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## RESEARCH ARTICLE OPEN ACCESS

# Linear or Cyclic? Theoretical Investigation of Astrophysically Relevant Magnesium-Bearing $\text{MgC}_n\text{H}$ Carbon Chains and Related Isomers

A. Karolyna M. S. Gomes<sup>1,2</sup>  | Ricardo R. Oliveira<sup>1</sup>  | Thiago M. Cardozo<sup>1</sup>  | Felipe Fantuzzi<sup>3</sup> <sup>1</sup>Instituto de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil | <sup>2</sup>Institut für Physik, Ruhr-Universität Bochum, Bochum, Germany | <sup>3</sup>Chemistry and Forensic Science, School of Natural Sciences, University of Kent, Canterbury, UK**Correspondence:** Thiago M. Cardozo ([thiago@iq.ufrj.br](mailto:thiago@iq.ufrj.br)) | Felipe Fantuzzi ([f.fantuzzi@kent.ac.uk](mailto:f.fantuzzi@kent.ac.uk))**Received:** 29 September 2024 | **Revised:** 13 December 2024 | **Accepted:** 16 December 2024**Funding:** This work was supported by the European Cooperation in Science and Technology, Conselho Nacional de Desenvolvimento Científico e Tecnológico (406804/2022-2), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (Financing Code 001), and Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro (E-26/200.249/2023).**Keywords:** astrochemistry | coupled cluster | DFT | magnesium | theoretical chemistry

## ABSTRACT

Magnesium-containing molecules, including  $\text{MgC}_2\text{H}$ ,  $\text{MgC}_4\text{H}$ , and  $\text{MgC}_6\text{H}$ , have been detected in the interstellar medium, largely facilitated by their high dipole moments. However, despite great efforts,  $\text{MgC}_{2m+1}\text{H}$  species remain elusive. Given the challenges in obtaining experimental data for these molecules, theoretical studies play a crucial role in guiding their detection. In this work, we present a theoretical analysis of  $\text{MgC}_n\text{H}$  isomers ( $n=4-7$ ) using density functional theory and coupled-cluster methods to identify low-lying isomers and characterize their structural and electronic properties. Our findings reveal that across the entire series investigated, the global minimum geometry is linear for even values of  $n$ , whereas for odd values, a cyclic geometry is favored. Additionally, our calculations highlight the enhanced stability of anionic  $\text{MgC}_n\text{H}^-$  systems, providing insights that could aid future astronomical detections in the interstellar medium.

## 1 | Introduction

To this day, more than 320 molecules have been identified in the interstellar medium (ISM) or circumstellar shells [1]. Given the presence of metals in these environments, the search for organometallic compounds has become increasingly important. Among the metals present in the ISM, magnesium stands out for its abundance and chemical significance. Notably, nearly half of the metal-containing molecules detected around the star IRC +10216 contain magnesium [2, 3]. IRC +10216, a carbon-rich circumstellar envelope, is renowned for its extraordinary molecular diversity and is one of the most chemically rich objects in the ISM. Magnesium is also the most prevalent metal in the solar system [4], which makes this element even

more central in the quest for understanding our astrochemical origins.

Beyond its relevance in astrochemistry, which continues to fuel both theoretical and experimental exploration [5, 6], magnesium plays a vital role in biological systems on Earth. As an essential element for life, magnesium forms chelates with various biomolecules, including adenosine triphosphate (ATP), and activates enzymes involved in multiple stages of metabolic processes in living organisms [7–10]. Magnesium is also a key component of chlorophyll, the molecule responsible for photosynthesis in plants [11]. In astrobiology, the detection of chlorophyll's absorption band at 670 nm is considered a potential biosignature, as its spectral signature could be preserved under Martian surface

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conditions, offering insights into the possibility of photosynthetic life beyond Earth [12].

Historically, the first magnesium-bearing molecule discovered in the ISM was magnesium isocyanide (MgNC), detected in 1986 via microwave spectroscopy around IRC +10216 [13]. Following this discovery, magnesium-containing compounds became prime targets for astronomical detection. Over time, several additional molecules were identified, including magnesium cyanide (MgCN) [14], HMgNC [15], MgC<sub>2</sub>H [16], MgC<sub>3</sub>N and MgC<sub>4</sub>H [17], MgC<sub>5</sub>N [18], MgC<sub>6</sub>H [18], and magnesium dicarbide (MgC<sub>2</sub>) [3]. Other recently detected Mg-bearing molecules include HMgCCCN, MgC<sub>4</sub>H<sup>+</sup>, MgC<sub>3</sub>N<sup>+</sup>, MgC<sub>6</sub>H<sup>+</sup>, MgC<sub>5</sub>N<sup>+</sup>, and MgS [19–21].

For MgC<sub>*n*</sub>H-type molecules, only those with even *n* values (*n* = 2, 4, 6) have been detected in IRC +10216, whereas analogs with an odd number of carbon atoms remain undetected. In a recent theoretical study, Panda et al. theoretically investigated isomers of MgC<sub>3</sub>H, and a total of 11 stationary points with doublet multiplicity (below 72 kcal/mol) were found [22]. Unlike the *n*-even MgC<sub>*n*</sub>H species, for which both theoretical [23] and experimental [16–18] studies have shown linear global minima with terminal magnesium atoms, the global minimum of MgC<sub>3</sub>H exhibits a cyclic geometry [22]. This structural difference may explain why *n*-odd species remain unobserved. Furthermore, the ISM contains species like C<sub>3</sub>H, C<sub>3</sub>H<sub>3</sub><sup>+</sup>, Mg, and Mg<sup>+</sup>, which could potentially react to form cyclic MgC<sub>3</sub>H compounds. This makes both c-MgC<sub>3</sub>H and c-MgC<sub>3</sub>H<sup>+</sup> promising targets for future detection, particularly in IRC +10216. However, the detection of c-MgC<sub>3</sub>H may be challenging due to its small dipole moment, which was calculated as 0.19 Debye [22].

Recently, various isomers of MgC<sub>4</sub>H were also theoretically predicted [24]. In addition to the previously known linear form with a terminal magnesium atom, new cyclic and linear structures were identified, all with energies less than 59 kcal/mol higher than the most stable form of MgC<sub>4</sub>H [24]. These findings suggest a trend in the global minimum geometries of MgC<sub>*n*</sub>H: for *n*-even, the preferred structure is linear with a terminal magnesium atom, whereas for *n*-odd, a cyclic structure is favored.

In this work, we provide a comprehensive analysis of the structure, stability, and bonding of MgC<sub>*n*</sub>H species, extending the study to systems with *n* up to 7. As part of a systematic investigation of astrophysically relevant molecules [25–30], we identify low-lying constitutional isomers for each MgC<sub>*n*</sub>H stoichiometry and compute their relative energies and thermodynamic stabilities using high-accuracy computational methods, providing a detailed understanding of the structural preferences within the series. Finally, we propose new viable magnesium-bearing candidates for future astrophysical detection.

