Induction of an Aromatic Six-Membered Nitrogen Ring via Cation−π Interaction

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Nitrogen clusters have been intensively studied for their potential application as high-energy density materials, but a six-membered nitrogen ring (N_6) was not found to be stable and aromatic. To explore the possibility of inducing an aromatic N_6 ring via cation−π interaction, quantum chemistry calculations were performed on the systems of Ca_2N_6, CaN_6, CaN_6^{2-}, N_6, and N_6^{4-} at the B3LYP/6-311+G* level. The optimized geometries reveal that the planar structure of the N_6 ring is stable only in the Ca_2N_6 complex. The computed NBO and CHelpG charges demonstrate that the planar N_6 moiety in the Ca_2N_6 complex is almost a 10π-electron system. The predicted nucleus-independent chemical shift (NICS) values demonstrate that the N_6 moiety is aromatic in comparison with the NICS values of benzene. The estimated enthalpy of formation for the Ca_2N_6 complex is 100.4 kcal/mol for the reaction of 2Ca and $3N_2$. The binding energy between the Ca^{2+} cation and the N_6^{4-} moiety is −1928.8 kcal/mol, with electrostatic interaction serving as the predominant component. When all the calculated results are taken into account, including the planar structure, 10π-electron system, identical bond length, and negative NICS value of the N_6^{4-} moiety in the Ca_2N_6 complex, it is deduced that the alkaline earth metal Ca is capable of inducing an aromatic N_6 ring through the cation−π interaction formed by electron transfer from the Ca atom to the N_6 ring.

1. Introduction

Polynitrogen molecules have been intensively studied for more than two decades since they are potential candidates as high-energy density materials (HEDMs).[1−5] Among them, theoretical studies on N_6 isomers have a substantial history[6−9] stimulated by the work of Vogel et al.,[10] who claimed to have experimental evidence for N_6 molecule in a matrix at low temperature. Many theoretical reports demonstrated that the N_6 molecule with a hexagonal ring structure is a nonplanar and twisted-boat D_2 structure without aromaticity, though it has six p electrons−.[7,8] A theoretical study at the Hartree−Fock level with 4-31G basis set by Li et al.[11] indicated a weak aromaticity of N_6^{4-} structure, but the calculation was carried out with a constraint of D_{6h} symmetry on the N_6^{4-} system. Our calculation at higher level (B3LYP/6-311+G*) shows that this D_{6h} structure has two imaginary frequencies and that a thorough optimization on the structure led to a twisted ring structure. Therefore, the energetically favored structure of either N_6 or N_6^{4-} ring is a nonplanar system without aromaticity. Thus, it is still an open question whether there is any way to induce a benzene-like N_6 or N_6^{4-} ring with aromaticity.

The cation−π interaction between a cation and an aromatic system plays important roles in diverse chemical and biological processes.[12] Many experimental and theoretical studies demonstrated that the interaction is rather strong and could be used to design new functional materials.[13−22] Our recent theoretical study suggested that the alkaline earth metal atoms Ca, Sr, and Ba can induce a nonaromatic boatlike cyclooctatetraene (COT) molecule to form a planar aromatic COT^{2-} via electron transfer.[23] The interaction between COT^{2-} and Ca^{2+} is a cation−π interaction. Accordingly, it might be possible to induce an aromatic ring of N_6^{4-} via the cation−π interaction. In this paper, we present our theoretical investigation on the possibility of inducing an aromatic six-membered nitrogen ring through the cation−π interaction. Our quantum chemistry calculations at the B3LYP/6-311+G* level reveal that calcium atom is indeed capable of inducing the distorted boatlike N_6 ring to form a planar structure. Furthermore, the calculated nucleus-independent chemical shift (NICS) values show that the planar N_6^{4-} moiety in the Ca_2N_6 complex has aromaticity. Therefore, this study opens a new way toward designing a class of planar nitrogen rings with aromaticity that could be used as potential high-energy density materials.

