

Energetics of the 2 + 2 cyclization of limonene

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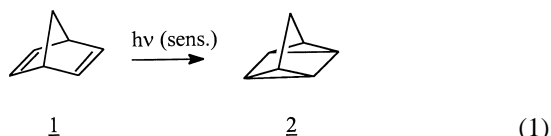
Abstract

The hydrocarbon 1,2-dimethyltricyclo[3.3.0.0^{2,7}]octane (**4**) was synthesized from carvone in two steps. Compound **4** is the product that would be obtained from the photochemical 2 + 2 intramolecular cyclization of limonene. The calculated enthalpy for the transformation of limonene to compound **4** is 7.2 kcal/mol, the endothermicity of the reaction being attributed to ring strain in the product. This strain energy, accompanied by the increase in specific gravity obtained upon cyclization, gives compound **4** a larger heat of combustion, on a volumetric basis, than jet fuel. Other naturally occurring terpenes, which are inexpensive and abundant, bear consideration as starting materials for easily prepared high energy density materials. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Limonene; Strain; Photocyclization; Fuel; Carvone; Camphor

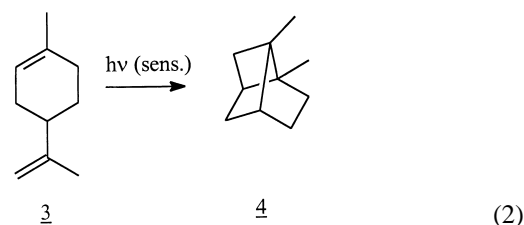
1. Introduction

Photoisomerization of organic compounds to produce strained and energy-rich products has received attention as a way to store solar energy [1]. Some of the most promising systems are based on the 2 + 2 photocyclization of norbornadiene to quadricyclane (Eq. (1)) [2–4] and derivatives of



this compound [5,6]. Other 2+2 photocyclizations have been explored for solar energy storage [1,7,8], but these systems generally have lower quantum yields and lower molar storage capacities. Intriguing systems based on the natural products carvone and limonene have been proposed [9], which have the advantage that the starting materials are cheap and abundant. Indeed, a report has been appeared [10] claiming that the sensitized photocyclization of limonene proceeds with a quantum yield near 0.5, according to Eq. (2). While

this photochemical transformation is unlikely to succeed based on well-known photochemical principles (*vide infra*),

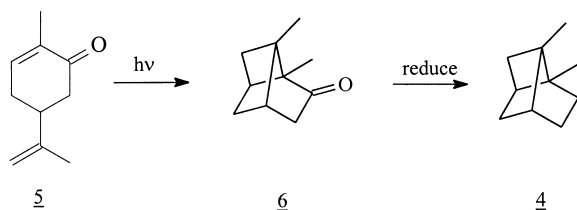


our interest in renewable resources, and the possibility that abundant plant-derived chemicals can be conveniently converted into high energy density materials [11], have prompted us to reinvestigate the photochemistry of limonene and compound **4** as a high energy density chemical. Since efforts at repeating the photochemistry depicted in Eq. (2) failed in our hands, we have prepared compound **4** (1,2-dimethyltricyclo[3.3.0.0^{2,7}]octane) by a different route, one that assembled its carbon skeleton photochemically from the plant-derived compound, carvone (**5**). This particular reaction is one of the earliest known examples of a photochemical transformation [12]. The photoproduct is tricyclic ketone **6** (carvone camphor), which was reduced to hydrocarbon **4** (Scheme 1). We report the full characterization of **4** and computational data on the heat of combustion

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Scheme 1.

of both limonene and 4, which provide information on the suitability of 4 as a high energy density fuel.

2. Experimental

2.1. Materials

Reagents were obtained from Aldrich Chemical Co. Carvone was distilled before use. Limonene cyclization experiments and the preparation of carvone camphor (6) were performed in Pyrex vessels using 365 nm light supplied by a Blak-Ray lamp situated a few centimeters from the reaction vessel. Density was measured in a 2-ml pycnometer using pure 4. Material was transferred to the flask as a supercooled liquid at a slightly elevated temperature (25°C). Infrared matrix spectra were obtained by depositing small amounts of analyte in an argon matrix at 6 K using an APD cryostat and a Nicolet Magna 550 FTIR spectrometer with an MCT detector.

2.2. Attempted photocyclization of limonene

The attempted photocyclization of limonene (Eq. (2)) was carried out according to the procedure in [10], using xanthone as sensitizer in cyclohexane solution. Both aerated and degassed solutions were subjected to prolonged irradiation (several hours), and no peaks could be found by gas chromatography–mass spectrometry (GC–MS) whose mass spectrum could be matched with the one reported [10] for compound 4. Numerous small peaks with long retention times relative to limonene were observed, the mass spectra of which were consistent with trace levels of photooxidation.

