energy&fuels

Open Access

This article is licensed under CC-BY 4.0

pubs.acs.org/EF

Article

Geometric and Positional Isomer Effects on Ignition Behavior of Cycloalkanes: Implications for Sustainable Aviation Fuels

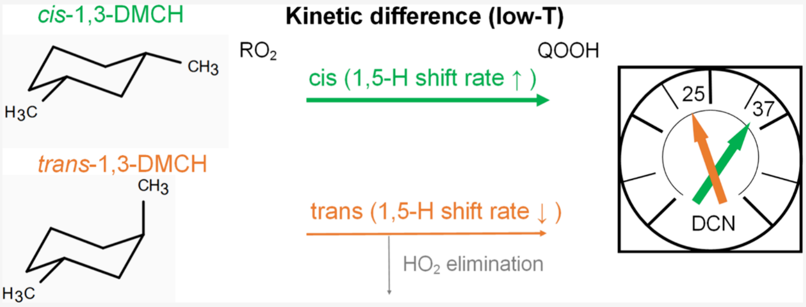
Zhibin Yang,* Conor Faulhaber, Randall Boehm, and Joshua Heyne

Cite This: *Energy Fuels* 2025, 39, 18641−18648

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

Downloaded via 192.225.176.122 on September 25, 2025 at 15:16:47 (UTC).
See https://pubs.acs.org/sharingguidelines for options on how to legitimately share published articles.



ABSTRACT: This study investigates the ignition behavior of six dimethylcyclohexane (DMCH) isomers and *cis-*/*trans*-decalin, focusing on the effects of molecular geometry and substitution patterns. Ignition delay and derived cetane number (DCN) were measured using a CFR ignition quality tester under ASTM D6890 conditions. Among the DMCH isomers, *cis*-1,3-DMCH exhibited the highest reactivity (DCN = 37.4), while *cis*-1,2-DMCH showed the lowest (DCN = 21.8). The most significant stereochemical effect was observed between *cis*- and *trans*-1,3-DMCH, with a 12-unit DCN difference. Temperature- and pressure-dependent tests of decalin isomers revealed that *cis*-decalin consistently ignited faster and exhibited stronger pressure sensitivity, supporting a mechanistic interpretation based on 1,5- versus 1,6-H shift pathways. Additionally, the impact of trace polar degradation products on ignition delay (ID) was assessed, revealing significant ID reduction in trans isomers after storage. These findings highlight the need to consider geometric isomerism in kinetic modeling, sustainable aviation fuel formulation, and surrogate design, particularly for fuels rich in cycloalkanes.

1. INTRODUCTION

The commercial aviation industry is facing mounting pressure to reduce greenhouse gas (GHG) emissions. In the United States, the Sustainable Aviation Fuel Grand Challenge has set ambitious goals: a 50% reduction in aviation-related GHG emissions and full substitution of fossil-based jet fuel with Sustainable Aviation Fuel (SAF) by 2050.[1] Similarly, the ReFuelEU Aviation Regulation mandates that SAF comprise at least 2% of jet fuel at EU airports by 2025, rising to 70% by 2050.[2] Achieving these targets requires not only scale-up of existing production but also the approval of new SAF production pathways. However, most currently certified ASTM D7566 pathways (e.g., A2 HEFA, A5 ATJ) primarily yield synthetic paraffinic kerosene (SPK), which consists almost entirely of n- and iso-alkanes. Although some pathways (e.g., A6 CHJ, A8 ATJ-SKA) can produce aromatic and cycloalkane components, their commercial-scale output remains limited.

There is growing interest in SAF candidates derived from novel feedstocks and conversion technologies, particularly those that produce predominantly aromatic and cycloalkane-rich fuels. Many of these are progressing through the ASTM D4054 approval process. However, due to limited research and historical uncertainty regarding cycloalkane behavior in combustion, original equipment manufacturers (OEMs) and regulatory bodies continue to limit the cycloalkane content within certain D7566 annexes and specifications. One key distinction between cycloalkanes and other hydrocarbon classes found in jet fuel (e.g., n- and iso-alkanes, aromatics) is the presence of cis−trans isomerism, also known as geometric isomerism. Although alkenes also exhibit geometric isomerism, their poor thermal stability renders them present only in trace amounts in conventional jet fuels and absent from all currently approved SAFs.

Ignition delay (ID) and derived cetane number (DCN) are key metrics used to characterize the combustion reactivity of liquid fuels.[3,4] Ignition delay is defined as the time between the start of fuel injection and the onset of significant combustion.

Received: July 22, 2025
Revised: August 29, 2025
Accepted: September 8, 2025
Published: September 16, 2025

ACS Publications

© 2025 The Authors. Published by
American Chemical Society

https://doi.org/10.1021/acs.energyfuels.5c03856

DCN, a dimensionless quantity, is inversely related to ignition delay and serves as a standardized indicator of ignition quality. For aviation turbine fuels, maintaining DCN in the range of 35 to 60 is critical to ensure safe and efficient engine operation.[5] Fuels with excessively low DCN (i.e., long ignition delay) may increase the risk of lean blowout (LBO), particularly under high-altitude or low-load conditions.[6] Conversely, fuels with excessively high DCN (i.e., short ignition delay) may contribute to hardware durability issues, especially upstream of the primary reaction zone where large heat release is not anticipated by the hardware designers. As a result, understanding and controlling ignition delay behavior is essential for SAF certification and performance optimization.

The ignition behavior of hydrocarbons is strongly influenced by their molecular structure, particularly in the case of cyclic and branched alkanes. Cycloalkanes like DMCH are of growing interest in SAF formulations and surrogate development due to their abundance in lignin-derived fuels.[7,8] Dimethylcyclohexane (DMCH), with its multiple positional and geometric isomers, offers an ideal molecular platform to examine the structural sensitivity of fuel reactivity. However, their behavior during autoignition differs substantially from linear or branched alkanes. The cis−trans configuration, resulting from the rigid ring structure, modulates steric strain, radical stability, and low-temperature reaction pathways. For instance, cis-isomers tend to ignite more readily than trans-isomers, owing to reduced conformational strain and more favorable intramolecular hydrogen shift (1,5-H shift) mechanisms.[9] This trend is consistent across several cycloalkane systems, including decalin, where Heyne et al.[10] reported a significantly higher derived cetane number (DCN ≈ 41.6) for cis-decalin than trans-decalin (DCN ≈ 32.0) under identical IQT conditions. This trend is further supported by detailed structural and experimental analysis of decalin. Decalin exists as a fused bicyclic cycloalkane with two ring junction configurations: cis-decalin, where both hydrogens at the ring junctions are on the same face, and trans-decalin, where they are on opposite faces. The cis isomer adopts a more flexible conformation, which allows for enhanced low-temperature reactivity due to more favorable hydrogen abstraction and chain-branching pathways. In contrast, the trans isomer exhibits a more rigid structure with lower reactivity under similar conditions.

