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## Dinitrogen complexes $N_2L_2$ ( $L = N_2, CO, CS, NO^+, CN^-$ )

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Quantum chemical calculations using *ab initio* methods and density functional theory have been carried out on the equilibrium structures and the vibrational spectra of the (valence) isoelectronic compounds  $N_2L_2$  ( $L = N_2, CO, CS, NO^+, CN^-$ ). The molecules have a *trans*-periplanar arrangement of the  $L_2$  ligands at the  $N_2$  unit. The complexes with  $L = N_2, CO, NO^+, CN^-$  are predicted as thermodynamically unstable for dissociation into  $N_2 + 2L$  with  $\Delta G^{298}$  value lying in between  $-257 \text{ kcal mol}^{-1}$  ( $L = NO^+$ ) and  $-73 \text{ kcal mol}^{-1}$  ( $L = CO$ ), but the adduct  $N_2(CS)_2$  is calculated as slightly stable with  $\Delta G^{298} = 4 \text{ kcal mol}^{-1}$ . The homolytic dissociation reaction into two fragments  $N_2L_2 \rightarrow 2 NL$  is energetically less favorable than the heterolytic fragmentation  $N_2L_2 \rightarrow N_2 + 2 L$ , which proceeds synchronously but asymmetrically. The activation barriers for the fragmentation reaction  $N_2L_2 \rightarrow N_2 + 2L$  have values between  $\Delta G^\ddagger(298 \text{ K}) = 17 \text{ kcal mol}^{-1}$  for  $L = N_2$  and  $\Delta G^\ddagger(298 \text{ K}) = 84 \text{ kcal mol}^{-1}$  for  $L = CS$ . The calculated vibrational frequencies suggest that the molecules  $N_2L_2$  can be identified by the IR active antisymmetric stretching mode  $\nu_{as}$  of the ligands  $L$ , which is blue shifted for  $L = CO$  ( $\Delta = 55 \text{ cm}^{-1}$ ) and  $L = NO^+$  ( $\Delta = 118 \text{ cm}^{-1}$ ) but it is red shifted for  $L = CS$  ( $\Delta = -242 \text{ cm}^{-1}$ ) and  $L = CN^-$  ( $\Delta = -133 \text{ cm}^{-1}$ ) relative to the  $\nu_{as}$  mode of  $L = N_2$ . The analysis of the bonding situation reveals that there is a total charge donation  $L \rightarrow ({}^1\Gamma-N_2) \leftarrow L$  in all complexes, ranging between 1.38 e ( $L = CN^-$ ) and 0.56 e ( $L = N_2$ ), except in the dication with  $L = NO^+$ , where a small backdonation in reverse direction  $L \leftarrow ({}^1\Gamma-N_2) \rightarrow L$  with 0.10 e is calculated. EDA-NOCV calculations of  $N_6$  show that the best description of the bonding situation is given in terms of dative interactions  $N_2 \rightarrow ({}^1\Gamma-N_2) \leftarrow N_2$  between central  $N_2$  in the excited ( $1^1\Gamma_g$ ) singlet state and the terminal  $N_2$  fragments in the  ${}^1\Sigma_g^+$  electronic ground state. In contrast, the best description of the complexes with  $L = CO, CS, NO^+$  is calculated for the interactions between the central  $N_2$  in the  ${}^5\Sigma_u^+$  quintet state and the terminal ligands in the symmetry-adapted ( $L_2$ ) quintet state. For  $N_2L_2$  with  $L = CN^-$ , it is found that the bonding is best described for the interaction between  $N_2^-$  in the electronic quartet ( ${}^4\Sigma_u^+$ ) state and the terminal ( $L_2^-$ ) ligand as symmetry-adapted quartet. In contrast to the common bonding model for  $N_6$  using Lewis structures  $N \equiv N^+ = N - N = N^+ \equiv N^-$ , the donor-acceptor model  $N_2 \rightarrow (N_2) \leftarrow N_2$  explains that the lowest activation barrier is found for the concerted cleavage of the two formal double bonds, leading to the experimentally observed dissociation into 3  $N_2$ .

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## Introduction

In 1964, Appel and Schöllhorn reported that triphenylphosphinazine, which was sketched with the formula  $Ph_3P=N-N=PPh_3$ , is a thermally stable diamagnetic species that has a melting point of  $184^\circ$ .<sup>1</sup> However, neither precise structural information about the compound was given in the

work, nor in their further study.<sup>2</sup> Later, quantum chemical calculations showed that  $N_2(PPh_3)_2$  is thermodynamically unstable for the release of  $N_2$  by  $\sim 90 \text{ kcal mol}^{-1}$ ,<sup>3</sup> which raised doubts about the structure of the isolated compound. A subsequent X-ray structure analysis confirmed that the species is indeed triphenylphosphinazine, which has an antiperiplanar arrangement of the phosphine groups in  $Ph_3P-(N_2)-PPh_3$  with bending angles P–N–N of  $107^\circ$ , and a long N–N bond of  $1.497 \text{ \AA}$ .<sup>4</sup> The theoretical analysis of the bonding situation suggested that the  $N_2$  moiety binds through its highly excited ( $1^1\Gamma_g$ ) state, where the out-of-plane  $\pi$  and  $\pi^*$  orbitals are doubly occupied and the in-plane  $\pi$  MO is vacant, which leads to strong dative interactions  $Ph_3P \rightarrow (N_2) \leftarrow PPh_3$  with  $N_2$  as a double Lewis acid. The same type of dative interactions was suggested for the related compound with NHC (N-Heterocyclic Carbene) ligand,  $NHC \rightarrow (N_2) \leftarrow NHC$ , which was reported to have an

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antiperiplanar arrangement of the NHC groups and a long N–N bond of 1.415 Å.<sup>5</sup>

Very recently, Qian, Mardyukov and Schreiner (QMS) reported the synthesis, *via* gas-phase reaction, of the new nitrogen allotrope N<sub>6</sub>, which was trapped in low-temperature argon matrices at 10 K and as a film at liquid nitrogen temperature of 77 K.<sup>6</sup> The molecule was identified by IR and UV-vis spectroscopy, and by *ab initio* calculations, which predict a structure where two N<sub>3</sub> fragments are bonded in a *trans*-arrangement through a long (1.460 Å) N–N bond. The viewpoint of N<sub>6</sub> as the dimer of N<sub>3</sub> is reasonable, because hexanitrogen was synthesized by treating AgN<sub>3</sub> with Cl<sub>2</sub>, which yields ClN<sub>3</sub> that reacts with AgN<sub>3</sub> and leads to the formation of the new nitrogen allotrope N<sub>6</sub>. Hexanitrogen was heralded as a molecule of the year 2025 with a long N–N bond connecting two N<sub>3</sub> fragments.<sup>7</sup> But the structural similarity to the N<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and N<sub>2</sub>(NHC)<sub>2</sub> species led us suspect that the N<sub>6</sub> species is another example of the compound class N<sub>2</sub>L<sub>2</sub> where the ligands L are bonded through dative interactions L→(<sup>1</sup>Γ-N<sub>2</sub>)←L. Dinitrogen N<sub>2</sub> is generally known as weakly bonded ligand, but the highly excited (1)<sup>1</sup>Γ<sub>g</sub> state of the central N<sub>2</sub> is a strong σ acceptor and strong π donor, which is capable to bind two N<sub>2</sub> ligands. The (1)<sup>1</sup>Γ<sub>g</sub> state of N<sub>2</sub> is 294.3 kcal mol<sup>-1</sup> above the X<sup>1</sup>Σ<sub>g</sub><sup>+</sup> ground state,<sup>8</sup> which, however, does not occur in N<sub>2</sub>L<sub>2</sub> as a free species, but as a reference state that is strongly stabilised by orbital interactions.

Another acceptor, which binds even eight N<sub>2</sub> ligands in the octa-coordinated complexes M(N<sub>2</sub>)<sub>8</sub> (M = Ca, Sr, Ba), is the alkaline-earth atom M in an excited triplet state with (n–1)d<sup>2</sup> electron configuration *via* strong M→(N<sub>2</sub>)<sub>8</sub> π backdonation.<sup>9</sup>

The new findings prompted us to investigate the electronic structure of N<sub>6</sub> in terms of dative bonding N<sub>2</sub>→(<sup>1</sup>Γ-N<sub>2</sub>)←N<sub>2</sub> and to compare the homolytic and heterolytic bond dissociation with quantum chemical methods. We also calculated the (valence) isoelectronic compounds N<sub>2</sub>L<sub>2</sub> (L = N<sub>2</sub>, CO, CS, NO<sup>+</sup>, CN<sup>-</sup>). Here, we report about the equilibrium geometries, bond dissociation energies (BDEs), and the vibrational spectra of the molecules. We also present a thorough analysis of the nature of the chemical bonds using a variety of methods. The results may be useful as a guideline for future experimental studies.

