



Thermochemical properties of iodinated cubane derivatives

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ABSTRACT

Since the initial synthesis of cubane, numerous derivatives have been made with a diverse range of physical, chemical, and biological properties. Some iodinated cubane derivatives have been reported to be thermolytically unstable and/or rearrange *in situ*. An iodinated cubane-containing, norbornene-based polymer showed rapid thermo-decomposition during TGA studies. Bis-(4-iodocubylmethyl)-dialkoxy disulfide undergoes fragmentation more easily than its non-iodinated counterpart. The synthesis and thermal behaviour of a library of iodinated cubane compounds are herein reported. Most of the iodinated cubane derivatives showed melting/decomposition with no exotherm upon cooling. 4-Iodo-1-vinylcubane was observed to rearrange to 4-vinyl-trans- β -iodostyrene and its cyclooctatetraene intermediate during DSC analysis. TGA studies on 1-iodo-4-(hydroxymethyl)-cubane suggest that this particular iodinated cubane scaffold is mostly prone to rapid thermo-decomposition.

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1. Introduction

Cubane and its derivatives have excited chemists since the first successful synthesis by Eaton and Cole in 1964 [1]. Numerous publications have highlighted the great diversity and utility of this simple scaffold [2]. Heteroatom bonding to the cube has revealed some rather unique phenomena. For example, nitrated cubane derivatives are explosive [3], whereas cubylamines are reported to possess anti-viral activity [2]. Cubanol undergoes spontaneous cage opening to yield vinylcyclobutenylketene [4]; whereas dicubyl disulfide [5] and its derivatives [6] are stable, and have unique bond lengths and intramolecular H-bonding. Cubyl halides have been demonstrated to be useful intermediates for subsequent transformations. In general, iodine is the most versatile halide as it can be easily attached to the cage from the cubyl carboxylic acid precursor via a Moriarty reaction [7], and can be transmetalated to magnesium [8] or lithium [5,9] for subsequent reactions. There are two reports of greater stability of non-iodofunctionalized cubane derivatives compared to their iodinated counterparts. One was with the dialkoxy disulfide functionality [10] and the other with a cubane-containing, norbornene-based polymer [11]. The latter revealed through thermogravimetric analysis that the iodinated cubane polymer underwent rapid decomposition at $\sim 250^\circ\text{C}$. Extensive work has been done on cubane and its derivatives

[12–14], however specific focus on iodinated cubane compounds has not been reported. This thus inspired us to examine the thermolytic behaviour of a family of iodinated cubane derivatives.

2. Experimental

2.1. Materials, preparation and characterization of compounds

All chemicals were reagent grade. 1,4-Dioxane was distilled over potassium benzophenone ketyl immediately prior to use. Melting points were obtained on a Gallenkamp apparatus and are uncorrected. ^1H (400 MHz) NMR spectra were obtained on a Varian instrument with solvent indicated with tetramethylsilane (TMS) as an internal standard and compared to authentic samples. Chemical shifts (δ) are given in ppm, coupling constants (J) in Hz, and spin multiplicities as s (single), d (doublet), and m (multiplet).

2.1.1. Cyclopentanone ethylene ketal (**2**)

Cyclopentanone (**1**, 250 mL, 3.0 mol), ethane-1,2-diol (200 mL, 3.59 mol), and Dowex 50W-X8 (H) cation exchange resin (3 g) were heated at reflux in benzene (500 mL) with simultaneous azeotropic removal of water over 30 h. The yellow solution which remained was cooled to room temperature, filtered, and washed with 4% aqueous NaOH (250 mL) and brine (500 mL), dried with MgSO_4 and concentrated by distillation through a Vigreux column (35 cm). Simple distillation of the residue ($59\text{--}63^\circ\text{C}/23\text{ mmHg}$) (Lit [15] $57^\circ\text{C}/18\text{ mmHg}$) yielded the ketal (**2**, 326.2 g, 90%) as a colorless liquid.

^1H NMR (400 MHz, CDCl_3): $\delta = 1.58\text{--}1.81$ (m, 8H), 3.87 (s, 4H).

