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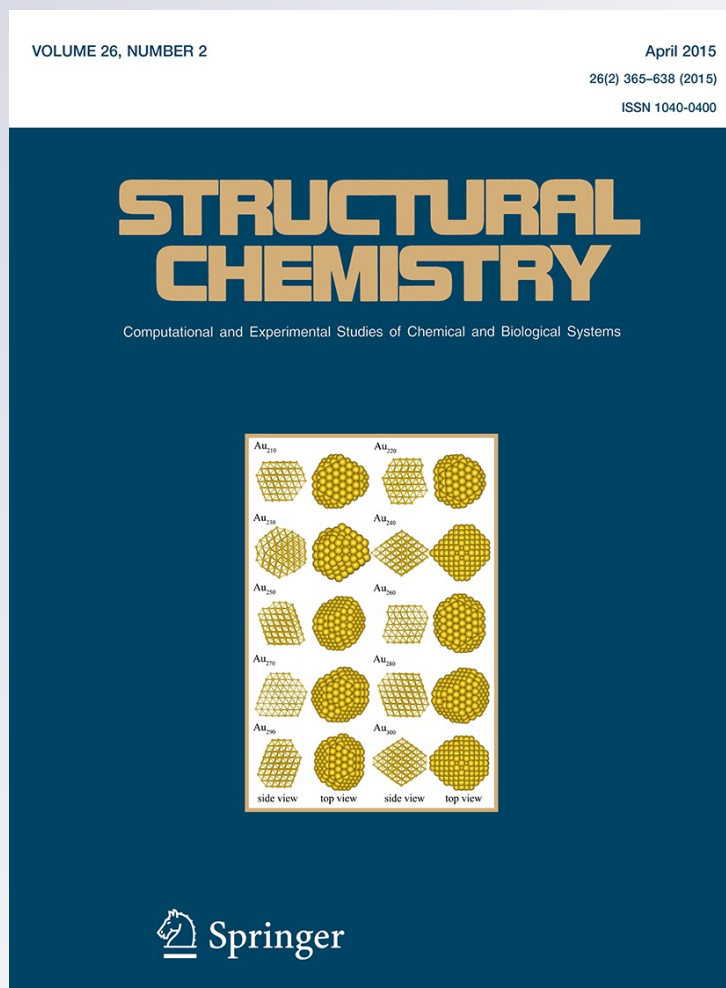
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Theoretical characterization of molecular complexes formed between triplet vinyl nitrene and Lewis acids

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Abstract In the current work, the complexes formed between triplet vinyl nitrene ($^3\text{CH}_2\text{CHN}$) and some Lewis acids YA (LiH, LiF, BeH₂, BeF₂, BH₃, BF₃, ClH, ClF, HCl, HF) have been investigated through calculations of the electronic structure. These calculations have been carried out in order to determine the energetic stability of the N \cdots Y (with Y = Li, Be, B, Cl, H) interactions and also to understand their chemical nature. Quantum chemical calculations predict that the molecular complexes $^3\text{CH}_2\text{CHN}\cdots\text{Y}-\text{A}$ are always more stable than the separated $^3\text{CH}_2\text{CHN}$ and Y–A species. The interaction energies range from $-0.98\text{ kcal mol}^{-1}$ (in $\text{CH}_2=\text{CHN}\cdots\text{ClH}$) to $-39.03\text{ kcal mol}^{-1}$ (in $\text{CH}_2=\text{CHN}\cdots\text{BH}_3$) at the CCSD(T)/6-311++G(2d,2p) level of theory. Accordingly, some of these complexes may serve to experimentally detect and characterize the elusive triplet vinyl nitrene species. Moreover, AIM theory, in particular the $L(\mathbf{r}) = -\frac{1}{4}\nabla^2\rho(\mathbf{r})$ function, reveals that the N \cdots Y interactions established between the electron lone pair of the nitrogen atom and the charge density depletion region of the Y atom are mainly of electrostatic character.