## Methods

The geometrical optimizations, followed by the frequency calculations of N<sub>2</sub>L<sub>2</sub> (L = N<sub>2</sub>, CO, CS, NO<sup>+</sup>, CN<sup>-</sup>) compounds, were first carried out at the M06-2X/cc-pVTZ level<sup>10</sup> in their respective singlet and triplet spin states. Taking the most stable spin state (singlet), further reoptimizations and frequency calculations were performed at the CCSD(T)-Full/cc-pVTZ level.<sup>11</sup> These calculations were done using the Gaussian 16 program.<sup>12</sup> Natural atomic charges and Mayer bond order<sup>13</sup> were calculated using NBO7 (ref. 14) and Multiwfn programs,<sup>15</sup> respectively.

Energy decomposition analysis (EDA)<sup>16</sup> in conjunction with the natural orbital for chemical valence theory (NOCV)<sup>17</sup> was carried out at the M06-2X/TZ2P-ZORA<sup>18</sup>//CCSD(T)/cc-pVTZ level using the ADF 2020 package.<sup>19</sup> The ZORA method considers

relativistic effects, which are unimportant for this work, but further work by us on heavier analogues requires a uniform level of theory. In the EDA-NOCV<sup>20</sup> analysis, the intrinsic interaction energy ( $\Delta E_{\text{int}}$ ) between two fragments is dissected into three distinct energy components, as follows:

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}} \quad (1)$$

The electrostatic  $\Delta E_{\text{elstat}}$  term represents the quasiclassical electrostatic interaction between the unperturbed charge distributions of the prepared fragments. The Pauli repulsion,  $\Delta E_{\text{Pauli}}$  accounts for the energy change during the transformation from the superposition of unperturbed electron densities of the individual fragments to a wavefunction that explicitly adheres to the Pauli principle, achieved through the necessary antisymmetrization and wavefunction renormalization. The orbital term  $\Delta E_{\text{orb}}$  comes from the mixing of orbitals, charge transfer, and polarization between the isolated fragments.

The EDA-NOCV enables the partition of the total  $\Delta E_{\text{orb}}$  into pairwise contributions of the orbital interactions that are very important to get a complete picture of the bonding. The charge deformation  $\Delta\rho_k(r)$ , resulting from the mixing of the orbital pairs  $\psi_k(r)$  and  $\psi_{-k}(r)$  of the interacting fragments presents the amount and the shape of the charge flow due to the orbital interactions (eqn (2)), and the associated energy term  $\Delta E_{\text{orb}}$  provides with the size of stabilizing orbital energy originated from such interaction (eqn (3)).

$$\Delta\rho_{\text{orb}}(r) = \sum_k \Delta\rho_k(r) = \sum_{k=1}^{N/2} \nu_k [-\psi_{-k}^2(r) + \psi_k^2(r)] \quad (2)$$

$$\Delta E_{\text{orb}} = \sum_k \Delta E_{\text{orb}}^k = \sum_k \nu_k [-F_{-k,-k}^{\text{TS}} + F_{k,k}^{\text{TS}}] \quad (3)$$

Several papers extensively discussed details of the EDA-NOCV method and its application, offering different perspectives and viewpoints.<sup>21</sup>

## Results and discussion

Fig. 1 shows the calculated geometries, atomic partial charges ( $q$ ), and bond orders ( $P$ ) of the compounds N<sub>2</sub>L<sub>2</sub> (L = N<sub>2</sub>, CO, CS, NO<sup>+</sup>, CN<sup>-</sup>) at the CCSD(T)/cc-pVTZ level. All molecules exhibit a *trans*-periplanar arrangement of the L<sub>2</sub> ligands at the N<sub>2</sub> unit with a C<sub>2h</sub> point group and <sup>1</sup>A<sub>g</sub> electronic state. The singlet-triplet gap computed at the M06-2X/cc-pVTZ level is very high (39.7–65.7 kcal mol; see Table S1 in SI). The central N–N bond lengths in N<sub>2</sub>(N<sub>2</sub>)<sub>2</sub> (1.450 Å) and [N<sub>2</sub>(CN)<sub>2</sub>]<sup>2-</sup> (1.488 Å) compare favorably with the bond length in H<sub>2</sub>N–NH<sub>2</sub> (1.445 Å),<sup>6</sup> whereas the N–N bonds in N<sub>2</sub>(CO)<sub>2</sub> (1.386 Å), N<sub>2</sub>(CS)<sub>2</sub> (1.355 Å) and [N<sub>2</sub>(NO)<sub>2</sub>]<sup>2+</sup> (1.382 Å) are significantly shorter. The small differences between our values for N<sub>6</sub> and the data reported by QMS are due to the fact that the CCSD(T)/cc-pVTZ calculations were carried out by us with the full core option, whereas the previous study used the frozen core approximation. Geometry optimisations of a *syn* isomer did not result in another



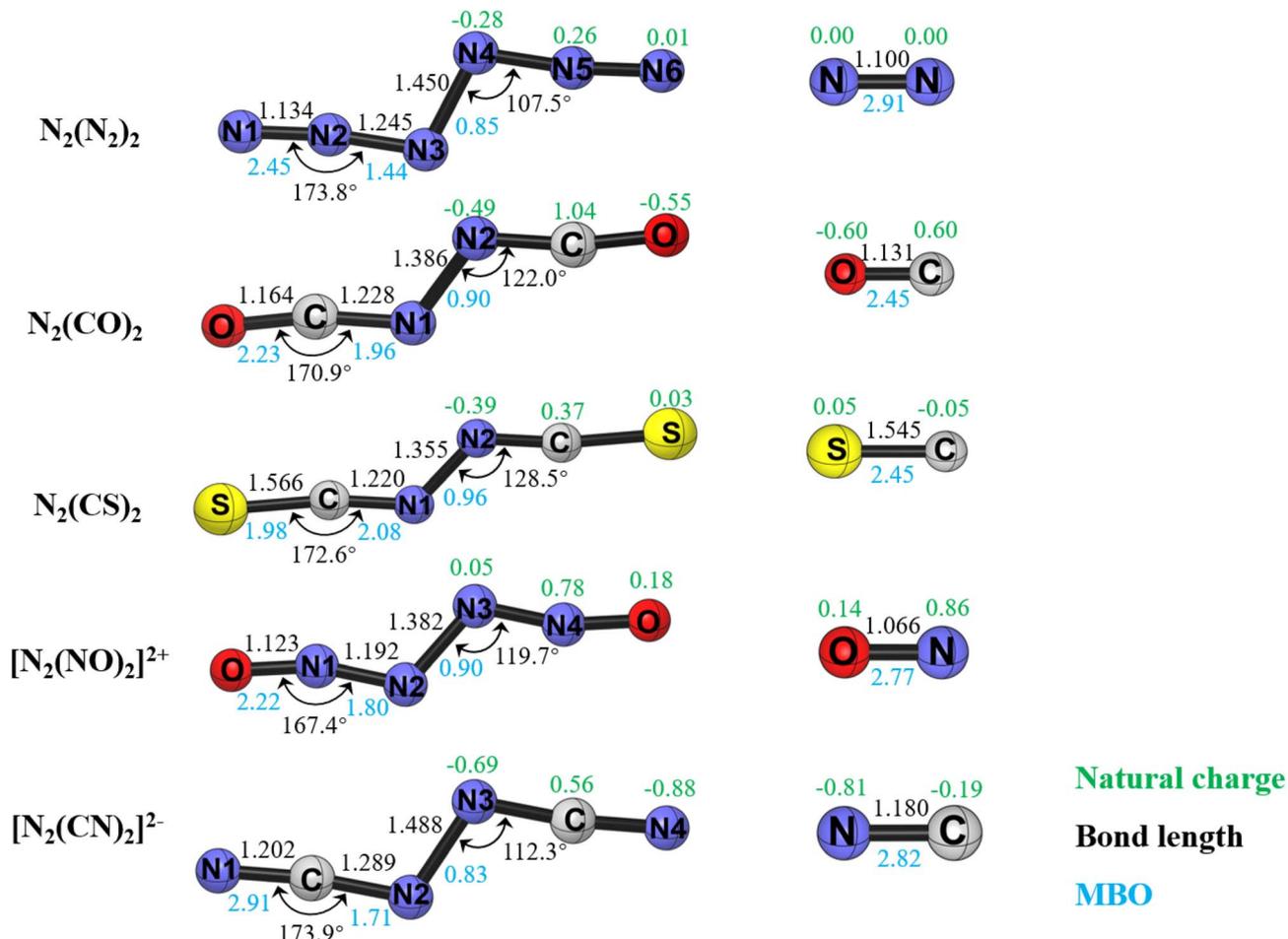


Fig. 1 Minimum energy geometries, partial charges ( $q$ ) and bond orders ( $P$ ) of the  $N_2L_2$  (L =  $N_2$ , CO, CS,  $CN^-$ ,  $NO^+$ ) compounds and the ligands L at the CCSD(T)/cc-pVTZ level. The bond lengths are given in Å, bond angles in degree. All molecules have a  $C_{2h}$  point group and  $^1A_g$  electronic state.

