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This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:

In search of phosphorus in astronomical environments: The reaction between the CP radical (X 2ς +) and methanimine / Alessandrini S.; Tonolo F.; Puzzarini C.. - In: THE JOURNAL OF CHEMICAL PHYSICS. - ISSN 0021-9606. - STAMPA. - 154:5(2021), pp. 054306.1-054306.8. [10.1063/5.0038072]

Availability:

This version is available at: https://hdl.handle.net/11585/867585 since: 2022-02-24

Published:

DOI: http://doi.org/10.1063/5.0038072

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S. ALESSANDRINI, F. TONOLO, C. PUZZARINI. IN SEARCH OF PHOSPHOROUS IN ASTRONOMICAL ENVIRONMENTS: THE REACTION BETWEEN THE CP RADICAL ($X^2\Sigma^+$) AND METHANIMINE. J. CHEM. PHYS. 154 (2021) 054306

The final published version is available online at: https://doi.org/10.1063/5.0038072

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In Search of Phosphorous in Astronomical Environments: The Reaction Between the CP radical ($X^2\Sigma^+$) and Methanimine.

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(Dated: 15 June 2023)

Phosphorus is of particular interest in astrochemistry because it is a biogenic element together with hydrogen, carbon, nitrogen, oxygen, and sulfur. However, the chemical evolution of such element in the interstellar medium (ISM) is still far from an accurate characterisation, with the chemistry of P-bearing molecules being poorly understood. To provide a contribution in this direction, we have carried out an accurate investigation of the potential energy surface for the reaction between the CP radical and methanimine (CH₂NH), two species already detected in the ISM. In analogy to similar systems, i.e. (CH₂NH + X, with X = OH, CN and CCH), this reaction can occur –from an energetic point of view– in the harsh conditions of the ISM. Furthermore, since the major products of the aforementioned reaction, namely *E*- and *Z*-2-phosphanylidyneethan-1-imine (HN=CHCP) and N-(phosphaneylidynemethyl)methanimine (H₂C=NCP), have not been spectroscopically characterised yet, some effort has been made for filling this gap by means of accurate computational approaches.

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I. INTRODUCTION

Phosphorous is an essential constituent of life on Earth due to the important roles played by its compounds in living systems. Therefore, it is considered a biogenic element together with hydrogen, carbon, nitrogen, oxygen, and sulfur.¹ While phosphorous is ubiquitous on our planet, the elemental abundance of gaseous P in the interstellar medium (ISM), i.e. due to P-bearing molecules, is still unclear, the reasons being its low cosmic abundance ($\sim 2.8 \times 10^{-7}$ with respect to hydrogen^{1–3}) and the poor comprehension of its chemistry.^{1,4,5} Concerning the former issue, phosphorous can only be formed by stars having a mass fifteen times greater than the solar mass, thus a small subgroup of astronomical objects.¹ Furthermore, the nuclear processes involved in the production of atomic phosphorous lead to a yield of only 2.5%.^{1,3} Another important consideration is related to the high condensation temperature of atomic phosphorous, which results in what is, probably, a high depletion of such element onto dust grains, thus reducing the possibility of gas-phase reactions involving atomic phosphorus to form P-containing species.⁴

Nonetheless, some small P-bearing molecules have been detected in the ISM and this apparent lack might be due to phosphorous molecules not yet discovered.⁶ In chronological order, the first molecule observed in molecular clouds was PN,^{7,8} followed a few years later by the CP radical $(X^2\Sigma^+)$.⁹ The latter is probably formed from photodissociation processes of the HCP molecule, also detected in the ISM, in 2007.¹⁰ Indeed, the latter species is considered the 'ferry' carry-ing phosphorous from the condensed state to the gas phase, via photodesorption. More recently, searches for PH₃, CCP and the PO molecules have been proven successful,^{11–13} with the latter being also the only species identified in space containing the P-O bond, whose relevance is correlated to its role in biochemistry. Tentative detections of other P-bearing species, like e.g. PH₂CN and CH₃PH₂, turned out to be unsuccessful.¹⁴

