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Theoretical Calculations on the NCCP Potential Energy Surface

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Ab initio and density functional theory (DFT) calculations have been used to study the isomerization process in the C−cyanophosphaethyne (NCCP) system. Minima and transition states have been optimized at the B3LYP/6-311G(2d) level, and single-point energies have been determined at the CCSD(T)/6-311G(2d) level. The lowest energy isomer is found to be the N≡C−C≡P isomer with $C_{\infty v}$ symmetry. The optimized geometry, rotational constant, and dipole moment are in good agreement with experiment. The heat of formation ($\Delta H°_{f,298.15K}$) of N≡C−C≡P has been computed to be 87.1 kcal/mol using an isodesmic reaction with G3 theory.

I. Introduction

Interstellar species have been of interest to chemists because of their unusual structures and reactivities.[1,2] Well-known compounds are carbon-chain rich interstellar molecules (e.g., C_nH, $n = 2, 3, 4, ...$)[2,3] and cyanocarbon species (e.g., $HC_{2n+1}N$, C_nN_n, $n = 1, 2, 3, ...$).[2]

In interstellar space, phosphorus and nitrogen-containing compounds such as CP and CN radicals have also been detected;[2,4] hence it might be possible to find new species such as C−cyanophosphaethyne (NCCP) by radio astronomy. It is known that Jupiter and Saturn have a rich phosphorus chemistry as well as a rich nitrogen and hydrocarbon chemistry in their atmospheres.[2] It is possible that reactions between known species such as CP and CN may produce NCCP in the atmospheres of these two planets, since it is known that CN radicals dimerize to form C_2N_2 in Titan's atmosphere.[5] While the astronomical observation of NCCP has not yet been reported, the laboratory microwave spectrum and dipole moment measurement have been known[6,7] from the reaction between cyanogen azide (NCN_3) and phosphaethyne (HCP) at high temperature (ca. 700 °C). Botschwina and co-workers newly reinvestigated the rotational spectrum of the NCCP by millimeter-wave spectroscopy and evaluated the accurate equilibrium structure of NCCP combined with coupled cluster calculations.[8]

Cyanogen (NCCN), isovalent to NCCP, has already been studied extensively by experiment and theory.[9] NCCN has recently attracted the attention of chemists due to the coordinative behavior of its isomer (CNCN) which acts as a π-acid ligand similar to CO.[10] In addition, cyanogen and related compounds have the potential of a high nonlinear optical (NLO) response.[11]

Recently, theoretical calculations have been made on another isovalent compound, 1,4-diphosphabutadiyne (PCCP), which is a known ligand with transition metals and may also exist in the interstellar medium.[12−14] In this sense, NCCP is a bridge between NCCN and PCCP with intermediate physical properties. Indeed, it is possible that theoretical calculations of NCCP may help to interpret astronomical spectroscopic results and could lead to the detection of this interesting molecule in outer space. In this work, theoretical calculations are applied to possible isomers of NCCP in order to investigate geometries, harmonic vibrational frequencies, thermochemistry, and dipole moments. In addition, transition states connecting isomers of NCCP were located to assess rearrangement barriers.

II. Computational Details

The Gaussian 98 program[15] was used for density functional theory (DFT),[16] coupled cluster (CC) method,[17] and G3 theory calculations.[18] Optimized geometries and vibrational frequencies for NCCP isomers and transition states (TS) were obtained at the B3LYP level[19] with the 6-311G(2d) basis set. The importance of ab initio electron correlation on the relative energy of various isomers was considered by single-point calculations using the CCSD(T)/6-311G(2d) (coupled cluster theory with single and double excitations incorporating the perturbative corrections for triple excitation) method based on the DFT-optimized geometries. All geometries have been analyzed by calculating vibrational frequencies at the B3LYP/6-311G(2d) level and characterized as minima with no imaginary frequency or as transition states with one imaginary frequency. The transition vector of each transition state was animated. If the pathway connecting the transition state to reactant and product was not obvious, a small distortion along the transition vector was added to the transition state geometry, which was then re-optimized to the corresponding reactant or product.

G3 theory has been applied to NCCP and related compounds such as NCCN and PCCP to obtain accurate heats of formation ($\Delta H°_{f,298.15K}$) and relative bond strengths between CN and CP. Finally, the potential energy surface (PES) for NCCP isomers has been determined by calculating transition states at the DFT level. Relative energies at the DFT and CCSD(T) levels have been improved by including zero-point correction (ZPC) energies computed at the B3LYP/6-311G(2d) level. Unless noted otherwise, our standard level of theory will be CCSD(T)/6-311G(2d)//B3LYP/6-311G(2d)+ZPC. Natural bond orbital (NBO) analysis[20a] (including Wiberg Bond Indices (WBI)[20b]) of isomers and transition states have also been computed at the B3LYP/6-311G(2d) level.

