

CATALYTIC SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION, DFT CALCULATIONS, AND EVALUATION OF PENTYLNORBORNANE AS A FUEL COMPONENT

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ABSTRACT

Pentylbornane, a bicyclic hydrocarbon combining the strained bicyclo[2.2.1]heptane framework with a linear C₅ alkyl substituent, was synthesized by Diels–Alder addition of cyclopentadiene (generated in situ by thermal cracking of dicyclopentadiene) to 1-heptene, followed by catalytic hydrogenation over a Ni/Cr₂O₃ catalyst. The structure of the target compound was confirmed by FT-IR and multinuclear (¹H, ¹³C) NMR spectroscopy, which also revealed a small residual fraction of unsaturated precursor consistent with the measured iodine value. Thermogravimetric analysis (TG/DTG/DTA) under nitrogen showed that pentylbornane remains thermally stable up to ≈83 °C and then undergoes a single dominant decomposition stage between 83.4 and 205.7 °C (maximum rate 13.15%/min at 144.4 °C), attributed to cleavage of strained C–C bonds and side-chain fragmentation. Density functional theory calculations (r2SCAN-3c/ORCA 6.1) gave a wide HOMO–LUMO gap (8.917 eV) and high chemical hardness (4.459 eV), indicating strong kinetic and electronic stability, and predicted a combustion enthalpy of –6546.53 kJ/mol and a gravimetric heat of combustion of 39.36 MJ/kg. When blended into TC-1 jet fuel (0.004 wt%) and hydrotreated diesel (0.05 wt%), pentylbornane improved density and viscosity and markedly enhanced thermo-oxidative stability (up to a 20-fold reduction in sediment) without compromising low-temperature properties, while remaining within GOST specification limits. These results identify pentylbornane as a promising energy-dense hydrocarbon component and multifunctional additive for aviation and diesel fuels.

Keywords: pentylbornane; Diels–Alder synthesis; catalytic hydrogenation; thermal stability; DFT calculations; combustion energetics; jet and diesel fuel additive.

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1. Introduction

The development of new synthetic hydrocarbon fuels with high energy density remains an important challenge in modern fuel chemistry, especially for volume-limited propulsion systems such as aircraft, rocket, and supersonic ramjet/scramjet engines. In these applications, volumetric rather than gravimetric energy density is particularly important, since increasing the energy stored within a fixed fuel-tank volume can directly improve flight range and payload capacity [1]. For this reason, considerable research has focused on saturated polycyclic and strained carbocyclic hydrocarbons, which can combine high density, thermal stability, and relatively low freezing points [2].

One of the best-known examples of this class of fuels is JP-10 [3], a commercial aviation and rocket fuel whose main

component is exo-tetrahydrodicyclopentadiene. This norbornane-derived tricyclic hydrocarbon is characterized by high thermal stability, a low freezing point, and significant ring strain, all of which contribute to its favorable energetic properties [4]. The norbornane (bicyclo[2.2.1]heptane) framework present in JP-10 has therefore attracted considerable attention as a structural basis for the development of new high-energy-density hydrocarbons. A variety of polycyclic and spirocyclic compounds can be prepared through reactions such as the catalytic dimerization of norbornene and norbornadiene, Diels–Alder reactions, and cyclopropanation. Some of these compounds have demonstrated specific impulse and volumetric heat of combustion values comparable to or higher than those of JP-10. In particular, spirocyclic norbornane derivatives have been reported to possess higher densities and volumetric energy densities than JP-10 [5].

In addition to the design of the hydrocarbon framework itself, alkyl substitution provides a useful way to adjust

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the physical and operational properties of potential fuels. The introduction of linear or branched alkyl groups into strained carbocyclic structures can influence melting and pour points, viscosity, and volatility, while generally causing only a moderate decrease in volumetric heat of combustion. This approach has also been investigated in high-density hydrocarbon fuels containing norbornane structures [6]. A similar strategy can be applied to the norbornane framework. In particular, the introduction of a pentyl group may provide a useful balance between the rigidity and ring strain of the bicyclic core and the favorable low-temperature and rheological properties associated with longer alkyl chains. More generally, the modification of liquid hydrocarbon and process-fluid systems (such as drilling compositions) with functional additives has demonstrated that even relatively low additive concentrations can influence important physicochemical and flow-related properties [7].

Thermal stability is another important consideration when evaluating such compounds as potential fuel components. Studies of norbornane and its alkyl derivatives indicate that thermal decomposition is largely associated with cleavage of strained C–C bonds in the bicyclic framework. The resulting radical species can undergo hydrogen-abstraction and ring-opening reactions, leading to further decomposition products. Among the alkyl-substituted derivatives, 2-ethyl-norbornane is of particular interest because of its structural similarity to the compound investigated in the present study. Pyrolysis studies performed over a range of pressures have identified the main radical pathways and primary decomposition products of this compound. Related investigations of dicyclopentadiene-derived polycyclic hydrocarbons have also addressed their synthesis and density characteristics [8]. Related decomposition behavior has also been reported for JP-10 and alkyladamantane fuels, where the presence of alkyl side chains creates additional pathways involving hydrogen abstraction and subsequent fragmentation of the side chain [9]. Therefore, tracking how elevated temperatures influence structural stability and basic thermophysical properties is vital for assessing such hydrocarbon candidates. Temperature-dependent thermal and thermophysical behavior has also been investigated in a range of inorganic and fluid systems [10, 11]. Parallel to this, spectroscopic methods such as Raman spectroscopy can provide useful information on temperature-dependent changes in material properties [12], while similar approaches can help clarify degradation pathways and energetic durability of the synthesized compounds.