Beyond geometry, positional isomerism also plays an important role. Prior studies report that 1,2-DMCH exhibits significantly lower reactivity than 1,3-DMCH, attributed to steric hindrance around the methyl groups and fewer accessible β-scission pathways.[11] Experimental work by Kang et al.[12] and Yang & Wang[13] supports this trend, demonstrating that 1,3-isomers produce earlier low-temperature heat release and higher radical concentrations in motored engine studies and quantum kinetic calculations.

These structural effects are also reflected in DCN measurements. Using IQT, Jameel et al.[14] measured a DCN of 24 for 1,2-DMCH and 30.5 for 1,3-DMCH, supporting the view that increased substitution near the ring reduces reactivity. However, their study did not provide detailed characterization of isomer purity or cis−trans ratios, limiting interpretation of configurational effects. Similarly, Do et al.[15] investigated ring-opening reactions of 1,2- and 1,3-DMCH over iridium-based catalysts and predicted cetane numbers using artificial neural networks, obtaining CN = 22 for 1,2-DMCH and CN = 30 for 1,3-DMCH. These predicted and experimental values align well with the trend that increased substitution near the ring reduces reactivity, but also highlight the sensitivity of these metrics to both position and geometry of substituents.

A recent comprehensive study by Yang et al.[16] provided direct comparative insight into the oxidation kinetics of 1,2- and 1,3-DMCH using flow reactor experiments and detailed chemical kinetic modeling. Their work revealed that 1,2-DMCH exhibits stronger high-temperature reactivity, whereas 1,3-DMCH is more reactive under low-temperature conditions, particularly within the negative temperature coefficient (NTC) regime. Their study contributed validated kinetic submodels for both isomers, yet did not differentiate cis- and trans- configurations, highlighting a critical gap in understanding the role of geometric isomerism in ignition behavior.

Other modeling efforts, such as those by Kubic,[9] used group contribution methods and neural networks to predict DCNs across a wide molecular domain. These models confirmed that ring substitution, branching, and unsaturation consistently reduce cetane numbers, primarily through their inhibitory effects on early stage radical formation and propagation. Additionally, Rosado-Reyes and Tsang[17] explored the isomerization kinetics of cis-1,2-DMCH in a single-pulse shock tube. Their findings showed unexpectedly slow cis-to-trans isomerization, suggesting kinetic bottlenecks due to steric hindrance in cyclic transition states.

Collectively, these findings emphasize the necessity of treating geometric and positional isomers as discrete species in kinetic models. Their differences are not merely of academic interest but bear significant implications for SAF performance metrics such as ignition delay, lean blowout risk, and nvPM emissions.[18] Despite growing understanding of DMCH oxidation chemistry, there remains a lack of experimental data that clearly isolates geometric isomerism effects under tightly controlled conditions. Many previous studies either used mixed isomer samples or did not specify isomeric purity, limiting mechanistic conclusions. As a result, detailed characterization of ignition delay and DCN as a function of cis−trans configuration remains an open research question.

In this work, we present a systematic investigation of the effect of geometric isomerism specifically cis vs trans configurations—on the ignition delay of high-purity dimethylcyclohexane and decalin isomers. This study aims to fill a critical knowledge gap in surrogate fuel modeling and contribute to the broader understanding of how molecular structure dictates fuel performance in advanced combustion systems.

2. MATERIAL AND METHODS

2.1. Reference Materials. All six configurations of DMCH and their mixtures were purchased for testing as shown in Table 1. Some configurations of fuel were purchased twice to acquire different lot numbers and used for cross referencing.

2.2. Sample Preparation. As with any hydrocarbon-based fuel, prolonged exposure to atmospheric oxygen can lead to the formation of trace oxygenates and peroxides. These oxidative degradation products can significantly affect ignition delay measurements by altering fuel reactivity. To minimize these effects and ensure consistent sample quality, solid phase extraction (SPE) was employed to remove potential contaminants prior to testing. The material retained in the SPE trap was subsequently analyzed by gas chromatography−mass spectrometry (GC−MS), and representative oxygenated species are reported in the results section.

A Thermo Scientific HyperSep Silica SPE cartridge (1000 mg) was used for this process. The procedure was as follows. An initial 5 mL

Table 1. Hydrocarbons Used in This Study, Including Source and Purity

molecules	purity	lot number	company
cis-1,2-dimethylcyclohexane	>98%	FIJ01-KU	TCI America
trans-1,2-dimethylcyclohexane	>99%	KRFHJ-QI	TCI America
cis-1,2-dimethylcyclohexane	>98%	FHA01-BN	TCI America
trans-1,2-dimethylcyclohexane	>99%	KRFHJ-BQ	TCI America
cis-1,3-dimethylcyclohexane	>99%	FB001-OX	TCI America
trans-1,3-dimethylcyclohexane	>95%	HD6TH-CM	TCI America
trans-1,3-dimethylcyclohexane	>98%	HD6TH-OK	TCI America
cis-1,4-dimethylcyclohexane	>98%	FHC01-NOJD	TCI America
trans-1,4-dimethylcyclohexane	>95%	G3HHM-US	TCI America
trans-1,4-dimethylcyclohexane	>95%	X7YKC-TT	TCI America
cis-decalin	>98%	TED3A-SN	TCI America
trans-decalin	>98%	7SQEF-LB	TCI America

portion of the fuel sample was passed through the cartridge to precondition the column and then discarded. Subsequently, 25 mL of test fuel was passed through the cartridge under positive pressure to maintain a uniform collection rate. After extraction, the sample was filtered through a fine membrane (0.2 μm) to remove any residual sorbent particles. The cleaned sample was then used directly for ignition delay measurements in the IQT system.