## 2 | Methods

Different isomeric starting structures of MgC<sub>*n*</sub>H (*n* = 4–7) were generated using the software CLUSTER 1.0 [31]. For all species, doublet multiplicities were assigned, and preliminary geometry optimizations were then performed at the UB3LYP/def2-SVP level of theory [32–36]. Higher-order multiplicities were also

tested for selected isomers to ensure all possible low-energy configurations were considered. From these calculations, low-energy isomers—up to about 50 kcal/mol above the lowest energy structure—were selected for further refinement. These selected isomers were subsequently reoptimized at the UB3LYP/aug-cc-pVTZ level [37–39]. Vibrational frequency calculations at this level of theory confirmed that all reported geometries correspond to true minima on their respective potential energy surfaces (PESs). The use of DFT to determine minimum geometries was validated by its strong agreement with CCSD(T) structural parameters for MgC<sub>4</sub>H isomers, reported by Bâldea [23]. For increased accuracy in the electronic energies, single-point calculations were performed at the optimized geometries using the CCSD(T) method, known for providing highly reliable energy values. These calculations employed the aug-cc-pVXZ basis sets, where *X* = T for *n* = 4, 5 and *X* = D for *n* = 6, 7. Quasi-restricted orbitals (QROs) obtained from unrestricted Hartree–Fock (UHF) calculations were used to construct the reference determinants to minimize spin contamination effects. All dipole moments reported in this work were calculated at the CCSD(T) level.

The distinct isomers obtained in this work are labeled as ***nx***, where ***n*** represents the number of carbon atoms in the MgC<sub>*n*</sub>H system. In turn, ***x*** is an alphabetical designation starting from ***a***, with ***a*** denoting the lowest-energy isomer. However, the linear carbon chain structures for MgC<sub>5</sub>H and MgC<sub>7</sub>H are labeled differently, as **5lin** and **7lin**, respectively. This distinction is made because these linear isomers exhibited exceptionally high spin contamination, with  $\langle S^2 \rangle$  values of 2.84 and 2.86, respectively. As a result, they were excluded from further analysis. Additional details are provided in the Supporting Information.

In addition to the structural optimizations, adiabatic and vertical ionization potentials (IPs) and electron affinities (EAs) were computed for selected species to gain further information on the electronic properties of MgC<sub>*n*</sub>H compounds. These properties were calculated as follows:

$$IP_{\text{ad}} = E^+(\text{cation}) - E^0(\text{neutral}) \quad (1)$$

$$EA_{\text{ad}} = E^0(\text{neutral}) - E^-(\text{anion}) \quad (2)$$

$$IP_{\text{vert}} = E^+(\text{neutral}) - E^0(\text{neutral}) \quad (3)$$

$$EA_{\text{vert}} = E^0(\text{neutral}) - E^-(\text{neutral}) \quad (4)$$

where  $E^q(M)$  refers to the total energy of the system with charge *q* at the geometry *M*. The adiabatic ionization potential ( $IP_{\text{ad}}$ ) and electron affinity ( $EA_{\text{ad}}$ ) were determined by the energy difference between the cation or anion in their optimized geometries and the neutral molecule in its optimized geometry, with zero-point energy (ZPE) corrections being considered. The vertical ionization potential ( $IP_{\text{vert}}$ ) and electron affinity ( $EA_{\text{vert}}$ ) were calculated by maintaining the geometry of the neutral molecule for the ionized species.

For selected cases, spin density calculations and bonding analyses were performed, with the former using Löwdin population analysis [40] and the latter employing the intrinsic bond orbital (IBO) method [41]. Additionally, selected fragmentation pathways involving the release of hydrogen and

magnesium from neutral and anionic  $\text{MgC}_n\text{H}$  structures were investigated. In total, 64 molecular structures with  $\text{MgC}_n\text{H}$  stoichiometry were thoroughly investigated in this work, providing a detailed examination of the Mg-bearing species. All electronic structure calculations were carried out using ORCA 5.0.3 [42, 43].

### 3 | Results and Discussion

#### 3.1 | General Trends in the $\text{MgC}_n\text{H}$ Series

Figure 1A shows the lowest energy structures obtained for  $\text{MgC}_n\text{H}$  isomers with  $n=4-7$ . These results reveal an alternating pattern in which cyclic structures are favored for odd-numbered carbon chains, whereas linear structures are preferred for even-numbered carbon chains. This trend is consistent with previously reported results for  $\text{MgC}_3\text{H}$ , which also favors a cyclic geometry as the lowest energy structure [22].

This pattern becomes clearer when examining the energy differences between the most stable cyclic and linear isomers across the  $\text{MgC}_n\text{H}$  series ( $n=4-7$ ), as shown in Figure 1B. For structures with an even number of carbons, the energy difference is positive, indicating a preference for linear geometries. Conversely, for the odd-numbered systems, the energy difference is negative, favoring the cyclic structures  $c\text{-MgC}_5\text{H}$  (**5a**) and  $c\text{-MgC}_7\text{H}$  (**7a**) over the linear isomers **5lin** and **7lin**. The most stable cyclic isomers of  $\text{MgC}_4\text{H}$  (**4a**) and  $\text{MgC}_6\text{H}$

