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In Quest of Strong Be–Ng Bonds among the Neutral Ng–Be Complexes

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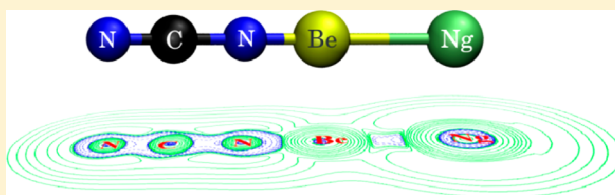
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S Supporting Information

ABSTRACT: The global minimum geometries of BeCN₂ and BeNBO are linear BeN–CN and BeN–BO, respectively. The Be center of BeCN₂ binds He with the highest Be–He dissociation energy among the studied neutral He–Be complexes. In addition, BeCN₂ can be further tuned as a better noble gas trapper by attaching it with any electron-withdrawing group. Taking BeO, BeS, BeNH, BeNBO, and BeCN₂ systems, the study at the CCSD(T)/def2-TZVP level of theory also shows that both BeCN₂ and BeNBO systems have higher noble gas binding ability than those related reported systems. ΔG values for the formation of NgBeCN₂/NgBeNBO (Ng = Ar–Rn) are negative at room temperature (298 K), whereas the same becomes negative at low temperature for Ng = He and Ne. The polarization plus the charge transfer is the dominating term in the interaction energy.



INTRODUCTION

Any attempt in predicting new noble gas (Ng) compounds appears to be a difficult task due to the chemical inactivity of Ng atoms that originated from their filled valence orbitals. Therefore, enough challenge persists in searching for new Ng compounds and in improving our understanding and ideas about the reactivity of Ng. The first member in the series of Ng compounds is xenon hexafluoroplatinate, Xe⁺[PtF₆][−] synthesized by Bartlett.^{1,2} This discovery came at a time when the inertness of group 18 elements was regarded as the fundamental law of nature and they were treated as the “loners” in the periodic table. This landmark success inspired other scientists to explore new Ng compounds, and within a short period, a large number of Kr-, Xe-, and Rn-containing compounds were reported.^{3–6} A series of compounds of type H(Ng)Y (Ng = noble gas atom; Y = electron-withdrawing group) was synthesized by Räsänen et al.^{7–14} following a similar technique, the photodissociation of HY in an Ng matrix. Employing electron irradiation techniques, the synthesis of Ng hydrides by Feldman and his co-workers^{15,16} is also a pioneering contribution in this field.

In fact, some theoretically predicted Xe compounds by Gerber et al.¹⁷ and Ghanty et al.¹⁸ were later identified experimentally by Feldman et al.¹⁹ and Räsänen et al.^{20,21} As a result of these findings, the existing myth about the inertness of an Ng had been removed, and a new field, namely, Ng chemistry having exciting prosperity, had been launched.^{22–28}

Although theoretical study on the stability of light Ng compounds was extensively carried out,^{29–32} the synthesis of the He and Ne compounds turns out to be the most challenging issue due to their very low polarizabilities and high ionization potentials owing to their small sizes. To date, there are only a few Ar^{33–39} and Ne^{38,39} (NeAuF, NeBeS) containing compounds that are experimentally detected. In a couple of papers, Frenking et al.^{40,41} highlighted the Ng-binding ability of a charged Be center by exploring the stability of NgBeO (Ng = He–Xe). Following Frenking's prediction, Andrews' group³³ successfully detected NgBeO (Ng = Ar–Xe) through matrix infrared spectroscopy.

In the BeO molecule, due to the presence of a highly electronegative O atom, Be possesses large positive charge, and it interacts with the Ng mainly through a charge-induced dipole type of interaction with some degree of covalent character for the case of Xe. Pyykkö⁴² suggested that a Lewis acid of the type SX (X = Be, B⁺, C²⁺, N³⁺, O⁴⁺) can form a strong bond with Ne. Therefore, the interaction between an electropositive center and an Ng is a donor–acceptor type of interaction. Now, because Be center acts as an electron acceptor by virtue of its electropositive nature, if one can improve the charge on it, it may behave as a better Lewis acid and hence a better Ng trapper. This is why the cationic systems possess a larger Ng

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binding energy than their neutral counterparts^{43–45} and the dissociation energy gradually decreases from NgBeO to NgBeTe.⁴⁵

Grandinetti et al.^{46–48} have contributed significantly to the understanding of the Ng-binding ability of neutral Be-containing systems. To make the Be center a better Ng trapper, they attached BeO with a BH₃ Lewis acid and substituted the H atom of BeNH with different groups.^{47,48} However, the main problem with these systems is that the most of the systems are not global minima, whereas the more stable isomers are those in which Be centers are no longer available for Ng binding.⁴⁹

