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A Theoretical Investigation of the Stability of HPC

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Several *ab initio* methods are applied to the study of two linear isomers of methylidyne phosphine, HCP and HPC. Single-reference correlation methods ranging from second-order Møller–Plesset theory to coupled cluster singles and doubles theory with noniterative inclusion of connected triple excitations were applied in a variety of basis sets of increasing size. In addition, complete active space self-consistent field wave functions, multireference singles and doubles configuration interaction, and averaged coupled pair functional theory were also applied to HPC. For HCP comparison of the single-reference based results is made with experimental data and previous theory to assess the accuracy of the methods employed. The same single-reference-based methods are then applied to linear HPC in order to assess whether it is a stable minimum or a transition state (imaginary frequencies in two dimensions). It is found that linear HPC is not a minimum on the ground-state potential surface. However, relatively high levels of correlation must be used when single-reference-based methods are employed to arrive at this conclusion. The multireference-based methods are then applied to HPC, and they too predict that it is not a minimum on the ground electronic potential surface. The qualitative nature of linear HPC is examined using CASSCF and CCSD wave functions.

I. Introduction

Hydrogen cyanide is a system which has received a great deal of theoretical and experimental attention recently.^{1–6} Much of this work has focused on the ground-state surface, which is made particularly interesting by the presence of two stable isomers, linear HCN (the lowest energy configuration) and HNC (approximately 0.64 eV above HCN¹). Since this system is well studied experimentally,^{5,6} the possibility exists of doing high-quality calculations of vibrational spectra on an accurate *ab initio* surface to yield theoretical spectra for comparison with experiment.

Experimental studies have also examined vibrational motion on the ground-state surface of HCP, a substituted analogue of HCN.^{7–10} It is known that the ground-state global minimum is linear and of the form H–C–P;¹¹ experimentally it is not known whether the isomer H–P–C exists. It is known from stimulated emission pumping experiments⁸ that the ground-state bending potential is more harmonic than was expected based on previous theory⁷ and that highly excited bending states can be accessed with little CP stretch being induced. One cannot yet infer from this data whether linear HPC exists, as the states studied were not high enough in energy to probe this portion of the potential surface (up to 54 kcal/mol above the HCP minimum, whereas HPC is calculated to be about 80 kcal/mol above HCP; see refs 7 and 12, and below).

Theoretically, HCP has been studied using a variety of methods and basis sets.^{7a,c,12–20} The earliest series of calculations used relatively small basis sets and modest correlation methods,^{13–18} but the first calculations to address the stability of HPC were performed by Lehmann et al.^{7a} They used frozen-angle restricted Hartree–Fock geometries followed by fourth-order Møller–Plesset (singles, doubles, and quadruples) to construct a bending potential for HCP, and predicted that HPC is not a stable species. The density of points near linear HPC was probably not sufficient to detect a small energy rise as the molecule departed from linearity, but their study has proven to be a quite useful point of comparison for later theory and

experiment. Karna et al.¹⁹ used multireference singles and doubles configuration interaction wave functions to examine the ground and certain excited states of HCP in a relatively large basis set. They suggested assignments for several excited states, obtained vibrational frequencies for several states, and calculated bending potentials at fixed bond lengths, but did not move far enough around in the bending coordinate to examine the HPC isomer. More recently, Bloor and Yu²⁰ examined the sensitivity of the geometry and many one-electron properties of HCP to the choice of basis set and correlation treatment. Their work emphasized the importance of extended basis sets and extensions of the correlation treatment beyond second-order Møller–Plesset perturbation theory (MP2) to achieve accurate geometries and properties. They too focused on the HCP isomer.

The most recent work to address the question of the stability of HPC is that of Goldstein et al.¹² They used up to triple zeta polarization (TZP) basis sets with either MP2 or CASSCF (complete active space self-consistent field) wave functions to examine both HCP and HPC. They concluded that the potential surface was flat in the region of HPC but the two correlation methods gave conflicting predictions as to whether HPC was a minimum (MP2, minimum; CASSCF, 2D saddle point). RHF results in all basis sets predicted that HPC was not a minimum. The CASSCF treatment (at most 10 electrons in 10 orbitals) gave excellent agreement with experiment in the case of HCP vibrational frequencies, but it was not clear whether its limited correlation recovery was yielding incorrect predictions for HPC. On the other hand, it could also be argued that the single-reference nature of the MP2 was inaccurate for the triply bonded system, or that higher order perturbation effects could be important in this system. Thus while both methods led to the conclusion that the surface is flat near linear HPC, the question of whether HPC is a true minimum was left open.

