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REGULAR ARTICLE

Theoretical study on the potential energy surface of NC_3P isomers

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Abstract Density functional theory (DFT) calculations have been used to study the isomerization process in the NC_3P system. At the DFT/B3LYP/6-311G(d) level, 28 triplet and 28 singlet minima were obtained on their respective potential energy surfaces. The linear triplet ^{3}NCCCP is the lowest-energy structure among the isomers. On the triplet PES, only linear isomers ^{3}NCCCP, ^{3}CNCCP, ^{3}CCCNP, and ^{3}CCNCP possess great kinetic and thermodynamic stabilities to exist under low-temperature conditions (such as in the dense interstellar clouds). At the same time, one chain-like and four three-membered-ring isomers on the singlet PES have been located with high kinetic and thermodynamic stabilities. Further CCSD(T)/6-311G(2df)//QCISD/6-311G(d), CCSD(T)/cc-pVTZ//DFT/B3LYP/cc-pVTZ, and CASPT2(14,12)/cc-pVQZ//CASSCF(14,12)/cc-pVQZ calculations are performed on the structures, frequencies, and energies of the relevant species. The bonding natures were analyzed and the results were compared with the analogous NC_3N and NC_2P molecules so as to aid their future experimental or astrophysical detection.

Keywords Theoretical study · Structure · Potential energy surface · NC_3P

1 Introduction

Structure and reactivity of small carbon, nitrogen, and phosphorus species have been of great interest to chemists from various aspects. For example, P-doped hetero-carbon cluster have important applications in microelectronic materials and surface chemistry. N- or P-containing carbon clusters are generally used as semiconducting materials [1]. The linear phosphaalkyne, phosphabutadiyue (HC_3P) and phosphahexatriyne (HC_5P) has also been detected by the microwave spectroscopy in the pyrolysis products [2–5].

An other interesting field is interstellar chemistry [6, 7]. Up to now, several species which contain N or P atom such as CP, CN, NP, CCCN, and CCNC radicals have been detected in interstellar space [8–12]. Long-chain molecule $HC_{11}N$ [13] have been detected by radio astronomy. Investigations show that small P-containing linear molecules such as C_2P, C_3P, and HC_2P might also exist if they are unreactive with oxygen atoms [14]. Species such as C_nX [8,14–16], Si_mX_n [18–22], and SiC_nX [23–27] (X = N or P) have been studied both in interstellar space and in the laboratory. They were expected to be carriers of some interstellar bands. The XC_nY (X, Y = N or P) species have received extensive study in both experimental and theoretic investigations. Understanding the structures, bonding natures, and stabilities of the XC_nY (X, Y = N or P, $n > 1$) series may be helpful for the formation mechanism and the further identification of new N- and P-containing hetero-carbon clusters.

As the first member of XC_nY (X, Y = N or P, $n > 1$) species, cyanogen (NCCN) was synthesized in 1815 [28]. Its isomers, CNCN and CNNC have been experimentally investigated and prepared since 1988 [29–31]. The laboratory microwave spectrum and the dipole moment

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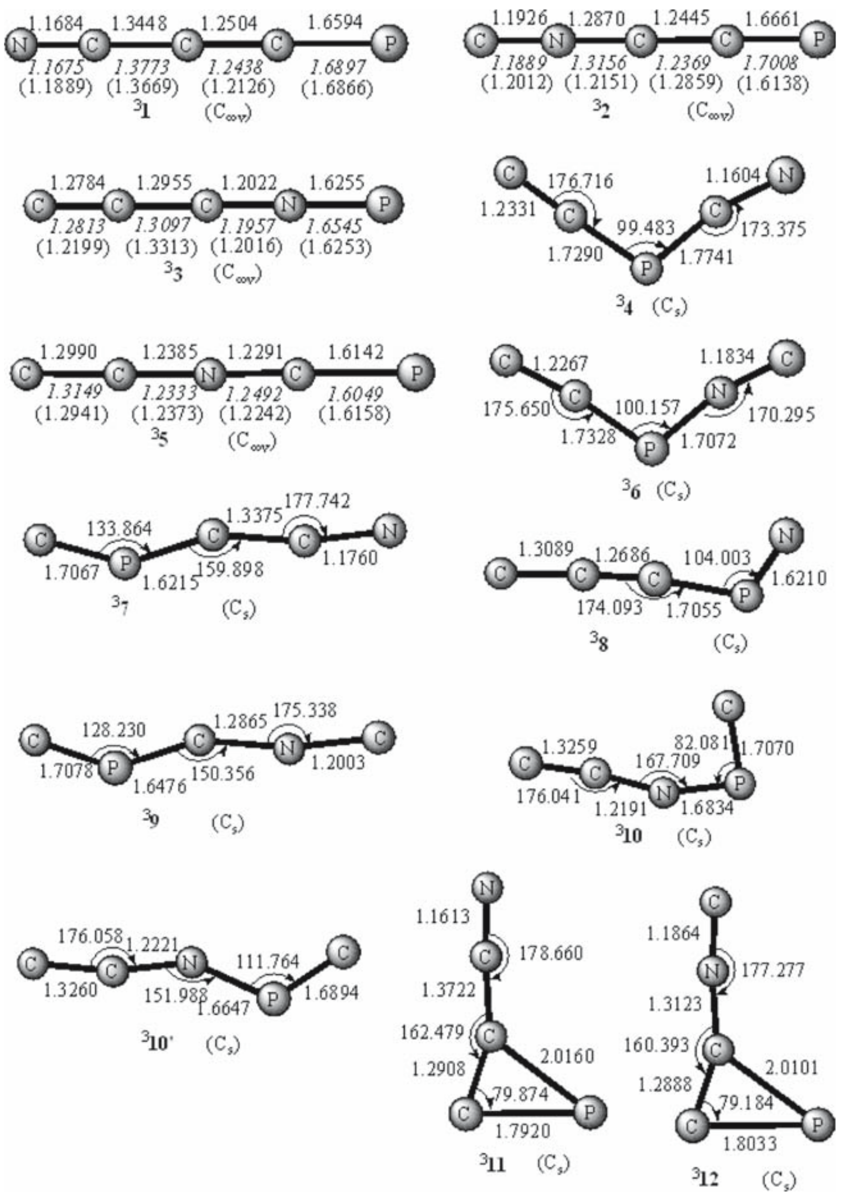


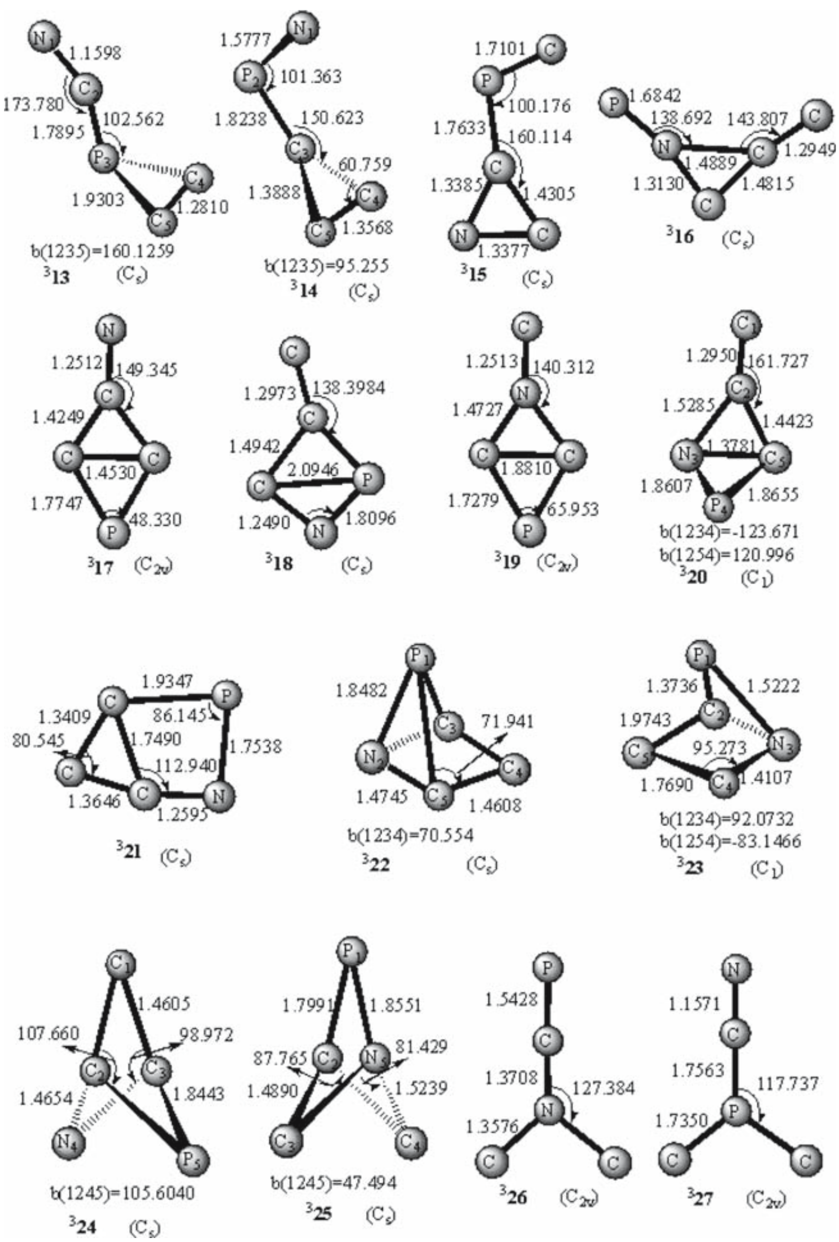
Fig. 1 Optimized geometries of the triplet NC_3P isomers at the DFT/B3LYP/6-311G(d) level. Bond lengths are in angstroms and angles in degrees. The values obtained at the QCISD/6-311G(d) level and with the DFT/B3LYP/cc-pVTZ method for some relevant isomers are also given in italics and in parentheses, respectively

measurement on NCCP have been known from the reaction between cyanogen azide (NCN_3) and phosphaethyne (HCP) at high temperature (ca. 700°C) in 1980 [32,33]. NC_2P species has another two kinetically very stable isomers (CNCP and CCNP), which may be detected in the near future [34]. Furthermore, both theoretical and experimental investigations have been done on the promising interstellar molecule NC_3N [35,36]. And in both neutral and ionized forms, dicyanocarbene (NCCCN) is found to be a stable and detectable species [37,38]. However, no theoretic, experimental, or astrophysical studies have been reported on the analogue NC_3P molecule. In this paper, we want to mainly resolve the following questions: (1) Which is the lowest-energy structure among the NC_3P isomers? (2) Are there cyclic NC_3P isomers that possess enough stability to be allowed in the laboratory or in interstellar space? (3) What are the bonding natures of the stable isomers? (4) What are the similarities and discrepancies between the NC_3P species and the well-known NC_2P and NC_3N molecules?

2 Computational methods

The Gaussian 98 program [39] is used for density functional theory (DFT), coupled cluster (CC) method and quadratic CI calculations. The optimized geometries and

Fig. 1 continued



harmonic vibrational frequencies of the local minima and transition states are obtained at the DFT/B3LYP/6-311G(d) [40] theory level. Further single-point energy evaluation is performed at the CCSD(T)/6-311G(2d) [41] level including the zero-point vibrational energies (ZPVEs) using the DFT/B3LYP/6-311G(d) geometries. To confirm whether the obtained transition states connect the right isomers, the intrinsic reaction coordinate (IRC) calculations [42,43] are performed at the DFT/B3LYP/6-311G(d) level. Furthermore, for the relevant species, the calculations on the structures and frequencies are carried out using the QCISD/6-311G(d) [44–46] and DFT/B3LYP/cc-pVTZ methods. At the same time, the single-point energies are carried out using the respective CCSD(T)/6-311G(2df) and CCSD(T)/cc-pVTZ methods. At last, the CASPT2(14,12)/cc-pVQZ//CASSCF(14,12)/cc-pVQZ method is performed to confirm the multi-configuration effects with the Molcas 6.0 program packages [47].