2.3. Experimental Setup and Procedure. The ID and DCN measurements were conducted using a CFR Ignition Quality Tester (IQT-LM model) in accordance with ASTM D6890. Traditionally, approximately 150 mL of fuel was required to complete a DCN test, but the new IQT system acquired by Washington State University in 2024 includes manufacturer updates that significantly reduce the fuel volume needed. In this method, the fuel is injected into a heated, temperature-controlled constant-volume combustion chamber (CVCC) precharged with compressed air. Each injection triggers a compression ignition event, and the ignition delay defined as the time between the start of fuel injection and the onset of significant combustion is recorded. Each test consists of 15 preinjections, used to condition the chamber and purge residual fuel, followed by 32 injections from which ignition delay values are averaged. An equation is used to correlate ID to CN using ASTM D613, resulting in a DCN. The eq 1) is used when ID ranges from 2.64 to 6.90 ms (75.1 DCN to 31.5 DCN).

$$DCN = 4.460 + 186.6/ID \quad (1)$$

The IQT is able to measure ID outside of this range, however the precision may be affected. When outside the ID range 2.64 to 6.90 ms, eq 2) should be used for the correlation of ID to DCN.

$$DCN = 83.99(ID - 1.512)^{(-0.658)} + 3.547 \quad (2)$$

It should be noted that the eq 1) and eq 2) are not equal at both end points (2.64 and 6.90 ms). However, the resolution of this discrepancy is outside the scope of this work. All measurements were calibrated following ASTM protocol using *n*-heptane (Haltermann solution, 99.86 vol %) with a measured ID of 3.78 ± 0.01 ms and methylcyclohexane (CFR Engine, purity unspecified) with an ID of 10.4 ± 0.5 ms. The charge air pressure was maintained at 310 psi, and the average charge air temperature was 582 °C.

3. RESULTS AND DISCUSSION

3.1. Experimental Ignition Delay Measurements. Ignition delay measurements were conducted for all six isomers of DMCH and two isomers of decalin using the CFR IQT system, and the corresponding DCNs are summarized in Table 2. Among the tested DMCH isomers, cis-1,3-DMCH exhibited the highest reactivity, with a DCN of 37.4, while cis-1,2-DMCH showed the lowest reactivity, with a DCN of 21.8. This represents a substantial difference of 15.6 DCN units among structurally similar isomers of DMCH, underscoring the significant influence of both positional and geometric isomerism on ignition behavior.

Table 2. Ignition Delay and DCN of Pure Compounds

compound	ignition delay, ms	DCN
cis-1,2-DMCH	11.690	21.8
trans-1,2-DMCH	11.404	22.1
cis-1,3-DMCH	5.660	37.4
trans-1,3-DMCH	9.250	25.4
cis-1,4-DMCH	9.742	24.5
trans-1,4-DMCH	7.797	28.6
cis-decalin	5.062	41.3
trans-decalin	6.734	32.2

For the 1,2-substituted isomers, cis-1,2-DMCH and trans-1,2-DMCH yielded nearly identical DCNs of 21.8 and 22.1, respectively. This suggests that geometric isomerism has a negligible effect on ignition delay for 1,2-DMCH. This observation is consistent with values reported in the NREL Compendium of Experimental Cetane Numbers,[19] which lists a DCN of 24.0 for a mixed 1,2-DMCH sample. In contrast, the effect of stereochemistry is most pronounced in the 1,3-substituted isomers. The DCN of cis-1,3-DMCH (37.4) is significantly higher than that of trans-1,3-DMCH (25.4), a difference of 12 DCN units. The DCN value of 30.5 reported in the NREL compendium for a mixed 1,3-DMCH sample falls between these two values, further supporting the sensitivity of ignition behavior to stereochemistry in this isomer group. For the 1,4-DMCH isomers, a moderate stereochemical effect is observed. The cis isomer exhibited a DCN of 24.5, whereas the trans isomer reached 28.6, resulting in a difference of 4.1 DCN units. When averaged across stereoisomers, the DCN trend by substitution position follows the order: 1,3-DMCH > 1,4-DMCH > 1,2-DMCH, indicating that positional isomerism also plays a significant role in ignition reactivity, independent of geometry. Figure 1 summarizes DCN comparison among DMCH isomers.

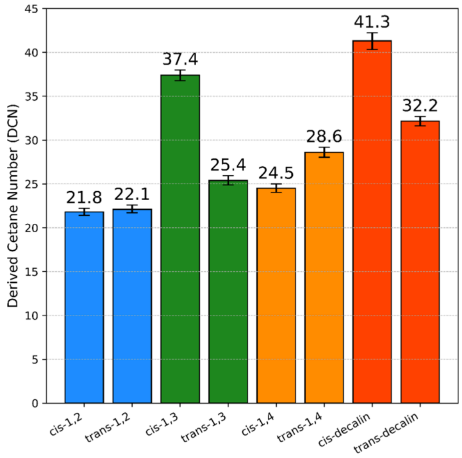
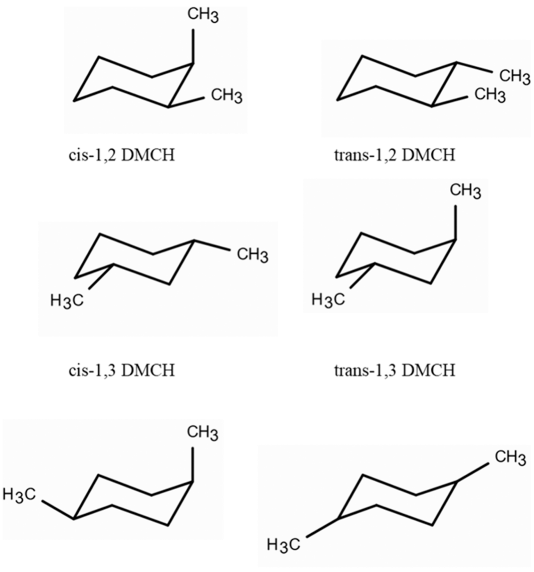


Figure 1. DCN comparison among DMCH and decalin isomers.

To further validate the role of stereochemistry, cis- and trans-decalin were also evaluated under identical IQT conditions. Cis-decalin yielded a DCN of 41.3, while trans-decalin yielded 32.2—a difference of 9.1 DCN units. These results closely match those of Heyne et al.,[10] who reported values of 41.6 and 32.0 for cis- and trans-decalin, respectively.

3.2. Possible Kinetic Explanation of DMCH Isomers.

The observed variation in DCN among the isomers of DMCH reflects differences in molecular conformation and the corresponding impact on low-temperature oxidation kinetics. These effects are governed by the steric accessibility of hydrogen abstraction sites, the population and stability of reactive conformers, and the propensity for chain-branching pathways such as 1,5-H shifts and β-scission. Collectively, these parameters influence the onset and rate of exothermic radical chemistry that drives low-temperature heat release. The ignition behavior differences among DMCH isomers can be mechanistically explained by examining their molecular conformations, particularly the accessibility of hydrogen abstraction sites and the feasibility of intramolecular hydrogen shifts. Figure 2 illustrates the most stable chair conformations of the six DMCH isomers, showing the relative positions of methyl groups and highlighting stereochemical effects that influence reactivity.



cis-1,2 DMCH trans-1,2 DMCH

cis-1,3 DMCH trans-1,3 DMCH

cis-1,4 DMCH trans-1,4 DMCH

Figure 2. Chair conformations of six DMCH isomers, highlighting the relative position and stereochemistry of the two methyl groups. Each structure represents the most stable conformer.