With these questions in mind, we undertook the present investigation. We used significantly larger basis sets than have been applied before to HPC, and single-reference correlation methods up to the coupled-cluster singles and doubles with noniterative inclusion of connected triples model²¹ (CCSD(T)). We have also applied several multireference-based correlation methods to HPC. It is found that it is critical to go beyond

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MP2 for HPC vibrational frequencies, as *the bending frequency oscillates from imaginary to real* for low orders of perturbation theory. We also find that while linear HCP appears to be well described by a single-reference-based correlation model, there are indications that there are significantly greater nondynamical correlation effects near the minimum for HPC, based on results of calculations of the T_1 diagnostic of Lee et al.²² (The CASSCF description indicates the difference arises due to greater excitation out of a σ orbital for HPC.) On the basis of the present results we predict that HPC is not a stable isomer of methylidyne phosphene.

In what follows, we examine both basis set and correlation treatment effects on the geometries and vibrational frequencies for HCP and HPC. In general it is found that a triple zeta plus polarization basis (TZP) is sufficient to yield a semiquantitative description of HPC, but that if single-reference methods are employed, high levels of correlation treatment are required to obtain converged results. In section II, the basis sets and correlation methods that were used are outlined, followed by a presentation of the results in section III. In section IV we discuss the results, and section V contains a brief summary of our conclusions.

II. Theoretical Methods

All restricted Hartree–Fock (RHF) and Moller–Plesset (MP) perturbation theory calculations were performed using the Gaussian 92 (G92) suite of electronic structure codes.²³ Most of the coupled cluster results (both coupled cluster singles and doubles (CCSD) and coupled cluster singles and doubles with noniterative inclusion of connected triples (CCSD(T)²¹) were performed with G92 as well, except that some single-point calculations were performed with PSI²⁴ in order to calculate the T_1 diagnostic.²² The T_1 diagnostic has been proposed as a measure of the degree of nondynamical correlation effects in the CC wavefunction, and hence an indicator of the reliability of the single-reference description for the case under study.²² The majority of the CASSCF calculations, and all multireference singles and doubles configuration interaction (MRSDCI) and averaged coupled pair functional²⁵ (ACPF) theory calculations, were performed using MOLCAS.²⁶ The MRSDCI and MRACPF calculations were performed using the interacting space option: double excitations from inactive to virtual orbitals were not allowed that would have the inactive and virtual electrons couple to a triplet.

All correlated calculations treat only the valence electrons, and only the valence electrons are correlated in the vibrational frequency calculations. In cases where the bending frequencies are not exactly degenerate due to numerical differentiation errors we have taken the average of the two values and quoted the average in the tables. In the multireference cases, the version of MOLCAS we used did not possess analytical gradients. We performed preliminary calculations on linear HCP using MRSDCI, MRSDCI+Q (+Davidson correction for quadruple excitations) and MRACPF, fitting the points to a quadratic in the two bond stretches plus a coupling term between the two stretches and found that the minima for the various methods were within 0.01 Å of those obtained by CCSD(T) in the 6-31G** basis. Thus, in all cases reported below we have frozen the R_{HP} and R_{CP} bond lengths at 1.4213 and 1.629 18 Å, respectively, these values being the CCSD(T) values in the 6-31G** basis. While geometry changes may have some effect on the computed force constants, they are expected to be modest over the geometry variations one might see as a function of basis set. The force constants obtained were obtained from a least-squares fit to a simple quadratic in bending angle, based on calculations at 180°,

TABLE 1: HCP Results in 6-311G** Basis

| method | E (au) +379.0 | R_{CH} (Å) | R_{CP} (Å) | ω_1, ω_2 | ω_3 | ω_4 |
|---------------------|--------------------|------------------------|------------------------|----------------------|------------|------------|
| RHF | -0.13836 | 1.064 | 1.514 | 818 | 1471 | 3518 |
| MP2 | -0.39556 | 1.076 | 1.559 | 683 | 1259 | 3359 |
| MP4(SDTQ) | -0.42687 | 1.080 | 1.567 | 663 | 1220 | 3392 |
| CCSD | -0.40873 | 1.076 | 1.547 | 692 | 1326 | 3363 |
| CCSD(T) | -0.42401 | 1.077 | 1.555 | 661 | 1289 | 3342 |
| Expt. ²¹ | — | 1.069 | 1.540 | 675 | 1278 | 3217 |

^a The theoretical frequencies are harmonic frequencies, the experimental values are fundamental frequencies; both are in cm^{-1} .

179°, and 178°. In the tables we quote bending frequencies, calculated at the rigid geometry, based on the fit force constant, using an expression from Herzberg.²⁷

In cases where the Davidson correction²⁸ for quadruple excitations was used the correction was calculated as $\Delta E_{\text{SDCI}}((1 - \sum c_{0i}^2)/\sum c_{0i}^2)$, where $\sum c_{0i}^2$ is the sum of the squares of the reference configurations in the final CI wave function.