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2.1.2. Endo-2,4-dibromodicyclopentadiene-1,8-dione bisethyl-ene ketal (**3**)

Anhydrous 1,4-dioxane (25 kg) was transferred into a 100 L reaction vessel under an atmosphere of nitrogen. To this was added cyclopentanone ethylene ketal (6.3 kg, 49.2 mol) and the mixture stirred under nitrogen. The system was cooled to 10 °C while stirring at 200 rpm. Anhydrous bromine (25 kg, 156 mol) was added slowly under nitrogen to the vigorously stirred reaction mixture keeping the temperature between 10 and 15 °C and ensuring the bromine was added directly into the stirred solution. Addition of bromine was complete after 6 h. The mixture was left stirring at room temperature with nitrogen blowing through the delivery vessel and over the reaction mixture to ensure removal of HBr. Sodium hydroxide (11 kg, 275 mol) in methanol (55 L) was added slowly maintaining the temperature below 10 °C. After half the NaOH solution had been added, the mixture turned a dark green color. After 4 h the addition was complete with the color having turned to brown. The mixture was then heated to reflux and left stirring for 16 h then subsequently cooled to room temperature and pumped out of the reactor into ice water (80 L). The precipitate was collected by vacuum filtration, washed with deionized water (90 L) and cold methanol (5 L), then the solid was then air-dried to yield the bis-ketal (**3**, 7.46 kg, 74.7%). mp. 174–176 °C (Lit [16] mp. 172–174 °C).

¹H NMR (400 MHz, CDCl₃): δ = 2.69–2.76 (m, 1H), 3.02–3.13 (m, 1H), 3.46–3.55 (m, 1H), 3.83–4.30 (m, 8H), 5.84 (d, *J* = 6.5 Hz, 1H), 6.07 (d, *J* = 2.3 Hz, 1H), 6.19 (dd, *J* = 3.5, 6.5 Hz, 1H).

2.1.3. Endo-2,4-dibromodicyclopentadiene-1,8-dione (**4**)

The bis-ketal **3** (14 kg, 34.5 mol) was slowly added to 98% sulphuric acid (45 L) keeping the temperature below 25 °C. The mixture was stirred at room temperature for 24 h then pumped from the reactor onto ice water (120 L) while stirring. The precipitate was collected by vacuum filtration, washed with water (2 × 20 L), and then air-dried to yield the dione, **4**, as a colorless solid (10.8 kg, 98.4%). mp. 156–157 °C (Lit [16] mp. 155–155.5 °C).

¹H NMR (400 MHz, CDCl₃): δ = 3.15–3.25 (m, 1H), 3.48–3.63 (m, 2H), 6.24–6.36 (m, 2H), 7.67 (d, *J* = 2.9 Hz, 1H).

2.1.4. Dimethyl 1,4-cubanededicarboxylate (**5**)

The dione, **4** (4.00 kg, 12.6 mol) was dissolved in methanol (68 L), deionized water (12 L) and conc. sulphuric acid (103 mL) in a 100 L reactor. The solution was pumped and circulated through a Syman-tec large scale photolysis unit irradiating the solution with UV light (2 kW Hg vapor lamp). Cooling was applied to the reactor to maintain a temperature of 25 °C. Conversion to the caged dione is quite slow with a maximum conversion rate of ca. 10 g per hour (monitored by ¹H NMR). When conversion was complete the reaction solution was concentrated to dryness under reduced pressure. The crude solid caged dione was dissolved in a 30% aq. sodium hydroxide solution (38 L) and the mixture was heated at reflux for 3 h. The solution was then cooled to 0 °C and acidified by the slow addition of conc. HCl (24 L) with vigorous stirring while maintaining the temperature below 10 °C. The resulting precipitate, crude cubane diacid, was collected by vacuum filtration and washed with ice-cold water (2 × 2 L), and then air-dried. The cubane diacid was dissolved in methanol (15 L), to which Dowex ion exchange resin (pre-washed with 500 mL methanol) was added, and the solution was heated at reflux overnight. The mixture was cooled to room temperature, filtered, and the filtrate evaporated to dryness under reduced pressure. The crude product was then purified by sublimation to afford a white solid of **5** (563 g, 78.7%). mp. 161–162 °C (Lit [17] mp. 161–162 °C).

¹H NMR (400 MHz, CDCl₃): δ = 3.70 (s, 6H, CH₃), 4.24 (s, 6H, cubyl H).

2.1.5. Cubane-1,4-dicarboxylic acid (**6**)

Dimethyl 1,4-cubanededicarboxylate (**5**, 5.04 g, 22.9 mmol) was added to a dissolved solution of NaOH (3.72 g, 93.0 mmol) in MeOH (150 mL) and H₂O (10 mL). After 10 min, **5** was completely dissolved. The mixture was heated at reflux for 4.5 h, at which time the solution was cloudy white. The solvent was removed via evaporation. The white residue was dissolved in H₂O (100 mL), and acidified to pH ~1 with conc. HCl. The white precipitate was vacuum filtered, washed with water and dried under vacuum to constant weight affording cubane-1,4-dicarboxylic acid (**6**, 4.35 g, 99%). mp. dec. 220–222 °C (Lit [18] 220 °C).