In this study, we have tried to identify a viable cluster that can trap Ng atoms with higher Be–Ng dissociation energies than that in the other reported Be-based neutral Lewis acids. It should be mentioned that here we have considered only those Be-based systems reported so far⁵⁰ in which the Be center occupies a terminal position and is bound to Ng atoms only. In a couple of papers, Ghanty et al.^{51,52} showed the metastability of HBeRgF and FBeRgF (Rg = Ar–Xe). They got very high bond energy values of Be–Rg bonds by studying the decomposition channel HBeRgF/FBeRgF → HBe/FBe + RgF. However, this high Be–Rg bond energy reflects the ability of the Be center present in HBe and FBe to bind RgF and not the Rg atom alone. Because the binding of one Ng atom alone and NgF together is not the same, we do not consider these types of systems for comparison in our present study.

Since the past decade, the probable crystal structure of BeCN₂ is a matter of interest for both theoreticians⁵³ and experimentalists⁵⁴ due to its semiconductor property originating from its band gap. Here, we have considered the global minimum structure of a single BeCN₂ molecule for our study, and its Ng binding ability is compared with those of the other reported neutral Ng–Be systems. Interestingly, the atomic arrangement in the global minimum structure of a single BeCN₂ molecule is linear Be–N–C–N, which is different from that in the proposed crystal structure.^{55,56} Moreover, we have replaced the –CN group of BeCN₂ with –BO and have identified its global minimum structure. Similar to the BeCN₂ molecule, our theoretically proposed BeNBO molecule is found to possess a linear geometry in which the Be center is available for further coordination with Ng atoms. The Ng binding ability of BeNBO is found to be slightly lower than that of BeCN₂.

COMPUTATIONAL DETAILS

The global minimum search is performed by means of a modified stochastic kick methodology called Bilatu.⁵⁷ Using the Mersenne twister algorithm,⁵⁸ this procedure first generates the atomic positions arbitrarily. Then, certain conditions are imposed to get optimized structures. First, the atomic positions of all of the atoms of the studied structure should be within a sphere of radius r (where r is the sum of the covalent radii of all the atoms); second, the corresponding distance between a pair of atoms should be less than the sum of the covalent radii of them; and third, the structure should fulfill the criteria of a cluster. If all three criteria are fulfilled then that structure is optimized. In this present study, initially, the search for the structures is made at the PBE0/LanL2DZ level, and then, they are further reoptimized at the MP2/def2-QZVPPD level. All of the Ng-bound systems are studied at the MP2/def2-QZVPPD level. Taking the five best systems obtained from the MP2 study, we have further carried out computations at the

CCSD(T)/def2-TZVP level of theory. A quasi-relativistic pseudopotential⁵⁹ is used for the Xe and Rn atoms. All of the MP2 and CCSD(T) computations are performed using the Gaussian 09 program package.⁶⁰ The correction of basis set superposition error (BSSE) is made using the standard counterpoise (CP) method of Boys and Bernardi.⁶¹ Natural population analysis (NPA) is performed to compute atomic charges (Q_{NPA}) at each center, and the Wiberg bond index (WBI)⁶² is computed to assess the bond order. The contour plots of the Laplacian of the electron density ($\nabla^2\rho(r)$) and the analysis of the electron density are done by Multiwfn software⁶³ using the wave functions generated at the MP2/def2-QZVPPD level. Energy decomposition analysis (EDA) is done at the CCSD(T)/def2-TZVP level by adopting the method proposed by Su and Li.⁶⁴

Ng-BINDING ABILITY OF BeCN₂ AND BeNBO AND COMPARISON WITH OTHER REPORTED Ng–Be SYSTEMS

The global minimum geometries of BeCN₂ and BeNBO systems and their Ng-bound analogues are depicted in Figure 1.

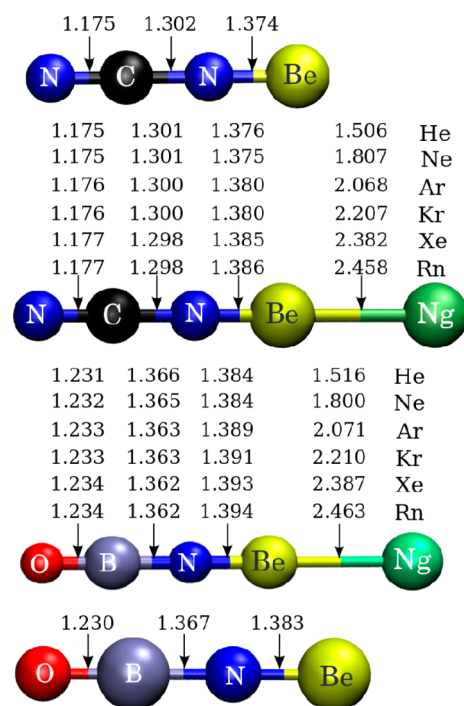


Figure 1. The global minimum-energy structures of BeCN₂ and BeNBO clusters and their Ng-trapped analogues computed at the CCSD(T)/def2-TZVP level of theory. All bond lengths are given within parentheses in Å units.