3 Results and discussions

All computations are carried out with Gaussian 98 and Molcas 6.0 programs. To include as many isomeric forms as possible, four types of isomers are considered, such

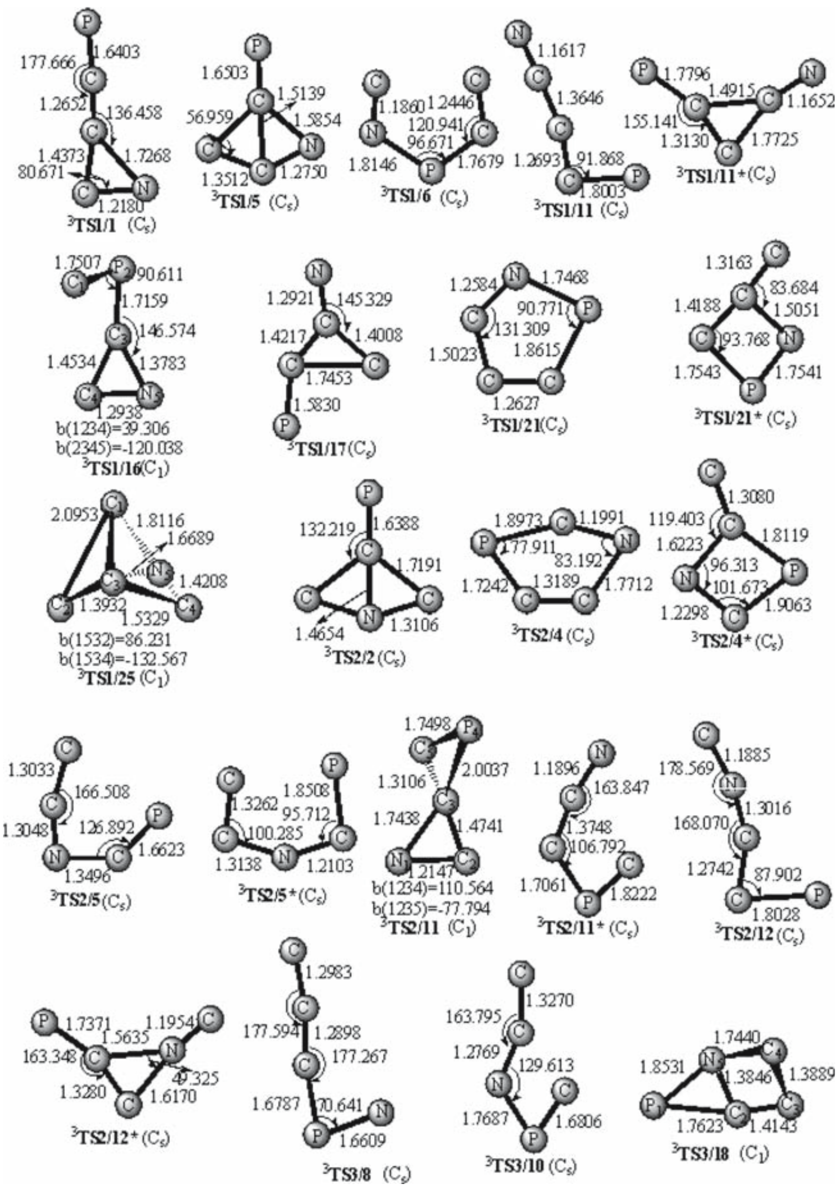
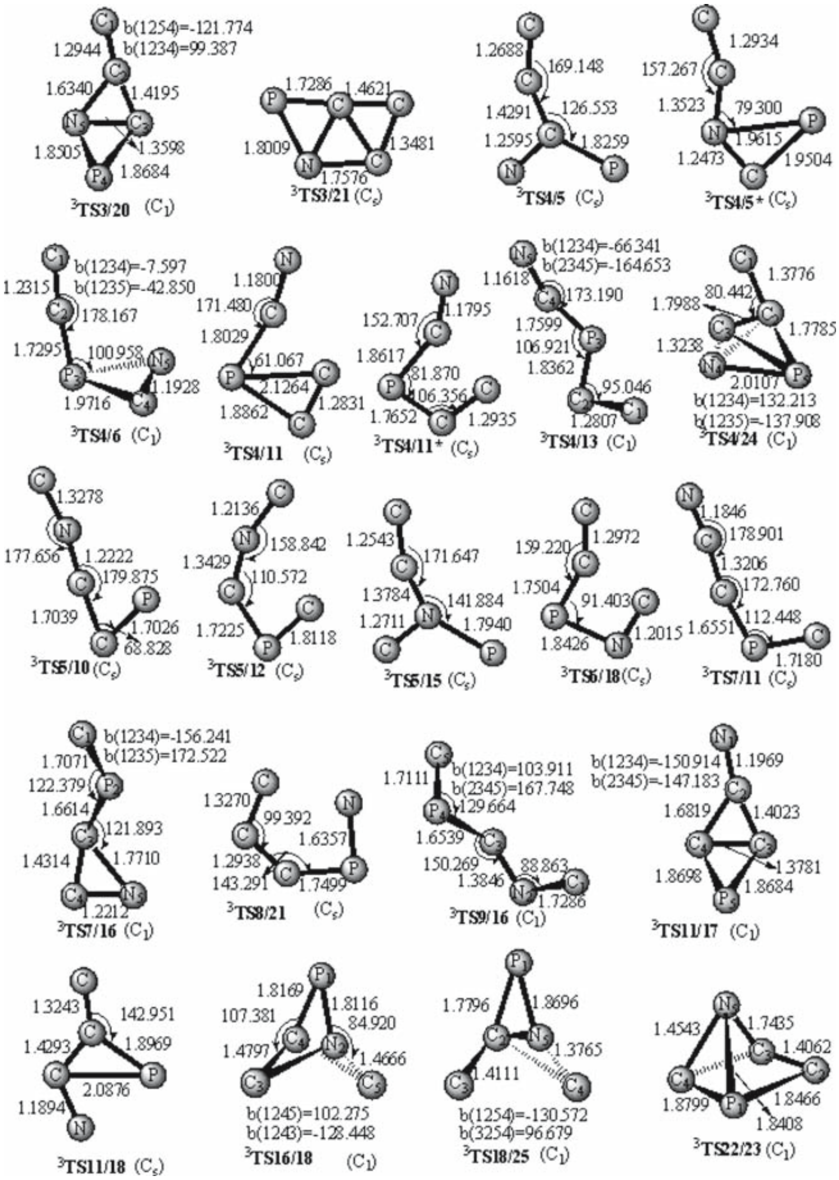


Fig. 2 Optimized geometries of interconversion transition states between the triplet NC_3P isomers at the DFT/B3LYP/6-311G(d) level. Bond lengths are in angstroms and angles in degrees

as chain-like, cyclic, cage-like, and branch-chain species. On the DFT/B3LYP/6-311G(d) level, 28 triplet isomers (shown in Fig. 1) were located on the triplet potential energy surface (PES), which are connected by 45 interconversion transition states (shown in Fig. 2). At the same time, there are 28 singlet isomers (shown in Fig. 3) on the singlet PES, which are connected by 56 interconversion transition states (shown in Fig. 4). The letter ^{S}**m** is used to denote various NC_3P isomers, and ^{S}**TSm/n** is used to denote the transition states which connect the species ^{S}**m** and ^{S}**n**. Note that the top left corner number *s* means the electronic state (1 for singlet and 3 for triplet) of the isomers or transition states. The relative energies of all the isomers and transition states are collected in Table 1. For the relevant species, the energies at the CCSD(T)//QCISD/6-311G(d)+ZPVE, CCSD(T)//DFT/B3LYP/cc-pVTZ+ZPVE, CCSD(T)//DFT/B3LYP/cc-pVTZ+ZPVE, and CASPT2//CASSCF (14,12)/cc-pVQZ levels are list in Table 2. The harmonic vibrational frequencies as well as the infrared intensities, dipole moments, and rotational constants are shown in Table 3. The possible dissociation product's energies are listed in Table 4. Finally, schematic triplet and singlet PES are presented in Figs. 5a and 6a, respectively. Figures 5b and 6b are the lowest isomerization channels for the relative isomers. Unless otherwise specified, the relative energies are at the CCSD(T)//DFT/B3LYP/6-311G(d)+ZPVE level.

Fig. 2 continued



3.1 Triplet NC_3P PES

Among the 28 triplet isomers, 11 have chain-like structures. Four isomers such as NCCCP ^{3}**1** (0.0), CNCCP ^{3}**2** (25.7), CCCNP ^{3}**3** (50.1), and CCNCP ^{3}**5**(65.0) are linear structures with the $^3\Sigma^-$ electronic state. The other chain-like isomers such as CCPCN ^{3}**4** (58.3), CCPNC ^{3}**6** (71.0), CPCCN ^{3}**7** (94.8), CCCPN ^{3}**8** (107.0), CPCNC ^{3}**9** (119.9), CCNPC ^{3}**10**(139.9), and ^{3}**10**′ (144.1) are of C_s symmetry with the ^{3} A″ electronic state.

Six C_s-symmetrized isomers with ^{3}A″ electronic state possess three-membered ring. Isomers NC-cCCP ^{3}**11** (36.3), CN-cCCP ^{3}**12** (60.2), and NC-cPCC ^{3}**13** (73.1) possess CCP ring; isomers PN-cCCC ^{3}**14** (114.1) and CP-cCNC ^{3}**15** (127.3) possess CCC and CNC rings, respectively; isomer P-cNCC-C ^{3}**16** (136.5) possess NCC three-membered ring with exocyclic NP and CC bonds. Amongst the four-membered ring isomers, C_{2v}-symmetrized N-cCCPC ^{3}**17** (85.3) and C-cNCPC ^{3}**19**(135.1) have CC cross-bonding with ^{3}**A**$_2$ and ^{3}B$_1$ electronic states, respectively; C_s-symmetrized C-cCCNP ^{3}**18** (92.6) has CP cross-bonding with ^{3}A″ electronic state; the C-cCNPC ^{3}**20** (137.7) having a CN cross-bonding is C_1 symmetrized. The only five-membered ring isomer cCC-CNP ^{3}**21** (83.8) is of C_s symmetry with ^{3}A″ electronic states.

Total four isomers can be viewed as cage-like structures. Cage-PNCCC ^{3}**22** (121.6) is C_s symmetried with ^{3}A″ electronic state and cage-PNCCC ^{3}**23** (133.0) is of C_1 symmetry. Both cage-CCCNP ^{3}**24** (132.6) and

