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Energetic Materials

Thermal and Sensitiveness Determination of Cubanes: Towards Cubane-Based Fuels for Infrared Countermeasures

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Abstract: As infrared seeking technology evolves, threats are better able to distinguish defensive infrared (IR) flares from true targets. Spectrally matched flares, which generally employ carbon-based fuels, are better able to decoy some advanced missiles by more closely mimicking the IR emission of the target. Cubane is a high-energy carbon-based scaffold which may be suitable for use as a fuel in spectrally matched flares. The enthalpy of formation and strain energy of a series of cubanes was predicted in silico, and their thermal and impact stability examined. All were found to undergo highly exothermic decomposition in sealed cell differential scanning calorimetry, and two cubanes subsequently underwent quantitative sensitiveness testing. Despite their *F* of *I* values being in the secondary explosive range, cubane-1,4-dicarboxylic acid (*F* of *I* = 70) and 4-carbamoylcubane-1-carboxylic acid (*F* of *I* = 90) were identified as potentially useful fuels for pyrotechnic infrared countermeasure flare formulations.

Introduction

High energy materials have a variety of uses in both military and civilian life. They can be classified by their end use, which include pyrotechnics, primary explosives, high (secondary) explosives, rocket fuels, fuel additives and propellants.[1] Each category can be further broken down into more specific groups, for example pyrotechnics include colourful fireworks, smoke producing flares, and infrared countermeasure flares (IRCMs). For military applications especially, constant innovation towards new pyrotechnic fuels is imperative.[2] For IRCMs, the technology in missile seekers is improving rapidly and there are now missiles equipped with seekers which can distinguish a true target (platform for example, aircraft) from the typical grey-body IR-emitting flares most commonly used today.[3]

One way of overcoming these new seekers is to create flares which more closely mimic the IR emission of the aircraft. These new flares, called spectrally matched flares, require fuels which are high in energy and which assist in the production of β-band (3.6–4.8 μm) emitting combustion products such as carbon dioxide, and limit the production of α-band (1.8–2.5 μm) emitters such as water and carbon soot.[3b] The development of spectrally matched flares and the theory behind them have been extensively reviewed elsewhere.[2b,4]

Since it was first synthesised by Eaton and Cole in 1964[5] cubane (pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane, **1**) has found uses in many areas of research including medicinal chemistry, materials, and as an internal NMR standard.[6] Cubane itself, and derivatives, are described as relatively stable despite the unusual geometry and huge strain energy of the eight carbon atoms configured in a cubic arrangement.[6g] Cubanes share the high C:H ratio of aromatics, suggesting that using the cubane carbon backbone would assist in minimising the production of α-band emitters, whilst increasing the overall energy of the formulation.

Previous high energy materials research into cubanes has produced mixed results regarding their stability. For example, 1,4-diisocyanocubane (**2**) has been reported as being highly thermally unstable, and detonates upon strong heating.[7] A variety of iodinated cubanes (e.g., **3** and **4**) have been described as undergoing rapid thermo-decomposition and being less stable than their non-iodinated counterparts.[8] Octanitro- (**5**) and heptanitrocubane (**6**) are reported as insensitive to hammer taps,[9] while 4-((nitrooxy)methyl)cubane-1-carboxylic acid (**7**), dimethyl cubane-1,4-dicarboxylate (**10**), and cubane-1,4-dicarboxylic acid (**11**) have been reported to exhibit sensitiveness to impact.[10] Azidocubanes are extremely sensitive to impact, with Eaton warning that the oils of cubyl azide (**8**) and methylcubyl azide (**9**) are "exceedingly shock sensitive and can (and have) detonated on touch".[11]

While cubanes (e.g., Scheme 1) have many potential applications as high-energy materials,[7,9,12] they have not been explored in the context of new fuels for spectrally matched flares. Considering the characteristics of flares formulated with oxygenated aromatic fuels[13] (i.e. favourable emission spectrum but low spectral efficiency), and the higher in energy but un-

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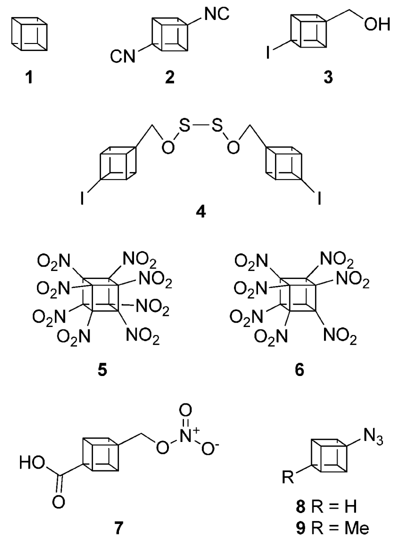
Supporting information containing full synthetic, computational, and sensitiveness testing details as well as the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/chem.201901086.