Details of other isomers of BeCN₂ and BeNBO are provided in Figures S1 and S2, respectively (Supporting Information). The global minima of both BeCN₂ and BeNBO are linear, with the Be center in one terminal position. They may be better represented as BeNH with a replacement of H by –CN and –BO groups.

Note that in BeCN₂ and BeNBO, the –CN and –BO electron-withdrawing groups attached with BeN will make the Be center more electron-deficient than that in BeNH (the NPA charges are +1.22, +1.39, and +1.45 e[–] at Be centers of BeNH, BeCN₂, and BeNBO, respectively). The results for NgBeCN₂,

Table 1. ZPE and BSSE Uncorrected Dissociation Energy (D_e , kcal/mol), ZPE Corrected Dissociation Energy (D_0 , kcal/mol), BSSE Corrected Dissociation Energy (D_e^{BSSE} , kcal/mol), Both ZPE and BSSE Corrected Dissociation Energy (D_0^{BSSE} , kcal/mol) of Be–Ng Bonds for the Dissociation Process $\text{NgBeCN}_2/\text{NgBeNBO} \rightarrow \text{Ng} + \text{BeCN}_2/\text{NgBeNBO}$, Reaction Enthalpy (ΔH , kcal/mol), Free Energy Change (ΔG , kcal/mol) at 298 K for the Process $\text{Ng} + \text{BeCN}_2/\text{NgBeNBO} \rightarrow \text{NgBeCN}_2/\text{NgBeNBO}$, HOMO–LUMO Gap (Gap, eV), Smallest Vibrational Frequency (ν_{\min} , cm^{-1}), NPA Charge at Be and Ng Centers (q , au), Wiberg Bond Indices of Be–Ng Bonds (WBI), and Be–Ng Bond Distances ($r_{\text{Be–Ng}}$, Å) at the CCSD(T)/def2-TZVP Level

clusters	D_e	D_0	D_e^{BSSE}	D_0^{BSSE}	ΔH	ΔG	Gap	ν_{\min}	$q(\text{Be})$	$q(\text{Ng})$	WBI	T_1^a	$r_{\text{Be–Ng}}$
HeBeCN ₂	6.4	5.2	6.0	4.8	−5.7	1.0	9.16	114.7	1.20	0.10	0.19	0.0188	1.506
NeBeCN ₂	5.7	5.0	4.7	4.1	−5.2	1.2	8.54	75.0	1.28	0.07	0.13	0.0195	1.807
ArBeCN ₂	14.8	14.1	13.4	12.7	−14.3	−7.6	8.93	73.4	1.14	0.18	0.33	0.0164	2.068
KrBeCN ₂	17.6	17.0	16.0	15.4	−17.1	−10.5	8.97	67.7	1.09	0.23	0.40	0.0141	2.207
XeBeCN ₂	20.9	20.3	19.2	18.6	−20.5	−14.0	8.96	64.7	1.02	0.29	0.50	0.0146	2.382
RnBeCN ₂	23.3	22.8	20.8	20.3	−22.9	−16.4	8.69	64.2	1.01	0.31	0.53	0.0132	2.458
HeBeNBO	6.0	4.8	5.7	4.4	−5.3	1.6	10.16	108.7	1.27	0.10	0.18	0.0202	1.516
NeBeNBO	5.7	5.0	4.7	4.0	−5.3	1.5	9.53	75.4	1.34	0.07	0.13	0.0173	1.800
ArBeNBO	14.5	13.8	13.1	12.4	−14.0	−7.2	9.88	67.9	1.20	0.18	0.33	0.0174	2.071
KrBeNBO	17.2	16.5	15.6	14.9	−16.7	−10.0	9.92	62.5	1.14	0.22	0.40	0.0149	2.210
XeBeNBO	20.3	19.7	18.5	17.9	−19.9	−13.2	9.92	58.5	1.08	0.29	0.50	0.0152	2.387
RnBeNBO	22.7	22.1	20.2	19.6	−22.3	−15.6	9.65	57.2	1.07	0.30	0.53	0.0137	2.463

^aThe T_1 diagnostic is obtained from the CCSD wave function.