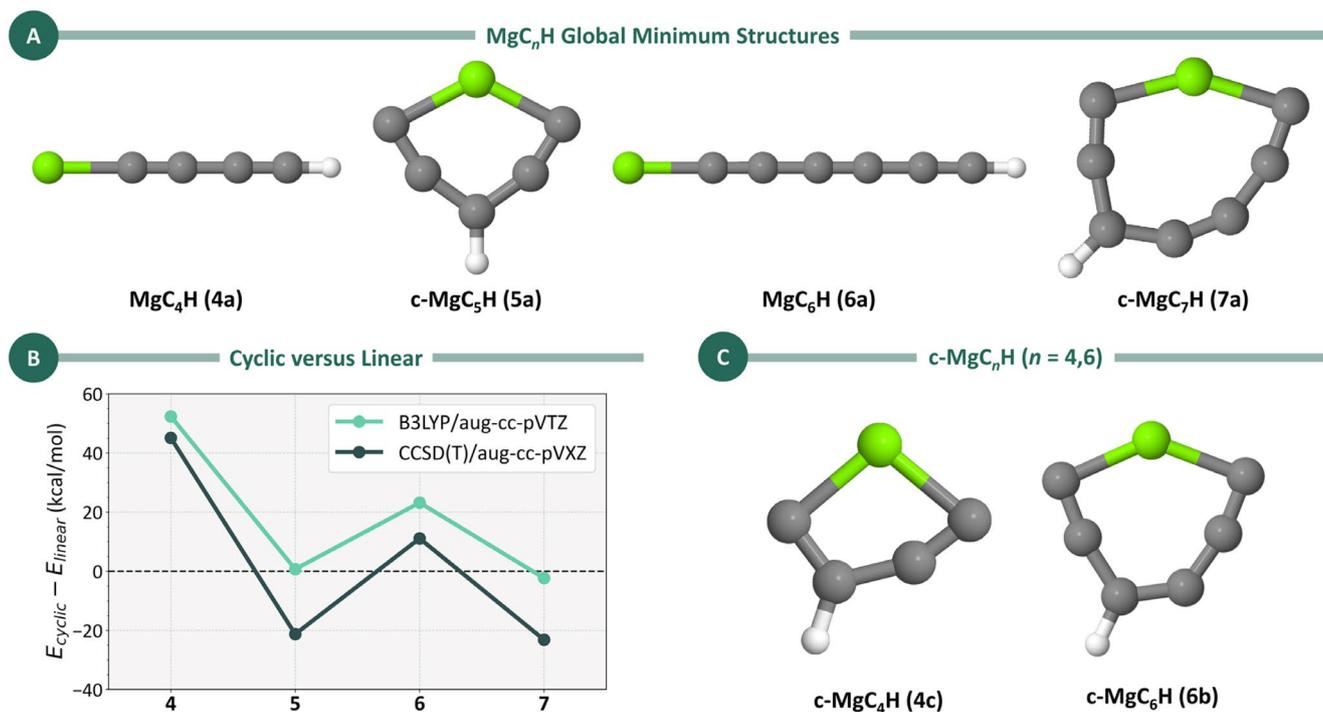
(**6a**), which were used in the plot of Figure 1B, are depicted in Figure 1C.

Figure 1B shows that DFT presents a bias toward the linear structures when compared to the CCSD(T) results. This is particularly dramatic in the case of  $\text{MgC}_5\text{H}$ , where DFT incorrectly predicts the linear geometry as the lowest energy configuration. This tendency is larger for odd  $n$  because the linear geometry often results in significant spin contamination in the calculated spin states, leading to artificially lower energy estimates due to the increased variational freedom caused by this effect. In the following sections, we discuss each  $\text{MgC}_n\text{H}$  series separately.

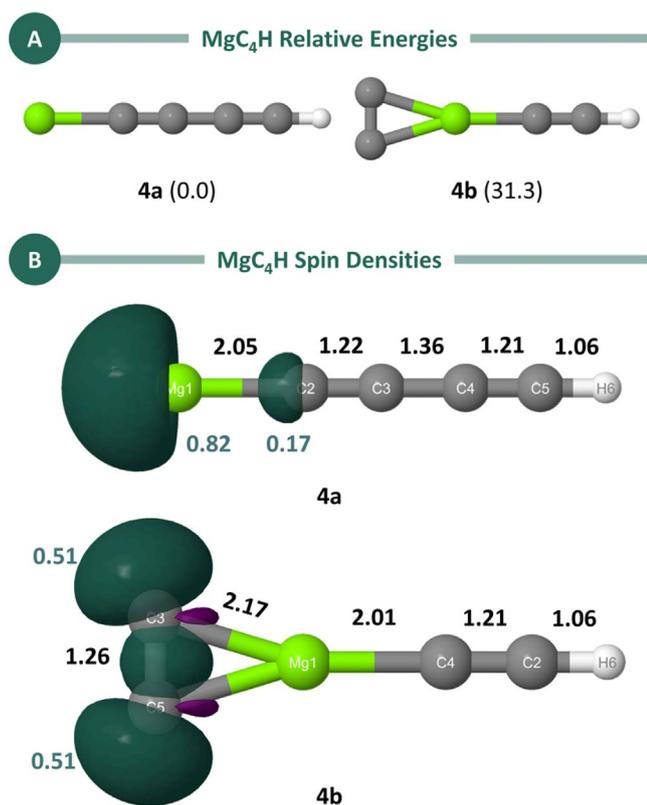
#### 3.2 | $\text{MgC}_4\text{H}$

The lowest-energy isomer identified for  $\text{MgC}_4\text{H}$ , referred to as Structure **4a**, is linear with an estimated dipole moment of approximately 2.2 Debye, as shown in Figure 2A. This isomer was previously studied by Bâldea [23], and its detection in IRC +10216 has already been reported by Cernicharo et al. [17]. The energies and structural parameters obtained in this work are in good agreement with those reported by Bâldea [23].

In Structure **4a**, it is possible to observe an alternation in carbon-carbon bond lengths, with the C2-C3 and C4-C5 bonds having lengths typical of triple bonds (1.20 Å), while the C3-C4 bond exhibits a length intermediate between typical



**FIGURE 1** | (A) Lowest-energy isomers for  $\text{MgC}_n\text{H}$  ( $n=4-7$ ) obtained at the CCSD(T)/aug-cc-pVXZ//UB3LYP/aug-cc-pVTZ level ( $X=T$  for  $n=4$  and 5 and  $X=D$  for  $n=6$  and 7). Isomers are labeled as described in the Section 2. (B) Energy differences (in kcal/mol) between cyclic and linear isomers for  $\text{MgC}_n\text{H}$  ( $n=4-7$ ) calculated at UB3LYP/aug-cc-pVTZ (green) and CCSD(T)/aug-cc-pVXZ (teal). The cyclic isomers considered here are the most stable cyclic structures, where all non-hydrogen atoms are incorporated into the ring. The linear  $\text{MgC}_5\text{H}$  and  $\text{MgC}_7\text{H}$  isomers considered here are labeled **5lin** and **7lin** (see text for details). (C) Most stable cyclic isomers for  $\text{MgC}_n\text{H}$  ( $n=4$  and 6), where all non-hydrogen atoms form part of the ring, obtained at the UB3LYP/aug-cc-pVXZ level.



**FIGURE 2** | (A) Low-energy isomers of  $\text{MgC}_4\text{H}$  calculated at the UB3LYP/aug-cc-pVTZ level. Relative energies (in kcal/mol, shown in parentheses) were refined using the CCSD(T)/aug-cc-pVTZ method with ZPE corrections from the UB3LYP/aug-cc-pVTZ level. Dipole moments were also calculated at the CCSD(T)/aug-cc-pVTZ//UB3LYP/aug-cc-pVTZ level and are 2.2 D for **4a** and 0.8 D for **4b**. (B) Spin density plots for the low-energy isomers of  $\text{MgC}_4\text{H}$ . Bond lengths (in Å, black), were obtained at the UB3LYP/aug-cc-pVTZ level. The Löwdin population analysis of the spin density (teal) was calculated at the CCSD(T)/aug-cc-pVTZ level.

double (1.34 Å) and single bonds (1.54 Å). The spin density plot (Figure 2B) reveals that the majority of the spin density is concentrated on the magnesium atom, a conclusion also reached by Bâldea [23] through natural bond orbital (NBO) [44] calculations.

