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Theoretical study of the potential-energy surface of C_2NP

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Abstract. The B3LYP/6-311G(d) and CCSD(T)/6-311G(2df) (single-point) methods have been used to investigate the singlet potential energy surface of C_2NP, in which seven stationary isomers and seventeen interconversion transition states are involved. At the final CCSD(T)/6-311G(2df)//B3LYP6-311G(d) level with zero-point vibrational energy correction the lowest-lying isomer is a linear NCCP followed by two linear CNCP isomers at 23.9 and CCNP at 65.8 kcal mol^{-1}, respectively. The three isomers are kinetically very stable towards both isomerization and dissociation, and CCNP is even more kinetically stable than CNCP – by 14.3 kcal mol^{-1} despite its high energy. Further comparative calculations were performed at the QCISD and QCISD(T) levels with the 6-311G(d) and 6-311G(2d) basis sets to obtain more reliable structures and spectroscopy for the three isomers. The calculated bond lengths, rotational constant, and dipole moment for NCCP were in close agreement with the experimentally determined values. Finally, similarities and discrepancies between the potential energy surface of C_2NP and those of the analogous species C_2N_2 and C_2P_2 were compared. The results presented in this paper might be helpful for future identification of the two still unknown yet kinetically very stable isomers CNCP and CCNP, both in the laboratory and in interstellar space.

Key words: Theoretical study – Potential-energy surface – C_2NP

Introduction

The molecule C_2N_2 has long been the subject of extensive experimental and theoretical studies [1, 2], because of its significance in, for example, photochemistry, combustion, interstellar research, and biochemistry. It is now established that the four linear isomers NCCN (cyanogen), CNCN (isocyanogen), CNNC (diisocyanogen), and CCNN (diazodicarbon) are all kinetically stable and should be experimentally observable, and the first three isomers have been synthesized or spectrometrically characterized. The most stable isomer NCCN has also been detected in interstellar space. The highest-energy isomer, which has a three-membered NNC ring, resides in a much more shallow potential well and its observation is less likely.

Theoretical investigations have also been performed on molecules analogous with C_2N_2, for example $SiCN_2$ [3], Si_2N_2 [4], C_2P_2 [5], and Si_2P_2 [6]. It has been shown that despite their analogous valence electrons, the structures, energetics, and stability of their isomers are significantly different. For example, SiNCN and SiNNSi, rather than the cyanogen analogues NSiCN and NSiSiN, are the lowest-energy isomers of the molecules $SiCN_2$ and Si_2N_2, respectively, whereas the cyclic structures are important for the molecule C_2P_2 [5c] and even dominate for Si_2P_2 [6].

Formally, the molecule C_2NP is isovalent and analogous with C_2N_2. In sharp contrast to the large bodies of data on C_2N_2, however, rather little attention has been paid to C_2NP. As far as we are aware only three experimental studies [7] have been concerned with the structure, rotational constant, and dipole moment of linear form NCCP, and the structural, spectroscopic, and stability properties of the analogous species of isocyanogen, diisocyanogen, and diazodicarbon, which are kinetically very stable for C_2N_2, are completely unclear. Moreover, as for C_2P_2 [5a, 5c] and Si_2P_2 [6], the introduction of phosphorus might lead to more complex structural diversity, for example the existence of stable four-membered ring structures, because phosphorus is more inclined than nitrogen to form single bonds. Without performing detailed calculations on the whole potential energy surface of C_2NP, it is certainly difficult and unsafe to judge the spectroscopic properties and stability of its different isomers, whether qualitatively or quantitatively.

The fragments CN, CP, C_2, and NP of the molecule C_2NP have all been detected within interstellar space [8].

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The direct association reaction between the doublet radicals CN and CP is expected to form NCCP, CNCP, NCPC, and CNPC, whereas that between the singlet molecules C_2 and NP might possibly produce CCNP and CCPN. Thus the molecule C_2NP should also be of interstellar interest. Because of the potential importance and the rather limited knowledge of C_2NP, we decide to perform a detailed ab initio investigation of its singlet potential energy surface. In addition to obtaining accurate theoretical structures and spectroscopy of the isomer NCCP, which has been experimentally synthesized [7], we have attempted to predict which other possible C_2NP isomers with high kinetic stability that might be experimentally observable. This work is reported in this paper.

