

Syntheses and Characterization of Cyclopropane-fused Hydrocarbons as New High Energetic Materials

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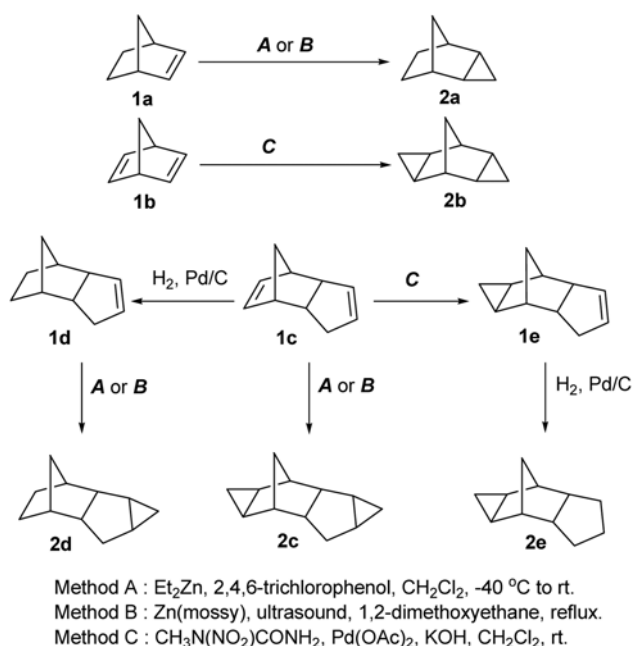
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Major increases in liquid-fueled propulsion performance have occurred in the past 100 years since the Wright brothers first flew in 1903. The fuel parameters most relevant to gas turbine engines and vehicle performances are the heat of combustion on a mass basis in air and the density.¹ The liquid propellant rockets, the key propellant-related parameters are specific impulse I_{sp} (thrust divided by propellant mass flow rate) and propellant density.² There are many other parameters that are important to reliable engine operation relating to fuel composition, volatility, combustion performance, stability, and cost. In general, I_{sp} is proportional to the square root of the ratio of the flame temperature to the combustion-product molecular weight, so that I_{sp} is maximized by high flame temperatures and low-molecular weight combustion products. A key parameter for both rockets and air breathing missiles is the propellant density.³ Several types of hydrocarbons are being examined as possible alternatives to RP-1, mainly focusing on high density and high heat of combustion.⁴ In this regard, highly strained hydrocarbons offer high I_{sp} and potentially increased density, but are relatively uncharacterized. We have programmed a research on developing and characterizing highly energetic cyclopropane-ring fused hydrocarbons and herein wish to report our preliminary results. It is known that hydrocarbons possessing a norbornane or dicyclopentane skeleton exhibited high densities and heats of combustions. Based on our hypothesis that hydrocarbons of cyclopropane-fused norbornanes and dicyclopentadienes might have high energy and high density, we designed several highly energetic molecules and their physical properties compared to those of known fuels.

Results and Discussion

There are numerous synthetic methods for cyclopropanes,⁵ among which cyclopropanations of carbene-related methods are most general for preparation of our target molecules. Basically, we employed three methods to obtain cyclopropane-fused hydrocarbons as shown in Scheme 1. Both method A⁶ and B⁷ were applicable to multi-gram scales of **2a** in 20% and 40% yields, respectively. *In-situ* generated diazomethane was used for preparation of bicyclic cyclopropane-fused molecule **2b**.⁸ Dicyclopentadiene was used for prepa-



Scheme 1

ration of **2c**, **2d**, and **2e**. Compound **2c** was prepared by utilizing method A or B. Preparation of **2d** was done in two steps: hydrogenation of **1c** to **1d** followed by cyclopropanation to **2d**. Use of a stoichiometric amount of carbene with **1c** afforded a mixture of product **1e** which upon hydrogenation furnished to **2e**. Since preparation of these compounds **2a-e** resulted in saturated hydrocarbons having similar polarities and boiling points, the most important factor in preparations of these compounds is in completion of reactions. In order to get pure compounds, we have used a slight excess of all reagents and finally isolated these compounds by distillation. Five synthetic compounds **2a-e** were evaluated for their densities and heats of combustion compared to known fuels, JP-5, JP-8, JP-9, JP-10, RJ-4, and RJ-5.

