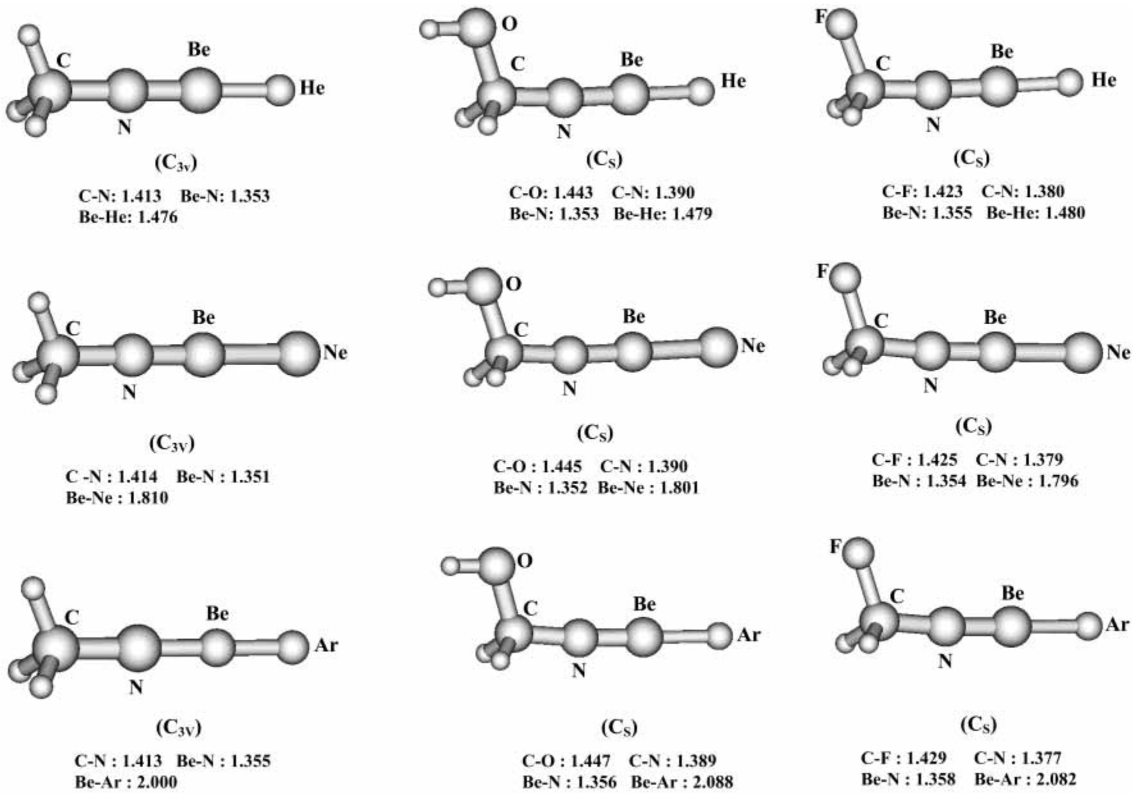

Figure 1. B3LYP/6-311G(d,p) optimized bond distances (Å) of X−CH_2−NBeNg (X = H, OH, F; Ng = He, Ne, Ar). (Unlabeled circles are hydrogen atoms.)

were invariably computed to be as low as ca. −0.04 for Ng = He, ca. −0.03 for Ng = Ne, and vanishingly small for Ng = Ar. We have also found that, irrespective of R and Ng, the total charge on the beryllium atom of RNBeNg was as large as ca. +1.50. The electrostatic character of the RNBeNg complexes is also consistent with their vibrational patterns, which invariably include, in particular, low-frequency N−Be−Ng bendings and Be−Ng stretchings. Exemplary values are 152.2 and 556.7 cm^{-1} (R = CH_3; Ng = He), 73.1 and 244.1 cm^{-1} (R = OH; Ng = Ne), and 96.8 and 226.3 cm^{-1} (R = F; Ng = Ar).