conformational isomer, but rather in the *trans* form as the only acyclic energy minimum structure. An extensive search of the potential energy surface using various starting geometries gave planar four-membered cyclic structures  $N_2(CX)_2$  (X = O, S) as energy minima, which are  $> 25$  kcal mol $^{-1}$  less stable than the acyclic  $N_2L_2$  forms. We also located nonplanar four-membered cyclic isomers for all species except for  $N_6$  where the central N–N bond is broken, which are  $> 40$  kcal mol $^{-1}$  higher in energy than the acyclic  $N_2L_2$  forms. They are shown in Fig. S1 of the SI. Since the present work focuses on the dinitrogen complexes  $N_2L_2$ , we do not discuss the cyclic isomers in this work.

Table 1 gives the calculated BDEs for the fragmentation  $N_2L_2 \rightarrow N_2 + 2L$  at the CCSD(T)/cc-pVTZ level, which show a remarkably high variation. The purely electronic values suggest that  $[N_2(NO)_2]^{2+}$  is even less stable ( $D_e = -233.3$  kcal mol $^{-1}$ ) than  $N_2(N_2)$  ( $D_e = -179.1$  kcal mol $^{-1}$ ). The exoenergetic values are much lower for  $[N_2(CN)_2]^{2-}$  ( $D_e = -116.7$  kcal mol $^{-1}$ ) and  $N_2(CO)_2$  ( $D_e = -49.5$  kcal mol $^{-1}$ ), and  $N_2(CS)_2$  is even predicted to be energetically stable ( $D_e = 27.7$  kcal mol $^{-1}$ ). The corrections by vibrational frequencies and entropic and thermal contributions lead to  $\Delta G^{298}$  values where the  $N_2L_2$  compounds are seen as thermodynamically unstable

in the order  $L = NO^+ > N_2 > CN^- > CO$ , but the molecule  $N_2(CS)_2$  is calculated as thermodynamically stable at room temperature with  $\Delta G^{298} = 3.6$  kcal mol $^{-1}$ .

Table 1 Computed bond dissociation energies  $D_e$ , zero-point energies corrected bond dissociation energies  $D_0$ , enthalpy change  $\Delta H$  and free energy change  $\Delta G$  of the processes (a)  $N_2L_2 \rightarrow N_2 + 2L$  and (b)  $N_2L_2 \rightarrow 2NL$  at the CCSD(T)/cc-pVTZ level. All values are given in kcal mol $^{-1}$

Complex	$D_e$	$D_0$	$\Delta H$	$\Delta G$
<b>(a) <math>N_2L_2 \rightarrow N_2 + 2L</math></b>				
$N_2(N_2)_2$	-179.1	-184.1	-182.0	-200.7
$N_2(CO)_2$	-49.5	-55.8	-53.7	-73.4
$N_2(CS)_2$	27.7	21.8	23.6	3.6
$[N_2(CN)_2]^{2-}$	-116.7	-122.2	-120.1	-139.7
$[N_2(NO)_2]^{2+}$	-233.3	-238.7	-236.5	-256.8
<b>(b) <math>N_2L_2 \rightarrow 2NL</math></b>				
$N_2(N_2)_2$	34.4	29.6	30.5	22.2
$N_2(CO)_2$	62.1	58.5	59.1	48.9
$N_2(CS)_2$	27.8	24.1	25.0	13.4
$[N_2(CN)_2]^{2-}$	-51.8	-56.8	-55.8	-60.8
$[N_2(NO)_2]^{2+}$	-70.2	-74.5	-73.7	-84.6



Table 1 also gives the BDEs for breaking the central N–N bond in the fragmentation  $N_2L_2 \rightarrow 2 NL$  at the CCSD(T)/cc-pVTZ level. It becomes obvious that the homolytic bond rupture of the N–N bond is thermodynamically strongly disfavoured compared with the heterolytic cleavage of the L–N<sub>2</sub>–L bonds, except for L = CS. The energies of the two fragmentation reactions of the latter species are very similar, but the free energy of the heterolytic process ( $\Delta G = 3.6 \text{ kcal mol}^{-1}$ ) makes it clearly more favourable than the homolytic fragmentation ( $\Delta G = 13.4 \text{ kcal mol}^{-1}$ ). The calculated BDEs at the M06-2X/cc-pVTZ level are very similar (Table S2 of SI) to the CCSD(T)/cc-pVTZ values, which indicates that the DFT values are quite reliable.

Fig. 2 shows the reaction profile for the heterolytic dissociation reaction  $N_2L_2 \rightarrow N_2 + 2 L$  along with the calculated activation free energy barriers  $\Delta G^\ddagger(298 \text{ K})$ , which vary between  $16.9 \text{ kcal mol}^{-1}$  (L = N<sub>2</sub>) and  $84.2 \text{ kcal mol}^{-1}$  (L = CS). The trend of the  $\Delta G^\ddagger$  follows, in general, the reaction energies, except for the very exergonic reactions where L = N<sub>2</sub>, NO<sup>+</sup>. The calculated barrier for the fragmentation of N<sub>2</sub> is in good agreement with the value reported by QMS ( $14.8 \text{ kcal mol}^{-1}$ ).<sup>6</sup> The computed value of the  $T_1$  diagnostics suggests that the multi-reference character of the CCSD(T) calculations of the N<sub>2</sub>L<sub>2</sub> complexes and the transition states is very low (Table S3, SI), which indicates that the single-reference approach is sufficient. The

activation barrier for the homolytic reaction  $N_6 \rightarrow 2 N_3$  was reported by QMS to be significantly higher ( $\Delta G^\ddagger(298 \text{ K}) = 26.1 \text{ kcal mol}^{-1}$ ) than the heterolytic process.<sup>6</sup> We carried out energy calculations with stretched N–N distances of the other L<sub>2</sub>L<sub>2</sub> species, which suggest that the barriers are also higher than for the heterolytic fragmentation. Since the NL fragments are also less stable than  $N_2 + 2 L$  (Table 1), it is unlikely that the homolytic reaction course plays a role in the fragmentation reaction of the N<sub>2</sub>L<sub>2</sub> species.

The higher barrier for breaking the bond in the central N<sub>2</sub> moiety of N<sub>6</sub> compared to breaking the (N<sub>2</sub>)–(N<sub>2</sub>)<sub>2</sub> bonds is surprising, given the calculated bond orders, which are much higher and have shorter distances in the latter bonds than the former one. It turns out that the energy required to break a bond depends not only on the strength of the bond, but also on the reorganisation of the electronic structure of the fragments during the cleavage reaction. The N<sub>3</sub>–N<sub>3</sub> bond in N<sub>6</sub> is weaker than the (N<sub>2</sub>)–(N<sub>2</sub>)<sub>2</sub> bonds, but the electronic charge migration during rupture of the latter heterolytic process is energetically more favourable than the homolytic reaction. The lower barrier for breaking the (N<sub>2</sub>)–(N<sub>2</sub>)<sub>2</sub> bonds than the N<sub>3</sub>–N<sub>3</sub> bond supports the use of our bonding model for N<sub>6</sub> in terms of dative interactions  $N_2 \rightarrow (N_2) \leftarrow N_2$  rather than the more conventional model using Lewis structures  $N^- = N^+ = N = N^+ = N^-$ , since it