The results are summarized in Table 1. Overall, all cyclopropane-fused compounds **2a-e** show comparable to higher than JP series and RJ-4 in terms of density and heat of combustion. Tricyclic compound **2a**, however, showed the least heat contenting compound. Tetracyclic compound **2b-e**

Table 1. Physical properties of cyclopropane-fused hydrocarbons

No	Compounds	Density	Heats of combustion		
			Btu/gal	MJ/kg	kcal/mol
1	2a	0.94	139,967	41.493	9.318
2	2b	1.00	154,201	43.091	10.265
3	2c	1.02	154,378	42.182	10.277
3	2d	0.99	153,373	42.331	10.210
3	2e	1.00	153,191	42.557	10.198
4	JP-5 (C₁₂H₂₂)	0.81	123,828	42.600	8.243
5	JP-8 (C₁₁H₂₁)	0.81	124,409	42.800	8.282
6	JP-9	0.94	142,000	42.106	9.453
7	JP-10	0.94	142,000	42.106	9.453
8	RJ-4	0.94	141,000	41.810	9.387
9	RJ-5	1.08	161,000	41.552	10.718

$Q_{\text{net}} = 10.479 \text{ kcal/g} \times 4.186 \text{ MJg/kcal/kg} - 0.2122 \times 11.18 \text{ (H wt\%)} = 41.493 \text{ MJ/kg} = 9.913 \text{ kcal/g} = 9.318 \text{ kcal/mL}$. JP-5: Aromatics (19 vol%), Naphthenes (34 vol%), Paraffins (45 vol%), Olefins (2 vol%). JP-8: Aromatics (18 vol%), Naphthenes (35 vol%), Paraffins (45 vol%), Olefins (2 vol%). JP-9: Methylcyclohexane (10 vol%), Tetrahydrodicyclopentadiene (65-70 vol%), hydrogenated norbornadiene dimer (20-25 vol%)

have high densities ranging from 0.99 to 1.02 almost similar to water and their heat of combustion ranging from 10,198 to 10,265 kcal/mL slightly lower than **RJ-5**. MJ/kg, the most important factor in high-energetic fuels, of compound **2b** is 43,091 which is about 5% higher than **RJ-5**. Although many other factors concerning fuel performance are to be considered, our approach to cyclopropane-fused hydrocarbons could be a future field in new high-energetic materials.

Experimentals

General Procedure for Preparation of 2a-e.

Method A: To a solution of 2,4,6-trichlorophenol (1.0 mmol) in CH₂Cl₂ (10 mL) at -40 °C was added Et₂Zn (1.0 mmol). After stirred for 15 min, CH₂I₂ (1.0 mmol) was added, and then after 15 min, **1** (0.5 mmol) was added. The reaction mixture was stirred for 12 h at room temperature. The reaction mixture was diluted with pentane (25 mL) and the organic phase was washed sequentially with 10% aq HCl (2 × 25 mL), and then saturated aq NaCl (25 mL). The organic layer was dried over MgSO₄ and concentrated under reduced pressure. Fractional distillation afforded the desired **2** as a colorless liquid.

Method B: To slurry of mossy zinc (210 mmol) in 1,2-dimethoxyethane (80 mL) activated by under ultrasound for 2 h was added rapidly **1** (100 mmol), and the mixture was heated to reflux. After diiodomethane (200 mmol) was added, the mixture was refluxed for 12 h. The mixture was then cooled to 25 °C, diluted with pentane (500 mL). The organic phase was washed sequentially with 10% aq HCl (2 × 200 mL), saturated aq NaCl (100 mL), dried over MgSO₄ and concentrated under reduced pressure. Fractional distillation afforded the desired **2** as a colorless liquid.

