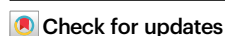


Low temperature synthesis of three cyanocyclopentadiene isomers and their role in interstellar cyano PAH formation

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The recent detection of polycyclic aromatic hydrocarbons and their cyano derivatives in the Taurus Molecular Cloud challenges existing models of their formation and survival under such harsh conditions. Cyanocyclopentadienes have emerged as fundamental molecular building blocks for cyano-substituted aromatics, yet their formation in the interstellar medium remains unknown. Here, we report the gas-phase formation of distinct cyanocyclopentadiene isomers through the bimolecular reaction of 1,3-cyclopentadiene with the cyano radical explored through molecular beam studies and electronic structure calculations. Three cyanocyclopentadiene isomers are identified: the astronomically observed 1-cyanocyclopentadiene and 2-cyanocyclopentadiene species and the elusive 5-cyanocyclopentadiene. Remarkably, the reaction predominantly forms the unobserved 5-cyanocyclopentadiene isomer accounting for two-third of the products, according to dynamics-guided statistical calculations. These results identify 5-cyanocyclopentadiene as a key precursor to cyano substituted aromatics, reveal a gap in current astronomical observations, and motivate targeted searches for this elusive molecule in cold molecular clouds.

Over the past decade, the unexpected molecular complexity of organic molecules detected in the deepest regions of space has captivated the astrochemical community^{1,2}. Cold molecular clouds, despite their extremely low temperatures (10 K)^{3,4}, exhibit a surprising richness of molecular species and have emerged as natural laboratories for nurturing our fundamental knowledge on the organic chemistry through astronomical observations merged with sophisticated laboratory experiments. The Taurus Molecular Cloud (TMC-1) represents a prototypical cold region and materialized as a benchmark for elucidating the complex low temperature organic gas phase chemistry hosting the remarkable inventory of diverse classes of molecules comprising hydrocarbons such as acyclic propylene (CH_3CHCH_2)⁵ and methylacetylene (CH_3CCH)⁶ and cyclic molecules like cyclopropenylidene ($\text{c-C}_3\text{H}_2$)^{7–9} and 1,3-cyclopentadiene ($\text{c-C}_5\text{H}_6$)^{8,9}

along with aromatic hydrocarbons (benzene, C_6H_6 ; indene, C_9H_8)^{8,10} (Fig. 1). These molecular structures are shown in Fig. 1 to provide a visual overview of representative species relevant to the present astrochemical context. Polycyclic aromatic hydrocarbons (PAHs) in particular account for up to 30% of the cosmic carbon budget^{11–14} and play a significant role in the astrobiological evolution of the interstellar medium through nucleation centers eventually accessing carbon-rich interstellar nanoparticles commonly referred to as dust grains¹⁵. However, PAHs have small or even no dipole moments; key tracers of molecular mass growth processes like benzene (C_6H_6), pyrene ($\text{C}_{16}\text{H}_{10}$), and coronene ($\text{C}_{24}\text{H}_{12}$) can only be observed astronomically via their cyano-tagged proxies, whose structures are displayed in Fig. 2 to illustrate their chemical complexity.

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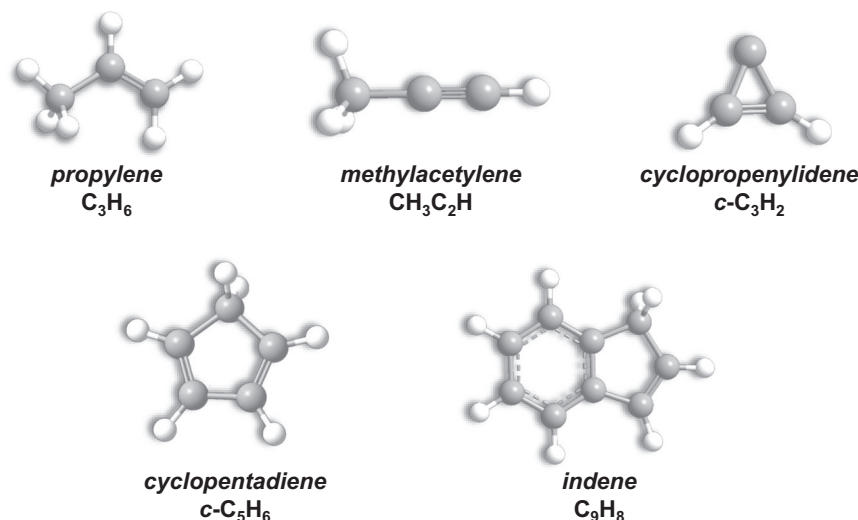


Fig. 1 | Molecular structures of selected hydrocarbons detected in TMC-1. Molecular structures of several hydrocarbons detected in TMC-1. The carbon and hydrogen atoms are color-coded in gray and white, respectively.

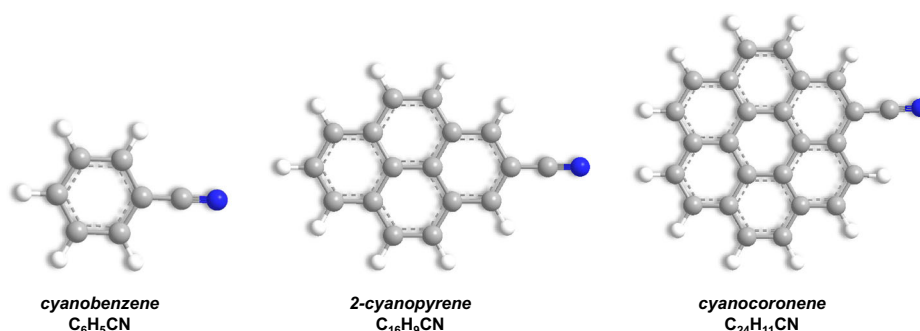


Fig. 2 | Molecular structures of selected cyano-substituted PAHs identified in the interstellar medium. Molecular structures of some cyano-PAHs identified in the interstellar medium and used as proxies for their corresponding PAHs. The carbon, hydrogen and nitrogen atoms are color coded in gray, white and blue, respectively.

