Al₂C₄H₂ Isomers with the Planar Tetracoordinate Carbon (ptC)/Aluminum (ptAl)

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Abstract: Forty-one isomers of Al₂C₄H₂ that lie within 50 kcal mol⁻¹ are theoretically identified in this work using density functional theory. Among these, isomers 3 and 14 contain a planar tetracoordinate carbon (ptC) atom that lies at 3.3 and 16.9 kcal mol⁻¹, respectively, and are above the global minimum geometry at the ωB97XD/6-311++G(2d,2p) level of theory. The other ten isomers that also contain unique bonding features are isomers 4, 18, 20, 21, 22, 27, 28, 31, 34, and 40. Out of these isomers, 4, 18, 20, 22, 27, 28, and 34 contain planar tetracoordinate aluminum (ptAl) whereas isomers 31 and 40 contain both ptC and ptAl atoms. Chemical bonding characteristic features are thoroughly analyzed for all these eleven isomers with various bonding and topological quantum chemical tools, such as NBO, AdNDP, WBI, and ELF, except isomer 27 due to the observed elongated Al-Al bond length. The current results indicate that ptC isomer 3 is more stable than other isomers because electron delocalization is more prevalent and it also has double aromaticity as observed from the ELF, NICS, and AdNDP analysis. Further, the structural stability of these isomers is investigated through ab initio molecular dynamics (AIMD) simulation. Isomer 21 shows the planar pentacoordinate aluminum but it is observed as a kinetically unstable geometry from AIMD and, further, one could notice that it isomerizes to isomer 12.

Keywords: Al₂C₄H₂; planar tetracoordinate carbon; planar tetracoordinate aluminum; delocalization; anti-van’t Hoff–Le Bel; computational chemistry

1. Introduction

Planar tetracoordinate carbon (ptC) has made tremendous progress in the past five decades both theoretically [1–10] and experimentally [11–20]. This concept is a fundamental deviation from the conventional ideas of tetrahedral tetracoordinate carbon, which was independently postulated by van’t Hoff and Le Bel in 1874 [18,21,22]. For a century, van’t Hoff and Le Bel’s tetrahedral carbon model went unchallenged. Later, computational predictions and experimental observations led to the initial discovery of planar tetracoordinate or hypercoordinate compounds [4,23]. In 1968, H. J. Monkhorst first proposed the idea of ptC as a transition state for a non-dissociative racemization process [24]. Two years later, in 1970, Hoffmann et al. proposed two ways to stabilize ptC, which have served as a basic guideline for the design of ptC species [25] to date. First, the mechanical strategy was employed with transition metals, conjugative rings, or cages to induce the formation of ptC. On the other hand, the electronic strategy involved using strong σ-donor and π-acceptor ligands or aromatic delocalization to stabilize the lone pair present in the p-orbital on the ptC center. Based on the latter strategy, Schleyer and coworkers theoretically identified the first set of ptC molecules in 1976 but they were not global minimum geometries [26]. Since then, the chemistry of ptC has been extensively studied both theoretically and experimentally as well. Further, it has been ex-
tended to planar hypercoordinate carbon (phC) [4,27] as well as nanosized systems [28–31]. These ptC molecules not only challenge our current understanding of “chemical bonding,” but also have potential applications in materials science [31,32].

Only a few ptC compounds, either global or local minimum energy structures, have been experimentally identified to date [13,15,16,33] and other ptC molecules are elusive in the laboratory to date. In this direction, the identification of a ptC structure for a particular elemental composition leads to a high chance of theoretical viability and it delineates a new path to synthetic feasibility [16,33–38]. Dong et al. and Zhang et al. experimentally achieved the ptC clusters of C₆Al₆ [37] and C₅Al₅ [39], respectively, and were predicted to be the global minimum theoretically [40,41]. These two outstanding experimental achievements on aluminum clusters demonstrated that ptC structures are substantially feasible in the experimental laboratory.