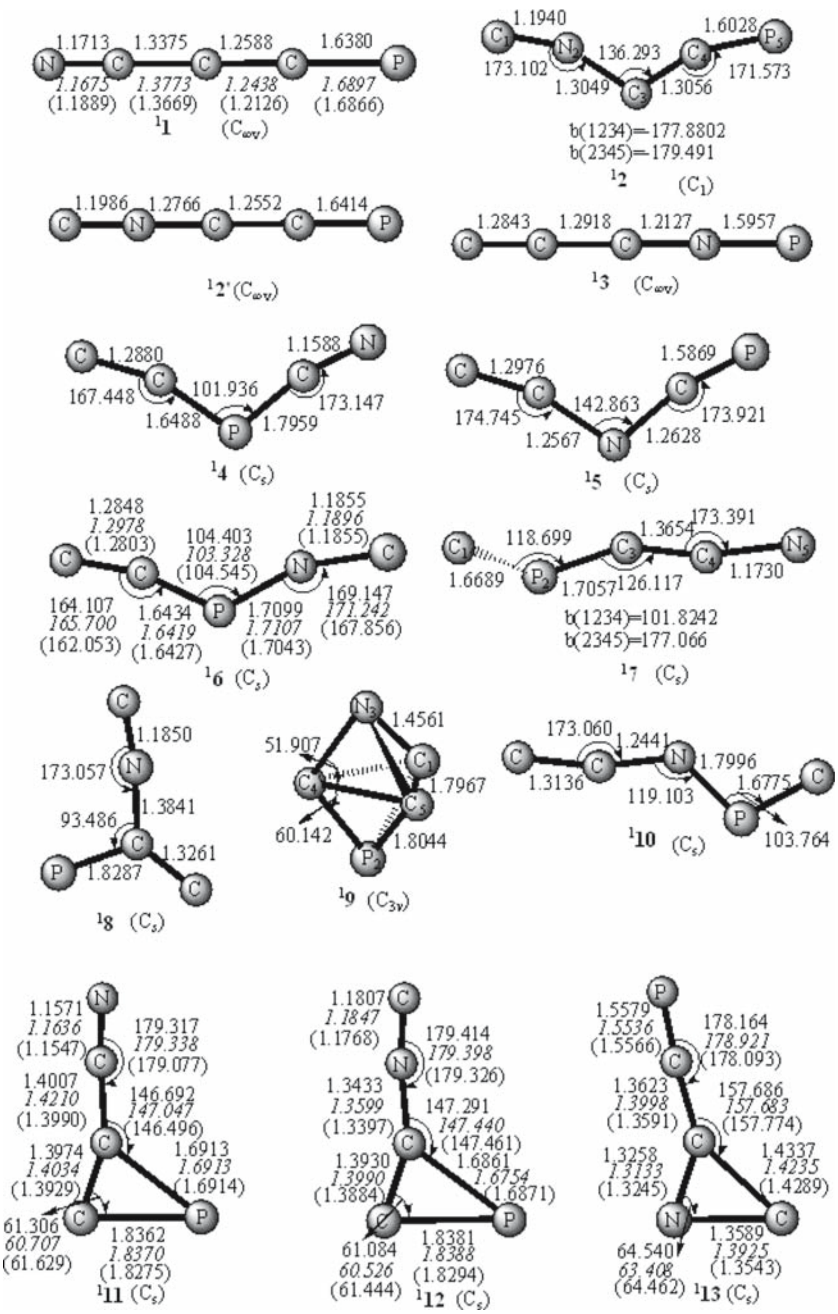
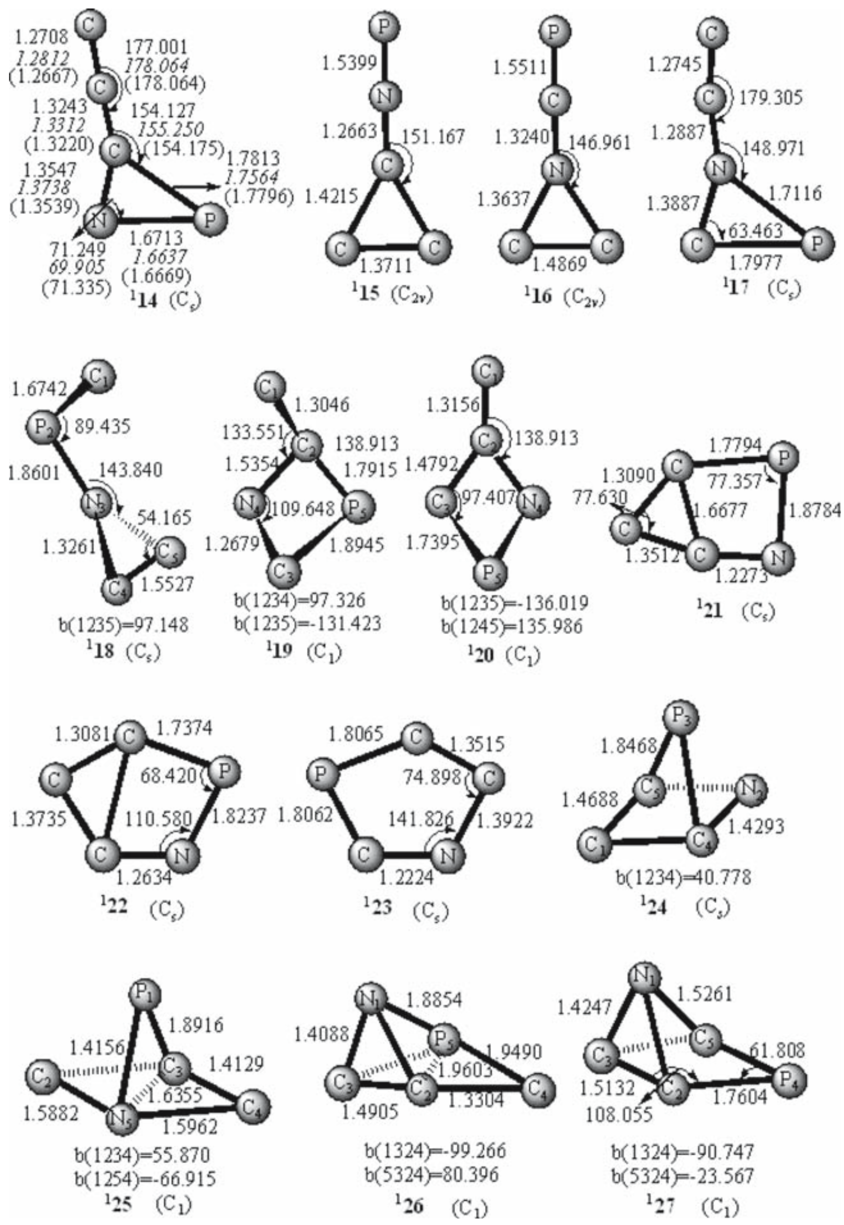


Fig. 3 Optimized geometries of the singlet NC_3P isomers at the DFT/B3LYP/6-311G(d) level. Bond lengths are in angstroms and Angles in degrees. The values obtained at the QCISD/6-311G(d) level and with the DFT/B3LYP/cc-pVTZ method for some relevant isomers are also given in italics and in parentheses, respectively

cage-PCNCC ^{3}**25** (154.6) are C_s symmetrized with $^3A'$ and $^3A''$ electronic states, respectively. Branch-chain isomers PCNC-C ^{3}**26** (141.0) and NCPC-C ^{3}**27** (158.0) are C_{2v} symmetrized with $^3A_2$ electronic state.

To discuss the kinetic stability, one needs to consider various isomerization and dissociation pathways. The lowest dissociation or isomerzation barriers usually govern the kinetic stability of isomers. From Table 4, we can see that the relative energies of the dissociation products are rather high (more than 96 kcal/mol). So the isomerization process determines the kinetic stability of NC_3P isomers. From the isomerization process depicted in Fig. 5, we can see that many cyclic, cage-like, and branch-chain structures can covert to the stable linear isomers through low isomerization barriers. These isomers are expected to be of little importance in the investigation. There are also many isomers which have high isomerization barriers such as ^{3}**1** (35.9, ^{3}**1** →^{3}**11**), ^{3}**2** (34.3, ^{3}**2** →^{3}**12**), ^{3}**3** (65.1, ^{3}**3** →^{3}**8**), ^{3}**4** (20.4, ^{3}**4** →^{3}**13**), ^{3}**5** (49.0, ^{3}**5** →^{3}**1**), ^{3}**6** (21.6, ^{3}**6** →^{3}**4**), ^{3}**9** (29.0, ^{3}**9** →^{3}**16**), ^{3}**15** (17.6, ^{3}**15** →^{3}**5**), ^{3}**22** (15.9, ^{3}**22** →^{3}**23**), and ^{3}**24** (15.5, ^{3}**24** →^{3}**4**). Considering the high relative energies

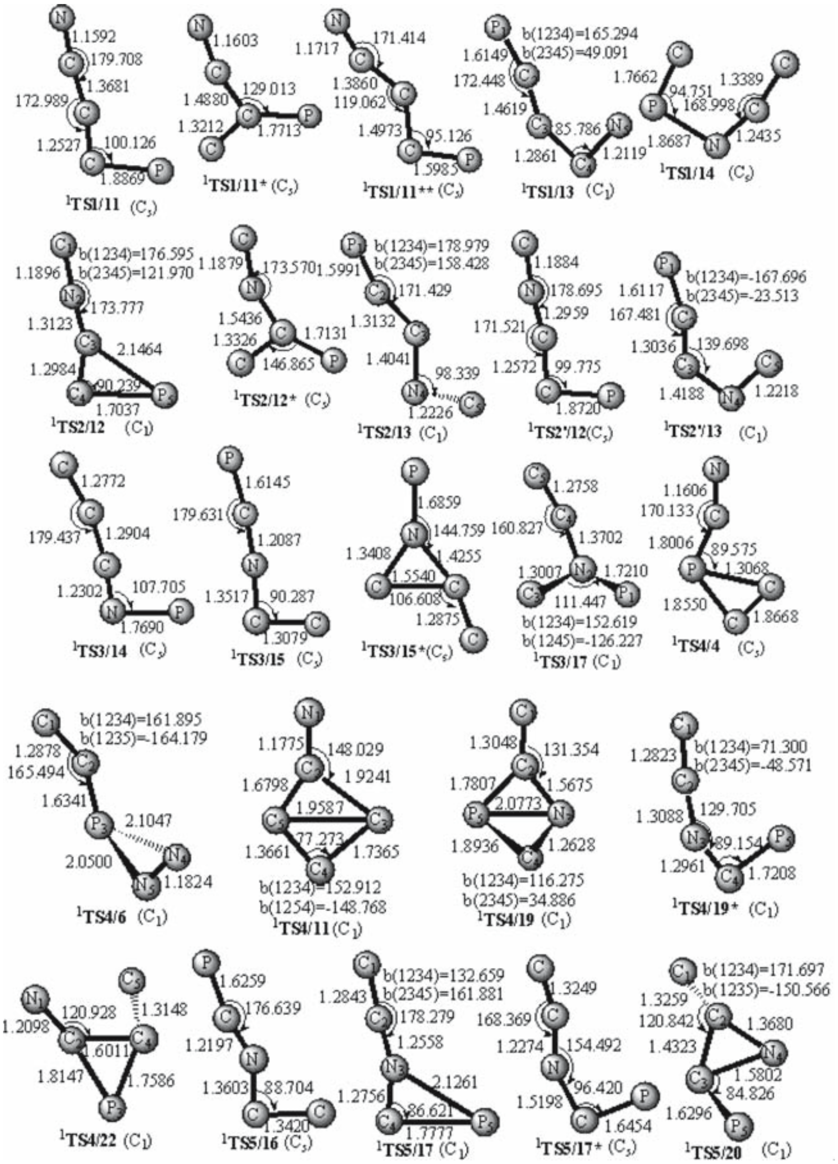
Fig. 3 continued



of isomers ^{3}**9**, ^{3}**15**, ^{3}**22**, and ^{3}**24** (more than 110 kcal/mol), only the isomers ^{3}**1**, ^{3}**2**, ^{3}**3**, ^{3}**4**, ^{3}**5**, and ^{3}**6** with considerable kinetic and thermodynamic stabilities may be detected in the laboratory or in space. Other isomers with small isomerization barriers such as ^{3}**7** (3.7, ^{3}**7** → ^{3}**11**), ^{3}**8** (8.2, ^{3}**8** → ^{3}**3**), ^{3}**10** (−1.2, ^{3}**10** → ^{3}**5**), ^{3}**11** (−0.4, ^{3}**11** → ^{3}**1**), ^{3}**12** (−0.2, ^{3}**12** → ^{3}**2**), ^{3}**13** (5.6, ^{3}**13** → ^{3}**4**), ^{3}**16** (3.4, ^{3}**16** → ^{3}**1**), ^{3}**17** (4.5, ^{3}**17** → ^{3}**11**), ^{3}**18** (4.2, ^{3}**18** → ^{3}**6**), ^{3}**20** (0.1, ^{3}**20** → ^{3}**3**), ^{3}**21** (9.1, ^{3}**21** → ^{3} **1**), ^{3}**23** (4.5, ^{3}**23** → ^{3}**22**), ^{3}**25** (1.0, ^{3}**25** → ^{3}**18**), and isomers with high relative energies such as ^{3}**10′** (144.1), ^{3}**14** (114.1), ^{3}**19** (135.1), ^{3}**26** (141.0), and ^{3}**27** (158.0) are of little importance in our research.

It is worth to mention that in order to test the stability of the isomers ^{3}**1**, ^{3}**2**, ^{3}**3**, ^{3}**4**, ^{3}**5**, and ^{3}**6**, we considered the relevant singlet isomers. The energies of triplet and singlet states at various levels are listed in Table 2. At the DFT/B3LYP/6-311G(d) level, isomers ^{1}**1** and ^{1}**3** are linear structures, while isomers ^{1}**2** and ^{1}**5** are bent structures. A singlet ^{1}**2′** with C_1 symmetry has also been found. Except ^{1}**3**, all the other singlet isomers are bent structures at higher QCISD/6-311G(d) level. From Table 2, we can conclude that the triplet isomers ^{3}**1**, ^{3}**2**, ^{3}**3**, and ^{3}**5** are more stable than their singlet counterparts (the energy differences are 21.5, 18.4, *21.4*, 18.4, and 8.8 kcal/mol, respectively). The italic value in

Fig. 4 Optimized geometries of interconversion transition states between the singlet NC$_3$P isomers at the DFT/B3LYP/6-311G(d) level. Bond lengths are in angstroms and angles in degrees



bracket is for isomer ^{1}**2**′. The triplet isomers ^{3}**4** and ^{3}**6** can transform to the relevant singlet states easily since the triplet isomers are of higher energy than the singlet ones for 19.4 and 23.3 kcal/mol, respectively. So the ^{3}**1**, ^{3}**2**, ^{3}**3**, and ^{3}**5** can be viewed as kinetically and thermodynamically stable isomers on the triplet PES.