Computational methods, particularly density functional theory (DFT), provide valuable information about the energetic properties and structural stability of new hydrocarbon architectures before extensive experimental work is undertaken. Quantum-chemical calculations and conceptual DFT reactivity descriptors (such as frontier molecular orbital energies, chemical hardness, and electronic potentials) allow for reliable screening of thermodynamic properties, heats of formation, and oxidative endurance across various organic systems [13–20]. Furthermore, heats of combustion can be estimated using atomization energies or isodesmic schemes, showing good agreement with experimental data [21]. To accelerate the screening and evaluation of potential high-energy-density fuels, DFT calculations are also increasingly coupled with group-contribution models and machine learning approaches [22–24].

In parallel, regional petrochemical research has shown that the practical performance of hydrocarbon products is governed not only by the base hydrocarbon composition but also by targeted functional additives and process chemistry, and field processing stability. Recent studies published in SOCAR Proceedings describe polymer-based additives that influence asphaltene–resin–paraffin deposition in highly paraffinic oils [25], corrosion inhibitors based on natural petroleum acyl amides for CO₂-containing media [26], and oligomeric imidazoline oxypropylates for oil-spill collection [27], as well as improving three-phase separation stability under transient well flow conditions [28], new scale-inhibitor formulations [29], and optimizing process conditions and equipment operations in oil and gas production [30]. Structural changes in petroleum-derived materials during catalytic and thermo-oxidative treatment are typically followed by combining FT-IR, NMR and elemental analysis [31], the same analytical toolset applied to pentylnorbornane in this work. Finally, efficiency-oriented fuel design is consistent with broader decarbonisation efforts in the sector, including geological CO₂ storage and its monitoring [32].

Although a substantial amount of information is available on the synthesis, thermal decomposition, and energetic properties of norbornane-based and related polycyclic hydrocarbons, pentyl-substituted norbornane derivatives have received comparatively little attention. In particular, studies combining their synthesis, experimental evaluation of thermal stability, and theoretical assessment of combustion energetics are limited. The present work therefore focuses on the synthesis and characterization of pentylnorbornane, with particular attention to its thermal stability and energetic properties.

2. Materials and methods

2.1. Experimental part

Technical-grade dicyclopentadiene (DCPD) was sourced and 1-heptene commercially and used as supplied, with one exception: DCPD was freshly cracked right before running the atmospheric-pressure reactions, since it doesn't store well once depolymerized. Hydroquinone (reagent grade) was added as a polymerization inhibitor to keep things stable. For the catalytic hydrogenation steps, relied on a heterogeneous catalyst, and the high-pressure reactions were run in a stainless-steel autoclave fitted with automated temperature and pressure monitoring.

Infrared spectra were recorded on a BRUKER LUMOS FT-IR microscope, and scanned across the relevant wavenumber range to pick out the key functional groups and track how the structures changed over the course of the reactions.

NMR data (¹H and ¹³C) were collected on a BRUKER-Fourier spectrometer at 300 MHz, at room temperature (20 °C). Deuterated chloroform (CDCl₃) was the solvent throughout, and chemical shifts are reported in ppm relative to TMS as the internal standard.

Thermal behavior was assessed using a NETZSCH STA 449 F3 Jupiter simultaneous thermal analyzer under a dynamic nitrogen atmosphere. We ran the measurements from 25 to 650 °C at a heating rate of 10 K/min, with nitrogen flowing at 20 mL/min. Roughly 10 mg of each sample was loaded into Al₂O₃ crucibles, which also served as the reference. The instrument recorded TG (mass loss, %), DTG (rate of mass loss, %/min), and DTA (thermal effects, μV) curves all at

once, since the STA 449 F3 combines thermogravimetric and differential thermal analysis to capture heat flow and mass change together under the same run.

2.2. Computational part

Quantum-chemical computations in this work were carried out with the Density Functional Theory (DFT) methodology, using the ORCA program suite (version 6.1) [33, 34]. Geometry optimizations and the accompanying vibrational analyses for both n-pentylbornane ($C_{12}H_{22}$) and the relevant oxidation products (O_2 , CO_2 , and H_2O) were performed with the rSCAN-3c composite method. This functional was chosen because it already accounts for dispersion effects, corrects for basis set superposition error via a counterpoise scheme, and compensates for basis-set incompleteness at short range, making it well suited to balancing accuracy against computational cost for larger hydrocarbon molecules. No symmetry restrictions were imposed, and all geometries

were optimized in the gas phase. To verify that each optimized geometry represented a genuine minimum rather than a saddle point on the potential energy surface, analytical harmonic frequencies were calculated at the same theoretical level; the absence of any imaginary frequencies confirmed this in every case. Thermochemical quantities zero-point energy corrections, enthalpy (H), and Gibbs free energy (G) were obtained at standard conditions (298.15 K and 1.0 atm) to assess the combustion energetics of the system. The energies of the frontier orbitals (HOMO and LUMO) were also taken from the converged SCF wavefunctions, allowing the standard reactivity descriptors to be calculated. These calculations were performed within the established theoretical framework of density-functional theory and related quantum-chemical model approaches [35–37].