Clusters of aluminum and carbon atoms have attracted a lot of attention because they can form non-classical and non-stoichiometric structures [4,42–44] different from most other metal carbide clusters with the cubic framework or layered structures. In 2022, Zhang and co-workers explored them both theoretically and experimentally and identified the most stable structure containing ptC in the carbon-doped aluminum clusters Al₃C₄ (n = 6–5) [45]. In the past, Naumkin explored the flat structural motifs of small alumino-carbon clusters CₙAlₙ (n = 2–3, m = 2–8) and identified unique clusters featuring ptC and phC [46]. Wu and co-workers identified the global minimum geometry of simple aluminum carbon clusters containing two ptCs [40]. Das et al. identified the global minimum ptC geometries of CSiGaAl₂⁻/0 and CGeGaAl₂⁻/0 systems, exhibiting both σ and π aromaticity [47].

The aluminum and carbon-based molecules could be used in cluster assembled materials [7,9], energy storage [48], aluminum nanoparticle protection, and two-dimensional donor materials in solar cells [49]. In 2021, the global minimum structures of aluminum-bearing planar tetracoordinate carbon isomers of CAI₂Mg⁻/0 [50] and planar tetracoordinate boron, as well as planar pentacoordinate boron isomers of BAL₂Mg⁻/0 [51], were also reported. Dong et al. synthesized Al₂CH₃, Al₂C₃H₃, Al₃C₃H₂, Al₄C₄H₂, Al₅C₄H₃, and Al₆C₆H clusters which have hydrogen storage properties [37]. Due to their ability to retain hydrogen and yield combustion products with minimal environmental impact, aluminum clusters have been the subject of several aspects of energy conversion materials development [8,52]. As said above, the exploration of aluminum, carbon, and hydrogen clusters with various molecular chemical compositions has been carried out in the recent past in both theoretical and experimental aspects and their potential applications have also been reported. Meanwhile, a lot of non-classical structure identification has also been carried out in this direction. They may have future potential as alternative fuel resources for overcoming one of the key challenges in developing a hydrogen economy [48] which is in line with one of the 17 UN Sustainable Development Goals [53]. Aluminum carbon clusters containing ptCs have moderate band gaps with wide applications in the areas of semiconductors, optoelectronics, and photovoltaics [28,49]. Al-doped carbon nanotubes have gained a lot of interest because of their nanocatalytic activity in reducing N₂ to NH₃ [54]. Al-doped single-walled carbon nanotubes are superior materials as sensors to detect air pollutants such as CO, NH₃, NOₓ, and SOₓ [55,56]. From this point of view, the Al₃C₄H₂ system has yet to be explored in detail, hence the present work demonstrates its importance in this field.

On the other hand, aluminum has also been touted as having a significant potential for astrochemical interest [57]. Aluminum is a generously available metallic element in the interstellar medium (ISM) that has a cosmic abundance of ~3 × 10⁻⁶ [58]. AlCl [59,60], AlF [59,61,62], AlNC [63–65], AlO [66,67], and AlOH [62] are aluminum-bearing molecules that have been detected in the ISM. The depletion of aluminum in interstellar space due to the formation of interstellar dust was well reported [68] and the existence of aluminum in interstellar space is reported as carbonaceous grains [69]. From this point of view, the present work aimed to explore the possible isomers of the Al₃C₄H₂ system the-
oretically and, in particular, the main focus is given to isomers that have ptC and ptAl isomers lying within 50 kcal mol\(^{-1}\).

2. Computational Methodology

The initial geometries of Al\(_2\)C\(_4\)H\(_2\) isomers are generated by chemical intuition. Density functional theory (DFT) was used to optimize the different possible geometries of Al\(_2\)C\(_4\)H\(_2\) isomers at the B3LYP/6-311++G(2d,2p) \([70–73]\) and \(\omega B97XD/6-311++G(2d,2p)\) \([70,71,74]\) level of theoretical methods. All the investigated Al\(_2\)C\(_4\)H\(_2\) isomers considered here correspond to the singlet spin state. Harmonic vibrational frequencies are calculated for all the energy minimized geometries to ensure the stationary point on the potential energy surface is a minimum, a transition state, or a higher-order saddle point. Natural bond order (NBO) analysis \([75]\), adaptive natural density partitioning (AdNDP) analysis \([76,77]\), and Wiberg bond indices (WBI) \([78]\) were used to examine the nature of chemical bonding in the planar tetracoordinate isomers at the \(\omega B97XD/6-311++G(2d,2p)\) level of theory. Nucleus-independent chemical shift (NICS) values were calculated to measure the \(\pi/\sigma\) dual aromaticity in isomer 3 \([79]\). Topological analysis of the electron localization function (ELF) \([80]\) was carried out for the planar tetracoordinate isomers using the Multiwfn program \([81]\). The ab initio molecular dynamics (AIMD) simulation using the atom-centered density matrix propagation (ADMP) \([82]\) method was performed for the planar tetracoordinate isomers to check their kinetic stability at the \(\omega B97XD/6-311++G(2d,2p)\) level of theory. In-house Python code was used to generate other possible atomic re-arrangements in the isomers of \(1, 2, 3, 4, 20, 22,\) and \(40\). All of these DFT calculations were carried out with the Gaussian suite of programs \([83]\).