At the CCSD(T)/6-311G(d,p) level of theory, singlet state $^1A_1$ of CH_3NBe (C_{3v} symmetry) was more stable than triplet state $^3A''$ by 4.1 kcal mol^{-1}. The B3LYP/6-311G(d,p) estimate is quite similar and amounts to 4.3 kcal mol^{-1}. Therefore,as with the HNBeNg adducts, all of the $H_3CNBeNg$ molecules emerge as additional examples of thermochemically stable compounds of the lightest noble gases. As for the HONBeNg and FNBeNg complexes, at the CCSD(T)/6-311G(d,p) level of theory the triplet state ($^3A''$) of HONBe is more stable than the singlet ($^1A'$) by 17.1 kcal mol^{-1}, and the triplet state ($^3A''$) of FNBe is more stable than the singlet ($^1A'$) by 7.2 kcal mol^{-1}. Therefore, none of the HONBeNg or FNBeNg adducts can be stated to be thermochemically stable. However, we cannot rule out the possibility that they could exist as metastable species because of the conceivable occurrence of an energy barrier that separates the singlet RNBeNg (R = OH, F; Ng = He, Ne, Ar) and the thermochemically favored dissociation products RNBe ($^3A''$) and Ng.

III. C. Structure and Stability of X−CH_2−NBeNg (X = OH, F), X−C(O)−NBeNg (X = H, OH, F), and C_6H_5−NBeNg (Ng = He, Ne, Ar). To appreciate the influence of more complex substituents on the structure and stability of the RNBeNg complexes, we have investigated saturated X−CH_2−NBeNg, (X = OH, F), unsaturated X−C(O)−NBeNg (X = H, OH, F), and aromatic C_6H_5−NBeNg. The relevant geometrical parameters of these species, optimized at the B3LYP/6-311G(d,p) level of theory, are shown in Figures 1 and 2, and their thermochemical stabilities, measured as the energy change at 0 K of reaction 2, are reported in Table 3.

Concerning the structure of singlet HO−CH_2−NBeNg and F−CH_2−NBeNg (Ng = He, Ne, Ar), we first note from Figure 1 that, for any substituent X, the structure of the X−CH_2−NBe moiety of the various X−CH_2−NBeNg adducts is practically independent of the noble gas Ng. In addition, irrespective of the substituent X, the Be−He, Be−Ne, and Be−Ar distances of the various X−CH_2−NBeHe, X−CH_2−NBeNe, and X−CH_2−NBeAr adducts are quite similar and are around 1.480, 1.800, and 2.080 Å, respectively. Consistent with these similarities in the computed structures, from Table 3 at the B3LYP/6-311G(d,p) level of theory the energy change of reaction 2 is computed to be 6.6 kcal mol^{-1} (Ng = He), 8.4 kcal mol^{-1} (Ng = Ne), and 10.0 kcal mol^{-1} (Ng = Ar) for X = OH and 6.7 kcal mol^{-1} (Ng = He), 8.8 kcal mol^{-1} (Ng = Ne), and 10.7 kcal mol^{-1} (Ng = Ar) for X = F. These values are also quite similar to the B3LYP/6-311G(d,p) dissociation energies of H_3C−NBeNg, which are computed to be 6.7 kcal mol^{-1} for Ng = He, 8.1 kcal mol^{-1} for Ng = Ne, and 9.4 kcal mol^{-1} for Ng = Ar. Therefore, as already evinced from the study of the simplest RNBeNg compounds (R = H, CH_3, OH, F), the presence of a substituent X does not seem to affect the stability of the X−CH_2−NBeNg complexes appreciably. Further confirmation of this minor influence of the substituent R on the stability of singlet RNBeNg has been obtained by finding that the dissociation energies at 0 K of additional exemplary species containing helium, including HCF_2−NBeHe, F_3C−NBeHe, $ClCH_2$−NBeHe, $HCCl_2$−NBeHe, and Cl_3C−NBeHe, are invariably around 6.7 kcal mol^{-1}. In addition, at the B3LYP/6-311G(d,p) level of theory, the triplet state $^3A''$ of FCH_2NBe and $HOCH_2$-