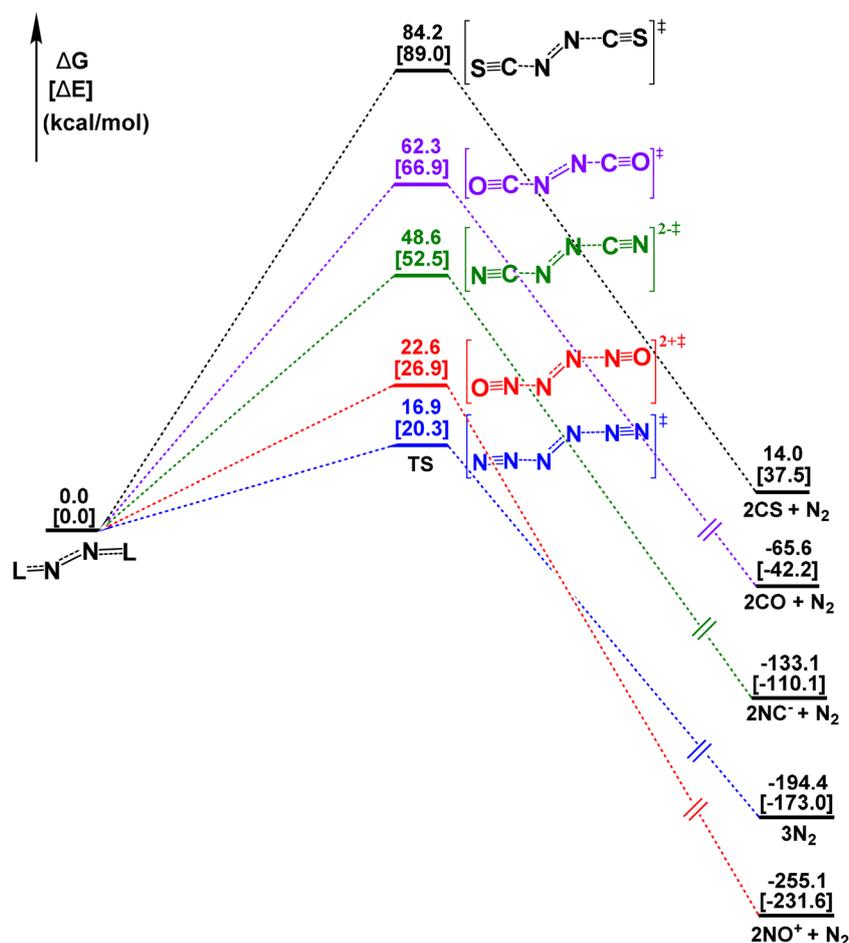


Fig. 2 Energy profile for the reaction  $N_2L_2 \rightarrow N_2 + 2L$  at the CCSD(T)/cc-pVTZ//M06-2X/cc-pVTZ level.



accounts for the experimental finding that  $N_6$  directly dissociated into 3  $N_2$ . The same applies for  $N_2(CO)_2$ , which photolytically dissociates into  $N_2 + 2 CO$  whereas cleavage into NCO radical was observed only to a small extent.<sup>22a</sup>

Examination of the transition state structures for the dissociation reaction reveals surprising features (Fig. 3). The geometries of  $[N_2L_2]^\ddagger$  possess a non-planar staggered geometry with a *syn* conformation of the ligands except for  $[N_2(CS)_2]^\ddagger$ , which exhibits a nearly linear NNCS moiety with one CS ligand, where the bond to the second CS ligand is significantly stretched. This implies that the fragmentation reaction may possibly be a two-step process in which an intermediate product, NN-L is formed along the dissociation reaction. We calculated the intrinsic reaction coordinate starting from the transition states and found that it smoothly connects to the reaction products  $N_2 + 2L$ . The fragmentation reaction is thus predicted as a concerted but highly asynchronous process where the two  $N_2-L$  bonds break one after the other. Note that the central N-N bond of the transition state  $[N_2L_2]^\ddagger$  is clearly shorter than in the equilibrium structures.

Hexanitrogen was clearly identified by spectroscopic signals, and the authors presented a careful analysis of the vibrational spectrum of the molecule.<sup>6</sup> The IR spectrum of  $N_6$  exhibits an intense vibrational band at  $2076.6\text{ cm}^{-1}$ , which comes from an asymmetric stretching mode of the terminal  $N_2$  ligands. Fig. 4 shows the calculated IR spectra of the five molecules  $N_2L_2$ . They show a similar pattern where the asymmetric stretching mode  $\nu_{as}$  of the terminal  $L_2$  ligands, which has the second largest wavenumber of all 12 fundamentals, exhibits the strongest signal. The symmetric stretching mode  $\nu_s$  with a slightly higher wavenumber is IR inactive. The calculated wavenumber of  $2263.7\text{ cm}^{-1}$  for the asymmetric mode of  $N_6$  is blue shifted for  $L = CO$  ( $\Delta = 55\text{ cm}^{-1}$ ) and  $L = NO^+$  ( $\Delta = 118\text{ cm}^{-1}$ ), but it is red shifted for  $L = CS$  ( $\Delta = -242\text{ cm}^{-1}$ ) and  $L = CN^-$  ( $\Delta = -133\text{ cm}^{-1}$ ). The calculated frequency shift of the intense asymmetric stretching mode  $\nu_s$  is very helpful information for identifying the molecules.

In addition to  $N_6$  [ $N_2(N_2)_2$ ], the complexes  $N_2(CO)_2$  and  $N_2(CS)_2$  have been synthesised and identified spectroscopically and they were also the subject of theoretical works. The

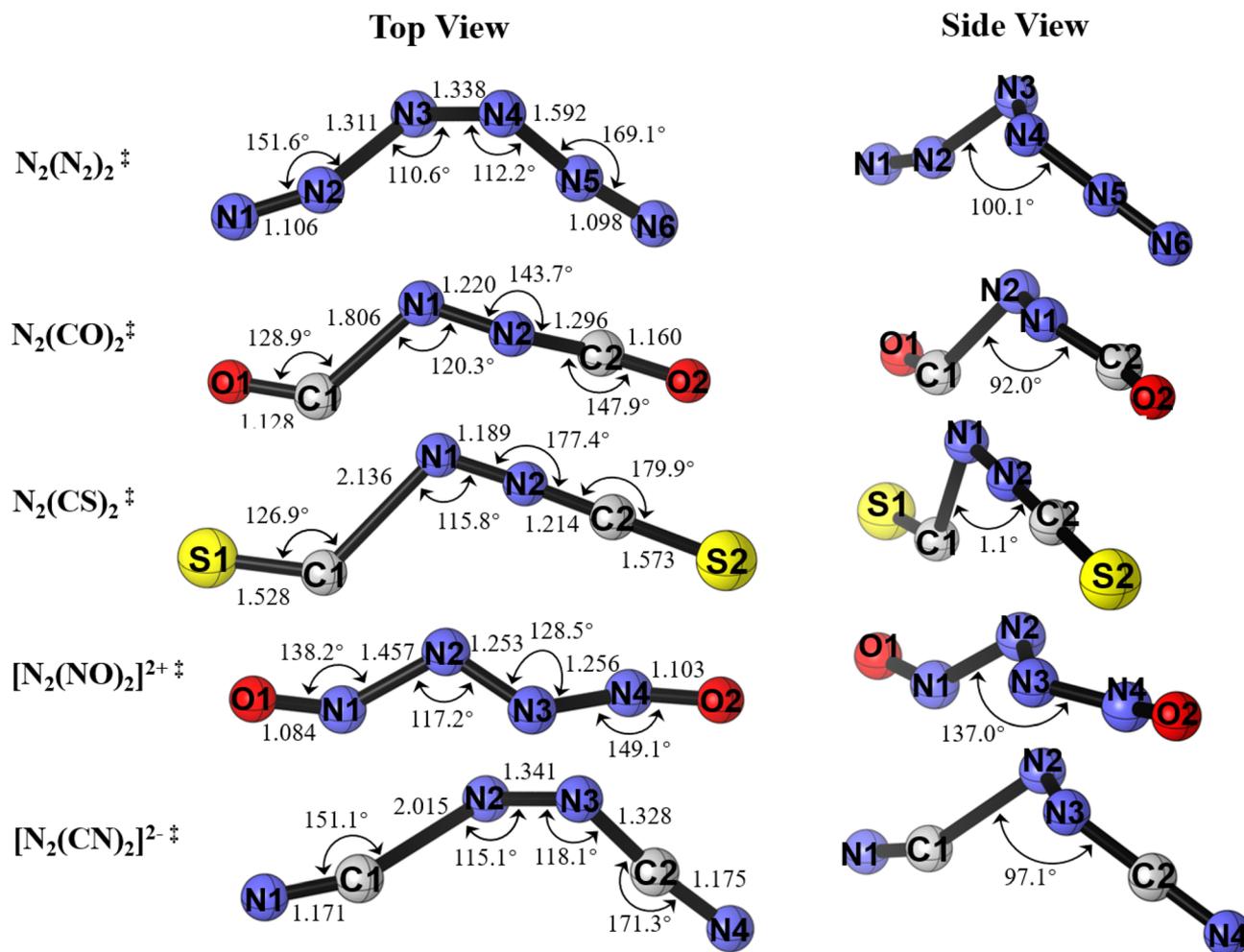


Fig. 3 Geometries of the transition states of  $N_2L_2$  ( $L = N_2, CO, CS, CN^-, NO^+$ ) compounds for the dissociation into  $2L$  and  $N_2$  at the M06-2X/cc-pVTZ level. The top view gives the bond lengths and bond angles, and the side view gives the dihedral angles  $L-N_2-L$ . The bond lengths are given in Å and the angles in degree.