The computational prediction of the second lowest energy isomer of  $\text{MgC}_4\text{H}$ , Structure **4b**, was recently reported [24]. This isomer features a three-membered  $\text{C}_2\text{Mg}$  ring (Figure 2A) and lies  $\Delta E = 31.6$  kcal/mol above Structure **4a**. The spin density plot for this isomer indicates a notable difference from the linear isomer, with higher spin density concentrated along the carbon chain, particularly over the C3–C5 atoms, rather than on the magnesium atom. This suggests a transfer of electron density from the magnesium atom to the carbon chain.

In fact, the bond length observed for C3–C5 (1.2585 Å) falls between the values reported for neutral  $\text{C}_2$  [45] and anionic  $\text{C}_2^-$  [46], but is closer to that of  $\text{C}_2^-$ . Furthermore, studies on  $\text{MgC}_2$  [3, 47, 48] also suggest an  $\text{Mg}^+\text{C}_2^-$  structure with a similar geometry to that observed in this work. According to these previous studies, the major interaction between the magnesium atom and the carbon chain is a  $\text{Mg} \rightarrow \text{C}_2$  charge transfer, with the cyclic

$\text{MgC}_2$  isomer stabilized relative to the linear congener due to a  $\text{C}_2 \rightarrow \text{Mg}$  backdonation, which can occur either in-plane or out-of-plane [48].

It is worth noting that a cyclic  $\text{MgC}_4\text{H}$  structure with  $\text{C}_{2v}$  symmetry was not identified, which is consistent with previous findings reported by Aoki at the DFT level [49]. Instead, c- $\text{MgC}_4\text{H}$  distorts to a  $\text{C}_s$  structure, as shown in Figure 1C.

Regarding the charged analogs of these neutral species, the vertical and adiabatic IPs and EAs of the linear  $\text{MgC}_4\text{H}$  Isomer **4a** have been previously reported by Bâldea [23]. Our results are in close agreement with those findings and confirm that, in all cases, the IPs and EAs are positive. These values are provided in Table S1.

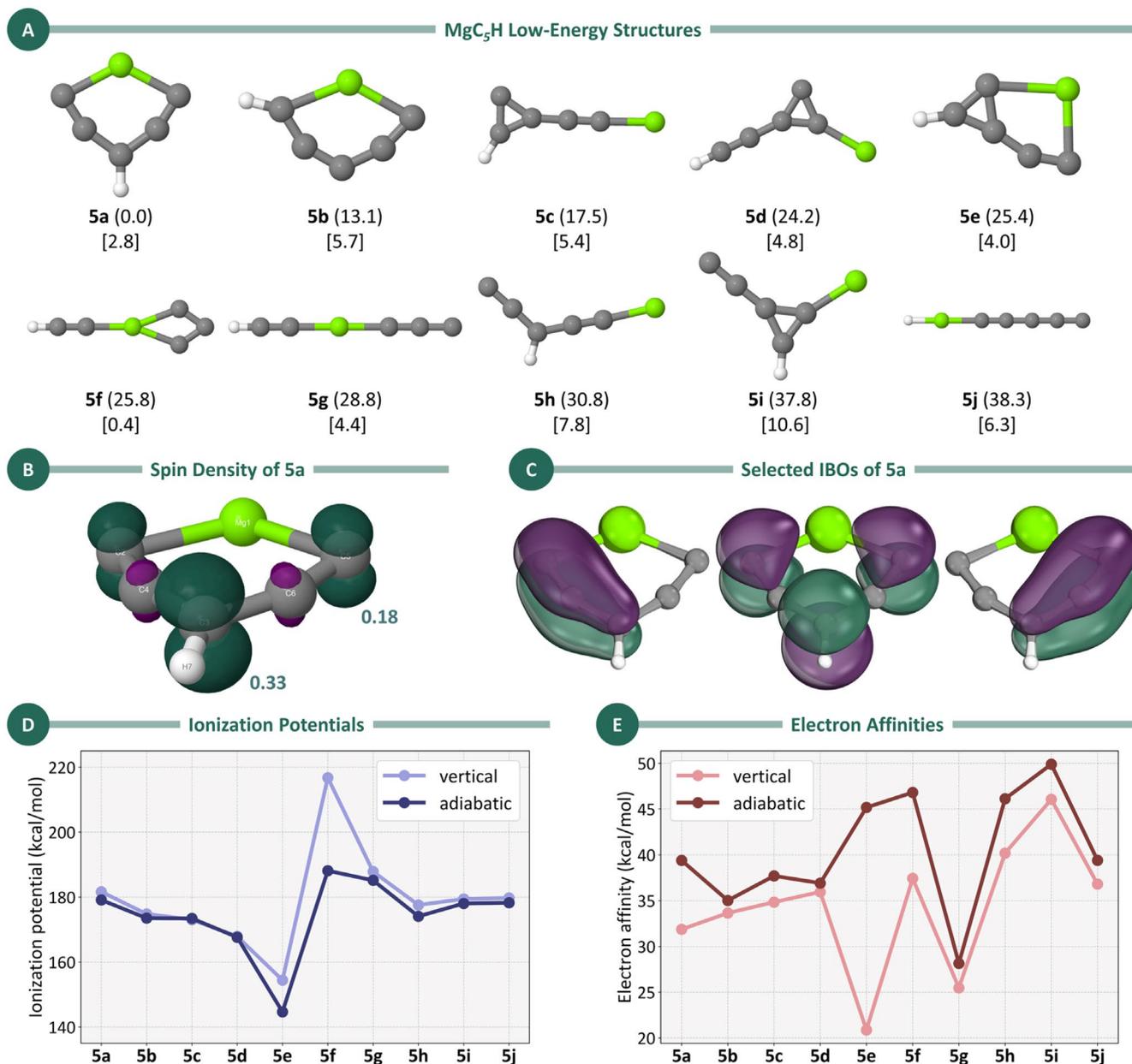
The positive IP and EA values indicate a stability hierarchy, with the anionic  $\text{MgC}_4\text{H}^-$  species being the most stable, followed by the neutral  $\text{MgC}_4\text{H}$  structures, and the cationic  $\text{MgC}_4\text{H}^+$  species as the least stable. Notably, the stabilization of the anionic form of **4b** is approximately twice as significant. Taken together, these results suggest that the still-elusive  $\text{MgC}_4\text{H}^-$  species, particularly the anion of **4b**, could be promising candidates for astronomical observation.