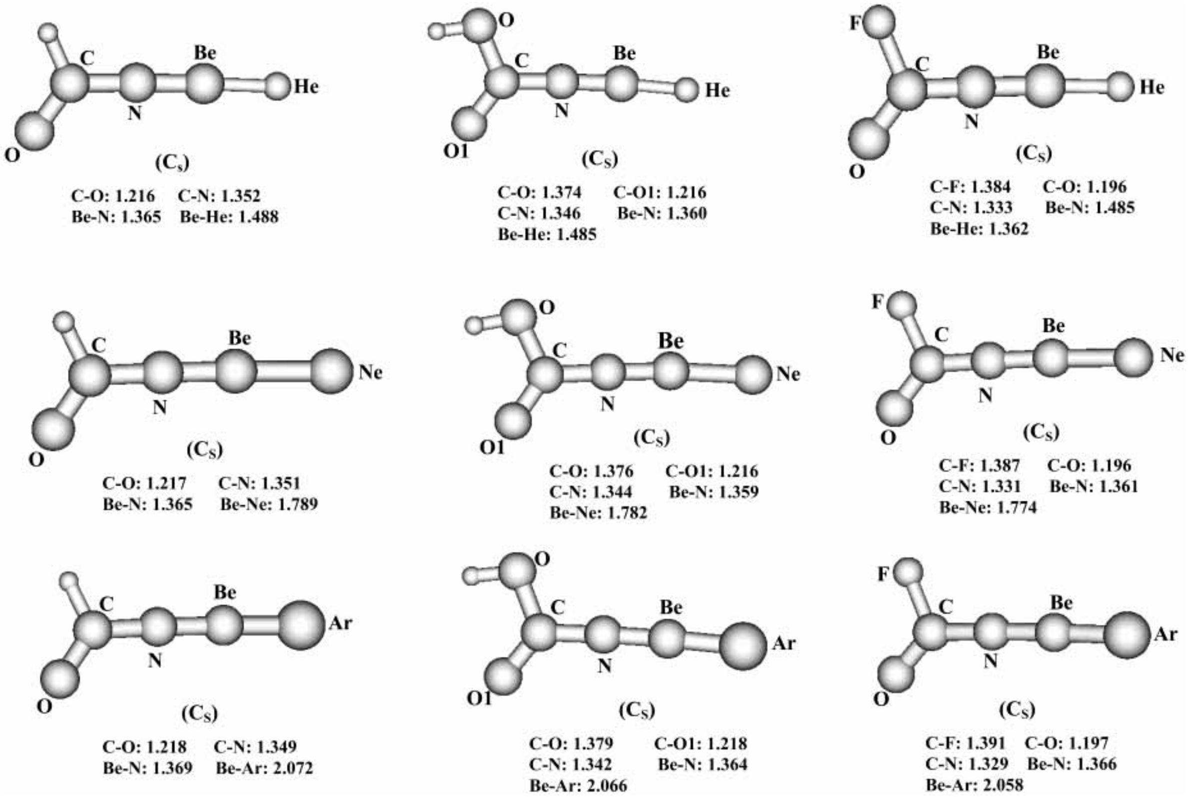

Figure 2. B3LYP/6-311G(d,p) optimized bond distances (Å) of X−C(O)−NBeNg (X = H, OH, F; Ng = He, Ne, Ar). (Unlabeled circles are hydrogen atoms.)