The ionization potential and electron affinity were estimated from the frontier orbital energies using the Koopmans approximation.

3. Results and discussion

This section reports the synthesis and physicochemical characterization of pentylbornane, its structural confirmation by FT-IR and NMR spectroscopy, an assessment of its thermal stability by TG/DTG/DTA analysis, and a DFT-based evaluation of its electronic structure and combustion energetics. The practical relevance of these properties is then examined through blending trials in TC-1 jet fuel and hydro-treated diesel fuel.

3.1. Synthesis at atmospheric pressure

The reaction between cyclopentadiene and 1-heptene went in the autoclave conditions. The dicyclopentadiene (as a result we received 164 ml of cyclopentadiene) (fig. 1) was filled to the autoclave and 281.2 ml 1-heptene was added there. In order to avoid polymerization of cyclopentadiene we add hydroquinone into the reaction.

The proportions of the reagents were 1:1 mol. The reaction went during 4-5 hours at 170-180 °C in intensive mixing mode.

The received product was separated and went through distillation. The physical and chemical properties of the substance: boiling temperature- 96-98 °C; density- 0.8755 g/cm³; refractive index- 1.4720, iodine value- 10.73 g I₂/100g.

The reaction went according to figure 2.

The obtained pentylbornane for the next step went through the catalytic hydrogenation and pentylbornane was synthesized. The reaction went at the autoclave conditions at 5-10 atm pressure (table 1), 100-130 °C temperature with addition of Ni/Cr₂O₃ as catalyst. The duration of the reaction is 8-10 hours.

The reaction went according to the figure 3.

After the reaction finished the obtained product was separated and went through distillation. The physical and chemical properties of the obtained pentylbornane: boiling temperature- 136 °C, density- 0.85 g/cm³, refractive index- 1.4605.

Structural study of the synthesized substances

The structure of the pentylbornane was studied by IR and NMR spectroscopy. The IR and NMR spectra of the synthesized compound are given below (figs. 4-6).

The FT-IR spectrum of the synthesized pentylbornane sample is presented in figure 4. The spectrum is dominated by strong aliphatic C–H stretching bands at 2960, 2924, and 2857 cm⁻¹, which correspond to the asymmetric and symmet-

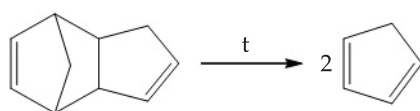


Fig. 1. Retro-Diels–Alder thermal cracking of dicyclopentadiene (DCPD) to regenerate monomeric cyclopentadiene

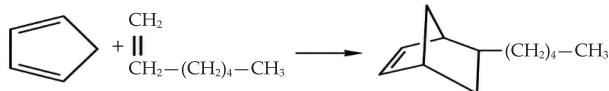


Fig. 2. Diels–Alder reaction scheme between cyclopentadiene and 1-heptene, yielding pentylbornene

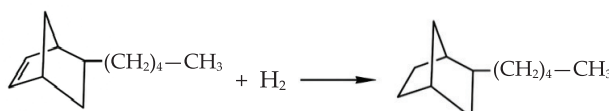


Fig. 3. Catalytic hydrogenation of pentylbornene to pentylbornane over a Ni/Cr₂O₃ catalyst

Table 1
Temperature and pressure profile recorded during the catalytic hydrogenation of pentylbornene

Time, min	Temperature, °C	Pressure, atm
0	34	10
20	103	10
50	114.2	8.9
80	94	7.7
110	109.9	7.4
140	158	7.2
170	104.5	5.9
200	96	5.1
230	99.4	4.4
260	93	3.8

ric vibrations of the $-\text{CH}_3$ and $-\text{CH}_2-$ groups of the pentyl chain and the norbornane ring. The bending vibrations of these groups are recorded at 1483 cm^{-1} ($-\text{CH}_2-$ scissor deformation) and 1379 cm^{-1} along with 1339 cm^{-1} ($-\text{CH}_3$ bending). The skeletal vibrations associated with the bicyclic core and the aliphatic chain appear in the fingerprint region at 1233 , 1150 , 1122 , 1094 , 935 , 907 , 849 , 826 , 755 , 716 , and 678 cm^{-1} .

In addition to the saturated hydrocarbon framework, a distinct peak is observed at 3069 cm^{-1} , which is characteristic of the olefinic $=\text{C}-\text{H}$ stretching vibration. Furthermore, low-intensity bands at 1620 and 1570 cm^{-1} are assigned to the $\text{C}=\text{C}$ double-bond vibrations. The presence of these bands suggests that the catalytic hydrogenation under the applied conditions did not proceed to completion, leaving a measurable fraction of unreacted double bonds in the product. This finding is consistent with the residual unsaturation indicated by the experimentally determined iodine value of the sample ($10.73\text{ g I}_2/100\text{ g}$).