3. Results and Discussion

The optimized geometries of Al\(_2\)C\(_4\)H\(_2\) isomers that lie within 50 kcal mol\(^{-1}\) at the \(\omega B97XD/6-311++G(2d,2p)\) level of theory are shown in Figure 1 and their total energy, ZPVE, and ZPVE corrected relative energies are listed out in Table S1. The B3LYP/6-311++G(2d,2p) level of theoretical results is provided in Table S2. Isomer 1 is a global minimum on the potential energy surface with a bent structure. Among these geometries, isomers 3, 4, 14, 18, 20, 22, 27, 28, 31, 34, and 40 are showing planar tetracoordinate structures that lie at 3.3, 4.3, 16.9, 21.3, 22.9, 24.6, 30.2, 30.9, 34.7, 40.0, and 49.6 kcal mol\(^{-1}\), respectively. Planar pentacoordinate aluminum (ppAl) is observed in isomer 21 which lies at 23.1 kcal mol\(^{-1}\) above isomer 1. All these planar tetracoordinate and pentacoordinate geometries with their bond lengths are shown in Figure 2. Among these, eleven isomers are local minima with zero imaginary frequencies except isomer 40, which is a first-order saddle point (transition state). Among all the isomers, only two isomers, 3 and 14, contain a ptC atom, while the other isomers such as 4, 18, 20, 22, 27, 28, and 34 contain ptAl. Isomers 3 and 4 have two planar tetracoordinate centers each. Isomer 3 contains two ptCs whereas isomer 4 contains two ptAls. Three planar tetracoordinate centers are present in isomers 31 and 40. In contrast to isomer 31, which has two ptCs and a ptAl, isomer 40 contains two ptAls and a ptC. Even though isomer 27 contains a ptAl center, because of the elongated Al-Al bond length of 3.10 Å, it is excluded from the bonding studies.
Figure 1. Isomers of Al₂C₄H₂ that lie within 50 kcal mol⁻¹ and their zero-point vibrational energy (ZPVE) corrected relative energies (in kcal mol⁻¹), dipole moments (in Debye), and the number of imaginary frequencies (NImag) obtained at the ωB97XD/6-311++G(2d,2p) level of theory.
3.1. Wiberg Bond Indices

The Wiberg bond indices (WBIs) of isomers 3, 4, 14, 18, 20, 21, 22, 28, 31, 34, and 40 are shown in Figure 3, which are the measure of electronic parameters related to electron population overlap between two atoms. It indicates the bond order and the characteristic bonding features of these isomers. In isomer 3, the WBI values for C1–C3, C1–C4, and C2–C4 (numbering scheme followed as shown in Figure 3) are 2.02, 1.22, and 2.02, respectively, which indicates resonance stabilization with alternate double bonds along ptCs. Among the four bonds of the ptC in isomers 14, 31, and 40, one of the bonds has a WBI value close to or greater than two which indicates the π bonds between them. The ppAl–Al bond in isomer 21 has a WBI value of 0.07 which indicates the interaction be-
tween them is electrostatic, but all four C–ppAl bonds have WBI values in the range of 0.36 to 0.76 which indicates the single bonds between them. In contrast to isomers with ptAl, which only have four σ bonds, isomers with ptC have one π bond and four σ bonds.

Figure 3. Wiberg bond indices of Al:C:H:isomers 3, 4, 14, 18, 20, 21, 22, 28, 31, 34, and 40 at the ωB97XD/6-311++G(2d,2p) level of theory.