2.3. Carvone camphor (6)

Carvone camphor was prepared from carvone by a modification of the published methods [12,13] using methanol as solvent, which gave very low levels of impurities. Typically, 10 g of carvone dissolved in 500 ml methanol was irradiated for several weeks with Blak-Ray lamps. Methanol was removed by rotary evaporation, and the residue was steam distilled to give the solid product (20–30% yield). This material was not further dried before being used in the next step. GC analysis indicated that it was greater than 99% pure (exclusive of water).

2.4. 1,2-Dimethyltricyclo[3.3.0.0^{2,7}]octane (4)

This material was prepared by the Huang–Minlon [14] modification to the Wolff–Kishner reaction. To a 25 ml diethylene glycol solution of moist carvone camphor (2.5 g, prepared as above), 4 ml hydrazine was added, and then solid KOH (5 g). This mixture was stirred and heated to 115°C for 15 min, and then the product was distilled out of the reaction mixture at 200°C through a short Vigreux column. The product was collected as a semi-solid, condensing on the walls of the distillation apparatus. It had to be removed from the glassware several times with a heat gun to prevent blockage and was finally separated from traces of diethylene glycol by extraction with pentane. It was isolated as a white low melting solid (65% yield). Purity was greater than 99% by GC analysis. A sample, sublimed at atmospheric pressure, melted to a liquid crystalline form at 56°C and melted completely at 83°C. ¹H NMR (300 MHz, CDCl₃): 0.88, s, 3H; 1.01, s, 3H; 1.14–1.22, m, 3H; 1.40–1.72, m, 6H; 1.85–1.96, m, 1H. ¹³C NMR (75.4 MHz, CDCl₃): 13.08 (CH₃), 14.72 (CH₃), 31.74, 32.20, 34.80, 39.64, 44.06, 44.76, 52.74 (4°), 54.42 (4°). Exact mass calculated for C₁₀H₁₆: 136.1252. Found: 136.1244.

2.5. Computational methods

Ab initio calculations were performed with Gaussian 98 [15] that help to determine the increase in strain energy for reaction (2). We used two methods for this study: density functional theory (B3LYP) [16,17] and complete basis set extrapolation (CBS-QB3) [18]. The B3LYP is the faster of the two techniques but typically provides less accuracy than the CBS technique. As a test of our calculations, we compared the calculated IR spectra for the molecules studied to those measured using matrix isolation FTIR spectroscopy.

2.6. Matrix isolation techniques

Matrix isolation experiments were conducted by depositing the argon mixtures containing the vapor phase of the samples to be studied. A mixing ratio of 1 part sample per 1000 parts argon was typically used. The individual samples (carvone, carvone camphor, limonene, or compound 4) were mixed with argon in a 1 l sample bulb to a total pressure of roughly 800 Torr. The mixtures were deposited on a cold (6 K) CsI window at a rate of about 4 Torr/min for roughly 20 min. Under these conditions, high signal to noise levels could be obtained with 20 min scans.

3. Results and discussion

3.1. Photoisomerization of limonene

Limonene will not undergo sensitized photocyclization, in contrast to the results reported in [10], which can be

readily explained by an examination of the energies involved. Limonene is a non-conjugated diene, and its triplet energy must lie well above that of conjugated dienes (e.g. 60 kcal/mol for 1,3-butadiene) [19], closer to the triplet energy of isolated double bonds (e.g. 78 kcal/mol for 2-butene). Xanthone (the sensitizer used in [10]), whose triplet energy is 74 kcal/mol and is easily accessible by irradiation with 365 nm light, is unable to transfer its excited state energy to limonene. Unfortunately, direct irradiation with higher energy light or sensitization with a higher energy sensitizer (such as atomic mercury) are both impractical and can lead to unwanted side products [19]. Norbornadiene, whose double bonds are held in close proximity (but are not conjugated), has a lower triplet state energy (67 kcal/mol), and does undergo sensitized photocyclization. Thus, limonene would require some unusual structural feature that would bring its double bonds in close proximity, which is clearly absent, as can be seen by examining the structure of limonene, and noting the relatively large distance between the double bonds.

Side by side tabulations of the mass spectrum for **4** obtained in this study, and the mass spectrum claimed for **4** earlier [10] are shown in Table 1. Our data are clearly in conflict with the earlier results, making it likely that the earlier data were obtained on a minor photoproduct, perhaps derived from photooxidation.³

3.2. Synthesis of (**4**)

In spite of the failed photochemical cyclization of limonene, we were still interested in the tricyclic product **4** as a high energy density material, since it should possess significant ring strain. In addition, a short synthesis of a strained hydrocarbon that could be obtained in bulk is of interest since these types of materials have been proposed as high energy additives to gasoline and jet fuel [11].