The ^1H NMR spectrum of the synthesized pentylnorbornane sample is shown in figure 5. In the aliphatic region, the triplet-like signal appearing at 0.80 – 0.95 ppm with an integral intensity corresponding to 3.00 H is assigned to the terminal methyl protons ($-\text{CH}_3$) of the pentyl side chain. The complex multiplet resonances observed between 1.00 and 2.80 ppm with a combined integral value of 19.36 H correspond to the methylene protons of the alkyl substituent ($-(\text{CH}_2)_4-$) together with the methine (bridgehead) and methylene protons of the bicyclic norbornane skeleton (theoretical value: 19 H).

In addition to the aliphatic proton signals of the target saturated product, weak multiplet peaks are visible in the olefinic region at 5.40 – 6.25 ppm . These residual signals confirm that the catalytic hydrogenation under the studied conditions proceeded with high conversion but did not reach completion, leaving a small fraction of unreacted double bonds in the hydrocarbon mixture. This observation is in good agreement with the presence of the olefinic bands in the FT-IR spectrum and the measured iodine value of the sample.

The ^{13}C NMR spectrum of the synthesized product is shown in figure 6. The spectrum displays distinct signals corresponding to the saturated framework of the molecule. The resonance at 14.14 ppm is assigned to the terminal methyl carbon ($-\text{CH}_3$) of the pentyl chain. The methylene carbons ($-\text{CH}_2-$) originating from both the linear alkyl substituent and the norbornane ring are observed at 22.69 , 28.42 , 32.16 , 32.49 , 34.81 , 38.77 , 42.52 , and 45.49 ppm . The signals appearing at 45.20 , 46.41 , and 49.57 ppm correspond to the tertiary methine carbons ($-\text{CH}-$) of the bicyclic norbornane core, including the bridgehead positions and the substituted ring carbon.

Along with these main aliphatic peaks, several weak low-intensity signals are visible in the 130 – 140 ppm region, which belong to residual sp^2 olefinic carbons. This indicates that a small portion of unreacted double bonds remained after hydrogenation.

3.2. Thermal analysis of pentylnorbornane

The thermal properties of the pentylnorbornane sample were investigated by TG/DTG/DTA methods under a nitrogen atmosphere in the temperature range of 25 – 650°C , at a heating rate of 10 K/min . Analysis of the TG curve shows that, as the temperature rises, the sample undergoes a multi-stage mass loss, comprising one clearly dominant thermal

decomposition stage together with several weaker subsequent thermal transformations. In the initial temperature range of 25 – 83.4°C , a mass loss of 4.09% is observed on the TG curve (fig. 7). This relatively low-temperature loss is not attributable to intense degradation of the main molecular backbone; it can instead be associated with the release of volatile components, low-boiling residues left over from the synthesis process, and other weakly bound species. A ther-

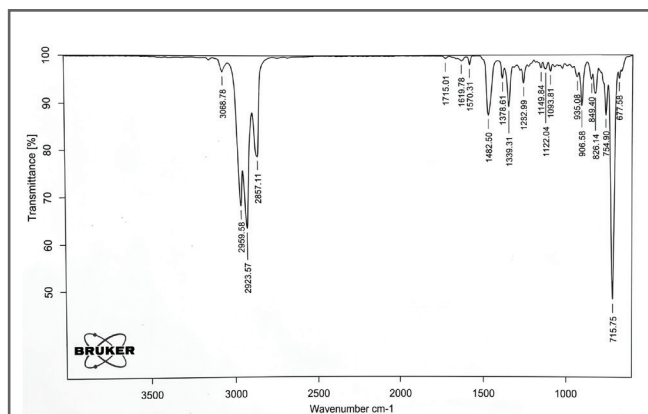


Fig. 4. FT-IR spectrum of the synthesized pentylnorbornane, showing characteristic aliphatic C–H and residual olefinic absorption bands

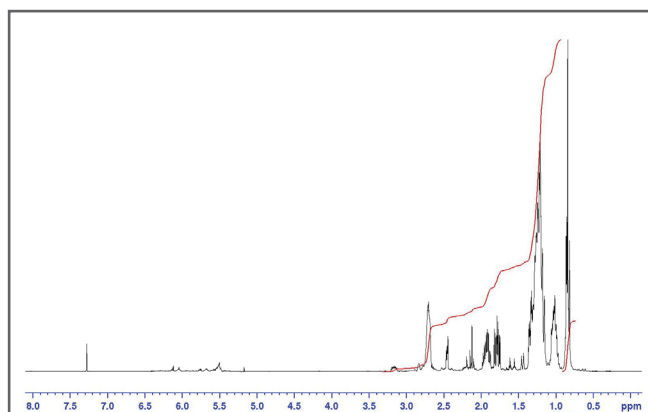


Fig. 5. ^1H NMR spectrum (300 MHz, CDCl_3) of the synthesized pentylnorbornane

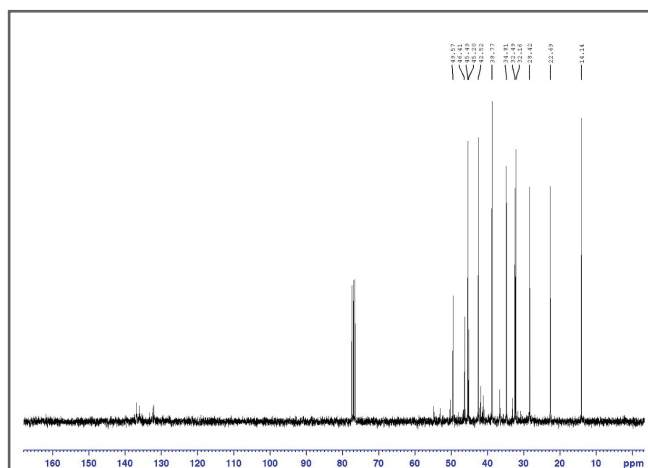


Fig. 6. ^{13}C NMR spectrum (300 MHz, CDCl_3) of the synthesized pentylnorbornane

