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Article

Keywords:

Posted Date: November 9th, 2026

DOI: https://doi.org/10.21203/rs.3.rs-11191906/v1

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Additional Declarations: No competing interests reported.

Carbon Di-carbene Allotrope as a Zero-Dimensional Carbon Platform for Small-Molecule Activation and Nitrogen-to-Ammonia Conversion

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Abstract

Carbon allotropes span molecular to extended architectures, with dimensionality playing a central role in determining their electronic structure and chemical reactivity. Inspired by the unique electronic characteristics of carbenes and the functional diversity of carbon allotropes, we computationally design a previously unexplored zero-dimensional carbon dicarbene allotrope (CDCA) at the ωB97XD/Def2-TZVP level. CDCA is composed exclusively of carbon atoms and incorporates two electronically communicating carbene centres within a cyclic molecular framework. Density-of-states analysis and ab initio molecular dynamics simulations are employed to characterize its electronic structure, reactive sites, and structural stability. The singlet state is substantially more stable than the triplet state, while the carbon framework remains structurally stable during the investigated finite-temperature dynamics. CDCA exhibits pronounced reactivity toward SO_2, SO_3, NO, NO_2, CO, CO_2, and H_2O through interactions involving its two carbene centres. Most notably, the two-centre architecture enables orientation-dependent activation of molecular nitrogen: interaction of N_2 with both carbene centres promotes N–N bond cleavage, whereas single-centre interaction yields an intact N_2 adduct. Subsequent stepwise hydrogenation of the activated nitrogen species provides a calculated pathway toward NH_3 formation. These results establish CDCA as a distinct zero-dimensional, carbon-only molecular architecture in which intrinsic carbene reactivity is integrated into a carbon allotrope, providing a new conceptual framework for small-molecule activation and the exploration of carbon-only systems for nitrogen chemistry.

Keywords: carbon allotrope; carbon di-carbene allotrope; carbene; small-molecule activation; nitrogen activation; ammonia synthesis; Molecular Handycam Technique

1 Introduction

Carbon, a fundamental element of organic chemistry and an essential constituent of living systems, occupies a unique position in modern chemistry, materials science, and chemical technology. The remarkable versatility of carbon arises from its ability to form stable and diverse chemical bonds, giving rise to an exceptionally broad range of molecular architectures and functional materials. Consequently, carbon-based materials have attracted considerable attention as potential platforms for addressing contemporary challenges in sustainable chemistry and technology. In the broader pursuit of green and sustainable technologies, the development of carbon-based alternatives to resource-intensive or environmentally burdensome materials represents an important research direction. The combination of carbon's natural abundance, structural diversity, tunable electronic properties, and capacity for chemical functionalization provides a compelling foundation for the design of next-generation materials with reduced environmental impact and enhanced technological utility. Thus, continued exploration of novel carbon architectures and their potential applications is essential for advancing sustainable chemical technologies and developing innovative materials for the future.

Carbon is unique among the elements in its ability to form structures spanning an extraordinary range of dimensionalities and bonding motifs. A diverse family of carbon allotropes [1–5], including molecular carbon clusters such as fullerenes [6, 7] and other zero-dimensional carbon species [8–10] represents the molecular limit of this structural continuum. At higher dimensionalities, graphene [11–14] and related two-dimensional carbon materials [15–18], carbon nanotubes [19–21], and three-dimensional carbon frameworks [22–24] extend carbon chemistry toward increasingly interconnected architectures. This remarkable dimensional diversity is accompanied by substantial variations in electronic structure, structural stability, and chemical reactivity [25, 26], thereby providing a broad platform for designing carbon materials with distinct physicochemical properties and functionalities.

The chemical versatility of carbon allotropes has traditionally been associated with extended π-conjugated networks, high surface areas, and unusual electronic properties [27]. These characteristics have made carbon-based materials attractive platforms for a wide range of applications, including catalysis [28–31] and catalyst supports [32–35], particularly in challenging transformations such as small-molecule activation [36–38], hydrogen storage [39], environmental remediation [40, 41], and nitrogen conversion [38, 42]. Beyond these applications, carbon allotropes and doped carbon materials have been investigated for their ability to interact with chemically inert molecules and provide alternative pathways for bond activation [43], as well as for the development of strong and lightweight materials [44–46], electrically conducting materials [47, 48], chemical and biological sensors [49, 50], and nonmetallic electrode materials [51–53]. These diverse applications demonstrate that the functionality of carbon materials can

be substantially modulated by controlling their dimensionality, bonding topology, and electronic structure.

An important but comparatively less explored direction is the deliberate incorporation of carbene-like carbon centres into carbon-based molecular frameworks. Carbenes are highly reactive species characterized by a divalent carbon centre bearing two nonbonding valence electrons [54–56]. Their distinct singlet and triplet electronic configurations give rise to markedly different chemical behaviours, making carbene chemistry an important platform for controlling bond activation and molecular transformations [57–59]. Incorporating two carbene centres within a single carbon-only molecular framework could therefore introduce an additional degree of electronic and structural control that is fundamentally different from that of conventional extended carbon materials. In particular, the presence of two electronically coupled carbene centres may provide opportunities for cooperative interactions with small molecules and facilitate chemical transformations that are difficult to achieve with conventional carbon allotropes. This concept motivates the exploration of a new class of carbon materials in which the intrinsic reactivity of carbene centres is integrated into an allotrope-like carbon framework.

In this work, we investigate a cyclic carbon dicarbene allotrope (CDCA) designed as a novel zero-dimensional carbon architecture. The proposed structure consists of sixteen carbon atoms arranged in a cyclic framework comprising a fourteen-membered ring fused to an additional four-membered ring. This structural arrangement generates two carbene centres that are positioned to interact cooperatively with external molecules. Quantum-chemical calculations identify CDCA as a singlet species and indicate that the singlet state is approximately 47.2 kcal mol^{-1} more stable than the corresponding triplet state. Although the experimental synthesis of CDCA has yet to be achieved, a closely related carbon framework was reported by Gao et al. as an intermediate during the synthesis of cyclo[16]carbon.[60] In the reported intermediate, the two carbene centres of CDCA are replaced by carbonyl groups, while the overall carbon framework remains closely related to that of the proposed allotrope. This experimentally characterized structural analogue provides a plausible synthetic precedent for the proposed CDCA framework and suggests that its synthesis may be accessible through suitable chemical transformation of an appropriate precursor.