Computational methods

All structures and vibration frequencies for the different C_2NP isomers and interconversion singlet transition states were obtained at the B3LYP/6-311G(d) level. Further single-point energy evaluation was performed at the CCSD(T)/6-311G(2df) level using B3LYP/6-311G(d)-optimized geometries. Zero-point vibration energies (ZPVE) calculated at the B3LYP/6-311G(d) level are included. The final energies are then denoted as CCSD(T)/6-311G(2df)//B3LYP/6-311G(d) + ZPVE. To test whether the transition states obtained connect the correct isomers, intrinsic reaction coordinate (IRC) calculations were performed at the B3LYP/6-311G(d) level. For kinetically stable isomers, further comparative calculations were performed on the structures and spectroscopy at the QCISD and QCISD(T) levels with the 6-311G(d) and 6-311G(2d) basis sets. For these isomers natural bond orbital analysis (NBO) was performed to determine the nature of the bonding. All calculations were performed with the Gaussian 98 program package.

Results and discussion

For C_2NP isomers and the corresponding transition states the optimized geometries are shown in Figs 1 and 2, respectively. A schematic potential energy surface of C_2NP is plotted in Fig. 3. The interatomic overlap density plots of the isomer CCNP **6**, C_2, and NP are given in Fig. 4. The relative energies for C_2NP isomers and transition states are given in Table 1. The harmonic vibration frequencies of the most relevant isomers NCCP **1**, CNCP **2**, and CCNP **6** are presented in Table 2.

Isomers

Figure 1 depicts thirteen C_2NP isomers labeled with Arabic numbers, **m**, from **1** to **13**. They can be classified into four groups – open forms (isomers **1** to **7**), three-membered rings (isomers **8** to **10**), four-membered rings (isomers **11** and **12**), and the tetrahedral species (isomer

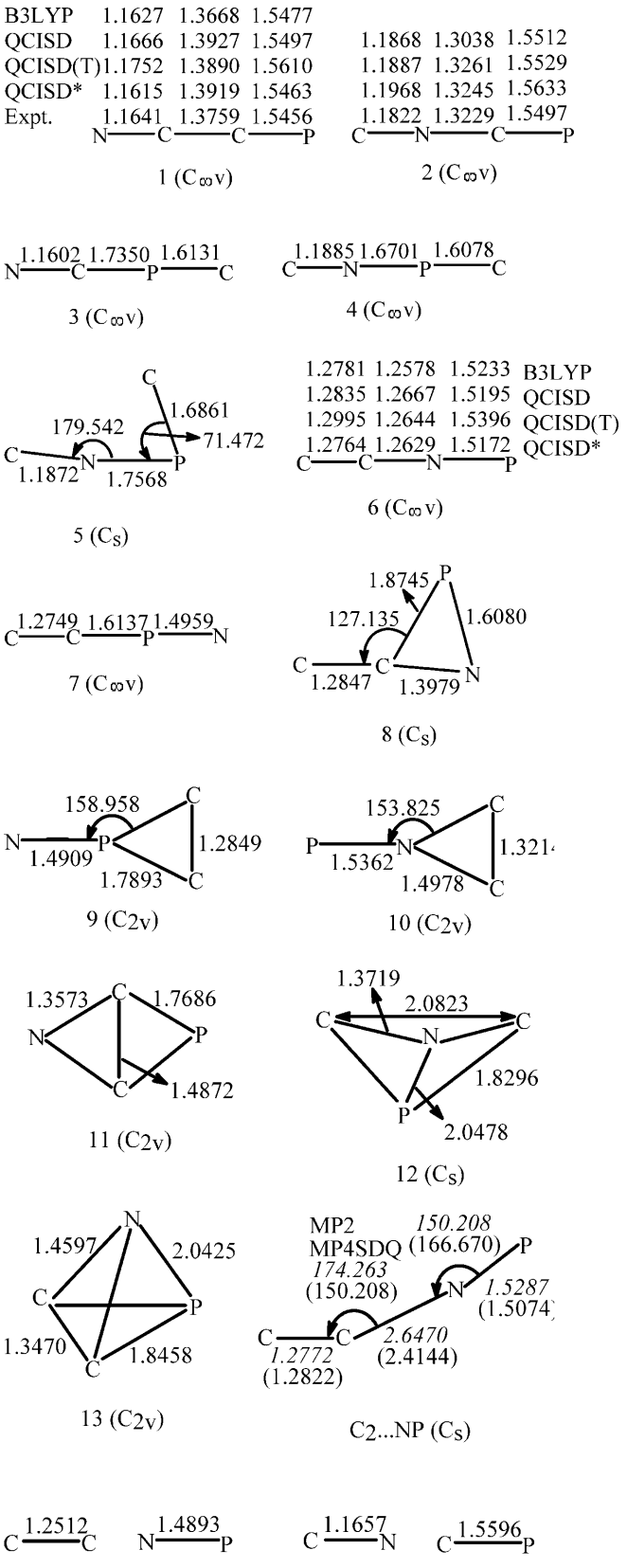
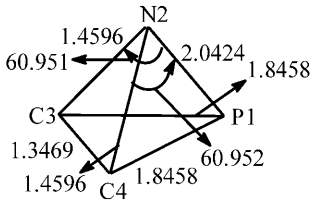
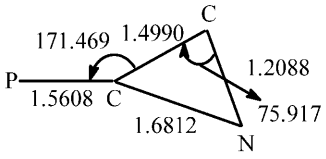