Keywords Vinyl nitrene · Lewis acid · Charge density · QTAIM · Laplacian · VSCC

Introduction

Molecular interactions represent an important class of intermolecular forces in chemistry, biology, and materials science and play important roles in molecular recognition [1–4]. The hydrogen bond (HB) has been the subject of many studies and its key role in different reactions and phenomena is very well known [5–8]. At present other noncovalent interactions are also being extensively analyzed. These are, for example, the halogen bond (XB) [9, 10], the chalcogen bond (ChB) [11, 12], the beryllium bond (BeB) [13, 14], the boron bond (BB) [15, 16], and the lithium bond (LiB) [17, 18]. According to Grabowski [5], the term “Lewis acid–Lewis base interaction” seems to be more proper than the term “noncovalent interaction” for the HB, XB, and all other interactions where the complex formation is connected with significant electron charge redistribution. In all these Lewis acid–Lewis base interactions, the electrostatic forces are very important since the positively charged Lewis acid center interacts with the negatively charged Lewis base center. This is in line with the σ -hole concept which was applied to the XB and to other noncovalent interactions [19, 20].

On the other hand, in the decomposition reactions of organic azides it is commonly believed [21–25] that photolysis and thermolysis of these molecules leads, in a first stage, to the release of molecular nitrogen and to the formation of a nitrene. Nitrenes are typically very reactive and short-lived intermediates thus making their experimental detection and characterization a very difficult task. In a previous work on the decomposition mechanism of vinyl

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azide [26], we found that triplet vinyl nitrene ($^3\text{CH}_2\text{CHN}$) is a minimum on the potential energy surface with one electron lone pair on the nitrogen atom centered along the C–N bond axis. Thus, this lone pair can act as a Lewis base that interacts electrostatically with a Lewis acid to form a Lewis adduct. These adducts are probably stable species and their study would be of great importance to experimentalists who seek to detect and isolate nitrenes.

Recently van der Waals complexes have been studied through the matrix isolation technique. For example, Romano et al. have trapped in an argon matrix complexes formed between CS_2 and dihalogen molecules XY, where XY = Cl_2 , Br_2 , BrCl , ICl , or IBr [27], and also HCl [28] and determined their IR spectra. Buchberger et al. [29] measured several IR bands of $\text{FCH}_2\text{CN}\cdots\text{BF}_3$ and $\text{ClCH}_2\text{CN}\cdots\text{BF}_3$ complexes in solid nitrogen, argon, and neon. To the best of our knowledge, there are no examples in the literature where triplet vinyl nitrene has been detected and characterized experimentally. Therefore, we wonder if this technique could be used to detect the experimentally difficult to find triplet vinyl nitrene.

In this paper, we report a theoretical study of 1:1 molecular complexes involving triplet vinyl nitrene and some Lewis acids YA (LiH , LiF , BeH_2 , BeF_2 , BH_3 , BF_3 , ClH , ClF , HCl , HF). The theoretical study of these systems may help experimentalists in the isolation of triplet vinyl nitrene.

Computational details

The geometries of all monomers (triplet vinyl nitrene and Lewis acids) and complexes were optimized, without any constraint, using the second order Møller–Plesset perturbation (MP2) [30] method with the 6-311++G(2d,2p) basis set. Frequency calculations at this computational level have been performed to confirm that the structures obtained correspond to minima. The electronic energy has been refined by means of single-point energy calculations at the CCSD(T) [31] level (CCSD augmented with a noniterative treatment of triple excitations) with the 6-311++G(2d,2p) basis set. The interaction energies have been calculated as the difference between the total energy of the complexes minus the sum of the energies of the isolated monomers. The basis set superposition error (BSSE) was taken into account using the counterpoise method proposed by Boys and Bernardi [32].

The calculations of local topological properties of the electron charge density at a critical point, as well as, the display of the molecular graphs were performed with the AIMAll [33] software, with the wave functions obtained at the MP2/6-311++G(2d,2p) level. All calculations of

electronic structure were carried out using the Gaussian 03 suite of programs [34].