We subsequently investigate the chemical reactivity of CDCA toward a representative series of small molecules, including SO_2, SO_3, NO, NO_2, NO_3, CO, CO_2, and H_2O. The calculations reveal a common feature of the proposed carbon architecture, namely, the activation of incoming molecules through interactions involving the two carbene centres. Particular attention is then devoted to molecular nitrogen, one of the most challenging small molecules to activate because of its strong N≡N triple bond. Our calculations demonstrate that the orientation of N_2 relative to the two carbene centres plays a decisive role in determining the reaction pathway, leading either to simple adduct formation through chemical bonding as C–N_2 or to N–N bond cleavage and separate binding to two different carbons of the carbene centers. Subsequent hydrogenation of the activated nitrogen species provides reaction pathways toward ammonia formation.

The central hypothesis of this study is that dimensional reduction of carbon into a deliberately designed molecular architecture can generate localized electronic sites capable of cooperative chemical activation. CDCA therefore provides a conceptual bridge between the structural diversity of carbon allotropes and the localized reactivity traditionally associated with reactive molecular carbon species. The present study consequently explores whether such a carbon-only dicarbene framework can combine the structural characteristics of a carbon allotrope with the capacity for small-molecule activation and, in particular, nitrogen conversion toward ammonia.

2 Computational Methodology

As described in the Introduction, the concept of the carbon dicarbene allotrope (CDCA) originates from a closely related intermediate reported by Gao et al. during the synthesis of cyclo[16]carbon.[60] The conversion of the C=O functionalities of such a framework into carbene centres provides an experimentally motivated basis for the proposed structure. Accordingly, the geometry of the reported intermediate, consisting of a C_{14} ring fused to a four-membered carbon ring, was adopted as the initial geometry for the construction of CDCA. In the resulting structure, the two carbon atoms of the four-membered ring that are not directly connected to the C_{14} ring possess only two C–C bonds, leaving two nonbonding valence electrons at each centre and thereby defining the two carbene centres of CDCA.

To investigate the structural and electronic properties of the proposed zero-dimensional carbon architecture, geometry optimization was performed using density functional theory (DFT) at the ωB97XD[61]/DEF2-TZVP[62] level of theory. All DFT calculations were carried out using the GAUSSIAN 16 program package[63]. The thermal stability of the optimized CDCA structure at 300 K was subsequently investigated using *ab initio* molecular dynamics (AIMD) simulations[64]. CP2K program package [65] is employed for this study. The optimized structure obtained from the DFT calculations was used as the reference geometry for all subsequent small-molecule activation calculations and AIMD simulations.

The electronic structure of CDCA was further examined using conventional electronic-structure analyses implemented through GAUSSIAN 16 and Multiwfn. The singlet and triplet electronic states of CDCA were independently optimized and analyzed to determine their relative energetic stability and identify the preferred spin state of the proposed structure.

For the small-molecule reactivity calculations, the individual reactant molecules were initially positioned in the vicinity of the reactive carbene centres of the optimized CDCA structure. Geometry optimizations followed by vibrational frequency calculations were then performed for the CDCA–SO_2, CDCA–SO_3, CDCA–NO, CDCA–NO_2, CDCA–NO_3, CDCA–CO, CDCA–CO_2, CDCA–H_2O, and CDCA–N_2 systems. The resulting optimized structures were subjected to vibrational analysis to confirm their characterization as stationary points corresponding to minima. The optimized structures were subsequently examined to determine the nature of the interaction between CDCA and each incoming molecule, including molecular adsorption, bond activation, fragmentation, and new bond formation.

Among the investigated small molecules, the N_2 activation process was examined in greater detail because of the chemical challenge associated with activation of the strong N≡N bond. Multiple initial orientations of N_2 with respect to the two carbene centres were considered to investigate the influence of molecular orientation on the resulting reaction pathways. For the nitrogen-containing intermediates obtained from these calculations, sequential hydrogenation calculations were performed by introducing H_2 molecules stepwise and optimizing the resulting structures at each stage. The Gibbs free-energy changes associated with the individual hydrogenation reactions were calculated and reported; however, activation free-energy barriers were not determined for these pathways. Accordingly, the present work focuses on the thermodynamic aspects of the proposed nitrogen-conversion pathways, while a complete kinetic investigation of these reactions will be presented separately.

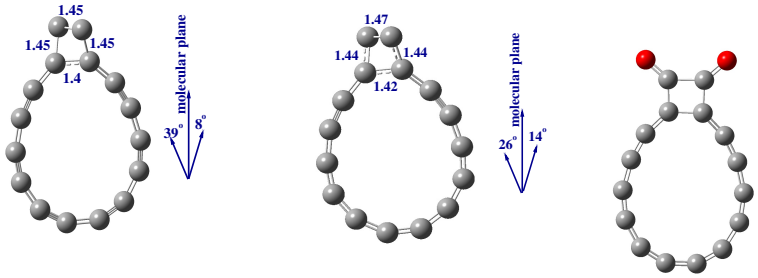
The convergence criteria, dispersion treatment, vibrational frequency calculations, transition-state methodology, and zero-point-energy corrections were applied following the standard computational protocol employed in the present study.