¹H NMR (400 MHz, MeOD): δ = 4.18 (s, 6H, cubyl H).

2.1.6. 1,4-Diiodocubane (**7**)

Dry benzene (350 mL) was added to cubane-1,4-dicarboxylic acid (**6**, 3.50 g, 18.3 mmol) under N₂, forming a suspension. To this IBDA (17.62 g, 54.7 mmol) and I₂ (14.40 g, 56.7 mmol) were added. The dark purple solution was refluxed for 6 h. After cooling to room temperature, sat. Na₂SO₃ (100 mL) was added, and the mixture was stirred until the top organic layer was light yellow (15–20 min). The layers were separated, the organic layer was washed with sat. Na₂SO₃ (2 × 100 mL), H₂O (2 × 100 mL), and brine (100 mL). The solution was dried with MgSO₄, filtered, and evaporated. The suspension that remained was triturated with cold hexanes to remove iodobenzene, affording the desired 1,4-diiodocubane (**7**, 5.45 g, 84%) as a white solid; mp. 225–227 °C (Lit [19] 226–227 °C).

¹H NMR (400 MHz, CDCl₃): δ = 4.39 (s, 6H, cubyl H).

2.1.7. Iodocubane (**7**)

1,4-Diiodocubane (**8**, 4.28 g, 12.0 mmol) was dissolved in dry THF (130 mL) under N₂. A 1.0 M EtMgBr in THF (48 mL) solution was added and cooled to –78 °C whereby the solution became off-white cloudy. A 1.6 M *n*-BuLi in hexanes (31 mL) solution was added till the mixture turned bright yellow. The mixture was stirred for an additional 5 min at –78 °C, whereupon cold MeOH (30 mL) was added. The cloudy white mixture was slowly warmed to room temperature and sodium methoxide in methanol (25 wt%, 35 mL) was added. The system was refluxed for 1 h to destroy the iodobutane by-product. After cooling to room temperature, pentane (200 mL) and H₂O (100 mL) were added. The mixture was acidified to pH 1 with concentrated HCl, extracted with pentane, and the combined organic layers were washed with H₂O (2 × 100 mL) and brine (100 mL). The solution was dried with MgSO₄, filtered and evaporated. Column chromatography with pentane as eluent afforded iodocubane (**8**, 2.38 g, 86%) as a white low-melting solid; mp. 31–33 °C (Lit [20] 32–34 °C).

¹H NMR (300 MHz, CDCl₃): δ = 4.17 (m, 4H, H-3,4,5,7), 4.31 (m, 3H, H-2,6,8).

¹³C NMR (75.5 MHz, CDCl₃): δ = 38.7, 47.9, 48.5, 58.1.

2.1.8. 4-(Methoxycarbonyl)cubane carboxylic acid (**9**)

A solution of NaOH (0.438 g, 10.9 mmol) dissolved in MeOH (7.1 mL) was added dropwise to a solution of dimethyl 1,4-cubanededicarboxylate, (**5**, 2.498 g, 11.3 mmol) in THF (85 mL) at room temperature. The mixture was stirred overnight and then evaporated to dryness. The resulting white solid was dissolved in water (100 mL), extracted with CHCl₃ (3 × 25 mL), dried with MgSO₄, filtered and evaporated. This afforded unreacted starting material (0.125 g, 5.5%). The aqueous layer from the extraction was acidified with conc. HCl to pH ~1, extracted with CHCl₃ (3 × 50 mL), dried with MgSO₄, filtered and evaporated, to afford 4-(methoxycarbonyl)cubane carboxylic acid (**9**, 1.70 g, 73.0%). mp. 181–183 °C (Lit [9a] mp. 182–183 °C).

¹H NMR (400 MHz, MeOD): δ = 3.71 (s, 3H, CH₃), 4.20 (s, 6H, cubyl H).

2.1.9. 4-Iodo-methyl-cubane carboxylate (**10**)

Iodobenzenediacetate (23.5 g, 72.2 mmol) and I₂ (18.5 g, 72.8 mmol) were added to a suspension of 4-(methoxycarbonyl)cubane carboxylic acid (5.00 g, 24.3 mmol) in dry benzene (390 mL) under argon. The mixture was heated at reflux for 7 h, cooled to room temperature, and hexane (175 mL) was added. The solution was washed with sat. Na₂SO₃ (2 × 60 mL), H₂O (2 × 60 mL), and brine (60 mL), dried over MgSO₄, and evaporated down to a reddish-brown oil. Column chromatography [EtOAc/hexanes (1:1)] afforded methyl 4-iodocubane-carboxylate (**10**, 4.89 g, 70%). mp. 115–117 °C (Lit [21] mp. 111–112 °C, [19] 124–125 °C).