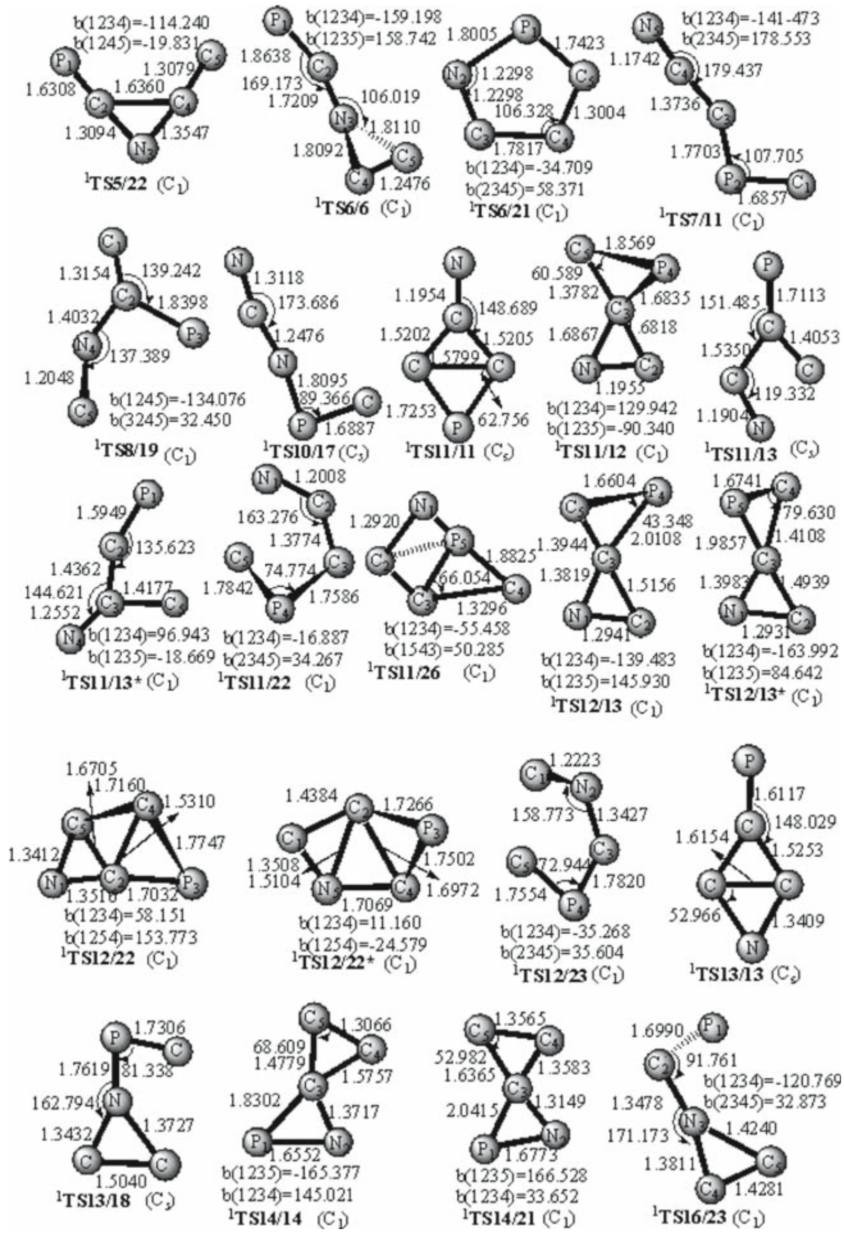
3.2 Singlet NC$_3$P PES

Except triplet isomers, there are 28 minima which have been located on the singlet PES (in Fig. 2). Amongst the nine chain-like isomers, ^{1}**1** (21.5), ^{1}**2**′(47.1), and ^{1}**3** (68.5) are linear structures with the $^1\Pi$ electronic state; except C_1 symmetrized isomers ^{1}**2** (44.0), ^{1}**7** (103.7), and ^{1}**10** (147.4), other isomers such as ^{1}**4** (67.5), ^{1}**5** (73.8), and ^{1}**6** (47.7) are all C_s symmetrized with the ^{1}A′ electronic state.

Total two three-membered ring isomers—^{1}**15** (78.3) and ^{1}**16** (84.3) are C_{2v} symmetrized with the ^{1}A$_1$ electronic state. The other six such as ^{1}**11** (17.2), ^{1}**12** (39.1), ^{1}**13** (39.8), ^{1}**14** (66.8), ^{1}**17** (108.1), and ^{1}**18** (153.6) are C_s symmetrized with the ^{1}A′ electronic state. Isomers ^{1}**19** (113.9) and ^{1}**20** (121.0) are four-membered ring structures without cross-bonding, and isomers ^{1}**21** (78.6), ^{1}**22** (83.8), and ^{1}**23** (113.5) are five-membered ring structures with CC cross-bonding in ^{1}**21** and ^{1}**22**. Isomers ^{1}**22** and ^{1}**23** are C_s symmetrized with the ^{1}A′ electronic state while ^{1}**19**, ^{1}**20**, and ^{1}**21** are C_1 symmetrized.

Amongst the five cage-like isomers ^{1}**9** (113.3), ^{1}**24** (91.5), ^{1}**25** (105.9), ^{1}**26** (108.7), and ^{1}**27** (113.7), only ^{1}**9**

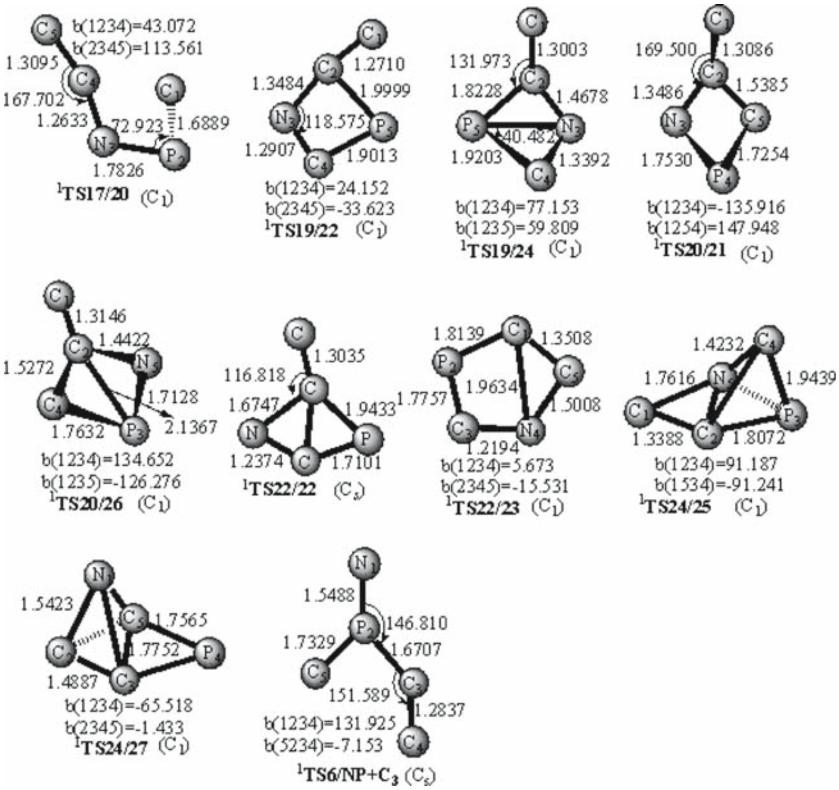
Fig. 4 continued



is of C_{3v} symmetry with the $^{1}A_{1}$ electronic state, and all the others are C_1 symmetrized. The only branch-chain isomer ^{1}**8** (118.7) is C_s symmetrized with the $^{1}A''$ electronic state.

The lowest-energy isomer of singlet PES is cyclic NC-CCP ^{1}**11**. The least isomerization barriers order of the singlet isomers is list as follows: ^{1}**11** (50.2, ^{1}**11** → ^{1}**1**) > ^{1}**1** (45.9, ^{1}**1** → ^{1}**11**) > ^{1}**5** (38.7, ^{1}**5** → ^{1}**22**) > ^{1}**12** (36.1, ^{1}**12** → ^{1}**2**) > ^{1}**16** (34.7, ^{1}**16** → ^{1}**5**) > ^{1}**13** (29.9, ^{1}**13** → ^{1}**2**) > ^{1}**24** (25.9, ^{1}**24** → ^{1}**27**) > ^{1}**2** (25.7, ^{1}**2** → ^{1}**13**) > ^{1}**17** (24.6, ^{1}**17** → ^{1}**5**) > ^{1}**14** (24.3, ^{1}**14** → ^{1}**3**) > ^{1}**2′** (22.9, ^{1}**2′** → ^{1}**16**) > ^{1}**6** (22.7, ^{1}**6** → ^{1}**4**) > ^{1}**3** (20.6, ^{1}**3** → ^{1}**15**) > ^{1}**25** (17.8, ^{1}**25** → ^{1} **24**) > ^{1}**22** (14.5, ^{1}**22** → ^{1}**4**) > ^{1}**21** (10.9, ^{1}**21** → ^{1}**6**) > ^{1}**15** (10.8, ^{1}**15** → ^{1}**3**) > ^{1}**18** (4.6, ^{1}**18** → ^{1}**13**) > ^{1}**8** (3.7, ^{1}**8** → ^{1}**19**) = ^{1}**27** (3.7, ^{1}**27** → ^{1}**24**) > ^{1}**4** (2.9, ^{1}**4** → ^{1}**6**) = ^{1}**7** (2.9, ^{1}**7** → ^{1}**11**) > ^{1}**26** (1.1, ^{1}**26** → ^{1}**11**) > ^{1}**20** (0.9, ^{1}**20** → ^{1}**21**) > ^{1}**19** (−0.4, ^{1}**19** → ^{1}**4**) > ^{1}**23** (−1.0, ^{1}**23** → ^{1}**22**) > ^{1}**10** (−1.1, ^{1}**10** → ^{1}**17**). Consider of this order, isomers ^{1}**1**, ^{1}**2**, ^{1}**2′**, ^{1}**3**, ^{1}**5**, ^{1}**6**, ^{1}**11**, ^{1}**12**, ^{1}**13**, ^{1}**14**, ^{1}**15**, ^{1}**16**, ^{1}**17**, ^{1}**21**, ^{1}**22**, ^{1}**24**, and ^{1}**25** represent considerable kinetic stability than other isomers. Among them, ^{1}**15** (78.3), ^{1}**16** (84.3), ^{1}**17** (108.1), ^{1}**21** (78.6), ^{1}**22** (83.8), ^{1}**24** (91.5), and ^{1}**25** (105.9) have high relevant energies (more than 75 kcal/mol) and of little chance to be formed. Isomers ^{1}**1**, ^{1}**2**, ^{1}**2′**, ^{1}**3**, and ^{1}**5** can convert to the counterpart triplet isomer easily (Table 2). Thus

Fig. 4 continued



only singlet ^{1}**6**, ^{1}**11**, ^{1}**12**, ^{1}**13**, and ^{1}**14** possessing large kinetic and thermodynamic stabilities can be viewed as stable isomers.

3.3 Properties of the stable isomers

From the fact mentioned above, we know that the isomers NCCCP ^{3}**1**, CNCCP ^{3}**2**, CCCNP ^{3}**3**, CCNCP ^{3}**5**, CCPNC ^{1}**6**, NC-cCCP ^{1}**11**, CN-cCCP ^{1}**12**, PC-cCNC ^{1}**13**, and CC-cCNP ^{1}**14** possess high kinetic and thermodynamic stabilities and may be observed in the laboratory or in interstellar space. We now analyze and discuss their structures and bonding natures.