III. Results and Discussions

A. NCCP Isomers. First, we have considered all possible linkage isomers for NCCP. From DFT geometry optimizations,

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TABLE 1: Calculated Vibrational Frequencies (cm^{-1}) with Infrared Intensities in Parentheses (km/mol) for NCCP Isomers and Transition States at B3LYP/6-311G(2d) Level

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7
A ($C_{\infty v}$)[a]	206 (0)	206 (0)	539 (14)	539 (14)	693 (0)	1598 (7)	2277 (0)
B ($C_{\infty v}$)	198 (0)	198 (1)	456 (6)	456 (6)	728 (2)	1620 (25)	2114 (319)
C ($C_{\infty v}$)	187 (2)	187 (2)	476 (6)	476 (6)	764 (3)	1511 (36)	2040 (1232)
D ($C_{\infty v}$)	17 (5)	17 (5)	189 (17)	189 (17)	742 (16)	1377 (3)	1940 (622)
E (C_s)	129 (4)	336 (1)	464 (9)	780 (25)	1065 (27)	1820 (217)	
F (C_{2v})	177 (56)	217 (14)	295 (20)	678 (61)	1383 (8)	1693 (1)	
G (C_s)	105 (2)	184 (0)	244 (0)	560 (17)	1012 (29)	2068 (231)	
TSB/B (C_{2v})	433i (15)	446 (47)	511 (0)	732 (5)	999 (34)	1481 (56)	
TSC/C (C_{2v})	613i (87)	356 (4)	401 (3)	625 (36)	1155 (147)	1575 (10)	
TSA/B (C_s)	397i (33)	262 (2)	351 (4)	661 (15)	1377 (13)	1879 (53)	
TSA/B* (C_s)	290i (10)	388 (0)	520 (2)	619 (10)	951 (14)	1929 (11)	
TSA/E (C_s)	1107i (21)	528 (12)	545 (27)	935 (41)	1069 (46)	1245 (27)	
TSA/E* (C_s)	693i (256)	315 (22)	416 (0)	627 (1)	1012 (10)	1395 (9)	
TSB/G (C_s)	176i (3)	194 (2)	278 (0)	546 (22)	1021 (20)	2002 (243)	
TSC/E (C_s)	873i (120)	221 (1)	259 (6)	874 (47)	1064 (77)	1829 (305)	
TSD/E (C_s)	427i (7)	124 (4)	124 (0)	642 (1)	1134 (16)	1883 (8)	
TSD/F (C_s)	181i (23)	196 (14)	211 (12)	830 (50)	1404 (20)	1695 (61)	
TSE/F (C_s)	311i (17)	249 (6)	403 (7)	656 (31)	1208 (6)	1607 (1)	

[a] The symmetries and normal mode description of the most stable NCCP isomer (**A**) are: $\nu_1,\nu_2 = \pi$, C−C−P bend; $\nu_3,\nu_4 = \pi$, N−C−C bend; $\nu_5 = \sigma$, CP/CC stretching; $\nu_6 = \sigma$, CC/CP stretching; $\nu_7 = \sigma$, CN stretching.

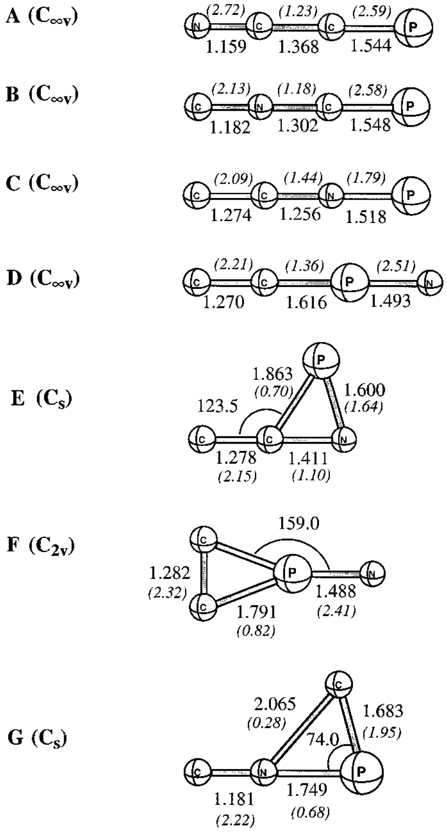


Figure 1. Optimized geometries of NCCP isomers at the B3LYP/6-311G(2d) level. Wiberg bond indices are in parentheses in italic. All bond lengths are in ångstroms and angles are in degrees.