3 Results and Discussions

The principal objective of the present study is to explore a new class of carbon allotrope containing intrinsically reactive carbene centres and to assess its potential as a platform for both catalytic and materials applications. Accordingly, the initial part of our investigation focuses on the structural stability and electronic properties of the proposed carbon dicarbene allotrope (CDCA). The broader potential of CDCA for materials and catalytic applications requires further systematic investigation and is beyond the scope of the present work. As an initial assessment of its chemical reactivity, a representative set of small-molecule activation processes is examined. Particular attention is subsequently given to the thermodynamic feasibility of ammonia formation from molecular nitrogen and hydrogen at ambient temperature in the presence of CDCA. These calculations are intended to establish the reactivity potential of the proposed carbon framework rather than to provide a complete mechanistic description of a catalytic process. In particular, a full kinetic analysis of the individual elementary steps and a complete catalytic cycle are not presented in the present study. The results therefore provide a preliminary computational assessment of CDCA as a reactive carbon architecture and establish a basis for further investigation of its catalytic and materials-related properties.

3.1 Structural and Electronic Characteristics of CDCA

The proposed CDCA consists exclusively of carbon atoms and represents a molecular, zero-dimensional carbon architecture. The optimized structures of CDCA together with its experimentally reported precursor are presented in Figure 1. The proposed framework contains a fourteen-membered carbon ring fused to a four-membered carbon ring, with the latter generating two adjacent carbene centres within the overall carbon framework.



(a) Singlet (b) Triplet (c) Precursor

Fig. 1 Optimized geometries of the (a) singlet CDCA (b) triplet CDCA and (c) A plausible precursor of CDCA

3.1.1 The optimized geometry of the singlet and triplet CDCA

Because the two carbene centres can give rise to different spin configurations, the singlet and triplet states of CDCA were independently optimized and compared. Higher-order spin states were not considered in the present study. The two adjacent carbene centres give rise to a characteristic set of closely spaced frontier molecular orbitals. In the singlet state, the four highest-energy electrons are paired and occupy two quasi-degenerate molecular orbitals. The corresponding orbital energies are −0.32643 and −0.32137 hartree, which correspond to the HOMO-1 and HOMO, respectively. The LUMO and LUMO+1 are likewise characterized by closely spaced orbital energies, indicating a near-degenerate pair of low-lying vacant orbitals.

The triplet state can be generated by promoting one electron from either member of the highest occupied quasi-degenerate pair, resulting in two unpaired electrons occupying two singly occupied molecular orbitals (SOMOs). Optimization of the resulting triplet configurations leads to essentially the same structural arrangement. In this electronic configuration, one carbene centre retains a paired electron configuration in its frontier occupied orbitals, whereas the two unpaired electrons occupy the two higher-energy orbitals of different orbital energy. The orbital energy associated with the doubly occupied orbital is −0.31726 hartree (HOMO-1), while the corresponding partially occupied orbitals (SOMO) have energies of −0.15522 hartree and −0.11201 hartree, respectively. The LUMO of the triplet CDCA is the same as that of the singlet CDCA. The spatial distributions of the relevant molecular orbitals for the singlet and triplet states are shown in Figure 2.

The optimized geometries reveal measurable differences between the singlet and triplet states (Figure 1). The C–C bond connecting the two carbon atoms common to the fourteen-membered and four-membered rings is approximately 1.40 Å in the singlet state and 1.42 Å in the triplet state. The bond connecting a carbon atom of the common ring to a carbon atom of the four-membered ring is 1.45 Å for the singlet and 1.44 Å for the triplet. A further difference is observed for the C–C bond between the two carbon atoms of the four-membered ring, which has calculated bond lengths of 1.45 Å and 1.47 Å for the singlet and triplet states, respectively. These variations

indicate a greater degree of bond-length asymmetry in the region surrounding the carbene centers for the triplet state.

The relative orientation of the carbene centres with respect to the C_{14} ring also differs between the two spin states. The dihedral angle between the C_{14} ring and the carbene-containing portion of the four-membered ring is approximately 43° for the singlet and 40° for the triplet. The individual angular parameters describing the orientations of the carbene centres relative to the C_{14} ring are 39° and 8° for the singlet state, compared with 26° and 14° for the triplet state. In addition, the two partially occupied orbitals of the triplet state exhibit an angular separation of approximately 65°, reflecting the distinct spatial orientation of the two unpaired-electron distributions.

3.1.2 The frontier molecular orbital analysis of CDCA

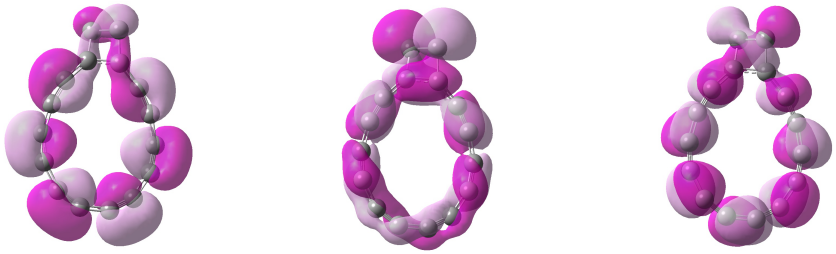
The frontier molecular orbitals provide further insight into the electronic structure of CDCA. The calculated HOMO, HOMO-1, HOMO-2, and LUMO orbitals reveal the electronic distribution associated with the carbon framework and, in particular, the regions surrounding the two carbene centres. The presence of closely spaced frontier orbitals is consistent with the electronically coupled nature of the two carbene centres and provides a molecular basis for their potential cooperative interaction with external molecules.

A particularly important characteristic of CDCA is its pronounced singlet-state preference. The optimized singlet structure is calculated to be approximately 47.2 kcal mol^{-1} lower in energy than the corresponding optimized triplet state. This substantial energetic separation indicates that the two carbene centres are strongly electronically coupled through the cyclic carbon framework rather than behaving as two independent triplet centres. The energetic preference for the singlet state therefore provides important evidence for the stability of the proposed CDCA electronic structure.

The combination of a strongly preferred singlet ground state with localized, electronically accessible carbene centres is particularly significant for the proposed carbon architecture. The singlet state provides substantial energetic stabilization of the overall framework, while the localized electronic character of the carbene centres provides chemically accessible sites for interaction with external molecules. This combination of structural stability and localized reactivity forms the basis for the subsequent investigation of small-molecule activation by CDCA.