A detailed understanding of the complex hydrocarbon chemistry in deep space and key molecular mass growth processes require knowledge how structural isomers—molecules with the same molecular formula, but distinct connectivities of atoms—are synthesized in the gas phase via bimolecular reactions³. This knowledge has to commence with the elucidation of the chemical dynamics of bimolecular reactions in the gas phase of molecular clouds on the most fundamental, molecular level. Recently, the cyclopentadiene moiety ($c-C_5H_6$) has emerged as an entrance point to aromatics¹⁶ as incorporated in, e.g., corannulene ($C_{20}H_{10}$), nanobowls ($C_{40}H_{10}$), and fullerenes (C_{60} and C_{70})^{17–20}. The cyclopentadiene molecule has also been recognized as a key molecular building block for hydrocarbons such as indene or naphthalene¹⁶, as well as their cyano derivatives such as cyanoindenes (C_9H_7CN) and cyanonaphthalenes ($C_{10}H_7CN$) toward TMC-1^{21,22}. The intermediate step towards the formation of the cyano-substituted PAHs from $c-C_5H_6$ has been proposed to be cyanocyclopentadiene isomers (C_5H_5CN)¹⁶, which exists in three isomeric forms (Fig. 3). Among these, 1-cyanocyclopentadiene (**p1**) and 2-cyanocyclopentadiene (**p2**) were identified in TMC-1 (Table 1)^{23–26}, yet the mechanisms leading to their formation under interstellar conditions has remained elusive. Yang et al.¹⁶ proposed cyanocyclopentadiene (C_5H_5CN) isomers could form via reactions between methyldiene radicals (CH) and 1-cyanobutadiene (C_4H_5CN) or via bimolecular collisions of cyano (CN) and 1,3-cyclopentadiene ($c-C_5H_6$). McCarthy et al.²³ also considered the cyano – cyclopentadiene system in analogy to the formation of cyanobenzene (C_6H_5CN) through the

fast reaction of cyano radicals with benzene (C_6H_6) reaction^{3,27–33}. This knowledge is of particular importance for the identification of specific structural isomers to be incorporated in reaction networks modeling the interstellar chemistry. For instance, 1-cyanocyclopentadiene (**p1**) can react with methyldiene (CH) to produce cyanobenzene (C_6H_5CN), whereas 2-cyanocyclopentadiene (**p2**) was proposed to be a precursor of cyanoindenes (C_9H_7CN)¹⁶. This denotes that reactions of different isomers can lead to a discrete chemical species.

Here, due to the lack of experimental and theoretical studies, we investigated the bimolecular gas-phase reaction between cyano radical (CN) and 1,3-cyclopentadiene ($c-C_5H_6$) by exploiting crossed molecular beams experiment. This allowed us to detect cyanocyclopentadiene isomers (C_5H_5CN) as the reaction products at a collision energy of $E_c = 17.9 \text{ kJ mol}^{-1}$. In combination with electronic structure calculations, the cyano–cyclopentadiene system has been revealed to be a barrierless and exoergic reaction, with all transition states and intermediates lying below the energy of the separated reactants, which opens this reaction in low-temperature environments such as TMC-1. Further, 1-cyanocyclopentadiene (**p1**) has been predicted to be formed in the title reaction as well as small amounts (up to 5%) of 2-cyanocyclopentadiene (**p2**). Interestingly, 5-cyanocyclopentadiene (**p3**), that has not yet been identified in the interstellar medium, is predicted to be the most dominant reaction product with fractional abundances of some 67 %. This finding demonstrates that astronomically ‘hidden’ species such as 5-cyanocyclopentadiene (**p3**) can efficiently be formed under the conditions of cold molecular clouds.

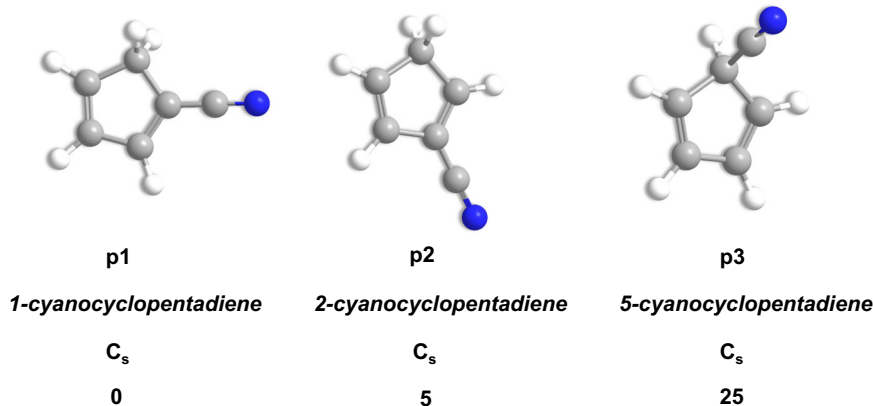


Fig. 3 | Most probable isomer products formed in the reaction of the cyano radical with 1,3 cyclopentadiene. Most probable isomer products formed in the reaction of cyano radicals (CN, $X^2\Sigma^+$) with 1,3-cyclopentadiene ($c\text{-C}_5\text{H}_6$, X^1A_1) along

with the name, point group and relative energies calculated at the CCSD(T)/CBS//B3LYP/cc-pVTZ level of theory shown in kJ mol^{-1} . The nitrogen, carbon and hydrogen atoms are color coded in blue, gray and white, respectively.

Table 1 | Astronomical observations and abundances of 1-cyanocyclopentadiene (p1) and 2-cyanocyclopentadiene (p2)

Molecule	Fractional abundance	Source	Reference
1-cyanocyclopentadiene (p1)	$(1.4 \pm 0.3) \times 10^{-10}$	TMC-1	23
1-cyanocyclopentadiene (p1)	$(8.3 \pm 0.9) \times 10^{-11}$	TMC-1	24
2-cyanocyclopentadiene (p2)	$(1.9 \pm 0.2) \times 10^{-11}$		
1-cyanocyclopentadiene (p1)	$(3.1 \pm 0.3) \times 10^{-11}$	TMC-1	25
2-cyanocyclopentadiene (p2)	$(1.3 \pm 0.2) \times 10^{-11}$		
1-cyanocyclopentadiene (p1)	6.6×10^{-12}	L1495B	26

To date 5-cyanocyclopentadiene (p3) has not been observed in the interstellar medium.