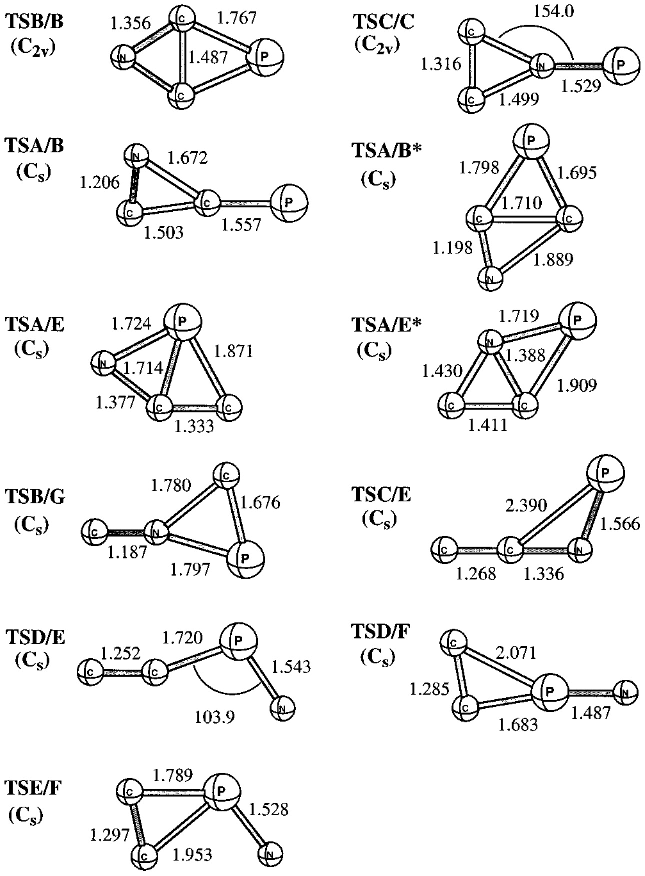


Figure 2. Optimized geometries of NCCP transition states. All bond lengths are in ångstroms and angles are in degrees.

seven minimum-energy structures on the NCCP isomerization potential energy surface have been located and characterized by vibrational frequency analyses. However, the possible linkage of C−P−C−N does not exist as an energy minimum or a transition state at the DFT level (two imaginary frequencies). Calculated vibrational frequencies at the B3LYP/6-311G(2d) level are listed in Table 1 with the optimized geometries for NCCP isomers and transition states in Figures 1 and 2, respectively. In Table 2, calculated energies and dipole moments of isomers and transition states are given. Since there is evidence of some diatomics such as CC, CP, CN, and NP in the interstellar medium,[1,2,4,5,21,22] these NCCP isomers may be expected to be of astrophysical importance.

Among NCCP isomers, **A**, **B**, **C**, and **D** have linear structures with $C_{\infty v}$ symmetry, while others (**E**, **F**, **G**) are nonlinear with planar structures (C_s or C_{2v}). Isomer **A** (N≡C−C≡P) is the most stable species. The calculated C−P bond distance (1.544 Å) is in excellent agreement with experiment (1.5456 Å),[8] which can be compared to a pure triple bond in HC≡P (1.540 Å).[23] The calculated C−C bond distance (1.368 Å) of NCCP is also in good agreement with experiment (1.3759 Å)[8] and somewhat

TABLE 2: Relative Energies (kcal/mol) and Dipole Moments (Debye) for NCCP Isomers and Transition States