The CP and CCP radicals have been detected, up to date, only in the carbon-rich circumstellar shell IRC+10216.^{9,12} Circumstellar envelopes of evolved stars are among the most remarkable chemical laboratories in the universe. Therefore, they are excellent bench tests to understand chemical synthesis in space. Among the molecules that might react with these radicals, a plausible and interesting species is methanimine (CH₂NH), whose presence in IRC+10216 was confirmed by Tenenbaum *et al.*.¹⁵ In this respect, this works aims at investigating the reaction between the CP radical and methanimine, which is particularly promising in view of the fact that the reaction involving the isoelectronic CN radical is the only formation route available so far for the production of *E*- and *Z*-cyanomethanimine (HNCHCN) in the gas phase.^{16,17} Furthermore, it has been recently demonstrated that the reaction between methanimine and the CCH radical leads to the formation of propargylimine,¹⁸ a newly detected species in the ISM,¹⁹ and it has been suggested that the reaction of CH₂NH with small radicals is a general mechanism for the production of complex imines.¹⁸ Among the successful reaction of methanimine, that with the OH radical²⁰ should also be mentioned.

In analogy with the works previously cited, the expected products of the CP + CH₂NH reaction are *E*- and *Z*-2-phosphanylidyneethan-1-imine (HN=CHCP) and N-(phosphaneylidynemethyl)methanimine (H₂C=NCP). In the present study, an accurate rotational spectroscopic characterisation of these species has also been carried out, with our spectral simulations providing a useful support to experimental measurements. The accurate knowledge of the experimental rotational spectra is, indeed, the mandatory requirement for astronomical searches.^{3,21}

This paper is organised as follows. In the next section, the computational methodologies employed for the accurate investigation of the potential energy surface (PES) of the reactive system, as well as those used for the computational spectroscopic investigations are outlined. In third section, the reactive PES is discussed in view of drawing the most important energetic considerations. Subsequently, the results of the spectroscopic characterisation for the products will be reported, together with the corresponding spectral simulations. In the last section, the conclusions will be sketched.

II. COMPUTATIONAL METHODS

The reactive PES of the CP + CH₂NH system has been explored employing the double-hybrid B2PLYP functional,²² including the D3 dispersion correction^{23,24} and using the partially augmented jun-cc-pVTZ basis set with an additional *d* function on second-row atoms, namely the jun-cc-pV(T+*d*)Z basis set^{25–28} (available on the Basis Set Exchange website^{29–31}). The nature of the stationary points located on the reactive PES has been confirmed by Hessian evaluations at the same level of theory, which also provide the corresponding harmonic zero-point vibrational energy (ZPE) corrections. To ensure the correct linking of the reaction pathways, each transition state (TS) has been connected to the corresponding minima by means of the intrinsic reaction coordinate (IRC) analysis.³²

To improve the quality of the $CP + CH_2NH$ reactive PES, the next step was the refinement

of the electronic energies, which have been computed using the junChS composite scheme.³³ This approach starts from a single-point energy calculation employing the CCSD(T) method (coupled cluster singles and doubles with a perturbative treatment of triples)³⁴ in conjunction with the jun-cc-pV(T+*d*)Z basis set and within the frozen-core approximation (fc). This leading term (E(CC/junTZ)) is then corrected by incorporating two terms, thus relying on the additivity approximation:

1. The extrapolation to the complete basis set (CBS) limit. This contribution (ΔE_{MP2}^{∞}) is obtained as described in eq. 1, with second-order Møller-Plesset perturbation theory³⁵ (MP2) being used in fc energy calculations in conjunction with the jun-cc-pV(T+*d*)Z and jun-cc-pV(Q+*d*)Z basis sets. The total fc-MP2 energies are then extrapolated to CBS limit by employing the n^{-3} formula by Helgaker *et al.*³⁶. The effective contribution is obtained by subtracting the MP2/jun-cc-pV(T+*d*)Z energy from the extrapolated value:

$$\Delta E_{\rm MP2}^{\infty} = \frac{4^3 E_{\rm MP2}^{\rm jun(Q+d)Z} - 3^3 E_{\rm MP2}^{\rm jun(T+d)Z}}{4^3 - 3^3} - E_{\rm MP2}^{\rm jun(T+d)Z}$$
(1)

2. The core-valence (CV) correlation contribution. This term, denoted as ΔE_{MP2}^{CV} , accounts for the correlation of core electrons. It is computed as the energy difference between all-electron (ae) and fc-MP2 computations, both performed with the polarized-weighted core valence triple- ζ basis set (cc-pwCVTZ)³⁷.