Both cis- and trans-1,2-DMCH exhibit similarly low DCNs (∼22), indicating that positional substitution at adjacent carbon atoms (C1 and C2) significantly hinders reactivity regardless of stereochemistry. This behavior stems from severe steric congestion between the two methyl groups, which limits access to secondary axial hydrogens, the preferred sites for initial hydrogen abstraction by OH or HO_2 radicals.[20] Quantum chemical studies confirm that these isomers predominantly occupy low-energy chair conformers with restricted conformational interconversion. In particular, Bian et al.[21] showed that inversion between conformers in cis-1,2-DMCH involves high energy barriers (>13 kcal/mol), and productive 1,5-H transfer is accessible only in rare, energetically disfavored geometries. Similarly, Sakurai et al.[22] found that radical cation fragmentation in 1,2-DMCH is stereoselective and limited, reinforcing the notion that conformational strain suppresses radical reactivity. Rossini and Pitzer[23] further support this conclusion with thermodynamic data: cis-1,2-DMCH has a higher enthalpy and lower entropy than its trans counterpart, reflecting its greater steric strain and reduced flexibility. Together, these findings indicate that 1,2-substitution locks the molecule into kinetically hindered conformations, reducing the formation of hydroperoxyalkyl radical (QOOH) and other chain-branching intermediates at low temperature.

In contrast, the 1,3-isomers show a pronounced stereochemical influence on DCN. The cis-1,3 isomer exhibits the highest DCN (37.4) of all isomers studied, while the trans form displays significantly lower reactivity (DCN = 25.4). Ab initio studies by Bian et al.[21] demonstrate that cis-1,3-DMCH favors low-energy conformers such as C13Cee, where both methyl groups occupy equatorial positions. This geometry is sterically favorable and facilitates intramolecular 1,5-hydrogen shifts via accessible transition states. At 500 K, the population of this conformer exceeds 99%, ensuring a high likelihood of radical isomerization and early OH regeneration through QOOH pathways. By contrast, trans-1,3-DMCH in its stable chair conformation must adopt an axial−equatorial (C13Cea) geometry due to the trans-1,3 substitution pattern. This configuration leads to more linear molecular geometries that are less favorable for internal hydrogen shift reactions, potentially delaying the onset of OH formation compared to the cis isomer. These conformers restrict chain-branching, delay low-temperature heat release, and result in a lower DCN. This stereochemical dependence on 1,5-H migration is consistent with prior kinetic models by Yang et al.,[16] which identify H-shift rates and QOOH formation as sensitive to ring geometry and substituent orientation.

The 1,4-DMCH isomers fall between the extremes observed in 1,2- and 1,3-substitution. Both cis and trans forms exhibit intermediate DCNs, with only a modest difference between stereoisomers. In these structures, the methyl groups are positioned at para-positions, on opposite poles of the cyclohexane ring, which minimizes steric interference and preserves conformational flexibility. Quantum calculations show relatively low energy differences among conformers and lower inversion barriers, suggesting that both isomers maintain access to reactive geometries over a wide temperature range.[24] This pattern is supported by pyrolysis data from Gillespie et al.,[25] who found that 1,4-DMCH readily undergoes radical fragmentation via ring hydrogen abstraction, consistent with the structural accessibility of reactive sites in these isomers.

These structure reactivity trends are reinforced by kinetic modeling and flow-reactor studies. Yang et al.[16] showed that 1,2-DMCH is more reactive at high temperatures, where ring-breaking dominates. While 1,3-DMCH exhibits enhanced reactivity under low-temperature conditions due to its propensity for H-migration and QOOH generation. Their sensitivity analyses confirmed that cis-isomers generally promote earlier formation of chain-branching intermediates, correlating with shorter ignition delays and higher DCN.

3.3. Temperature and Pressure Dependence of Decalin Isomers.

To further investigate the mechanistic differences between cis- and trans-decalin in low temperature oxidation chemistry, a comprehensive series of ID measurements were conducted over a range of temperatures (400−620 °C) and pressure (250−350 psi). These conditions span the peroxy radical chemistry and hydrogen shift isomerization regime, allowing detailed investigation of conformational effects. During the temperature sweep, pressure was held constant at 310 psi, while the pressure sweep was performed at a fixed temperature of 450 °C, enabling isolated analysis of each variable's influence on ignition behavior.

Figure 3 illustrates the pressure and temperature dependence of ID for cis- and trans-decalin. The top panel displays strong Arrhenius behavior, with high linearity for both cis- and trans-decalin (R2 = 0.992 and 0.992, respectively). Although both exhibit similar slopes, the cis isomer consistently displays shorter ID times across the entire temperature range studied. This indicates that the overall reactivity of cis-decalin is higher, likely due to greater accessibility of low-temperature chain-branching pathways, particularly below 550 °C, where RO2 and QOOH intermediates play key roles.[26−29] As these reactions involve complex networks rather than single elementary steps, the observed differences in ID may reflect variations in the number or efficiency of reactive pathways available to each isomer, rather than differences in a single activation energy barrier.

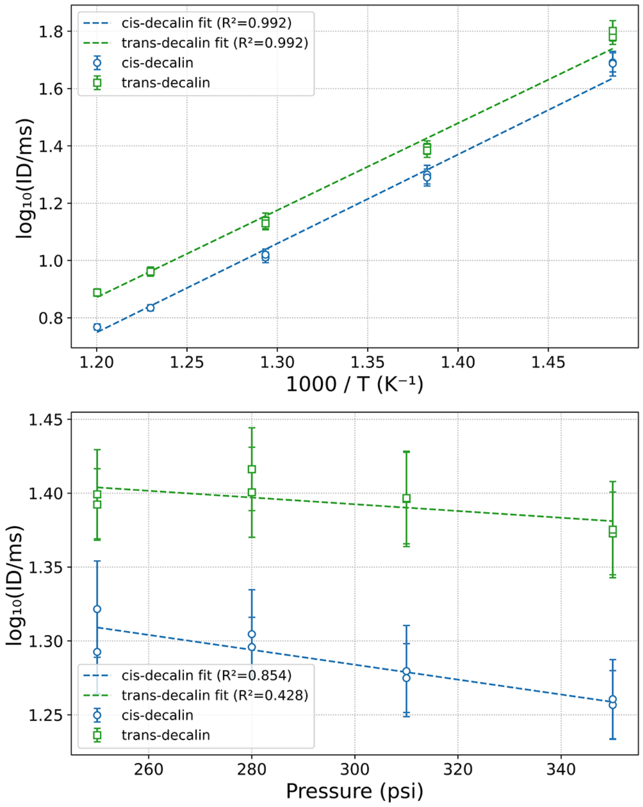


Figure 3. Pressure and temperature dependence of ignition delay for *cis*- and *trans*-decalin. ID is expressed in milliseconds before taking the logarithm. Data points represent duplicate measurements with error bars showing one standard deviation (SD). Each point is the mean of 32 injections; error bars are one SD across injections; two markers at a condition indicate independent duplicate tests. Dashed lines are linear fits to the logarithm of ignition delay, with coefficients of determination (R^2) included in the legend.