Method C: **1** (0.2 mol), CH₂Cl₂/diethyl ether (40 mL/40 mL) and ~80 mL of aqueous KOH solution (40%) were

placed in a flask equipped with a stirrer, a coiled condenser. Then the solution of *N*-methyl-*N*-nitrosourea⁹ (2-3 g) and Pd(OAc)₂ (0.3 mmol) in CH₂Cl₂ (5 mL) were added at 10-20 °C. After nitrogen gas evolution was ceased, solid *N*-methyl-*N*-nitrosourea (~1.5 g/min, total amount 30-40 g) was added in several portions over 30 min. Upon completion of the reaction, the organic layer was extracted with hexane, washed with saturated NaCl solution, dried over anhydrous MgSO₄, filtered, and evaporated under reduced pressure. Fractional distillation afforded the desired **2** as a colorless liquid.

Tricyclo[3.2.1.0^{2,4}]octane (2a): *Method A:* 110 mg, 20%. *Method B:* 4.2 g, 40%.

¹H NMR (400 MHz, CDCl₃) δ 2.21 (s, 2H), 1.41-1.45 (m, 2H), 1.22-1.27 (m, 2H), 0.88-0.93 (m, 1H), 0.65-0.68 (dd, *J* = 6.8, 3.6 Hz, 2H), 0.56-0.58 (d, *J* = 10.4 Hz, 2H), 0.26-0.29 (m, 1H), -0.13 ~ -0.08 (dd, *J* = 12.8, 6.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 35.62, 29.76, 26.76, 14.61, 0.98.

Tetracyclo[3.3.1.0^{2,4}.0^{6,8}]nonane (2b): *Method B:* 1.2 g, 10%. *Method C:* 8.41 g, 70%.

¹H NMR (400 MHz, CDCl₃) δ 2.26 (s, 2H), 0.97-0.99 (dd, *J* = 7.2, 3.2 Hz, 4H), 0.71-0.74 (m, 2H), 0.39-0.40 (t, *J* = 1.6 Hz, 2H), 0.20-0.25 (dd, *J* = 13.2, 6.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 35.58, 18.75, 14.23, 6.21.

Pentacyclo[6.3.1.0^{2,7}.0^{3,5}.0^{9,11}]dodecane (2c): *Method A:* 385.6 mg, 88%. *Method B:* 7.97 g, 58%.

¹H NMR (400 MHz, CDCl₃) δ 2.30 (s, 1H), 2.23-2.28 (m, 2H), 2.12 (s, 1H), 1.96-2.02 (m, 1H), 1.47-1.52 (m, 1H), 1.32-1.38 (m, 1H), 1.16-1.21 (m, 1H), 1.04-1.08 (dt, *J* = 10.8, 2 Hz, 1H), 1.00-1.02 (dd, *J* = 7.6, 2.4 Hz, 2H), 0.83-0.89 (m, 1H), 0.73-0.75 (d, *J* = 10 Hz, 1H), 0.54-0.59 (tdd, *J* = 8.4, 4.4, 1.2 Hz, 1H), 0.43-0.46 (dt, *J* = 5.2, 3.2 Hz, 1H), -0.08 ~ -0.20 (m, 1H), -0.36 ~ -0.33 (dd, *J* = 8.0, 4.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 52.78, 48.15, 40.42, 39.91, 30.94, 27.66, 22.49, 19.40, 13.78, 9.84, 9.03, 0.83.

Tetracyclo[6.2.1.0^{2,7}.0^{3,5}]undecane (2d): 10% Pd/C (0.126 g, 0.118 mmol) was added the solution of **1c** (11.42 g, 82.1 mmol) in *n*-Hexane (37.00 g) and then was degassed. The solution was saturated with H₂ gas under hydrogen atmosphere and was stirred at rt for 4 h. The reaction mixture was filtered, and the resultant filtrate was evaporated. Thermal crack of the residue afforded the crude **1c**. The crude product was purified with vacuum distillation to give **1d** as colorless oil (8.20 g, 74%).

¹H NMR (400 MHz, CDCl₃): δ 5.62-5.65 (m, 1H), 5.52-5.55 (m, 1H), 2.96-3.01 (m, 1H), 2.48-2.55 (m, 1H), 2.17-2.26 (m, 3H), 2.08-2.11 (d, *J* = 10.4 Hz, 1H), 1.38-1.45 (m, 2H), 1.28-1.20 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 132.92, 130.36, 52.93, 42.43, 41.14, 40.95, 39.53, 32.24, 25.22, 21.99.