Fig. 1. B3LYP/6-311G(d)-optimized geometries for C_2NP isomers and dissociation products. Bond lengths are in angstroms and bond angles in degrees. "QCISD*" denotes the QCISD/6-311G(2d) values from this work and "Expt." denotes the experimental values [7c]

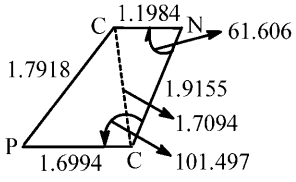


D(4213)=63.712

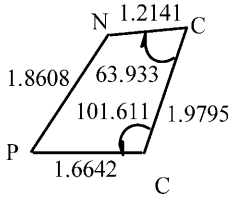
TS1/1 (C_1)



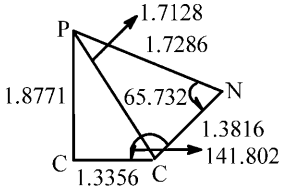
TS1/2 (C_S)



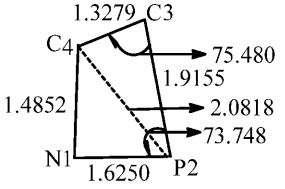
TS1/2* (C_S)



TS1/5 (C_S)

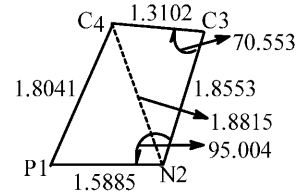


TS1/8 (C_S)



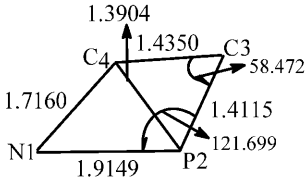
D(4312)=35.151

TS1/8* (C_1)

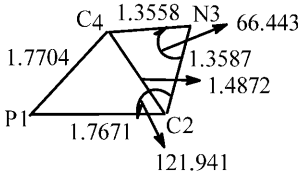


D(4321)=35.028

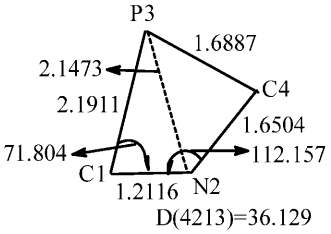
TS1/8** (C_1)



TS1/8*** (C_S)

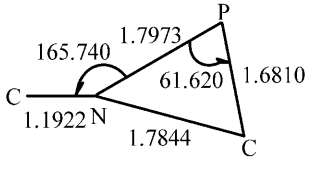


TS2/2 (C_S)

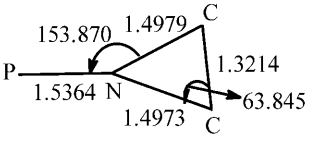


D(4213)=36.129

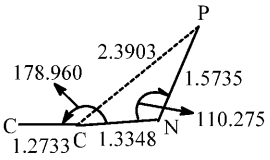
TS2/2* (C1)



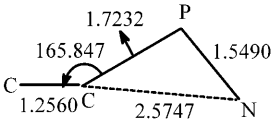
TS2/5 (C_S)



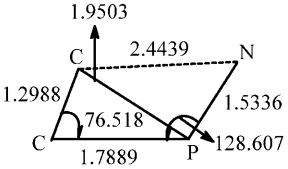
TS6/6 (C_S)