2. Calculation Methods

The initial structures of the N_6, N_6^{4-}, CaN_6, CaN_6^{2-}, and Ca_2N_6 were designed in such a way that the six-membered ring of nitrogen has a planar structure and that each metal atom could interact directly with the six nitrogen atoms. Density functional theory (DFT) is known as a powerful algorithm because the Kohn−Sham orbital interaction includes electron correlation effects. In this study, the DFT B3LYP method[24,25] was employed to optimize these initial structures with the 6-311+G* basis set,[26,27] as the method would utilize computational resources sparingly and provide precise results comparable to those generated by the MP2 method for some cation−π systems.[12] No structural symmetry was constrained during the geometrical optimization, and both singlet and triplet electronic states were tested for each of the initial structures. To characterize their

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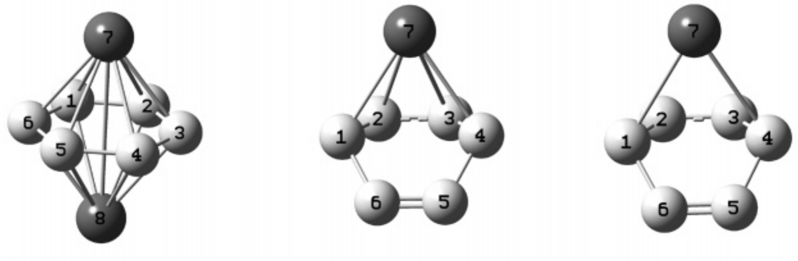
(a) N_6 (D_2-singlet) (b) N_6^{4-} (C_{2v}-triplet)



(c) Ca_2N_6 (D_{6h}-singlet) (d) CaN_6 (C_s-singlet) (e) $[CaN_6]^{2-}$ (C_s-singlet)

Figure 1. Optimized structures of the N_6, N_6^-, Ca_2N_6, CaN_6, and N_6^{4-} systems

stationary points and estimate their enthalpies of formation, the harmonic vibrational frequencies of these structures were also calculated at the same level of the theory.

To explore the details of the binding between the calcium and the nitrogen ring, the Morokuma−Ziegler energy partitioning scheme[28] was used to decompose the interaction energy E_{int}:

$$E_{int} = E_{es} + E_{Pauli} + E_{oi} \tag{1}$$

where E_{es} is the electrostatic interaction energy; E_{Pauli} is the Pauli, or exchange repulsion, which accounts for steric repulsion; and E_{oi} is the orbital interaction energy, including charge transfer and polarization effects. Here, the geometry optimization and the decomposition of the interaction energy between the Ca^{2+} and the N_6^{4-} ring in the Ca_2N_6 complex were performed by use of Becke's 1988 exchange combined with Lee, Yang, and Parr's correlation functional (BLYP)[25,29] with the standard triple-ζ exponential (TZ2P)[30] basis sets including double polarization functions encoded in the program ADF.[31]

To further explore the characteristic of the optimized structures of the nitrogen ring, the nucleus-independent chemical shift (NICS), which has been widely used as a criterion of aromaticity in recent theoretical studies,[32] was employed to study the aromaticity of the six-membered nitrogen ring.

All the geometrical optimizations and frequency calculations were performed with the Gaussian 03 program on a SGI Power Challenge R10000 supercomputer.[33]

3. Results and Discussion

3.1. Optimized Geometrical Structures. Figure 1 shows the optimized structures, and Table 1 lists the calculated geometrical parameters of the N_6, N_6^{4-}, CaN_6, CaN_6^{2-}, and Ca_2N_6 systems. The geometrical optimization for N_6 shows that the D_2 structure (singlet) is the most stable one, with two different N−N distances of 1.326 Å for R_{1-6} and R_{3-4} and 1.315 Å for the rest of the bonds (Figure 1a). They are both between the N−N single bond length (1.450 Å) and N═N double bond length (1.250 Å).[34] The planar D_{6h} isomer of the N_6 molecule is unstable with three large imaginary frequencies and with a higher energy of 2.58 kcal/mol than the most stable D_2 structure (singlet), which is very similar to the reported results by Engelke[7] and Tobita and Bartlett.[8]