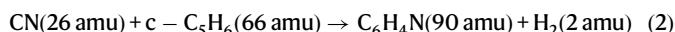
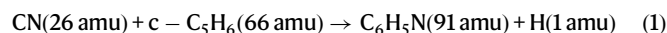
These results reveal a critical gap in current astronomical observations and identify 5-cyanocyclopentadiene (p3) as a key precursor to cyano-substituted aromatics thus challenging conventional wisdom that cyano-substituted PAHs are predominantly accessed by cyano radical reactions with PAHs. This study bridges laboratory experiments, computations, and astrochemical models, highlighting the need for targeted astronomical searches of this astronomically elusive molecule in cold molecular clouds eventually deciphering the origin of cyano-substituted aromatics in our Galaxy.

Results and discussion

Laboratory frame

The gas-phase reaction of the cyano radical (CN; $X^2\Sigma^+$; 26 amu) with 1,3-cyclopentadiene ($c\text{-C}_5\text{H}_6$; X^1A_1 ; 66 amu) was investigated under single collision conditions in a crossed molecular beams machine^{34,35}. The reactive scattering signal was recorded at mass-to-charge (m/z) ratio $m/z = 91$ ($\text{C}_6\text{H}_5\text{N}^+$) suggesting the formation of a molecule with the formula $\text{C}_6\text{H}_5\text{N}$ plus a neutral hydrogen atom (H) (reaction (1)). No signal was observed at $m/z = 90$ ($\text{C}_6\text{H}_4\text{N}^+$) for a potential molecular hydrogen elimination route (reaction (2)) and/or dissociative electron impact ionization of the $\text{C}_6\text{H}_5\text{N}$ neutral product (91 amu). To obtain the laboratory angular distribution (LAD), angle-resolved time-of-flight (TOF) spectra were collected, integrated, and normalized relative to the TOF data recorded at the center-of-mass (CM) angle of $53.4 \pm 0.6^\circ$. The TOF spectra were recorded in 5° intervals between 27.25° and 62.25° along with 64.25° within the scattering plane with accumulation times of up to 17 h (1.7×10^6 time of flight spectra) per angle. These TOFs were some 400 μs wide spanning a range between 600 and 1000 μs . Figure 4a,b shows the resulting LAD and representative TOF spectra recorded at $m/z = 91$ for the title reaction. The LAD reveals an

apparent symmetry with a broad maximum near the CM angle. This feature is suggestive of an indirect reaction mechanism along with the formation of intermediate(s) ($\text{C}_6\text{H}_6\text{N}$); the latter then eliminate a hydrogen atom (H) to form $\text{C}_6\text{H}_5\text{N}$ isomers.



Center-of-mass frame

To investigate the underlying chemical dynamics and reaction mechanisms, a forward convolution method transforming the laboratory measurements (TOFs, LADs) into the center-of-mass (CM) reference frame was employed^{3,36,37}. Using this approach, the CM translational energy ($P(E_T)$) and angular ($T(\theta)$) flux distributions are obtained as illustrated in Fig. 4c,d with θ denoting the CM scattering angle. This figure exhibits the best-fit CM functions employing a single-channel hydrogen atom loss fit of the data obtained at $m/z = 91$ via reaction (1) for the $\text{CN}(X^2\Sigma^+)/\text{C}_5\text{H}_6(X^1A_1)$ system. Turning first to a detailed examination of the $P(E_T)$ (Fig. 4c), the maximum translational energy released (E_{max}) was determined to be $152.0 \pm 20.9 \text{ kJ mol}^{-1}$. Accounting for the conservation of energy, E_{max} represents the sum of the collision energy E_c ($17.9 \pm 0.6 \text{ kJ mol}^{-1}$) plus the reaction exoergicity for those product molecules born without internal energy. Therefore, the reaction was determined to be exoergic by $134.2 \pm 20.9 \text{ kJ mol}^{-1}$. The $P(E_T)$ exhibits further a broad distribution maximum at $61 \pm 8 \text{ kJ mol}^{-1}$, suggesting the existence of at least a tight transition state upon unimolecular decomposition of the $\text{C}_6\text{H}_6\text{N}$ reaction intermediates along with a substantial electron density organization during product formation³⁸. In addition, the products were found to exhibit an average translational energy of $68 \pm 9 \text{ kJ mol}^{-1}$ corresponding to $45 \pm 12\%$ of the total available energy channeled into their translational degrees of freedom. This observation also suggests the formation of a covalently bound intermediate³. The angular flux distribution $T(\theta)$ (Fig. 4d) depicts intensity over the full angular range, which strengthens the interpretation of an indirect reaction mechanism involving bound reaction intermediates^{3,39}. Furthermore, the $T(\theta)$ reveals a noticeable forward asymmetry, with intensity ratios $I(0^\circ)/I(180^\circ)$ of approximately $(1.9 \pm 0.6):1.0$. This pattern indicates the presence of at least one reaction pathway involves an oscillating complex³ and hence a complex lifetime too short to undergo multiple rotations. These findings are reflected in the flux contour map (Fig. 4e), which presents the differential cross-section as $I(\theta, u) - P(u) \times T(\theta)$. This