Results and discussion

In the current work, the complexes formed between triplet vinyl nitrene ($^3\text{CH}_2\text{CHN}$) and some Lewis acids YA (LiH , LiF , BeH_2 , BeF_2 , BH_3 , BF_3 , ClH , ClF , HCl , HF) have been investigated.

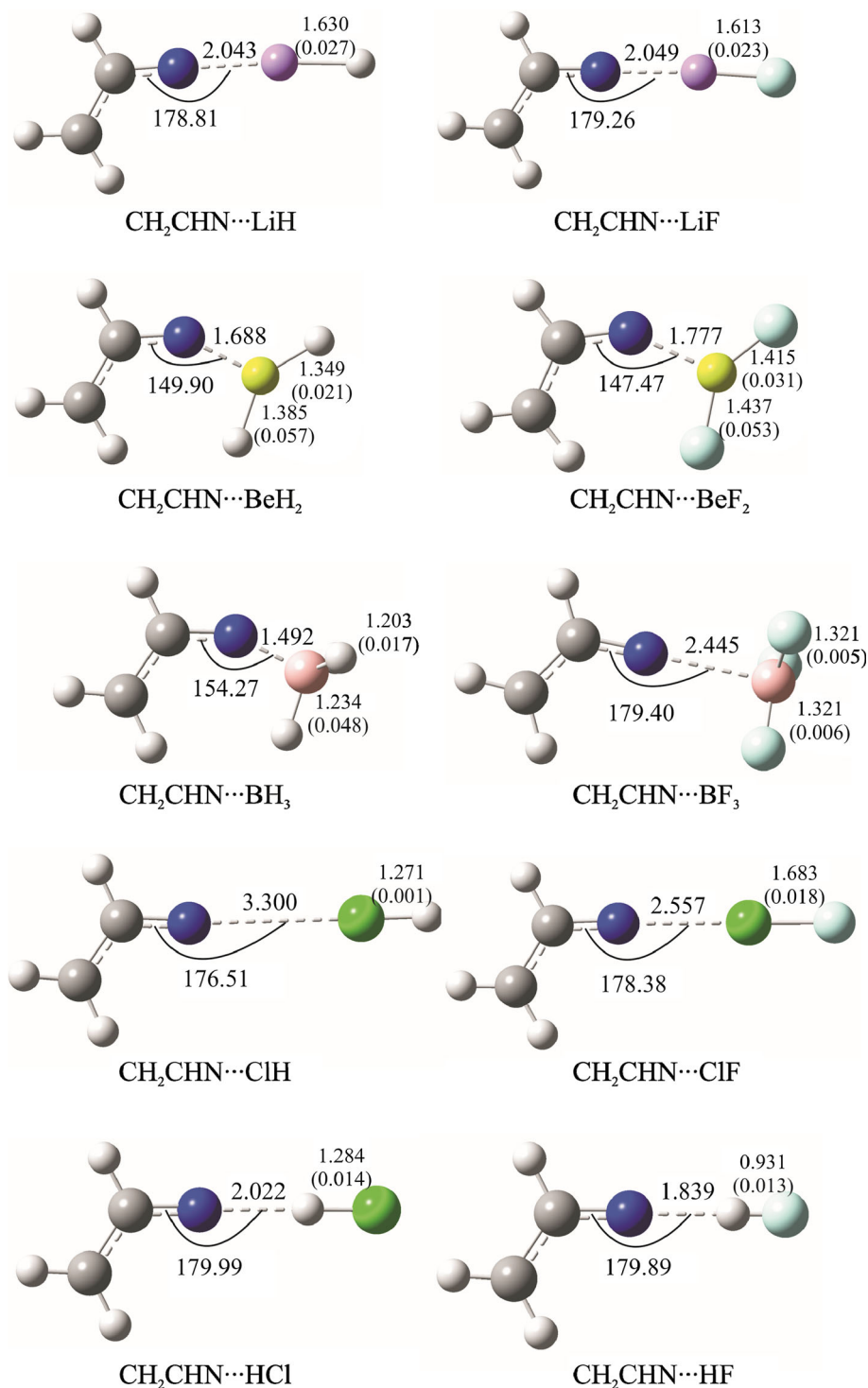
Geometries of the complexes

Optimized geometries and selected geometrical parameters of the complexes under consideration, obtained at the MP2/6-311++G(2d,2p) level of theory, are shown in Fig. 1. It can be observed in this figure that the interatomic distances between the nitrogen atom and the acidic site Y (Li, Be, B, Cl, H) of the Lewis acids are relatively short, from 1.688 to 3.300 Å. The distances $d(\text{N}\cdots\text{Y})$ are in agreement with the proposed range for the LiB [18], BeB [13], BB [15, 16], XB [35, 36], and HB [7], respectively. The short $\text{N}\cdots\text{Y}$ is indicative of the existence of a significant interaction between the two monomers forming the complex and is result of the mutual penetration of N and Y atoms electronic densities. An interesting aspect of the results presented in Fig. 1 is the fact that the presence of the electron-withdrawing fluorine atom leads to an increase of the binding distance in the LiB, BeB, and BB, while in the XB and HB there is a decrease in the binding distance. It is also evident that all Y–A bonds are systematically lengthened upon complexation (see values in parentheses). These results reveal that the $\text{N}\cdots\text{Y}$ interaction weakens the Y–A bonds. Except for the boron complexes all the other complexes present a planar structure. The equilibrium angle, C–N \cdots Y, is close to 180° in all complexes except for the $^3\text{CH}_2\text{CHN}\cdots\text{BeH}_2$, $^3\text{CH}_2\text{CHN}\cdots\text{BeF}_2$, and $^3\text{CH}_2\text{CHN}\cdots\text{BH}_3$ complexes where the equilibrium angle C–N \cdots Y is close to 150°.