### 3.3 | $\text{MgC}_5\text{H}$

For  $\text{MgC}_5\text{H}$ , 10 distinct low-energy isomers (plus **5lin**) were identified, and their geometries are shown in Figure 3A, along with ZPE-corrected energies and dipole moments. Our results indicate that, similar to  $\text{MgC}_3\text{H}$  [22], the global minimum of  $\text{MgC}_5\text{H}$  (**5a**) adopts a cyclic structure with  $\text{C}_{2v}$  symmetry, in contrast to the linear isomer observed for  $\text{MgC}_4\text{H}$  [23]. Notably, many of the  $\text{MgC}_5\text{H}$  isomers exhibit calculated dipole moments exceeding 2 Debye. Given that species with smaller dipole moments—such as the CH radical, with a  $\mu$  value of 1.46 Debye [50]—have been successfully detected by rotational spectroscopy [51], these findings suggest a promising potential for future experimental investigations of magnesium-containing systems, particularly for targeted observations using radio telescopes.

Before diving into low-lying isomers, we first focus on further characteristics of the global minimum **5a**. In terms of bond lengths (Figure S2), the Mg–C2 and Mg–C5 distances are consistent with typical Mg–C single bonds [52]. The C2–C4 and C5–C6 bonds display lengths intermediate between those of triple and double bonds, whereas the C3–C4 and C3–C6 bonds fall between double and single bond lengths. This suggests that multiple bonding schemes (i.e., resonance structures) might contribute to the final structure of this isomer. The spin density (Figure 3B) is concentrated among the  $\alpha$  and  $\gamma$  carbon atoms, especially the latter.

Figure 3C shows selected IBOs for Structure **5a**. These orbitals reveal significant delocalization over three carbon atoms, indicating the presence of a delocalized  $\pi$  system across them. This finding is consistent with the structural parameters displayed in Figure 3B. Spin density plots for all structures depicted in Figure 3A were also generated and are available in Figure S4,



**FIGURE 3** | (A) Low-energy isomers for MgC<sub>5</sub>H obtained at the UB3LYP/aug-cc-pVTZ level. Relative energies (in kcal/mol, in parentheses) were refined using the CCSD(T)/aug-cc-pVTZ method with ZPE corrections from the UB3LYP/aug-cc-pVTZ level. Dipole moments (in square brackets) were also determined at the CCSD(T)/aug-cc-pVTZ//UB3LYP/aug-cc-pVTZ level. (B) Spin density of the ground-state geometry of MgC<sub>5</sub>H, with the Löwdin populational analysis of the spin density (CCSD(T)/aug-cc-pVTZ) shown in teal. (C)  $\pi$ -Space IBOs for Structure **5a**. (D) Vertical and adiabatic ionization potentials (in kcal/mol) for MgC<sub>5</sub>H isomers. Geometries and ZPE were obtained at the UB3LYP/aug-cc-pVTZ level, with energies calculated at the UCCSD(T)/aug-cc-pVTZ level. (E) Vertical and adiabatic electron affinities (kcal/mol) for the isomers with the chemical formula MgC<sub>5</sub>H. Geometries and ZPE were obtained at the UB3LYP/aug-cc-pVTZ level, with energies calculated at the UCCSD(T)/aug-cc-pVTZ level.

highlighting the distribution of spin density across the various isomers, with some structures showing spin delocalization across the carbon chain, rather than concentrated on the magnesium atom. Although these higher-energy isomers may be less abundant in astrochemical environments, determining their structures is crucial, as they could act as key intermediates in chemical reactions.

Out of the 10 lowest-energy MgC<sub>5</sub>H isomers (excluding **5lin**), seven adopt cyclic configurations, with ring sizes varying from three to six atoms. Isomer **5b** ( $\Delta E = 13.1$  kcal/mol) stands out

with its planar six-membered ring, where the hydrogen atom is attached to a carbon in the  $\alpha$  position relative to magnesium, unlike Isomer **5a**, in which the hydrogen occupies the  $\gamma$  position. This shift in hydrogen placement leads to a more compact ring structure, resulting in an increase in the C–Mg–C bond angle from 124.6° in **5a** to 129.3° in **5b**. Additionally, the distance between the magnesium atom and the  $\gamma$  carbon shortens from 2.82 Å in **5a** to 2.55 Å in **5b**.

Among the cyclic structures, four isomers—**5c** ( $\Delta E = 17.5$  kcal/mol), **5d** ( $\Delta E = 24.2$  kcal/mol), **5e** ( $\Delta E = 25.4$  kcal/mol), and **5i**

( $\Delta E = 37.8$  kcal/mol)—feature a distinctive three-membered  $C_3$  ring. In Isomer **5c**, one of the carbon atoms in the ring is dicoordinate, with no attached substituents, whereas the other two carbon atoms are tricoordinate, with one bonded to a hydrogen atom and the other connected to a linear  $C_2Mg$  fragment. Interestingly, in Isomer **5d**, the positions of the hydrogen and magnesium atoms are interchanged: the hydrogen atom migrates to the  $C_2Mg$  fragment, whereas the magnesium atom occupies the former position of the hydrogen. This rearrangement results in a destabilization of 6.7 kcal/mol compared to **5c** and a modest decrease in dipole moment from 5.4 Debye in **5c** to 4.8 Debye in **5d**. It is worth highlighting that none of the low-lying  $MgC_5H$  isomers feature the  $C_5^{2-}$  cluster with a planar tetracoordinate carbon, which was theoretically predicted for  $MgC_5$  in earlier works [53, 54].

Isomer **5e** is unique among the 10 lowest-energy structures, featuring a fused bicyclic arrangement. In this case, a three-membered  $C_3$  ring is fused to a five-membered  $C_5Mg$  ring, with two carbon atoms participating at the junction of the two rings. This structure is planar and exhibits  $C_s$  symmetry. On the other hand, the least stable structure with a three-membered ring is Isomer **5i**. In this isomer, all the carbon atoms in the  $C_3$  ring are tricoordinate, bonded respectively to a hydrogen atom, a magnesium atom, and a  $C_2$  fragment. Among the 10 isomers, **5i** stands out with the highest dipole moment of 10.6 Debye.

Isomer **5f** ( $\Delta E = 25.8$  kcal/mol) is the only one with a four-membered ring structure among the 10 lowest-lying isomers. The four-atom cycle adopts a rhombic geometry, reminiscent of the structure reported by Redondo et al. for  $MgC_3$  [55]. In this case, the remaining  $C_2H$  group is connected to the magnesium atom via one of the carbon atoms. Notably, its dipole moment is only 0.4 Debye, making it the least polar  $MgC_5H$  isomer by a considerable margin.