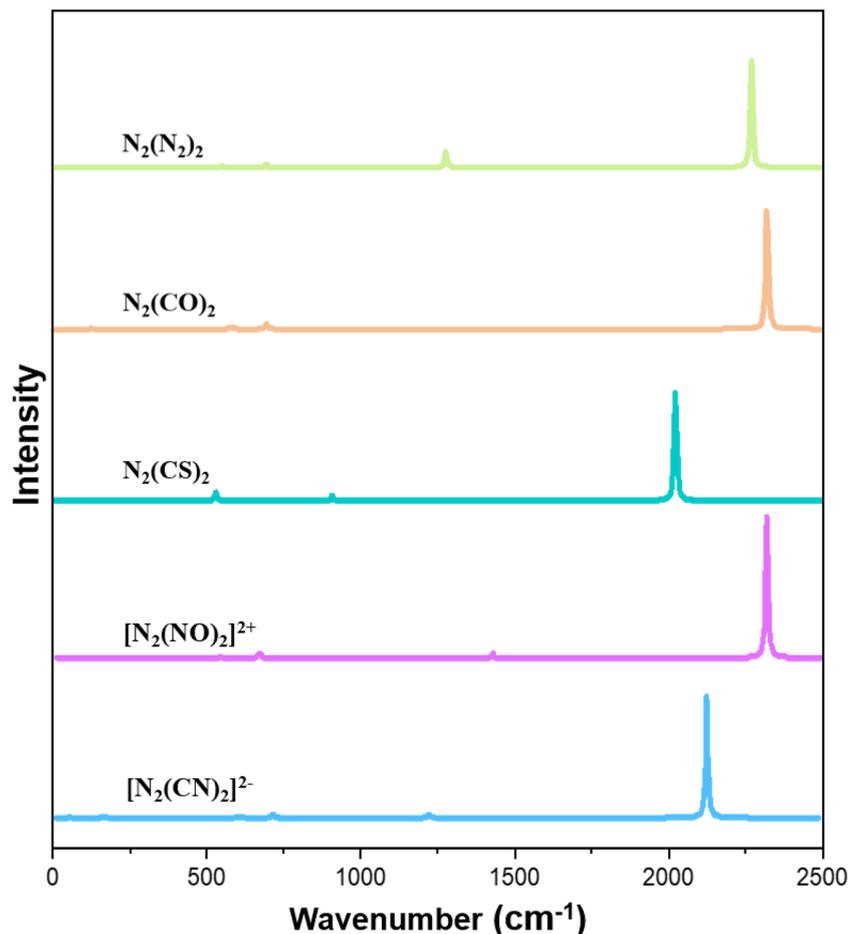


Fig. 4 Calculated IR spectra of  $N_2L_2$  complexes ( $L = N_2, CO, CS, CN^-, NO^+$ ) at the M06-2X/cc-pVTZ level.

dicarbonyl adduct was introduced as diisocyanate  $O=C=N-N=C=O$  following the conventional descriptions using Lewis structures.<sup>22</sup> Photolysis of the matrix-isolated  $N_2(CO)_2$  gives  $N_2 + 2 CO$  as products, which agrees with our calculated reaction profile (Fig. 2). The IR spectrum shows one very intensive band at  $2200.6\text{ cm}^{-1}$  for the asymmetric NCO stretching mode besides several signals with lower intensity.<sup>22a</sup> The comparison with the IR spectrum of  $N_6$  gives a red shift of  $124\text{ cm}^{-1}$ , which agrees with the direction but is higher than our computed value of  $54\text{ cm}^{-1}$ . The diisothiocyanate complex  $N_2(CS)_2$  was identified as product of the photolysis of the energetically lower lying isomer  $S_2(CN)_2$  with a characteristic vibrational mode of the IR spectrum at  $1910\text{ cm}^{-1}$ .<sup>23</sup> The experimental red-shift compared to the asymmetric stretching mode of  $N_6$  is also given by our calculations, but the observed value of  $-166\text{ cm}^{-1}$  is smaller than our computed value of  $-242\text{ cm}^{-1}$ . The computed wavenumber for  $[N_2(NO)_2]^{2+}$  ( $2382\text{ cm}^{-1}$ ) agrees quite well with the experimental value of  $NO^+$  ( $2340\text{ cm}^{-1}$ ) whereas the calculated value for  $[N_2(CN)_2]^{2-}$  ( $2131\text{ cm}^{-1}$ ) is red-shifted compared with an approximately interaction-free anion  $CN^-$  ( $2244\text{ cm}^{-1}$ ).<sup>24</sup> The complete set of the calculated vibrational spectra of the five molecules  $N_2L_2$  is given in Table S4 of the SI.

We analyzed the bonding situation in  $N_2L_2$  with a variety of methods. Fig. 1 shows that the Mayer bond order (MBO) of the

central N-N bond is between 0.83 ( $L = CN^-$ ) and 0.96 ( $L = CS$ ), which is a rather small variation considering the differences in the N-N bond length between  $1.488\text{ \AA}$  ( $L = CN^-$ ) and  $1.355\text{ \AA}$  ( $L = CS$ ). The atomic partial charges suggest that there is a total charge donation in the neutral complexes  $L \rightarrow (N_2) \leftarrow L$  with  $0.98 e$  ( $L = CO$ ),  $0.78 e$  ( $L = CS$ ), and  $0.56 e$  ( $L = N_2$ ). There is an even stronger charge donation of  $1.38 e$  in the dianion ( $L = CN^-$ ) and a small backdonation in reverse direction  $L \leftarrow (N_2) \rightarrow L$  with  $0.10 e$  in the dication ( $L = NO^+$ ).

We proposed in our earlier study that the diatomic  $N_2$  species in  $N_2(PPh_3)_2$  binds through its highly excited  $(1)^1\Gamma_g$  state where the out-of-plane  $\pi$  and  $\pi^*$  orbitals are doubly occupied.<sup>4</sup> Fig. 5 shows schematically the valence MOs of  $N_2$  in the  $(1)^1\Gamma_g$  state. The donation of the  $L_2$  ligands  $L \rightarrow (N_2) \leftarrow L$  may take place into the vacant  $1\pi_u'$  (bonding) and  $1\pi_g'$  (antibonding) orbitals of  $N_2$ . Note that the assignment of  $\pi$  symmetry refers to free  $N_2$ , which has two mirror planes that contain the atoms. The complexes  $L-N_2-L$  have only one mirror plane and the donation is correctly assigned as in-plane  $\sigma(+,-)$  and  $\sigma(+,+)$  orbital interaction.

There are two occupied out-of-plane  $\pi$  MOs,  $1\pi_u$  (bonding) and  $1\pi_g$  (antibonding), in the  $(1)^1\Gamma_g$  state of  $N_2$ . If this holds true also for the  $N_2L_2$  complexes in the present study, the number of occupied valence  $\pi$  MOs should be four ( $\pi$  and  $\pi^*$



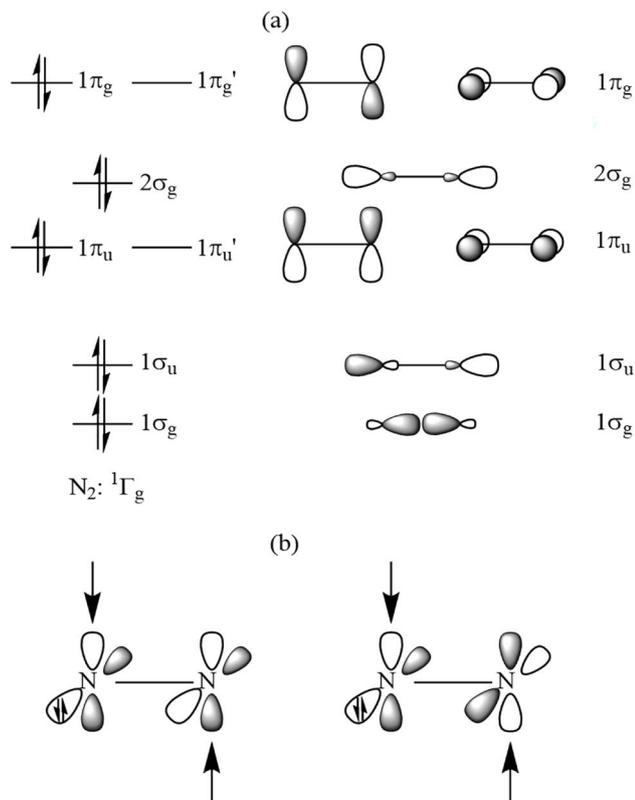


Fig. 5 (a) Schematic representation of the  $(1)^1\Gamma_g$  state of  $N_2$  and the associated orbitals. (b) Donation of the plus and minus combination of the lone-pair donor orbitals of L into the vacant in-plane  $\pi$  and  $\pi^*$  orbitals of  $N_2$ . The orbital numbering refers to the valence orbitals of  $N_2$ .

