Through computational analysis we found that pentazine and hexazine, two hypothetical high-energy density materials, exhibit inherent instability due to quantum tunneling effects. This instability remains even near the absolute zero, and therefore they can be deemed as unsynthesizable. We propose substituents that could potentially stabilize pentazine, especially dimethylamine.

Hexazine (N₆) and pentazine (N₅CH) are the only two six-membered unsaturated N-heterocyclic rings that have not been synthesized yet.¹⁻³ The quest for their detection and characterization is rooted not only in their academic and aesthetic value,⁴⁻⁸ but also in their characteristics as energetic materials⁹⁻¹¹ (even if their proposed low decomposition barriers¹,¹²,¹³ would make them highly dangerous). Herein we analyze with computational means the intrinsic stability of hexazine and pentazine, with the aim of predicting their potential for being synthesized.

In the context of molecular stability, a molecule is expected to be isolatable, at least at sufficiently low temperatures, if it corresponds to a minimum in the potential energy surface (including the zero-point energy, ZPE).¹⁴ Considering the synthetic procedure can be surmounted, the plausibility of observing hypothetical molecules is often predicated upon this theoretical notion, prompting many endeavors trying to create and detect intriguing new species.

Nonetheless, it is important to acknowledge that certain molecules, despite being predicted to be minima on the potential energy surface, may be inherently unstable due to quantum tunneling (QT) effects,¹⁵⁻²¹ or what we called quantum tunneling instability (QTI).²²,²³ Consequently, the decomposition might proceed regardless of the temperature if the reaction complies with specific conditions that enhance the QT process. This would make the detection and synthesis of these molecules exceptionally difficult.

The elusiveness of pentazine and hexazine can be attributed to their semi-classical (SC) barrier leading to their decomposition (Fig. 1), independent of tunneling effects. Hexazine is likely to decompose into three nitrogen molecules, while pentazine, with analogous vibrations, is expected to yield two nitrogen molecules and one hydrogen cyanide, both through overwhelmingly exothermic reactions. The threshold energies are relatively low (∼4 kJ mol⁻¹ for hexazine, ∼17 kJ mol⁻¹ for...
pentazine, see below). Nevertheless, a low enough temperature should, in principle, stabilize them. On the other hand, conforming to the Hammond postulate, the high exothermicity producing low barriers and short movements can increase the probability of QT.24–26

Our study shows with computational methods that the stability of pentazine and hexazine is directly contingent on the occurrence of molecular quantum tunneling. It becomes evident that this effect represents the limiting factor in stabilizing these molecules at very low temperatures.

The theoretical investigation of hexazine presents challenges due to varying outcomes from different computational methods. Generally, density functional theory (DFT) methods converge on hexazine being a minimum on the PES,1,13,27,28 with a small barrier for breaking into three N₂ molecules.29,30 However, coupled cluster methods exhibit ambiguity in their predictions.13 Through the optimization of hexazine using diverse levels of theory, we confirmed that DFT methods tend to favor the hexazine in a D₂ symmetry. Nevertheless, optimizations employing DLPNO-CCSD(T)/CC-PVTZ with ORCA 531 indicate that the bonded D₂ geometry is a transition state between two 3 × N₂ geometries. It is worth noting that the system has considerable static correlation (%TAE ~ 10, T₁ ~ 0.3),32,33 suggesting that CCSD(T) might not be suitable for accurately describing hexazine. Consequently, uncertainty remains regarding whether D₂-hexazine is indeed a minimum or not. The ultimate solution for resolving the question of hexazine’s stability would involve energies and geometries computed with coupled cluster with higher excitations33 or heavy multireference methods, techniques that can deal both with static and dynamic correlation; these are intractable problems for us. Instead, we turned to the MN15 DFT functional to address this issue for two reasons: first, this functional was specifically designed to handle both types of correlations;34 second, among the five tested functionals (see ESI†), MN15 provides the highest barrier (4.2 kJ mol⁻¹ including ZPE) for decomposition, serving as an upper limit for the compound’s half-life in our evaluating of tunneling instability. In other words, if with this functional the QT decomposition rate is substantial, we can confidently expect that the experimental rate will be even faster. Therefore, all the hexazine computations were carried out with MN15/Def2-TZVP using Gaussian16,35 with all stationary structures tested with frequency analysis. Tunneling computations were conducted employing the Small Curvature Tunneling (SCT) method.36 Noteworthy, SCT rates were found to be faster, and therefore more adequate, than Large Curvature Tunneling (LCT), which would have been the method of choice if there was extreme corner-cutting (see ESI†). The non-tunneling semi-classical (SC) rates were carried out with Canonical Variational Transition State Theory (CVT)37 with Polyrate1738 (and Gassrater17B39 for the interface with Gaussian16), with a step size of 0.001 Bohr and Quasi-Rectangular-Stepping (QRST)40 in the lower region of temperatures.