The remaining isomers—**5lin** ( $\Delta E = 21.3$  kcal/mol), **5g** ( $\Delta E = 28.8$  kcal/mol), **5h** ( $\Delta E = 30.8$  kcal/mol), and **5j** ( $\Delta E = 38.3$  kcal/mol)—are open-chain structures, with **5g** and **5j** adopting linear configurations. Isomer **5g** is characterized by a linear  $C_3MgC_2H$  arrangement, whereas **5j** consists of a  $C_5MgH$  chain. Other potential linear structures were found to be too high in energy and were therefore excluded from further analysis. In contrast, Isomer **5h** features an open-chain  $MgC_5$  structure, where the central carbon of the  $C_5$  chain is hydrogenated.

Optimized geometries for the cations and anions associated with the distinct  $MgC_5H$  isomers are provided in Figure S5. These geometries were computed at the UB3LYP/aug-cc-pVTZ level of theory. The figure highlights the most significant variations in bond lengths and angles observed during the transitions between neutral, cationic, and anionic states. Particularly, bonds and angles involving the magnesium atom undergo the most significant changes. In the case of the lowest-energy isomer, changes in C–C bond lengths are also observed, which aligns with the spin density distribution predominantly located along the carbon chain.

The adiabatic and vertical IPs and EAs for all structures shown in Figure 3A are presented in Figure 3D,E, respectively, with

the numerical values provided in Table S2. The adiabatic IP values range from 140 to 190 kcal/mol, with **5f** showing the highest value and **5e** the lowest. Interestingly, these two isomers also exhibit the largest deviations between their vertical and adiabatic IP values, whereas the other isomers have vertical IPs closely matching their adiabatic counterparts. This indicates that, except for **5e** and **5f**, the geometries of the neutral  $MgC_5H$  isomers are quite similar to their corresponding cationic forms.

In terms of EAs, adiabatic EA values range from 27 to 50 kcal/mol, with **5g** showing the lowest EA and **5i** the highest. Once more, **5e** stands out by displaying the largest difference between its vertical and adiabatic EA values, similar to the case of the IP. This suggests that both the cationic and anionic forms of **5e** undergo significant geometric changes compared to their neutral structure.

Finally, it is also worth mentioning that, as observed for  $MgC_4H$ , the IP and EA values for all  $MgC_5H$  cases are positive. Again, this indicates that the anionic species are the most stable, followed by the neutral structures, with the cationic species being the least stable. These findings suggest the potential viability of detecting  $MgC_5H^-$  species. We hope these results will inspire further efforts to detect anionic magnesium-bearing carbon chains in the ISM, particularly in IRC +10216, where such species remain elusive.

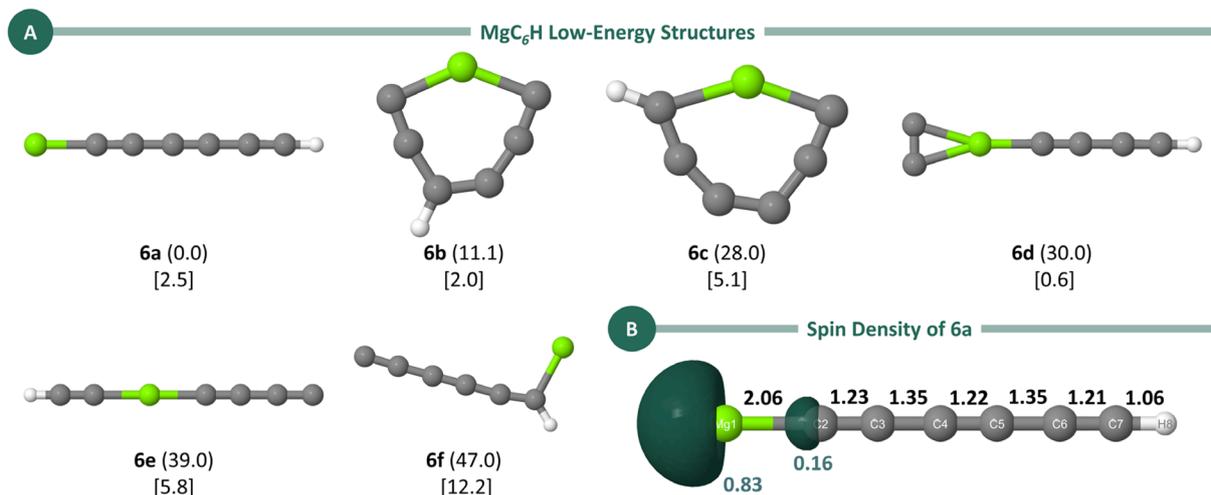
### 3.4 | $MgC_6H$

For  $MgC_6H$ , six distinct structures were identified, as shown in Figure 4A. Consistent with previously reported results for  $MgC_4H$ , the global minimum for  $MgC_6H$  features a linear structure with a terminal magnesium atom.

We begin by discussing the structural and bonding characteristics of Isomer **6a**. Upon examining the geometric parameters of this linear structure (Figure 4B), a similar alternation of bond lengths to that observed in  $MgC_4H$  is evident. Specifically, the C2–C5, C7–C3, and C4–C6 bonds exhibit lengths typical of triple bonds ( $\sim 1.20$  Å), whereas the C2–C7 and C3–C6 bonds have longer bond lengths. However, these lengths are shorter than those observed in  $MgC_4H$ , suggesting double bond characteristics ( $\sim 1.34$  Å) rather than single bonds ( $\sim 1.54$  Å).

The spin density plot and its population analysis for the linear structure are also presented in Figure 4B. These results show that, similar to  $MgC_4H$ , the majority of the spin density is localized on the magnesium atom. Spin density plots for the other low-lying isomers of  $MgC_6H$  are provided in Figure S6.