3.1.3 Density of state analysis of CDCA

Figure 3 presents the density of states (DOS) profiles of the singlet and triplet states of CDCA. The total density of states (TDOS) and overlap population density of states (OPDOS) for the singlet and triplet states are shown in Figures 3a and 3b, respectively. To obtain a more localized picture of the electronic states associated with the two carbene centres, the projected density of states (PDOS) corresponding to the carbon atoms of the carbene centres was additionally analyzed for both spin states, as presented in Figures 3c and 3d.



(a) HOMO-1 (b) HOMO (c) LUMO

Orbitals of the singlet CDCA



(a) Orbital of the Paired electron (b) Orbital of lower energy SOMO

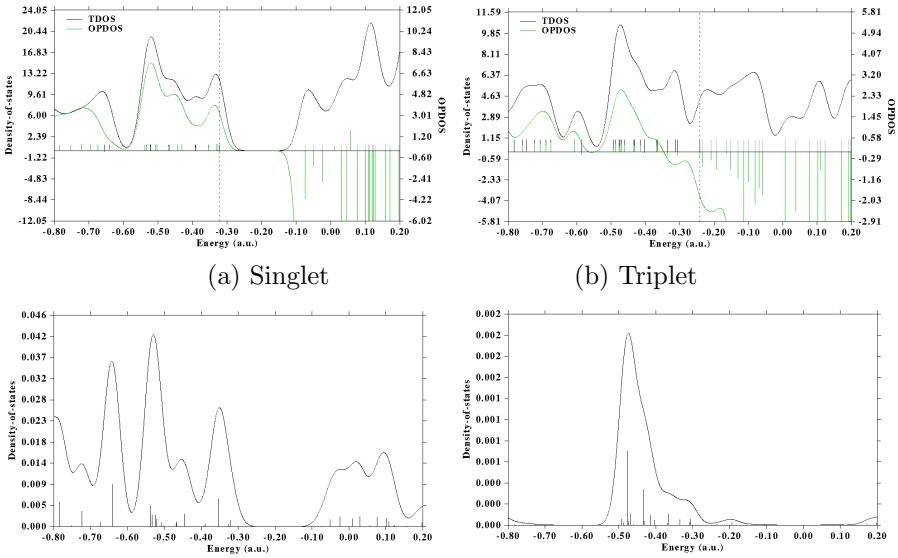


(c) Orbital of higher energy SOMO (d) LUMO

Orbitals of the triplet CDCA

Fig. 2 Frontier molecular Orbitals of the singlet and triplet CDCA.

The TDOS profiles of both spin states exhibit a dense manifold of occupied electronic states below the Fermi level, located at approximately -0.32 a.u. for the singlet and -0.24 a.u. for the triplet state. This distribution reflects the closely spaced electronic states associated with the extended carbon framework. For singlet CDCA (Figure 3a), a pronounced TDOS feature is observed near -0.50 a.u., accompanied by a positive OPDOS contribution in the same energy region. The positive OPDOS indicates a bonding contribution associated with the corresponding electronic states of the carbon framework. Another distinct TDOS feature appears near -0.35 a.u., where a weaker but still positive OPDOS contribution is observed. Above the Fermi



(a) Singlet (b) Triplet

(c) Singlet (d) Triplet

Fig. 3 Density of states of singlet and triplet CDCA. TDOS is the Total Density of States. OPDOS is the Overlap Population Density of States. (a) and (b) represent the TDOS and OPDOS of the singlet and triplet CDCA, respectively. (c) and (d) represent the density of states near the carbene carbons of the singlet and triplet CDCA.

level, a positive OPDOS contribution extends over a relatively narrow energy range from approximately −0.32 to −0.28 a.u. This feature indicates that some low-lying unoccupied states retain bonding character, suggesting that the corresponding virtual electronic states can participate in stabilizing interactions upon electron population.

The DOS characteristics change appreciably upon conversion to the triplet state (Figure 3b). The highest occupied TDOS feature is shifted toward the Fermi level, while its intensity is reduced relative to the corresponding feature in the singlet state. In contrast to the singlet state, for which the TDOS approaches zero over the energy interval from approximately −0.28 to −0.10 a.u., the triplet state retains a finite density of states throughout this region. The OPDOS remains predominantly positive within the occupied region but becomes more fragmented, reflecting the altered electronic structure associated with the presence of two unpaired electrons. The reduced and more discontinuous OPDOS contribution near the Fermi level further indicates a substantial reorganization of the bonding interactions accompanying the change in spin state.

The carbene-centred PDOS profiles (Figures 3c and 3d) provide a more localized representation of these electronic differences. For singlet CDCA (Figure 3c), distinct peaks are observed near −0.55, −0.48, and −0.35 a.u., indicating substantial contributions from the carbene-centred electronic states to the occupied manifold. These features are consistent with the presence of localized electronic states associated with the two divalent carbon centres and their interaction with the surrounding carbon framework. In the triplet state (Figure 3d), a pronounced peak near −0.48 a.u.

dominates the carbene-centred PDOS. The substantially different distribution of carbene-centred states between the singlet and triplet configurations indicates a redistribution of electronic density associated with the formation of the triplet state. In particular, the more localized character of the carbene-centred states in the triplet configuration is consistent with the presence of the two unpaired electrons and the reduced participation of these states in the delocalized electronic manifold.

Taken together, the DOS and OPDOS analyses reveal a pronounced electronic reorganization upon changing the spin state of CDCA. The singlet state exhibits a more continuous distribution of bonding contributions and stronger coupling between the carbene-centred states and the surrounding carbon framework, whereas the triplet state displays a more fragmented DOS/OPDOS profile and enhanced localization of the electronic states associated with the carbene centres. These differences provide further electronic-structure evidence for the distinct nature of the two spin states and are relevant to understanding the reactivity of CDCA toward external molecules. In particular, the coexistence of a strongly stabilized singlet state with localized electronic states at the carbene centres provides a useful electronic basis for the subsequent investigation of small-molecule activation.