from  $N_2$  and one  $\pi$  from each ligand L) and not three. Examination of the shape of the Kohn–Sham MOs shows that this is indeed the case. Fig. 6 displays the four occupied valence  $\pi$  MOs of  $N_6$ . The number of nodes follows the common symmetry rules with zero (HOMO-8), one (HOMO-7), two (HOMO-2), and three (HOMO). The same number of occupied valence  $\pi$  is found for the other  $N_2L_2$  complexes. The complete set of occupied valence MOs of all  $N_2L_2$  complexes is presented in Fig. S2–S6. Fig. 6 shows also the HOMO of the  $N_2L_2$  complexes, which can be identified with the out-of-plane  $\pi^*$  orbital of  $N_2$  mixing with the antibonding  $\pi^*$  orbitals of the ligands L.

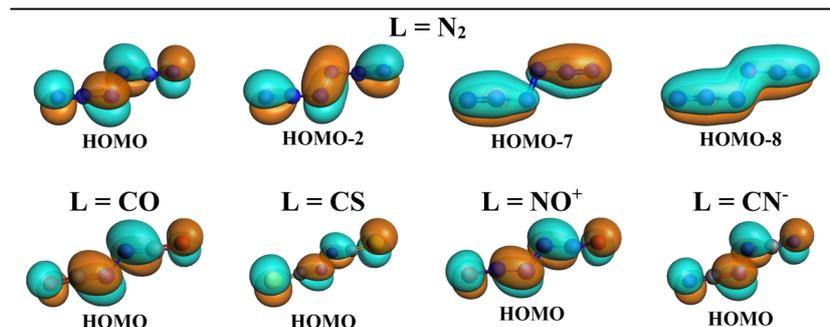


Fig. 6 Top row: plot of the four occupied valence  $\pi$  MOs of  $N_6$ . Bottom row: plot of the HOMO of  $N_2L_2$  with L = CO, CS,  $NO^+$ ,  $CN^-$ .

A more detailed insight into the nature of the  $N_2$ – $L_2$  bonds is provided by the EDA–NOCV analysis of the interactions between the fragments. In our previous study of  $N_2(PPh_3)_2$ , we considered only neutral  $N_2$  in the excited  $(1)^1\Gamma_g$  state and 2  $PPh_3$  ligands in the electronic ground state.<sup>4</sup> We analyzed  $N_2L_2$  using various electronic states and charges of the fragments  $N_2$  and 2L. Numerous studies have shown that the strength of the orbital term  $\Delta E_{orb}$ , which considers the change in the wave function during bond formation, is a reliable indicator of the optimal fragments for describing the bond between them.<sup>7,25</sup> The fragments with the lowest absolute values of  $\Delta E_{orb}$  are the best choice for explaining the bonding interactions. Table 2 shows the numerical results for L =  $N_2$ .

It becomes obvious that the chemical bonds in  $N_6$  between the central  $N_2$  moiety and the terminal  $N_2$  species are indeed best described in terms of dative interactions  $N_2 \rightarrow (N_2) \leftarrow N_2$  between central  $N_2$  in the excited  $(1)^1\Gamma_g$  singlet state and two terminal  $N_2$  fragments in the  $^1\Sigma_g^+$  electronic ground state. The interactions between central  $N_2$  in the  $^3\Sigma_u^+$  triplet state and the terminal ligands in the symmetry-adapted  $(N_2)_2$  triplet state, which exhibit a mixture of electron-sharing and dative bonds, give a bigger  $\Delta E_{orb}$  value. The same holds for the formation of electron-sharing double bonds between central  $N_2$  in the  $^5\Sigma_u^+$  quintet state and the terminal ligands in the symmetry-adapted  $(N_2)_2$  quintet state. EDA–NOCV calculations using central  $N_2^-$  as an anion in the electronic doublet ( $^2\Sigma_g^+$ ) or quartet ( $^4\Sigma_u^+$ ) state and the terminal  $(N_2)_2^+$  ligand as a cation in the symmetry-adapted doublet or quartet state also result in bigger  $\Delta E_{orb}$  values.

Further examination of the dative interactions between central  $N_2$  and the terminal  $N_2$  ligands reveals that they come mainly from  $N_2 \rightarrow (N_2) N_2$   $\sigma$  donation through out-of-phase ( $\Delta E_{orb(1)}$ ) and in-phase ( $\Delta E_{orb(2)}$ ) orbital pairs, which provide 75% of the total orbital (covalent) bonding. The  $\pi$  backdonation  $N_2 \leftarrow (N_2) \rightarrow N_2$  via out-of-phase ( $\Delta E_{orb(3)}$ ) and in-phase ( $\Delta E_{orb(4)}$ ) orbital interactions deliver only 17% of  $\Delta E_{orb}$ . The nature of the individual orbital interactions  $\Delta E_{orb(1)} - \Delta E_{orb(4)}$  becomes clear when considering the corresponding deformation densities and the associated orbitals, which are shown in Fig. 7. The dominant orbital interactions through (+,–) and (+,+)  $\sigma$  donation  $N_2 \rightarrow (N_2) \leftarrow N_2$  nicely explain the bond shortening of the central  $N_2$  moiety compared to free  $N_2$  in the  $^1\Gamma$  state, which has



**Table 2** EDA-NOCV results of the complex  $N_2L_2$  ( $L = N_2$ ) considering  $L_2$  as one fragment and central  $N_2$  as another fragment at the M06-2X/TZ2P-ZORA//CCSD(T)/cc-pVTZ level. Energy values are given in kcal mol<sup>-1</sup>

Energies	Orbital interaction	$N_2$ (singlet) + 2L (singlet)	$N_2$ (triplet) + 2L (triplet)	$N_2$ (quintet) + 2L (quintet)	$N_2^-$ (doublet) + 2L <sup>+</sup> (doublet)	$N_2^-$ (quartet) + 2L <sup>+</sup> (quartet)
$\Delta E_{\text{int}}$		-165.0	-368.7	-401.3	-387.3	-519.0
$\Delta E_{\text{Pauli}}$		1036.0	1022.8	1028.3	1042.8	1090.1
$\Delta E_{\text{elstat}}^a$		-364.9 (30.4%)	-388.8 (27.9%)	-438.1 (30.6%)	-538.1 (37.6%)	-615.1 (38.6%)
$\Delta E_{\text{orb}}^a$		-836.1 (69.6%)	-1002.7 (72.1%)	-991.5 (69.4%)	-894.5 (62.4%)	-980.0 (61.4%)
$\Delta E_{\text{orb}(1)}^b$	L-NN-L $\sigma$ -bond (+,-)	-328.7 (39.3%)	-317.3 (31.6%)	-328.7 (33.2%)	-329.8 (36.9%)	-350.4 (35.8%)
$\Delta E_{\text{orb}(2)}^b$	L-NN-L $\sigma$ -bond (+,+)	-296.4 (35.5%)	-296.9 (29.6%)	-314.1 (31.7%)	-261.4 (29.2%)	-337.7 (34.5%)
$\Delta E_{\text{orb}(3)}^b$	L-NN-L $\pi$ -bond (+,-)	-98.6 (11.8%)	-174.9 (17.4%)	-151.4 (15.3%)	-123.1 (13.8%)	-90.9 (9.3%)
$\Delta E_{\text{orb}(4)}^b$	L-NN-L $\pi$ -bond (+,+)	-44.7 (5.3%)	-86.5 (8.6%)	-94.8 (9.6%)	-54.0 (6.0%)	-56.2 (5.7%)
$\Delta E_{\text{orb}(\text{rest})}^b$		-67.7 (8.1%)	-127.1 (12.7%)	-102.2 (10.3%)	-126.2 (14.1%)	-144.8 (14.8%)