Overall, the total junChS electronic energy is given by:

$$E(\text{junChS}) = E(\text{CC/junTZ}) + \Delta E_{\text{MP2}}^{\infty} + \Delta E_{\text{MP2}}^{\text{CV}}$$
(2)

To avoid spin-contamination of higher electronic spin-states, the junChS approach was evaluated using the restricted open-shell Hartree-Fock wave function (ROHF) for both the $CCSD(T)^{38,39}$ and MP2^{40,41} methods, as pointed out in ref. 42. In contrast, B2PLYP-D3 energies have been computed using the unrestricted version of the reference wave function (UHF) in view of the fact that density functional theory (DFT) is less affected by spin-contamination.⁴³ While the accuracy of the junChS model has been demonstrated for the interaction energy of noncovalent complexes, this is its first application in reaction energies. For this reason, its accuracy has been checked by evaluating a small portion of the PES using an HEAT-like protocol, which is described in detail in refs. 42, 44–48. According to ref. 42, the cc-pVnZ basis sets^{25,27} have been employed to compute the extrapolation to the CBS limit of the Hartree-Fock self consistent field (HF-SCF; with *n*=T,Q, and 5) and fc-CCSD(T) correlation (*n*=T and Q) energies. The contribution due to the correlation of inner electrons has been included at the CCSD(T)/cc-pCVTZ^{37,49} level. However, to reach the "sub-kJ accuracy", also other additive terms have been considered: (i) the full account of triple excitation at the CCSDT/cc-pVTZ level of theory;^{50,51} (ii) the contribution of quadruple excitation by means of the CCSDT(Q) method^{52–54} in conjunction with the cc-pVDZ basis set; (iii) the scalar relativistic correction (the mass-velocity and Darwin terms) using perturbative techniques,^{55,56} computed at the CCSD(T)/aug-cc-pCVDZ level; (iv) the diagonal Born-Oppenheimer correction (DBOC) computed at the HF-SCF level⁵⁷ in conjunction with the aug-cc-pVDZ basis set.^{27,58}

The energetic investigation of the CP + CH₂NH reactive PES has been complemented by the spectroscopic characterisation of the three major products, namely *E*- and *Z*-HN=CHCP and H₂C=NCP. To accurately simulate their rotational spectra, the rotational and centrifugal distortion constants should be computed at the highest possible level of theory.⁵⁹ Since equilibrium rotational constants (B_e) are straightforwardly derived from the equilibrium structure, an accurate geometry optimisation has been carried out. In detail, the fc-CCSD(T)/CBS(Q,5)+CV/(pwCVTZ) 'gradient' composite scheme^{60,61} has been exploited, the following energy gradient thus being minimised:

$$\frac{dE_{\text{CBS+CV}}}{dx} = \frac{dE_{\text{HF}}^{\text{CBS}}}{dx} + \frac{d\Delta E_{\text{CCSD}(\text{T})}^{\text{CBS}}}{dx} + \frac{d\Delta E_{CV}}{dx}, \qquad (3)$$

where the first term on the right-hand side is the extrapolation of the HF-SCF energy to the CBS limit using the 3-point expression by Feller⁶² in combination with the cc-pV(n+d)Z basis sets, with n=T, Q, and 5. The second term is the extrapolation to the CBS limit of the CCSD(T) correlation energy obtained with the n^{-3} formula, previously introduced for the junChS model, and employing the cc-pV(Q+d)Z and cc-pV(5+d)Z sets. The last term is the CV contribution, which is computed at the CCSD(T)/cc-pwCVTZ level. Further details, can be found in refs. 60, 61, and 63. To move from equilibrium to the vibrational ground state, vibrational corrections to the equilibrium rotational constants have to be included.^{59,64} Within second-order vibrational perturbation theory (VPT2),^{65,66} these corrections require the knowledge of the vibration-rotation interaction constants, which in turn involve anharmonic force field computations (full cubic and semi-diagonal quartic force constants). These have been carried out at the B2PLYP-D3/jun-cc-pV(T+d)Z level.

The other parameters needed for a reliable simulation of the rotational spectrum are:

- the quartic centrifugal-distortion constants, which have been obtained from a harmonic force field computed at the ae-CCSD(T)/cc-pwCVQZ level of theory.
- the electric dipole moment components, which have been obtained combining the equilibrium values at the ae-CCSD(T)/pwCVQZ level with the vibrational corrections at the B2PLYP-D3/jun-cc-pV(T+d)Z level.

All DFT computations together with the single-point energy calculations within the junChS scheme have been carried out using the Gaussian suite of program,⁶⁷ while geometry optimisations and force-field evaluations involving the CCSD(T) method have performed employing the CFOUR quantum chemical program package^{68,69}.