Scheme 1. Cubane (**1**) and high energy derivatives (**2**–**9**).

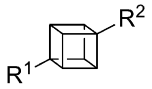
stable carbonitriles[14] (i.e. good spectral efficiency but unfavourable emission spectrum), we envisioned cubanes as having the potential to satisfy both criteria. That is, cubanes share the low carbon to hydrogen ratio of aromatic fuels, which should assist in producing a favourable emission spectrum. Moreover, they are high in energy, and thus should result in an increase in the enthalpy of combustion which in turn should increase the spectral efficiency.[2,4] Furthermore, in the view that cubanes have demonstrated a spectrum of stability through pharmaceutical development, this situation suggested that identifying optimal characteristics that would meet modern day criteria for the development of new high energy fuels could be achieved.

Reported herein are in silico prediction methods and subsequent validation using a series of simplified and synthetically practicable cubanes. The thermal decomposition characteristics of the cubanes were examined using thermogravimetric analysis (TGA) and sealed cell differential scanning calorimetry (scDSC), and the results compared to thresholds used within the pharmaceutical industry to flag compounds and reagents which require extra safety precautions.

Results and Discussion

A series of known mono and 1,4-disubstituted cubanes (**10**–**17**; Table 1) were chosen to refine our knowledge of cubane sensitiveness, most of which had no reported issues, except for that of cubane-1,4-dicarboxylic acid (**11**) and dimethyl cubane-1,4-dicarboxylate (**10**).[10] This selection was predicated on the ready availability of dimethyl cubane-1,4-dicarboxylate (**10**), which can be prepared on kilogram scale, as developed by Tsanaktsidis et al.,[15] and has since become commercially available.

Table 1. Structure and substituents of cubanes **10**–**17**.



Cubane	R^1	R^2
dimethyl cubane-1,4-dicarboxylate (diester, **10**)	COOMe	COOMe
cubane-1,4-dicarboxylic acid (diacid, **11**)	COOH	COOH
4-methoxycarbonylcubane-1-carboxylic acid (acid ester, **12**)	COOH	COOMe
methyl cubane-1-carboxylate (ester, **13**)	H	COOMe
cubane-1-carboxylic acid (acid, **14**)	H	COOH
cubane-1-carboxamide (amide, **15**)	H	$CONH_2$
methyl 4-carbamoylcubane-1-carboxylate (amide ester, **16**)	$CONH_2$	COOMe
4-carbamoylcubane-1-carboxylic acid (amide acid, **17**)	COOH	$CONH_2$

Enthalpy of formation

Considering fuels with large, positive enthalpies of formation ($\Delta_f H^o_{solid}$) assist in yielding sufficient flare spectral efficiency,[14] high $\Delta_f H^o_{solid}$ values are a desirable characteristic. However, we were unable to achieve complete combustion of diester **10** in bomb calorimetry, and thus were unable to experimentally determine the $\Delta_f H^o_{solid}$ value. Spiking with benzoic acid using a stacked pellet approach, as described previously for this compound,[29,39] did not reliably produce complete combustion, and therefore computational methods were explored to predict the $\Delta_f H^o_{solid}$ values for **10**–**17**. $\Delta_f H^o_{solid}$ can be calculated by Equation (1) in which $\Delta_f H^o_{gas}$ is the gas phase enthalpy of formation and $\Delta_{sub}H^{\circ}$ is the enthalpy of sublimation.[17]

$$\Delta_f H^o_{solid} = \Delta_f H^o_{gas} - \Delta_{sub}H^o \tag{1}$$

Several predictive methods for $\Delta_{sub}H^{\circ}$ are available including group additivity,[18] quantitative structure-property relationships (QSPR),[19] atom–atom potential,[20] and electrostatic surface potential (ESP) methods.[21] All of these methods rely on experimental $\Delta_{sub}H^{\circ}$ values for the construction of a training set, and the accuracy of each application is contingent upon both the selection of the training library and the reliability of the experimental values therein. Therefore, it is often necessary to utilise a training set based on the targets of interest. That said, using a training set to predict $\Delta_{sub}H^{\circ}$ of a compound with functional groups or characteristics which are not well represented in the training set will often lead to large errors.[21a]