We performed a variety of CASSCF calculations, denoted as n/m CASSCF, where n denotes the number of electrons correlated and m denotes the number of orbitals used. In all CASSCFs we correlated at least the 4π electrons and 2σ electrons in 4π and 2σ orbitals (6/6 CASSCF). In the 10/10 CASSCFs four σ electrons and 4σ orbitals were added to the 6/6 CAS respectively. The 10/12 CASSCF adds two more π orbitals to the 10/10 CASSCF.

For the single-reference methods all basis sets used were built upon the 6-31G²⁹ or 6-311G³⁰ basis sets. Note that for P the “6-311G” basis is the triple zeta basis due to McLean and Chandler.³¹ The polarization and diffuse function sets were also those internal to Gaussian 92.^{32,33} In the results presented in the 6-31G** basis, only the five $l = 2$ components of the six Cartesian d functions are included in the calculation. In the 6-311G basis sets all six Cartesian d functions but only the seven $l = 3$ Cartesian f-type functions were used. In test calculations we have seen that the inclusion or exclusion of the lower l components of the Cartesian d functions has essentially no effect on the results. In the multireference cases we used the averaged natural orbital (ANO) basis sets of Widmark et al.³⁴ The lower angular momentum contaminants were not deleted for the ANO basis sets. The specific basis sets used are given in the Results section.

In order to investigate the qualitative nature of HCP and HPC near their respective linear stationary points we have performed 10/10 CASSCFs in the 6-31G** basis (six Cartesian d functions) using GAMESS.³⁵ Natural orbital occupations were calculated based on the converged results and are discussed below.

III. Results

(a) **Single-Reference-Based Methods.** We first present results for HCP using various basis sets and wave functions in order to assess the quality of the methods to be applied to HPC. Table 1 contains a series of results in the 6-311G** basis for HCP. Included are total energies, geometries, and vibrational frequencies. It is seen that there is little change in the geometry or vibrational frequencies in this basis once one goes beyond the Hartree–Fock level of approximation. The frequencies are quite good for the bend and CP stretch; the CH stretch is high by about 100 cm^{-1} . Both bond lengths are long by about 0.01 Å at the CCSD(T) level, and it is also seen that inclusion of triple excitations has a significant effect on both the CP bond length and the CP stretching frequency. This is to be expected since in HCP the CP bond is a triple bond, and single-reference methods tend to require relatively high levels of excitations in order to properly describe multiple bonding. However, we have

TABLE 2: MP2 Results for HCP vs Basis Set^a

| basis | <i>E</i> (au) +379.0 | <i>R</i> _{CH} (Å) | <i>R</i> _{CP} (Å) | ω_1, ω_2 | ω_3 | ω_4 |
|---------------------|-------------------------|-------------------------------|-------------------------------|----------------------|------------|------------|
| 6-311G** | -0.3956 | 1.076 | 1.559 | 683 | 1259 | 3359 |
| 6-311++G** | -0.3969 | 1.077 | 1.559 | 672 | 1258 | 3356 |
| 6-311G(2d,2p) | -0.4159 | 1.070 | 1.558 | 606 | 1232 | 3356 |
| 6-311G(2df,2pd) | -0.4458 | 1.071 | 1.553 | 707 | 1259 | 3372 |
| 6-311G(3df,3pd) | -0.4506 | 1.072 | 1.553 | 693 | 1259 | 3340 |
| Expt. ²¹ | | 1.069 | 1.540 | 675 | 1278 | 3217 |

^a The theoretical frequencies are harmonic frequencies, the experimental values are fundamental frequencies; both are in cm⁻¹.

computed the *T*₁ diagnostic in the 6-31G** basis at essentially the minimum for the CCSD(T) result of Table 1 and found a value of 0.017, indicating that the single-reference description provided by CCSD or CCSD(T) should be quite reliable for HCP near its minimum.^{22,36} The correlated results in this basis are quite similar to those obtained in our previous work¹² using a 10/10 CASSCF wave function in a triple zeta polarized basis, except that the CASSCF bond lengths are another 0.01 Å too long, and the CH stretching frequency is about 50 cm⁻¹ lower for the CASSCF result. This lower frequency for the CASSCF may be due to a cancellation of errors in force constants and geometries,³⁷ or could arise from the limited correlation treatment, and so should not be taken as necessarily being more accurate for "the right reasons".