Interaction energies

The interaction energy provides a measure of the strength of the interaction between N and Y (Y=Li, Be, B, Cl, H). Table 1 presents the interaction energies for the complexes calculated at the HF, MP2, and CCSD(T) levels of theory. It can be seen from Table 1 that the CCSD(T) method predicts a significant range of strength: from –0.98 (in $\text{CH}_2=\text{CHN}\cdots\text{ClH}$ complex) to –39.03 kcal/mol (in $\text{CH}_2=\text{CHN}\cdots\text{BH}_3$ complex) indicating that these interactions are comparable in strength to the well-documented hydrogen bonding interactions [37].

Fig. 1 Optimized geometries of the complexes between ${}^3\text{CH}_2\text{CHN}$ and the Lewis acids YA (LiH, LiF, BeH_2 , BeF_2 , BH_3 , BF_3 , ClH, ClF, HCl, HF). In addition, the variation of the Y–A bond length (defined as the difference between the bond length in the complex and isolated molecule) upon complex formation is indicated in parentheses. Bond lengths are in Å and bond angles in degrees



In the LiBs, the interaction energies at the HF, MP2, and CCSD(T) levels are practically identical, which means that the electronic correlation has not effect on the strength of the interactions $\text{N}\cdots\text{Li}$, in the rest of the complexes the electronic correlation significantly affects the interaction energy.

It is known that the higher the electron-withdrawing capacity of A (group bonded to Y, hydrogen and halogen, respectively) the stronger is the interaction [9].