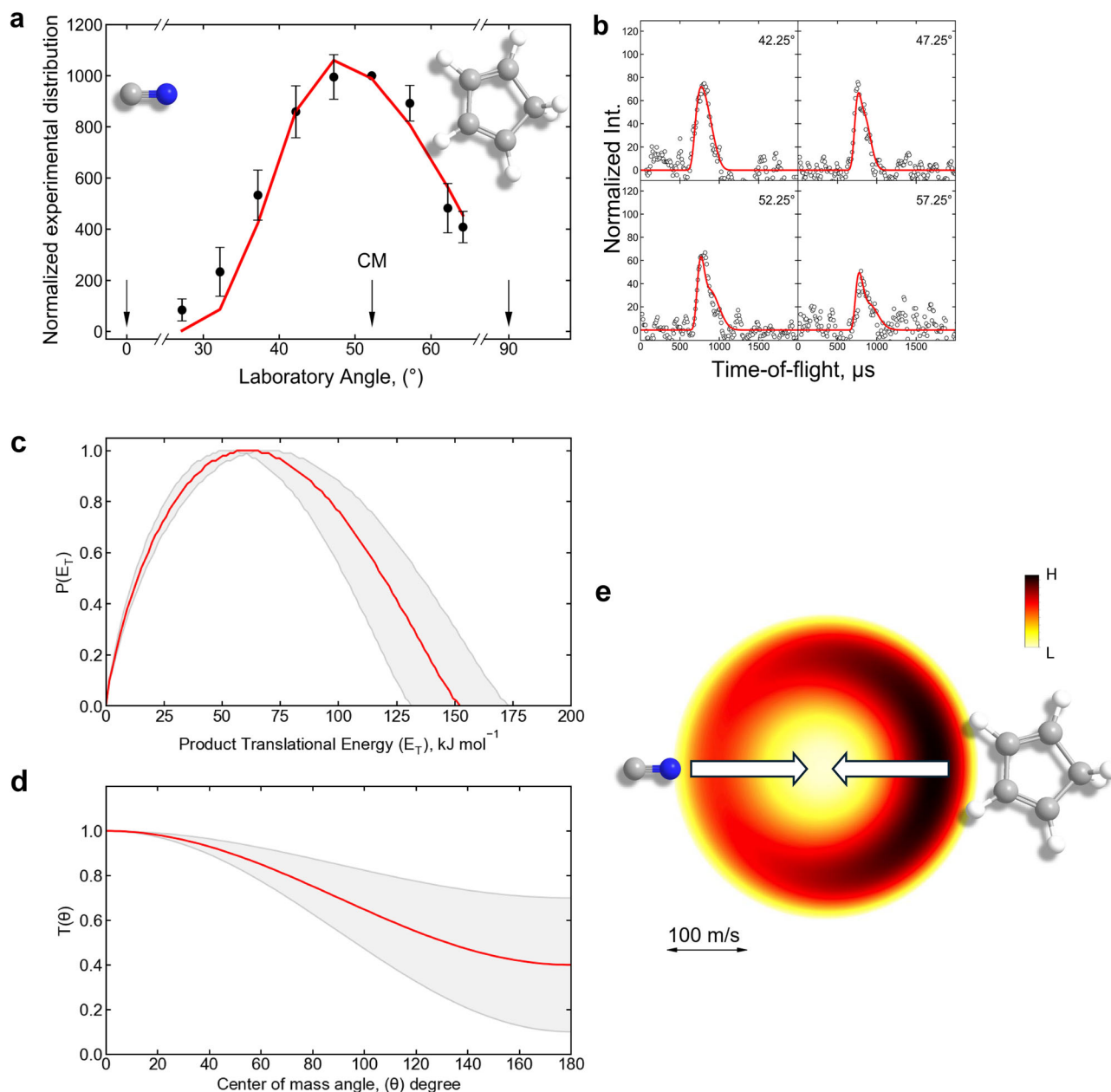


Fig. 4 | Experimental scattering results, angular and translational energy distributions, and flux contour map for the reaction of cyano radicals with 1,3-cyclopentadiene. **a** Laboratory angular distribution and **b** time-of-flight (TOF) spectra recorded at $m/z = 91$, **c** Center-of-mass translational energy ($P(E_T)$), **d** angular distributions ($T(\theta)$), and **e** corresponding flux contour map for the reaction of the cyano radicals ($\text{CN}, X^2\Sigma^+$) with 1,3-cyclopentadiene ($\text{c-C}_5\text{H}_6, X^1A_1$) with laboratory data recorded at $m/z = 91$. The bar errors in **(a)** denote $\pm 1\sigma$ (standard

deviation of the TOF integrals at each angle). The black circles in **(b)** represent the experimental and the solid red lines are the best fits. The red solid lines in **(c)** and **(d)** represent the best fit of the laboratory data and shaded areas are the error limits. For the $T(\theta)$, the direction of the cyano radical beam is defined as 0° and of the 1,3-cyclopentadiene as 180° and the color bar indicates flux gradient from high (H) to low (L) intensity.

reports the intensity of the reactively scattered $\text{C}_6\text{H}_5\text{N}$ products and hence provides an overall image of the reaction.

Electronic structure calculations and reaction mechanism

To reveal the nature of the products found in the experiments along with the reaction mechanism, electronic structure calculations were performed. The reaction energy diagram (Fig. 5) features the formation of seven energetically accessible reaction intermediates (**i1-i7**), six atomic hydrogen elimination products (**p1-p6**), and seventeen transition states. For simplicity, high energy intermediates **i8** and **i9** (Fig. S2) with energies of 53 and 55 kJ mol^{-1} above the separated reactants, respectively, are not included in this figure since they are energetically

not accessible under our experimental conditions. The bimolecular gas phase reaction is initiated via the barrierless addition of the cyano radical with its carbon or nitrogen atom to the C1 and/or C2 carbon atoms of the carbon-carbon double bonds of $\text{c-C}_5\text{H}_6$ accessing the initial cyano- (**i1** (C_1, X^2A) and **i2** (C_1, X^2A)) and/or isocyano- (**i3** (C_1, X^2A) and **i4** (C_1, X^2A)) cyclopentenyl doublet radical intermediates. These intermediates are stabilized by 264, 212, 175, and 123 kJ mol^{-1} , respectively, with respect to the separated reactants. The products of this bimolecular reaction (**p1-p6**) can be obtained from each of these intermediates by eliminating a hydrogen atom: **i1** can yield 1-cyanocyclopentadiene (**p1**, $\text{C}_s, X_1A', -103 \text{ kJ mol}^{-1}$) or 5-cyanocyclopentadiene (**p3**, $\text{C}_s, X_1A', -78 \text{ kJ mol}^{-1}$) passing exit