A modification of the ESP method was utilised to predict $\Delta_{sub}H^{\circ}$ values.[21d,22] The ESP method is widely used in high energy material predictions,[23] and is especially attractive as it has been suggested that electrostatic surface potential parameters may also be related to other physical properties such as density and impact sensitiveness.[24] The modification, proposed by Suntsova and Dorofeeva, introduces an additional parameter (Π) to improve predictions.[21a] The relationship between $\Delta_{sub}H^{\circ}$ and ESP parameters is shown in Equation (2) where SA is the surface area, σ^2_{tot} is a measure of variability on the surface potential, ν is the degree of balance between the positive and negative areas on the surface, and Π is a measure of local polarity. Using Gaussian09[25] and Gaussian16[26] software, all structures were first optimised at the B3LYP/ccpVTZ level of theory, and then frequency calculations were performed using the same level of theory. ESP parameters were calculated on the 0.001 electrons bohr^{-3} contour of the electron density,[27] and were obtained using the Multiwfn computer program.[28] The coefficients *a*, *b*, *c*, and *d* were determined from a least squares fitting of a training set with known $\Delta_{sub}H^{\circ}$ and their ESP parameters (Equation (2), Table 2).

$$\Delta_{sub}H^{o} = a(SA)^{2} + b\sqrt{\sigma^{2}_{tot}\nu} + c + d\Pi \tag{2}$$

Table 2. Coefficients for Equation (2).

a	*b*	*c*	*d*
0.000244 8164	−0.505274 1293	4.328415 1896	1.089548 2769

The paucity of experimental $\Delta_{sub}H^{\circ}$ data for cubanes, and similarly highly strained caged hydrocarbons, unfortunately placed limitations on training set selection. However, by combining both strained systems and selecting carboxylic acid and related amide functional groups, a training set of twelve members was developed, which gave good prediction levels for the test set (Table 3). The uncertainty of the predicted $\Delta_{sub}H^{\circ}$ values was defined as two times the root-mean-square deviation of the training set, ±21 kJ mol^{-1} (see Supporting Information), which was comparable to the uncertainty of previously reported training sets that are much larger.[21a]

Table 3. Literature and calculated $\Delta_{sub}H^{o}$ values for the test set. All values are in kJ mol^{-1}.

Compound	Literature	Calculated	Δ
dimethyl 1,4-cubane dicarboxylate (**10**)	117.19[29]	121.8	4.6
cubane-1,4-dicarboxylic acid (**11**)	126.50[30]	103.8	−22.7
dimethyl 2,6-cuneane dicarboxylate (**19**)	106.80[29]	119.7	12.9
pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (**20**)	55.85[31]	60.1	4.3
malonamide (**21**)	126.40[32]	103.4	−23.0
propanamide (**22**)	75.00[32]	81.4	6.4
adamantane carboxamide (**23**)	108.00[32]	91.3	−16.7
piperidine-1-carboxamide (**24**)	100.20[32]	91.5	−8.7
2-methyl propanamide (**25**)	86.19[32]	83.2	−3.0
malonic acid (**26**)	111.40[32]	116.1	4.7
1,1-cyclobutanedicarboxylic acid (**27**)	111.29[32]	95.6	−15.7
dimethyl malonate (**28**)	111.71[32]	100.9	−10.8
homocubane-4-carboxylic acid (**29**)	82.01[32]	81.7	−0.3
	Root Mean Square Deviation		**12.5**

To validate the accuracy of the experimentally determined $\Delta_{sub}H^{\circ}$ values presented in Table 3, as well as demonstrate the importance of accurate and reliable experimental training/test sets, 3-oxopentanedioic acid (literature $\Delta_{sub}H^{\circ} = 160.21$ kJ mol^{-1}[32]) was chosen as a test substrate. The method used in the literature measurement of the $\Delta_{sub}H^{\circ}$ of 3-oxopentanedioic acid has revealed inconsistent values with other experimental methods, and so it is possible that the reported value is unreliable.[33] The training set herein predicted a value of 129.4 kJ mol^{-1}, which was a difference of −30.8 kJ mol^{-1} from the literature value, and thus was outside the uncertainty value of ±21 kJ mol^{-1}. This demonstrated that unreliable experimental values in the test set can reduce confidence in predictions.