In the ${}^3\text{CH}_2\text{CHN}\cdots\text{Li}-\text{A}$ and ${}^3\text{CH}_2\text{CHN}\cdots\text{Be}-\text{A}$ (with $\text{A}=\text{H}, \text{F}$) complexes, the electron-withdrawing fluorine atom has practically no effect on the strength of the $\text{N}\cdots\text{Li}$

Table 1 Interaction energies calculated using the HF, MP2, and CCSD(T) methods (kcal/mol)

Complexes	ΔE^{HF}	ΔE^{MP2}	$\Delta E^{\text{CCSD(T)}}$
CH ₂ =CHN...LiH	-15.33	-15.99	-15.99
CH ₂ =CHN...LiF	-15.00	-15.91	-15.69
CH ₂ =CHN...BeH ₂	-7.60	-15.54	-25.37
CH ₂ =CHN...BeF ₂	-12.53	-15.69	-26.59
CH ₂ =CHN...BH ₃	-4.79	-22.41	-39.03
CH ₂ =CHN...BF ₃	-2.86	-4.41	-6.22
CH ₂ =CHN...ClH	0.31	-0.40	-0.98
CH ₂ =CHN...ClF	-1.62	-4.76	-4.69
CH ₂ =CHN...HCl	-2.42	-4.52	-4.61
CH ₂ =CHN...HF	-5.45	-7.10	-7.53

All calculated interaction energies are BSSE corrected

and N...Be interactions (the interaction energies are approximately equal).

In the case of the BBs, the interaction energy is more negative for ³CH₂CHN...BH₃ than for ³CH₂CHN...BF₃ complexes, despite the strong electron-withdrawing effect of the fluorine atom; thus some additional factor is involved. A similar situation occurs when analyzing the relative Lewis acidity of boron trihalides [16]. The Lewis acidity of these acids increases in the order BF₃ < BC1₃ < BBr₃. According to Politzer and co-workers [16], this fact can be better understood and explained with the concept of “charge capacities”. According to these authors, the relative Lewis acidity of these molecules is due to the ability to accept charge density. This magnitude is increased in the order BF₃ < BC1₃ < BBr₃. It is logical to think that the major relative Lewis acidity of the BH₃ molecule is due to its higher “charge capacities” in relation to the BF₃ molecule.

In XBs and HBs, the stronger N...Y (with Y=Cl, H) interactions occur when Y is bonded to fluorine.

Vibrational analysis

The formation of a complex also has a strong effect on the frequencies of the vibrational normal modes of the Lewis acid. Table 2 presents selected vibrational modes of the Lewis acids and the complexed species.

A characteristic of conventional HBs, also called proper HBs, B...H-A, is that its formation leads to a weakening of the H-A bond [38]. This weakening is accompanied by a bond elongation and a concomitant decrease of the H-A stretch vibration frequency (shifted to the red), compared with the isolated H-A molecule. In contrast, in the formation of the so-called improper HBs, the H-A bond shortens, and its vibrational frequency increases (shift to the blue). In addition, it has been reported that the formation of XBs can also lead to a lengthening (red shift) or shortening (blue shift) of the X-Y bond (with X, Y=F, Cl, Br) [39]. For this

Table 2 Selected computed frequencies (cm⁻¹) at MP2/6-311++G(2d,2p) level of theory

Complex	Vibrational mode	$\nu_{\text{Mon}}^{\text{a}}$	$\nu_{\text{Dim}}^{\text{b}}$	$\Delta\nu^{\text{c}}$
CH ₂ =CHN...LiH	$\nu(\text{LiH})$	1419.46	1349.33	-70.13
CH ₂ =CHN...LiF	$\nu(\text{LiF})$	889.38	878.46	-10.92
CH ₂ =CHN...BeH ₂	$\delta_{\text{s}}(\text{BeH}_2)$	741.95	838.23	96.28
	$\nu_{\text{s}}(\text{BeH})$	- ^d	1864.26	
	$\nu_{\text{a}}(\text{BeH})$	2286.48	2073.18	-213.30
CH ₂ =CHN...BeF ₂	$\delta_{\text{s}}(\text{BeF}_2)$	363.37	450.85	87.48
	$\nu_{\text{s}}(\text{BeF})$	- ^d	811.69	
	$\nu_{\text{a}}(\text{BeF})$	1571.54	1327.49	-244.05
CH ₂ =CHN...BH ₃	$\delta_{\text{s}}(\text{BH}_3)$	1171.54	1096.59	-74.95
	$\nu_{\text{s}}(\text{BH})$	- ^d	2508.12	
	$\nu_{\text{a}}(\text{BH})$	2738.06	2556.22	-181.84
CH ₂ =CHN...BF ₃	$\delta_{\text{s}}(\text{BF}_3)$	693.28	615.69	-77.59
	$\nu_{\text{s}}(\text{BF})$	- ^d	868.21	
	$\nu_{\text{a}}(\text{BF})$	1449.36	1423.74	-25.62
CH ₂ =CHN...ClH	$\nu(\text{ClH})$	3003.93	2996.4	-7.53
CH ₂ =CHN...ClF	$\nu(\text{ClF})$	752.15	749.81	-2.34
CH ₂ =CHN...HCl	$\nu(\text{HCl})$	3003.93	2820.77	-183.16
CH ₂ =CHN...HF	$\nu(\text{HF})$	4168.97	3870.77	-298.20