3.1.4 Thermal Stability of CDCA

The stability of carbene species at room temperature and their existence as isolable molecular entities were initially considered challenging because of their high intrinsic reactivity. However, with the development of suitable molecular frameworks and steric and electronic stabilization strategies, a variety of persistent carbene architectures have been developed, including cyclic (alkyl)(amino) carbenes (CAACs), CAArCs, N-heterocyclic carbenes (NHCs), abnormal N-heterocyclic carbenes (aNHCs), cyclic (alkyl)(aryl) carbenes (CABC), and bicyclic CAACs (BicAACs). Several members of these carbene families are now known as stable compounds and have found widespread applications in organic synthesis and catalysis. The assessment of the structural stability of CDCA is therefore an important aspect of establishing the feasibility of the proposed carbon dicarbene architecture.

For this purpose, an *ab initio* molecular dynamics (AIMD) simulation was performed using the CP2K program package [65] at 300 K. Owing to the computational cost associated with the simulation, the trajectory considered in the present analysis was limited to 0.16 ps. The time-dependent structural parameters obtained from the AIMD simulation are presented in Figure 4. The individual C–C bond-length trajectories show continuous thermal fluctuations but do not exhibit any progressive elongation toward the adopted bond-breaking criterion of 1.8 Å. The two carbon atoms constituting the carbene centres remain spatially separated from the C_{14} ring throughout the trajectory, as expected from the fused C_{14}/C_4 architecture of CDCA; this persistent separation is therefore an intrinsic structural feature of the molecule rather than evidence of bond dissociation. The remaining C–C bonds of the carbon framework undergo only moderate thermal fluctuations and retain their characteristic bonding distances throughout the simulation.

The structural dynamics are further reflected in the RMSD, out-of-plane distortion, and bond-length alternation parameters. The RMSD initially increases as

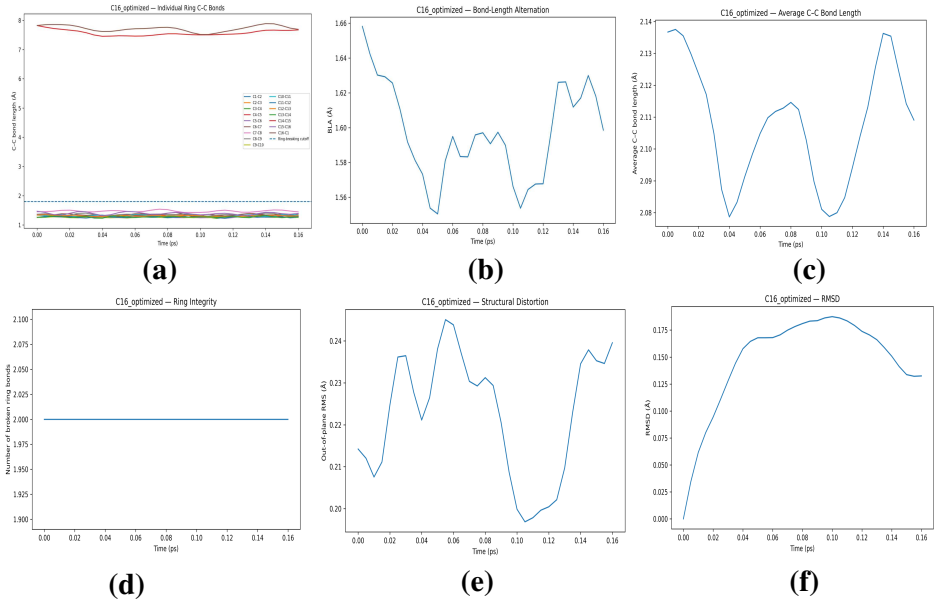


Fig. 4 Thermal stability of CDCA at 300 K investigated using *ab initio* molecular dynamics (AIMD) simulations with the CP2K program package. The simulations were performed using the PBE-D3/GPW/GTH-PBE-q4/DZVP-MOLOPT-SR-GTH level of theory with a 400 Ry cutoff and 60 Ry relative cutoff in a $24 \times 24 \times 24$ Å^3 isolated cell with PERIODIC NONE and the Martyna–Tuckerman Poisson solver. A CSVR thermostat with a 100 fs time constant and a timestep of 0.5 fs was employed. The trajectory analysed here corresponds to 0.16 ps (320 MD steps).

the optimized structure responds to thermal excitation, reaching approximately 0.19 Å, and subsequently decreases, indicating reversible structural fluctuations rather than progressive structural deformation. The out-of-plane distortion remains within approximately 0.20–0.25 Å throughout the trajectory, demonstrating that the carbon framework undergoes moderate thermal deformation while maintaining its overall structural arrangement. Similarly, the bond-length alternation parameter exhibits oscillatory behaviour without a systematic drift, indicating dynamic redistribution of the C–C bond lengths rather than irreversible structural rearrangement.

Taken together, the AIMD results indicate that the characteristic C_{14}/C_4 fused carbon framework of CDCA is retained during the 300 K simulation. No progressive C–C bond elongation, irreversible geometric distortion, or disruption of the characteristic separation of the two carbene centres from the C_{14} ring is observed within the simulated time window. These results provide preliminary computational evidence that the proposed CDCA architecture can withstand thermal fluctuations at 300 K and retains its fundamental structural integrity under the simulated conditions.

3.2 Reactivity towards small molecules

The optimized CDCA structure was subsequently employed as a platform for investigating its reactivity towards a representative set of small molecules, including SO_2, SO_3, NO, NO_2, N_2, CO, CO_2, and H_2O. The optimized structures of the end products

of these reactions are presented in Figure 5. These calculations reveal a common feature across the investigated systems, namely, the involvement of both carbene centres in the interaction with the incoming molecule. Rather than forming weak noncovalent complexes, the calculated structures generally involve cleavage of a heteronuclear bond within the incoming molecule, followed by the formation of new C–X bonds between the resulting molecular fragments and the two carbene centres of CDCA. Notably, the C–C bond connecting the two carbene centres remains intact for all reactions except molecular nitrogen in the investigated systems. In the case of molecular nitrogen, the C–C bond between the two carbene carbons breaks down upon the addition of an N_2 molecule (in type-b), while it is not observed for type-a addition of N_2.