TABLE 3: B3LYP/6-311G(d,p) Energies at 0 K (kcal mol^{-1}) for the Dissociation of Singlet RNBeNg into Singlet RNBe and Ng

RNBeNg	Ng = He	Ng = Ne	Ng = Ar
H−NBeNg	6.3	8.1	9.5
HO−NBeNg	7.1	8.0	9.6
F−NBeNg	7.1	8.6	10.6
H_3C−NBeNg	6.7	8.1	9.4
FCH_2−NBeNg	6.7	8.8	10.7
$HOCH_2$−NBeNg	6.6	8.4	10.0
H−C(O)−NBeNg	5.7	8.5	10.8
HO−C(O)−NBeNg	6.5	9.3	11.8
F−C(O)−NBeNg	6.8	9.8	12.8
C_6H_5−NBeNg	7.1	9.2	11.1
F_2CH−NBeNg	6.7		
F_3C−NBeNg	6.8		
$ClCH_2$−NBeNg	6.9		
Cl_2CH−NBeNg	7.0		
Cl_3C−NBeNg	7.2		

NBe was less stable than the corresponding singlet state $^1A'$ but only by 4.1 and 2.5 kcal mol^{-1}, respectively. Therefore, all of the HO−CH_2NBeNg and F−CH_2NBeNg compounds are predicted to be thermochemically stable with respect to the dissociation into triplet XCH_2NBe (X = OH, F) and Ng.

At the B3LYP/6-311G(d,p) level of theory, all of our investigated X−C(O)−NBeNg compounds (X = H, OH, F; Ng = He, Ne, Ar) were characterized as true energy minima on the potential energy surface. From Figure 2, as already noted for the saturated compounds X−CH_2−NBeNg (X = H, OH, F; Ng = He, Ne, Ar), for any substituent X the structure of the X−C(O)−NBe moiety of the various X−C(O)−NBeNg compounds is practically independent of the noble gas Ng. In addition, irrespective of the substituent X, the Be−He, Be−Ne, and Be−Ar distances of the various X−C(O)−NBeHe, X−C(O)−NBeNe, and X−C(O)−NBeAr compounds are quite similar—around 1.485, 1.780, and 2.065 Å, respectively. In addition, we note again the minor influence of the substituent on the stability of the singlet X−C(O)−NBeNg adducts with respect to the dissociation into RNBe and Ng. Thus, from Table 3 at the B3LYP/6-311G(d,p) level of theory for X = H, the energy change of reaction 2 is computed to be 5.7 kcal mol^{-1} for Ng = He, 8.5 kcal mol^{-1} for Ng = Ne, and 10.8 kcal mol^{-1} for Ng = Ar. For X = OH, the corresponding values amount to 6.5, 9.3, and 11.8 kcal mol^{-1}, respectively, and become 6.8, 9.8, and 12.8 kcal mol^{-1}, respectively, for X = F. In addition, as already noted for the X−CH_2−NBeNg (X = H, OH, F; Ng = He, Ne, Ar) adducts, all of the X−C(O)−NBeNg (X = H, OH, F; Ng = He, Ne, Ar) adducts are predicted to be thermochemically stable. In fact, at the B3LYP/6-311G(d,p) level of theory, the singlet state $^1A'$ of the X−C(O)−NBe imides is invariably more stable than the triplet $^3A''$, and the singlet−triplet gap has been computed to be 4.2 kcal mol^{-1} for X = H, 2.0 kcal mol^{-1} for X = OH, and 5.1 kcal mol^{-1} for X = F.

The C_6H_5−NBeNg (Ng = He, Ne, Ar) adducts are prototype cases of RNBeNg compounds containing aromatic groups. At the B3LYP/6-311G(d,p) level of theory, all of these species in their singlet state $^1A_1$ (C_{2v} symmetry) were characterized as true energy minima on the potential energy surface, and the computed Be−Ng bond distances of 1.476 (Ng = He), 1.797 (Ng = Ne), and 2.079 Å (Ng = Ar), were in line with the above results concerning the geometries of X−CH_2−NBeNg and X−C(O)−NBeNg. In addition, the C_6H_5−NBeNg adducts were found to be stable with respect to dissociation into singlet C_6H_5−NBe ($^1A_1$) and Ng by 7.1 (Ng = He), 9.2 (Ng = Ne), and 11.1 kcal mol^{-1} (Ng = Ar). However, the triplet C_6H_5−NBe ($^3B_1$) was more stable than the singlet by 9.9 kcal mol^{-1}. Therefore, probably only C_6H_5−NBeAr can be considered to be thermochemically stable, although we cannot rule out the possibility that C_6H_5−NBeHe and C_6H_5−NBeNe could exist as metastable species because of the conceivable occurrence of an energy barrier that separates the singlet $C_6H_5{-}NBeNg$ (Ng = He, Ne) and the thermochemically favored dissociation products $C_6H_5{-}NBe$ ($^3B_1$) and Ng.