III. RESULTS

A. The reactive PES of the CP + CH₂NH system

The severe conditions of the interstellar clouds, namely low temperatures (10-100 K) and low number density $(10-10^7 \text{ cm}^{-3})$ pose tight constraints on reactivity, thus allowing only reactions that can occur without overcoming activation barriers, with the only exception due to tunnelling effects. For this reason, we focused on reaction pathways presenting only submerged barriers. Based on previous studies,^{17,18} the nucleophilic attacks of the C-end of the CP radical on both the carbon and nitrogen side of methanimine have been considered. The resulting reaction paths are depicted in Figure 1, which also shows the structures of all the stationary points identified.

The strong nucleophilicity of the CP radical leads to three barrierless entrance channels:

- The CP attack to the methanimine C-end. This forms two isomers of the pre-reactive complex MIN1, MIN1e and MIN1z, which can easily interconvert through TSi because of the low isomerization barrier (~10 kJ mol⁻¹).
- 2. The CP attack to the methanimine N-end. This leads to the formation of a planar pre-reactive complex, **MIN4**.
- 3. The CP attack to the π -system of the imine double bond. This leads to the formation of a stable cyclic adduct (**MIN3**), which links the left (N-end) and right (C-end) portions of the reactive PES through barriers of the order of 50-60 kJ mol⁻¹.



Reaction Coordinate

FIG. 1. CP+CH₂NH reaction pathways: junChS relative energies (**black**) and their harmonic ZPE-corrected (**blue**) counterparts.

Despite the weaker electrophilic character of nitrogen compared to the carbon atom of methanimine, the **MIN4** intermediate is the most stable pre-reactive complex from an energetic point of view, analogously to what occurs in the reactions of methanimine with CN or CCH.^{17,18} This might be attributed to the stabilising effect of electronic delocalisation. However, the crucial interconversion barriers between the first intermediates, i.e. **MIN4**, **MIN3**, and **MIN1e/z**, are slightly different from those obtained for the CCH radical¹⁸. The intermediates **MIN4** and **MIN1** (both the *E* and *Z* isomers) evolve into the products **CH**₂**NCP** and **HNCHCP** (both the *E* and *Z* isomers), respectively, by elimination of a hydrogen atom. The elimination mechanism can occur in two different ways: either through a path (depicted in **black** in Figure 1) involving only one transition state at high energy (**TS6**, **TS1e** and **TS1z**), but still submerged with respect to reactants, or through a two-step path (depicted in **blue** in Figure 1), which involves the formation of the most stable intermediates (**MIN5** and **MIN2**) of the entire PES.

Table I collects the B2PLYP-D3/jun-cc-pV(T+d)Z and junChS relative energies, together with

the ZPE-corrected counterparts, for all stationary points of the reactive PES. While the junChS model does not change the trends resulting from DFT calculations, it reduces the relative energies by about 14-30 kJ mol⁻¹. In particular, the largest change occurs for **TS6** which increases the relative energy by about 30 kJ mol⁻¹, thus approaching the energy of the reactants (albeit being still submerged). Overall, we can note that the reaction barriers are approximately left unchanged.

As mentioned in the previous section, to validate the accuracy of the junChS approach, the path **Reactants** \rightarrow **MIN1** (both the *E* and *Z* isomers) \rightarrow **TS1** (both the *E* and *Z* isomers) \rightarrow **HNCHCP** (both the *E* and *Z* isomers) has been re-investigated employing the HEAT-like protocol^{42,44–48} on top of B2PLYP-D3/jun-cc-pV(T+*d*)Z geometries. The comparison between junChS and HEAT-like energies is reported in Table II and shows a maximum absolute deviation of ~0.8 kJ mol⁻¹ and an average absolute deviation of ~0.6 kJ mol⁻¹. Therefore, it has been confirmed that the approach adopted for this investigation has the required accuracy for reactive PES investigation.

B. Spectroscopic Characterisation of *E*/Z--HNCHCP and CH₂NCP

As mentioned in the Introduction, the identification of new molecules in astronomical environments is driven by the observation of their rotational transitions,⁷⁰ which are unambiguous fingerprints. With only few exceptions,^{71–73} experimental rotational transition frequencies are required for the assignment of the spectra collected by radio-telescopes and/or interferometers. However, whenever there is a complete lack of information, computed spectra are the mandatory starting point for experiment in the laboratory, especially if the species of interest is unstable and produced inside the spectrometer cell via, e.g., electric discharge or pyrolysis.