NgBeNBO, and other reported Ng–Be systems obtained at the MP2/def2-QZVPPD level are summarized in Table S1 (Supporting Information). A comparison of the result of NgBeCN₂ with those of the other Be systems reveals that there are only two systems (BeOBH₃ and BeNCCl₃) among those studied here that show higher dissociation energy values of Be–Ng bonds than that of BeCN₂ for Ng = Ne–Rn (Table S1, Supporting Information). However, BeCN₂ shows the highest He-binding ability among the studied Be systems. Here, it should be noted that neither of the BeOBH₃ and BeNCCl₃ systems in the studied geometry is a global minimum.⁴⁹ Hence, they are very unlikely to be synthesized in these forms. Moreover, like the improvement of the dissociation energy of NgBeO due to attachment with BH₃, one can also tune BeCN₂ as a better Ng trapper by attaching it with any electron-withdrawing group. We have considered here NgBeCN₂–BH₃ as an example to examine this. It possesses a better dissociation energy of Be–Ng bonds, reaction enthalpy, and free energy change values than those of BeCN₂ (see the result in Table S2, Supporting Information). It may be mentioned that BeCN₂–BH₃ is not a global minimum and H–BeCN₂–BH₂ is more stable than this.⁶⁵ Therefore, selection of a proper electron-withdrawing group is very important, and one has to make an appropriate choice of it in order to make BeCN₂ a better Ng trapper.

Now, taking both their Ng-binding ability and global minimum structures under consideration, we have chosen NgBeCN₂, NgBeNBO, NgBeNH, NgBeO, and NgBeS systems for further study at the CCSD(T)/def2-TZVP level of theory. The corresponding results for NgBeCN₂ and NgBeNBO are provided in Table 1, and those for NgBeNH, NgBeO and NgBeS systems are given in Table 2. We have calculated the T_1 diagnostic⁶⁶ to know whether using of single reference-based electron correlation procedure is appropriate for these systems. The values of T_1 given in Table 1 are less than 0.02 in all cases except for HeBeNBO. It shows that our chosen level of theory is adequate to give reliable results for these systems. In the case of HeBeNBO, the value of T_1 (0.0202) is almost equal to 0.02; therefore, still, we believe that our chosen level is adequate to represent this system properly. The uncorrected dissociation energy (D_e) values of Be–Ng bonds in NgBeCN₂ and

Table 2. ZPE and BSSE Uncorrected Dissociation Energy (D_e , kcal/mol), ZPE Corrected Dissociation Energy (D_0 , kcal/mol), BSSE Corrected Dissociation Energy (D_e^{BSSE} , kcal/mol), and Both ZPE and BSSE Corrected Dissociation Energy (D_0^{BSSE} , kcal/mol) of Be–Ng Bonds for the Dissociation Process $\text{NgBeX} \rightarrow \text{Ng} + \text{BeX}$, Reaction Enthalpy (ΔH , kcal/mol) and Free Energy Change (ΔG , kcal/mol) at 298 K for the Process $\text{Ng} + \text{BeX} \rightarrow \text{NgBeX}$, and Be–Ng Bond Distance ($r_{\text{Be–Ng}}$, Å) at the CCSD(T)/def2-TZVP Level

clusters	D_e	D_0	D_e^{BSSE}	D_0^{BSSE}	ΔH	ΔG	$r_{\text{Be–Ng}}$
HeBeNH	5.7	4.0	5.4	3.7	−4.7	2.0	1.510
NeBeNH	4.1	3.1	3.3	2.3	−3.5	2.7	1.859
ArBeNH	11.3	10.2	10.0	8.9	−10.6	−4.1	2.101
KrBeNH	13.5	12.4	12.1	11.0	−12.9	−6.3	2.237
XeBeNH	16.1	15.0	14.5	13.4	−15.5	−9.1	2.408
RnBeNH	17.9	16.9	15.7	14.6	−17.3	−10.9	2.484
HeBeO	3.6	2.3	3.2	1.9	−2.9	3.8	1.560
NeBeO	3.6	2.7	2.6	1.8	−3.1	3.3	1.869
ArBeO	10.6	9.6	9.1	8.1	−10.0	−3.4	2.110
KrBeO	12.8	11.9	11.2	10.3	−12.3	−5.8	2.247
XeBeO	15.3	14.4	13.5	12.6	−14.8	−8.3	2.427
RnBeO	17.4	16.5	14.8	14.0	−16.8	−10.4	2.500
HeBeS	1.5	0.5	1.1	0.0	−0.9	5.6	1.637
NeBeS	2.0	1.4	1.1	0.5	−1.6	4.6	1.971
ArBeS	8.7	7.9	7.3	6.5	−8.2	−1.6	2.141
KrBeS	11.0	10.3	9.5	8.7	−10.6	−4.0	2.273
XeBeS	13.7	13.0	11.9	11.2	−13.2	−6.7	2.451
RnBeS	15.9	15.2	13.4	12.7	−15.4	−8.9	2.523