		B3LYP/6-311G(2d)//B3LYP/6-311G(2d)			CCSD(T)/6-311G(2d)//B3LYP/6-311G(2d)	
species[a]	point group	dipole moment	rel *E*	rel *E* (+ZPC)[b]	rel *E*	rel *E* (+ZPC)[b]
A	$C_{\infty v}$	3.4	0.0[c]	0.0[d]	0.0[e]	0.0[f]
B	$C_{\infty v}$	2.3	23.0	22.6	24.7	24.3
C	$C_{\infty v}$	5.3	61.9	61.3	67.1	66.5
D	$C_{\infty v}$	1.0	111.9	109.7	112.7	110.5
E	C_s	4.4	96.6	94.5	98.1	96.0
F	C_{2v}	1.4	113.6	111.2	112.8	110.5
G	C_s	3.2	96.5	93.9	94.7	92.1
TSB/B	C_{2v}	1.8	79.1	76.4	81.8	79.1
TSC/C	C_{2v}	3.7	116.0	113.2	119.6	116.8
TSA/B	C_s	1.4	63.7	61.6	63.7	61.5
TSA/B*	C_s	2.9	81.7	79.3	82.1	78.7
TSA/E	C_s	2.7	106.9	104.4	109.0	106.5
TSA/E*	C_s	2.3	124.2	121.1	127.4	124.1
TSB/G	C_s	3.1	96.8	93.9	95.9	93.0
TSC/E	C_s	6.3	114.2	111.6	120.3	117.7
TSD/E	C_s	3.2	136.1	133.0	130.4	127.3
TSD/F	C_s	1.4	114.4	111.9	113.0	110.5
TSE/F	C_s	2.1	129.6	126.8	125.8	123.0

[a] All species are closed shell singlets. Calculations for the triplet spin states of **C**−**G** and **TSC/C** showed the open shell triplet to be higher in energy than the closed shell singlet (See text). [b] Zero-point correction energy is calculated at the B3LYP/6-311G(2d) level. [c] Absolute energy is −472.30779 hartree. [d] Absolute energy is −472.29399 hartree. [e] Absolute energy is −471.50412 hartree. [f] Absolute energy is −471.49032 hartree.

TABLE 3: Comparison of the Structural Parameters of NCCP with Those of Related Compounds at the B3LYP/6-311G(2d) Level

molecules	*r*(CC) (Å)	*r*(CN) (Å)	*r*(CP) (Å)
NCCP	1.368	1.159	1.544
CN		1.162	
CP			1.555
HCN		1.146	
HCP			1.535
NCCN	1.378	1.153	
PCCP	1.341		1.562
HCC−CN	1.371	1.155	
HCC−CP	1.357		1.552

longer than the experimental CC distance in $CH_2{=}CH_2$ (1.339 Å)[24] but very similar to the CC bond in N≡C−C≡N (1.3839 Å).[9a] The C−N bond distance is computed to be 1.159 Å, which is close to the experimental value of 1.1641 Å.[8]

Comparison is made with the structural parameters of NCCP and those of related molecules done at the same theoretical level in Table 3. C≡N and C≡P bond distances in NCCP are longer than those in HC≡N and HC≡P (Table 3), which implies the bonding between carbon and nitrogen/phosphorus in N≡C−C≡P is less than a pure triple bond. The Wiberg bond indices (WBI), a computational measure of bond order, for the C≡N and C≡P bonds in NCCP (WBI = 2.72 and 2.59, respectively) indicate some delocalization compared to the C≡N bond in HCN (WBI = 2.99) or the C≡P bond in HCP (WBI = 2.91). It is noted that the CN bond in NCCP is longer than in NCCN while the CP bond in NCCP is shorter than in PCCP, and while the length of the CC bond in NCCP is intermediate to the CC bond in NCCN and PCCP. It is suggested that the triple/single bonds in NCCP are more delocalized than in NCCN but less delocalized than in PCCP (Table 3). This may be due to the difference in π-bonding strength for CN and CP, as it is known that CN π-bonds are stronger than CP because C and N use 2p orbitals for π-bonding while P uses 3p orbitals.

TABLE 4: Bond Dissociation Enthalpies (BDEs) of NCCP and Related Compounds at 298.15 K (kcal/mol)

species	products	G3	exp	Δ(G3 − exp)
NC−CP	CN + CP	144.6		
NC−CN	CN + CN	139.7	137.1[a]	2.6
PC−CP	CP + CP	148.1[b]		
H−CN	H + CN	127.5	124.8 ± 0.4[c]	2.7
H−CP	H + CP	121.6	123.8[d]	2.2
H−CCH	H + CCH	133.5	131.3 ± 0.7[c]	2.2
HCC−CN	HCC + CN	153.8	156.0[e]	−2.2
HCC−CP	HCC + CP	154.7		
HCC−CCH	HCC + HCC	161.9	159.2[f]	2.7

[a] $\Delta H°_{f,298.15K}$ of CN from ref 26, and $\Delta H°_{f,298.15K}$ of NCCN from ref 25. [b] A calculated bond dissociation enthalpy at 298 K of 152.2 kcal/mol has been reported from ref 13. [c] Reference 26. [d] Reference 25. However, the calculated BDE of HCP based on G3 isodesmic heats of formation (eqs 2 and 3) is 117.8 kcal/mol. [e] $\Delta H°_{f,298.15K}$ of HCC and CN from ref 26, and $\Delta H°_{f,298.15K}$ of HCCCN from ref 25. [f] $\Delta H°_{f,298.15K}$ of HCC from ref 26, and $\Delta H°_{f,298.15K}$ of HCCCCH from ref 25.