The laboratory synthesis of species like HNCHCP and CH_2NCP is not feasible and their production *in situ* is challenging. Indeed, a suitable precursor for pyrolysis needs to be envisaged which, according to the works on propargylimine¹⁹ and cyanomethanimine⁷⁴, should be a substituted N-containing phosphine or P-bearing amine. In view of the complexity of the experimental investigation, the accurate computational characterisation of rotational spectra of HNCHCP and CH_2NCP is particularly important.

Table III collects the spectroscopic parameters computed with the protocol described in section 2. According to ref. 63, the expected accuracy of the vibrational ground-state rotational constants is ~0.06%, while the uncertainty affecting the quartic centrifugal-distortion constants is about one order of magnitude greater.^{75,76} Figure 2 depicts the simulation of the rotational spectra of the Z

	B2PLYP-D3/jun-cc-pV(T+d)Z		junChS	
	Energy	ZPE Corrected ^a	Energy	ZPE Corrected ^a
Reactants	0.00	0.00	0.00	0.00
MIN1z	-201.48	-196.38	-180.59	-175.49
TSi	-189.85	-184.06	-169.57	-163.79
MIN1e	-196.65	-190.57	-176.29	-170.22
TS1e	-42.40	-54.73	-24.24	-36.58
TS1z	-47.15	-58.82	-29.46	-41.12
TS2z	-79.03	-80.38	-59.62	-60.98
TS2e	-69.92	-71.80	-51.19	-53.08
MIN2	-326.45	-315.89	-303.66	-293.10
TS3e	-60.41	-72.16	-38.18	-49.92
TS3z	-64.43	-75.96	-42.45	-54.00
E-HNCHCP+H	-73.10	-90.17	-46.67	-63.74
Z-HNCHCP+H	-68.14	-85.71	-51.41	-68.97
TS5	-147.84	-143.05	-129.44	-124.62
MIN3	-214.53	-201.92	-197.30	-184.75
TS4	-152.28	-144.29	-138.47	-130.48
MIN4	-241.05	-234.78	-215.36	-209.02
TS6	-36.00	-48.47	-5.68	-18.26
TS7	-58.84	-63.19	-34.76	-39.19
MIN5	-321.65	-311.06	-293.22	-282.53
TS8	-50.70	-65.57	-27.29	-42.04
CH ₂ NCP+H	-58.87	-78.08	-30.77	-49.96

TABLE I. Relative electronic energies (kJ mol⁻¹) of the stationary points for the CP + CH₂NH reaction.

^a Harmonic ZPE corrections at the B2PLYP-D3/jun-cc-pV(T+*d*)Z level.

and E isomers of HNCHCP, at a temperature of 100 K, based on the spectroscopic parameters of Table III. This figure shows that, while the maximum of intensity is around 180 GHz for both species, the larger dipole moment components of the E isomer result in a more intense spectrum.

	junChS	HEAT-like	$ \Delta E ^{\mathrm{a}}$
MIN1z	-180.59	-179.86	0.73
MIN1e	-176.29	-175.50	0.79
TS1e	-24.24	-24.67	0.43
TS1z	-29.46	-29.90	0.44
Z-HNCHCP+H	-51.41	-51.12	0.29
E-HNCHCP+H	-46.67	-45.86	0.81

TABLE II. Relative electronic energies (kJ mol⁻¹) for the $CH_2NH + CP \rightarrow MIN1e/z \rightarrow TS1e/z \rightarrow Z/E$ -HNCHCP+H path.

^a Absolute junChS - HEAT-like energy difference.



FIG. 2. Left panel: Simulated rotational spectra of *Z*- and *E*-HNCHCP, blue and red lines, respectively, up to 400 GHz. Right panel: Zoom of the rotational spectra between 30 and 100 GHz. Intensity in nm²MHz

Since the uncertainties on the computed parameters propagate by increasing the rotational quantum number *J* (denoting the lowest rotational level involved in the transition), the most accurate estimates are obtained for rotational transitions with low *J* values, which usually lie at low frequencies. For this reason, Figure 2 also reports a zoom of the rotational spectra in the 30 - 100 GHz frequency range, with the different K_a -components of each transition being evident. It has to be noted that, for both isomers, *a*- and *b*-type transitions are observable; however, the μ_b component of the dipole moment is rather small, in particular for the *Z*-HNCHCP species. As a consequence, the *b*-type spectrum of *Z*-HNCHCP is not discernible in Figure 2; for the *E* isomer, instead, this type of transitions becomes well visible at frequencies greater than 250 GHz (darker red lines).