NgBeNBO are 6.4 and 6.0 kcal/mol for He, 5.7 kcal/mol for Ne, 14.8 and 14.5 kcal/mol for Ar, 17.6 and 17.2 kcal/mol for Kr, 20.9 and 20.3 kcal/mol for Xe, and 23.3 and 22.7 kcal/mol for Rn, respectively. However, both corrections of the BSSE and zero point energy (ZPE) reduce the dissociation energy to some extent. Both BSSE and ZPE corrected dissociation energy values (D_0^{BSSE}) are 4.8 and 4.4 kcal/mol for He, 4.1 and 4.0 kcal/mol for Ne, 12.7 and 12.4 kcal/mol for Ar, 15.4 and 14.9 kcal/mol for Kr, 18.6 and 17.9 kcal/mol for Xe, and 20.3 and 19.6 kcal/mol for Rn in NgBeCN₂ and NgBeNBO,

respectively. Note that the dissociation energy values of Be–Ng bonds in NgBeNBO are slightly smaller than those in NgBeCN₂, although the Be center of BeNBO is more electron-deficient (+1.45 e[−]) than that of BeCN₂ (+1.39 e[−]). Therefore, although the Ng binding ability generally improves with an increase in the cationic character of the Be center, it does not seem to carry a direct proportionality with the charge. We have plotted the variation of the D_e value with Be–Ng bond distances (see Figure S3, Supporting Information). Generally, for a particular Ng atom, one may expect an increase in the D_e value with a decrease in the Be–Ng bond distance and vice versa. This is obviously the case for the heavier Ng atoms (Ng = Ar–Rn), but for He and Ne, we have obtained different results. The D_e value of the He–Be bond in HeBeNBO is larger (6.0 kcal/mol) than that in HeBeNH (5.7 kcal/mol), although the Be–He distance in HeBeNH (1.510 Å) is slightly smaller than that in HeBeNBO (1.516 Å). A similar result is obtained for NeBeCN₂ and NeBeNBO, in which they have same D_e value (5.7 kcal/mol) despite the fact that the Be–Ne distance in NeBeNBO (1.800 Å) is slightly smaller than that in NeBeCN₂ (1.807 Å). The group attached with the Be center seems to be responsible for this.

The HOMO–LUMO gap (Gap), also called the hardness, is generally used as a stability indicator.⁶⁷ The hardness value of the product is generally greater than that of the reactants for an exothermic process.⁶⁸ The HOMO–LUMO gap values of the bare BeCN₂ and BeNBO clusters are 6.78 and 7.96 eV, respectively. These values are improved significantly upon binding with Ng (Table 1). It indicates the greater stability of Ng-loaded clusters with respect to the bare clusters.

The higher dissociation energy values of Be–Ng bonds in NgBeCN₂ and NgBeNBO than those in NgBeNH, NgBeO, and NgBeS clearly show their higher potency to bind with Ng atoms (Tables 1 and 2). Note that the dissociation energy values obtained at the CCSD(T)/def2-TZVP level are smaller to some extent than the corresponding values at the MP2 level. All of the Ng-binding processes on BeCN₂ and BeNBO are exothermic in nature ($\Delta H < 0$), and in the case of BeCN₂, it is −5.7 for He and −5.2 kcal/mol for Ne binding, whereas it is −5.3 kcal/mol for both He and Ne binding in BeNBO. Thereafter, it gradually becomes more and more negative in going from Ar to Rn. In both cases, the free energy change values (ΔG) for He and Ne trapping are positive at 298 K, whereas other Ng (Ng = Ar–Rn) binding processes are exergonic ($\Delta G < 0$) at that temperature (298 K). It should be noted that for such a type of trapping processes, the entropy change (ΔS) is negative; hence, ΔG will be negative if favorable ΔH terms are dominant over unfavorable $T\Delta S$ terms. For Ar–Rn cases, ΔH is large enough to overshadow $T\Delta S$, but in the cases of He and Ne, $T\Delta S$ dominates over ΔH at 298 K. However, at lower temperature, say at 200 K, ΔG turns out to be negative for these systems as well (see Table 3). Note that the ΔG value for the formation of NgBeO (Ng = He, Ne) is still positive at 200 K; it becomes negative only at much lower temperature (77 K) (Table 3).

NATURE OF BONDING

WBI values are very low for He (0.19 and 0.18) and Ne (0.13) cases, highlighting a dominant van der Waals interaction. However, it improves gradually from Ar to Rn (see Table 1). It shows almost a half bond between Be and Kr–Rn, showing some degree of covalent character therein. The descriptors obtained from the analysis of the electron density⁶⁹ are

Table 3. Free Energy Change (ΔG , kcal/mol) at Different Temperatures for the Process Ng + BeCN₂/BeNBO/BeO → NgBeCN₂/NgBeNBO/NgBeO (Ng = He, Ne) at the CCSD(T)/def2-TZVP Level

clusters	ΔG				
	at 273 K	at 250 K	at 200 K	at 150 K	at 77 K
HeBeCN ₂	0.4	−0.1	−1.2	−2.3	−3.9
NeBeCN ₂	0.7	0.2	−0.9	−2.0	−3.6
HeBeNBO	1.0	0.5	−0.7	−1.8	−3.5
NeBeNBO	0.9	0.4	−0.7	−1.9	−3.5
HeBeO	3.2	2.7	1.6	0.5	−1.1
NeBeO	2.8	2.3	1.2	0.1	−1.4

tabulated in Table 4 for NgBeCN₂ and Table S3 (Supporting Information) for NgBeNBO clusters. The existence of a