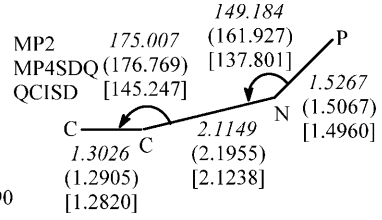
TS6/8 (C_S)



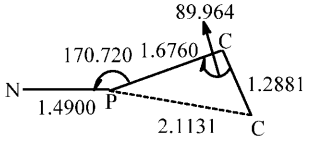
TS7/8 (C_S)



TS8/9 (C_S)



TS6/C_2...NP (C_S)



TS7/9 (C_S)

Fig. 2. B3LYP/6-311G(d)-optimized geometries for C_2NP interconversion and dissociation transition states. Bond lengths are in angstroms and bond angles in degrees

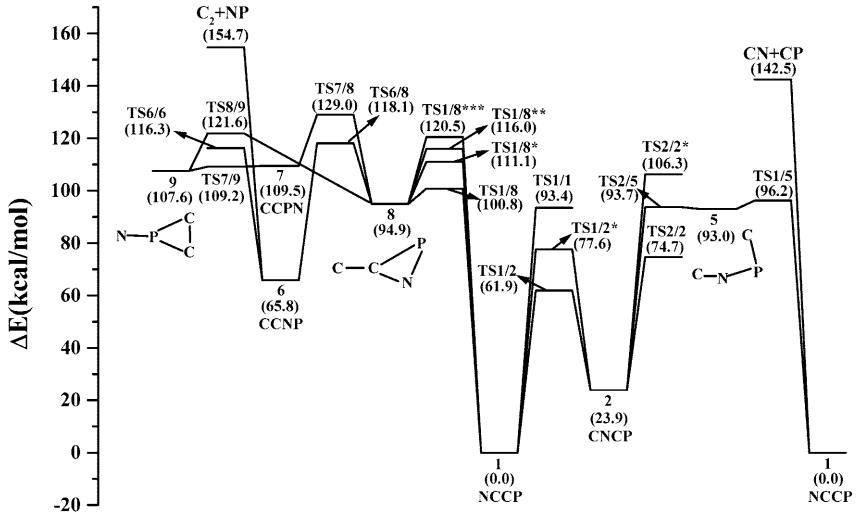


Fig. 3. Schematic potential energy surface of C_2NP at the CCSD(T)/6-311G(2df)//B3LYP/6-311G(d) + ZPVE level

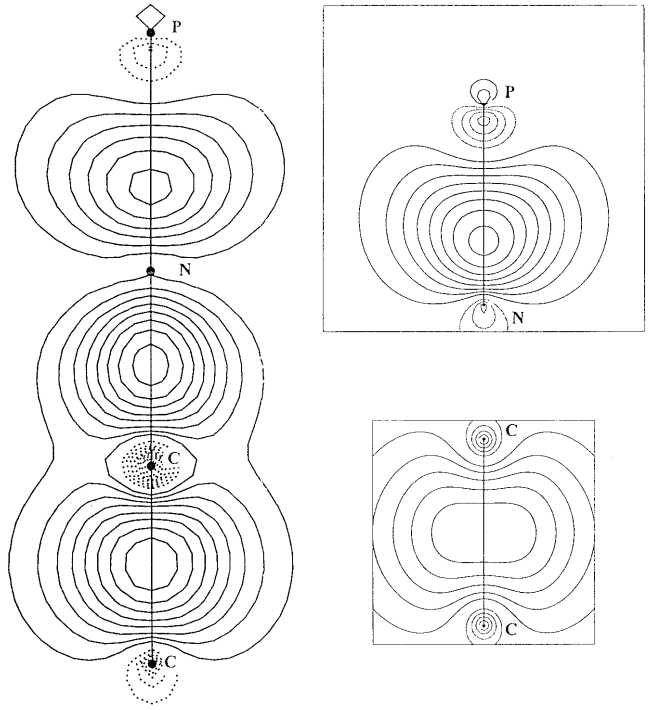


Fig. 4. Interatomic overlap density plots of the isomers CCNP 6, C_2, and NP

13). We will discuss the structural features of the isomers in these four groups.