TABLE 1: Optimized Geometrical Parameters[a] of CaN_6, $[CaN_6]^{2-}$, and Ca_2N_6 and of Free N_6 and N_6^{4-} Structures at the B3LYP/6-311+G* Level

bond	Ca_2N_6	$[CaN_6]^{2-}$	CaN_6	N_6	N_6^{4-}
N1−N2	1.432	1.422	1.405	1.315	1.413
N2−N3	1.432	1.277	1.298	1.315	1.293
N3−N4	1.432	1.422	1.405	1.326	1.413
N4−N5	1.432	1.444	1.455	1.315	1.413
N5−N6	1.432	1.240	1.228	1.315	1.293
N6−N1	1.432	1.444	1.455	1.326	1.413
Ca7−N1	2.332	2.433	2.315		
Ca7−N2	2.332	2.433	2.399		
Ca7−N3	2.332	2.608	2.399		
Ca7−N4	2.332	2.608	2.315		
Ca7−N5	2.332	3.233			
Ca7−N6	2.332	3.233			
$Ca^{2+}−N_{ring}$	1.840				

[a] Bond distances are given in angstroms.

The geometry optimization of the singlet N_6^{4-} molecule from an initial planar structure resulted in a boatlike C_{2v} geometry without any imaginary frequencies, but it is higher in energy than its corresponding triplet state by 3.37 kcal/mol, demonstrating that the triplet-state structure of N_6^{4-} with C_{2v} symmetry is a more stable one at the B3LYP/6-311+G* level. However, the difference is not great enough to exclude the singlet of C_{2v} structure. The singlet planar D_{6h} structure is higher in energy than the triplet C_{2v} structure by 38.60 kcal/mol, demonstrating that the D_{6h} structure is not a stable conformation of the N_6^{4-} ring. This C_{2v} triplet-state structure also has two different N−N bond lengths of 1.293 Å for R_{2-3} and R_{5-6} and 1.413 Å for the rest of the bonds. The calculated longer N−N bond lengths of N_6^{4-} on average compared with those of N_6 indicate that this 10 π-electron N_6^{4-} structure might not be more stable than the 6 π-electron N_6 system, possibly, because of the antibonding MO occupation in the 10 π-electron system. All the calculated results show that the free N_6 and N_6^{4-} rings are energetically unfavorable to keep a planar conjugated aromatic structure and, consequently, are not good aromatic systems.

The geometrical optimization of the singlet Ca_2N_6 structure without constraint generated a structure with the symmetry of D_{6h} without imaginary frequencies, suggesting that the optimized structure is stable. The moiety of the six-membered nitrogen ring in the Ca_2N_6 complex is totally a planar structure, which is different from the free N_6 or N_6^{4-} ring discussed above. The optimized N−N bond lengths of the ring are all identical with a value of 1.432 Å. The calculated distance between the calcium and the nitrogen ring is 1.840 Å, which is much shorter than

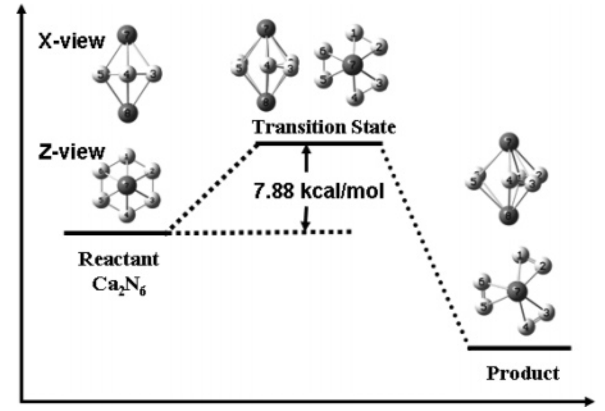


Figure 2. Most probable decomposition approach of Ca_2N_6.