^a ν_{Mon} represents the monomer (Lewis acid) vibrational frequency

^b ν_{Dim} represents the dimer vibrational frequency

^c $\Delta\nu$ represents the frequency shift, defined as the difference between the frequency of the certain vibrational mode in the complex and in the Lewis acid YA

^d $\nu_{\text{s}}(\text{BeA})$ and $\nu_{\text{s}}(\text{BA})$ are not listed because these symmetric stretches are IR inactive

reason, the effects of the formation of the complexes on the Y-A bond were also explored in this work.

The variation in the Y-A bond distance upon complexation, $\Delta d(\text{Y-A})$, that is, the difference between the distance $d(\text{Y-A})$ in the complexes and in the isolated monomers (YA), is presented in Fig. 1 and the IR spectrum and the predicted shifts with respect to the free monomers at MP2/6-311++G(2d,2p) level are presented in Table 2. All $\Delta d(\text{Y-A})$ values are positive; that is, the Y-A bond is stretched as result of the complexation. The elongation of the Y-A bond is accompanied by a decrease in the strength of the Y-A bond. This idea is supported by the analysis of the vibrational frequencies (see Table 2). In all cases, it is observed a decrease of the frequency of the vibration associated with the stretching of the Y-A bond, compared with the isolated molecule. Therefore, the interactions studied here, we can consider as conventionals.

In the LiBs, XBs, and HBs studied here, there is a single Y-A (with Y=Li, Cl, H and A=H, F) stretching mode [$\nu(\text{YA})$] that is in every case shifted to the red in comparison with the isolated molecule. That is, the formation of the complex weakens the Y-A bond.

Table 3 Local topological properties of the electronic charge density distribution calculated at the position of the NY...BCPs

Complexes	$\rho(\mathbf{r}_b)$	$\nabla^2\rho(\mathbf{r}_b)$	$ \lambda_1/\lambda_3 $	$H(\mathbf{r}_b)$
CH ₂ =CHN...LiH	0.0234	0.1593	0.1689	0.0071
CH ₂ =CHN...LiF	0.0231	0.1566	0.1672	0.0071
CH ₂ =CHN...BeH ₂	0.0655	0.4433	0.2186	-0.0047
CH ₂ =CHN...BeF ₂	0.0519	0.3316	0.2056	-0.0021
CH ₂ =CHN...BH ₃	0.1411	0.6823	0.2227	-0.1047
CH ₂ =CHN...BF ₃	0.0190	0.0553	0.1168	0.0004
CH ₂ =CHN...ClH	0.0057	0.0228	0.1191	0.0012
CH ₂ =CHN...ClF	0.0252	0.1028	0.1369	0.0027
CH ₂ =CHN...HCl	0.0223	0.0717	0.2167	0.0013
CH ₂ =CHN...HF	0.0311	0.0944	0.2467	0.0009