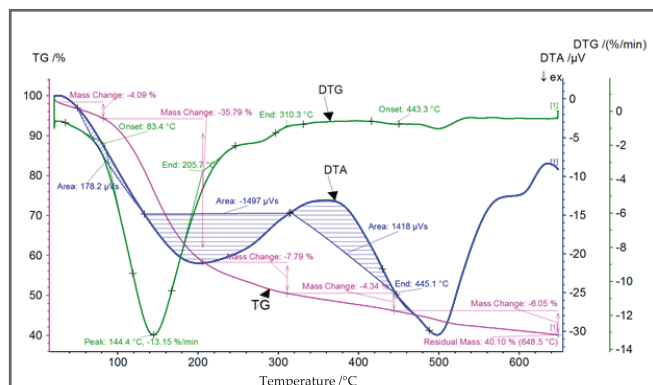


Fig. 7. Simultaneous TG/DTG/DTA thermal-decomposition profiles of pentylbornane recorded under a nitrogen atmosphere (25–650 °C, 10 K/min)

mal effect with an area of 178.2 $\mu\text{V}\cdot\text{s}$, recorded on the DTA curve between 49.5 and 132.6 °C, may be associated with the release of volatile components and/or evaporation-related processes in this region.

The main thermal transformation of the sample occurs in the range of 83.4–205.7 °C, where a mass loss of 35.79% is observed on the TG curve — the largest among all the stages recorded. A maximum peak is seen on the DTG curve at 144.4 °C, where the rate of mass change reaches 13.15 %/min; accordingly, 144.4 °C can be regarded as the characteristic temperature at which the sample's thermal decomposition reaches its highest intensity. It is presumed that this main mass-loss stage is associated with the breaking of C–C bonds in the pentylbornane structure, together with destructive transformations of the side chain and/or the norbornane skeleton, giving rise to more volatile, lower-molecular-weight hydrocarbon fragments.

On the DTA curve, a pronounced thermal effect with an area of $-1497 \mu\text{V}\cdot\text{s}$ is observed in the same temperature region. The fact that the thermal effects on the DTA and DTG curves coincide in the same temperature range shows that the sample's intensive mass loss is accompanied by a notable thermal transformation.

After 205.7 °C the mass loss on the TG curve weakens progressively. In the range of 205.7–310.3 °C an additional mass loss of 7.79% is observed, followed by further losses of 4.43% (310.3–445.1 °C) and 6.05% (445.1–650 °C). These can be attributed to the gradual transformation and decomposition of thermally more stable intermediate products formed after the main decomposition stage; the correspondingly weak DTG signal in this range indicates that these processes proceed at a comparatively low rate. A moderate thermal

effect with an area of 1418 $\mu\text{V}\cdot\text{s}$, recorded on the DTA curve between 310.3 and 445.1 °C, shows that this later-stage transformation is likewise accompanied by a measurable thermal effect, and not solely by mass loss.

At the end of the analysis, the residual mass of the sample at 650 °C is 41.85%. Such a high residual mass for a low-molecular-weight compound such as pentylbornane suggests that the sample contains a noticeable proportion of thermally stable and/or non-volatile components, which may be related to oligomeric or polymerization-type by-products of the synthesis, or to other non-volatile substances. However, it is not possible to precisely determine the chemical nature of the residual mass based solely on the TG/DTG/DTA results.

Overall, the main thermal decomposition of the pentylbornane sample occurs in the temperature range of 83.4–205.7 °C, with the maximum mass-loss rate of 13.15 %/min occurring at 144.4 °C. The main thermal transformation is accompanied by an intense DTA effect. Above 205.7 °C, the mass loss weakens progressively and continues as a series of lower-intensity thermal transformations, leaving a substantial fraction of the sample (41.85%) as residue at 650 °C.

3.3. Evaluation of fuel component performance and physicochemical properties

In order to confirm the effectiveness of the synthesized pentylbornane as a promising component and stabilizing additive in aviation fuels, it was introduced into the base TC-1 reactive fuel in a micro-amount (0.004 wt%). The main physicochemical and performance properties of the resulting fuel composition were tested according to the relevant standards (GOST), and the results are summarized in table 2.

The analysis of the test results presented in table 2 shows that the addition of only 0.004% pentylbornane leads to positive changes in the main quality and performance parameters of the TC-1 base fuel. At 20 °C, the fuel's density increased from an initial value of 805.81 kg/m³ to 808.679 kg/m³, which fully satisfies and exceeds the requirement set by the GOST 10227-86 standard (minimum 780.0 kg/m³). This slight increase in density allows for more efficient use of the fuel within the limited volume of fuel tanks in aviation technology and increases the energy supply carried per unit volume of the aircraft. At the same time, the kinematic viscosity measured at 20 °C decreased from 2.935 mm²/s to 2.864 mm²/s, fully meeting the minimum standard requirement of 1.30 mm²/s and ensuring reliable lubrication of the parts in fuel systems.