In comparisons of experimental and theoretical vibrational frequencies it is important to note that the experimental values quoted are fundamental frequencies, whereas the theoretical values are harmonic frequencies. (We associate the mode with frequency near 1300 cm⁻¹ with the CP stretch and the 3400 (HCP) or 2300 (HPC) cm⁻¹ modes with the HX stretches. The degenerate mode is the bending frequency.) In studies of HCN^{1,38} it is seen that the fundamental frequency for the H-C stretch is significantly lower (100 cm⁻¹) than the experimental or theoretical harmonic values. The other two modes are somewhat less affected. It does not appear that enough data has been gathered for the two stretching modes of HCP to obtain accurate harmonic frequencies,⁹ but for the bend the harmonic value is 687.9 cm⁻¹, as opposed to the fundamental value of 674.7 cm⁻¹.⁹ A simple fit to the first two vibrational transitions involving the ground state for each of the stretching modes yields values of 3273 cm⁻¹ for the HC stretch and 1284 cm⁻¹ for the CP stretch; each in somewhat better agreement with the correlated results of Table 1 (and later results), especially for the HC stretch.

We have examined HCP in larger basis sets (6-311++G** to 6-311G(3df,3pd)) using RHF and MP2 wave functions (Table 2). We find that diffuse functions have little effect on the geometry or vibrational frequencies, but there are sizable effects upon inclusion of a second set of first polarization (d,p) and upon inclusion of a first set of second polarization functions (f,d) (added sequentially). In the MP2 case the second set of (d,p) functions leads to a significant drop in the bending frequency (75 cm⁻¹) followed by a 100 cm⁻¹ increase in the bend when the (f,d) set is added to the (2d,2p) basis. A third set of first polarization functions has little additional effect. Overall, we conclude there is little net gain in accuracy for calculated vibrational frequencies or geometries at the MP2 level with basis set extension.

The calculations presented above are not absolute "converged," but the similarity of the results for the various correlated calculations in Table 1, coupled with the apparent convergence of the MP2 results as a function of basis, suggests that there are no surprises awaiting if we could extend the theoretical methods to the complete basis set, full CI limit. Were

TABLE 3: HPC Results in 6-31G Basis^a**

| method | <i>E</i> (au) +379.0 | <i>R</i> _{HP} (Å) | <i>R</i> _{CF} (Å) | ω_1, ω_2 | ω_3 | ω_4 |
|-----------|-------------------------|-------------------------------|-------------------------------|----------------------|------------|------------|
| RHF | +0.041 4 | 1.384 | 1.576 | 646 <i>i</i> | 1310 | 2695 |
| MP2 | -0.217 45 | 1.414 | 1.636 | 334 | 1047 | 2419 |
| MP3 | -0.218 96 | 1.398 | 1.598 | 452 <i>i</i> | 1245 | 2537 |
| MP4(SDTQ) | -0.260 28 | 1.421 | 1.684 | 197 | 790 | 2338 |
| CCSD | -0.232 30 | 1.412 | 1.612 | 393 <i>i</i> | 1179 | 2414 |
| CCSD(T) | -0.252 17 | 1.421 | 1.629 | 326 <i>i</i> | 1108 | 2323 |

^a Frequencies are harmonic frequencies, in cm⁻¹. Only the *l* = 2 components of the d functions are included.

TABLE 4: HPC Results in 6-311G Basis^a**

| method | <i>E</i> (au) +379.0 | <i>R</i> _{HP} (Å) | <i>R</i> _{CP} (Å) | ω_1, ω_2 | ω_3 | ω_4 |
|---------|-------------------------|-------------------------------|-------------------------------|----------------------|------------|------------|
| RHF | 0.010 79 | 1.385 | 1.573 | 646 <i>i</i> | 1203 | 2606 |
| MP2 | -0.262 74 | 1.414 | 1.630 | 344 | 1059 | 2408 |
| MP3 | -0.263 38 | 1.398 | 1.593 | 450 <i>i</i> | 1254 | 2531 |
| CCSD | -0.276 50 | 1.411 | 1.608 | 397 <i>i</i> | 1185 | 2416 |
| CCSD(T) | -0.297 96 | 1.420 | 1.624 | 328 <i>i</i> | 1118 | 2324 |

^a Frequencies are harmonic frequencies, in cm⁻¹.

one to extrapolate these results to the seemingly similar case of linear HPC, one might conclude that the third set of polarization functions is relatively unimportant for the description of the vibrational frequencies and the geometry and that diffuse functions will have a modest effect on the vibrational frequencies. While the former statement appears to be true, it turns out that for HPC diffuse functions seem to have a larger quantitative effect on the bending frequency at the correlated level.