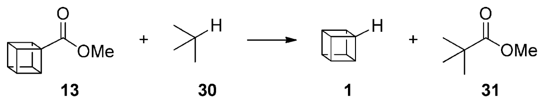
In the test set, listed in Table 3, both malonamide (**21**) and cubane diacid **11** are predicted outside the uncertainty range at −23.0 and −22.7 kJ mol^{-1} difference, respectively. Considering other amides in the test set are well predicted, the malonamide discrepancy was unexpected, although the reported experimental value was determined over a narrow temperature range (397.4–403.2 K), and then extrapolated to 298.15 K. It is therefore possible that the experimental value for malonamide is likely erroneous. The prediction for diacid **11** presented more of an issue, however other highly strained compounds [that is, dimethyl 1,4-cubane dicarboxylate (**10**), dimethyl 2,6-cuneane dicarboxylate (**19**), 1,1-cyclobutanedicarboxylic acid (**27**), and homocubane-4-carboxylic acid (**29**)] are predicted within uncertainty, which provided sufficient confidence in the predicted value for diacid **11**. Unfortunately, these findings suggested that for cubanes there is not yet enough experimental data available to validate modern training or test set libraries, however the ESP method performed satisfactorily for the majority of cases.

To complete the requirements for Equation (1) values of $\Delta_{f}H^{o}_{gas}$ were determined for **10**–**17** using the isodesmic reaction protocol.[34] Recently the C–C bonds of the cube have been shown to be bent, with electron density sitting outside C–C vectors which make up the edges of the cube.[35] The exocyclic bonds are also shorter than equivalent bonds in unstrained molecules.[36] To maintain this unusual bonding, and the resulting strain energy, the cubane core was preserved in the designed reactions, as outlined in Scheme 2 for ester **13**. The $\Delta_{f}H^{o}_{gas}$ of cubane (**1**), isobutane (**30**), and methyl pivalate (**31**) are known, facilitating the prediction of $\Delta_{f}H^{o}_{gas}$ of ester **13** through Equations (3) and (4). From Equation (3) the enthalpy of the reaction ($\Delta_{r}H^{\circ}$) was calculated from the sum of the electronic and thermal enthalpies ($\Sigma(\varepsilon_{0} + H_{corr})$) obtained from frequency calculations. Then, by rearranging Equation (4), the $\Delta_{f}H^{o}_{gas}$ of the unknown compound can be predicted.

$$\Delta_{r}H^{\circ}\ (298K) = \Sigma(\varepsilon_{0} + H_{corr})_{products} - \Sigma(\varepsilon_{0} + H_{corr})_{reactants} \tag{3}$$

$$\Delta_{r}H^{o} = \Sigma\Delta_{f}H^{o}_{products} - \Sigma\Delta_{f}H^{o}_{products} \tag{4}$$

The predicted $\Delta_{f}H^{o}_{gas}$, $\Delta_{sub}H^{\circ}$, and resulting $\Delta_{f}H^{o}_{solid}$ values are presented in Table 4, and a comparison of predictions to literature values for diester **10** and diacid **11** are given Table 5. The



Scheme 2. Designed reaction for the prediction of the $\Delta_{f}H^{o}_{gas}$ of **13**.

Table 4. Predicted enthalpies of formation and strain energies for cubanes **10**–**17**. All values are in kJ mol^{-1}.

Compound		$\Delta_f H^o_{gas}$	$\Delta_{sub}H^o$	$\Delta_f H^o_{solid}$	E_s
diester	**10**	−141.0	121.8	−262.8	645.3
diacid	**11**	−206.0	103.8	−309.8	602.1
acid ester	**12**	−118.3	134.3	−252.7	680.1
ester	**13**	+269.5	99.6	169.9	699.1
acid	**14**	+222.0	95.3	126.7	663.0
amide	**15**	+411.6	86.1	325.5	661.7
amide ester	**16**	+69.3	128.7	−59.4	676.8
amide acid	**17**	+22.2	125.8	−103.6	641.0

literature $\Delta_f H^o_{gas}$ values for **10** and **11** are both derived from experimental $\Delta_f H^o_{solid}$ and $\Delta_{sub}H^\circ$ values,[29,30] however, various $\Delta_f H^o_{solid}$ values are reported, and therefore different $\Delta_f H^o_{gas}$ values can be derived. Using the experimental $\Delta_{sub}H^\circ$ values from Roux et al. (117.2 kJ mol^{-1} for diester **10**[29] and 126.5 kJ mol^{-1} for diacid **11**[30]) and adding them to the various $\Delta_f H^o_{solid}$ values available in the literature gave the derived $\Delta_f H^o_{gas}$ values seen in Table 5.