	-		
Parameter ^a	Z-HNCHCP	E-HNCHCP	CH ₂ NCP
A_e	50319.38	58098.90	61454.73
B_e	2846.04	2796.71	2997.13
C_e	2693.69	2668.27	2857.76
$\Delta A_{\rm vib}$	272.77	52.49	1372.17
$\Delta B_{ m vib}$	-11.55	-6.82	-17.25
$\Delta C_{ m vib}$	-12.34	-8.66	-16.54
A_0	50592.15	58151.39	62826.90
B_0	2834.49	2789.89	2979.88
C_0	2681.35	2659.61	2841.22
D_J	0.65×10^{-3}	$0.54 imes 10^{-3}$	0.63×10^{-3}
D_{JK}	-0.056	-0.066	-0.080
D_K	3.9	6.2	7.7
d_1	$-0.90 imes 10^{-4}$	$\textbf{-0.70}\times10^{-4}$	$-0.88 imes 10^{-4}$
d_2	-0.47×10^{-5}	-0.32×10^{-5}	-0.45×10^{-5}
$ \mu_a $ / D	1.58	1.90	1.68
$ \mu_b $ / D	0.06	0.37	1.39
$ \mu_c $ / D	0.00	0.00	0.00

TABLE III. Rotational spectroscopic parameters (MHz, if not otherwise stated) of E-/Z-HNCHCP and CH₂NCP (Watson's *S* reduction, I^r representation).

^a Equilibrium rotational constants at the fc-CCSD(T)/CBS(Q,5)+CV/(pwCVTZ) level. Anharmonic corrections (ΔB_{vib} 's) at the B2PLYP-D3/jun-cc-pV(T+d)Z level. Quartic centrifugal distortion constants at the ae-CCSD(T)/cc-pwCVQZ level. Equilibrium dipole moment components (in debye) at the ae-CCSD(T)/cc-pwCVQZ level corrected for vibrational contributions at the B2PLYP-D3/jun-cc-pV(T+d)Z level.

In Figure 3, the rotational spectrum for CH₂NCP, simulated at T=100 K, is shown in the 0-500 GHz frequency range. Both *a*- and *b*-type transitions are evident, and the maximum of intensity is above 500 GHz. However, at such frequencies, the predictions are less accurate, and higher frequencies have not thus been considered. A good candidate for the observation in the case of CH₂NCP is the transition $J_{K_a,K_c} = 2_{1,2} \leftarrow 1_{1,1}$, which is predicted at 11503.8 MHz with an error,



FIG. 3. Simulated rotational Spectrum of CH_2NCP in the 0-500 GHz frequency range. Intensity in nm^2MHz .

according to estimates addressed above, of only 5.4 MHz.

IV. CONCLUSIONS

In analogy to the addition of the CN and CCH radicals to methanimine, the CP radical is expected to lead to reaction paths that are 'open' (i.e. energetically accessible) in the harsh conditions of the ISM. Interestingly, the reactive CP + CH₂NH PES is, in any detail, analogous to that of the CN + CH₂NH and CCH + CH₂NH systems, thus supporting the idea of a general mechanism for the formation of complex imines in interstellar clouds. Furthermore, the present work is the first application of the new junChS model for energetic studies of reactive PESs. The comparison with the results issuing from an extremely accurate HEAT-like approach pointed out to a great accuracy and suitability for energy evaluations of reactive systems, despite its limited computational cost. Finally, this work has been complemented by the spectroscopic characterisation of the major reaction products, namely *E*-/*Z*-HNCHCP and CH₂NCP, with a methodology at the state of the art, able to predict rotational transitions with an accuracy better than 0.2%.

DEDICATION

This work is dedicated to Laura Bassi-Veratti (Bologna, 1711-1778) as the symbol of all women who pursued or are pursuing a scientific academic career. She was the second woman to achieve a university degree, the very first to obtain a PhD in a scientific subject and a teaching position at the University of Bologna. She fought for equal rights for women and men in academics.

ACKNOWLEDGMENTS

This work has been supported by the University of Bologna (RFO funds). The SMART@SNS Laboratory (http://smart.sns.it) is acknowledged for providing high-performance computing facilities. Support by the Italian Space Agency (ASI; 'Life in Space' project, N. 2019-3-U.0) is also acknowledged.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Watts and the integral packages MOLECULE (J. Almlöf and P.R. Taylor), PROPS (P.R. Taylor), ABACUS (T. Helgaker, H.J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wüllen. For the current version, see http://www.cfour.de.

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