IV. Conclusions

In this study, we have obtained computational evidence for a new class of thermodynamically stable compounds containing the noble gases helium, neon, and argon. These species have the general formula RNBeNg, and in their singlet state, they must be viewed as electrostatic complexes between a noble gas Ng and an RNBe Lewis acid. The small radius of the beryllium atom and its total charge, computed to be as large as ca. +1.5, produce an electric field strong enough to fix the noble gas, including helium, into a relatively deep potential energy well. We have also found that the nature of the substituent R has a minor influence on the charge of Be. The energy of dissociation ΔE into singlet RNBe and Ng have consistently been found to be practically independent of the nature of R and are around 6.5 kcal mol^{-1} for Ng = He, 8.5 kcal mol^{-1} for Ng = Ne, and 11.0 kcal mol^{-1} for Ng = Ar. However, the thermochemical stability of the RNBeNg molecules depends not only on ΔE but also on the energy difference between the singlet state and the triplet state of RNBe. In particular, for most of the investigated RNBeNg molecules, the singlet state of RNBe is more stable than the triplet, or for RNBe with a triplet ground state, the singlet−triplet gap is lower than ΔE. These findings support the prediction that the class of thermochemically stable RNBeNg compounds can actually be very large, and the conceivable existence of these species could stimulate future experimental work aimed at their observation and structural characterization. Any successful attempt along this direction could realize one of the still elusive chemical dreams, namely, the isolation of stable compounds of helium and neon.

Acknowledgment. We thank the Italian Ministero dell′ Istruzione, dell′ Università e della Ricerca (MIUR) and the Consiglio Nazionale delle Ricerche (CNR) for financial support.

References and Notes

(1) Bartlett, N. *Proc. Chem. Soc.* **1962**, 218.

(2) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley & Sons: New York, 1999.

(3) (a) Seidel, S.; Seppelt, K. *Science (Washington, D.C.)* **2000**, *290*, 117. (b) Pyykkö, P. *Science (Washington, D.C.)* **2000**, *290*, 64.

(4) Christe, K. O. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 1419 and references therein.

(5) Thompson, C. A.; Andrews, L. *J. Am. Chem. Soc.* **1994**, *116*, 423.

(6) Evans, C. J.; Gerry, M. C. L. *J. Chem. Phys.* **2000**, *112*, 1321.

(7) Evans, C. J.; Gerry, M. C. L. *J. Chem. Phys.* **2000**, *112*, 9363.

(8) Evans, C. J.; Lesarri, A.; Gerry, M. C. L. *J. Am. Chem. Soc.* **2000**, *122*, 6100.

(9) (a) Khriachtchev, L.; Pettersson, M.; Runeberg, N.; Lundell, J.; Räsänen, M. *Nature (London)* **2000**, *406*, 874. (b) Frenking, G. *Nature (London)* **2000**, *406*, 836.

(10) Lee, L.; Busten, B. E.; Liang, B.; Andrews, L. *Science (Washington, D.C.)* **2002**, *295*, 2242.

(11) (a) Koch, W.; Frenking, G.; Gauss, J.; Cremer, D.; Collins, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 5917. (b) Frenking, G.; Koch, W.; Gauss, J.; Cremer, D. *J. Am. Chem. Soc.* **1988**, *110*, 8007.

(12) Frenking, G.; Koch, W.; Deakyne, C. A.; Liebman, J. F.; Bartlett, N. *J. Am. Chem. Soc.* **1989**, *111*, 31.