Table 4. Electron Density Descriptors (au) at the BCPs of Ng and BeCN₂ Clusters Obtained from the Wave Functions Generated at the MP2/def2-QZVPPD Level

clusters	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$G(r_c)$	$V(r_c)$	$H(r_c)$	$-G(r_c)/V(r_c)$
HeBeCN ₂	0.032	0.345	0.072	−0.058	0.014	1.241
NeBeCN ₂	0.027	0.296	0.062	−0.051	0.011	1.216
ArBeCN ₂	0.036	0.242	0.059	−0.057	0.002	1.035
KrBeCN ₂	0.036	0.196	0.051	−0.053	−0.002	0.962
XeBeCN ₂	0.036	0.149	0.044	−0.050	−0.006	0.880
RnBeCN ₂	0.036	0.124	0.039	−0.048	−0.009	0.813

gradient path connecting the Ng with the beryllium fragment is obvious (between two maxima should exist a minimum).^{70,71} Nevertheless, some interesting results could be obtained from this analysis. The negative and positive values of the Laplacian of the electron density, $\nabla^2\rho(r_c)$, indicate the concentration of electron density and charge depletion. In the case of NgBeCN₂, for the lighter Ng atoms (He, Ne), the Laplacian at the Ng–Be bond critical point (BCP) is positive (0.345 and 0.296 au), whereas it decreases for heavier Ng atoms and becomes 0.149 and 0.124 au for Xe and Rn cases, respectively. The contour plots of $\nabla^2\rho(r)$ for NgBeCN₂ and NgBeNBO clusters are provided in Figures 2 and S4 (Supporting Information), respectively. In both cases, the gradual deformation in the shape of this scalar field moving from He to Rn implies increased “covalent” character along the bottom of the group. Finally, in cases of Xe and Rn, a well-defined region of charge concentration ($\nabla^2\rho(r) < 0$, shown by dotted blue lines) in between Be and Ng centers is developed.

Further, in order to evaluate the nature of interaction in Ng–Be bonds, various parameters such as local electron energy density ($H(r_c)$) and its components, the local kinetic energy density ($G(r_c)$) and local potential energy density ($V(r_c)$), are computed at the BCPs. The balance between $G(r_c)$ and $V(r_c)$ could help to understand the nature of the interaction. Cremer et al.⁷² proposed that if $\nabla^2\rho(r_c) > 0$ and $H(r_c) < 0$, then the interaction is partly covalent in nature. Hence, it is clear from Tables 4 and S3 (Supporting Information) that for He to Ar analogues, the interaction is purely noncovalent in nature, whereas the degree of covalency in bonding arises for heavier Ng atoms, and it increases from Kr to Rn. Another parameter, the $-G(r_c)/V(r_c)$ ratio, also provides clues for the existence of covalency in bonding.⁷³ If $-G(r_c)/V(r_c) > 1$, then the nature of the interaction is purely noncovalent, and if it ranges between