Sediment content an indicator of a fuel's resistance to oxidation and gum formation at elevated temperatures decreased slightly from 16.9 mg/100 ml in the unmodi-

Physicochemical and performance indicators of TC-1 base jet fuel and its blend with 0.004 wt% pentylbornane

Table 2

Indicators	TC-1	TC-1 + pentylbornane (0.004%)	GOST (Standard)
Density at 20 °C, kg/m ³ (by pycnometer)	805.81	808.679	GOST 3900-85 / GOST 10227-86
Kinematic viscosity at 20 °C, mm ² /s	2.935	2.864	GOST 33-82
Thermo-oxidative stability, sediment amount, mg/100 ml	16.9	15.9	GOST 11802-88
Aniline point, °C	57	58.4	—
Lower heating value (Q _d), kJ/kg	43110.63	43122.63	GOST 11065-75

fied fuel to 15.9 mg/100 ml with the addition of n-pentyl-norbornane, with both values remaining well within the 18.0 mg/100 ml limit specified by GOST 11802-88. This modest reduction is consistent with the bicyclic compound having a beneficial effect on thermo-oxidative stability. On the other hand, the increase in the aniline point from 57.0 to 58.4 °C confirms an increase in the share of saturated hydrocarbons in the mixture.

To determine the energy value of the fuel, the empirical calculation methodology of the GOST 11065-75 standard was used:

$$Q_a = [9940 + (t_{\text{aniline}} + 17.8) \cdot K] \cdot 4.1868$$

Taking into account the values of the aniline point ($t_{\text{aniline}} = 58.4$ °C) and the density-dependent coefficient ($K = 4.72$) in the formula:

$$Q_a = [9940 + (58.4 + 17.8) \cdot 4.72] \cdot 4.1868 = [9940 + 359.664] \cdot 4.1868 = 10299.644 \cdot 4.1868 = 43122.63 \text{ kJ/kg}$$

The calculated lower heating value increased to 43122.63 kJ/kg compared with 43110.63 kJ/kg for the base TC-1 fuel. Taken together, these results show that, despite a slight reduction in heating value and a decrease in sediment formation at this concentration, pentyl-norbornane improves several other key performance properties of TC-1 fuel notably density and viscosity while remaining within the limits required by the relevant GOST standards for those parameters.

Along with this, in order to study the effectiveness of the synthesized pentyl-norbornane as a stabilizing and inhibiting agent in engine fuels, its effect on the performance properties of hydrotreated diesel fuel was also investigated. For this purpose, a sample prepared by adding pentyl-norbornane to diesel fuel at a concentration of 0.05 wt% was tested for thermo-oxidative stability and low-temperature characteristics using standard methods. The results obtained are presented in table 3.

The analysis of the results shown in table 3 demonstrates that when only 0.05% pentyl-norbornane is added to the diesel fuel, a sharp improvement is observed in the fuel's thermo-oxidative stability. Specifically, the amount of sediment formed as a result of oxidation decreased from 2.0 mg/100 ml in the base diesel fuel to 0.1 mg/100 ml in the modified fuel. This 20-fold reduction in sediment content clearly proves that the bicyclic structure of the synthesized substance strongly slows down gum formation and oxidation processes in the diesel fraction, exhibiting a powerful antioxidant and inhibiting effect.

Regarding low-temperature behavior, adding pentyl-norbornane caused no deterioration in the cloud point, which shifted from -34 to -37 °C. The freezing point moved further, from -41 to -42 °C in the treated fuel, confirming that the diesel retains fully acceptable low-temperature handling characteristics. These complex results obtained confirm that pentyl-norbornane is a promising additive that increases the operational reliability and storage life of diesel fuels.

3.4. Computational study

The fully optimized geometry of pentyl-norbornane (fig. 8) clearly highlights the structural contrast between its flexible linear side chain and the rigid bicyclic core. As seen in the optimized model, the pentyl chain settles into a relaxed, staggered all-trans conformation, which minimizes steric strain along the alkyl backbone. Within this chain, the carbon-carbon (C-C) bond lengths remain close to 1.527–1.529 Å, while the aliphatic C-H bonds fall in the range of 1.094–1.099 Å. In contrast, the bicyclic norbornane framework shows slightly longer C-C single bonds, ranging from about 1.540 up to 1.564 Å, especially around the ring-junction and bridgehead positions. This elongation directly reflects the inherent ring strain of the bridged bicyclic system. The bridgehead C-H bond lengths stay close to 1.094–1.096 Å. Overall, this balanced spatial arrangement between the bulky bicyclic head and the uncoiled alkyl tail yields a highly stable minimum-energy structure, providing a solid baseline to evaluate the molecule's thermodynamic behavior.