Method A: 5.07 g, 90%

¹H NMR (400 MHz, CDCl₃) δ 2.20-2.28 (m, 3H), 2.02 (s, 1H), 1.76-1.81 (m, 1H), 1.57-1.67 (m, 2H), 1.45-1.51 (dd, *J* = 13.6, 8.8 Hz, 1H), 1.42-1.44 (m, 2H), 1.31-1.37 (m, 1H), 1.25-1.30 (m, 2H), 1.06-1.11 (m, 1H), 0.56-0.61 (tdd, *J* = 8.4, 4.0, 0.8 Hz, 1H), -0.35 ~ -0.32 (dd, *J* = 8.4, 3.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 51.06, 46.66, 42.86, 41.79,

41.47, 28.70, 22.64, 22.56, 21.25, 20.31, 13.96.

Tetracyclo[6.2.1.0^{2,6}.0^{8,10}]undecane (2e): Method C: **1e** (113.5 g, 95%) was reduced with hydrogenation

To an oven-dried 100 mL was placed 3-tetracyclo[6.2.1.0^{2,6}.0^{8,10}]undecene (113.5 g, 776 mmol) in *n*-Hexane (380 mL), and 5% Pd/C (4.00 g, 1.87 mmol). The reaction mixture was cooled down to -78 °C bath and evacuated air and any moisture under vacuum, then charged with hydrogen gas. The reaction mixture was warmed up to room temperature and stirred for 12 h. The reaction mixture was filtered with an aid of celite545, and the filtrate was concentrated under reduced pressure. Fractional distillation afforded the desired Tetracyclo[6.2.1.0^{2,6}.0^{8,10}]undecane (115 g, 100%) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ 2.26 (s, 2H), 0.97-0.99 (dd, *J* = 7.2, 3.2 Hz, 4H), 0.71-0.74 (m, 2H), 0.39-0.40 (t, *J* = 1.6 Hz, 2H), 0.20-0.25 (dd, *J* = 13.2, 6.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 35.58, 18.75, 14.23, 6.21.

Density Measurement: Automatic pycnometer (Model AccuPyc 1330, made by Micrometrics, USA) was used. The volume of the empty cell (*V*_{cell}) was measured. This cell, charged with the sample (*M* g), was pressurized at 25 psi by helium atmosphere and measured the cell pressure (*P*₁). Then, when its expand valve was opened, the cell pressure was changed to *P*₂. The volume of the sample in Table 1 was calculated by the following equation:

$$V_{\text{sample}} = V_{\text{cell}} + V_{\text{exp}}(P_2 - P_{\text{air}})/(P_2 - P_1)$$

$$\text{Density} = M/V_{\text{sample}}$$

Heat of Combustion: The heat of combustion was measured by using 1261 Bomb calorimeter (made by Parr, USA). Calibration of the bomb calorimeter was done by using benzoic acid. Thus, benzoic acid (1.00 g) was placed in a capsule connected with Ni-Cr wire and charged with 450 psi of oxygen gas. Water (2,000 g) was charged in bucket of the calorimeter. The combustion was done and the temperature changed was measured as *T*.

Heat of combustion was calculated as the follows.

$$W = (H_b m_b + e_1 + e_2 + e_3) / T$$

$$H_c (\text{cal/g}) = (WT - e_1 - e_2 - e_3) / m$$

$$Q_{\text{net}} (\text{MJ/Kg}) = H_c \text{ kcal/g} \times 4.186 \text{ MJ}\cdot\text{g/kcal}\cdot\text{kg} \\ - 0.2122 \times H \text{ wt\%}$$

*Q*_{net} = Net of heat of combustion

*H*_c = Gross heat of combustion.

T = Observed temperature rise.

*e*₁ = Heat produced by burning the nitrogen portion of the air trapped in the bomb to form nitric acid.

*e*₂ = The heat produced by the formation of sulfuric acid from the reaction of the reaction of sulfur dioxide, water and oxygen.

*e*₃ = Heat produced by the heating wire and cotton thread.

m = Mass of the sample.

*H*_b = Gross heat of combustion with benzoic acid.

*m*_b = Mass of benzoic acid.

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