While the values are not particularly close, they demonstrate that no consensus on enthalpies of formation could be determined for **10** and **11** making it difficult to validate the predictions. Isodesmic reactions have been used to predict gas phase enthalpies of formation in many studies and have been found to be one of the most accurate methods.[37] Elioff et al. state that the goal for any method of $\Delta_f H^o_{gas}$ prediction should be errors no larger than ±2 kcal mol^{-1} (±8.37 kJ mol^{-1}),[38] and the predictions for diester **10** and diacid **11** are clear outliers. When comparing the predicted $\Delta_f H^o_{solid}$ values of **10** and **11** there was a spread of values available as seen in Table 5. Three literature values are available for diester **10**; Roux et al. give −232.62 kJ mol^{-1},[29] Avdonin et al. give −231.2 kJ mol^{-1},[39] and Kirklin et al. give −218.99 kJ mol^{-1}.[40] Our prediction (−262.8 kJ mol^{-1}) was closer to the first two values, however this also highlighted little literature consensus. Roux et al. were unable to achieve complete combustion without using an auxiliary substance, whereas Avdonin et al. accomplished this goal, and we were unable to achieve complete combustion even with an auxiliary substance. Although the value determined by Roux et al. agreed with that determined by Avdonin et al. they used the same procedure as Kirklin et al. to achieve complete combustion. For diacid **11** there are two different values; −355.9 kJ mol^{-1} from Roux et al.[30] and −318.5 kJ mol^{-1} from Avdonin et al.[39] The prediction determined herein (−309.8 kJ mol^{-1}) was closer to that provided by Avdonin et al., but 46 kJ mol^{-1} higher than the value measured by Roux et al. Overall, the scarcity and variety of experimental values for enthalpy of formation for cubanes creates a considerable challenge for developing predictions in this area, which inspired a search for alternative determinants.

Strain energy

Cubane (**1**) is by definition a highly strained molecule (681.18±9.8 kJ mol^{-1}),[29] and it is this strain which is the major contributor to its high heat of formation. Therefore the strain energy (E_S) of cubanes **10**–**17** were estimated by the method of Fan et al. using the reaction described by Equation (5).[37,41]

$$C_8H_{8-m}X_m + 12C_2H_6 \rightarrow (8-m)(CH_3)_3CH + m(CH_3)_3CX \tag{5}$$

Taking the total energy and the zero-point vibrational energy (ZPE) from the frequency calculations, the change in energy (ΔE_n) between the reactants and the products was calculated using Equation (6). Due to the strain free nature of the other components in Equation (5), ΔE_n is taken as the E_S of the cubane target.[37b,41]

$$\Delta E_n = \Sigma E_{products} - \Sigma E_{reactants} + ZPE \tag{6}$$

In order to validate this E_S predictive method for cubane derivatives the E_S for cubane (**1**) was evaluated using the reaction $C_8H_8 + 12C_2H_6 \rightarrow 8(CH_3)_3CH$ and Equation (6) (Table 6). The predicted value was determined to be 685.1 kJ mol^{-1}, which was close to the value calculated by Roux et al. of 681.0 kJ mol^{-1},[29] although it is 22.5 kJ mol^{-1} lower than the value predicted by Fan et al. (707.64 kJ mol^{-1}).[41] Additionally, the E_S calculated for 1,4-dinitrocubane (**32**, 692.0 kJ mol^{-1}) is 17.6 kJ mol^{-1} lower than the value predicted by Fan et al. (709.65 kJ mol^{-1}).[41] Importantly, both predictions herein and those by Fan et al. indi-

Table 6. Comparison of predicted and literature strain energies. All values are in kJ mol^{-1}.

Compound		E_s	Δ from cubane prediction
cubane **1**	this work	685.1	
	Fan et al.[41]	707.64	
1,4-dinitrocubane **32**	this work	692.0	6.9
	Fan et al.[41]	709.65	2.01
azidocubane **7**	this work	674.6	−10.5
	Fan et al.[41]	696.22	−11.42

Table 5. Comparison of predicted values of **10** and **11** to values derived from literature. All values are in kJ mol^{-1}.