In contrast to the linear structure of **6a**, the next three low-lying isomers adopt cyclic configurations. Isomer **6b** ( $\Delta E = 11.1$  kcal/mol) features a seven-membered  $MgC_6$  ring with  $C_s$  symmetry, where the hydrogen atom is bonded to one of the carbons in the *para* position relative to magnesium. Similarly, isomer **6c** ( $\Delta E = 28.0$  kcal/mol) also contains a seven-membered ring, but with the hydrogen atom attached to a carbon in the *ortho* position to magnesium. No low-lying structures with six-, five-, or four-membered rings were identified. The final



**FIGURE 4** | (A) Low-energy isomers for MgC<sub>6</sub>H obtained at the UB3LYP/aug-cc-pVTZ level. Relative energies (in kcal/mol, in parentheses) were refined using the CCSD(T)/aug-cc-pVTZ method with ZPE corrections from the UB3LYP/aug-cc-pVTZ level. Dipole moments (in square brackets) were also obtained at the CCSD(T)/aug-cc-pVTZ//UB3LYP/aug-cc-pVTZ level. (B) Spin density distribution for Isomer **6a** at the CCSD(T) level. Bond lengths (in Å) are given in black, while the Löwdin population analysis of the spin density, calculated at the CCSD(T)/aug-cc-pVTZ level, is shown in teal.

cyclic structure, Isomer **6d** ( $\Delta E = 30.0$  kcal/mol), consists of a three-membered MgC<sub>2</sub> ring, with a C<sub>4</sub>H group bonded to the magnesium atom. Among the two low-lying open-chain structures, Isomer **6e** ( $\Delta E = 39.0$  kcal/mol) features a linear C<sub>4</sub>MgC<sub>2</sub>H chain, whereas **Isomer 6f** ( $\Delta E = 47.0$  kcal/mol) has a quasi-linear C<sub>6</sub> unit, where one of the terminal carbon atoms is tricoordinate and bonded to both the hydrogen and magnesium atoms. It is worth noting that, except for Isomer **6d** (0.6 Debye), all MgC<sub>6</sub>H isomers exhibit dipole moments of 2.0 Debye or higher, with Isomer **6f** having the largest dipole moment at 12.2 Debye.

### 3.5 | MgC<sub>7</sub>H

The final stoichiometry examined in this study is MgC<sub>7</sub>H, for which we identified 18 isomers within a 50 kcal/mol energy threshold. The first 10 of these isomers are presented in Figure 5A, whereas the others are shown in the Supporting Information. Consistent with the findings for MgC<sub>5</sub>H and MgC<sub>3</sub>H [22], the lowest-energy structure for MgC<sub>7</sub>H (**7a**) is also cyclic. However, unlike the previous cases, this cyclic structure exhibits C<sub>s</sub> symmetry rather than C<sub>2v</sub>, with the hydrogen atom attached to a carbon atom in the  $\gamma$  position relative to magnesium. This isomer appears to be analogous to the one found for MgC<sub>5</sub>H, with the addition of an ethylene group to one side of the carbon chain. This similarity is supported by comparable bond lengths and spin density patterns.

Figure 5B displays the geometric parameters, spin density plot, and Löwdin population analysis for the spin density. As with MgC<sub>5</sub>H, the lowest-energy isomer of MgC<sub>7</sub>H exhibits an alternation of C–C bond lengths along the carbon chain. These bond lengths fall between those typical of single and double bonds or double and triple bonds. Additionally, the spin density shows a nodal plane, with the highest concentration located on carbon atom C5 and significant contributions on atoms C2, C3, and C8.

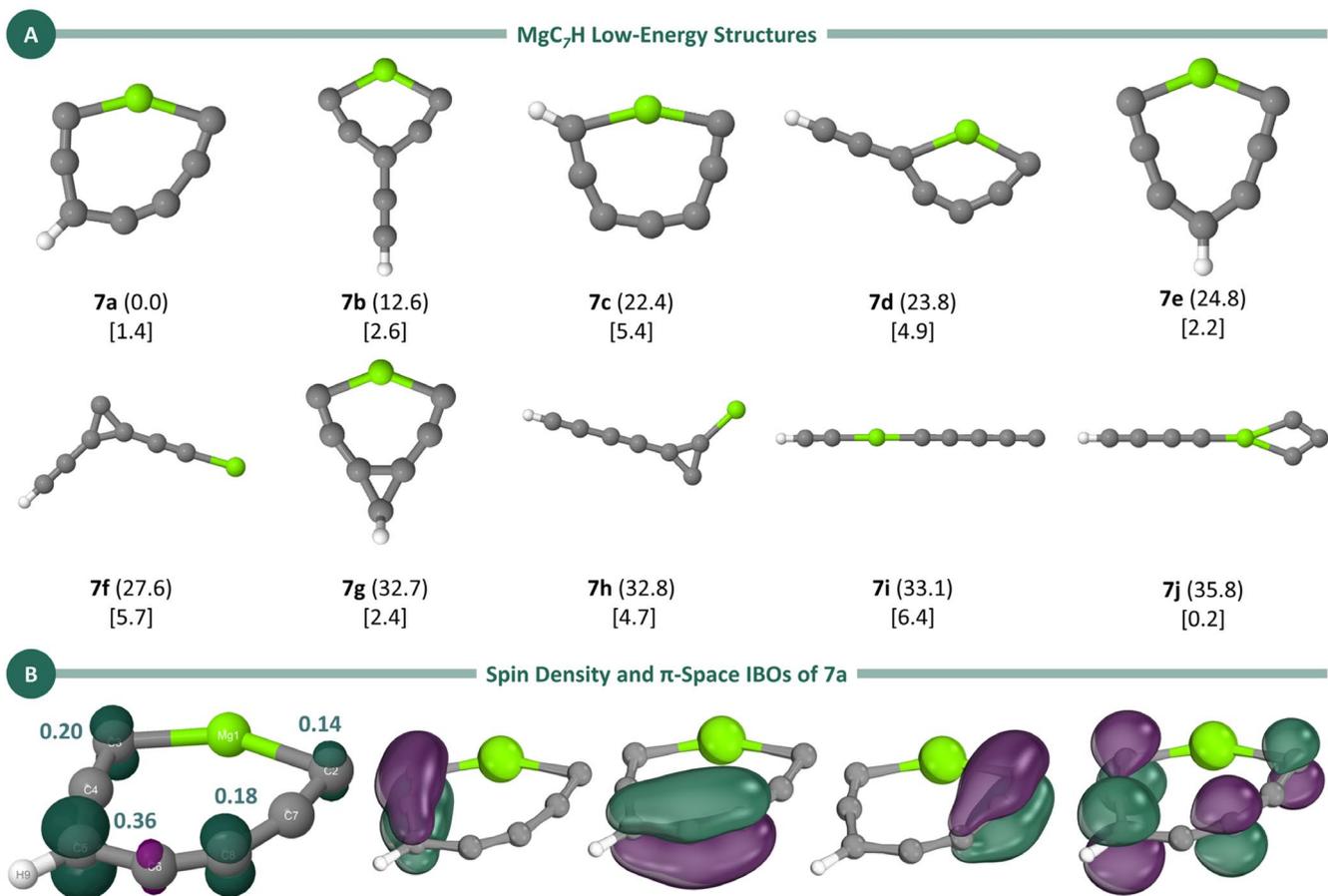
In addition to **7a**, the Isomers **7b** ( $\Delta E = 12.6$  kcal/mol), **7c** ( $\Delta E = 22.4$  kcal/mol), **7d** ( $\Delta E = 23.8$  kcal/mol), **7e** ( $\Delta E = 24.8$  kcal/mol), **7f** ( $\Delta E = 27.6$  kcal/mol), **7g** ( $\Delta E = 32.7$  kcal/mol), **7h** ( $\Delta E = 32.8$  kcal/mol), and **7j** ( $\Delta E = 35.8$  kcal/mol) are also cyclic. Three of these Isomers—**7a**, **7c** and **7e**—feature eight-membered rings in planar structures, with **7c** having the hydrogen attached to a carbon atom *ortho* to magnesium, and **7e** displaying a 1,5-substitution pattern. In contrast, **7b** and **7d** each feature a six-membered ring with a C<sub>2</sub>H substituent at one of the carbon atoms— $\gamma$  to magnesium in **7b** and  $\alpha$  to magnesium in **7d**.