The bottom panel of Figure 3 shows that cis-decalin also exhibits stronger pressure dependence (R^2 = 0.854), while trans-decalin shows weak sensitivity to pressure changes (R^2 = 0.428). This differential response implies that cis-decalin benefits significantly from pressure assisted stabilization of radical intermediates, which is consistent with unimolecular reaction pathways that involve third-body collisions.[27,30]

Figure 4 expands on these observations by directly comparing the ratio of ID (cis/trans-decalin) across temperature and pressure sweeps. In the top panel, the ID ratio decreases slightly with increasing temperature but remains below one across the full range. This reinforces the conclusion that cis-decalin is consistently more reactive, particularly at lower temperatures where peroxy radical isomerization dominates. The weak temperature dependence and low R^2 (0.006) indicate that the ratio of ignition delays between cis- and trans-decalin remains nearly constant across the studied temperature range. This supports the earlier observation that both isomers have similar apparent activation energies in this regime. Each point represents one of many pairwise combinations between individual cis- and trans- measurements, with error bars reflecting the propagated uncertainty from both isomers. The resulting scatter reflects real experimental variability while still preserving the overall trend.

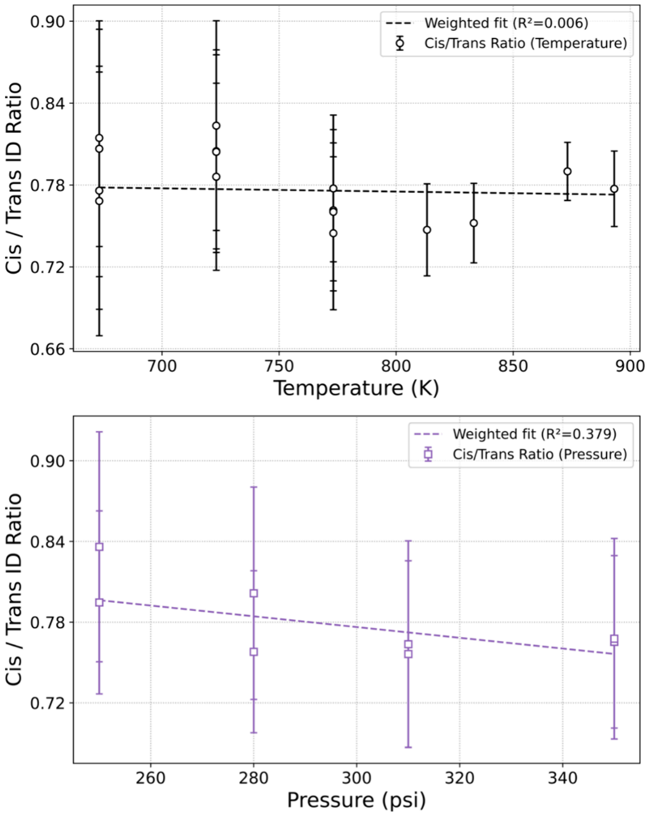


Figure 4. Effect of temperature and pressure on *cis*/*trans* ignition delay ratio of decalin isomers. Data points represent ratios derived from independent replicate measurements of *cis*- and *trans*-decalin; error bars were propagated from the replicate standard deviations. Dashed lines show linear fits with R^2 reported in the legend.

In contrast, the bottom panel of Figure 4 reveals a negative correlation between the ID ratio and pressure (R^2 = 0.379). This supports the interpretation that the pressure-enhanced reactivity of cis-decalin is not matched by trans-decalin, likely due to geometric constraints that limit efficient 1,6-H shift isomerization in the trans isomer. As pressure increases, the efficiency of pressure-dependent low-temperature pathways[27,30] (e.g., $RO_2 \rightleftharpoons$ QOOH and O_2QOOH formation) disproportionately benefits cis-decalin, driving the ratio lower. Figure 5 illustrates a representative 1,5-H abstraction transition state in cis-decalin, where axial hydrogen accessibility supports

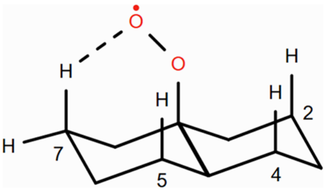


Figure 5. Illustration of a 1,5-hydrogen abstraction transition state in *cis*-decalin. The axial hydrogen at the 7-position is abstracted by a peroxy radical (ROO·), initiating QOOH formation. The adjacent equatorial hydrogen and other abstractable sites are shown for reference. This geometry supports efficient low-temperature chain branching, consistent with the enhanced reactivity and pressure sensitivity observed experimentally. Adapted from Heyne et al.[10] Copyright 2009 Energy Fuels.

faster QOOH formation under low-temperature and high-pressure conditions.

Taken together, the temperature and pressure dependence of ID in cis- vs trans-decalin highlight the mechanistic role of H-shift pathways. The data support a scenario where 1,5-H shift isomerization in cis-decalin is more accessible and pressure-enhanced, whereas trans-decalin is constrained to slower or less pressure-responsive 1,6-H pathways. These insights clarify the structure−reactivity relationship and aid in modeling low-temperature oxidation behavior of bicyclic hydrocarbons. A full computational treatment of the isomer-dependent oxidation pathways lies beyond the scope of this work, but represents an important avenue for future study.

3.4. Polar Contaminant Effect on Ignition Delay. Trace polar species, particularly peroxides and oxygenates, are well-known to accelerate low temperature combustion chemistry and reduce ID. These compounds can form during ambient storage through slow autoxidation of hydrocarbons in the presence of oxygen, and even at ppm levels, they can significantly bias DCN measurements by promoting radical generation and chain branching.

To assess this effect, each DMCH isomer was tested immediately upon opening ("as received"), then stored under ambient, light-protected conditions for 135 days in sealed amber bottles (although no purge using inert gas was performed). No further purification was applied prior to retesting. Figure 6 compares ID values before and after storage, with error bars representing standard deviations from 32 injections per test.