To evaluate the electronic stability and chemical reactivity of pentyl-norbornane, the spatial distributions of its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were analyzed. As shown in the orbital maps (fig. 9), the HOMO electron density is fully delocalized across the entire molecule, spanning both the flexible pentyl tail and the bicyclic norbornane core via σ -bond networks. In contrast, the LUMO is concentrated mainly over the strained bicyclic framework, with little amplitude on the distal side-chain carbons. This spatial localization highlights the norbornane core as the primary site susceptible to electron acceptance during thermal excitation or degradation. Crucially, the frontier orbitals exhibit a wide energy gap of 8.917 eV, which directly translates to high kinetic stability and low chemical reactivity under operational conditions. This substantial electronic inertia indicates that pentyl-norbornane is highly resistant to premature oxidation and side reactions, supporting its potential as a thermally stable synthetic fuel candidate.

To systematically evaluate the overall chemical reactivity,

Table 3 Effect of pentyl-norbornane (0.05 wt%) on the thermo-oxidative stability and low-temperature properties of hydrotreated diesel fuel		
Indicators	Hydrotreated diesel (base)	Diesel + pentyl-norbornane (0.05%)
Thermo-oxidative stability (sediment), mg/100 ml	2.0	0.1
Cloud point, °C	-34	-37
Freezing point, °C	-41	-42

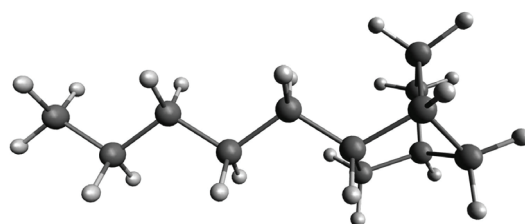
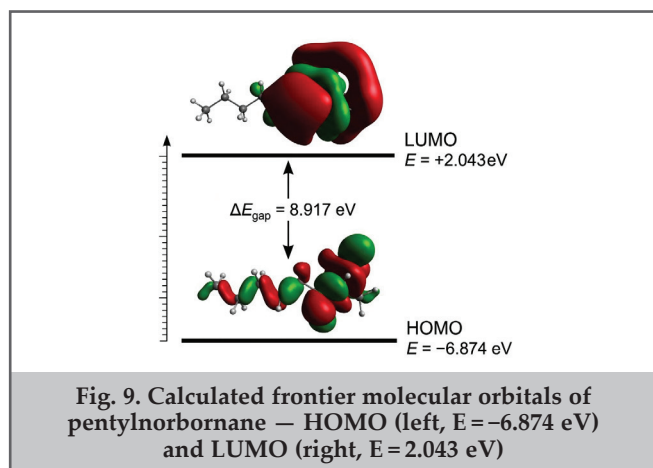


Fig. 8. DFT-optimized (r2SCAN-3c) equilibrium geometry of pentyl-norbornane, with selected bond lengths (Å) labeled



Parameter	Formula / Relation	Value	Unit
E_{HOMO}	Highest Occupied Molecular Orbital	-6.874	eV
E_{LUMO}	Lowest Unoccupied Molecular Orbital	+2.043	eV
Energy gap (ΔE)	$E_{\text{LUMO}} - E_{\text{HOMO}}$	8.917	eV
Ionization potential (I)	$-E_{\text{HOMO}}$	6.874	eV
Electron affinity (A)	$-E_{\text{LUMO}}$	-2.043	eV
Electronegativity (χ)	$(I+A)/2$	2.415	eV
Chemical potential (μ)	$-\chi$	-2.415	eV
Chemical hardness (η)	$(I-A)/2 = \Delta E/2$	4.459	eV
Chemical softness (S)	$1/(2\eta)$	0.112	eV ⁻¹
Electrophilicity index (ω)	$\mu^2/(2\eta)$	0.654	eV

Parameter	Symbol / Relation	Calculated Value	Unit
Combustion Enthalpy	$\Delta H^\circ_{\text{comb}}$	-6546.53	kJ/mol
Combustion Gibbs Free Energy	$\Delta G^\circ_{\text{comb}}$	-6726.61	kJ/mol
Specific Heat of Combustion	Q_{net}	39.36	MJ/kg

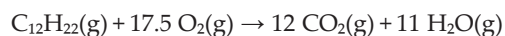
electronic resistance, and structural stability of pentylbornane, conceptual DFT global reactivity descriptors were calculated using the frontier molecular orbital energy levels (table 4). The calculated ionization potential ($I = 6.874$ eV) and electron affinity ($A = -2.043$ eV) demonstrate that removing an electron from the saturated skeleton requires considerable energy, while the negative electron affinity confirms that the molecule has no thermodynamic drive to accept free electrons. The wide HOMO–LUMO energy gap (8.917 eV) directly correlates with high electronic stability and low chemical reactivity under operating conditions.

This pronounced electronic inertia is further reinforced by the global reactivity indices. The compound exhibits a moderate electronegativity ($\chi = 2.415$ eV) and a correspond-

ing negative chemical potential ($\mu = -2.415$ eV), reflecting an electron-dense yet chemically unreactive non-polar framework. Crucially, pentylbornane displays a high chemical hardness ($\eta = 4.459$ eV) paired with a low chemical softness ($S = 0.112$ eV⁻¹), classifying it as a distinctly hard molecular system. In fuel chemistry, high chemical hardness is an essential metric because it ensures that the saturated hydrocarbon core resists radical attacks, thermal isomerization, and spontaneous electronic degradation prior to the actual combustion process. Finally, the low electrophilicity index ($\omega = 0.654$ eV) confirms the non-corrosive and chemically passive nature of the molecule, indicating that this fully saturated bicyclic framework possesses good thermal and electronic endurance for high-density synthetic fuel applications.