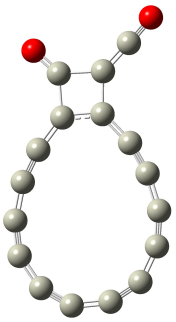
For SO_2, interaction with CDCA results in activation and cleavage of an S–O bond, followed by the formation of new bonds between the resulting fragments and the two carbene centres. A similar transformation is observed for SO_3, where interaction with the two carbene centres is accompanied by S–O bond breaking and subsequent formation of a CDCA-bound product. These results indicate that the adjacent carbene centres can cooperatively interact with sulfur–oxygen bonds and promote their activation within the carbon framework.

The nitrogen oxides display similarly pronounced reactivity towards CDCA. In the case of NO, interaction with the two carbene centers leads to N–O bond cleavage, with the resulting nitrogen- and oxygen-containing fragments becoming associated with the reactive carbon centers. Here it is observed that the nitrogen atom also breaks the C–C bond between two carbene carbons and gets inserted into it to form a C–N–C bond. NO_2 also undergoes N–O bond activation upon interaction with CDCA, resulting in the formation of a nitrogen/oxygen-containing product bound to the carbon framework.

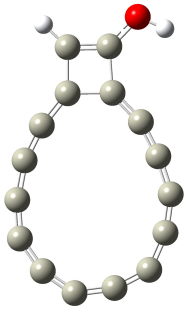
The carbon oxides are also activated upon interaction with CDCA. CO interacts with the two carbene centres in a manner that results in the incorporation of both the carbon and oxygen atoms into the carbon framework through the formation of new C–C and C–O interactions. Similarly, CO_2 undergoes C–O bond activation, producing carbon- and oxygen-containing fragments that become associated with the two reactive carbon centres. These results further demonstrate the ability of the CDCA framework to promote activation of otherwise relatively stable heteronuclear bonds.

Water provides another example of bond activation by CDCA. Interaction between H_2O and the two carbene centres leads to cleavage of an O–H bond, followed by the formation of new bonds between the resulting H and OH fragments and the reactive carbon centres. Thus, even the O–H bond of water can undergo activation through interaction with the two carbene sites of CDCA.

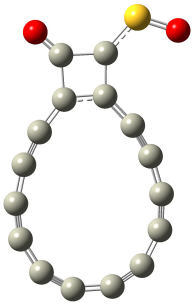
Collectively, these results demonstrate that the reactivity of CDCA is not limited to a single class of small molecules. The proposed carbon dicarbene framework exhibits a broad capacity for activating S–O, N–O, C–O, and O–H bonds through interactions involving its two carbene centres. The recurrent involvement of both reactive carbon sites suggests that the two carbene centres can participate cooperatively in small-molecule activation, highlighting an important feature that distinguishes CDCA from conventional carbon allotropes and different classes of carbenes. The preservation of the C–C bond connecting the two carbene centres in most of the investigated



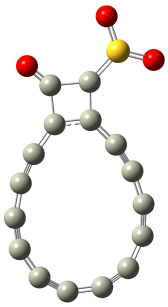
(a) CDCA–CO_2



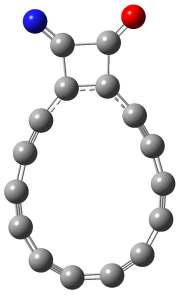
(b) CDCA–H_2O



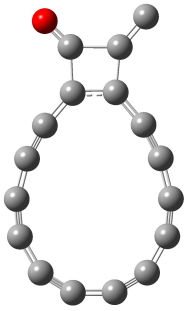
(c) CDCA–SO_2



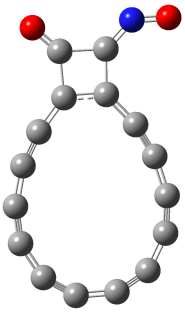
(d) CDCA–SO_3



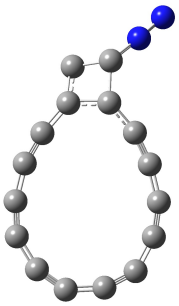
(e) CDCA–NO



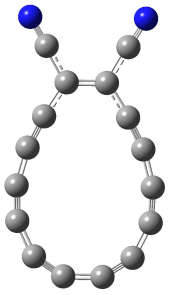
(f) CDCA–CO



(g) CDCA–NO_2



(h) CDCA–N_2a



(i) CDCA–N_2b

Fig. 5 The products of CDCA–X reaction where X = CO, NO, N_2, CO_2, H_2O, SO_2, SO_3 and NO_2

products further indicates that the intrinsic carbon framework can accommodate substantial chemical transformations while retaining its fundamental structural connectivity. Thus, CDCA could be treated as a super carbene and a new class of highly active zero-dimensional carbon allotrope.

Table ref tab: fre summarizes the calculated changes in reaction free energy (ΔG) for the CDCA–X reactions. The calculated free energies reveal a pronounced dependence of the thermodynamic favourability on the identity and orientation of the incoming molecule. Except for the CDCA–NO reaction and the Type-a interaction of N_2, all investigated reactions have negative reaction free energies, indicating

Reaction	Reaction free energy (kcal/mol)
CDCA + NO $\longrightarrow$ CDCA–NO	129.4
CDCA + CO $\longrightarrow$ CDCA–CO	-29.2
CDCA + NO_2 $\longrightarrow$ CDCA–NO_2	-128.0
CDCA + CO_2 $\longrightarrow$ CDCA–CO_2	-72.9
CDCA + SO_2 $\longrightarrow$ CDCA–SO_2	-95.0
CDCA + H_2O $\longrightarrow$ CDCA–H_2O	-80.3
CDCA + SO_3 $\longrightarrow$ CDCA–SO_3	-93.3
CDCA + N_2 $\longrightarrow$ CDCA–N_2 (Type-a)	15.9
CDCA + N_2 $\longrightarrow$ CDCA–N_2 (Type-b)	-87.2

Table 1 Calculated reaction free energies (ΔG) for the CDCA–X reactions presented in Figure 5.