In Table 3 a series of calculations are presented in the 6-31G** basis for HPC. This basis is only double zeta with one set of polarization functions, but the data presented in Table 4 show that 6-311G** results are quite similar both for geometries and for vibrational frequencies. Results in both basis sets are presented to show that the unusual behavior is not unique to either the double zeta or the triple zeta basis. The most startling result from this series of calculations is the oscillation in the bending frequency from real to imaginary as the order of the perturbation theory increases. The RHF results predict that the linear geometry is unstable with respect to bending, but as one moves up in order on the MP perturbation series the linear geometry is either a minimum or saddle point. The CCSD result, which sums the singles and doubles portion of the perturbation series to infinite order, predicts that the linear geometry is unstable with respect to bending. The inclusion of connected triples within the CCSD(T) model suggests the same result, albeit with somewhat smaller imaginary frequency. It is also important to note that the energy contribution of the triples correction is somewhat larger for HPC (approximately -0.020 h for HPC vs -0.014 h for HCP in the 6-31G** basis, which is also consistent with a larger *T*₁ diagnostic for HPC (0.041) than HCP (0.017)). This leads to a small lowering of the energy difference between HCP and HPC, of about 4 kcal/mol, when comparing CCSD and CCSD(T) (see Table 5).

Due to the quantitative similarity of the 6-31G** and 6-311G** results, we chose to examine the effects of diffuse functions in a 6-31++G** basis; these results are shown in Table 6. It is seen that diffuse functions have a relatively large effect on the bending frequency at the MP2 level, but little effect on the two stretching frequencies. The trend is to lower the bending force constant (make more negative) in all methods. This was observed in the larger basis sets at the MP2 level as well, but in those basis sets we did not use diffuse functions in the CCSD calculations. Thus in those cases we will assume

TABLE 5: $\Delta E(\text{HPC}-\text{HCP})$ as a Function of Method and Basis Set^a

| basis set | method | ΔE (kcal/mol) |
|-----------------|---------|-----------------------|
| 6-311G** | RHF | 93.6 |
| | MP2 | 83.3 |
| | MP3 | 87.2 |
| | CCSD | 83.0 |
| | CCSD(T) | 79.1 |
| 6-311++G** | MP2 | 82.8 |
| 6-311G(2d,2p) | MP2 | 83.6 |
| 6-311G(2df,2pd) | MP2 | 83.0 |
| 6-311G(3df,3pd) | MP2 | 82.2 |

^a ΔE is defined as the energy of HPC minus that of HCP, each at its own stationary point for the method and basis.

TABLE 6: HPC Results in 6-31++G Basis^a**

| method | E (au) +379.0 | R_{HP} (Å) | R_{CP} (Å) | ω_1, ω_2 | ω_3 | ω_4 |
|---------|--------------------|------------------------|------------------------|----------------------|------------|------------|
| MP2 | -0.223 82 | 1.414 | 1.633 | 271 | 1051 | 2410 |
| MP3 | -0.224 50 | 1.398 | 1.596 | 473 <i>i</i> | 1247 | 2531 |
| CCSD(T) | -0.257 92 | 1.421 | 1.627 | 372 <i>i</i> | 1110 | 2323 |

^a Frequencies are harmonic frequencies, in cm^{-1} .

TABLE 7: CCSD Results for HPC vs Basis Set^a

| basis | E (au) +379.0 | R_{HP} (Å) | R_{CP} (Å) | ω_1, ω_2 | ω_3 | ω_4 |
|-----------------|--------------------|------------------------|------------------------|----------------------|------------|------------|
| 6-311G** | -0.2765 | 1.411 | 1.608 | 397 <i>i</i> | 1185 | 2416 |
| 6-311G(2d,2p) | -0.2952 | 1.413 | 1.610 | 469 <i>i</i> | 1153 | 2339 |
| 6-311G(2df,2pd) | -0.3243 | 1.412 | 1.605 | 436 <i>i</i> | 1181 | 2397 |

^a Frequencies are harmonic frequencies, in cm^{-1} .

that the net effect of expanding the basis set to include diffuse functions would be to make the force constant more negative.

For the smaller basis sets the perturbation series is oscillatory for the character of the linear HPC geometry. In order to investigate the effects of extended basis sets we performed MP2 (results not presented) and CCSD calculations. The results of Table 7 show that CCSD in larger basis sets predicts that HPC is not a minimum but is instead a saddle point, unstable with respect to bending. Basis set extensions beyond the 6-311G** level lead to little change in the stretching force constants and small changes in the size of the (imaginary) bending frequency. On the basis of the results presented above for the 6-31G** and 6-31++G** basis sets, we predict that extension to the CCSD(T) level would lead to somewhat smaller imaginary frequencies but that inclusion of diffuse functions would tend to increase the magnitude of the imaginary frequency a similar amount, yielding results similar to the CCSD value in a given basis without diffuse functions. On the basis of the MP2 results we also expect that the further extension to the 6-311G(3df,3pd) basis would not significantly alter the present conclusions.