¹H NMR (400 MHz, CDCl₃): δ = 3.71 (s, 3H, CH₃), 4.30 (m, 3H, cubyl H), 4.39 (m, 3H, cubyl H).

¹³C NMR (100 MHz, CDCl₃): δ = 36.1, 50.2, 51.7, 54.9, 56.1, 172.2.

2.1.10. 4-Iodocubane-carboxylic acid (**11**)

Iodobenzenediacetate (9.06 g, 28.1 mmol) and I₂ (7.14 g, 28.1 mmol) were added to a suspension of 4-(methoxycarbonyl)cubane carboxylic acid (**9**, 1.94 g, 9.38 mmol) in dry benzene (150 mL) under argon, and the mixture heated at reflux for 7 h. The mixture was then cooled to RT and hexanes (75 mL) were added. The solution was washed with saturated Na₂SO₃ (2 × 25 mL), H₂O (25 mL), and brine (25 mL), dried with MgSO₄, filtered, and evaporated to near dryness. The resulting red-brown liquid was dissolved in THF (50 mL) and a mixture of NaOH (3.75 g, 93.8 mmol) dissolved in MeOH (40 mL) and H₂O (15 mL) was added and the mixture stirred overnight. The solution was evaporated to near dryness then dissolved in water (25 mL), acidified with concentrated HCl to pH < 1, whereby a white precipitate formed which was collected under vacuum filtration, yielding 4-iodocubane-carboxylic acid (**11**, 1.91 g, 74.3%). mp. 212 °C (dec.) (Lit [9a] mp. 215 °C (dec.)).

¹H NMR (400 MHz, MeOD): δ = 4.24 (m, 3H, cubyl H), 4.36 (m, 3H, cubyl H).

2.1.11. 1-Iodo-4-(hydroxymethyl)cubane (**12**)

4-Iodocubane-carboxylic acid (**11**, 676 mg, 2.46 mmol) was dissolved in dry THF (25 mL) under argon and cooled to 0 °C. To it, borane dimethyl sulfide complex (0.78 mL, 3.91 mmol) was added and stirred for 20 min at 0 °C, then at RT for 4 h. The solution was quenched with water and stirred overnight. After adding EtOAc (20 mL), the solution was washed with water (2 × 15 mL) and brine (20 mL), dried with MgSO₄, filtered, and evaporated to dryness. Column chromatography (1:1 CHCl₃:EtOAc) afforded the white solid, 1-iodo-4-(hydroxymethyl)cubane (**12**, 438 mg, 68.4%). mp. 109–111 °C (Lit [9a] mp. 109–111 °C).

¹H NMR (400 MHz, CDCl₃): δ = 3.80 (s, 2H, CH₂), 4.07 (m, 3H, cubyl H), 4.23 (m, 3H, cubyl H).

2.1.12. 1-Iodocubane-4-carboxaldehyde (**13**)

A stirring solution of oxalyl chloride (0.16 mL, 1.89 mmol) in dry CH₂Cl₂ (4 mL) was prepared under argon at –78 °C. To it, dry DMSO (0.28 mL, 3.86 mmol) in dry CH₂Cl₂ (4 mL) was added dropwise. After 20 min at –78 °C, 1-iodo-4-(hydroxymethyl)cubane (**12**, 403 mg, 1.56 mmol) dissolved in dry CH₂Cl₂ (17 mL) under argon was added dropwise to the system. The mixture was maintained at –78 °C for 1.5 h and then dry Et₃N (0.42 mL, 7.02 mmol) was added via syringe. The mixture was warmed to RT and quenched with water (15 mL). The aqueous layer was extracted with CH₂Cl₂ (2 × 15 mL) and the organic layers were combined and washed with water (15 mL) and brine (15 mL), dried with MgSO₄, filtered, and evaporated to dryness. Column chromatography (CH₂Cl₂) afforded 1-iodocubane-4-carboxaldehyde as a white solid (**13**, 326 mg, 80.9%). mp. 106–109 °C (Lit [20] mp. 108–110 °C).

¹H NMR (400 MHz, CDCl₃): δ = 4.31 (m, 3H, cubyl H), 4.53 (m, 3H, cubyl H), 9.76 (s, 1H, CHO).