The synthesis started from the readily available natural product carvone (Scheme 1). Photocyclization of carvone proceeds in modest yield to produce carvone camphor of high purity. The purification of this material is somewhat tedious [12] and was found to be unnecessary in the present instance; after steam distillation, the moist carvone camphor was subjected directly to Wolff–Kischner reduction conditions. The final hydrocarbon was isolated by simple distillation in 13–20% yield based on the starting carvone.

3.3. Heat of combustion of (**4**)

Prior to pursuing a sophisticated and accurate experimental heat of combustion study on **4**, which would require at a minimum the scale up of the synthesis and a lengthy purifi-

³ That the authors in [10] used 250 nm light does not alter our conclusion, since triplet xanthone was produced in their experiment. Possibly, the small amount of short wavelength light that did not get absorbed by xanthone contributed to the photooxidation.

Table 1
Comparison of the reported mass spectrum for compound **4** and results from this work

<i>m/z</i>	Relative intensity (%)	
	Ref. [10]	This work
39	40.5	10.1
40	16.0	2.2
41	68.0	9.6
42	22.0	0.8
43	100	1.0
50	13.0	1.1
51	3.8	12.0
52	–	1.8
53	24.0	8.8
55	33.0	7.7
63	–	1.3
65	–	5.0
66	–	2.1
67	–	29.8
68	65.0	28.9
69	43.0	2.4
77	15.0	14.9
78	–	3.2
79	26.0	23.9
80	–	10.4
81	25.0	7.9
91	19.0	17.0
92	12.0	15.4
93	51.5	54.2
94	20.0	21.6
95	22.0	100
96	–	7.5
105	–	4.1
107	–	18.5
108	19.5	6.4
117	25.0	0.4
119	12.0	0.7
121	8.0	17.9
122	–	1.68
136	12.0	1.8

cation, high quality calculational results were obtained in order to determine if this endeavor would be worth the effort. Ab initio calculations were conducted on limonene, cyclized limonene (**4**), carvone (**5**), carvone camphor (**6**). For the purposes of this discussion in these systems, the enthalpy of the transformation from the open to the cyclized product is taken as the added ring strain for each system. As a benchmark for the ab initio techniques that were used, the enthalpy for the norbornadiene (**1**) to quadricyclane (**2**) (Eq. (1)) system was first computed. This isomerization has been well studied and the enthalpy for the reaction has been measured to be 19–21 kcal/mol [20–22]. Our calculated results are shown in Table 2, which show that the measured isomerization energy for the norbornadiene to quadricyclane system is reproduced well by calculations. Furthermore, these tests show that the lower level of theory (B3LYP) is sufficient for estimating the ring strain energy in these molecules.

As a further test of the accuracy of our computational methods, we have compared the computed IR spectra of the

Table 2
Calculated enthalpies for molecules considered in this study

System	Ab initio technique	Open form (Hartrees)	Closed form (Hartrees)	Difference (kcal/mol)	Experimental (kcal/mol)
Norborene to quadricyclane	CBS-QB3	−270.94232	−270.906875	22.2	21.3 (0.3) ^a
	B3LYP	−271.359555	−271.32631	20.9	19.0 (0.2) ^b 21.2 (0.2) ^c 19.2 (1.0) ^d
Limonene to 4 5 to 6	B3LYP	−390.44536	−390.43392	7.2	
	B3LYP	−464.48923	−464.47580	8.4	

^a Ref. [20].

^b Ref. [21].

^c Ref. [22] (toluene solution).

^d Ref. [22] (gas phase).

compounds of interest to the spectra obtained on authentic materials at 6 K by matrix isolation techniques. The comparison is good in all cases; the computed and the authentic spectra for compound **4** and limonene are shown in Fig. 1. Note that in comparisons of this type, there are slight variations in the assumption that each IR band corresponds to a harmonic oscillator in the molecule.