On the triplet PES, four stable isomers are all linear structures with $^{3}\Sigma^{-}$ electronic states. The global minimum is NCCCP ^{3}**1** followed by CNCCP ^{3}**2** at the 25.7 kcal/mol. Their terminal CN bond lengths (1.1684 and 1.1926 Å for ^{3}**1** and ^{3}**2**, respectively) are a little longer than the normal CN triple bond (1.1486 Å) [48]. Their terminal CP bond lengths (1.6594 and 1.6661 Å for ^{3}**1** and ^{3}**2**, respectively) are between the typical CP double (1.7183 Å) and triple (1.5392 Å) bonds. The spin densities of isomer ^{3}**1** (0.391, −0.215, 0.823, −0.421, and 1.422 e for N, C, C, C, and P, respectively) and isomer ^{3}**2** (0.315, −0.123, 0.707, −0.376, and 1.477 e for C, N, C, C, and P, respectively) show that their single electrons are mainly on the terminal P atoms and secondarily on the middle C atoms. The bond lengths and the spin densities suggest that isomer ^{3}**1** resonates among the following three forms:

$|N{\equiv}C{-}C{\equiv}C\overset{\leftarrow}{-}\overset{\bullet}{\underset{\bullet}{\mathrm{P}}}$ $|N{\equiv}C{-}C{\equiv}C\overset{\leftarrow}{\equiv}\overset{\bullet}{\underset{\bullet}{\mathrm{P}}}$ and

$|\overset{\bullet}{\mathrm{N}}{=}C{=}C{=}C{=}\overset{\bullet}{\mathrm{P}}|$

while isomer ^{3}**2** resonates among

$|C\overset{\leftarrow}{\equiv}N{-}C{\equiv}C\overset{\leftarrow}{-}\overset{\bullet}{\underset{\bullet}{\mathrm{P}}}$ $|C\overset{\leftarrow}{\equiv}N{-}\overset{\bullet}{\mathrm{C}}{=}C\overset{\leftarrow}{\equiv}\overset{\bullet}{\mathrm{P}}$ and

$|\overset{\bullet}{\mathrm{C}}\overset{\leftarrow}{-}N{=}C{=}C{=}\overset{\bullet}{\mathrm{P}}|$

where "|" denotes the lone electron pair, and "•" denotes the single electron. The resonant structures are confirmed by the natural bond orbital (NBO) [49–56] analysis.

For isomer CCCNP ^{3}**3**, both of the CC bond lengths (1.2784 Å for the terminal one and 1.2955 Å for the internal one) are shorter than the normal CC double bond (1.3269 Å). Its CN bond length (1.2022 Å) is shorter than the normal CN double bond, and the NP bond (1.6255 Å) is closed to the normal NP double bond (1.6432 Å). The spin densities of the CCCNP ^{3}**3** are 0.370, −0.011, 0.240, −0.161, and 1.563 e for C, C, C, N, and P, respectively. Form the bond lengths and the

Table 1 Relative energies (kcal/mol) of the NC_3P Isomers and Transition States at the DFT/B3LYP/6-311G(d) and Single-Point CCSD(T)/6-311G(2d) Levels^a

species	B3LYP^a	ΔZPVEB3LYP^a	CCSD(T)^b //B3LYP^a	Total
NCCCP ^{3}**1**^{c}($^3\Sigma^-$)	0.0	0.0	0.0	0.0
CNCCP ^{3}**2**($^3\Sigma^-$)	26.5	−0.4	26.1	25.7
CCCNP ^{3}**3**($^3\Sigma^-$)	46.4	−0.2	50.3	50.1
CCPCN ^{3}**4**($^3A''$)	70.0	−1.4	59.7	58.3
CCNCP ^{3}**5**($^3\Sigma^-$)	58.9	−0.7	65.7	65.0
CCPNC ^{3}**6**($^3A''$)	83.3	−1.6	72.6	71.0
CPCCN ^{3}**7**($^3A''$)	99.0	−2.0	96.8	94.8
CCCPN ^{3}**8**($^3A''$)	110.3	−2.2	109.2	107.0
CPCNC ^{3}**9**($^3A''$)	124.3	−2.4	122.3	119.9
CCNPC ^{3}**10**($^3A''$)	143.5	−2.8	142.7	139.9
CCNPC ^{3}**10′**($^3A''$)	146.5	−2.6	146.7	144.1
NC-cCCP ^{3}**11**($^3A''$)	40.8	−0.4	36.7	36.3
CN-cCCP ^{3}**12**($^3A''$)	65.2	−0.9	61.1	60.2
NC-cPCC ^{3}**13**($^3A''$)	86.0	−1.5	74.6	73.1
PN-cCCC ^{3}**14**($^3A''$)	121.8	−2.8	116.9	114.1
CP-cCNC ^{3}**15**($^3A''$)	132.1	−2.5	129.8	127.3
P-cNCC-C ^{3}**16**($^3A''$)	143.5	−2.6	139.1	136.5
N-cCCPC ^{3}**17**($^3A_2$)	88.8	−1.4	86.7	85.3
C-cCCNP ^{3}**18**($^3A''$)	99.7	−1.7	94.3	92.6
C-cNCPC ^{3}**19**($^3B_1$)	145.2	−3.3	138.4	135.1
C-cCNPC ^{3}**20**	144.7	−2.5	140.2	137.7
cCCCNP ^{3}**21**($^3A''$)	90.0	−1.0	84.8	83.8
Cag-ePNCCC ^{3}**22**($^3A''$)	131.7	−1.0	122.6	121.6
cage-PNCCC ^{3}**23**	143.0	−1.5	134.5	133.0
cage-CCCNP ^{3}**24**($^3A'$)	145.2	−1.4	134.0	132.6
cage-PCNCC ^{3}**25**($^3A''$)	168.8	−2.9	157.5	154.6
cage-CNC-C ^{3}**26**($^3A_2$)	150.7	−3.2	144.2	141.0
NCPC-C ^{3}**27**($^3A_2$)	172.4	−3.1	161.1	158.0
^{3}**TS1/1**($^3A''$)	62.8	−2.0	61.6	59.6
^{3}**TS1/5**($^3A''$)	120.5	−2.5	116.5	114.0
^{3}**TS1/6**($^3A''$)	116.0	−2.2	105.9	103.7
^{3}**TS1/11**($^3A''$)	41.7	−0.8	36.7	35.9
^{3}**TS1/11***($^3A''$)	71.3	−1.7	62.0	60.3
^{3}**TS1/16**	144.5	−3.0	142.9	139.9
^{3}**TS1/17**($^3A''$)	108.5	−2.5	104.5	102.0
^{3}**TS1/21**($^3A''$)	101.0	−2.0	94.9	92.9
^{3}**TS1/21***($^3A''$)	142.2	−2.5	136.7	134.2
^{3}**TS1/25**	177.6	−3.7	167.6	163.9
^{3}**TS2/2**($^3A''$)	152.8	−3.3	148.4	145.1
^{3}**TS2/4**($^3A''$)	111.5	−2.5	103.3	100.8
^{3}**TS2/4***($^3A''$)	122.8	−3.0	116.7	113.7
^{3}**TS2/5**($^3A''$)	126.7	−2.4	123.4	121.0
^{3}**TS2/5***($^3A''$)	136.6	−1.9	131.2	129.3
^{3}**TS2/11**	99.0	−2.3	95.0	92.7
^{3}**TS2/11***($^3A''$)	123.0	−2.1	115.9	113.8
^{3}**TS2/12**($^3A''$)	65.6	−1.3	61.3	60.0
^{3}**TS2/12***($^3A''$)	106.8	−2.7	99.4	96.7
^{3}**TS2/12****	141.8	−3.2	135.3	132.1
^{3}**TS3/8**($^3A''$)	118.5	−2.7	117.9	115.2
^{3}**TS3/10**($^3A''$)	148.8	−3.1	144.8	141.7
^{3}**TS3/18**	147.3	−2.5	140.3	137.8
^{3}**TS3/20**	144.9	−2.9	140.7	137.8
^{3}**TS3/21**($^3A''$)	153.9	−3.2	148.4	145.2
^{3}**TS4/5**($^3A''$)	124.7	−2.5	119.2	116.7
^{3}**TS4/5***($^3A''$)	138.8	−2.5	133.7	131.2
^{3}**TS4/6**	105.7	−2.6	95.2	92.6
^{3}**TS4/11**($^3A''$)	101.5	−2.6	92.4	89.8

Table 1 continued

species	B3LYP^a	ΔZPVEB3LYP^a	CCSD(T) ^{b} //B3LYP^a	Total
^{3}**TS4/11**∗(^{3}A")	106.6	−2.8	100.5	97.7
^{3}**TS4/13**	91.2	−2.3	81.0	78.7
^{3}**TS4/24**	160.3	−3.1	151.2	148.1
^{3}**TS5/10**(^{3}A")	143.9	−3.2	141.9	138.7
^{3}**TS5/12**(^{3}A")	147.5	−3.0	139.3	136.3
^{3}**TS5/15**	153.6	−3.1	148.0	144.9
^{3}**TS6/18**(^{3}A")	106.5	−2.6	99.4	96.8
^{3}**TS7/11**	102.9	−2.6	101.1	98.5
^{3}**TS7/16**	158.2	−3.7	154.2	150.5
^{3}**TS8/21**(^{3}A")	145.2	−2.6	138.2	135.6
^{3}**TS9/16**	157.3	−3.8	152.7	148.9
^{3}**TS11/17**	95.0	−2.2	92.0	89.8
^{3}**TS11/18**(^{3}A")	107.4	−2.3	102.3	100.0
^{3}**TS16/18**	176.0	−3.5	164.9	161.4
^{3}**TS18/25**	169.6	−3.4	159.0	155.6
^{3}**TS22/23**	149.3	−2.1	139.6	137.5
NCCCP ^{1}**1**($^1\Pi$)	20.7	0.2	21.3	21.5
CNCCP^1**2**	45.9	−1.0	45.0	44.0
CNCCP^1**2′**($^1\Pi$)	46.9	−0.6	47.7	47.1
CCCNP^1**3**($^1\Pi$)	66.3	−0.2	68.7	68.5
CCPCN^1**4**($^1A'$)	51.1	−1.2	68.7	67.5
CCNCP^1**5**($^1A'$)	75.4	−1.0	74.8	73.8
CCPNC^1**6**($^1A'$)	59.6	−1.6	49.3	47.7
CPCCN^1**7**	115.0	−1.9	105.6	103.7
CNCC-P^1**8**(^{1}A′)	130.8	−1.8	120.5	118.7
pNCCCP^1**9**(^{1}A$_1$)	133.6	−2.3	115.6	113.3
CCNPC^1**10**	158.3	−2.8	150.2	147.4
NC-cCCP^1**11**(^{1}A′)	26.6	0.0	17.2	17.2
CN-cCCP^1**12**(^{1}A′)	47.9	−0.4	39.5	39.1
PC-cCNC^1**13**(^{1}A′)	45.5	−0.4	40.2	39.8
CC-cCNP^1**14**(^{1}A′)	73.6	−0.7	67.5	66.8
PN-cCCC^1**15**(^{1}A$_1$)	80.5	−0.9	79.2	78.3
PC-cNCC^1**16**(^{1}A$_1$)	93.2	−0.8	85.1	84.3
CC-cNCP^1**17**(^{1}A′)	114.1	−1.1	109.2	108.1
CP-cNCC^1**18**(^{1}A′)	166.5	−2.8	156.4	153.6
C-cCPCN^1**19**	127.0	−2.4	116.3	113.9
C-cCNPC^1**20**	135.0	−1.8	122.8	121.0
cCCCNP^1**21**	85.3	−0.1	78.7	78.6
cNCCPC^1**22**(^{1}A′)	92.4	−0.6	84.4	83.8
cPCNCC^1**23**(^{1}A′)	122.7	−1.3	114.8	113.5
pPCCCN^1**24**	107.5	−1.2	92.7	91.5
pPNCCC^1**25**	123.5	−2.2	108.1	105.9
pCNCCP^1**26**	122.1	−1.7	110.4	108.7
pPNCCC^1**27**	131.0	−1.7	115.4	113.7
^{1}**TS1/11**(^{1}A′)	77.3	−0.4	67.8	67.4
^{1}**TS1/11***(^{1}A′)	94.0	−1.9	84.7	82.8
^{1}**TS1/11****(^{1}A′)	99.0	2.2	89.0	91.2
^{1}**TS1/13**	80.7	−1.1	77.4	76.3
^{1}**TS1/14**(^{1}A′)	173.3	−2.9	160.4	157.5
^{1}**TS2/12**	84.6	−1.6	76.8	75.2
^{1}**TS2/12***	121.4	−3.0	113.8	110.8
^{1}**TS2/13**	76.3	−2.1	71.8	69.7
^{1}**TS2′/12**(^{1}A′)	98.3	−0.8	90.6	89.8
^{1}**TS2′/13**	76.7	−2.1	72.1	70.0
^{1}**TS3/14**(^{1}A′)	93.6	−1.0	92.1	91.1
^{1}**TS3/15**(^{1}A′)	92.1	−1.2	90.3	89.1
^{1}**TS3/15***(^{1}A′)	153.7	−2.4	149.9	147.5
^{1}**TS3/17**	164.3	−2.4	158.8	156.4