The linear isomers NCCP **1**, CNCP **2**, NCPC **3**, CNPC **4**, CCNP **6**, and CCPN **7** are the respective analogues of the well-known C_2N_2 isomers, i.e., cyanogen, isocyanogen, diisocyanogen, and diazodicarbon. Only isomers **1**, **2**, **6**, and **7** are minima with all real frequencies, however. Relaxation of structure **3** leads to isomer **1**. Notice that at the HF/6-311G(d) level, a bent NCPC structure can be optimized with all real frequencies. When the structure of **4** is relaxed, a non-linear isomer

Table 1. Relative energies (kcal mol^{-1}) of different C_2NP isomers, interconversion transition states, and dissociation products at the B3LYP/6-311G(d) and single-point CCSD(T)/6-311G(2df) levels. The B3LYP/6-311G(d) and CCSD(T)/6-311G(2df)//B3LYP/6-311G(d) total energies of the reference isomer NCCP 1 are −472.3037715 and −471.5655238 hartree, respectively

Species	B3LYP/6-311G(d)	CCSD(T)/6-311G(2df) //B3LYP/6-311G(d) + ZPVE
NCCP **1**	0.0	0.0
CNCP **2**	23.8	23.9
NCPC **3**	95.1	
CNPC **4**	113.3	
CNPC **5**	99.2	93.0
CCNP **6**	63.0	65.8
CCPN **7**	115.8	109.5
CCPN **8**	100.1	94.9
CCPN **9**	119.0	107.6
CCPN **10**	117.0	
CCPN **11**	79.8	
CCPN **12**	115.0	
CCPN **13**	157.5	
TS1/1	157.5	93.4
TS1/2	64.5	61.9
TS1/2*	83.7	77.6
TS1/5	103.0	96.2
TS1/8	112.3	100.8
TS1/8*	119.7	111.1
TS1/8**	125.7	116.0
TS1/8***	125.7	120.5
TS2/2	80.0	74.7
TS2/2*	112.8	106.3
TS2/5	99.4	93.7
TS6/6	117.0	116.3
TS6/8	117.0	118.1
TS7/8	140.4	129.0
TS7/9	120.2	109.2
TS8/9	135.4	121.6
CN + CP	149.6	142.5
C_2 + NP	189.4	154.7

*The weakly bound species C_2…NP are obtained at the MP2/6-311G(d) and MP4SDQ/6-311G(d) levels and the transition state **TS6/C_2…NP** are obtained at the MP2/6-311G(d), MP4SDQ/6-311G(d) and QCISD/6-311G(d) levels. So the energies of the two species are not listed

Table 2. Vibration frequencies (cm^{-1}) and infrared intensities in parentheses (km mol^{-1}) of the most relevant isomers NCCP **1**, CNCP **2** and CCNP **6**

Species	Frequencies (intensities)		
	B3LYP/ 6-311G(d)	QCISD/ 6-311G(d)	QCISD/ 6-311G(2d)
NCCP **1**	2292 (0)	2296 (0)	2285 (0)
	1614 (7)	1602 (2)	1579 (3)
	1297 (0)	676 (0)	669 (0)
	559 (16)	527 (15)	512 (14)
	211 (0)	199 (0)	199 (0)
CNCP **2**	2119 (332)	2140 (393)	2133 (383)
	1633 (21)	1616 (32)	1595 (38)
	729 (1)	710 (3)	706 (4)
	473 (4)	439 (3)	420 (5)
	204 (0)	190 (0)	179 (1)
CCNP **6**	2059 (1221)	1999 (1686)	1980 (1671)
	1515 (30)	1504 (128)	1492 (146)
	766 (3)	768 (1)	762 (1)
	489 (6)	495 (3)	462 (4)
	192 (1)	178 (1)	175 (1)

with CNPC atomic ordering with all real frequencies is obtained; this is isomer **5**.

Three optimized isomers had three-membered rings. Isomer **8** is a PNC three-membered ring structure with exocyclic CC bonding whereas isomer **9** is a CCP three-membered ring structure with exocyclic PN bonding. Both isomers are calculated to have all real frequencies. Notice that the analogous C_2N_2 isomer with the three-membered NNC ring bonded by an exocyclic CC bond is also stable, whereas that bearing a CCN three-membered ring with an exocyclic NN bond is unstable [2b]. Isomer **10**, a three-membered CCN ring with an exocyclic NP bond, is actually an automerization transition state **TS6/6**. Other isomers with CPC or CNC three-membered rings cannot be located.