In Table 1 and Fig. 2 we present the Arrhenius plot and the SC and QT rate constants at selected temperatures for hexazine (along with pentazine, see below). As evident from the data, hexazine exhibits a strong propensity for QT, in line with the Hammond postulate which in this case favors the tunneling conditions toward decomposition.25,26 The MN15 SC results show a hypothetical half-life of 10⁴⁶ seconds at 4 K (close to liquid He conditions, calculated as a first-order reaction with t₁/₂ = ln 2/k, indicating the possibility for isolation if hexazine would be synthesized. However, the QT results point to a prompt disintegration of hexazine into nitrogen molecules with a half-life of picoseconds at all temperatures (even considering that MN15 provides an upper bound). Therefore, hexazine can be deemed as unsynthesizable.

Considering the importance of the mass for the QT rates, we studied the ¹⁴N/¹⁵N kinetic isotope effect by substituting all the nitrogen atoms. Close to the absolute zero the obtained KIE was 1.41 (see Table 1), a significantly slower rate for the heavier species, but negligible from a synthetic perspective.

While the question of whether hexazine represents a minimum or not remains unsolved, the analysis presented here supports the argument that hexazine simply cannot be synthesized. Even if hexazine is a minimum (as DFT predicts, see above), the QT mechanism will ensure its exceptionally rapid disintegration into N₂ molecules, precluding its isolation and characterization. Consequently, molecular hexazine is likely to remain indefinitely a hypothetical chemical entity due to a quantum tunneling effect.

Pentazine can be decomposed similarly to hexazine (see Fig. 1), but it has some differences. Previous studies yielded

### Table 1 Semi-classical and quantum tunneling included reaction rate constants for decomposition of hexazine and pentazine at different temperatures, and kinetic isotope effects

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>SC (s⁻¹)</th>
<th>QT (s⁻¹)</th>
<th>N₂ (s⁻¹)</th>
<th>KIE</th>
<th>SC (s⁻¹)</th>
<th>QT (s⁻¹)</th>
<th>N₂ (s⁻¹)</th>
<th>KIE</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>4 x 10⁻⁷</td>
<td>4 x 10⁻⁷</td>
<td>1.41</td>
<td>KIE⁺</td>
<td>4 x 10⁻⁷</td>
<td>4 x 10⁻⁷</td>
<td>1.41</td>
<td>KIE⁺</td>
</tr>
<tr>
<td>20</td>
<td>2</td>
<td>4 x 10⁻⁷</td>
<td>1.41</td>
<td>KIE⁺</td>
<td>1 x 10⁻⁷</td>
<td>4 x 10⁻⁷</td>
<td>1.41</td>
<td>KIE⁺</td>
</tr>
<tr>
<td>50</td>
<td>3 x 10⁻⁷</td>
<td>5 x 10⁻⁷</td>
<td>1.37</td>
<td>KIE⁺</td>
<td>3 x 10⁻⁷</td>
<td>4 x 10⁻⁷</td>
<td>1.37</td>
<td>KIE⁺</td>
</tr>
<tr>
<td>77</td>
<td>7 x 10⁻⁷</td>
<td>7 x 10⁻⁷</td>
<td>1.32</td>
<td>KIE⁺</td>
<td>2 x 10⁻⁷</td>
<td>4 x 10⁻⁷</td>
<td>1.32</td>
<td>KIE⁺</td>
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<td>KIE⁺</td>
<td>3 x 10⁻⁷</td>
<td>1.08</td>
<td>1.08</td>
<td>KIE⁺</td>
</tr>
</tbody>
</table>