Bond dissociation enthalpies (BDEs) of NCCP and related compounds have been computed to understand the nature of bonding of CN and CP species. First, an isodesmic reaction (eq 1) has been considered since there is no experimental heat of formation ($\Delta H°_{f,298.15K}$) for NCCP. From this isodesmic (and isogyric) reaction, the reaction enthalpy

$$NCCN + PH_3 \rightarrow NCCP + NH_3 \qquad (1)$$

($\Delta H_{r,298.15K}$) has been computed to be −3.3 kcal/mol by using G3 theory, and the heat of formation ($\Delta H°_{f,298.15K}$) of NCCP can be computed to be 87.1 kcal/mol based on this reaction enthalpy (−3.3 kcal/mol) and the known experimental heats of formation of NCCN (73.9 kcal/mol), PH_3 (5.5 kcal/mol), and NH_3 (−11.0 kcal/mol).[25] Second, calculated bond dissociation enthalpies (BDEs) of NCCP and related compounds are listed in Table 4. Computed G3 enthalpies agree with the available experimental data within 3 kcal/mol.

However, there is a serious disagreement between experiment and theory in the heat of formation of CP. When we use the experimental heat of formation (107.5 kcal/mol)[25] of CP for the dissociation reaction of NCCP into CN and CP, the calculated heat of formation (66.9 kcal/mol) of NCCP is quite different from the value (87.1 kcal/mol), which is computed from the above isodesmic reaction (eq 1). Therefore, we considered the isodesmic reactions (eqs 2 and 3) in order to obtain G3 heats of formation for HCP and CP.

$$HCP + NH_3 \rightarrow HCN + PH_3 \qquad (2)$$

$$HCN + CP \rightarrow HCP + CN \qquad (3)$$

The calculated heats of formation ($\Delta H°_{f,298.15K}$) of HCP and CP from eq 2 and eq 3 using G3 theory are 56.3 and 122.1 kcal/mol, respectively, which deviate significantly from the experimental values (HCP, 35.8 kcal/mol; CP, 107.5 kcal/mol).[25] Fast et al.[27] calculated the atomization energy of CP at the CCSD(T) level with an extrapolation to infinite basis set. Using experimental data for atoms and the atomization energy from Fast et al. (123.5 kcal/mol) with zero-point correction and heat capacity contributions computed at the B3LYP/6-311G(2d) level, we obtain a standard heat of formation of 124.4 kcal/mol for CP, in good agreement with our result (122.1 kcal/mol).[28]

The calculated G3 C−C BDE of NCCP (144.6 kcal/mol) is between those of NCCN and PCCP (139.7 and 148.1 kcal/mol, respectively), which is consistent with a C−C bond distance in NCCP of 1.368 Å between NCCN (1.378 Å) and PCCP (1.341

TABLE 5: Evaluated Electronegativities (χ) of CN, CP, and CCH Species[a]

	χ(Cl)	χ(CN)	χ(CP)	χ(CCH)
F (χ = 3.98)[b]	3.22[c]	2.74[c]	2.77[c]	2.82[c]
Cl (χ = 3.16)[b]		2.67[d]	2.87[d]	2.91[d]
averaged χ	3.22	2.71[e]	2.82	2.87

[a] Electronegativities have been evaluated with the Pauling relationship:[30] $\chi_A - \chi_B = 0.0244(\Delta)^{1/2}$, where $\Delta = D_{AB} - 0.5[D_{AA} + D_{BB}]$. The G3 bond dissociation enthalpies (D) in kcal/mol at 298 K come from Table 4 for NCCN, PCCP, HCCCCH. In addition, the following G3 bond dissociation enthalpies (kcal/mol) were calculated: F−F (37.2), Cl−Cl (56.8), F−Cl (60.4), F−CN (123.8), Cl−CN (103.8), F−CP (126.4), Cl−CP (104.4), F−CCH (130.4), Cl−CCH (110.8). [b] Reference 30. [c] Electronegativities were calculated by Pauling's definition of electroneagtivity using G3 bond enthalpies with respect to the Pauling's electronegativity value (χ = 3.98) of fluorine. [d] Electronegativities were calculated by Pauling's definition of electroneagtivity using G3 bond enthalpies with respect to the Pauling's electronegativity value (χ = 3.16) of chlorine. [e] A Mulliken electronegativity (χ_M) of 8.92 has been reported for CN.[31] This value can be converted to 2.66 on the Pauling scale with the relationship[30] $\chi_P = 1.35(\chi_M)^{1/2} - 1.37$.