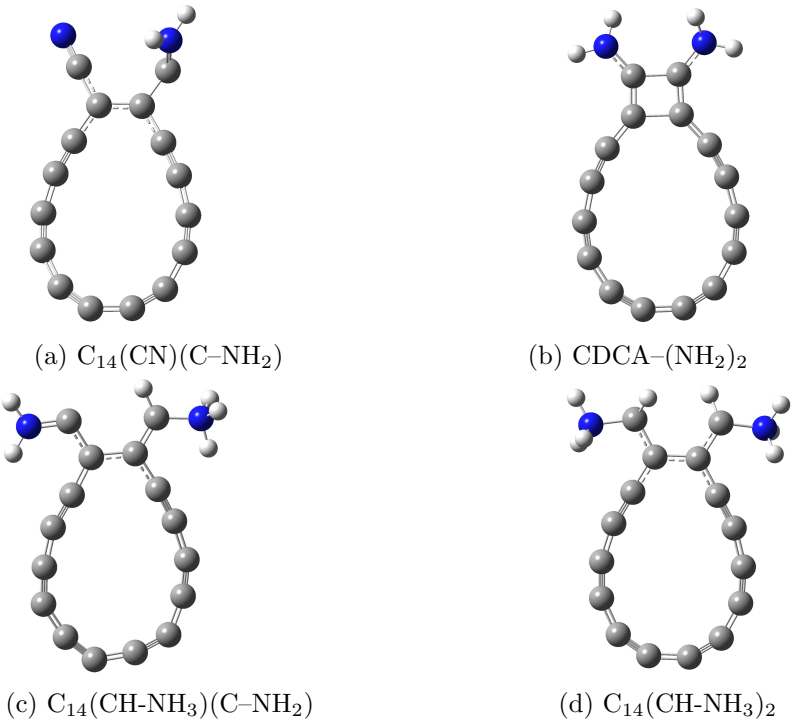
that the corresponding product formation is thermodynamically favourable under the conditions considered. The CDCA–NO reaction has a positive ΔG of 129.4 kcal/mol, indicating that the calculated product is strongly thermodynamically disfavoured relative to the separated reactants. Similarly, the Type-a orientation of N_2 gives a positive ΔG of 15.9 kcal/mol, whereas the alternative Type-b orientation is strongly exergonic, with a ΔG of -87.2 kcal/mol. This pronounced difference shows that the orientation of N_2 relative to the two carbene centres critically determines the thermodynamic feasibility of its interaction with CDCA.

Among the remaining small molecules, CO exhibits the least negative reaction free energy, with $\Delta G = -29.2$ kcal/mol. In contrast, substantially larger negative free-energy changes are obtained for the other favourable reactions, ranging from -72.9 kcal/mol for CDCA–CO_2 to -128.0 kcal/mol for CDCA–NO_2. The reactions with SO_2, SO_3, and H_2O are also strongly exergonic, with calculated ΔG values of -95.0, -93.3, and -80.3 kcal/mol, respectively. These results indicate that CDCA can engage in thermodynamically favourable interactions with a broad range of small molecules, although the magnitude of the free-energy change depends strongly on the nature of the substrate and its mode of interaction with the two carbene centres.

Taken together, the reaction free energies demonstrate that the chemical reactivity of CDCA is highly dependent on the nature and orientation of the interacting molecule. In particular, the substantially different free energies obtained for the two N_2 orientations highlight the importance of molecular approach geometry in determining the thermodynamic outcome of small-molecule activation. The strongly favourable Type-b N_2 interaction provides a thermodynamic basis for further investigation of nitrogen activation and subsequent hydrogenation towards ammonia formation.

3.3 Conversion of the activated molecular nitrogen to ammonia

Among the investigated molecules, N_2 is particularly important because its activation represents a central challenge in nitrogen chemistry. Molecular nitrogen possesses an exceptionally strong N≡N triple bond, and its cleavage or substantial weakening requires effective electronic interaction with a sufficiently reactive center.



(a) $C_{14}(CN)(C–NH_2)$ (b) $CDCA–(NH_2)_2$

(c) $C_{14}(CH\text{-}NH_3)(C–NH_2)$ (d) $C_{14}(CH\text{-}NH_3)_2$

Fig. 6 Optimized geometries of hydrogenated products.

The calculations reveal that the orientation of N_2 relative to the two carbene centers of CDCA has a decisive influence on the resulting chemistry. When N_2 approaches only one of the carbene centers, an adduct is formed without cleavage of the N–N bond, while the C–C bond connecting the two carbene centers remains intact (Type-a interaction, Figure 5h). However, this interaction is thermodynamically unfavorable, with a calculated free-energy change of +15.9 kcal/mol, indicating that formation of the Type-a adduct is not favored under the conditions considered. In contrast, when N_2 approaches approximately parallel to the two carbene centers, both carbon centers can interact cooperatively with the N_2 molecule, leading to cleavage of the N–N bond (Type-b interaction, Figure 5i). Remarkably, this process is associated with a substantially negative free-energy change of −87.2 kcal/mol. The N–N bond cleavage, however, is accompanied by disruption of the C–C bond connecting the two carbene centers. This observation provides important mechanistic insight into the reactivity of CDCA: the two carbene centers can participate cooperatively in N_2 activation, while

the orientation of the incoming N_2 molecule determines whether the interaction results in simple adduct formation or N–N bond cleavage. Thus, the two-center architecture of CDCA is not merely a structural feature but can directly influence the reaction pathway and the mode of nitrogen activation.

It is also worth noting that, following the Type-a interaction, the remaining unreacted carbene center could in principle interact with a second N_2 molecule. Such a pathway may therefore permit the uptake of two N_2 molecules by the carbon framework without cleavage of the C–C bond connecting the two carbene centers. However, detailed investigation of this alternative pathway is beyond the scope of the present study. Instead, we further investigated the subsequent conversion of the activated nitrogen species into ammonia through systematic stepwise hydrogenation. For this purpose, the Type-b N_2-activated structure was selected as the starting point.