(b) Multireference-Based Methods. The T_1 diagnostic for HPC in the CCSD(T) wave function suggests the multireference character of the wave function is significant enough to view the results with caution.²² In addition, the oscillatory character of the perturbation theory results leads one to ask whether CCSD(T) is robust enough to accurately describe HPC and predict the curvature of the potential surface near the linear geometry. With these questions in mind we have applied a variety of multireference based methods to HPC near the linear geometry. The force constants are based on rigid bending of the molecule and are obtained from a fit to three angles. While these are clearly not the "exact" force constants for HPC for the given basis and method (since we are not at the true minimum) they should assess the curvature of the potential near enough to the minimum to test the CCSD and CCSD(T) results. The calculations we performed can be separated into two classes.

TABLE 8: Multireference-Based Results in VDZP ANO Basis^a

| method | $E(\text{linear})$ | k - (hartrees/deg ²) | ω (cm^{-1}) |
|----------------------|--------------------|---------------------------------------|----------------------------------|
| CASSCF(6/6) | -379.113 770 15 | -8.19E-06 | 339 <i>i</i> |
| CASSCF(8/8) | -379.139 339 34 | -1.05E-05 | 384 <i>i</i> |
| CASSCF(10/10) | -379.159 466 24 | -1.15E-05 | 403 <i>i</i> |
| CASSCF(6/6)/MRSDCI | -379.291 210 61 | -7.31E-06 | 321 <i>i</i> |
| CASSCF(6/6)/MRSDCI+Q | -379.310 623 32 | -7.45E-06 | 324 <i>i</i> |
| CASSCF(6/6)/MRACPF | -379.308 295 95 | -7.53E-06 | 325 <i>i</i> |

^a All force constants and frequencies obtained from rigid bending at standard geometry (see text). Energies are in hartrees.

In the first, we used a small ANO basis to compare the various multireference methods. We then use a subset of the methods to examine the effects of basis set extensions.

The first basis set used is an ANO basis³⁴ which is essentially valence double zeta with one set of polarization functions (denoted VDZP below) and is (8s4p/2s1p) for H, (14s9p4d/3s2p1d) for C, and (17s12p5d/4s3p1d) for P. The energies for HPC in this basis at the standard linear geometry, the force constants obtained from the quadratic fit to the three angles, and the estimated vibrational frequency (in cm^{-1}) are given in Table 8. This is a modest basis, but serves to compare the various methods. It is seen that all methods predict that HPC is unstable with respect to bending, with force constants similar in size to those found using CCSD and CCSD(T). The CASSCF frequencies are all quite similar to those obtained in the CCSD and CCSD(T) calculations, with a modest increase in magnitude as the CAS is increased in size. Inclusion of further correlation using all single and double excitations relative to all functions in the 6/6 CASSCF wave function (second-order CI or second-order ACPF) yields the MRSDCI, MRSDCI+Q, and MRACPF results quoted (CASSCF(6/6)/MRSDCI indicates a single and doubles CI calculation based using the configurations of the 6/6 CASSCF wave function as a reference space). All three methods produce quite similar estimates of the force constant and the vibrational frequency, and while somewhat different from the various CASSCF results, the frequencies are all within 20% of each other. In the 10/10 CASSCF wave function for the linear geometry the σ occupation numbers for the natural orbitals are 1.98, 1.97, 1.92, 0.09, 0.01, and 0.01, while the π occupation numbers are 1.90 and 0.10 (two sets of π orbitals). The 6/6 active space corresponds to removing the two σ orbitals with highest occupation numbers and the two σ orbitals with lowest occupation numbers from the active space. Since the occupation numbers of the σ orbitals neglected in the 6/6 CAS are close to 2 and 0, respectively, it is reasonable to assume that the effects due to correlating the electrons in these orbitals could be treated in the second-order treatment based on the 6/6 CAS.

We tried a variety of other approaches in the VDZP basis as well. We examined the use of only a subset of the CAS functions as reference functions for all valence-electron CI or ACPF equations. The reference functions were chosen as those with coefficients greater than 0.05 or 0.025 in the 6/6 CASSCF wave function at the linear geometry. It was found that either reference space led to a zeroth-order wave function which increased in energy upon bending (contrary to the full CASSCF result). In addition, the MRSDCI result in this smaller reference space predicted the linear configuration was a minimum, while the MRSDCI+Q and MRACPF results predicted HPC was unstable with respect to bending. Finally, it was found that the bending force constants for the MRSDCI+Q and MRACPF results in the smaller reference space calculations were significantly larger than those obtained with the full CAS as a