Table 1 continued

species	B3LYP[a]	ΔZPVEB3LYP[a]	CCSD(T) [b] //B3LYP[a]	Total
^{1}**TS4/4**	73.8	−2.1	60.9	58.8
^{1}**TS4/6**	83.8	−2.4	72.8	70.4
^{1}**TS4/11**	88.0	−2.0	75.3	73.3
^{1}**TS4/19**	127.0	−2.7	116.2	113.5
^{1}**TS4/19***	137.2	−1.9	130.7	128.8
^{1}**TS4/22**	113.5	−2.2	100.5	98.3
^{1}**TS5/16**($^1A'$)	120.6	−1.0	120.0	119.0
^{1}**TS5/17**	133.6	−2.1	134.8	132.7
^{1}**TS5/17***	162.2	−2.1	157.1	155.0
^{1}**TS5/20**	148.2	−2.8	139.8	137.0
^{1}**TS5/22**	119.0	−2.5	115.0	112.5
^{1}**TS6/6**	82.0	−2.1	68.3	66.2
^{1}**TS6/21**	105.2	−2.4	91.9	89.5
^{1}**TS7/11**	118.5	−2.4	109.0	106.6
^{1}**TS8/19**	135.1	−2.2	124.6	122.4
^{1}**TS10/17**($^1A'$)	158.6	−3.0	149.3	146.3
^{1}**TS11/11**($^1A'$)	85.7	−2.0	78.5	76.5
^{1}**TS11/12**	89.8	−2.1	79.3	77.2
^{1}**TS11/13**	104.4	−2.1	96.7	94.6
^{1}**TS11/13***	132.4	−2.1	118.3	116.2
^{1}**TS11/22**	121.3	−2.0	108.4	106.4
^{1}**TS11/26**	125.8	−2.3	112.1	109.8
^{1}**TS12/13**	100.4	−2.1	93.6	91.5
^{1}**TS12/13***	104.3	−2.4	97.7	95.3
^{1}**TS12/22**	111.9	−2.0	103.0	101.0
^{1}**TS12/22***	137.2	−2.8	126.3	123.5
^{1}**TS12/23**	145.6	−2.7	132.1	129.4
^{1}**TS13/13**($^1A'$)	89.0	−2.5	83.2	80.7
^{1}**TS13/18**($^1A'$)	173.3	−3.1	161.3	158.2
^{1}**TS14/14**	109.6	−2.3	101.1	98.8
^{1}**TS14/21**	111.3	−2.2	101.1	98.9
^{1}**TS16/23**	160.9	−3.3	154.1	150.8
^{1}**TS17/20**	154.8	−2.7	144.6	141.9
^{1}**TS19/22**	131.8	−2.0	120.0	118.0
^{1}**TS19/24**	134.3	−2.7	123.2	120.5
^{1}**TS20/21**	136.4	−2.0	123.9	121.9
^{1}**TS20/26**	151.4	−2.7	137.9	135.2
^{1}**TS22/22**($^1A'$)	116.6	−2.0	108.6	106.6
^{1}**TS22/23**	123.3	−2.2	114.7	112.5
^{1}**TS24/25**	139.9	−2.7	126.4	123.7
^{1}**TS24/27**	135.1	−2.5	119.9	117.4
^{1}**TS6/NP + C3**	218.0	−3.2	199.1	195.9

[a] The basis set is 6-311G(d)

[b] The basis set is 6-311G(2d)

[c] The total energy of reference isomer ^{3}**1** at DFT/B3LYP/6-311G(d) level is –510.3621738 au, and at CCSD(T)/6-311G(2d)//DFT/B3LYP/6-311G(d) level is –509.4533316 au

spin densities, the isomer can be viewed as resonating forms between

$$|C{=}C{=}C{=}N\overset{\rightarrow}{-}\overset{\bullet}{\underset{\bullet}{\mathrm{p}}}| \qquad \text{and} \qquad |C{=}C{=}\overset{\bullet}{\mathrm{C}}\overset{\leftarrow}{-}N{=}\overset{\bullet}{\mathrm{p}}|$$

The CC bond length of isomer CCNCP ^{3}**5** (1.2990 Å) is shorter than the normal CC double bond, and both of the CN bond lengths (1.2385 Å for the one connected to the terminal C and 1.2291 for the other one) are close to the normal CN double bond (1.2409 Å). The CP bond length (1.6142 Å) is between the normal CP double (1.7183 Å) and triple (1.5392 Å) bonds. The spin densities (0.775, 0.092, 0.433, −0.370, and 1.071 e for C, C, N, C, and P, respectively) suggest that the isomer is resonated between

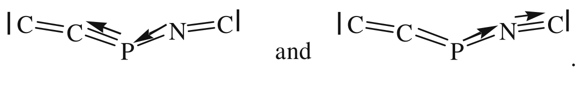
Table 2 Relative Single-Point Energies (kcal/mol) of the relevant Triplet and Singlet NC_3P Isomers at the CCSD(T)//DFT/B3LYP, CCSD(T)//QCISD, and CASPT2//CASSCF levels

species	state	CCSD(T)[b]//DFT/ B3LYP[a] + ZPVE	CCSD(T)[b] //QCISD[a] + ZPVE	CCSD(T)[c] //DFT/B3LYP[c] + ZPVE	CASPT2[d] //CASSCF[d]
NCCCP ^{3}**1**[e]	$^3\Sigma^-$	0.0	0.0	0.0	0.0
NCCCP ^{1}**1**	$^1\Pi$ (^{1} A′)[f]	21.5	19.7	20.0	
CNCCP ^{3}**2**	$^3\Sigma^-$	25.7	25.9	26.1	28.9
CNCCP ^{1}**2**	^{1} A′	47.1	45.7	46.4	
CNCCP ^{1}**2**′		44.1	44.5	44.2	
CCCNP ^{3}**3**	$^3\Sigma^-$	50.1	49.8	49.3	50.6
CCCNP ^{1}**3**	$^1\Pi$	68.5	66.7	66.8	
CCPCN ^{3}**4**	^{3} A′	58.3	60.3	59.6	63.3
CCPCN ^{1}**4**	^{1} A′	38.9	40.7	40.5	
CCNCP ^{3}**5**	$^3\Sigma^-$	65.0	64.4	64.6	61.7
CCNCP ^{1}**5**	^{1} A′	73.8	73.5	74.1	
CCPNC ^{3}**6**	^{3} A′	71.0	73.4	72.7	80.5
CCPNC ^{1}**6**	^{1} A′	47.7	49.5	49.2	59.7
NC-cCCP ^{3}**11**	^{3} A′	36.3	36.0	34.3	
NC-cCCP ^{1}**11**	^{1} A′	17.3	17.2	16.0	24.0
CN-cCCP ^{3}**12**	^{3} A′	60.2	60.1	58.4	
CN-cCCP ^{1}**12**	^{1} A′	39.1	38.9	37.6	46.6
CN-cCCP ^{1}**13**	^{1} A′	39.8	39.1	38.2	47.4
CN-cCCP ^{1}**14**	^{1} A′	66.8	66.2	64.2	70.1

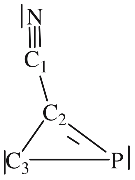
[a] The basis set is 6-311G(d)
[b] The basis set is 6-311G(2df)
[c] The basis set is cc-pVTZ
[d] The cc-pVQZ basis set and 14*12 electrons and active orbitals are used for the CASSCF and CASPT2 methods
[e] at the QCISD/6-311G(d) level is –509.3788281 au, at the CCSD(T)/6-311G(2df)// QCISD/6-311G(d) level is –509.5282328 au, at the DFT/B3LYP/cc-pVTZ level is –510.3859173 au, at CCSD(T)/6-311G(2d)//DFT/cc-pVTZ level is –509.5441711 au, and at the CASPT2//CASSCF(14,12) level is –509.7236452 au. The ZPVE at DFT/B3LYP/6-311G(d), QCISD/6-311G(d) and DFT/B3LYP/cc-pVTZ level are 0.017425, 0.016883, and 0.017368 au
[f] The electronic states at the QCISD/6-311G(d) level

$\dot{\mathrm{C}} \equiv C \overset{\leftarrow}{\equiv} N{=}C{=}\dot{\mathrm{p}}\,|$ and $\dot{\mathrm{C}} \equiv C-\dot{\mathrm{N}} \overset{\rightarrow}{-} C \equiv \mathrm{p}\,|$

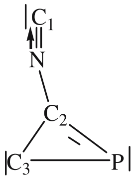
The singlet isomer CCPNC ^{1}**6** is a chain-like structure with ^{1}A′ electronic state. Its CC bond length (1.2848 Å) is close to the normal CC double bond, and the CP bond length (1.6434 Å) is between the normal double and triple bonds. The PN bond length (1.7099 Å) is a little longer than the double bond (1.6432 Å), and the NC bond length (1.1885 Å) is between the double and triple bond. From the bond lengths and the result of NBO analysis, the isomer can be viewed as resonance structures between



Three-membered-ring isomers NC-cCCP ^{1}**11** and NC-cCCP ^{1}**12** are of interest with considerable kinetic stability on the singlet PES. Formally, these two isomers can be considered as the products when the P-atom attacks the terminal CC triple bond of the linear NCCC and CNCC isomers. In both of the two isomers, the bond lengths of C_2P (1.6913 Å for isomer ^{1}**11** and 1.6861 Å for isomer ^{1}**12**) are shorter than the bond lengths of C_3P (1.8362 Å for isomer ^{1}**11** and 1.8381 Å for isomer ^{1}**12**). Considering the bond lengths and the result of NBO analysis, the following forms can describe the structures of isomers ^{1}**11** and ^{1}**12**, respectively.



^{1}**11**



^{1}**12**

Three-membered-ring isomer PC-cCNC ^{1}**13** is of C_s symmetry with ^{1}A′ electronic state. Its PC bond length is 1.5579 Å, only a little longer than the typical CP

Table 3 Harmonic Vibrational Frequencies (cm^{-1}), Infrared Intensities (km/mol) (in Parentheses), Dipole Moment (Debye), and Rotational Constants (GHz) of the Relevant NC$_3$P Structures at the DFT/B3LYP/6-311G(d), QCISD/6-311G(d)^{a}, and DFT/B3LYP/ cc-pVTZ Levels^{b}