2.1.13. 4-Iodo-1-vinylcubane (**14**)

To a suspension of methyltriphenylphosphonium bromide (0.76 g, 2.21 mmol) in dry THF (20 mL), at –78 °C, under N₂, 2.50 M *n*-BuLi in hexanes (0.60 mL, 1.50 mmol) was slowly added. The yellow mixture was stirred for 20 min, whereupon 1-iodocubane-4-carboxaldehyde (**13**, 0.26 g, 1.01 mmol) dissolved in dry THF (10 mL), under N₂, was cannulated in and maintained at –78 °C for 1 h. After an additional hour at room temperature the mixture was quenched with H₂O (15 mL). Hexanes (25 mL) were added and the layers were separated. The aqueous layer was extracted with hexanes (2 × 25 mL), and the combined organic layer was washed with H₂O (2 × 25 mL) and brine (25 mL), dried with MgSO₄, filtered, and evaporated to dryness. Column chromatography (hexanes) afforded 4-iodo-1-vinylcubane (**14**, 0.23 g, 88%) as a white solid. mp. 77–79 °C (Lit [22] mp. 77–79 °C).

¹H NMR (300 MHz, CDCl₃): δ = 4.09 (m, 3H), 4.19 (m, 3H), 4.92 (dd, 1H, *J* = 1.95, 17.10 Hz), 5.06 (dd, 1H, *J* = 1.95, 10.60 Hz), 6.05 (dd, 1H, 10.60, 17.10 Hz).