Å). However, the G3 C−C BDE of NCCP (144.6 kcal/mol) is smaller than those of HCCCN and HCCCP (153.8 and 154.7 kcal/mol, respectively).

The CN radical is sometimes called a pseudohalogen[30] because its properties are so similar to that of the halogens. Since CP and CCH are isoelectronic to CN, they might also be considered as pseudohalogens. Therefore, it is interesting to compute group electronegativities[31−34] of the CN, CP, and CCH radicals from the Pauling relationship (Table 5) and compare with the Pauling electronegativities of halogens. Using the data from Tables 4 and 5, Pauling electronegativities of 2.71, 2.82, and 2.87 were computed for CN, CP, and CCH, respectively. The 2.71 value for CN can be compared to a value of 2.66 (converted from the Mulliken scale) reported by Pearson[31] (see Table 5). Thus, the Pauling electronegativity order is Br (2.96) > CCH (2.87) > CP (2.82) > CN (2.71) > I (2.66).

The rotational constant (B_e) of isomer **A** has been computed to be 2724.47 MHz at the B3LYP/6-311G(2d) level which can be compared with the experimental B_0 value (vibrational-averaged) of 2704.48 MHz.[6−8] Also, the calculated dipole moment of isomer **A** is 3.37 D (the dipole direction is from P to N), in good agreement with experiment (3.44 ± 0.03 D).[6,7]

Isomers **B**, **C**, and **D** are linkage isomers of NCCP, among which **B** (C≡N−C≡P) is only 24.3 kcal/mol higher than the lowest isomer **A** at the CCSD(T) level. The rotational constants (B_e) of isomers **B**, **C**, and **D** have been computed to be 2938.43, 3024.24, and 3447.22 MHz, respectively, at the DFT level. Thus, there are differences of 100−400 MHz among the rotational constants of these linear isomers. Such a difference is likely to be sufficient to distinguish these symmetric-top isomers by high-resolution rotational spectroscopy. The IR intensities of the vibrational transitions of isomer **A** are all very small (Table 1), which is in contrast to isomers **B**, **C**, and **D** which show one very strong IR mode at 2114 cm^{-1} (IR$_{int}$ = 319 km/mol, CN stretching), 2040 cm^{-1} (IR$_{int}$ = 1232 km/mol, coupled CC and CN stretching), and 1940 cm^{-1} (IR$_{int}$ = 621 km/mol, CC stretching), respectively. The probable reason is that the bonds of isomer **A** are less polar than the bonds in isomers **B**−**D**. Thus, the formal charges of all atoms are zero for the dominant resonance structure of **A** while they are not for isomers **B**−**D**.

Isomers **E**, **F**, and **G** possess a three-membered ring with a phosphorus atom. Isomer **E** acts as an intermediate on the isomerization surface and is 96.0 kcal/mol higher than isomer **A** at the standard level as shown in Figures 3 and 4. For isomer **E**, the calculated C−P bond distance is slightly longer than the typical C−P single bond distance (1.84 Å).[30] In isomer **F**, the two carbon atoms are bonded by a partial triple bond (C−C, 1.282 Å; WBI, 2.32) and coordinated side-on to the P end of PN (WBI(CP), 0.82; WBI(PN) 2.41). Isomer **G** has a partially closed ring in which the carbon atom is weakly bonded to the nitrogen atom (2.065 Å). The calculated CN and CP distances (1.181 and 1.683 Å, respectively) are somewhat longer than the CN bond in CN/HCN or the CP bond in CP/HCP at the same theoretical level (See Table 3).