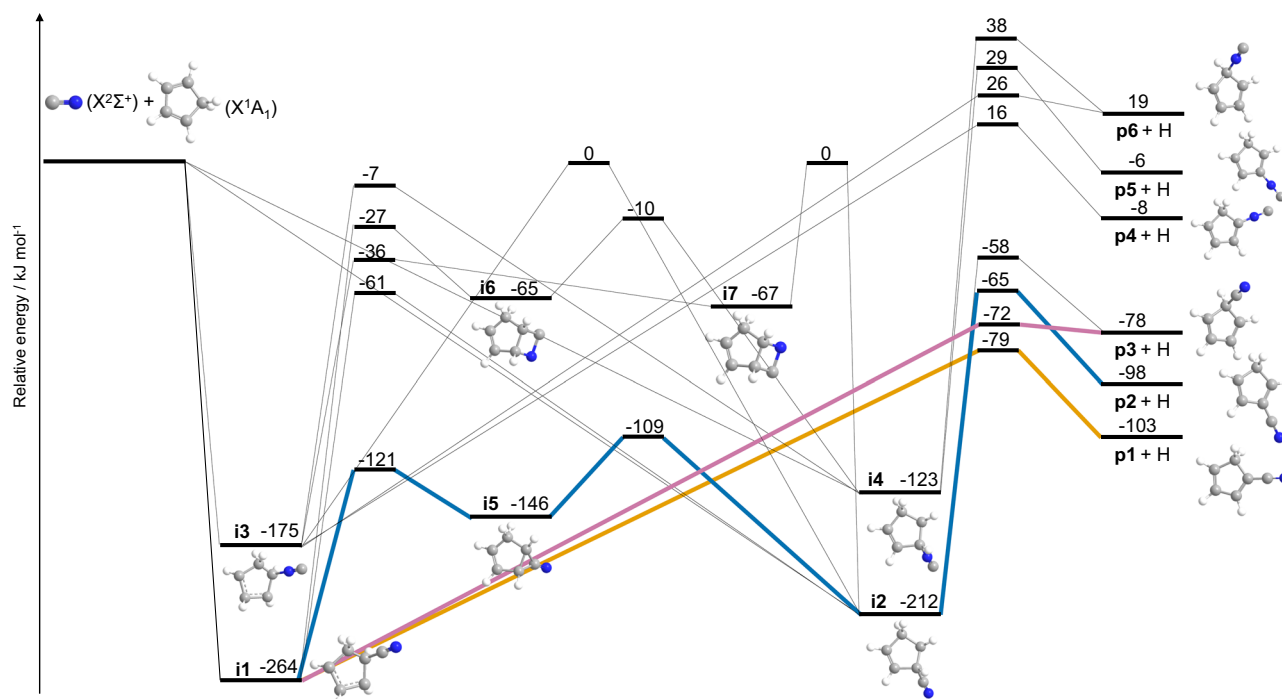


Fig. 5 | Reaction energy diagram for the formation of products from the cyano radicals and 1,3-cyclopentadiene reaction. Reaction energy diagram derived from the potential energy surface for the reaction of the cyano radical (CN) with 1,3-cyclopentadiene ($c\text{-C}_5\text{H}_6$) leading to products **p1–p6** calculated at the CCSD(T)/

CBS//B3LYP/cc-pVTZ level. Intermediates **i8** and **i9** are not included since they represent high energy intermediates which are not accessible at the experimental collision energy (Fig. S2). Color lines represent the pathways to the most probable products **p1** (orange), **p2** (blue), and **p3** (rose).

transition states located 24 and 6 kJ mol^{-1} above **p1** and **p3**. **i2** could produce either 2-cyanocyclopentadiene (**p2**, C_s , X_1A' , -98 kJ mol^{-1}) or 5-cyanocyclopentadiene (**p3**), through exit tight transition states 33 and 20 kJ mol^{-1} above the separated products. On the other hand, 1-isocyanocyclopentadiene (**p4**, C_s , X_1A' , -8 kJ mol^{-1}) could be formed from **i3** and 2-isocyanocyclopentadiene (**p5**, C_s , X_1A' , -6 kJ mol^{-1}) from **i4**, overcoming barriers of 16 and 29 kJ mol^{-1} above the reactants. Regarding 5-isocyanocyclopentadiene (**p6**, C_s , X_1A' , 19 kJ mol^{-1}), it can be formed via **i3** and **i4** through transition states of 26 and 38 kJ mol^{-1} above the separated reactants. It is important to note that the initial collision complexes can isomerize via cyano group migration forming exotic bicyclic reaction intermediates. In detail, intermediate **i1** isomerizes to **i2** via intermediate **i5** (C_1 , X^2A) through a ring closure – ring opening pathway which de-facto migrates the cyano group from the C1 to the C2 carbon atom of the cyclopentenyl moiety. Alternatively, **i1** may undergo ring closure to a bicyclic intermediate **i6** (C_1 , X^2A), which then ring opens to **i4**; further, **i3** could isomerize via intermediate **i7** (C_1 , X^2A) also by ring closure followed once again by ring opening to **i2**. These isomerization sequences resemble the 1-cyanoethyl-2 radical (C_2H_4CN) to 1-isocyanoethyl-2 radical (C_2H_4NC) conversion in the cyano–ethylene system explored earlier^{32,40}. Lastly, **i1** and **i3** can isomerize to **i2** and **i4**, respectively, via [4,5] hydrogen shifts with barriers located 203 kJ mol^{-1} and 168 kJ mol^{-1} above **i1** and **i3**. Considering the heights of this barrier, **i1** is anticipated to preferentially isomerize to **i2** via ring–opening–ring closure reaction rather than hydrogen shifts. Additionally, **i3** can also isomerize to **i2** via CN-group migration having to overcome a barrier of 175 kJ mol^{-1} .

Having discussed the energy diagram, we are exploring the question of what is/are the actual reaction pathways. A comparison of the experimental reaction energy of $134.2 \pm 20.9 \text{ kJ mol}^{-1}$ with the computationally predicted values for 1-cyanocyclopentadiene (**p1**) ($-103 \pm 10 \text{ kJ mol}^{-1}$), 2-cyanocyclopentadiene (**p2**) ($-98 \pm 10 \text{ kJ mol}^{-1}$), and 5-cyanocyclopentadiene (**p3**) ($-78 \pm 10 \text{ kJ mol}^{-1}$) suggests that at least 1-cyanocyclopentadiene (**p1**) plus atomic hydrogen is formed;