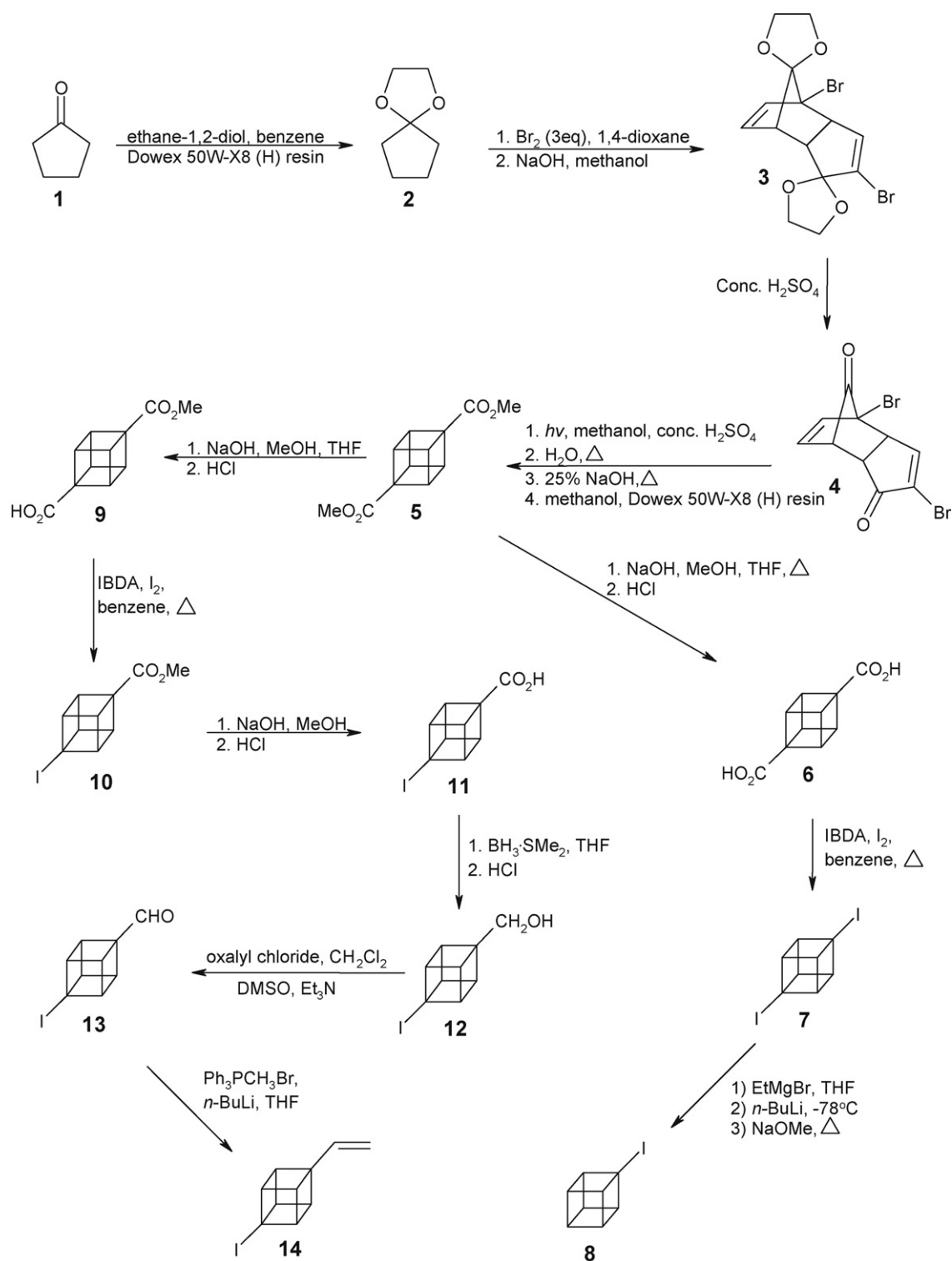
2.1.14. Measurements

Thermal properties were examined by thermogravimetric analysis, TGA, with TA instruments TGA Q50 System in a N₂ atmosphere and heated at a rate of 10 K/min. The differential scanning calorimetry, DSC, was run with a Perkin-Elmer Pyris 6 calorimeter in a N₂ atmosphere. The solid sample was placed in an aluminum capsule, heated and cooled at the rate of 5 K/min. All results were taken from the multiple heating and cooling runs, detecting the level of enthalpy change that is associated with a respective phase transition. The transition enthalpy, Δ*H* (kJ/mol), was determined from the peak area of the DSC thermogram. The transition entropy, Δ*S* (kJ/molK), was calculated with the equation Δ*S* = Δ*H*/*T*, where *T* was the transition temperature corresponding to the DSC maximum. The thermodynamic data were mean values of several independent measurements carried out on different samples.

3. Results and discussion

3.1. Synthesis

As Aldrich no longer sells any cubane starting materials, we synthesized the dimethyl 1,4-cubanedicarboxylate from cyclopentanone directly (Scheme 1) [23]. The synthesis of the cubane frame was accomplished by initial ketalization of cyclopentanone, **1**, with ethane-1,2-diol in presence of a Dowex 50W-X8 (H) cation exchange resin to give **2**. The ketal, **2**, was treated with bromine in 1,4-dioxane and the unpurified tribromide was dimerized to yield endo-2,4-dibromodicyclopentadiene-1,8-dione bisethyl-ene ketal, **3**, upon refluxing in MeOH. Stirring in concentrated H₂SO₄ afforded the dione, **4**, which upon irradiation underwent two consecutive Favorskii ring contractions, and subsequent esterification to afford the dimethyl 1,4-cubanedicarboxylate, **5**. The simple monoiodocubane, **8**, was synthesized from the dimethyl 1,4-cubanedicarboxylate, **5**, by initially performing a base hydrolysis with excess NaOH to yield the diacid, **6** [18]. After a Moriarty reaction we obtained the diiodocubane, **7** [19], whereby we selectively removed one iodine to yield the monoiodocubane, **8** [20]. By only reacting one equivalent of NaOH with the starting dimethyl 1,4-cubanedicarboxylate, **5**, we obtained the acid/ester, **9**. A Moriarty reaction yielded the iodo/ester, **10**. Base hydrolysis afforded the iodo/acid, **11**, which could be further reacted with borane to give the iodo/alcohol, **12**. Swern oxidation provided the iodo/aldehyde, **13**, followed by Wittig gave the iodo/vinyl, **14** [22].



Scheme 1. Synthetic path for all iodinated cubane derivatives.

3.2. Thermogravimetric analysis

The thermogravimetric analysis on the iodinated cubane derivatives (**7**, **8**, **10–14**, Fig. 1) all showed no weight loss prior to decomposition curve, suggesting that no crystal and/or hygroscopically bound solvent was present. From Table 1, it can be seen that monoiodo, **8**, and iodo/vinyl, **14**, had the lower onset of degradation temperature of 376 and 386 K, respectively; while iodo/acid, **11**, had the highest at 479 K. Monoiodo (**8**), iodo/acid (**11**), iodo/alcohol

(**12**), and iodo/aldehyde (**13**) had a small amount of residual material remaining of 1.68, 2.84, 1.64, and 3.82% of weight, respectively. What was most remarkable was the onset to end temperature range was 35–47 K, for all but one of the iodinated cubane compounds. Iodo/alcohol (**12**) had a relatively steep 2nd tangent, hence a narrow onset to end temperature range of 28 K. This phenomenon was also observed with the cubane-containing, norbornene-based polymer synthesized from the iodo/alcohol [14]. It appears that this particular cubane scaffold is prone to rapid thermo-decomposition.

Table 1
Temperature at onset, inflection, and end for iodinated cubane derivatives, **7**, **8**, **10**–**14**.