isomers	frequencies (cm^{-1}) (km·mol^{-1})	Dipole moment	rotational constant
NCCCP $^{3}\mathbf{1}$	125 (1) 125 (1) 354 (6) 354 (6) 522 (2) 522 (2) 537 (3) 1084 (1) 1851 (1) 2175 (14)	3.1382	1.42951
NCCCP $^{3}\mathbf{1}^{a}$	121 (2) 121 (1) 281 (3) 281 (3) 486 (4) 486 (4) 507 (6) 1024 (13) 1867 (1) 2237 (9)	3.2478	1.392095
NCCCP $^{3}\mathbf{1}^{b}$	122 (2) 122 (2) 353 (7) 353 (7) 507 (2) 507 (2) 534 (4) 1080 (2) 1863 (1) 2181 (15)	3.2466	1.424638
CNCCP $^{3}\mathbf{2}$	129 (1) 129 (1) 314 (4) 314 (4) 417 (1) 417 (1) 545 (2) 1126 (0) 1922 (12) 2039 (78)	1.9271	1.497862
CNCCP $^{3}\mathbf{2}^{a}$	126 (1) 126 (1) 281 (4) 281 (4) 386 (1) 386 (1) 514 (12) 1077 (4) 1964 (3) 2159 (241)	2.1082	1.466766
CNCCP $^{3}\mathbf{2}^{b}$	129(1) 129 (1) 315 (5) 315 (5) 423 (1) 423 (1) 542 (3) 1125 (0) 1930 (9) 2048 (78)	2.0439	1.501988
CCCNP $^{3}\mathbf{3}$	118 (3) 118 (3) 253 (6) 253 (6) 527 (16) 527 (16) 562 (10) 1081 (12) 1906 (114) 2166 (816)	4.967	1.550147
CCCNP $^{3}\mathbf{3}^{a}$	103 (2) 103 (2) 208 (3) 208 (3) 535 (60) 538 (27) 538 (27) 1065 (52) 1945 (68) 2204 (2081)	5.8077	1.527138
CCCNP $^{3}\mathbf{3}^{b}$	116 (4) 117 (3) 251 (6) 252 (6) 520 (9) 520 (9) 562 (10) 1083 (11) 1910 (106) 2158 (874)	5.1516	1.556194
CCNCP $^{3}\mathbf{5}$	123 (5) 123 (5) 317 (9) 317 (9) 436 (0) 436 (0) 604 (3) 1124 (83) 1751 (0) 1919 (471)	4.1377	1.56277
CCNCP $^{3}\mathbf{5}^{a}$	116 (4) 116 (4) 315 (10) 315 (10) 399 (0) 339 (0) 609 (5) 1062 (115) 1586 (28)1872 (355)	4.3560	1.551922
CCNCP $^{3}\mathbf{5}^{b}$	123 (5) 125 (5) 318 (8) 319 (8) 436 (0) 437 (0) 600 (5) 1120 (103) 1753 (2) 1914 (514)	4.3585	1.567836
CCPNC $^{1}\mathbf{6}$	99 (5) 122 (4) 179 (0) 201 (0) 431 (15) 654 (165) 829 (29) 1903 (744) 2082 (441)	2.9520	14.79872, 2.66225, 2.25634
CCPNC $^{1}\mathbf{6}^{a}$	89 (2) 100 (4) 184 (0) 202 (0) 446 (17) 670 (203) 831 (12) 1878 (678) 2089 (476)	2.9606	13.81059, 2.71259, 2.26727
CCPNC $^{1}\mathbf{6}^{b}$	100 (7) 121 (7) 179 (0) 203 (0) 428 (8) 661 (155) 835 (28) 1906 (749) 2089 (437)	2.9669	15.46287, 2.64763, 2.26056
NC-cCCP $^{1}\mathbf{11}$	187 (7) 227 (11) 521 (2) 567 (1) 614 (1) 719 (1) 1050 (11) 1463 (9) 2315 (1)	3.4907	18.65982, 2.58257, 2.26859
NC-cCCP $^{1}\mathbf{11}^{a}$	189 (8) 225 (9) 518 (2) 555 (1) 614 (1) 731 (1) 1087 (13) 1493 (10) 2316 (1)	3.6555	18.61760, 2.55742, 2.24855
NC-cCCP $^{1}\mathbf{11}^{b}$	184 (8) 226 (13) 515 (2) 556 (0) 616 (1) 720 (1) 1042 (9) 1464 (9) 2311 (0)	3.5064	18.77818, 2.58915, 2.27542
CN-cCCP $^{1}\mathbf{12}$	179 (4) 191 (6) 453 (4) 491 (3) 625 (1) 732 (3) 1089 (19) 1477 (42) 2146 (326)	3.1018	18.88653, 2.78105, 2.42410
CN-cCCP $^{1}\mathbf{12}^{a}$	174 (4) 182 (4) 453 (6) 477 (3) 627 (1) 744 (8) 1126 (21) 1506 (57) 2167 (392)	3.3396	18.80126, 2.76358, 2.40942
CN-cCCP $^{1}\mathbf{12}^{b}$	180 (5) 192 (7) 450 (4) 493 (3) 631 (2) 731 (3) 1082 (18) 1477 (39) 2150 (307)	3.1126	19.10182, 2.78684, 2.43202
PC-cCNC $^{1}\mathbf{13}$	173 (0) 178 (0) 501 (12) 567 (27) 572 (1) 995 (16) 1176 (19) 1478 (20) 1741 (19)	3.2478	42.84555, 2.00154, 1.91221
PC-cCNC $^{1}\mathbf{13}^{a}$	169 (0) 175 (0) 510 (15) 560 (29) 565 (1) 1002 (12) 1268 (27) 1510 (4) 1781 (8)	3.5846	40.89163, 1.98802, 1.89585
PC-cCNC $^{1}\mathbf{13}^{b}$	174 (0) 175 (0) 504 (10) 572 (1) 572 (27) 1000 (16) 1174 (20) 1473 (17) 1731 (18)	3.3995	43.10871, 2.00828, 1.91888
CC-cCNP $^{1}\mathbf{14}$	147 (8) 161 (4) 443 (0) 458 (1) 609 (32) 770 (0) 1013 (50) 1501 (70) 2062 (985)	6.5969	21.87428, 2.57179, 2.30123
CC-cCNP $^{1}\mathbf{14}^{a}$	126 (5) 159 (2) 440 (2) 461 (2) 646 (18) 790 (10) 1040 (21) 1492 (129) 2032 (1247)	6.8383	22.02685, 2.56692, 2.29900
CC-cCNP $^{1}\mathbf{14}^{b}$	159 (11) 164 (5) 444 (0) 497 (1) 608 (30) 770 (1) 1018 (47) 1500 (72) 2062 (1001)	6.7305	21.98304, 2.57980, 2.30885

Table 4 Relative Energies (kcal/mol) of the Possible Dissociation Products of NC_3P isomers at the DFT/B3LYP/6-311G(d) and Single-Point CCSD(T)/6-311G(2d) Levels

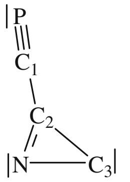
species	B3LYP[b]	ΔZPVE B3LYP[b]	CCSD(T)[c] //B3LYP[b]	Total
$C(^1D) + NCCP(^1\Sigma)$[a]	169.1	−2.2	146.7	144.5
$C(^1D) + CNCP(^1\Sigma)$	192.9	−2.6	171.3	168.7
$C(^1D) + CCNP(^1\Sigma)$	232.0	−2.8	213.6	210.8
$C(^3P) + NCCP(^1\Sigma)$	127.0	−2.2	110.5	108.3
$C(^3P) + CNCP(^1\Sigma)$	150.8	−2.6	135.1	132.5
$C(^3P) + CCNP(^1\Sigma)$	190.0	−2.8	177.4	174.6
$N(^2D) + CCCP(^2\Pi)$	226.5	−3.4	203.9	200.5
$P(^2D) + CCCN(^2A')$	156.5	−2.5	113.1	110.6
$P(^2D) + CNCC(^2A')$	180.4	−2.7	136.8	134.1
$P(^2D) + cNCCC(^2B_1)$	210.9	−3.9	198.7	194.8
$CC(^1\Sigma_g) + NCP(^3\Sigma)$	177.1	−3.5	138.3	134.8
$CC(^1\Sigma_g) + NPC(^3\Sigma)$	289.6	−5.5	248.3	242.8
$CC(^1\Sigma_g) + PNC(^3\Sigma)$	191.0	−3.7	152.1	148.4
$CC(^3\Pi_u) + NCP(^3\Sigma)$	154.4	−3.7	172.3	168.6
$CC(^3\Pi_u) + NPC(^3\Sigma)$	266.9	−5.7	282.3	276.6
$CC(^3\Pi_u) + PNC(^3\Sigma)$	168.4	−4.0	186.2	182.2
$NC(^2\Sigma) + CCP(^2\Pi)$	133.9	−3.6	105.5	101.9
$NC(^2\Sigma) + CPC(^2A'')$	224.9	−5.2	189.8	184.6
$PC(^2\Sigma) + CCN(^2\Sigma)$	173.7	−4.0	120.7	116.7
$PC(^2\Sigma) + CNC(^2\Pi)$	171.7	−4.5	119.7	115.2
$NP(^1\Sigma) + CCC(^1\Sigma_g)$	117.2	−3.8	100.3	96.5
$NP(^3\Pi) + CCC(^1\Sigma_g)$	208.0	−3.4	197.5	194.1
$NP(^1\Sigma) + CCC(^3\Pi_u)$	167.4	−5.4	155.2	149.8
$NP(^3\Pi) + CCC(^3\Pi_u)$	258.2	−5.8	252.5	246.7

[a] The total energies of reference isomer ^{3}**1** at the DFT/B3LYP and single point CCSD(T) levels as well as the ZPVE at the DFT/B3LYP level are listed in footnote *c* of Table 1. The symbols in parentheses of the column denote the electronic states

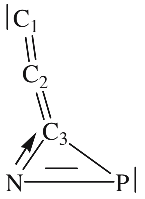
[b] The basis set is 6-311G(d)

[c] The basis set is 6-311G(2d)

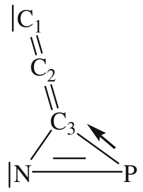
triple bond. The CC bond lengths (1.3623 for C_1C_2 and 1.4337 Å for C_2C_3) and the CN bond lengths (1.3258 Å for C_2N and 1.3589 Å for C_3N) are between the normal single and double bonds. The bond lengths and the NBO analysis suggest the following Lewis structure:



Three-membered-ring isomer CC-cCNP ^{1}**14** is of C_s symmetry with a $^1A'$ electronic state. Both the CC bonds (1.2708 Å for C_1C_2 and 1.3243 Å for C_2C_3) are close to the normal CC double length (1.3269 Å). The CN (1.2547 Å) and CP bond (1.7813 Å) are between the normal single and double bond lengths. The NP bond length (1.6713 Å) is very close to the normal NP double bond.



and



In order to investigate the validity of the computational approaches used in the present paper, the structures (in Fig. 1) and spectroscopic properties (in Table 3) of the most relevant species ^{3}**1**, ^{3}**2**, ^{3}**3**, ^{3}**5**, ^{1}**6**, ^{1}**11**, ^{1}**12**, ^{1}**13**, and ^{1}**14** are calculated at the QCISD/6-311G(d) and DFT/B3LYP/cc-pVTZ levels. At the same time, the single-point energies are carried out using the further CCSD(T)/6-311G(2df) and CCSD(T)/cc-pVTZ methods. The values are in good agreement with the DFT/B3LYP/6-311G(d)-based results and thus the one-particle basis sets 6-311G(d) and 6-311G(2d) are enough for the prediction of the species' geometries, spectros-