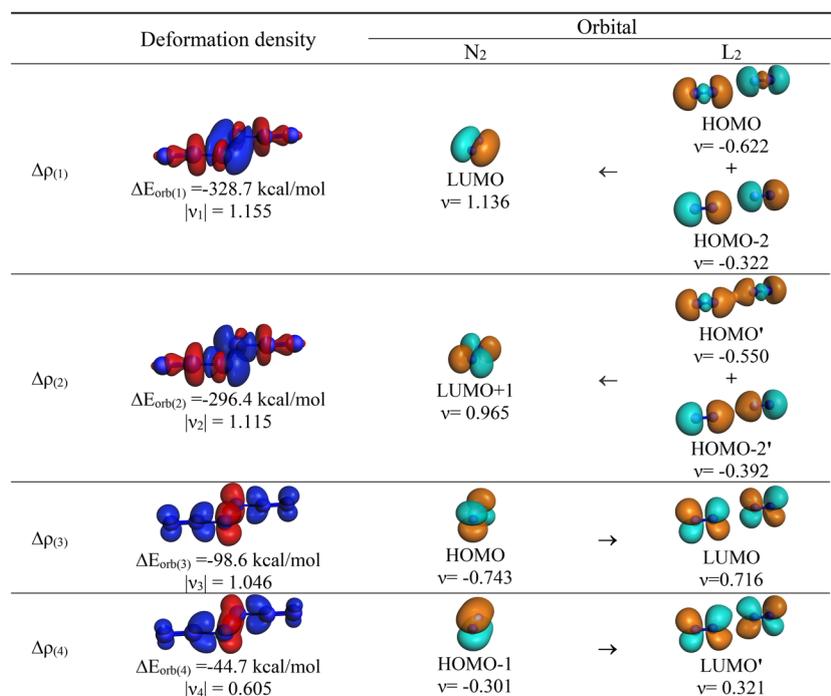
<sup>a</sup> The values in parentheses give the percentage contribution to the total attractive interactions  $\Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$ . <sup>b</sup> The values in parentheses give the percentage contribution to the total orbital interactions  $\Delta E_{\text{orb}}$ .

a calculated bond length of 1.608 Å and is 294.3 kcal mol<sup>-1</sup> above the  $X^1\Sigma_g^+$  ground state.<sup>8</sup> The donation takes place into the vacant in-plane and out-of-plane  $\pi$  orbitals of  $N_2$ , which are bonding orbitals (see Fig. 5). Note that the  $(1)^1\Gamma_g$  state of  $N_2$  is a reference state which is strongly stabilized by the orbital interaction. It is not formed as a free species during the reaction process.

The numerical EDA-NOCV results of the other  $N_2L_2$  compounds are given in Tables S5–S8 of SI. In contrast to the results for  $N_6$ , the lowest  $\Delta E_{\text{orb}}$  values with  $L = \text{CO}, \text{CS}, \text{NO}^+$  are calculated for the interactions between the central  $N_2$  in the  $^5\Sigma_u^+$  quintet state and the terminal ligands in the symmetry-adapted  $(L)_2$  quintet state, which indicate electron-sharing

double bonds between the fragments. The central N–N bond in the latter species is much shorter (between 1.355–1.386 Å) than in  $N_6$  (1.450 Å). The lowest  $\Delta E_{\text{orb}}$  value of  $N_2L_2$  with  $L = \text{CN}^-$  is found for the interactions between  $N_2^-$  in the electronic quartet ( $^4\Sigma_u^+$ ) state and the terminal  $(\text{CN})_2^-$  ligands as symmetry-adapted quartets. The individual orbital interactions are identified by the corresponding deformation densities and the associated orbitals, which are shown in Fig. S7–S14. The latter electron-sharing interactions also lead to four occupied  $\pi$  valence MOs in all five  $N_2L_2$  molecules.

In order to compare the  $N_2L_2$  compounds with each other, we have chosen the same fragments with the central  $N_2$  in the excited  $(1)^1\Gamma_g$  singlet state and two terminal  $N_2$  fragments in the



**Fig. 7** Plot of the deformation densities,  $\Delta\rho_{(1-4)}$  shown as the electronic charge corresponding to  $\Delta E_{\text{orb}(1-4)}$  and the related interacting orbitals of  $N_2L_2$  ( $L = N_2$ ) at the M06-2X/TZ2P-ZORA//CCSD(T)/cc-pVTZ level using  $NN$  ( $^1\Gamma_g$ ) +  $L_2$  (singlet) as interacting fragments. The eigenvalues  $\nu$  indicate the size of the charge flow. The direction of charge flow is red  $\rightarrow$  blue. The isovalue for  $\Delta\rho_{(1-4)}$  is 0.003 au.



**Table 3** EDA-NOCV results of complexes  $N_2-L_2$  ( $L = N_2, CO, CS, NO^+, CN^-$ ) considering  $L_2$  as one fragment and central  $N_2$  as another fragment in the singlet states ( $^1\Gamma_g$  state of  $N_2$  and symmetry adapted singlet state of  $L_2$ ) at the M06-2X/TZ2P-ZORA//CCSD(T)/cc-pVTZ level. Energy values are given in kcal mol $^{-1}$

Energies	Orbital interaction	L = N <sub>2</sub>	L = CO	L = CS	L = NO <sup>+</sup>	L = CN <sup>-</sup>
$\Delta E_{int}$		-165.0	-306.0	-387.0	-202.5	-301.4
$\Delta E_{Pauli}$		1036.0	1400.4	1542.2	1242.3	1155.6
$\Delta E_{elstat}^a$		-364.9 (30.4%)	-530.8 (31.1%)	-595.4 (30.9%)	-356.9 (24.7%)	-484.9 (33.3%)
$\Delta E_{orb}^a$		-836.1 (69.6%)	-1175.7 (68.9%)	-1333.8 (69.1%)	-1088.0 (75.3%)	-972.1 (66.7%)
$\Delta E_{orb(1)}^b$	L-NN-L in-plane( $\sigma$ )-bond (+,-)	-328.7 (39.3%)	-483.0 (41.1%)	-536.4 (40.2%)	-373.2 (34.3%)	-405.8 (41.7%)
$\Delta E_{orb(2)}^b$	L-NN-L in-plane( $\sigma$ )-bond (+,+)	-296.4 (35.5%)	-434.3 (37.4%)	-493.4 (37.0%)	-322.3 (29.6%)	-400.0 (41.1%)
$\Delta E_{orb(3)}^b$	L-NN-L out-of-plane( $\pi$ )-bond (+,-)	-98.6 (11.8%)	-76.1 (6.5%)	-134.6 (10.1%)	-182.1 (16.7%)	-70.4 (7.2%)
$\Delta E_{orb(4)}^b$	L-NN-L out-of-plane( $\pi$ )-bond (+,+)	-44.7 (5.3%)	-45.2 (3.8%)	-48.0 (3.6%)	-75.5 (6.9%)	-34.6 (3.6%)
$\Delta E_{orb(rest)}^b$		-67.7 (8.1%)	-137.1 (11.7%)	-121.4 (9.1%)	-134.9 (12.4%)	-61.3 (6.3%)

<sup>a</sup> The values in parentheses give the percentage contribution to the total attractive interactions  $\Delta E_{elstat} + \Delta E_{orb}$ . <sup>b</sup> The values in parentheses give the percentage contribution to the total orbital interactions  $\Delta E_{orb}$ .