Among the DMCH isomers, trans-1,2-DMCH showed the most significant ID reduction from 11.40 to 9.81 ms, well beyond experimental uncertainty. Smaller but measurable decreases were also observed for trans-1,3-DMCH and trans-1,4-DMCH. In contrast, the cis isomers exhibited less change over time, indicating greater oxidative (storage) stability which is likely due to conformational constraints that hinder peroxide formation or radical propagation.

A similar trend was observed in trans-decalin, which initially showed an abnormally low ID of 5.33 ms (DCN = 39.5), inconsistent with literature values (≈32). Following SPE to remove polar contaminants, the ID increased to 6.73 ms (DCN = 32.2), aligning with prior reports and confirming that oxidative degradation had artificially enhanced the sample's reactivity. This validates both the susceptibility of trans-fused cycloalkanes to oxidative change and the efficacy of SPE purification.

GC-MS analysis of the SPE retained polar fraction from trans-decalin confirmed the presence of multiple oxygenated species, including ketones and hydroxylated decalin derivatives, further supporting the hypothesis that oxidative byproducts were responsible for the observed ID reductions. A full chromatogram, annotated peak identities, and mass spectra are provided in Supporting Information (SI). It should be noted that while SPE GC-MS analysis is qualitative in nature, these results reinforce the need for careful fuel handling and

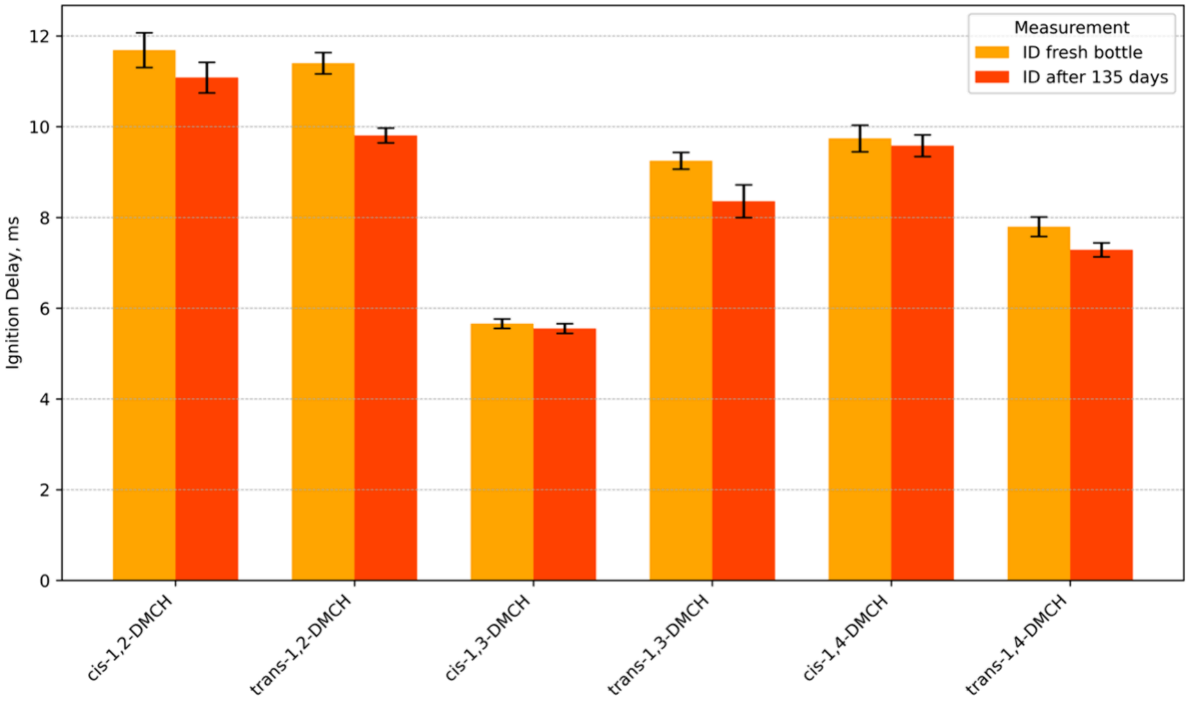


Figure 6. Ignition delay comparison of DMCH isomers before and after 135 days of storage.

purification when evaluating ignition properties particularly for fuels prone to peroxide formation. This is especially important for accurate kinetic model validation and experimental repeatability in surrogate fuel testing. The scope of this polar study is not to quantify the kinetics or concentrations of these impurities, but rather to alert the community to their potential impact on ignition measurements.

It should be noted that while the IQT provides a standardized and certification relevant platform for ignition delay and DCN determination, it does not capture the full range of autoignition behavior accessible with complementary equipment such as shock tubes or rapid compression machines. IQT measurements are most sensitive to mid temperature reactivity, whereas low-temperature chain branching and high-pressure kinetics are better resolved by other devices. Thus, while the present work emphasizes relative trends among isomers under ASTM D6890 conditions, a broader mechanistic picture will require integration with complementary methods in future studies. Although a comprehensive ab initio calculation/kinetic modeling of the isomer dependent oxidation network (conformers, H-abstraction sites, RO_2/QOOH isomerization, and pressure effects) would be valuable, it lies beyond the scope of this experimental study and would constitute a separate contribution. Here we focus on delivering an isomer-resolved, internally consistent IQT data set under certification-relevant conditions (ASTM D6890), together with a literature based mechanistic context that can be used to benchmark and refine future models and surrogate fuel formulations.

4. CONCLUSIONS

Here, we investigated the impact of stereochemistry on the ID behavior of DMCH isomers. Among the isomers tested, cis-1,3-DMCH exhibited the highest reactivity, with a DCN of 37.4, while cis-1,2-DMCH was the least reactive, with a DCN of 21.8. The most pronounced stereochemical effect was observed between cis- and trans-1,3-DMCH, which showed a significant DCN difference of 12.0. In contrast, the effect was minimal for cis- and trans-1,2-DMCH, with only a 0.3 DCN difference. These variations are attributed to differences in molecular conformation, which directly influence low-temperature oxidation pathways and the formation of reactive intermediates during combustion.

To validate and extend these findings, cis- and trans-decalin were examined under a range of temperatures and pressures. Cis-decalin consistently exhibited faster ignition and stronger pressure sensitivity, consistent with its ability to access more favorable low-temperature chain-branching mechanisms (e.g., 1,5-H shift). The trans isomer, in contrast, was limited by conformational rigidity and exhibited weaker pressure dependence, likely due to inefficient 1,6-H isomerization. These results clarify the mechanistic basis for structure−reactivity trends among fused bicyclic hydrocarbons.