Compound	Extrapolated onset temperature for degradation (K)	Temperature of inflection point (K)	Extrapolated end temperature for degradation (K)
Diiodo (7)	441	468	479
Monoiodo (8)	376	405	418
Iodo/ester (10)	417	448	460
Iodo/acid (11)	479	507	514
Iodo/alcohol (12)	438	460	466
Iodo/aldehyde (13)	418	448	465
Iodo/vinyl (14)	386	416	427

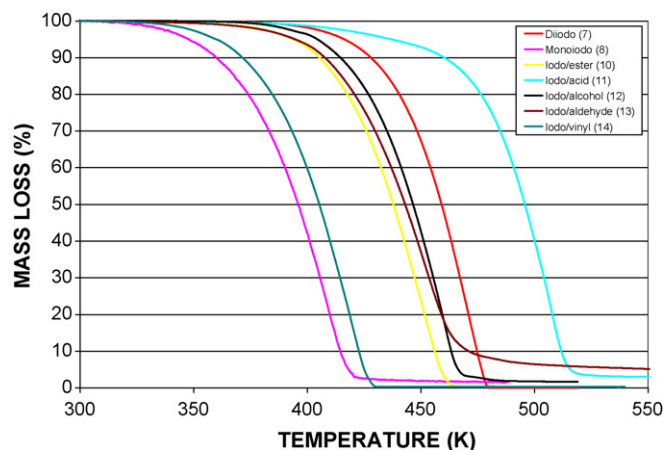


Fig. 1. TGA curves for **7**, **8**, **10**–**14**.

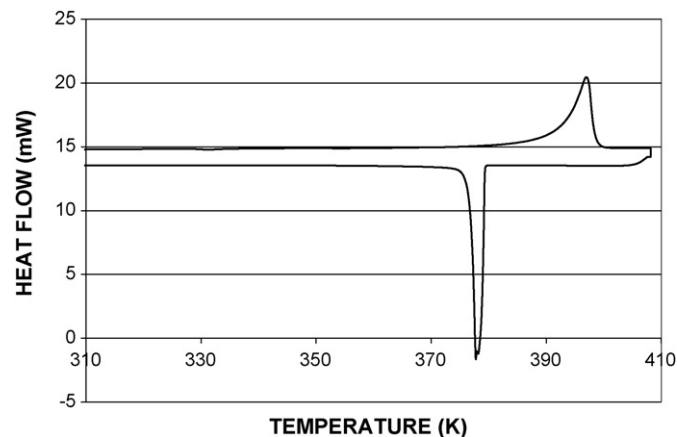


Fig. 2. DSC thermogram of iodo/ester, **10**.

3.3. DSC analysis

Only the iodo/ester, **10**, demonstrated the classic melting/freezing DSC thermogram profile of a pure compound (Fig. 2). An endotherm was observed at 395 K with a ΔH of 22.3 kJ/mol and a ΔS of 56.4 J/mol K. Upon cooling, an exotherm was observed at 380 K with a ΔH of -103.2 kJ/mol and a ΔS of -271.5 J/mol K. The sample could be heated and cooled repeatedly and exhibited temperature hysteresis. Diiodo, **7**, and iodo/alcohol, **12**, both yielded endotherms at 499 and 393 K, respectively; however, neither produced an exotherm upon cooling (Table 2). This is not surprising as these temperatures were near the inflection points of degradation from the TGA results (Table 1). The aluminum capsules were opened and NMR spectra were run on the material, revealing no starting cube compound. Monoiodo (**8**) gave an endotherm at 301 K with no exotherm upon cooling. It was assumed that this was due to the low-melting point of this compound. Even upon cooling the sample in dry ice and then re-running, the DSC did not provide an endotherm on a second run. When the aluminum capsule was opened indeed monoiodo, **8**, was a liquid and post-

DSC NMR revealed no detectable degradative products. The ΔH for **7**, **8**, **10**, and **12** were between 9 and 22 kJ/mol. In comparison cubane itself has a reported ΔH of fusion of 8.7 kJ/mol [24], whereas dimethyl 1,4-cubanedicarboxylate (**5**) has a ΔH of ~ 38 kJ/mol [14]. Interestingly, both iodo/acid, **11**, and iodo/aldehyde, **13**, yielded an exotherm upon heating at 516 and 465 K respectively. Both of these temperatures were virtually identical to the extrapolated end temperature for degradation from the TGA (Table 1). Post-DSC NMRs revealed that no starting cubane remained. When the residues were partially dissolved in water, the pH was ~ 4 and a precipitate was formed when AgNO_3 was added suggesting the formation of hydroiodic acid. The dissolved residue was also active to starch paper which indicated the presence of iodine. Mass spectrometry did indeed reveal signals that correspond to I_2 (254) and HI (128).