3.2. Topological Analysis

The electron localization function (ELF) analysis was carried out to measure the extent of electron delocalization in molecular systems. The color-filled ELF plots of isomers 3, 4, 14, 18, 20, 21, 22, 28, 31, 34, and 40 are shown in Figure 4. In isomer 3, the electron density is localized between the ptC–C bonds in the range of 0.80 to 1.00 which indicates strong localization of electrons, and also the electron density is delocalized through the
ptC–C bonds, contributing to its stability. Furthermore, both of the aluminum atoms are involved in the delocalization of electrons, which enhances the stability of isomer 3. In isomers 14, 22, 31, and 34, the electron density is delocalized along the C–C bonds, contributing to their structural stability. In the case of isomers 4, 20, 22, 31, and 34, aluminum-attached hydrogen has electronegative values in the range of \(-0.345\) to \(-0.378\) e\(^{-}\) as listed in Table S3 due to the high electropositive nature of aluminum compared to carbon. The Al–Al bonds in isomers 21, 28, and 40 have ELF values in the range of 0.00 to 0.50 which indicates the poor localization of electrons between these atoms.

Figure 4. Color-filled map of ELF for isomers 3, 4, 14, 18, 20, 21, 22, 28, 31, 34, and 40 obtained at the ωB97XD/6-311++G(2d,2p) level of theory.
3.3. Kinetic Stability

To explore the kinetic stability of ptC and ptAl isomers in the AlC4H2 system, ab initio molecular dynamics simulations were carried out using the ADMP approach. This study enables us to explore the structural variation through the atomic arrangement in the elemental composition. Isomers 3, 4, 14, 18, 20, 21, 22, 28, 31, 34, and 40 were considered for these simulations at 298 K and 1 atm pressure, and the simulations were carried out for up to 1000 fs. The structural stability in the time evolution of total energy for these isomers is given in Figure 5. The oscillations in the energy plots result from an increase in nuclear kinetic energy during the structural deformation of the systems throughout the simulation. These plots demonstrate well-balanced energy oscillations for isomers 3, 4, 14, 18, 20, 21, 31, 34, and 40. These isomers’ structural stability is well retained throughout the simulated time scale, and no isomerization or other structural modifications take place in these molecules and they are kinetically stable except for isomer 21. In the case of isomer 21, the geometry deforms by entirely shattering the geometry and isomerizing it into the low-energy isomer 12, confirming that it is kinetically unstable.

Figure 5. Energy evolution of isomers 3, 4, 14, 18, 20, 21, 22, 28, 31, 34, and 40 at 298 K, 1 atm pressure for 1000 fs of time in the ADMP simulation performed at the ωB97XD/6311++G(2d,2p) level.
3.4. Adaptive Natural Density Partitioning and Natural Bond Order analysis

The adaptive natural density partitioning (AdNDP) analysis was performed for isomers 3, 4, 14, 18, 20, 21, 22, 28, 31, 34, and 40 which are illustrated in Figure 6 for multi-center–2e bonds and Figure S2 for lone pairs and 2c–2e bonds. It gives insight into delocalized multi-center–2e bonds as well as Lewis bonding components. In a Lewis structure, the good electron pair should have an occupancy number (ON) greater than 1.90 |e|. The 2c–2e σ bonds in all of the isomers have an ON value above 1.90 |e| that dictates the electron density which is localized between the planar tetracoordinate centers and their adjacent atoms. The presence of multi-center–2e π bonds in isomers 3, 14, 22, 31, 34, and 40 shows how the electrons participate in delocalization along C-C carbon bonds. In isomer 3, four 3c–2e σ bonds with ON 1.99 and 1.98 |e|, two 3c–2e π bonds with ON 1.93 |e|, 4c–2e π bonds with ON 2.00 |e|, and a 5c–2e π bond with ON 1.99 |e| are observed and are in accord with the concept of double aromaticity in the molecule as shown by the negative values of NICS (0) and NICS (1) in Figure S3. Delocalization encompasses the whole system, making isomer 3 more stable than other isomers. All the other isomers also have multi-center–2e bonds with ON greater than 1.90 |e|. In isomer 3, the aluminum LP orbitals with low ON 1.80 |e|, as shown in Figure S2, confirm that the electrons are shared by aluminum atoms which is consistent with NBO and ELF analysis.