We also evaluated the impact of trace polar contaminants formed during ambient storage. Trans isomers, particularly trans-decalin, showed notable ignition delay reductions due to oxidative degradation. SPE and GC-MS confirmed the presence of oxygenated byproducts, such as ketones and hydroxylated species. These findings underscore the need for careful sample preparation to ensure accurate ignition property comparisons across isomer classes.

Taken together, these findings demonstrate that molecular stereochemistry and positional isomerism play critical roles in governing ignition behavior. This work deepens the mechanistic understanding of structure−reactivity relationships in cycloalkanes and offers valuable guidance for surrogate fuel formulation, SAF pathway evaluation, and chemical kinetic model development. Although this study focused on pure cis- and trans-cycloalkanes, such measurements are directly relevant to multi component SAF mixtures. Because DCN typically follows a linear by volume blending rule, accurate pure-component data expand the DCN database and support both hydrocarbon type analysis and quantitative structure property relationship (QSPR) modeling. These insights help address knowledge gaps on cycloalkanes and strengthen confidence in their role within sustainable aviation fuel blending strategies.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.5c03856.

GC-MS analysis of the SPE retained polar fraction (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Zhibin Yang − *Bioproducts, Sciences, and Engineering Laboratory, School of Engineering and Applied Sciences, Washington State University, Richland, Washington 99354, United States;* orcid.org/0000-0003-2857-720X; Email: zhibin.yang@wsu.edu

Authors

Conor Faulhaber − *Bioproducts, Sciences, and Engineering Laboratory, School of Engineering and Applied Sciences, Washington State University, Richland, Washington 99354, United States;* orcid.org/0009-0003-5634-0864

Randall Boehm − *Bioproducts, Sciences, and Engineering Laboratory, School of Engineering and Applied Sciences, Washington State University, Richland, Washington 99354, United States;* orcid.org/0000-0003-2983-1337

Joshua Heyne − *Bioproducts, Sciences, and Engineering Laboratory, School of Engineering and Applied Sciences, Washington State University, Richland, Washington 99354, United States; Energy Processes and Materials Division, Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, Washington 99352, United States;* orcid.org/0000-0002-1782-9056

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.energyfuels.5c03856

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to acknowledge funding from the U.S. Federal Aviation Administration Office of Environment and Energy through ASCENT, the FAA Center of Excellence for Alternative Jet Fuels and the Environment, project 65 through FAA Awards Number 13-CAJFE- WASU-035 (PI: Dr. Joshua Heyne) under the supervision of Ana Gabrielian and project 103 through FAA award number 13-CAJFE-WASU-044 under the supervision of Bahman Habibzadeh. Any opinions, findings, conclusions, or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the FAA or other sponsors. This work was done under the auspices of the WSU−PNNL Bioproducts Institute, which is a joint research collaboration of Washington State University and the U.S. Department of Energy's Pacific Northwest National Laboratory. The authors also gratefully acknowledge the M. J. Murdock Charitable Trust for funding the acquisition of the Ignition Quality Tester (IQT) used in this study.

REFERENCES

(1) US DOE; USDA; EPA; US Department of Transportation. *SAF Grand Challenge Roadmap*; 2022. https://www.energy.gov/eere/bioenergy/articles/sustainable-aviation-fuel-grand-challenge-roadmap-flight-plan-sustainable.

(2) *Regulation - EU - 2023/2405 - EN - EUR-Lex*. https://eur-lex.europa.eu/eli/reg/2023/2405/oj (accessed 2025−06−11).

(3) Colket, M.; Heyne, J. *Fuel Effects on Operability of Aircraft Gas Turbine Combustors*; American Institute of Aeronautics and Astronautics, Inc., 2021. .

(4) Luecke, J.; Naser, N.; Yang, Z.; Heyne, J.; McCormick, R. L. Measurement of Spray Chamber Ignition Delay and Cetane Numbers for Aviation Turbine Fuels. *Energy Fuels* **2025**, *39* (22), 10479−10487.

(5) *ASTMD4054: Standard Practice for Evaluation of New Aviation Turbine Fuels and Fuel Additives*; West Conshohocken, 2022. .

(6) Boehm, R. C.; Colborn, J. G.; Heyne, J. S. Comparing Alternative Jet Fuel Dependencies Between Combustors of Different Size and Mixing Approaches. *Front. Energy Res.* **2021**, *0*, 440.

(7) Ruan, H.; Qin, Y.; Heyne, J.; Gieleciak, R.; Feng, M.; Yang, B. Chemical Compositions and Properties of Lignin-Based Jet Fuel Range Hydrocarbons. *Fuel* **2019**, *256* (May), No. 115947.

(8) Yang, Z.; Xu, Z.; Feng, M.; Cort, J. R.; Gieleciak, R.; Heyne, J.; Yang, B. Lignin-Based Jet Fuel and Its Blending Effect with Conventional Jet Fuel. *Fuel* **2022**, *321* (March), No. 124040.

(9) Kubic, W. L. *A Group Contribution Method for Estimating Cetane and Octane Numbers*; Los Alamos National Laboratory **2016**.

(10) Heyne, J. S.; Boehman, A. L.; Kirby, S. Autoignition Studies of Trans- and Cis-Decalin in an Ignition Quality Tester (IQT) and the Development of a High Thermal Stability Unifuel/Single Battlefield Fuel. *Energy Fuels* **2009**, *23* (12), 5879−5885.

(11) Kang, D.; Kirby, S.; Agudelo, J.; Lapuerta, M.; Al-Qurashi, K.; Boehman, A. L. Combined Impact of Branching and Unsaturation on the Autoignition of Binary Blends in a Motored Engine. *Energy Fuels* **2014**, *28* (11), 7203−7215.

(12) Kang, D.; Lilik, G.; Dillstrom, V.; Agudelo, J.; Lapuerta, M.; Al-Qurashi, K.; Boehman, A. L. Impact of Branched Structures on Cycloalkane Ignition in a Motored Engine: Detailed Product and Conformational Analyses. *Combust. Flame* **2015**, *162* (4), 877−892.

(13) Yang, M.; Wang, J. Comprehensive Multipath Variational Kinetics Study on Hydrogen Abstraction Reactions from Three Typical Dimethylcyclohexane Isomers by Hydroxyl Radicals: From the Electronic Structure to Model Applications. *J. Phys. Chem. A* **2024**, *128* (22), 4517−4531.

(14) Abdul Jameel, A. G.; Naser, N.; Emwas, A. H.; Dooley, S.; Sarathy, S. M. Predicting Fuel Ignition Quality Using 1H NMR Spectroscopy and Multiple Linear Regression. *Energy Fuels* **2016**, *30* (11), 9819−9835.

(15) Do, P. T.; Alvarez, W. E.; Resasco, D. E. Ring Opening of 1,2- and 1,3-Dimethylcyclohexane on Iridium Catalysts. *J. Catal.* **2006**, *238* (2), 477−488.