TABLE 2: Enthalpies of Formation of CaN_6, $[CaN_6]^{2-}$, and Ca_2N_6 and of Free N_6 and N_6^{4-} Systems at the B3LYP/6-311+G* Level

reaction	ΔH (kcal/mol)
$3N_2(g) \rightarrow N_6(g)$	198.06
$3N_2(g) \rightarrow N_6^{2-}(g)$	232.33
$3N_2(g) + 4e^- \rightarrow N_6^{4-}(g)$	791.82
$Ca(g) + 3N_2(g) \rightarrow CaN_6(g)$	144.14
$Ca(g) + 3N_2(g) + 2e^- \rightarrow [CaN_6]^{2-}(g)$	146.79
$2Ca(g) + 3N_2(g) \rightarrow Ca_2N_6(g)$	100.36

the reported distances of the metal cation Ca^{2+} and benzene ring (2.33−2.43 Å) at the MP2/6-31G** level.[21] The sum of the covalent radius of N atom (0.75 Å) and that of Ca atom (1.74 Å) is 2.49 Å.[35] The optimized Ca−N distance is only 2.332 Å, thus, shorter than the sum of the corresponding atomic covalent radii, demonstrating that the interaction between the metal and the planar ring structure is very strong.

To examine the kinetic stability of the Ca_2N_6 complex as a potential HEDM, three possible decomposition approaches of the complex were designed, viz., the breaking of the N−N bond, the leaving of the calcium atom from the N_6 moiety along the normal of the N_6 plane, and the sliding of the calcium over the N_6 plane. The calculations at the B3LYP/6-311+G* level reveal three different decomposition barriers of 7.9, 24.6, and 9.0 kcal/mol, respectively, indicating that the first designed decomposition approach (breaking of the N−N bond) is the most feasible way (Figure 2). These barriers show that Ca_2N_6 might be slightly more stable than some other nitrogen HEDMs, such as Ti(η^6-N_6) complex that has a decomposition barrier of 4.5 kcal/mol with the B3LYP method.[36]

To study whether one calcium atom is enough to induce a planar six-membered nitrogen ring structure, both CaN_6 and CaN_6^{2-} structures were also optimized at the B3LYP/6-311+G* level. The results show that their singlet C_s structures are more stable than those with a planar N_6 ring. For instance, the optimized triplet C_{6v} structure of the CaN_6 complex with two imaginary frequencies is higher in energy than the singlet C_s one by 17.48 kcal/mol. Regarding CaN_6^{2-}, two structures, viz., triplet C_{2v} and singlet C_s, were obtained through geometry optimization. The singlet C_s structure is more stable than the triplet C_{2v} one by 18.52 kcal/mol. Therefore, it could be concluded that one metal atom is not capable of inducing a planar six-membered nitrogen ring.

3.2. Enthalpies of Formation. The calculated enthalpies of formation for the complexes of CaN_6, $[CaN_6]^{2-}$, and Ca_2N_6 and the free N_6 and N_6^{4-} systems in Table 2 demonstrate that all the systems are energetically unfavorable structures relative to the reactants of these reactions, namely, calcium and nitrogen molecules (Table 2). Therefore they are metastable and, thus, could be candidates for potential high-energy density materials (HEDMs). The formation enthalpy of the free N_6 ring is 198 kcal/mol, which is very close to the previously reported results,[7,8] while those of N_6^{2-} and N_6^{4-} are 232 and 792 kcal/mol, respectively. Remarkably, the introduction of electrons to the nitrogen ring leads to a significant destabilization of the N_6 ring. Furthermore, the effect of introducing electrons to the isolated N_6 ring is much greater than that for the CaN_6 molecule. For instance, the formation enthalpies (ΔH) of the CaN_6 and CaN_6^{2-} molecules, 144 and 147 kcal/mol, respectively, are very close to each other.