The energies of donor–acceptor interaction of lone pairs of aluminum obtained for isomers 3, 4, 18, 21, 22, 28, and 31 with NBO analysis are presented in Table S4. The occupancies of lone pairs for isomers 3, 14, 18, 21, 22, 28, 31, and 40 from NBO analysis are given in Table S5. The E(2) is the hyperconjugative interaction between acceptor and donor which governs the stabilization energy. The LP(Al5) → π*(C1–C4) and LP(Al6) → π*(C1–C4) in isomer 3 have larger stabilization energy of 36.71 kcal mol⁻¹, as compared to other isomers, which confirms that the electrons from both of the aluminum atoms are shared and accepted by surrounding atoms that is consistent with the delocalization nature of the structure obtained from ELF analysis.
Figure 6. AdNDP bonding patterns of Al-Cd-H isomers 3, 4, 14, 18, 20, 21, 22, 28, 31, 34, and 40 at the ωB97XD/6-311++G(2d,2p) level of theory.
4. Conclusions

In summary, the isomers of Al₂C₄H₂ have been explored at the ωB97XD/6-311++G(2d,2p) level of theory. The isomers containing planar tetracoordinate carbon/aluminum that lie within 50 kcal mol⁻¹ are subjected to chemical bonding analysis. Isomers 3 and 4 are planar tetracoordinate systems that are energetically close to global minimum geometry 1. The isomers that have the ptCs are energetically more stable than the isomers that contain ptAl because of the electron delocalization nature of ptC compared to ptAl. The isomers with ptC have one π bond and four σ bonds, while the isomers with ptAl have only four sigma bonds. Among the planar tetracoordinate isomers, isomer 3 is energetically stable due to its high delocalization nature and double aromaticity as observed in the ELF, NICS, and AdNDP analysis. So, the stability of isomer 3 is achieved by the tendency of the electron-donating nature of the aluminum atom. The ab initio molecular dynamics simulations revealed that all these planar tetracoordinate molecules are kinetically stable except isomer 21 which isomerizes to isomer 12. Exploring the electron density distribution and orbital orientation of these isomers provides insight into the nature of chemical bonding and may lead to potential applications in the future. The insights of this work would impart great interest to experimentalists to find Al₂C₄H₂ isomers in the laboratory which remain elusive to date.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/atoms10040112/s1. The optimized geometries of all the isomers are given in Figure S1, AdNDP for lone pairs and 2c–2e bonds of isomers 3, 4, 14, 18, 20, 21, 22, 28, 31, 34, and 40 are given in Figure S2, NICS for isomer 3 is given in Figure S3, total energies (in a.u), zero-point vibrational energies (ZPVEs; in a.u.), ZPVE corrected total energies (E+ZPVE; in a.u.), relative energies (ΔE+ZPVE; in kcal mol⁻¹), and the number of imaginary frequencies (NImag) of Al₂C₄H₂ isomers calculated at ωB97XD/6-311++G(2d,2p) and B3LYP/6-311++G(2d,2p) level are given in Tables S1 and S2, respectively, natural atomic charges of hydrogen in isomers 3, 4, 14, 18, 20, 21, 22, 28, 31, 34, and 40 are given in Table S3,  the donor → acceptor orbitals of lone pairs of aluminum in isomers 3, 4, 14, 18, 20, 21, 22, 28, and 31 are given in Table S4, occupancies of lone pairs for isomers 3, 14, 18, 21, 22, 28, 31, and 40 from NBO analysis are given in Table S5, cartesian coordinates of all isomers at ωB97XD/6-311++G(2d,2p) and B3LYP/6-311++G(2d,2p) level are given in Tables S6 and S7.

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Abbreviations

The following abbreviations are used in this manuscript:

AdNDP  Adaptive Natural Density Partitioning
ADMP  Atom-centered Density Matrix Propagation
DFT  Density Functional Theory
ELF  Electron Localization Function
NBO  Natural Bond Order
ON  Occupation Number
ptC  Planar Tetracoordinate Carbon
phC  Planar Hypercoordinate Carbon
ptAl  Planar Tetracoordinate Aluminum
ppAl  Planar Pentacoordinate Aluminum
WBI  Wiberg Bond Index
LP  Lone Pair

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