however, any contribution of 2-cyanocyclopentadiene (**p2**) and 5-cyanocyclopentadiene (**p3**) can be masked in the lower energy section of the center of mass translational energy distribution. Since these three isomers differ by only 25 kJ mol^{-1} , the contribution of 2-cyanocyclopentadiene (**p2**) and 5-cyanocyclopentadiene (**p3**) cannot be derived from the experimental data alone. Therefore, statistical Rice-Ramsperger-Kassel-Marcus (RRKM) calculations were conducted to predict the branching ratios of **p1–p3** at distinct collision energies from 0 to 30 kJ mol^{-1} for four different scenarios with an assumed exclusive formation each of the intermediates **i1–i4** (Supplementary Table 2). Overall, these results suggest average fractions of 28 %, 5 % and 67 % for **p1**, **p2**, and **p3**, respectively, at the experimental collision energy ($E_c = 17.9 \text{ kJ mol}^{-1}$). Note that the branching ratio is nearly independent on which collision complex is formed initially for **p1** and **p3**; whereas a small increase by around 3.5 % for **p2** is observed when **i2** is solely considered. For the low-temperature conditions of the cold molecular clouds such as TMC-1 ($E_c = 0 \text{ kJ mol}^{-1}$), a slight increase on the formation of 1-cyanocyclopentadiene (**p1**) is predicted with respect to 17.9 kJ mol^{-1} with calculated branching ratios of 32 %, 4 % and 64 % for **p1**, **p2** and **p3**, respectively. The remaining isomers have negligible contributions of up to 0.5 % in the best-case scenario. The RRKM calculations also predict the dominating pathway to each of these three isomeric products as highlighted in Fig. 5 in orange (1-cyanocyclopentadiene, **p1**), blue (2-cyanocyclopentadiene, **p2**) and rose (5-cyanocyclopentadiene, **p3**). All the possible routes leading to the most energetically stable **p1–p3** products assuming an exclusive formation each of the intermediates **i1–i4** are discussed in detail in Supplementary Note 2. To summarize, according to RRKM calculations the most likely channels to **p1–p3** from each initial intermediate **i1–i4** exclusively considered include the following:

- 1) **i1** $\rightarrow$ **p1** + H
- 2) **i2** $\rightarrow$ **i5** $\rightarrow$ **i1** $\rightarrow$ **p1** + H
- 3) **i3** $\rightarrow$ **i2** $\rightarrow$ **i5** $\rightarrow$ **i1** $\rightarrow$ **p1** + H
- 4) **i4** $\rightarrow$ **i3** $\rightarrow$ **i2** $\rightarrow$ **i5** $\rightarrow$ **i1** $\rightarrow$ **p1** + H

Table 2 | AIMD-derived association ratios

Intermediate	Relative population (%)
i1	63.89
i2	12.27
i3	17.87
i4	5.98
i5	0

- 5) **i1** → **i5** → **i2** → **p2** + H
- 6) **i2** → **p2** + H
- 7) **i3** → **i2** → **p2** + H
- 8) **i4** → **i3** → **i2** → **p2** + H
- 9) **i1** → **p3** + H
- 10) **i2** → **i5** → **i1** → **p3** + H
- 11) **i3** → **i2** → **i5** → **i1** → **p3** + H
- 12) **i4** → **i3** → **i2** → **i5** → **i1** → **p3** + H

As it is explained in the supplementary information (Supplementary Note 2), these results can be easily understood in terms of the inherent barriers of isomerization and the calculated unimolecular rate constants. An interesting feature is that the calculated branching ratios for the different products **p1**–**p3** are independent regardless of the initial complex considered. In this context, the bicyclic intermediates **i5**, **i6** and **i7** formed during the course of the reaction apparently can potentially play a critical role since they act as connectors between **i1**–**i4** in their isomerization pathways, providing stable structures with energies well below the separated reactants. Lastly, as already described and observed in Fig. 5, the most dominant pathway to **p3** is from **i1** over **i2**, involving the formation of a loose transition state of only 6 kJ mol^{−1} above **p3** + H. On the other hand, the formation of tight transition states of 24 kJ mol^{−1} and 33 kJ mol^{−1} to form **p1** and **p2** from **i1** and **i2**, respectively, agrees with the experimental findings as observed in Fig. 4c.

Molecular dynamics simulations

Rate constant theories such as RRKM predict product branching ratios of unimolecular reactions. It assumes that the lifetime of the reaction intermediates is much longer than the intramolecular energy redistribution (IVR), as well as that the reaction strictly follows the intrinsic reaction coordinate (IRC), i.e., no direct reactions in which products formed immediately after the bimolecular collision without an intermediate. To use RRKM theory to predict the product branching ratio of the titled reaction, the populations of the collision-induced intermediates, e.g., **i1**, **i2**, **i3**, and **i4** in Fig. 5, are required. These populations cannot be derived from the potential energy profiles alone, as they depend on the access energy and entrance channel. In the absence of direct reactions, immediately after the collision-induced intermediates are formed, the excess energies are largely localized in newly formed bonds, which is then deposited to the entire molecule through IVR. Therefore, ab initio molecular dynamics (AIMD) simulations were performed to determine the population of these intermediates and whether direct reaction makes up a significant portion. These simulations were carried out long enough - longer than IVR - until the population of the intermediate becomes stable, after which their decomposition can be assumed to be statistical and hence follows RRKM. It is important to note that while AIMD simulations could be in theory extended until products eventually formed, under the condition of the titled reaction, the collision-induced intermediates do not dissociate to products within a practical AIMD simulation time frame. Across all 280 bimolecular collision AIMD trajectories, 124 formed an intermediate and there was no direct reaction. No hydrogen atom loss products were observed up to 3 ps and an overwhelming majority of

the trajectories remains as the collision induced intermediates (Supplementary Fig. 4). This is in line with experimental findings revealing long lived reaction intermediates. The AIMD simulations show that association of the reactants occurs predominantly through intermediate **i1**, with smaller contributions from **i3** and **i2**, while formation of **i4** is comparatively rare and no trajectories were observed to associate through **i5** (Table 2). The only observed isomerization was between **i1** and **i2** through **i5**, although they are statistically insignificant (3 out of 124 trajectories). This “trapping” phenomena is common in other bimolecular collision systems that form stable intermediates^{41–43}. These dynamics-guided intermediate population has been used to predict product branching ratios with RRKM theme reported. As Table 2 shows, since AIMD simulations show no direct reactions, the dynamics-guided, RRKM branching ratio of **p1** (29 %), **p2** (4 %) and **p3** (67%) aligns well with the intermediate-independent RRKM branching ratio (Supplementary Table 9).