$^1\Sigma_g^+$  electronic ground state as model for the bonding interactions. Table 3 gives the numerical results. The calculated interaction energies  $\Delta E_{int}$  show the same order  $CS > CO > CN^- > NO^+ > N_2$  as the calculated activation barriers  $\Delta E^\ddagger$  (Fig. 2), which indicates that the choice of the singlet fragments is a valid model for the trend of the chemical bonds. The orbital (covalent) interactions always make the largest percentage contribution to the chemical bonds, which is particularly high for  $L = NO^+$  (75%). The breakdown of  $\Delta E_{orb}$  into the pairwise orbital interactions reveals that the  $\sigma$  donations through out-of-phase ( $\Delta E_{orb(1)}$ ) and in-phase ( $\Delta E_{orb(2)}$ ) orbital pairs are always the largest components of the total orbital bonding. The percentage contribution of  $\Delta E_{orb(1)}$  and  $\Delta E_{orb(2)}$  is higher for  $L = CN^-$  and lower for  $L = NO^+$ , which is due to the charges of the ligands. A surprising result concerns the low contribution of the  $\pi$  backdonation  $\Delta E_{orb(3)}$  and  $\Delta E_{orb(4)}$  for  $L = CO$ , which is smaller than for  $L = N_2$ . CO is known to be a better  $\pi$  acceptor than  $N_2$  in transition metal complexes.<sup>26</sup> The peculiar results for the orbital interactions in the neutral  $N_2L_2$  compounds can be explained with the dominance of the  $\sigma$  donation  $L \rightarrow N_2 \leftarrow L$  over  $\pi$  backdonation  $L \leftarrow N_2 \rightarrow L$ , which comes to the fore by the calculated partial charges (Fig. 1). The energy of the  $\sigma$  lone-pair HOMO suggests that the donor strength of the ligands has the order  $CS$  ( $\epsilon = -10.1$  eV)  $>$   $CO$  ( $\epsilon = -12.2$  eV)  $>$   $N_2$  ( $\epsilon = -13.9$  eV). But the overall strength of the dative interactions cannot simply be derived from the orbital interactions. The orbital interaction  $\Delta E_{orb}$  of the negatively charged  $CN^-$  is significantly weaker ( $-972.1$  kcal mol $^{-1}$ ) than that of  $NO^+$  ( $-1088.0$  kcal mol $^{-1}$ ), but the total interaction energy  $\Delta E_{int}$  of the former ligand is clearly higher ( $-301.4$  kcal mol $^{-1}$ ) than the latter ( $-202.5$  kcal mol $^{-1}$ ). The electrostatic interaction  $\Delta E_{elstat}$  but also the Pauli repulsion  $\Delta E_{Pauli}$ , which makes the largest contribution to  $\Delta E_{int}$ , are equally relevant for the trend of the interatomic interactions. It has been shown that the Pauli repulsion is the crucial factor for the equilibrium geometry of molecules.<sup>27</sup>

We also want to comment on the  $\Delta E_{orb(rest)}$  term, which is comparatively large in the systems with  $L = CO, CS, NO^+$ . It stems from the relaxation of the fragment orbitals with respect to the isolated species. The central  $N_2$  moieties in the latter complexes have significantly shorter N-N distances than in the

$^1\Gamma_g$  singlet state (1.606 Å at the M06-2X/cc-pVTZ level), and the electronic relaxation is, therefore, larger than in the complexes with  $L = N_2, CN^-$  which have longer central N-N bonds (Fig. 1). The impact of the geometry relaxation on the BDE and the stability of molecules has been pointed out by Bickelhaupt in his activation strain model.<sup>28</sup> The strong influence of the fragment relaxation and the geometry of the interacting species becomes obvious when the trend of the interaction energy  $\Delta E_{int}$  between the frozen fragments ( $L = CS > CO > CN^- > NO^+ > N_2$ ) is compared with the BDEs that are calculated using the fragments at their equilibrium geometries and electronic ground state ( $L = CS > CO > CN^- > N_2 > NO^+$ ). Finally, we want to mention that the chemistry of  $N_2(PPh_3)_2$  was recently studied in joint experimental and theoretical works by the groups of Stephan and Grimme, which showed a surprising reactivity of the member of the  $N_2L_2$  compound class.<sup>29</sup>

## Summary and conclusion

Geometry optimizations of the compounds  $N_2L_2$  ( $L = N_2, CO, CS, NO^+, CN^-$ ) at the CCSD(T)/cc-pVTZ level give the energy minimum structures with a *trans*-periplanar arrangement of the  $L_2$  ligands at the  $N_2$  unit. Attempts to localize a *syn* isomer failed, and the calculations gave the *trans* isomer as the only conformational minimum. Energy calculations suggest that all compounds  $N_2L_2$  ( $L = N_2, CO, CS, NO^+, CN^-$ ) may be synthesized and should be observable under appropriate conditions. The complexes with  $L = N_2, CO, NO^+, CN^-$  are predicted as thermodynamically unstable for dissociation into  $N_2 + 2 L$  with  $\Delta G^{298}$  value lying in between  $-257$  kcal mol $^{-1}$  ( $L = NO^+$ ) and  $-73$  kcal mol $^{-1}$  ( $L = CO$ ), but the adduct  $N_2(CS)_2$  is calculated as slightly stable with  $\Delta G^{298} = 4$  kcal mol $^{-1}$ . The homolytic dissociation reaction into two fragments  $N_2L_2 \rightarrow 2 NL$  is energetically less favorable than the heterolytic fragmentation  $N_2L_2 \rightarrow N_2 + 2 L$ , which proceeds synchronously but asymmetrically. The activation barriers for the fragmentation reaction  $N_2L_2 \rightarrow N_2 + 2 L$  have values between  $\Delta G^\ddagger(298 K) = 17$  kcal mol $^{-1}$  for  $L = N_2$  and  $\Delta G^\ddagger(298 K) = 84$  kcal mol $^{-1}$  for  $L = CS$ . The calculated vibrational frequencies show that all molecules  $N_2L_2$  have a characteristic vibrational mode with the



second highest wavenumber  $\nu_{\text{as}}$  that comes from the antisymmetric stretch of the ligands L, which is blue shifted for L = CO ( $\Delta = 55 \text{ cm}^{-1}$ ) and L = NO<sup>+</sup> ( $\Delta = 118 \text{ cm}^{-1}$ ) but it is red shifted for L = CS ( $\Delta = -54 \text{ cm}^{-1}$ ) and L = CN<sup>-</sup> ( $\Delta = -133 \text{ cm}^{-1}$ ) relative to the  $\nu_{\text{as}}$  mode of L = N<sub>2</sub>.

The analysis of the bonding situation using the charge distribution reveals that there is a total charge donation L → (N<sub>2</sub>) ← L in all complexes ranging between 1.38 e (L = CN<sup>-</sup>) and 0.56 e (L = N<sub>2</sub>), except in the dication with L = NO<sup>+</sup>, where a small backdonation in reverse direction L → (N<sub>2</sub>) ← L with 0.10 e is calculated. EDA-NOCV calculations of N<sub>6</sub> using the central N<sub>2</sub> moiety and the terminal N<sub>2</sub> ligands as interacting fragments in various electronic states and with different partial charges show that the best description of the bonding situation is given in terms of dative interactions N<sub>2</sub> → (N<sub>2</sub>) ← N<sub>2</sub> between central N<sub>2</sub> in the excited (1)<sup>1</sup>Γ<sub>g</sub> singlet state and the terminal N<sub>2</sub> fragments in the <sup>1</sup>Σ<sub>g</sub><sup>+</sup> electronic ground state. In contrast to the results for N<sub>6</sub>, the best description of the complexes with L = CO, CS, NO<sup>+</sup> is calculated for the interactions between the central N<sub>2</sub> in the <sup>5</sup>Σ<sub>u</sub><sup>+</sup> quintet state and the terminal ligands in the symmetry-adapted (L)<sub>2</sub> quintet state, which indicates electron-sharing double bonds between the fragments. For N<sub>2</sub>L<sub>2</sub> with L = CN<sup>-</sup>, it is found that the bonding is best described for the interaction between N<sub>2</sub><sup>-</sup> in the electronic quartet (<sup>4</sup>Σ<sub>u</sub><sup>+</sup>) state and the terminal (L)<sub>2</sub><sup>-</sup> ligand as symmetry-adapted quartet. A comparative analysis of the five N<sub>2</sub>L<sub>2</sub> compounds using the same fragments with central N<sub>2</sub> in the excited (1)<sup>1</sup>Γ<sub>g</sub> singlet state and the terminal L<sub>2</sub> fragments in the <sup>1</sup>Σ<sub>g</sub><sup>+</sup> electronic ground state reveals that the σ donation L → (N<sub>2</sub>) ← L makes the largest contribution to the stabilizing interactions and that the π backdonation L ← (N<sub>2</sub>) ← L is much weaker. In contrast to the common bonding model for N<sub>6</sub> using Lewis structures N<sup>-</sup> = N<sup>+</sup> = N = N = N<sup>+</sup> = N<sup>-</sup>, the donor-acceptor model N<sub>2</sub> → (N<sub>2</sub>) ← N<sub>2</sub> explains that the lowest activation barrier is found for the concerted cleavage of the two formal double bonds, leading to the experimentally observed dissociation into 3 N<sub>2</sub>.

## Author contributions

G. F. and S. P. conceived the project, wrote the draft and finalized it, Y. L., C. D. and L. X. performed the calculations, Y. L. analyzed the data. All authors took part in the discussions and approved the final version.

## Conflicts of interest

The authors declare no conflict of interest.

## Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5sc08399k>.

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