Iodo/vinyl, **14**, gave the most unique data (Fig. 3). On the first DSC cycle an endotherm at 357 K ($\Delta H = 13.4$ kJ/mol; $\Delta S = 37.6$ J/mol K) and an exotherm upon cooling at 344 K ($\Delta H = -52.6$ kJ/mol; $\Delta S = -153.0$ J/mol K) was observed. This heating/cooling was repeated three more times. Each time there was a decrease in the temperature of the endotherm, ΔH and ΔS upon heating. On the cooling runs the temperature of the exotherm decreased as

Table 2
Transition temperatures, T , enthalpies, ΔH , and entropies, ΔS for iodinated cubane derivatives, **7**, **8**, **10**–**14**.

Compound	Heating			Cooling		
	T (K)	ΔH (kJ/mol)	ΔS (J/mol K)	T (K)	ΔH (kJ/mol)	ΔS (J/mol K)
Diiodo (7)	499	16.7	33.5			
Monoiodo (8)	301	9.0	29.9			
Iodo/ester (10)	395	22.3	56.4	380	-103.2	-271.5
Iodo/acid (11)	516	-485.4	-940.7			
Iodo/alcohol (12)	393	22.4	57.1			
Iodo/aldehyde (13)	465	-302.6	-651.1			
Iodo/vinyl (14)	357	13.4	37.6	344	-92.6	-273.0
	351	11.7	33.3	335	-87.7	-261.6
	350	10.9	31.1	331	-85.7	-259.3
	349	10.7	30.6	319	-80.3	-251.5

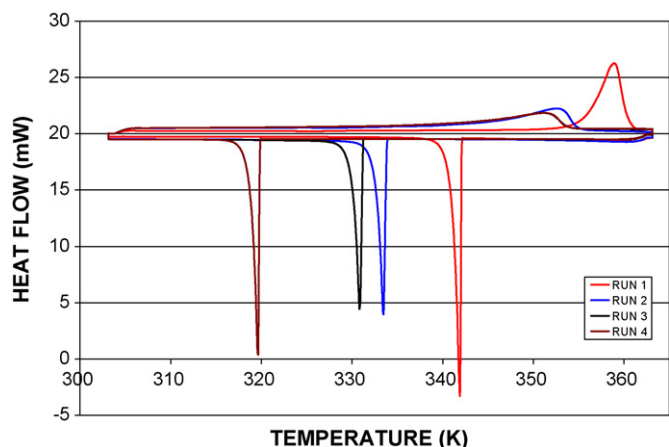
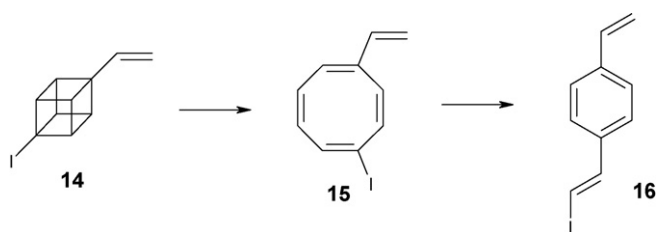


Fig. 3. DSC thermogram of iodo/vinyl, **14**.



Scheme 2. Reported thermolytic rearrangement of iodo/vinyl, **14**, to 4-vinyl-trans- β -iodostyrene, **16** [22].

well as the ΔH and ΔS increased. The changes from run 1 to 4 is proposed to be due to the formation of a new product; hence introducing an impurity into the mix. Previous work in our lab has shown that iodo/vinyl cubane, **14**, rearranges under heat to yield 4-vinyl-trans- β -iodostyrene, (**16**, Scheme 2) [22]. The ΔH of fusion of pure cyclooctatetraene and styrene have been reported to be 11.27 kJ/mol [25] and 10.95 kJ/mol [26], respectively, each being lower than that of the starting iodo/vinyl, **14**. Their respective melting points are 268 K [25] and 242 K [26], which are also lower than that of compound **14**, at 351 K [22]. Indeed, post-DSC NMR did reveal small quantities of 4-vinyl-trans- β -iodostyrene, **16** as well as the cyclooctatetraene intermediate, **15**.

4. Conclusion

A range of iodinated cubane derivatives were successfully synthesized and analyzed for their thermochemical behaviour. All compounds contained no crystal and/or hygroscopically bound sol-

vent as observed from TG analysis. Iodo/alcohol, **12**, showed the most rapid thermo-decomposition as was previously reported from a polymer containing this moiety. The iodo/vinyl, **14**, underwent cage opening/rearrangement to 4-vinyl-trans- β -iodostyrene, **16**, during the heating with DSC.

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