TABLE 3: Calculated NBO and CHelpG Charges (*q*/*Q*) at the B3LYP/6-311+G* Level

	NBO	CHelpG
Ca	+1.69	+1.62
N_6	−3.36	−3.25
N	−0.56	−0.54

The formation enthalpy of Ca_2N_6 is 100.36 kcal/mol, about 33.5 kcal/mol per N_2 unit above the energy of its reactants. The energy densities per N_2 unit of the reported N_5ThN_7, ThN_6, and $Fe(N_5)_2$ complexes are 22, 24, and 59 kcal/mol, respectively.[36−38] Thus, Ca_2N_6 falls in the range of the stability of the reported systems and could be a potential HEDM. Noticeably, the metal atoms in the reported systems are all transition metal elements.[36−38] The nitrogen ring acts as both a π donor and a π^* acceptor with respect to the metal d and f electrons.[36] Thus, both d and f orbitals are involved in the interactions between the transition metal atoms and the nitrogen ring. In other word, the stabilization of the planar N_6 ring could be attributed to the coordination bond between the transition metal atoms and the nitrogen atoms in the nitrogen ring. Differently, the metal atom in our studied system is an alkali earth metal element, calcium. There is no f orbital involved in the interaction between the calcium and the planar N_6 ring. Therefore, the planarity of the N_6 ring in Ca_2N_6 should result from electron transfer from the calcium to the N_6 ring (refer to section 3.3 for details). Therefore, different from the reported systems, the interaction between calcium and the nitrogen ring is ionic in nature.

3.3. Charge Transfer. Our attempt is to induce an aromatic N_6 ring via electron transfer from the calcium atom to the N_6 ring. Thus, the charge distribution in Ca_2N_6 is another key issue that we should address. Two different types of charges, namely, NBO[39] and CHelpG[40] charges, are shown in Table 3. As expected, indeed, all the calculated charge distribution indicates that the electron transfer takes place from the metal atoms to the nitrogen ring. The calcium is positively charged, and the N_6 ring is negatively charged. In detail, both the NBO and CHelpG charge analyses show that each of the two calcium atoms transfers more than 1.6 electrons to the N_6 ring, while the whole nitrogen ring obtains ~3.3 electrons. This significant charge transfer demonstrates a strong interaction between the positively charged calcium cation and the negatively charged N_6 ring. Differently, the calculated natural orbital occupation numbers are 1.12, 1.70, 1.85, and 2.62 on the metal atom in the complexes TiN_6, ZrN_6, HfN_6, and ThN_6, respectively,[36] indicating that the N_6 ring moiety in the complexes is not a 10-electron system. To estimate the binding strength between the positively charged calcium cation and the negatively charged N_6 ring, the binding energy of the complex of Ca_2N_6 was calculated at the B3LYP/6-311+G* level. Noteworthily, the calculated binding energy between the Ca^{2+} cation and the N_6^{4-} moiety extracted directly from the optimized Ca_2N_6 structure is as great as −1928.8 kcal/mol, demonstrating an extraordinarily strong interaction between the cation and the ring.