(13) (a) Wong, M. W. *J. Am. Chem. Soc.* **2000**, *122*, 6289. (b) Chaban, G. M.; Lundell, J.; Gerber, R. B. *J. Chem. Phys.* **2001**, *115*, 7341.

(14) Grandinetti, F.; Hrušák, J.; Schröder, D.; Karrass, S.; Schwarz, H. *J. Am. Chem. Soc.* **1992**, *114*, 2806.

(15) Cacace, F.; Grandinetti, F.; Pepi, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 123.

(16) Grandinetti, F.; Pepi, F.; Ricci, A. *Chem.*−*Eur. J.* **1996**, *2*, 495.

(17) Grandinetti, F.; Cecchi, P.; Vinciguerra, V. *Chem. Phys. Lett.* **1997**, *281*, 431.

(18) Aschi, M.; Grandinetti, F.; Vinciguerra, V. *Chem.*−*Eur. J.* **1998**, *4*, 2366.

(19) Aschi, M.; Grandinetti, F. *Int. J. Mass Spectrom.* **1999**, *184*, 89.

(20) Aschi, M.; Grandinetti, F. *J. Mol. Struct.: THEOCHEM* **2000**, *497*, 205.

(21) Grandinetti, F.; Vinciguerra, V. *J. Mol. Struct.: THEOCHEM* **2001**, *574*, 185.

(22) Grandinetti, F.; Vinciguerra, V. *Int. J. Mass Spectrom.* **2002**, *216*, 285.

(23) Aschi, M.; Grandinetti, F. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 1690.

(24) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.

(25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

(26) MOLPRO 2000.1 is a package of ab initio programs written by Werner, H.-J. and Knowles, P. J., with contributions from Amos, R. D.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Leininger, T.; Lindh, R.; Lloyd, A. W.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Peterson, K.; Pitzer, R.; Pulay, P.; Rauhut, G.; Schütz, M.; Stoll, H.; Stone, A. J.; Thorsteinsson, T.

(27) (a) Werner, H.-J.; Knowles, P. J. *J. Chem. Phys*. **1985**, *82*, 5053. (b) Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett*. **1985**, *115*, 259.

(28) (a) Werner, H.-J.; Knowles, P. J. *J. Chem. Phys*. **1988**, *89*, 5803. (b) Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett*. **1988**, *145*, 514.

(29) Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *8*, 61.

(30) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(31) Hampel, C.; Peterson, K.; Werner, H.-J. *Chem. Phys. Lett*. **1992**, *190*, 1.

(32) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(33) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(34) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frish, M. J. *J. Phys. Chem*. **1994**, *98*, 11623.

(35) Boys, S.; Bernardi, F. *Mol. Phys*. **1970**, *19*, 553.

(36) Cioslowski, J.; Mixon, S. T. *J. Am. Chem. Soc.* **1991**, *113*, 4142.

(37) Cioslowski, J.; Surján, P. R.; Mixon, S. T. *J. Mol. Struct.: THEOCHEM* **1992**, *255*, 9.

(38) Cioslowski, J. *Chem. Phys. Lett.* **1992**, *194*, 73.

(39) Cioslowski, J.; Nanayakkara, A.; Challacombe, M. *Chem. Phys. Lett.* **1993**, *203*, 137.

(40) Cioslowski, J.; Nanayakkara, A. *Chem. Phys. Lett.* **1994**, *219*, 151.

(41) Jacobs, H.; Juza, R. *Z. Anorg. Allg. Chem.* **1969**, *370*, 248.

(42) Linde, G.; Juza, R. *Z. Anorg. Allg. Chem.* **1974**, *409*, 199.

(43) Roberto-Neto, O.; Ornellas, F. R. *J. Phys. Chem.* **1994**, *98*, 81 and references therein.

(44) Sana, M.; Leroy, G. *Theor. Chim. Acta* **1990**, *77*, 383.

(45) Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem., Quantum Chem. Symp*. **1989**, *23*, 199.

(46) *CRC Hanbook of Chemistry and Physics*, 74th ed. Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1993; Section 10-194.