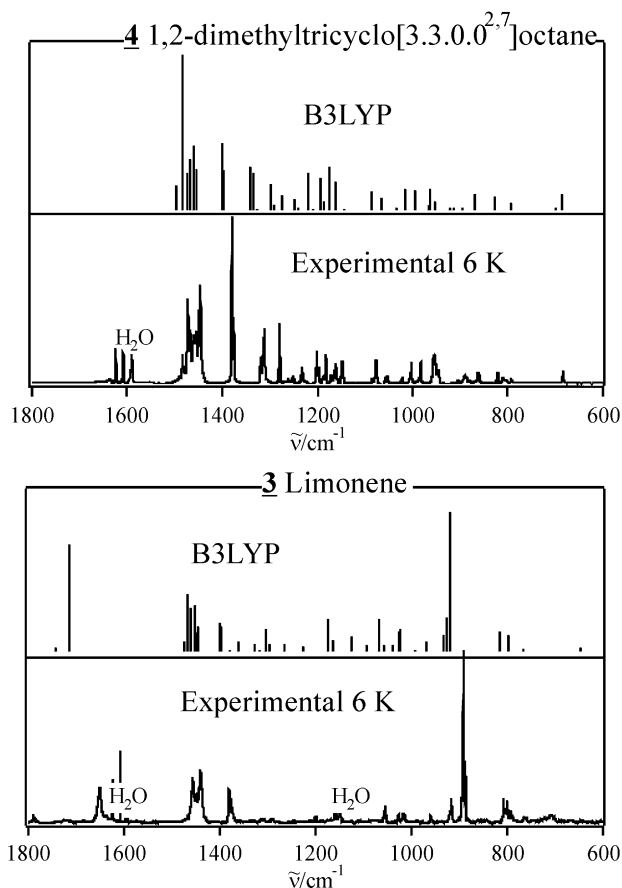


Fig. 1. Computed and authentic infrared spectra for compound **4** and limonene.

Note that the calculated difference for each system in Table 2 is positive, indicating that the reaction to form the closed species is endothermic. These results imply that on a per mole basis, only about one-third of the energy that can be stored in the quadricyclane system can be stored in the limonene system.

3.4. Energy density

In considering a high energy density fuel, two values are important: energy available per mole, and energy available per unit volume. In Table 3 the densities and energy gains obtained upon cyclization, as well as heats of combustion for various high density fuels are collected. Values for a kerosene jet fuel are also included for comparison. Note that on a mass basis, both quadricyclane and compound **4** are very close to kerosene in energy content, but on a volumetric basis, both cyclized compounds contain more energy than kerosene: 12.7% more in the case of quadricyclane, and 7.0% more in the case of compound **4**. Thus, the strain energy in these compounds, coupled with the increase in specific gravity upon cyclization, contribute to the enhanced energy content as compared to kerosene.

Other molecules have been considered for high energy density fuels. One is cubane (m.p. 130°C), which has a strain energy of 166 kcal/mol [11,27]. This molecule is difficult to compare directly to the present systems, since there exists no unstrained isomer for thermochemical comparisons. But clearly, compound **4** does not possess nearly the strain energy of cubane. However, the ready availability of terpenes makes them attractive candidates as starting materials for high energy density fuels. Moreover, if one considers the amount of strain energy obtained per synthetic step, quadricyclane and compound **4** have certain advantages over cubane, since cubane requires 10 steps at a minimum to make, and does not start with a natural product. Terpenes, or terpene-derived compounds with multiple double bonds, bear further consideration as starting materials for high energy density fuels.

Table 3
Densities, energy gains per mole and heats of combustion (ΔH_c) for various fuels

Compound	Density (g/ml)	Energy gain (kcal/mol)	ΔH_c (kcal/mol)	ΔH_c (kcal/g)	ΔH_c (kcal/ml)
Norbornadiene	0.854 ^a		−982.72 ^b	−10.68	−9.12
Quadricyclane	0.919 ^a	21	−1003.8 ^b	−10.91	−10.03
Limonene	0.847 ^a		−1464.7 ^c	−10.77	−9.12
4	0.880 ^d	7.2	−1471.9 ^e	−10.82	−9.52
Cubane	1.29 ^f	n/a	−1155.2 ^g	−11.11	−14.33
Kerosene	0.805 ^h	n/a	n/a	−11.05 ^h	−8.90

^a Ref. [23].

^b Ref. [25].

^c Ref. [26].

^d This work.

^e Computed from ΔH_c of limonene and the energy gain of cyclization.

^f Ref. [11].

^g Ref. [27].

^h Ref. [24].

4. Conclusions

We have circumvented the unsuccessful sensitized photochemical 2 + 2 intramolecular cyclization of limonene, and produced the product that would be formed from such a cyclization by an independent route. The mass spectrum of this compound does not match the mass spectrum reported earlier [10]. It was found computationally that this cyclized isomer of limonene contains about 7.2 kcal/mol more energy than limonene, which can be attributed to ring strain. This strain energy, coupled with the larger specific gravity of cyclized isomer as compared to limonene, provides the cyclized product with 7.0% more energy density on a volumetric basis than kerosene jet fuel. The readily available and inexpensive starting materials represented by the terpenes as a whole, coupled with simple and short syntheses of high energy density products, make terpenes attractive candidate starting materials for high energy density fuel applications.

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