$\rho(\mathbf{r}_b)$: electron density; $\nabla^2\rho(\mathbf{r}_b)$: Laplacian of the electron density; $|\lambda_1/\lambda_3|$: ratio of the perpendicular contractions of $\rho(\mathbf{r}_b)$ to its parallel expansion at the N...Y BCP; $H(\mathbf{r}_b)$: electronic energy density. The values of all properties are in atomic units

In the BeB, the Be–A stretching modes appear as symmetric [$\nu_s(\text{BeA})$] and asymmetric [$\nu_a(\text{BeA})$] combinations. In CH₂CHN...BeA₂ complexes, the asymmetric stretching appears significantly shifted to the red. These results agree with those reported by Yáñez et al. [13] for similar systems (B...BeCl₂, with B: Lewis base). In addition, the symmetric deformation mode of the BeA₂ subunits [$\delta_s(\text{BeA}_2)$] is significantly blue-shifted in both complexes. This is so because in the complexes the BeA₂ subunits are bent, and therefore the symmetric deformations [$\delta_s(\text{BeA}_2)$] are unavoidably coupled with the stretching of the N...Be interactions. In other words, the symmetric deformations lead to a compression of the N...Be interaction and vice versa.

In the BB, both subunits BA₃ (with A = -H, -F) have two B–A stretching modes, the B–A symmetric stretch [$\nu_s(\text{BA})$] and the B–A asymmetric stretch [$\nu_a(\text{BA})$]. In addition, the symmetric deformation or “umbrella” mode [$\delta_s(\text{BA}_3)$] is also observed. From the data in Table 2, it can be seen that $\nu_a(\text{BA})$ and $\delta_s(\text{BA}_3)$ vibrational modes are found shifted toward the red. These results reveal that the N...B interaction weakens the B–A bonds.

Understanding of the nature of these intermolecular interactions requires a deep analysis. For this purpose, we describe in the following sub-section a topological analysis of the electron charge density and its Laplacian function within the framework of the quantum theory of atoms in molecules, QTAIM.

QTAIM analysis

The topological analysis of the electron density, $\rho(\mathbf{r})$, and its Laplacian function, $\nabla^2\rho(\mathbf{r})$, was performed to understand the origin of the interactions studied here, and the results are summarized in Table 3 and Fig. 2. According to the AIM

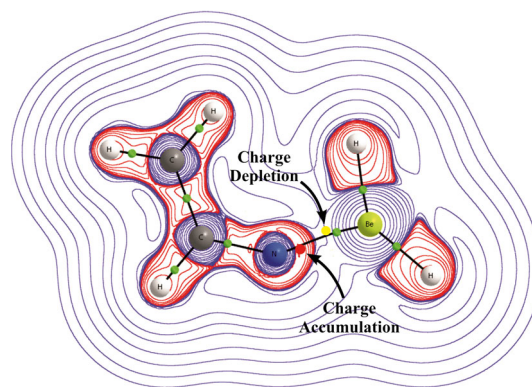


Fig. 2 Contour map of $L(\mathbf{r}) = -1/4\nabla^2\rho(\mathbf{r})$ function for ${}^3\text{CH}_2\text{CHN}\cdots\text{BeH}_2$ complex. Blue lines denote $L(\mathbf{r}) < 0$ and red lines $L(\mathbf{r}) > 0$. In addition, the CP (3, -3) of the nitrogen atom (red dot) and the CP (3, +1) (yellow dot) of the $L(\mathbf{r})$ function are shown. The black lines indicate the bond paths and the green dots indicate the BCP of the $\rho(\mathbf{r})$ topology. Note the anisotropic distribution of the charge concentration in the VSCC of the N atom (Color figure online)

theory, the presence of a bond path, BP, is a universal indicator of the existence of a chemical bond [40]. In all complexes, a BP is formed between the N and Y (with Y = Li, Be, B, Cl, H) atoms (molecular graphs shown in Fig. S1 of Supplementary Material). In addition, in the CH₂CHN...BeF₂ complex, it can also be observed a line of maximum electronic charge density between F and H atoms. That is, a hydrogen bond C–H...F is formed. However, properties at the bond critical point (BCP) H...F and at the ring critical point (RCP) [$\rho(\mathbf{r}_b) = 0.0083$ au, $\epsilon_{\text{RCP}} = 0.37$] and the distance between the BCP and the RCP of only 0.41 Å, reflect structural instability; that is, the bond can be easily broken [41].