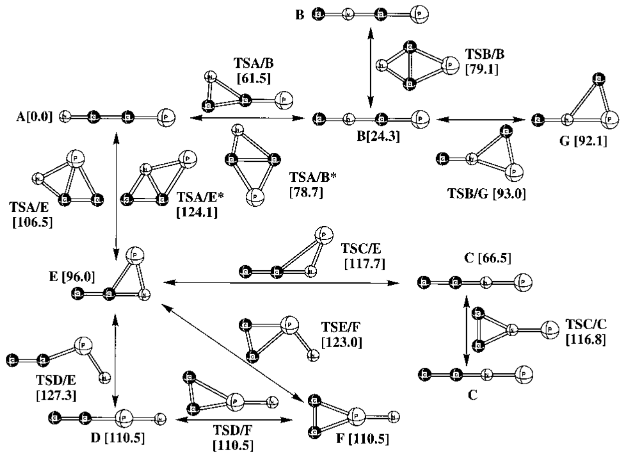


Figure 3. Structural correlations of NCCP isomers and transition states on the potential energy surface. Numbers in brackets are relative energies in kcal/mol at the CCSD(T)/6-311G(2d)//B3LYP/6-311G-(2d)+ZPC level.

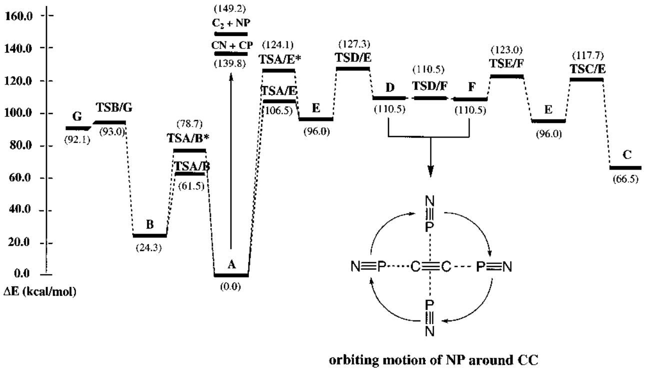
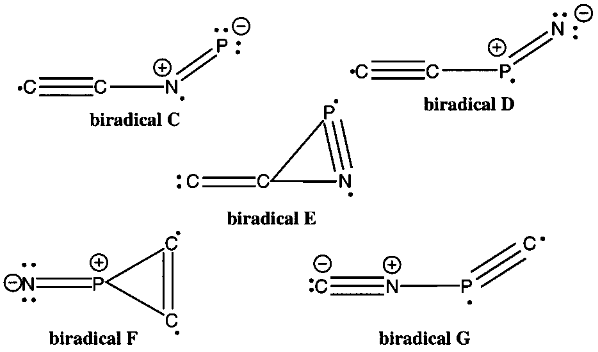


Figure 4. Schematic reaction profile for the NCCP system. Relative energies (kcal/mol) are obtained at the CCSD(T)/6-311G(2d)//B3LYP/6-311G(2d)+ZPC level.

All NCCP calculations discussed above are based on closed-shell wave functions. However, several isomers (**C**, **D**, **E**, **F**, and **G**) might have biradical forms (Scheme 1).

To access the relative stabilities of triplet biradicals relative to closed-shell singlets, calculations were made at the UB3LYP/6-311G(2d)+ZPC level ($\langle S^2 \rangle$ values varied from 2.01 to 2.05). For isomers **C** and **D**, the bent triplet biradicals are 32.2 and 14.4 kcal/mol higher in energy than the linear closed shell structure, respectively. The triplet biradical of isomer **E** is only 1.0 kcal/mol higher than the closed-shell singlet. Thus, it is possible that the ground state of isomer **E** may contain significant biradical character and, for that reason, the CCSD(T) calculation of isomer **E** may be less reliable.[35] For isomers **F** and **G**, the triplet biradicals are also local minima and are higher than closed-shell singlet states by 52.2 and 11.9 kcal/mol, respectively.

SCHEME 1



B. Transition States and Isomerization. Schematic structural correlations among isomers and transition states are depicted in Figure 3 while the reaction profile for NCCP isomerizations is shown in Figure 4. The transition states **TSB/B** and **TSC/C** are associated with the interchange of the two carbon atoms in the isomers **B** and **C**. At our standard level, the interchange barriers of isomers **B** and **C** have been computed to be 54.8 (via **TSB/B**) and 50.3 kcal/mol (via **TSC/C**). From the optimized structure of **TSC/C** in Figure 2, the C−C bond distance (1.316 Å) implies double-bond character and suggests that biradical character may be present in **TSC/C**. However, the optimized triplet biradical structure of isomer **TSC/C** (zero imaginary frequencies in C_{2v} symmetry) is 10.9 kcal/mol higher in energy than **TSC/C** at the DFT+ZPC level.