Note that the experimental collision energy ($E_c = 17.9$ kJ mol^{−1}) corresponds to a temperature of approximately 2160 K, which is typical from circumstellar envelopes of carbon stars like IRC + 10216. Nevertheless, the dominant pathways for the studied reaction were found to proceed barrierlessly and with all intermediates and transition states located below the energy of the separated reactants. These requisites render the reaction feasible under the low-temperature conditions prevalent in cold molecular clouds. Amongst the cyano-cyclopentadiene isomers (C₅H₃CN) mainly formed in the reaction between cyano (CN) radical and 1,3-cyclopentadiene (c-C₅H₆) according to the statistical calculations, 1-cyanocyclopentadiene (**p1**) and 2-cyanocyclopentadiene (**p2**) have been detected in the interstellar medium and, specifically, in TMC-1 (see Table 1)^{23–25}. Although there are some discrepancies between these studies on the reported relative abundances of these species as previously discussed²⁵, it is clear that 1-cyanocyclopentadiene (**p1**) is more abundant than 2-cyanocyclopentadiene (**p2**). Astrochemical models have found that the main pathways to produce indistinguishably both isomers in low-temperature environments include the CH plus C₄H₅CN and CN plus c-C₅H₆ reactions¹⁶. Yet, these simulations do not take into account the branching ratio for the different isomers formed in these processes. The calculations from this work reveals that the CN+c-C₅H₆ reaction produces 1-cyanocyclopentadiene (**p1**) and 2-cyanocyclopentadiene (**p2**) in fractions of 32 and 4 % at the conditions of the cold molecular clouds. Surprisingly, the presence of the most dominant product predicted to be formed in the titled reaction, 5-cyanocyclopentadiene (**p3**), remains elusive in space. Therefore, these computational results suggest that this undetected isomer should not only be at detectable levels in the interstellar medium but also have a higher abundance than 1-cyanocyclopentadiene (**p1**) and 2-cyanocyclopentadiene (**p2**) if the CN plus c-C₅H₆ is the main considered pathway leading these species. However, it cannot be ruled out that other pathways are major contributors to the formation of **p1** and **p2** such as the aforementioned CH plus C₄H₅CN route. The latter reaction would shed some light about its role on the formation of **p1**–**p3** but it has not been investigated either theoretically or experimentally. Additionally, the cyano radical is iso-electronic to the ethynyl radical (C₂H, X^{2Σ+}) and, therefore, should have similar reaction dynamics with the cyclopentadiene molecule. Although the gas-phase dynamics of the ethynyl–cyclopentadiene system has not been studied yet, the title reaction can provide a useful prediction for this system, which is also of relevance for the modeling of TMC-1. Analogously to the cyano radical reaction, the corresponding possible reaction products for the latter system would be ethynylcyclopentadiene (C₅H₃C₂H), which has also three different isomeric species (Fig. 6). Similar to cyanocyclopentadiene, 1-ethynylcyclopentadiene and 2-ethynylcyclopentadiene were detected in TMC-1²⁵, whereas 5-ethynylcyclopentadiene remains undetected in space. Furthermore, the presence of fulvenallene (C₅H₄C₂H₂), an ethynylcyclopentadiene isomer, in TMC-1⁹, arises the interest of the

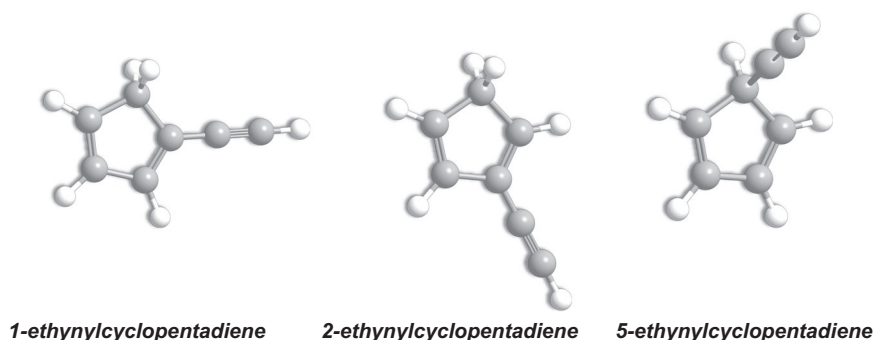


Fig. 6 | Molecular structures of three ethynylcyclopentadiene isomers. Three isomers of ethynylcyclopentadiene ($C_5H_5C_2H$). These isomers are isovalent to 1-cyanocyclopentadiene (**p1**), 2-cyanocyclopentadiene (**p2**), and

5-cyanocyclopentadiene (**p3**). The carbon and hydrogen atoms are color coded in gray and white, respectively.

study of the gas-phase dynamics of the ethynyl – cyclopentadiene system, since this reaction could be a fulvenallene source in the interstellar medium.

In conclusion, we investigated the previously unexplored gas-phase reaction of the cyano radical (CN) with 1,3-cyclopentadiene ($c\text{-}C_5H_6$) under single-collision conditions using crossed molecular beam experiments. The obtained results, combined with high-level electronic structure calculations and dynamics guided RRKM studies, demonstrate that this reaction is exoergic and barrierless, leading to the formation of all three cyanocyclopentadiene isomers (C_5H_5CN , **p1–p3**) under low-temperature conditions relevant to cold molecular clouds. Statistical calculations based on Rice-Ramsperger-Kassel-Marcus (RRKM) theory predict that 5-cyanocyclopentadiene (**p3**) is the dominant product, despite its absence in current astronomical observations, whereas the less abundant isomers, 1- and 2-cyanocyclopentadiene (**p1** and **p2**), have already been detected in TMC-1. The quantitative data reported here provide critical constraints for astrochemical reaction networks and call for a reassessment of assumed isomeric distributions of cyano-substituted hydrocarbons in space. By revealing that the primary formation pathway leads to a currently unobserved species, our study highlights the indispensable role of laboratory benchmarks combined with calculations in guiding targeted astronomical searches. In this context, 5-cyanocyclopentadiene (**p3**) emerges as a compelling candidate for detection with facilities such as the Green Bank Observatory and Yebes Radio Telescope. More broadly, these findings suggest that additional, yet-undetected nitrogen-bearing hydrocarbons may contribute significantly to molecular mass growth and PAH evolution in the interstellar medium, thereby advancing our understanding of the carbonaceous chemistry of the universe we live in.