TABLE 9: Multireference-Based Methods in Larger ANO Basis Sets^a

| basis, method | $E(\text{linear})$ | k (hartrees/deg ²) | ω (cm ⁻¹) |
|---------------------------------|--------------------|-------------------------------------|---------------------------------|
| VTZ2P, CASSCF(6/6) | -379.118 755 81 | -7.04E-06 | 315i |
| VTZ2P, CASSCF(10/10) | -379.164 988 49 | -1.05E-05 | 384i |
| VTZ2P, CASSCF(10/12) | -379.195 324 02 | -8.34E-06 | 342i |
| VTZ2P, CASSCF(6/6)/ MRSDCI | -379.316 091 67 | -6.36E-06 | 299i |
| VTZ2P, CASSCF(6/6)/ MRSDCI+Q | -379.337 822 27 | -6.67E-06 | 306i |
| VQZ3P+(FD), CASSCF(6/6) | -379.122 962 85 | -8.80E-06 | 352i |

^a All force constants and frequencies obtained from rigid bending at standard geometry (see text). Energies are in hartrees.

reference; thus we have not considered using the truncated reference space in the larger basis sets.

We were unable to perform second-order CIs based on the 10/10 CASSCF due to the low symmetry upon bending and the large number of configurations generated. However, in order to estimate the effects of reference space expansion in further correlated calculations we examined use of the recently developed CASPT2 method. The CASPT2 method³⁹ is a second-order perturbation theory based on a CASSCF wave function as a zeroth-order wave function. The zeroth-order Hamiltonian is a sum of Fock-like operators, and the theory reduces to MP2 in the limit that the zeroth-order wave function is a single configuration. We used the form of the theory based on the full nondiagonal Fock operator. We found that the nondiagonal form predicted HPC was unstable with respect to bending for both CASSCFs (6/6 and 10/10) but the results were quite nonquadratic and tended to flatten out as the angle increased. We thus have not included quadratic force constants for CASPT2. However, we did find that the multireference second-order method reverses the prediction of MP2 as to the stability of HPC and that there is no significant alteration in the conclusions obtained from the 6/6 reference space when the larger CAS wave functions are used as reference functions.

In Table 9 we present results in an ANO basis set of the form H 3s2p, C 4s3p2d, P 5s4p2d (denoted valence triple zeta plus 2 polarization functions; VTZ2P). Due to the similarity between the MRSDCI+Q and MRACPF results quoted above (and in other tests) we only present MRSDCI+Q results. It is seen that HPC is still unstable in the larger basis set, with force constants of similar size to those obtained previously. Further extension to an ANO basis of form H 3s2p1d, C 5s4p3d1f, P 6s5p4d1f (denoted VQZ3P+FD) were examined using the 6/6 CASSCF wave function; these results are also presented in Table 9. It is seen that little change occurs upon basis set extension, relative to the TZ2P basis.

IV. Discussion

The questions we set out to address in the present work were (1) "Is there a stable minimum for HPC at the linear geometry?", and (2) "What is the qualitative nature of the wave function for linear HPC?" We now address them in light of the data presented above.

Concerning question 1, the present results provide strong evidence that linear HPC is not a minimum on the ground-state surface. All of the CCSD and CCSD(T) results indicate that the bending frequency is imaginary with a magnitude of between 300 and 400 cm⁻¹. However, on the basis of the T_1 diagnostic tests performed above one predicts that HPC has significantly more multireference character than HCP at its minimum, and on this basis one may still view the CCSD(T) results with some caution. Using a 10/10 CASSCF wave function in the 6-31G** basis, we found that the difference between HCP and HPC lies

largely in additional excitation out of a σ orbital in HPC (natural orbital occupation 1.91, compared to the lowest σ NO occupation of 1.97 in HCP). The π natural orbital occupations are actually quite similar in the two cases (1.90, HPC; 1.91, HCP). This led us to examine HPC using methods that build in the multireference character of HPC at zeroth-order. These methods uniformly lead to the same conclusion as CCSD(T): linear HPC is not a minimum on the ground-state potential surface. Once one uses a CASSCF wave function as a starting point, even a second-order theory predicts this, and the more extensive correlation treatments support this result quantitatively as well as qualitatively.

Of course, the multireference results are based on fixed bond length bending calculations, at a geometry appropriate to CCSD(T) in the 6-31G** basis, and one might wonder to what extent this geometry choice affects the computed force constants and frequencies. In preliminary test calculations we found that CCSD(T) bending force constants calculated at geometries differing by 0.01 Å in both bond lengths could change by approximately 5%, and thus the values quoted above are not definitive for the given multireference method. However, this also suggests that the qualitative result, that linear HPC is not a minimum, is not seriously called into question by possible geometry variations.