Compound	Literature $\Delta_f H^o_{solid}$	Literature $\Delta_{sub}H^o$	Derived $\Delta_f H^o_{gas}$	Predicted $\Delta_f H^o_{gas}$	Δ (Predicted−Derived)
diester **10**	−232.62±5.84[29]	117.2[29]	−115.4±7.0[29]	−141.0	−25.6
	−231.2±2.5[39]		−114.0		−27.0
	−218.99±2.12[40]		−101.8		−39.2
diacid **11**	−355.9±11.7[30]	126.5[30]	−229.4±14.8[30]	−206.0	23.4
	−318.5±12.6[39]		−192.0		−14.0

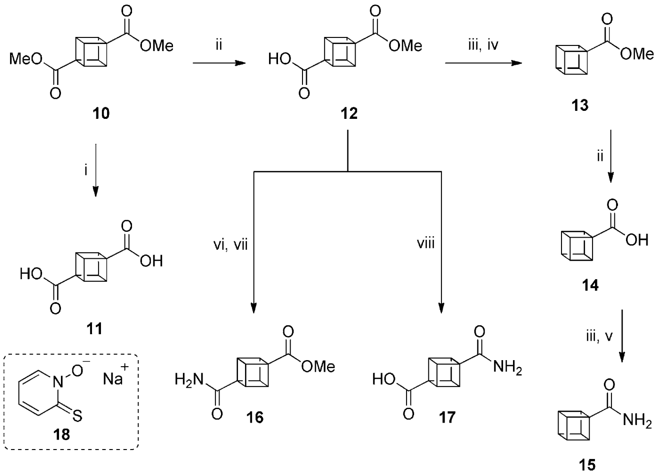
cate an increase in E_S between cubane (**1**) and 1,4-dinitrocubane (**32**). Our prediction for azidocubane (**7**, 674.4 kJ mol^{-1}) is also lower than the literature value (696.22 kJ mol^{-1}),[41] but the differences between **1** and **7** from this work (−10.5 kJ mol^{-1}) and from Fan et al. (−11.42 kJ mol^{-1}) are comparable. The predictions herein are consistently around 20 kJ mol^{-1} lower than those of Fan et al., however the change in E_S between unsubstituted cubane (**1**) and the substituted derivatives azido **7** and dinitro **32** are comparable. As the prediction for cubane itself was very close to the value calculated by Roux et al.,[29] and the change in strain energy between cubane and the derivatives was comparable to those reported by Fan et al., this method was validated with confidence.

Synthesis

In brief the synthesis of the selected cubanes were achieved as follows: the half hydrolysis of diester **10** (e.g., acid ester **12**) was performed using one equivalent of hydroxide in tetrahydrofuran (THF) and methanol, whereas the fully hydrolysed diacid (**11**) was obtained with excess base in methanol. Monosubstituted cubanes can be accessed from acid ester **12**, by Barton decarboxylation, to give methyl cubane-1-carboxylate (**13**).[42] Hydrolysis of ester **13** gave carboxylic acid **14** in excellent yield. Subsequent conversion to the acid chloride and reaction with aqueous ammonia in situ afforded cubane-1-carboxamide (**15**) in 63 % yield over four steps. Treatment of acid ester **12** with ethyl chloroformate followed by ammonia in THF gave amide ester **16**, while reacting the acid ester **12** with aqueous ammonia provided amide acid **17** (Scheme 3).

Thermal characterisation

The melting and decomposition temperatures of pyrotechnic ingredients play a key role in the pyrotechnic reaction.[43] Thus the thermal properties of the cubanes were investigated using simultaneous thermogravimetric analysis/differential scanning calorimetry (TGA/DSC). Pleasingly, all cubanes were observed to be stable to above 100 °C except ester **13** which melted at 51.48 °C.[42a] Cubanes diester **10** and ester **13** effectively lost 100 % mass in one step while all others displayed multi-step mass loss (Figure 1). The simultaneous DSC data recorded during the TGA analysis showed that both **10** and **13** (Figure 2) only underwent endothermic transitions while the main mass loss events for **11**, **12**, and **14**–**17** were accompanied by exothermic decomposition. Amide acid **17** displayed a particularly steep TGA slope, and the accompanying heat flow curve showed a sharp and narrow peak, suggesting that this derivative underwent particularly rapid thermal decomposition.[8a]



Scheme 3. Synthetic Scheme for compounds **11**–**17**. i) NaOH, MeOH; ii) NaOH, MeOH/THF; iii) $(COCl)_2$, DMF, CH_2Cl_2; iv) **18**, DMAP, $CHCl_3$, $h\nu$, Δ; v) NH_3, CH_2Cl_2, vi) TEA, ethyl chloroformate, THF; vii) NH_3, THF; viii) NH_3, MeOH. TEA = triethylamine; DMAP = 4-*N*,*N*-dimethylaminopyridine; DMF = *N*,*N*-dimethyformamide].