Properties at the BCP of a BP allow to classify the interaction between two atoms as a shared-shell (covalent) or a closed-shell (ionic or van der Waals interaction) interaction [42]. In all N...Y intermolecular interactions, the BCP (see data in Table 3) presents properties typical of closed-shell interactions: $\rho(\mathbf{r}_b)$ relatively low, $\nabla^2\rho(\mathbf{r}_b) > 0$ and $|\lambda_1/\lambda_3| < 1$.

The $L(\mathbf{r}) = -1/4\nabla^2\rho(\mathbf{r})$ function is more sensitive and provides complementary information from the molecular electronic system under observation. This function shows the regions of the space where $\rho(\mathbf{r})$ is locally concentrated [$L(\mathbf{r}) > 0$] or depleted [$L(\mathbf{r}) < 0$] [35, 36]. In previous works, we have used this function to characterize XBs [35, 36] and we have determined that triplet vinyl nitrene has lone pairs available to interact electrostatically with a Lewis acid to form a Lewis adduct [26]. Figure 2 shows the contour map of the $L(\mathbf{r})$ function and molecular graph for the ${}^3\text{CH}_2\text{CHN}\cdots\text{BeH}_2$ complex. In this figure, it can clearly be observed a lump–hole interaction. That is to say, the N...Be interaction is the result of the combination of a local charge concentration [lump – CP (3, -3) in $L(\mathbf{r})$] in the valence shell charge concentration (VSCC) of the nitrogen

atom with a local charge depletion [hole – CP (3,+1) in $L(\mathbf{r})$] in the VSCC of the beryllium atom. Popelier called this statement “the Laplacian complementary principle” [43]. In every complex, it can be observed a similar situation. Therefore, the topological analysis of the $L(\mathbf{r})$ function reveals that the formation of the studied complexes is electrostatic in nature. These interactions are established between the charge density provided by the lone pair of the nitrogen atom and the charge density depletion region of the Y atom. In addition, the localization of the thinning of the electron density in the VSCC of the Y atom determines the geometry of these complexes.

Conclusions

The present study has afforded the first theoretical evidence of the formation of complexes between triplet vinyl nitrene ($^3\text{CH}_2\text{CHN}$) and some Lewis acids YA (LiH, LiF, BeH_2 , BeF_2 , BH_3 , BF_3 , ClH, ClF, HCl, HF). Quantum chemical calculations predict that the molecular complexes $^3\text{CH}_2\text{CHN}\cdots\text{Y}-\text{A}$ are always more stable than the separated $^3\text{CH}_2\text{CHN}$ and Y–A species. Accordingly, some of these complexes may serve to detect and characterize experimentally the elusive triplet vinyl nitrene. In addition, in most cases (except in $^3\text{CH}_2\text{CHN}\cdots\text{BH}_3$ and $^3\text{CH}_2\text{CHN}\cdots\text{BF}_3$ complexes) a planar structure is observed between the $^3\text{CH}_2\text{CHN}$ subunit and the Lewis acids. Complex formation results in the decrease in the strength of the Y–A bond as observed by the elongation of the Y–A bond and the decrease of the frequency of the vibration (shift to red) associated with the stretching of the Y–A bond, compared with the isolated molecule. According to QTAIM, the formation of the studied complexes results from the atomic interaction between the N and Y atoms. Additionally, the $L(\mathbf{r})$ function reveals that the stability of the complexes is mainly of character electrostatic and is established between the lone pair of the nitrogen atom and the charge density depletion region of the Y atom. Moreover, the localization of the depletion charge density in the VSCC of Y atom determines the geometry of the complexes.

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