(16) Yang, M.; Liang, Y.; Wang, J. A Comparative Experimental and Kinetic Modeling Study on the Oxidation Chemistry of 1,2- and 1,3-Dimethylcyclohexanes: Key Cyclic Components in Sustainable Biofuels and Fossil Fuels. *Fuel* **2025**, *387*, No. 134417.

(17) Rosado-Reyes, C. M.; Tsang, W. Isomerization of Cis-1,2-Dimethylcyclohexane in Single-Pulse Shock Tube Experiments. *J. Phys. Chem. A* **2014**, *118* (36), 7707−7714.

(18) Boehm, R. C.; Yang, Z.; Heyne, J. S. Threshold Sooting Index of Sustainable Aviation Fuel Candidates from Composition Input Alone: Progress toward Uncertainty Quantification. *Energy Fuels* **2022**, *36* (4), 1916−1928.

(19) Yanowitz, J.; Ratcliff, M. A.; Mccormick, R. L.; Taylor, J. D.; Murphy, M. J. *Compendium of Experimental Cetane Numbers*; National Renewable Energy Lab: Golden CO., 2017.

(20) Klimkowski, V. J.; Manning, J. P.; Schafer, L. Molecular Structures and Intramolecular Interactions in Dimethyl Cyclohexane Isomers. *J. Comput. Chem.* **1985**, *6* (6), 570−580.

(21) Bian, H.; Ye, L.; Li, J.; Sun, J.; Liang, T.; Zhong, W.; Zhao, J. Impact of Conformational Structures on Primary Decomposition of Cis-1,2-Dimethylcyclohexyl Isomers: A Theoretical Study. *Combust. Flame* **2019**, *205*, 193−205.

(22) Sakurai, H.; Shiotani, M.; Ichikawa, T. Hydrogen Molecule Detachment in Irradiated 1,2-Dimethyl Cyclohexane: Stereo-Selective Reaction. *Radiat. Phys. Chem.* **1999**, *54* (3), 235−240.

(23) Rossini, F. D.; Pitzer, K. S. Relabeling of the Cis and Trans Isomers of 1,3-Dimethylcyclohexane. *Science (80-.)* **1947**, *105* (2738), 647.

(24) Bian, H.; Zhang, Y.; Wang, Y.; Zhao, J.; Ruan, X.; Li, J. Computational Study of Inversion-Topomerization Pathways in 1,3-Dimethylcyclohexane and 1,4-Dimethylcyclohexane: Ab Initio Conformational Analysis. *Int. J. Quantum Chem.* **2021**, *121* (11), 1−13.

(25) Gillespie, H. M.; Gowenlock, B. G.; Johnson, A. F. The Pyrolysis of Cyclic Hydrocarbons. Part 1. 1.4- Dimethylcyclohexane. *J. Chem. Soc. Perkin Trans. 2* **1979**, 317−324.

(26) Burke, U.; Somers, K. P.; O'Toole, P.; Zinner, C. M.; Marquet, N.; Bourque, G.; Petersen, E. L.; Metcalfe, W. K.; Serinyel, Z.; Curran, H. J. An Ignition Delay and Kinetic Modeling Study of Methane, Dimethyl Ether, and Their Mixtures at High Pressures. *Combust. Flame* **2015**, *162* (2), 315−330.

(27) Zádor, J.; Taatjes, C. A.; Fernandes, R. X. Kinetics of Elementary Reactions in Low-Temperature Autoignition Chemistry. *Prog. Energy Combust. Sci.* **2011**, *37* (4), 371−421.

(28) Peeters, J.; Nguyen, T. L.; Vereecken, L. HOx Radical Regeneration in the Oxidation of Isoprene. *Phys. Chem. Chem. Phys.* **2009**, *11* (28), 5935−5939.

(29) Westbrook, C. K.; Pitz, W. J.; Herbinet, O.; Curran, H. J.; Silke, E. J. A Comprehensive Detailed Chemical Kinetic Reaction Mechanism for Combustion of N-Alkane Hydrocarbons from n-Octane to n-Hexadecane. *Combust. Flame* **2009**, *156* (1), 181−199.

(30) Glowacki, D. R.; Wang, L.; Pilling, M. J. Evidence of Formation of Bicyclic Species in the Early Stages of Atmospheric Benzene Oxidation. *J. Phys. Chem. A* **2009**, *113* (18), 5385−5396.

Technical Report Documentation Page

1. Report No.
acs.energyfuels.5c03856

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
Geometric and Positional Isomer Effects on Ignition Behavior of Cycloalkanes:
Implications for Sustainable Aviation Fuels

5. Report Date
September 2025

6. Performing Organization Code

7. Author(s)
Zhibin Yang, Conor Faulhaber, Randall Boehm, and Joshua Heyne

8. Performing Organization Report No.

9. Performing Organization Name and Address
Center of Excellence for: Alternative Jet Fuels and Environment

Washington State University, Pullman, WA 99164

10. Work Unit No. (TRAIS)

11. Contract or Grant No.
13-C-AJFE-WaSU-035, 044

12. Sponsoring Agency Name and Address
Federal Aviation Administration
Office of Environment and Energy

13. Type of Report and Period Covered
Journal Article

14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

This study investigates the ignition behavior of six dimethylcyclohexane (DMCH) isomers and cis-/trans-decalin, focusing on the effects of molecular geometry and substitution patterns. Ignition delay and derived cetane number (DCN) were measured using a CFR ignition quality tester under ASTM D6890 conditions. Among the DMCH isomers, cis-1,3-DMCH exhibited the highest reactivity (DCN = 37.4), while cis-1,2-DMCH showed the lowest (DCN = 21.8). The most significant stereochemical effect was observed between cis- and trans-1,3-DMCH, with a 12-unit DCN difference. Temperature- and pressure-dependent tests of decalin isomers revealed that cis-decalin consistently ignited faster and exhibited stronger pressure sensitivity, supporting a mechanistic interpretation based on 1,5- versus 1,6-H shift pathways. Additionally, the impact of trace polar degradation products on ignition delay (ID) was assessed, revealing significant ID reduction in trans isomers after storage. These findings highlight the need to consider geometric isomerism in kinetic modeling, sustainable aviation fuel formulation, and surrogate design, particularly for fuels rich in cycloalkanes.

17. Key Words
ASCENT

18. Distribution Statement
This article is licensed under CC-BY 4.0

19. Security Classif. (of this report)
Unclassified

20. Security Classif. (of this page)
Unclassified

21. No. of Pages

22. Price

Form DOT F 1700.7 (8-72) Reproduction of completed page authorized