Two transition states **TSA/B** and **TSA/B*** connect isomers **A** and **B**. The lower barrier via **TSA/B** (61.5 kcal/mol), which involves insertion of nitrogen into the C−C bond, is 17.2 kcal/mol more favorable than **TSA/B***. In turn, **TSB/G** connects isomer **B** to isomer **G**, which is not predicted to be stable since the reverse barrier is only 0.9 kcal/mol.

Isomer **E** acts as an intermediate on the pathway between isomers **A** and **D** or **F**. Two transition states, **TSA/E** and **TSA/E***, have been found connecting isomers **A** and **E**. The two transition states differ by the coordination number of phosphorus and nitrogen. The lower transition state energy for **TSA/E** (compared to **TSA/E***) is consistent with the higher coordination number of phosphorus compared nitrogen (coordination number of P = 3; coordination number of N = 2) since it is known that phosphorus has a greater propensity for smaller angles compared to nitrogen.[30]

Isomer **E** can isomerize either into isomer **D** via transition state **TSD/E**, or into isomer **C** via transition state **TSC/E**. As seen in Figure 4, the calculated conversion barrier is smaller for **E** → **C** (21.7 kcal/mol) than **E** → **D** (31.3 kcal/mol). It is noted that **D**, **F**, and **TSD/F** all have the same relative energy, which suggests that the NP diatomic orbits the C_2 moiety with essentially no activation at a radius of 1.6 Å (distance from P to C−C midpoint) with the phosphorus lone pair pointing toward the C_2 (See Figure 4). There are two minima in this orbiting surface that can be best described as a “planetary system”.[36] One is the isomer **D** in which NP is linear with C_2; the other is the isomer **F** in which NP is directed toward the C_2 midpoint. This orbiting motion can also be found from the PES of LiCN/LiNC.[37] Isomer **F** can be converted into isomer **E** via transition state **TSE/F** with a barrier of 12.5 kcal/mol. The reverse barriers for **E** → **A** and **E** → **C** are 10.5 and 21.7 kcal/mol, which indicates that isomer **E** may be thermally unstable toward conversion to isomers **A** and **C**, as seen in Figure 4.

To investigate the relationship between fragment molecules such as CN, CP, C_2 and NP and isomers **A** and **C**, the following unimolecular reactions can be considered. The calculated reaction energies of eqs 4 and 5 at the standard level are −139.8 and −82.7 kcal/mol, respectively (see Figure 4).

$$\mathrm{CN} + \mathrm{CP} \rightarrow \mathrm{NCCP}\ (\text{isomer } \mathbf{A}) \tag{4}$$

$$\mathrm{C_2} + \mathrm{NP} \rightarrow \mathrm{CCNP}\ (\text{isomer } \mathbf{C}) \tag{5}$$

In the conversion of **C** to **A**, there is an overall barrier of 51.2 kcal/mol via **TSC/E**, which is 31.5 kcal/mol less than the CC−NP bond energy (eq 5). Thus, if C_2 and NP bind to form isomer **C**, isomer **A** will eventually be formed unless there are stabilizing collisions. Therefore, we predict that isomer **A** is the most probable NCCP isomer to be detected in the interstellar medium.

IV. Conclusion

B3LYP/6-311G(2d) and CCSD(T)/6-311G(2d) calculations have been carried out in order to investigate geometries, energetics, and isomerization processes in the NCCP system. It is shown that isomer **A** is the global minimum with $C_{\infty v}$ symmetry, and the optimized geometry, rotational constant, and dipole moment compare well with experiment. The heat of formation ($\Delta H^\circ_{\mathrm{f,298.15K}}$) of NCCP has been computed to be 87.1 kcal/mol using an isodesmic reaction with G3 theory. Bond dissociation enthalpies (BDE) for breaking the C−C bond of NCCP and related compounds have also been computed using G3 theory. From the Pauling relationship group electronegativities of CN, CP, and CCH have been computed to be 2.71, 2.82, and 2.87, respectively.

From the study of the potential energy surface, it is found that transition states **TSB/B** and **TSC/C** are associated with the interchange of the two carbon atoms in isomers **B** and **C**. The conversion between isomers **D** and **F** (∼0 activation barrier via **TSD/F**) resembles the Moon−Earth “planetary system” in that NP (Moon) orbits C_2 (Earth) with its P-side always facing C_2. If either C_2 + NP or CN + CP enter the NCCP potential energy surface, then the exothermicity from bond formation provides sufficient internal energy to cross transition states to the global minimum ($N\equiv C-C\equiv P$, isomer **A**). We hope that this study will help identify the microwave spectrum of NCCP and related isomers in interstellar space.

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