Methods

Crossed molecular beams

The bimolecular reaction between the cyano radical (CN; $X^2\Sigma^+$) and 1,3-cyclopentadiene ($c\text{-}C_5H_6$; X^1A_1) was exploited by using the crossed molecular beams apparatus⁴⁴. The primary supersonic beam of cyano radicals was produced in situ via laser ablation of a rotating graphite rod at 266 nm, generated by a Nd:YAG laser (8 mJ per pulse, 30 Hz; Quanta-Ray). Nitrous oxide (N_2O , Matheson, 99.999 %) was used both as a reactant and seeding gas released by a Porch-Trickl pulsed valve operating at 60 Hz and at a backing pressure of 4 atm. The cyano radical beam passed through a skimmer, and a four-slot chopper wheel selected a specific part of the pulsed beam with a peak velocity (v_p) of $1228 \pm 26 \text{ m s}^{-1}$ and a speed ratio (S) of 4.3 ± 0.3 . The secondary supersonic beam of 1,3-cyclopentadiene (Supplementary Note 1) seeded at a level of 5 % in argon (99.9999 %, Air Gas) was released by a Porch-Trickl pulsed valve operating at 60 Hz with a backing pressure of 520 Torr. This molecular beam was characterized with a v_p of

$638 \pm 13 \text{ m s}^{-1}$ and S of 24.0 ± 1.1 ; since both beams have distinct velocities, the secondary pulsed valve was triggered 35 μs prior to the primary pulsed valve allowing both beams to cross perpendicularly in the interaction region. This results in a collision energy (E_c) of $17.9 \pm 0.6 \text{ kJ mol}^{-1}$ and a center of mass angle (θ_{CM}) of $53.4 \pm 0.6^\circ$. Reactively scattered products were detected using a rotatable, triply differentially pumped mass spectrometric detection system operating under ultrahigh-vacuum conditions (6×10^{-12} Torr). Neutral species were ionized via electron impact using a Brink-type ionizer (80 eV, 2 mA emission current). The resulting ions were then extracted and filtered by their mass-to-charge ratio (m/z) using a quadrupole mass spectrometer (QMS, Extrel, QPS, 2.1 MHz) and subsequently detected by a Daly-type particle ion counter. Time-of-flight (TOF) data were recorded at different angles. The laboratory data were transformed into the center-of-mass (CM) frame using a forward-convolution approach^{3,36,37}. This process begins by assuming trial center-of-mass translational energy ($P(E_T)$) and angular flux ($T(\theta)$) distributions. The corresponding laboratory data (TOF spectra and lab angular distributions (LAD)) are then calculated from these distributions averaging over the instrument and beam functions. This process is iteratively repeated, adjusting $P(E_T)$ and $T(\theta)$ until satisfactory fit agreement of the experimental laboratory data is obtained. Finally, the flux contour map portrays the overall image of the outcome of the reaction.

Electronic structure calculations

On adiabatic doublet ground state potential surface of CN plus cyclopentadiene reaction, the geometries of species along H dissociation channels (Figs. 3 and 5) are located and optimized with density functional B3LYP^{45,46}/cc-pVTZ calculations. The energies are further refined to complete basis set limits⁴⁷ [CCSD(T)/CBS] by extrapolating the CCSD(T)/cc-pVDZ, CCSD(T)/cc-pVTZ, and CCSD(T)/cc-pVQZ energies, with B3LYP/cc-pVTZ zero-point energy corrections. The energy-dependent RRKM rate constants⁴⁸ (0 to 30 kJ/mol in step of 5) are then calculated with B3LYP/cc-pVTZ harmonic frequencies and zero-point-corrected CCSD(T)/CBS energies. The saddle-point approach^{48,49} is utilized in computing the number of states for transition states and the density of states for intermediates. All species are considered as a collection of harmonic oscillators. Finally, the product branching ratios (Supplementary Table 2) are predicted by solving the ab initio path-based rate equations with the numerical Runge–Kutta method. Gaussian16 programs⁵⁰ are used in the electronic structure calculations.

AIMD simulations

Candidate electronic structure methods for AIMD simulations were benchmarked using single-point calculations against the stationary-point energies of the reference potential energy surface (Supplementary Table 10). Because B3LYP/6-31 + G^* provided accuracy comparable

to larger basis sets while maintaining a lower computational cost, this level of theory was selected for the AIMD simulations^{45,51}. Although the B3LYP/cc-pVDZ method⁵² has a slightly lower RMSD value, the largest-deviation energy was notably greater than the 6-31+G* method selected. AIMD simulations were performed using the VENUS molecular dynamics package interfaced with NWChem for electronic structure calculations⁵³. Initial conditions were generated over a range of impact parameters, with 20 trajectories propagated at each impact parameter in increments of 0.50 Å until no intermediates were formed, above 6.75 Å, for a total of 280 trajectories. A timestep of 0.15 fs was used to conserve the total energy of the system. Center-of-mass collision energy was set to 18 kJ mol⁻¹ with a vibrational and rotational energy distribution corresponding to a microcanonical ensemble at 10 K to best replicate experimental conditions. Following trajectory propagation, molecular geometries were extracted and converted to InChI identifiers using Open Babel⁵⁴. These identifiers were then used to classify the first associated structure formed in each trajectory. For each impact parameter, the fractional population of each observed intermediate was weighted by the corresponding annular impact-parameter area to obtain effective association cross sections.

Data availability

The data generated in this study are provided in the Supplementary Information and Source Data File. All data are available from the corresponding author upon request. Source data are provided with this paper.

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Author contributions

R.I.K. supervised and designed the experiments. D.G., I.A.M., S.M., and S.J.G. carried out the experimental measurements and RRKM calculations. D.G. analyzed the data. S.F. and A.H.H.C. conducted the electronic structure calculations. N.M. conducted the AIMD simulations, T.B. and Z.Z. helped with the c- C_5H_6 synthesis. D.G. and R.I.K. wrote the original draft, reviewed and edited the paper. D.G., R.S., and R.I.K. revised the manuscript. All authors discussed the data.

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Competing interests

The authors declare no competing interests.

Additional information

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