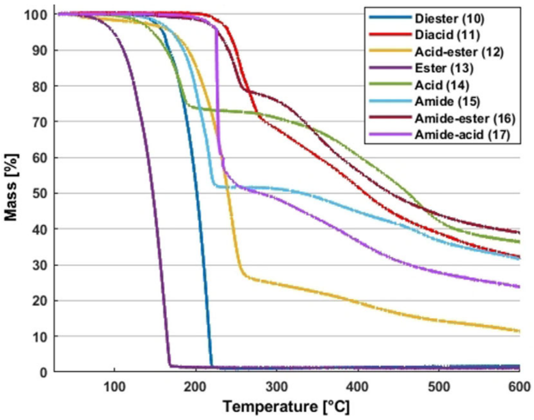


Figure 1. Thermogravimetric analysis (TGA) mass loss curves for cubanes **10**–**17**.

Impact sensitiveness testing

As mentioned above, the ESP method has been applied to predicting impact sensitiveness of high energy compounds. The prediction of impact sensitiveness is an especially attractive goal, both for safety reasons and to direct synthetic resources away from targets which are likely to be unsuitable for their intended application. The ESP method has seen some success in predicting impact sensitiveness, however much like predicting $\Delta_{sub}H^\circ$ each application can only be used for compounds which are well represented in the training set.[24a,44] Unfortunately, a suitable training set could not be constructed from the literature for cubanes **10**–**17**, and thus empirical testing was investigated.

In high energy materials research initial impact sensitiveness testing is carried out by striking a small amount of material with a hammer.[45] When this preliminary test was carried out on **10**–**17**, diacid **11** was the only substrate to result in a "go-event", which mirrored results reported by Nesterenko et al. who disclosed that cubane-1,4-dicarboxylic acid (**11**) reacted to 18 out of 25 hammer strikes.[10] The authors also reported that diester **10** reacted to one hammer strike out of 25, however we were unable to elicit any go-events for this compound. This was perhaps of no surprise as sensitiveness to impact and other stimuli (friction, electrostatic discharge [ESD]) is not only