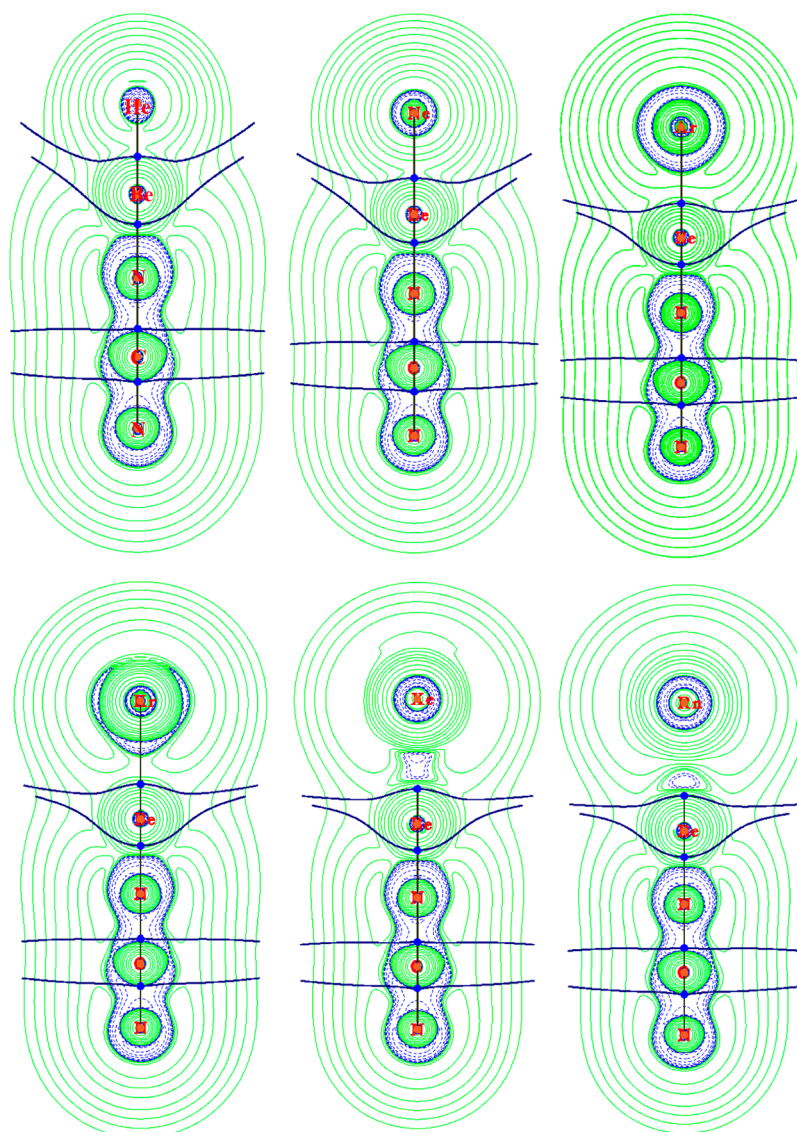


Figure 2. Contour line diagrams of the Laplacian of the electron density of different NgBeCN₂ clusters. (Green solid lines show areas of the charge depletion ($\nabla^2\rho(\mathbf{r}) > 0$), and blue dotted lines show areas of the charge concentration ($\nabla^2\rho(\mathbf{r}) < 0$)).

0.5 and 1, then the interaction is partially covalent in nature.⁷³ One can conclude from the $-G(r_c)/V(r_c)$ ratio and H_C values that there exists some degree of covalent character in bonding between Be and Kr–Rn. Very recently, Boggs et al.⁷⁴ carried out the analysis of the electron density of a series of rare-gas-containing systems and classified the weak interaction between the rare gas (Rg) and binding center as Rg bonds similar to hydrogen bonds, lithium bonds, and halogen bonds. They termed the interaction of Rg (Rg = He–Ar) and Be in RgBeO as W^n (W^n implies weak interaction with some noncovalent properties), whereas for those for the heavier Rg atoms, the interaction is of W^c type (W^c implies weak interaction with some covalent properties). The results for RgBeO and our NgBeCN₂ and NgBeNBO are quite similar. Therefore, we can also say that Be–Ng (Ng = He–Ar) interaction is of W^n type, and those for Ng = Kr–Rn are of W^c type.

To provide more insight into the nature of bonding, we have performed NPA charge calculation and EDA. To perform EDA, we have used the scheme proposed by Su and Li.⁶⁴ As shown in Table 5, ΔE^{ex} , $\Delta E^{\text{pol+ct}}$, and ΔE^{dis} (always negative in sign) stabilize the complexes, whereas ΔE^{rep} and ΔE^{ele} (always

positive in sign, with the exception the ΔE^{ele} of Ne) are destabilizing contributions.

The magnitudes of ΔE^{ex} and $\Delta E^{\text{pol+ct}}$ terms indicate a significant orbital overlap between Ng and the beryllium fragment. As evidenced in Table 1 by NPA charges, there is a significant amount of charge transfer to Be upon binding to Ng. Similar trends in $\Delta E^{\text{pol+ct}}$ have been observed in ionic Ng clusters such as Rg_2H^+ ⁷⁵ (Rg = rare gas), which are considered to be bound by polar-covalent bonds.⁷⁶ Interestingly, only a small percentage of the Ng–Be dissociation energy in both complexes arises from ΔE^{dis} . These results contrast the values found for other Ng trapping molecules, such as lithium complexes (O_2Li_5^+ and C_5Li_7^+),⁷⁷ where percentages range between 18 and 91%. It is generally accepted that a large contribution from the dispersion term indicates dominant van der Waals forces to the interaction energy. This reinforces the idea that the nature of the bond in the title systems is more of covalent nature.