Reaction	Reaction free energy (kcal/mol)
CDCA + N_2 $\longrightarrow$ CDCA–N_2 (Type-b)	-87.2
CDCA–N_2 + H_2 $\longrightarrow$ C_{14}(CN)(C–NH_2)	16.9
C_{14}(CN)(C–NH_2) $\longrightarrow$ CDCA–$(NH_2)_2$	-11.8
CDCA–$(NH_2)_2$ $\longrightarrow$ C_{14}(CH-NH_3)(C–NH_2)	18.3
C_{14}(CH-NH_3)(C–NH_2) $\longrightarrow$ C_{14}(CH-NH_3)$_2$	15.0
Total Free Energy Change	-48.8

Table 2 Calculated reaction free energies (ΔG) for the hydrogenation to the activated nitrogen.

The calculated free-energy changes (ΔG) are presented in Table 2, while the corresponding optimized geometries are shown in Figure 6. During the stepwise hydrogenation process, the C–C bond between the two carbene centers undergoes alternating formation and disruption, indicating substantial structural reorganization of the CDCA framework as hydrogen is transferred to the activated nitrogen species. A similar alternation is reflected in the stepwise free-energy changes. The first hydrogenation step is associated with a positive free-energy change of +16.9 kcal/mol, whereas the second hydrogenation is exergonic, with a free-energy change of −11.8 kcal/mol. The third hydrogenation step again requires a positive free-energy change of +18.3 kcal/mol and leads to the formation of the corresponding ammonium-containing product. However, further addition of hydrogen converts the remaining amine group to ammonia, though the free energy change for this step is also positive (+15.0 kcal/mol). Despite the positive free-energy requirements of the first, third, and fourth hydrogenation steps, the overall transformation is associated with a substantially negative free-energy change of −48.8 kcal/mol.

These results demonstrate that, within the computational model considered, CDCA can strongly promote the thermodynamic conversion of molecular nitrogen into an ammonia-derived product through cooperative activation of N_2 followed by stepwise hydrogenation. Nevertheless, the positive free-energy changes encountered during individual hydrogenation steps indicate that the overall thermodynamic driving force alone is insufficient to establish the feasibility of the complete catalytic cycle. In particular, the kinetic barriers, hydrogen-transfer mechanism, regeneration of the CDCA active structure, and possible competing pathways must be investigated before assessing whether CDCA can mediate ammonia synthesis from molecular nitrogen and hydrogen under ambient conditions. Therefore, the present results should be regarded as evidence for the potential of the two-carbene architecture of CDCA for N_2 activation and subsequent hydrogenation, rather than as definitive evidence of catalytic ammonia synthesis under ambient conditions.

4 Conclusions

A novel carbon dicarbene allotrope (CDCA) has been computationally designed as a zero-dimensional, carbon-only molecular architecture containing two electronically communicating carbene centres. The singlet state is calculated to be substantially more stable than the triplet state by 47.2 kcal mol^{-1}, while finite-temperature AIMD simulations indicate that the carbon framework retains its structural integrity under the investigated conditions. Despite this electronic and structural stability, the two carbene centres remain highly reactive, demonstrating that stability and chemical functionality can coexist within a molecular carbon allotrope.

CDCA exhibits pronounced reactivity toward a diverse range of small molecules, including SO_2, SO_3, NO, NO_2, NO_3, N_2, CO, CO_2 and H_2O. The calculated transformations demonstrate that the two carbene centres can participate cooperatively in small-molecule activation, highlighting the role of the two-centre architecture in determining the chemical behaviour of CDCA. Among these reactions, N_2 activation provides the most significant demonstration of this cooperative effect. A single-centre interaction with N_2 produces an adduct without N–N bond cleavage, whereas simultaneous interaction of N_2 with both carbene centres promotes N–N bond cleavage. Subsequent stepwise hydrogenation of the activated nitrogen species leads toward ammonia formation, with an overall negative free-energy change for the investigated sequence.

Taken together, these results establish CDCA as a distinct conceptual class of zero-dimensional carbon allotrope in which specific carbon centres serve as intrinsic reactive sites. Rather than relying on extended carbon surfaces or heteroatom functionalization, CDCA incorporates chemical reactivity directly into an all-carbon molecular framework. The present study therefore demonstrates that dimensionality and molecular architecture can serve as design parameters for controlling the chemical reactivity of carbon allotropes and provides a molecular-level framework for exploring carbon-only systems for small-molecule activation and nitrogen chemistry.

The present results should, however, be regarded as a computational proof of concept rather than evidence of an experimentally established catalytic process. In

particular, transition-state barriers, hydrogen activation, product release, regeneration of the CDCA framework, competing reaction pathways, and the stability of CDCA under realistic reaction conditions remain to be established. Experimental synthesis and characterization will therefore be essential to determine whether the predicted reactivity of CDCA can be translated into an experimentally accessible carbon-only platform for nitrogen fixation and other small-molecule transformations.

Data availability. The underlying optimized structures, computational input files, output files are reported either in the main manuscript or in the supporting information file.

Acknowledgments. The authors acknowledge the computational resources and institutional facilities of MAKAUT WB, West Bengal, India used for the theoretical investigation reported in this manuscript.

Author contributions. Rahul Das carried out the computational work. All authors were involved in the result analysis and draft writing of this manuscript. Conceptualization, mentoring, project guiding, resource management, validation, and manuscript finalization were done by Arijit Bag.

Competing interests. The authors declare that there is no competing interests.

Declarations

- Funding: Not Applicable
- Conflict of interest/Competing interests: There is no conflict of interests.
- Ethics approval and consent to participate: Not Applicable
- Consent for publication: Not Applicable
- Data availability: Available in the supporting information file.
- Materials availability: Not Applicable
- Code availability: Not Applicable
- Author contribution: Rahul Das carried out the computational work. All authors were involved in the result analysis and draft writing of this manuscript. Conceptualization, mentoring, project guiding, resource management, validation, and manuscript finalization were done by Arijit Bag.

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