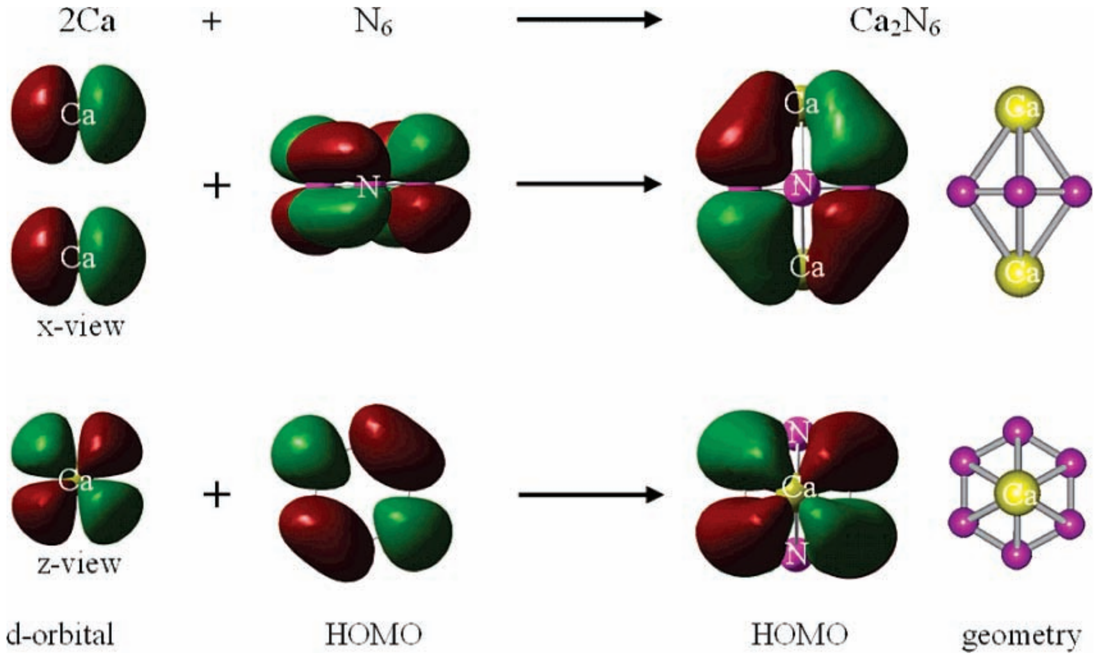


Figure 3. Orbital interaction between the Ca and N_6 moieties in the Ca_2N_6 complex.

TABLE 4: Decomposition of Interaction Energy between Ca^{2+} and N_6^{4-} Moieties in Ca_2N_6[a]

	kcal/mol
E_{es}	−1998.09
E_{Pauli}	246.70
E_{oi}	−311.14
E_{int}	−2062.53

[a] By the Morokuma−Ziegler decomposition approach at the BLYP/TZ2P level.

3.4. Energy Decomposition and Molecular Orbital Interaction. The total interaction energy E_{int} is decomposed into three parts, namely, E_{es}, E_{Pauli}, and E_{oi}, according to the Morokuma−Ziegler energy partitioning scheme.[28] As shown in Table 4, the contribution of the electrostatic interaction is as strong as 97% of the total interaction energy, suggesting that the interaction between the calcium cation and the N_6^{4-} ring is undoubtedly electrostatic in nature. On the other hand, the orbital interaction also makes a certain contribution to the total interaction energy ($E_{oi} = -311$ kcal/mol). To further address the orbital interaction between the calcium atom and the N_6^{4-} ring, the first 10 highest occupied molecular orbitals of the Ca_2N_6 molecule were checked. Only the HOMO is contributed simultaneously by both the Ca and N_6 ring. As shown in Figure 3, the HOMO of the Ca_2N_6 molecule is composed of the empty 3d orbital of the calcium and the HOMO of the N_6 ring. Thus, all the calculated results show that the interaction between the Ca^{2+} and the N_6^{4-} moieties is mainly ionic in nature, which is different from the previously reported covalent cation−π interaction between the alkaline earth metal cation M^{2+} and benzene[21,22] but is very similar to the interaction between the alkaline earth metal cation M^{2+} and the COT^{2-} moiety in M^{2+}−COT^{2-} complexes.[23]

3.5. Aromaticity of N_6 Ring. The NICS values were calculated by three different methods, viz., HF/6-31+G*, B3LYP/6-311+G*, and MP2/6-311+G*. All the data indicate that the N_6 moiety in Ca_2N_6 is aromatic. For HF/6-31+G*, as an example, the NICS(0) (i.e., at the ring center) and NICS(1) (i.e., at the point of 1 Å above the ring center) values of the N_6 moiety in the Ca_2N_6 are −16.2 and −27.4 ppm, respectively (Table 5), indicating that the planar N_6 ring is of aromatic character. To further explore whether the calcium atom can induce aromaticity of the ring, NICS calculations were performed on the planar N_6^{4-} ring extracted directly from the Ca_2N_6 complex without further geometrical optimization, which produced NICS(0) and NICS(1) values of −6.9 and −6.6 ppm, respectively (Table 5). Remarkably, the introduction of two calcium atoms into the N_6 ring significantly enhances the aromaticity of the N_6 moiety in the complex of Ca_2N_6. Meanwhile, NICS values were also calculated for the optimized N_6^{4-} ring with D_{6h} symmetry constraint (a planar structure), obtaining almost the same NICS(0) and NICS(1) values as those extracted directly from the complex of Ca_2N_6 (Table 5). Furthermore, the NICS(0) and NICS(1) values of a typical aromatic system, benzene, were calculated to be −9.7 and −11.5 ppm, respectively. Thus, on the basis of the calculated NICS(0) and NICS(1) values for different systems, it could be concluded that the N_6^{4-} moiety in the complex of Ca_2N_6 is obviously aromatic. As the calcium is located at 1.84 Å above the nitrogen ring, it may affect the calculated NICS values of