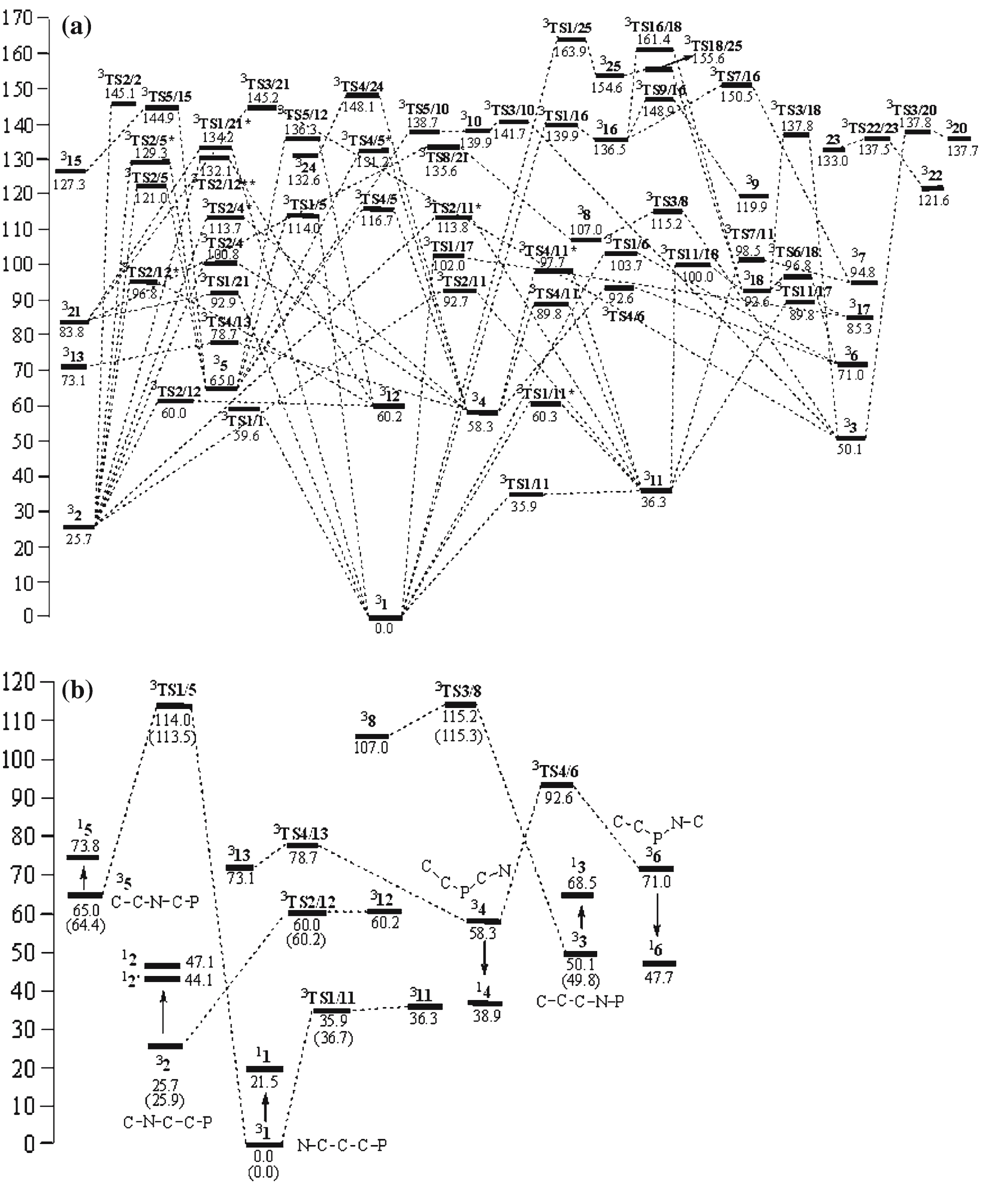


Fig. 5 **(a)** Schematic potential energy surface of the triplet NC3P at the CCSD(T)/ 6-311G(2d)//DFT/B3LYP/6-311G(d)+ZPVE level. **(b)** The lowest isomerization channels for the relative isomers. The values in parentheses for the relevant species ^{3} **1**, ^{3} **2**, ^{3} **3**, and ^{3} **5** are obtained at the CCSD(T)/6-311G(2df)// QCISD/6-311G(d)+ZPVE level

copies, and energies. At the DFT/B3LYP/6-311G(d) level, the $< S^2 >$ values of the triplet isomers are close to the expected value 2.0 of a pure triplet state (2.0638, 2.0494, 2.0364, and 2.0786 for ^{3}**1**, ^{3}**2**, ^{3}**3**, and ^{3}**5**, respectively), indicating that the spin contamination is small enough to be neglected.

The harmonic vibrational frequencies, infrared intensities, dipole moments, and rotational constants of the relevant isomers at various levels have been listed in Table 3. It can be seen that almost all the relevant isomers are reasonable for microwave detection with large dipole moment. The dominant vibrational frequencies give another way to detect them. Moreover, the CASPT2//CASSCF calculations are performed to check the multi-configurational properties of the isomers. The geometrical structures and relative energies at the CASPT2//CASSCF level are in good agreement with the DFT/B3LYP/6-311G(d) and QCISD/6-311G(d) results. The leading electronic configurations occupied by ^{3}**1**, ^{3}**2**, ^{3}**3**, ^{3}**5**, ^{1}**6**, ^{1}**11**, ^{1}**12**, ^{1}**13**, and ^{1}**14** (88.60%, 88.48%, 88.36%, 80.67%, 83.11%, 87.01%, 87.13%, 87.07%, and 85.29%, respectively) indicate that both the triplet and the singlet state of NC_3P system have negligible multi-configurational effects, and the DFT/B3LYP method is adequate for the calculations of the structures, vibrational spectra, and energies.

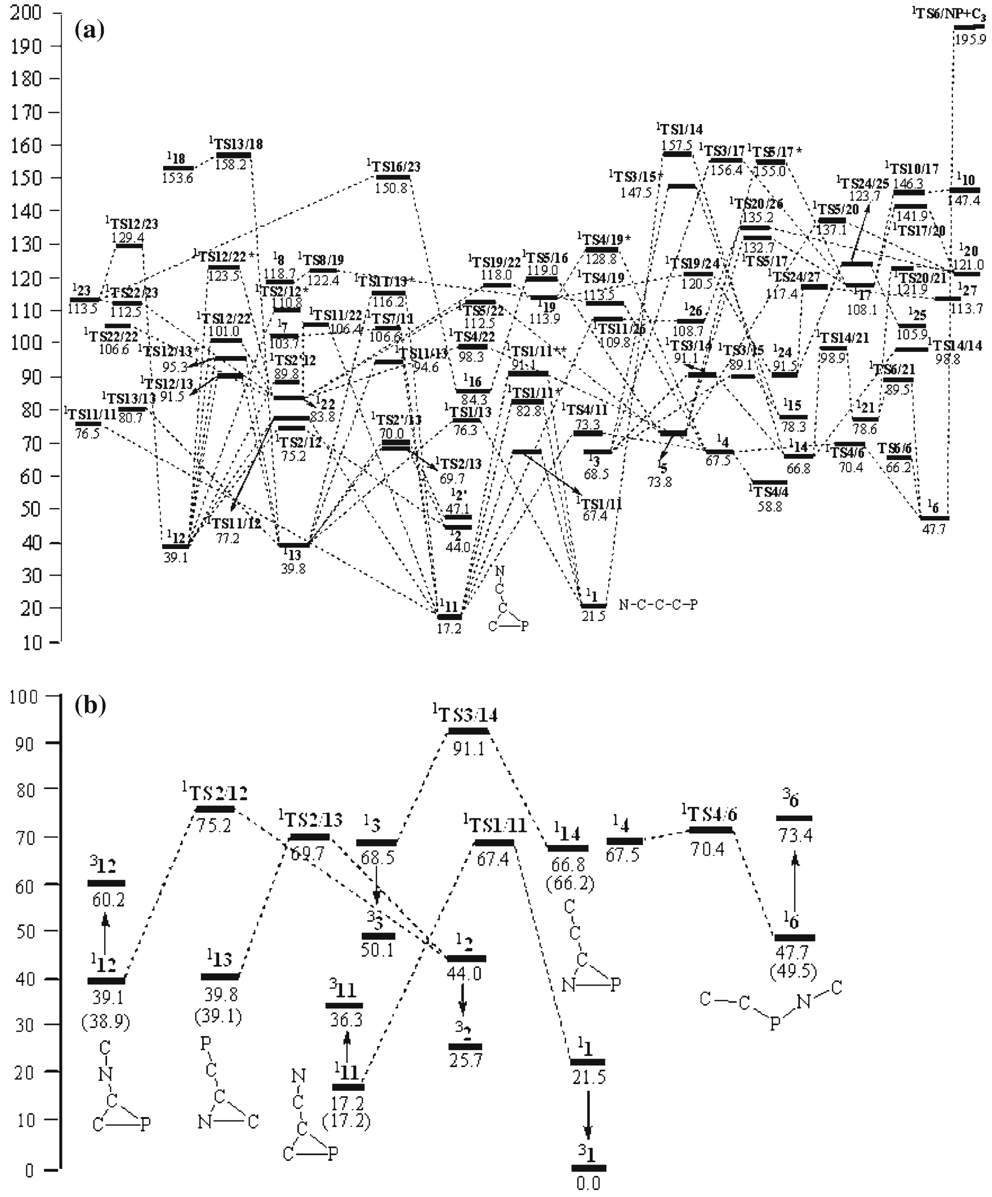


Fig. 6 **(a)** Schematic potential energy surface of the singlet NC_3P at the CCSD(T)/ 6-311G(2d)//DFT/B3LYP/6-311G(d)+ZPVE level. **(b)** The lowest isomerization channels for the relative isomers. The values in parentheses for the relevant species ^{1} **6**, ^{1} **11**, ^{1} **12**, and ^{1} **14** are obtained at the CCSD(T)/6-311G(2df)// QCISD/6-311G(d)+ZPVE level

3.4 Comparison with analogous species

It is desirable to compare the NC_3P isomers with the isovalent NC_3N and NC_2P species which have been previously studied. In the available experimental data [32], the linear triplet NCCCN isomer is the ground state on NC_3N potential energy surface. Two kinds of resonance structures were suggested as $|N{\equiv}C{-}{}^{\bullet}C^{\bullet}{-}C{\equiv}N| \longleftrightarrow {}^{\bullet}|N{=}C{=}C{=}C{=}N|^{\bullet}$ [30] and $|N{\equiv}C{-}C{\equiv}C{-}{}^{\bullet}N|^{\bullet} \longleftrightarrow {}^{\bullet}|N{=}C{=}C{=}C{=}N|^{\bullet}$ [31] with $^3\Sigma_g^-$ electronic state. Both of the two opinions express a resonance of hyperconjugate multiple bond and cumulene bond. Considering the spin density on the center C atom, the former resonance structure will be more accurate. Compare with the first row N atom, the second row P atom processes fewer tendencies to form π-bonding with C atom, because the C and N atoms use the $2p$ orbital to form π-bonding, while P atom uses the $3p$ orbital. The ground isomer NCCCP ^{3}**1**with $^3\Sigma^-$ electronic state can be viewed as resonating among

$$|N \equiv C{-}C \equiv C \leftrightarrows \overset{\bullet}{\underset{\bullet}{\mathrm{P}}} \qquad |N \equiv C{-}C \equiv C \leftrightarrows \overset{\bullet}{\underset{\bullet}{\mathrm{P}}} \quad \text{and}$$

$$|\overset{\bullet}{\mathrm{N}} \equiv C{=}C{=}C{=}\overset{\bullet}{\mathrm{P}}|$$

The linear NCCP, CNCP, and CCNP are kinetically stable isomers of NC_2P, whereas no three-membered-ring or cyclic isomers can be located as minima on NC_2P's PES. Singlet NCCP ($|N{\equiv}C{-}C{\equiv}P|$) is the most stable species with CP triple bond. On the contrary, triplet NCCCP isomer (resonate among $|N \equiv C{-}C \equiv C \overset{\leftarrow}{=} \underset{\bullet}{\overset{\bullet}{\mathrm{P}}}$ $|N \equiv C{-}\overset{\bullet}{\mathrm{C}}{=}C \overset{\leftarrow}{=} \overset{\bullet}{\mathrm{P}}$ and $|\overset{\bullet}{\mathrm{N}} \equiv C{=}C{=}C{=}\overset{\bullet}{\mathrm{P}}|$) is the ground species of NC_3P. For those species contain $2n+2$ π-electrons, when the n is odd number (NCCP), the highest π orbitals are completed occupied, giving rise to a closed-shell electron configuration and a $^1\Sigma$ electronic ground state. For n even (NCCCP), however, the highest doubly degenerate π orbital is occupied with only two electrons and the lowest electronic state is the $^3\Sigma$ state.

4 Conclusions

The potential energy surface of triplet and singlet NC_3P is theoretically investigated by means of the DFT/B3LYP/6-311G(d) and single-point CCSD(T)/6-311G(2d) methods to determine the structures, energies, vibrational frequencies, and kinetic stability of possible low-lying isomers. Total four triplet and five singlet NC_3P isomers can be kinetically and thermodynamically stable toward isomerization and dissociation. Among them, the triplet isomer NCCCP is the ground state, and other stable triplet isomers are all linear structures. Singlet ^{1}**6** is bent structure with C_s symmetry and singlet isomers ^{1}**11**, ^{1}**12**, ^{1}**13**, and ^{1}**14** are all three-membered-ring structures. The similarities and discrepancies between the NC_3P and the other analogous molecules such as NC_3N and NC_2P are compared and discussed. The NC_2P has a singlet ground isomer while the NC_3N and the NC_3P have triplet ground isomers. We hope that our calculations may be useful for future laboratory or interstellar detection of the NC_3P molecular.

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48. For parallel comparison, the following bond distances are calculated at the DFT/B3LYP/6-311G(d,p) (p for H atom) level (with frequency confirmation as stationary points) for the model systems NH_2CH_3, NCH_2, NCH, CH_3CH_3, CH_2CH_2, CHCH, CH_3PH_2, CH_2PH, CHP, PNH_3, PNH_2, and PNH respectively: N–C (1.4664 Å), N=C (1.2409 Å), N≡C (1.1486 Å), C–C (1.5305 Å), C=C (1.3269 Å), C≡C (1.1981 Å), C–P (1.8730 Å), C=P (1.7183 Å), C≡P (1.5392 Å), N–P (1.9927 Å), N=P (1.6432 Å), N≡P (1.5527 Å).
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