* In the KIE, "N" is for ¹⁴N/²¹²N, "C" is for ¹²C/¹³C, and "H" is for H/D.
less ambiguous results on the geometry of N$_2$CH compared to N$_6$, as it is predicted to be a C$_{2v}$ symmetry minimum using DFT, MP2, and coupled cluster. Additionally, the decomposition barrier into 2 N$_2$ + HCN is expected to be relatively higher, thus laying the groundwork for possible isolation at low temperatures. Furthermore, a notable difference between hexazine and pentazine from a technical viewpoint is observed in terms of static correlation, with the latter exhibiting significantly lower values (%TAE $\sim$ 5 and T1 $\sim$ 0.2), and therefore CCSD(T) energies are reliable in this case. For this species the decomposition kinetics were computed using the much more robust CCSD(T)/CBS/MN15/Def2-TZVP method (with ORCA-5, extrapolating to a complete basis set from cc-pVTZ and cc-pVQZ bases), improving the DFT potential surface (and consequently the rate constants) with coupled cluster energies using the Intrinsic Symmetry-Projected Energy (ISPE) method.

The resulting decomposition $\Delta$E$^f$ + ZPE for pentazine was the relatively high value of 16.5 kJ mol$^{-1}$, rendering the molecule semi-classically stable below 50 K. However, even with the much higher threshold energy compared to hexazine, pentazine is expected to break apart due to its narrow barrier, with a QT rate constant of $4 \times 10^5$ s$^{-1}$ close to the absolute zero (see Fig. 2 and Table 1), equivalent to a half-life of microseconds. This again poses an insurmountable challenge for experimentalists seeking pentazine isolation.

To further evaluate the impact of tunneling, various isotopic substitutions were explored involving $^{14}$N/$^{15}$N, $^{12}$C/$^{13}$C, H/D, and an all-isotopically substituted molecule as a test for the upper limit of the suppression of QT, as depicted in Table 1. The hydrogen atom exhibits minimal movement throughout the reaction, resulting in an anticipated relatively small H/D KIE. On the contrary, the carbon plays a significant role in the decomposition dynamics, leading to a $^{12}$C/$^{13}$C KIE = 1.14 at low T. Substituting all the N atoms also results in varying degrees of motion during the breakage, contributing to distinct KIE values. While the KIEs can be significant, from a synthetic point of view carrying out isotopic substitutions will again be futile.

Thus far, our computations show that both pentazine and hexazine should be unattainable. However, pentazine derivatives are promising candidates for further theoretical investigation, as the hydrogen can be substituted. These species may not only change the barrier height, but they can, in principle, also raise the QT effective mass. We selected substituents broadly according to their inductive effects, with results indicating that the barrier changes, but the reaction energy remains highly exothermic (obtained at the same level of theory of the parent pentazine). We observed that plotting the activation energy against the resonance parameter ($R$) of the Swain–Lupton equation$^{45}$ reveals a correlated trend ($R^2 = 0.87$, see Table 2 and ESI†), with elevated energy barriers observed toward the π electron-pushing groups (for reference, the $R^2$ for the σ-para Hammett parameters was 0.67, and for the field Swain–Lupton ones it was 0.15).