TABLE 5: Calculated NICS Values[a] with Different Methods

	Ca_2N_6			N_6^{4-} [b]			N_6^{4-} (D_{6h})			C_6H_6 (D_{6h})		
	HF[c]	DFT[d]	MP2[e]	HF[c]	DFT[d]	MP2[e]	HF[c]	DFT[d]	MP2[e]	HF[c]	DFT[d]	MP2[e]
NICS(0)	−16.2	−23.3	−22.8	−6.9	−4.0	−6.0	−6.9	−4.2	−6.1	−9.7	−7.9	−9.5
NICS(1)	−27.4	−30.3	−31.2	−6.6	−5.3	−7.4	−6.6	−5.6	−7.5	−11.5	−10.1	−11.3
NICS(0.25)	−16.6	−23.8	−23.1	−7.3	−4.7	−6.7	−7.4	−4.9	−6.7	−10.4	−8.5	−10.0
NICS(0.50)	−17.3	−24.3	−23.4	−8.0	−5.9	−7.8	−8.1	−6.2	−7.9	−11.5	−9.8	−11.2
NICS(0.75)	−18.7	−24.7	−24.1	−7.8	−6.2	−8.2	−7.9	−6.6	−8.3	−12.1	−10.5	−11.7

[a] Calculated values are given in parts per million (ppm). [b] Structure extracted from the Ca_2N_6 molecule directly. [c] HF/6-31+G*. [d] B3LYP/6-311+G*. [e] MP2/6-311+G*.

the complex of Ca_2N_6. To study the effect of the calcium on the NICS value, NICS(0.25), NICS(0.50), and NICS(0.75) values were calculated at 0.25, 0.50, and 0.75 Å, respectively, above the nitrogen ring (Table 5). While the data show that the N_6^{4-} moiety in the Ca_2N_6 is aromatic, they also demonstrate that the calcium atoms really affect the calculated NICS values.

4. Summary

The quantum chemistry calculations at the B3LYP/6-311+G* level on the systems of Ca_2N_6, CaN_6, CaN_6^{2-}, N_6, and N_6^{4-} reveal that the planar structure of the six-membered nitrogen ring is stable only in the complex Ca_2N_6. The calculated distance between the Ca atom and N atom was found to be even shorter than the theoretical covalent bond length of Ca−N. In addition, the optimized N−N bond lengths in the Ca_2N_6 complex are all identical. The computed NBO and CHelpG charges demonstrate that about 3.3 electrons are transferred from two calcium atoms to the nitrogen ring during the complexation, indicating that the N_6 moiety in the Ca_2N_6 complex is almost a 10 π-electron system and implying that the N_6 moiety is aromatic. On the other hand, the significant charge transfer leads to a strong electrostatic interaction between the cation Ca^{2+} and the negatively charged nitrogen ring. Indeed, the calculated binding energy between Ca^{2+} and N_6^{4-} is −1928.8 kcal/mol. The energy decomposition calculations reveal that the electrostatic interaction is absolutely a predominant component in comparison with the contributions of orbital interaction and exchange repulsion. The calculated NICS values indicate the six-membered ring moiety in the complex of Ca_2N_6 has indeed aromaticity with reference to the typical aromatic system benzene. When the characteristics of the N_6 moiety in the Ca_2N_6 complex are taken into account, including its planar structure, 10 π-electron system, identical bond lengths, and negative NICS values, it should be acceptable that the N_6^{4-} moiety in the Ca_2N_6 complex is aromatic. Consequently, the interaction between the cations and the N_6 moiety is a typical cation−π interaction but is ionic in nature. In conclusion, the alkaline earth metal Ca atom is capable of inducing an aromatic six-membered nitrogen ring through electron transfer from the Ca atom to N_6 ring, which could serve as a potential high-energy density material.

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