Isomers **11** and **12** are consistent with a four-membered ring description. Isomer **11** is a planar C_{2v}-symmetrized structure with C–C cross bonding. It corresponds, in fact, to the automerization transition state **TS2/2**. Isomer **12** is formally a NP cross-bonded CNCP cyclic structure with C_s symmetry, and it is not a minimum point. Searching for a CCNP four-membered ring isomer often leads to isomer **6** or **8**.

Finally, isomer **13** can be described as a tetrahedral structure, although the peripheral NP bond is somewhat long (2.0425 Å). Frequency calculations show that it is not a minimum structure – it is, actually, the automerization transition state **TS1/1**. It should be noted that the analogous C_2P_2 isomer is a minimum structure [5a, 5c].

Let us now consider the energetics of the seven minimum C_2NP isomers **1**, **2**, **5**, **6**, **7**, **8**, and **9**. As shown in Table 1, the lowest-lying isomer is linear NCCP **1** followed by linear CNCP **2** (23.9) and linear CCNP **6** (65.8). The values in parentheses are relative energies at the CCSD(T)/6-311G(2df)//B3LYP/6-311G(d) + ZPVE level, relative to isomer **1**. It is noteworthy that the relative energies of CNCN and CCNN with reference to NCCN are 23.6 and 82.7 kcal mol^{-1}, respectively. This might indicate that the thermodynamic stability of CNCP and CNCN is similar, whereas that of CCNP is higher than that of CCNN. The bent isomer **5** (93.0) with the CNPC skeleton, linear CCPN **7** (109.5), and the three-membered ring isomers **8** (94.9) and **9** (107.6) lie much higher.

Kinetic stability

Seventeen transition states were located for the interconversion or dissociation of the seven C_2NP isomers, as shown in Fig. 2. The connection of these transition states was checked by IRC calculations. The symbol **TSm/n** is referred to as the transition states between the isomers **m** and **n**. By means of the seven stable isomers, seventeen transition states, and the corresponding energetics, a schematic potential energy surface of C_2NP is established in Fig. 3. For simplicity, the structural details of these transition states are not discussed.

By simple consideration of the depth of the potential wells in which the isomers reside, we can readily find from Fig. 3 that only three linear isomers, NCCP **1**, CNCP **2**, and CCNP **6**, can be kinetically stable towards both isomerization and dissociation. Like the situation for NCCN and CNCN, the three-membered ring transition state **TS1/2** governs the kinetic stability of isomers **1** and **2**. The barriers from **1** to **2** and from **2** to **1** are 61.9 and 38.0 kcal mol^{-1}, respectively. The corresponding barriers for NCCN↔CNCN are 59.7 and 36.1 kcal mol^{-1} [2c]. The direct ring-closure of **6** to form isomer **8** governs the kinetic stability of isomer **6** with the conversion barrier 52.3 kcal mol^{-1}. Notably, the dissociation barrier 42.1 kcal mol^{-1} separating singlet molecules C_2 and N_2 determines the kinetic stability of CCNN. This means that CCNP might be kinetically more stable than CCNN. Interestingly, the kinetic stability of CCNP is 14.3 kcal mol^{-1} higher than that of CNCP, even though CCNP is thermodynamically much less stable than CNCP – by 41.9 kcal mol^{-1}. This is similar to the situation for CCNN and CNCN. Because of the high kinetic stability (more than 38 kcal mol^{-1}), the three linear isomers are all expected to be experimentally observable.

The other four isomers **5**, **7**, **8**, and **9**, however, reside in much more shallow potential wells, because the barriers for **5**→**2**, **7**→**9**, **8**→**1** and **9**→**7** conversions are just 0.7, -0.3, 5.9, and 1.6 kcal mol^{-1}, respectively (the negative sign results from single-point calculations). Their experimental observation thus seems much less likely.

It should be pointed out that at the 6-311G(d) MP2, MP4SDQ, and QCISD levels, we can obtain a transition state **TS6/C_2…NP** connecting CCNP and a weakly bound complex C_2...NP. Yet, both **TS6/C_2…NP** and C_2...NP cannot be located at the B3LYP/6-311G(d) level, and are thus not presented in Fig. 3 (they will not affect our discussion on the kinetic stability of CCNP). Interestingly, **TS6/C_2…NP** is found to lie lower in energy than the dissociation product C_2 + NP by 1.6, 5.8, and 13 kcal mol^{-1}, respectively, at the three levels. This is quite different from the situation for CCNN, for which the dissociation transition state lies 5.5 kcal mol^{-1} higher than the dissociation limit $C_2 + N_2$ [2c].