The QT kinetics of the pentazine derivatives are shown in Table 2. The substituent effect goes from mild to remarkable, with dimethylamino emerging as the most effective pentazine stabilizing group, significantly augmenting the molecule’s half-life by about ten orders of magnitude, from microseconds to days. That is, we estimate that there is a solid chance for dimethylamine-pentazine of being detected below liquid nitrogen conditions (if the synthetic procedure can be carried out from a technical point of view). The amino and hydroxy groups were also effective as tunneling suppressors, but with $t_1 \sim 1$ minute they will probably be impossible to detect. Conversely, electron withdrawing groups such as CF$_3$, CN, or NO$_2$ actually reduced the stability by approximately an order of magnitude compared to the parent pentazine.

Examination of the vibrational dynamics during the decomposition transition state shows that the motion of atoms during the breaking process is predominantly influenced by the cleavage of the ring C–N and N–N bonds, fairly independent of the substituents’ mass. Since the breakage solely involves the pentazine ring, the barrier width remains comparable across all substituents. Therefore, there is no discernible influence or correlation between the QT rate constant and the substituents’ mass for this particular family of reactions. This agrees with the good correlation between the Swain–Lupton equation and the QT rate regardless of the substituent mass, and the fact that pentazine has a low H/D KIE. In this case it appears that only the electronic properties modulate the tunneling. Considering that the ground state tunneling rate can be roughly estimated as$^{46}$

$$k_{QT} \sim \nu e^{-2w\sqrt{\Delta E^f}}$$  \hspace{1cm} (1)

where $w$ is the barrier width, $\mu$ the reduced mass of the tunneling entity, $\nu$ a factor of the barrier shape, and $\nu$ the reactant frequency of the normal mode leading to the transition state (i.e. the encountering frequency with the barrier), then a linear relationship between In $k_{QT}$ and $\Delta E^f$ indicates that the barrier height is the main variable of the tunneling rate. Indeed, despite the significant mass variation among all the tested molecules, there is a straight correlation between the energy and logarithmic
rate ($R^2 = 0.94$), which can be explained by the limited motion of the substituents at the critical stages of the reaction.

To summarize, we studied the tunneling dynamics of the highly sought-after but still unobserved hypothetical pentazine and hexazine compounds due to their unique properties, especially as potential energetic materials. We present computational evidence that a substantial portion of their elusiveness can be attributed to quantum tunneling instability. Hexazine, an archetypical model for a synthetically elusive molecule, presents a computationally challenging scenario; until better evidence is obtained, we believe it to be a very shallow and reactive local minimum. According to our upper bound results the molecule should be semi-classically stable only under harsh conditions, such as in liquid He temperature. However, if quantum tunneling influence is considered, it will be perpetually unobservable in its neutral molecular form, with a unimolecular decomposition half-life of picoseconds at any temperature.

Pentazine is unequivocally predicted to be a local minimum on the potential energy surface, with a higher degradation barrier, and therefore in principle it should be stable up to ~50 K. But again, when QT is considered, the observation of pentazine is anticipated to also be an exceedingly tricky endeavor, with a predicted half-life of microseconds even close to the absolute zero. Therefore, we can presuppose that the only ways to stabilize these species may be at exorbitant pressures, high enough to counteract their large exergonicity, or maybe with vastly intense fields. We alternatively propose some pentazine derivatives as an avenue for the stabilization of these systems, with dimethylenimine as the most promising ($k_{QT} \approx 10^{-6} \text{s}^{-1}$ up to liquid N$_2$ conditions).

The quantum tunneling instability exhibited by pentazine and hexazine not only underscores their perpetual elusiveness, but also calls for the previously overlooked consideration of the instability of many other hypothetical energetic molecules.

**Conflicts of interest**

There are no conflicts to declare.

**Notes and references**

3. As a matter of fact, only one tetrazine isomer has been synthesized, 1,2,4,5-tetrazine, the other two isomers of tetrazine are still unknown.