We have also analyzed the bond dissociation energy trend in going from He to Rn. On the basis of polarizability values of Ng atoms, one may expect a periodic increase in bond dissociation

Table 5. Su and Li Decomposition Analysis⁶⁴ of the Electron Interaction Energy (ΔE^{total}) between Ng Atoms and the BeCN₂/BeNBO Complex, Including Values of Electrostatic (ΔE^{ele}), Exchange (ΔE^{ex}), Polarization and Charge Transfer ($\Delta E^{\text{pol+ct}}$), Dispersion (ΔE^{dis}), and Repulsion (ΔE^{rep}) Interaction Energy Terms Calculated at the CCSD(T)/def2-TZVP Level^a

clusters	ΔE^{ele}	ΔE^{ex}	ΔE^{rep}	$\Delta E^{\text{pol+ct}}$	ΔE^{dis}	ΔE^{total}
HeBeCN ₂	0.37	-2.61	6.57	-9.11	-1.25	-5.79
NeBeCN ₂	-0.08	-2.75	6.61	-7.83	-0.69	-4.74
ArBeCN ₂	0.41	-6.76	15.77	-20.81	-2.03	-13.42
KrBeCN ₂	0.70	-7.66	17.44	-24.15	-2.50	-16.15
XeBeCN ₂	1.31	-8.71	19.38	-28.16	-3.13	-19.31
RnBeCN ₂	1.58	-8.93	19.70	-29.49	-3.83	-20.97
HeBeNBO	0.35	-2.54	6.45	-8.95	-1.08	-5.77
NeBeNBO	-0.07	-2.71	6.61	-8.09	-0.73	-4.99
ArBeNBO	0.41	-6.50	15.32	-20.75	-2.03	-13.55
KrBeNBO	0.71	-7.37	16.99	-23.85	-2.45	-15.96
XeBeNBO	1.43	-8.38	18.87	-27.72	-3.05	-18.85
RnBeNBO	1.73	-8.60	19.18	-29.00	-3.76	-20.43

^aBSSE corrected energies are in kcal/mol.

energy along the group. However, we have observed that in NgBeCN₂ and NgBeNBO, the bond dissociation energy value for Ne is smaller than that of He (Table 1). This unusual behavior of Ne is already known and very nicely represented by Grochala⁷⁸ and Grandinetti⁷⁹ in their articles “On Chemical Bonding between Helium and Oxygen”⁷⁸ and “Neon Behind the Signs”, respectively.⁷⁹ A look at D_0^{BSSE} values in Tables S1 and S2 (Supporting Information) further shows the inconsistent behavior of Ne; in a few cases, it shows a higher bond dissociation energy than He, whereas in some other cases, just the reverse is the situation. Therefore, such types of results further prove the strange character of Ne. Values of ΔE^{dis} and $\Delta E^{\text{pol+ct}}$ decrease for Ne compared to those in He. NPA shows the lower charge transfer from Ne than He. Therefore, this factor does not allow one to improve the polarization term as one expects based on polarizability knowledge in going from He to Ne. Therefore, the improvement in the attractive interaction energy terms for Ne cannot compensate for the decrease in the dispersion and polarization terms and the increase in the repulsive term in the case of Ne with respect to He. It results in a slight decrease in ΔE^{total} for Ne compared to that of He.

All attractive terms gradually increase in going from Ar to Rn. However, polarization and exchange terms are the most and the second most dominating factors in stabilizing such Ng–BeCN₂ and Ng–BeNBO complexes. High values of $\Delta E^{\text{pol+ct}}$ for Ar–Rn cases suggest that the corresponding orbitals suffer considerable change in their shapes, which is a characteristic in the formation of a covalent bond. This result also supports the conclusions obtained from the analysis of the electron density (Table 4 and Figure 2).

CONCLUSIONS

We have shown that the global minimum geometries of BeCN₂ and BeNBO are linear in shape, having a Be center in a terminal position. At the MP2 level, BeCN₂ can bind a He atom with the highest dissociation energy among the studied neutral Ng–Be complexes. There are only two systems among those studied by us, namely, BeNCCl₃ and BeOBH₃, that show a higher dissociation energy of Be–Ng bonds (Ng = Ne–Rn) than

BeCN₂, but none of them is a global minimum in their studied geometries. Both BeCN₂ and BeNBO are found to be better candidates as Ng trappers than the well-known BeO, BeS, and BeNH systems at the CCSD(T) level. Further, one can make them a better Ng trapper by attaching a proper electron-withdrawing group. All Ng-binding processes are found to be thermodynamically spontaneous at room temperature (298 K) except for He and Ne. For these two cases, lower temperature is required. Polarization plus charge transfer is the key term in binding Ng atoms. Significant covalent contribution is found to be present for the heavier Ng atoms, especially for Xe and Rn.

ASSOCIATED CONTENT

Supporting Information

Figures S1–S4, including different isomers of BeCN₂ and BeNBO, plots of the ZPE and BSSE uncorrected dissociation energies, and contour line diagrams, Tables S1–S3, including ZPE and BSSE uncorrected dissociation energies and calculated topological properties of the BCPs, and Cartesian coordinates of the optimized geometries of BeCN₂, NgBeCN₂, BeNBO, and NgBeNBO clusters at the CCSD(T)/def2-TZVP level. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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