One might wonder why it is that the CCSD(T) method yields results in good agreement with multireference-based methods in a case where it is apparent from the T_1 diagnostic that multireference character is important. However, a variety of tests of CCSD(T) have been made and it appears to be unusually robust in cases at least as demanding as the present. For example, CCSD(T) results with values of T_1 in the range of 0.04–0.05 have shown to yield good total energies, geometries, and/or vibrational frequencies when compared with full CCSDT, full CI, or CASSCF studies.^{40,41} In addition, even when T_1 does get large (e.g., T_1 equals 0.08, $^1\Sigma$ state of BN) the error in vibrational frequency relative to a multireference based treatment⁴² is on the order of 50–60 cm⁻¹. When the T_1 diagnostic is on the order of 0.04 for the $^3\Pi$ state of BN the error in vibrational frequency is much less, on the order of 15 cm⁻¹. Even if our errors are of the same order, this will have no effect on determining whether HPC is a minimum. Thus, it appears that even relatively significant multireference character (it is significant here, note the difference in second-order perturbation theory predictions in going from MP2 to CASPT2N) can be handled by CCSD(T), and HPC is another example of the robustness of the method.

In comparison with our previous results which were unable to determine whether linear HPC was a minimum, it appears that the flatness of the HPC surface and the multiple bond between C and P led to a case where it was important to be able to (a) sum portions of the perturbation series to a higher order (go beyond second order for a single-reference treatment), and/or (b) explicitly treat the state using a multiconfigurational zeroth-order state. Only when one of these approaches was used could one obtain a consistent description of HPC.

It is apparent from previous studies^{12–20} and the above results that the HCP/HPC system is fundamentally different from HCN/HNC in several respects. A recent series of calculations by Bentley et al.² obtains a 14.7 kcal/mol energy difference between HCN (lowest energy conformer) and HNC; our previous¹² and present results suggest that the difference in energy between HCP and HPC is on the order of 80–85 kcal/mol. The HP bond in HPC is much weaker than the HN bond in HNC, if one assumes that the HC bonds are of comparable strengths. On the basis of average bond enthalpies⁴³ one would expect

the difference to be on the order of about 16 kcal/mol for conventional HN and HP single bonds, but this accounts for only about one-quarter of the difference in stabilities of the two less stable structures. Another difference is seen in comparing the HN and HP stretching frequencies in HNC and HPC. For HNC the HN stretch is actually somewhat larger than the HC stretch in HCN, but in HPC the HP stretch has dropped significantly relative to the HC stretch in HCP. This is consistent with the significantly weaker HP bond as well. Finally, the CN bond in HCN and HNC are within 0.01 Å of one another, whereas the CP bonds in HCP and HPC differ by on the order of 0.06–0.07 Å. The associated CX vibrational frequency is also reduced to a greater extent in HPC than in HNC, as would be expected based on the lengthened CP bond. Finally, one sees that experimentally and theoretically, HNC is predicted to be a stable minimum, whereas HPC has not been isolated or observed experimentally.

One can rationalize the differences in stability between HPC and HNC based on simple ideas of hybridization, and the nature of the bonding required in the two species. In order to preserve the triple bond character in the CX moiety, X is forced to hybridize its *s* and *p_z* orbitals when the HXC species is formed if a triple bond to C is to be maintained. However, when HCX is formed, X need not hybridize the *ns* pair significantly (although it likely does in the case of HCN). Thus one can attribute the large difference between HPC and HNC to the relative ease of hybridization for second-row atoms when compared with third-row atoms. Of course, this qualitative picture still does not allow one to predict whether HPC is a stable species or not, except in the limit of an HP bond strength of zero. However, on the basis of the above results it is seen that HPC is, in fact, not a minimum on the ground-state potential.

It is of interest to note that our present conclusions are consistent with the results of Lehmann et al.⁷ and support our previous CASSCF conclusions.¹² The unusual harmonicity of the HCP bending potential remains to be treated at high levels, but the present work suggests that CCSD(T) wave functions will be the minimum level of single-reference correlation treatment adequate to the task. The (T) correction will be important as the molecule bends, as one expects large rearrangements in the orbitals upon correlation for the bent system.

V. Conclusions

We have performed calculations using a variety of wave functions to examine the stability of HPC. For single-reference-based methods, depending on the order of the perturbation series, it was found that the MP perturbation series predicts HPC is either a minimum or a saddle point. CCSD and CCSD(T) predict HPC is a saddle point. Rigid bending force constants obtained using several multireference correlation treatments support the CCSD and CCSD(T) results. Extensions to the basis sets alter the frequencies to some extent but do not alter this conclusion in a qualitative way.

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