It is worth considering the closed/open-shell nature of the singlet C_2NP isomers and dissociation products. The calculated ||t1|| diagnostic [9] values for NCCP **1**, CNCP **2**, CCNP **6**, C_2 and NP at the QCISD/6-311G(d) level are approximately 0.017, 0.021, 0.021, 0.040, and 0.019, respectively. It can be readily seen that the singlet C_2 has the largest ||t1|| value and might have considerable multireference character, whereas other species do not. Because the dissociation energy of CCNP to C_2 and NP is very large (76.6 kcal mol^{-1}), however, and the dissociation process does not govern the kinetic stability of CCNP, we still expect that our employed level CCSD(T)/6-311G(2df)//B3LYP/6-311G(d) + ZPVE is adequate and reliable for the singlet C_2NP potential energy surface.

QCISD study on NCCP **1**, *CNCP* **2** *and CCNP* **6**

To compare previous identification and to aid future identification of the three kinetically stable isomers NCCP, CNCP, and CCNP in the laboratory and in interstellar space, QCISD and QCISD(T) calculations are performed for the structures, rotational constants, dipole moments, and vibration frequencies.

NCCP **1** and CNCP **2**

Several experimental investigations [7] of the lowest-lying isomer NCCP **1** are now available. As shown in Fig. 1, the predicted bond lengths at all levels are very close to the experimental values [7c]. At the QCISD/6–311(2d) level, the calculated rotational constant and dipole moment are 2.683775 GHz and 3.4722 Debye, respectively, which are in close agreement with the experimental values 2.704480 GHz and 3.44 Debye [7a, 7b]. The direction of the dipole moment points to the terminal P-atom. The experimental vibration frequencies of isomer **1** are not available. The dominant low vibration, 512 cm^{-1}, is predicted to be very weak (14 km mol^{-1}) at the QCISD/6-311G(2d) level.

The second low-lying isomer CNCP **2** is completely experimentally unknown. At the QCISD/6-311G(2d) level, the dominant and very intense vibration is of high frequency 2133 cm^{-1}. Its rotational constant, 2.901292 GHz, is larger than that of NCCP yet the dipole moment, 2.5233 Debye, is smaller than that of NCCP. It is interesting to note that the direction of the dipole moment of CNCP **2** points to the terminal P-atom, whereas that of CNCN points to the terminal C-atom with a very small value less than 1.0 Debye. This is certainly because of different electronegativities of P and N.

As shown in Fig. 1, the CN and CP bond lengths of NCCP **1** and CNCP **2** are close to those of the separate CN and CP radicals. Each can, therefore, be considered as a dimer of CN and CP radicals. NBO analysis suggests that **1** and **2** can best be described as the valence structure formula |N≡C—C≡P| and |C≡N—C≡P| with conjugate triple bonding, similar to NCCN and CNCN. Note that "|" denotes the lone electron pair. It should be remarked that agreement between the B3LYP and QCISD results is good for isomers **1** and **2**.

CCNP **6**

The high-lying yet kinetically quite stable isomer CCNP **6** might represent a very interesting species, which is still experimentally unknown. As shown in Fig. 1, the CC and NP bond lengths are close to those of the separate singlet molecules C_2 and NP. The central CN bond length is very short. In this context CCNP can be considered as a strongly bonded co-dimer of two singlet molecules C_2 and NP just like CCNN described by Scheller et al. [2a] and Ding et al. [2c]. In addition, the interatomic overlap density plots of CCNP, C_2, and NP at the QCISD/6–31G(d) level, as shown in Fig. 4, clearly show that the charge is transferred from NP to C_2. CCNP can, therefore, also be viewed as a charger-transfer species comprising the ionic structure $(C_2^-)(NP^+)$ like CCNN. NBO analysis indicates that CCNP **6** might have a valence formula |C≡C—N≡P|.