The Isomers **7f**, **7g** and **7h** possess a three-membered C<sub>3</sub> ring, whereas **7j** features a four-membered C<sub>3</sub>Mg ring reminiscent of **5f**. In turn, **7g** consists of a bicyclic structure where a seven-membered MgC<sub>6</sub> ring is fused to the C<sub>3</sub> ring via two carbon atoms, with the hydrogen atom connected to the third carbon of the C<sub>3</sub> cycle.

Finally, the two lowest-energy open-chain structures are **7lin** ( $\Delta E = 23.2$  kcal/mol) and **7i** ( $\Delta E = 33.1$  kcal/mol), the latter containing a linear C<sub>5</sub>MgC<sub>2</sub>H chain. Among these structures, the dipole moments range from 0.2 Debye for **7j** to 6.4 Debye for **7i**.

### 3.6 | Fragmentation Studies

A critical factor influencing the likelihood of detecting these molecules is their stability against fragmentation. To address this, we performed a systematic fragmentation analysis of the **na** isomers ( $n = 4-7$ ), including their anionic counterparts. Although fragmentation can occur through various pathways, this study focuses on the loss of hydrogen and magnesium for the neutral species and magnesium loss for the anionic forms. These pathways, identified as the lowest-energy dissociation reactions for the linear MgC<sub>4</sub>H in previous studies [23], are particularly relevant to our analysis.



**FIGURE 5** | (A) Low-energy isomers for MgC<sub>7</sub>H calculated at the UB3LYP/aug-cc-pVTZ level. Relative energies (in kcal/mol, in parentheses) were refined using the CCSD(T)/aug-cc-pVTZ method with ZPE corrections from the UB3LYP/aug-cc-pVTZ level. Dipole moments (in square brackets) were also obtained at the CCSD(T)/aug-cc-pVTZ//UB3LYP/aug-cc-pVTZ level. (B) Spin density and  $\pi$ -space IBOs for Structure **7a**. The Löwdin population analysis of the spin density, calculated at the CCSD(T) level, is shown in teal.

As shown in Table S3, all dissociation enthalpies are positive, ranging from +23.0 kcal/mol (**6a**<sup>-</sup> → C<sub>6</sub>H<sup>0</sup> + Mg<sup>0</sup>) to +145.8 kcal/mol (**6a** → MgC<sub>6</sub> + H). For the linear Isomers **4a** and **6a**, the Mg–C bond is more prone to breaking compared to the C–H bond. However, this trend does not apply to the cyclic species, where the C–H bond is more susceptible to fragmentation than the Mg–C bond. This behavior arises because, in cyclic species, the magnesium atom interacts with two carbon atoms, making magnesium dissociation less favorable.

For the anionic species, a similar pattern is observed: the cyclic structures exhibit greater stability than their linear counterparts with respect to magnesium loss. This enhanced stability suggests that cyclic anionic species could be particularly promising candidates for experimental observation.

### 3.7 | MgC<sub>n</sub>H Versus MgC<sub>n</sub><sup>-</sup>

When examining the full dataset of MgC<sub>n</sub>H species investigated in this work, along with data reported by Panda et al. [22] for MgC<sub>3</sub>H, a clear trend emerges: for even *n*, the linear structure is energetically favored, whereas for odd *n*, the cyclic structure is preferred. Interestingly, for even *n*, the most stable structure consistently appears to be linear with the spin density centered on the magnesium atom. This finding contrasts with prior

studies on isoelectronic species of the MgC<sub>n</sub><sup>-</sup> type, where cyclic structures were reported to be more stable for even *n*, and linear structures for odd *n* [55]. The discrepancy likely arises from differences in the computational methods employed. More recent high-level CC calculations for MgC<sub>4</sub>H and MgC<sub>3</sub>H align with the trends observed in this work, further supporting the validity of the current results [22, 23].

## 4 | Conclusions

In this study, we investigated the low-energy isomeric structures of MgC<sub>n</sub>H (*n* = 4–7) to explore the significance of magnesium in interstellar chemistry and the absence of MgC<sub>n</sub>H compounds with odd carbon numbers in the interstellar medium. The results reveal distinct structural characteristics depending on whether *n* is even or odd. For even *n*, the lowest-energy isomers, including two and six low-energy isomers for *n* = 4 and 6, respectively, were linear MgC<sub>n</sub>H chains exhibiting alternating C–C bond lengths akin to polyynic structures, though with shorter bond lengths indicating a partial cumulenic character. In contrast, odd *n* isomers displayed greater structural diversity, with 10 and 17 low-energy isomers found for MgC<sub>5</sub>H and MgC<sub>7</sub>H, surpassing the number of isomers found for their even *n* counterparts. This diversity arises from the stability of linear structures in even *n* cases, where an unpaired electron on the

magnesium atom is feasible, whereas for odd  $n$ , cyclic structures are favored. The lowest-energy  $\text{MgC}_5\text{H}$  structure adopts a cyclic geometry with  $C_{2v}$  symmetry, similar to that of  $\text{MgC}_3\text{H}$ . In contrast,  $\text{MgC}_7\text{H}$  exhibits a comparable cyclic form, but without  $C_{2v}$  symmetry, as the hydrogen atom is preferentially positioned  $\gamma$  to the magnesium atom, facilitating the formation of three  $\text{C}\equiv\text{C}$  triple bonds. The IBO analysis for  $\text{MgC}_7\text{H}$  reveals a bonding pattern closely resembling that observed in the  $\text{MgC}_5\text{H}$  species. In both cases, the IBOs display significant electron delocalization along the carbon backbone. Additionally, all  $\text{MgC}_5\text{H}$  isomers demonstrated positive EA, suggesting the formation of stable anions under astrochemical conditions. Many isomers exhibited dipole moments suitable for rotational spectroscopy detection, indicating a promising avenue for further experimental studies and radio telescope observations.

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## Data Availability Statement

The data that supports the findings of this study are available in the supplementary material of this article.

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### Supporting Information

Additional supporting information can be found online in the Supporting Information section.