3.5. Quantum-chemical combustion energetics and performance indicators

The energetic potential and heat-release capability of pentylbornane ($C_{12}H_{22}$) as a candidate high-density synthetic fuel component were theoretically investigated through its full stoichiometric combustion process:



Standard thermodynamic relations and quantum-chemical conversion protocols were applied to process the thermochemical data obtained from vibrational frequency calculations. The gas-phase optimization yielded a total enthalpy of -470.05733055 Eh and a Gibbs free energy of -470.10820748 Eh for pentylbornane. Incorporating these values alongside reference energies for molecular oxygen, carbon dioxide, and water vapor computed at the same level of theory (O_2 , $H = -150.31075959$ Eh, $G = -150.33403975$ Eh; CO_2 , $H = -188.55483115$ Eh, $G = -188.57909714$ Eh; H_2O , $H = -76.39373550$ Eh, $G = -76.41516087$ Eh) enabled the direct determination of the reaction enthalpy (ΔH_{comb}) and Gibbs free energy change (ΔG_{comb}). Furthermore, the gravimetric specific energy (Q_{net}) was derived by normalizing the absolute combustion enthalpy over the molecular weight of the fuel ($M = 166.31$ g/mol), following the same fuel-characterization methodology. The resulting thermochemical metrics are given in table 5.

The calculated thermochemical metrics summarized in table 5 illustrate the substantial thermodynamic driving force behind the oxidation process. The complete combustion of pentylbornane releases a large amount of heat, as evidenced by the strongly exothermic reaction enthalpy ($\Delta H_{\text{comb}} = -6546.53$ kJ/mol). This significant thermal output is further supported by a heavily negative Gibbs free energy change ($\Delta G_{\text{comb}} = -6726.61$ kJ/mol), confirming that the oxidative degradation of the hydrocarbon is thermodynamically spontaneous and irreversible under standard operating conditions.

From an applied energy standpoint, the achieved gravimetric energy output ($Q_{\text{net}} = 39.36$ MJ/kg) reflects the structural advantage provided by the bridged bicyclic skeleton: strained polycycloalkane frameworks store additional internal ring-strain energy, which is liberated during high-temperature C–C bond cleavage, offering enhanced thermal performance relative to conventional acyclic hydrocarbons of comparable size.

These DFT-derived parameters are internally consistent with the thermal-analysis results presented above: the high

chemical hardness ($\eta = 4.459$ eV) and wide HOMO–LUMO energy gap (8.917 eV) determined for pentylnorbornane are in line with a compound that remains largely intact up to ≈ 83 °C and then decomposes sharply and predominantly in a single main stage (83.4–205.7 °C), rather than degrading grad-

ually from the outset behavior consistent with a kinetically stable, electronically «hard» saturated hydrocarbon. The high computed gravimetric combustion energy ($Q_{\text{net}} = 39.36$ MJ/kg) further indicates that, structurally, pentylnorbornane is an energy-dense hydrocarbon component.

Conclusion

Pentylnorbornane was successfully synthesized in a two-step sequence Diels–Alder cycloaddition of in situ generated cyclopentadiene with 1-heptene followed by catalytic hydrogenation and its structure was confirmed by FT-IR and $^1\text{H}/^{13}\text{C}$ NMR spectroscopy. Minor residual unsaturation detected consistently by the iodine value, IR, and NMR data indicates that the hydrogenation step, while efficient, did not proceed to full completion under the conditions studied.

Thermogravimetric analysis established that the compound is thermally robust below ≈ 83 °C and decomposes predominantly through a single, well-defined stage between 83.4 and 205.7 °C, with a substantial non-volatile residue (41.85%) remaining at 650 °C. This behavior is consistent with the DFT-derived electronic structure: the wide HOMO–LUMO gap (8.917 eV), high chemical hardness (4.459 eV), and low electrophilicity index (0.654 eV) all point to a kinetically and electronically stable saturated hydrocarbon that resists premature oxidative and radical degradation.

Quantum-chemical combustion calculations predict a strongly exothermic reaction enthalpy ($\Delta H^\circ_{\text{comb}} = -6546.53$ kJ/mol) and a gravimetric heat of combustion ($Q_{\text{net}} = 39.36$ MJ/kg), values that place pentylnorbornane among energy-dense, JP-10-type norbornane derivatives. Practical fuel-blending trials support this theoretical picture: incorporation of pentylnorbornane into TC-1 jet fuel (0.004 wt%) increased density and lowered viscosity while remaining within GOST limits, and its addition to hydrotreated diesel (0.05 wt%) produced up to a 20-fold reduction in oxidation sediment together with improved cloud and freezing points.

Taken together, these experimental and computational results indicate that pentylnorbornane combines adequate thermal stability, favorable combustion energetics, and a measurable stabilizing/antioxidant effect in real fuel matrices, supporting its potential as a high-density hydrocarbon component and multifunctional additive for aviation and diesel fuels. Further work should address optimization of the hydrogenation step to eliminate residual unsaturation, a broader concentration screening in both fuel types, and direct experimental determination of the heat of combustion to validate the DFT predictions.

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