For CCNP, there are two intense vibration bands at 1980 (dominant) and 1492 (side) cm^{-1} with the IR intensities 1671 and 146 km mol^{-1}, respectively, at the QCISD/6-311G(2d) level. Note that the B3LYP/6-311G(d) IR intensities, 1221 and 30 km mol^{-1}, are much smaller. The calculated QCISD/6-311G(2d) rotational constant (3.011996 GHz) and dipole moment (6.0298 Debye) for CCNP are larger than those for NCCP and CNCP. The direction of the dipole moment of CCNP **6** is towards the terminal P-atom, as is consistent with the interatomic overlap density plots. The dipole moment of CCNP is much larger than that of CCNN (3.3486 Debye at the QCISD/6-311G(d) level [2c]). This is understandable because:

1. although the symmetric N_2 molecule is not polar, the separate singlet NP molecule originally has a large dipole moment pointing to P (2.7244 Debye at the QCISD/6-311G(d) level); and
2. charge transfer from NP to C_2 further enlarges the dipole moment.

The rather large dipole moment makes CCNP a very promising candidate for astronomical detection.

Comparison with other molecules

Because the molecule C_2NP contains the elements N and P, which are in the same group, comparison of C_2NP with analogous molecules such as C_2N_2 and C_2P_2 might be helpful.

For the well-known molecule C_2N_2, theoretical investigations [2c] have shown that all four linear isomers NCCN, CNCN, CNNC, and CCNN are kinetically very stable, whereas the NNC three-membered ring isomer is relatively much less stable. No C_2N_2 isomers with four-membered rings or closed ring structures could be located as minima. Similarly for C_2NP, the linear isomers NCCP **1**, CNCP **2**, and CCNP **6**, which are analogous with NCCN, CNCN, and CCNN, are all kinetically very stable. Another CNCN-like isomer NCPC **3** and the CNNC-like isomer CNPC **4** are not minima at all, however. Although a bent CNPC isomer **5** can be located, it can be converted to isomer CNCP **2** with almost no barrier. This indicates that, unlike the -NC group, the

-PC group is not able to form stable species consistent with the well known "double bond rule" [10], i.e., the second-row elements are reluctant to form multiple bonds. For C_2NP no four-membered ring or closed-ring isomers can be located as minima, although phosphorus prefers to form single bonds to multiple bonds. It seems that for C_2NP, the bonding of nitrogen overwhelms that of phosphorus.

The C_2P_2 molecule has been paid much less attention [5, 11] – only the linear NCCN-like isomer PCCP has been tentatively detected [11]. Theoretical investigations [5] have shown that the lowest energy isomer is PCCP. In sharp contrast to C_2N_2 and C_2NP, however, several C_2P_2 isomers containing CPCP and CCPP four-membered ring structures and the closed-ring isomer have been found as minima. A planar CPCP four-membered ring isomer with CC cross bonding is even the second thermodynamically stable isomer with considerable kinetic stability. The CCNN-like isomer CCPP is also a high-energy yet kinetically stable species. Similar to C_2NP, the isomers CPCP and CPPC that contain the -PC group are not minima for C_2P_2. Overall, C_2NP seems to have more similarities to C_2N_2 than to C_2P_2.

Conclusions

Detailed ab-initio calculations have been performed to investigate the structures, spectroscopy, and stability of various singlet C_2NP isomers at the CCSD(T)/6-311G(2df)//B3LYP/6-311G(d) level. Whereas seven isomers were identified as local minima, only three linear isomers NCCP **1** (0.0 kcal mol^{-1}), CNCP **2** (23.9 kcal mol^{-1}), and CCNP **6** (65.8 kcal mol^{-1}) are kinetically very stable towards both isomerization and dissociation. Similar to the analogue CCNN, the isomer CCNP **6**, a formally charge-transfer species comprising the ionic structure $(C_2^-)(NP^+)$, is kinetically more stable than isomer **2** by approximately 14 kcal mol^{-1}. Further calculations at the QCISD and QCISD(T) levels were performed for the three kinetically stable isomers **1**, **2**, and **6**, to enable accurate theoretical prediction of structures, vibration frequencies, rotational constants, and dipole moments for their future detection in the laboratory and in interstellar space. The calculated rotational constant and dipole moment of NCCP **1** are in close agreement with experimental values. Finally, the potential energy surface features of C_2NP were compared with those of the analogous species C_2N_2 and C_2P_2, and C_2NP was found to be closer to C_2N_2 than to C_2P_2. We hope that our theoretical results might stimulate future experimental and interstellar investigations on the three kinetically stable isomers **1**, **2**, and **6**, among which the isomers **2** and **6** are completely unknown, even in laboratory.

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