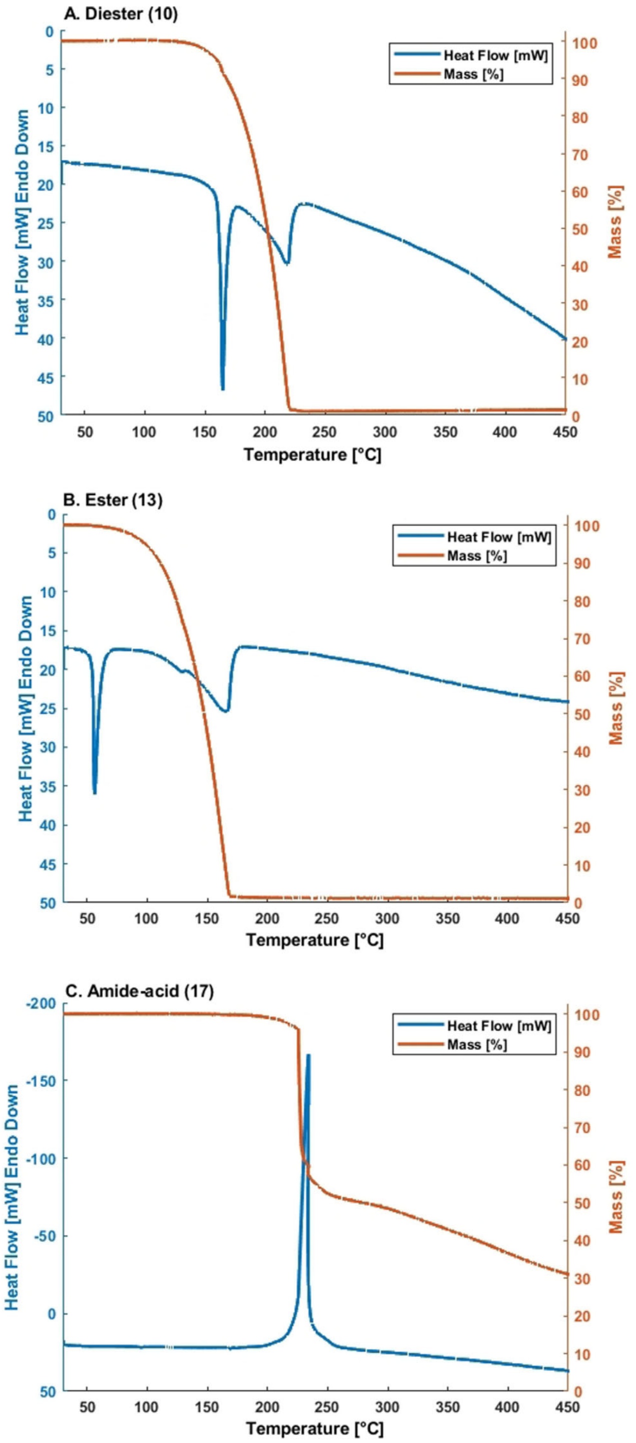


Figure 2. Simultaneous TGA/DSC plots of A) diester **10**; B) ester **13**; C) amide acid **17**.

affected by the molecular structure, but by particle size, crystallinity, and environmental factors (e.g., humidity, and temperature).[1,43,46] Despite this report, cubane-1,4-dicarboxylic acid (**11**) has been used in many laboratories worldwide, and there have been no reported incidents of impact initiated accidents.

While the hammer test is routinely used as an evaluation method for high energy materials it has been shown to be highly subjective, with the amount of force applied by individuals performing the test varying.[45] The amount of material required for standardised quantitative testing is much larger than that for a hammer test, and therefore diacid **11** and amide acid **17** were selected to undergo further sensitiveness testing (Table 7) due to a demonstrated positive hammer test and a steep TGA curve, respectively. Impact sensitiveness for both **11** and **17** were found to be in the range of secondary explosives, although they are insensitive to friction, and only slightly sensitive to ESD. While these data confirmed that care should be taken when handling cubanes **11** and **17**, it was not sufficient to classify either as explosive. Sensitiveness data for secondary explosive RDX and primary explosive TATP are shown for comparison.

Table 7. Sensitiveness data for **11**, **17**, secondary explosive RDX, and primary explosive TATP.

	Diacid **11**	Amide acid **17**	RDX (**47**)	TATP (**48**)
F of *I*[a]	70	90	80	<10
friction	>360 N	>360 N	120 N	0.1 N
ESD	ignition at 4.5 J but not at 0.45 J	ignition at 4.5 J but not at 0.45 J	ignition at 4.5 J but not at 0.45 J	ignition at <0.045 J

[a] Figure of Insensitiveness (*F* of *I*) standardised to RDX (*F* of $I=80$); a smaller number is more sensitive to impact.

Calculations made little suggestion that **11** and **17** should be more or less impact sensitive than the other cubanes. Diacid **11** registered the lowest enthalpy of formation and the lowest strain energy yet displayed highly exothermic decomposition under DSC analysis with a relatively sharp curve. Whereas amide acid **17** displayed the second lowest strain energy and fourth lowest enthalpy of formation but produced an almost vertical TGA curve and very sharp DSC curve, indicating rapid thermal decomposition.

Inspired by these results, an investigation to determine a correlation between energy of decomposition, onset temperature, and impact sensitiveness was undertaken. In the pharmaceutical industry Yoshida correlations are utilised to predict potentially problematic chemical reagents in scaled up reactions, and thus were deemed appropriate in this instance. Yoshida correlations are simple mathematical equations which relate the DSC measured onset temperature (T_{DSC}), and energy of the exotherm (Q_{DSC}), to the potential for a molecule to be impact sensitive and/or to propagate an explosion.[48] To quantitatively measure Q_{DSC} mass loss must be prevented during measurement, and therefore high-pressure rated capsules were used to carry out sealed cell DSC (scDSC), as opposed to the open pans used for TGA/DSC measurements. Using the lower energy threshold recommended by Sperry et al.,[48b] compounds falling above the green line are potentially impact sensitive and those above the red line could potentially propagate an explosion (Table 8 and Figure 3).

Cubanes **10**–**17** were all flagged as potentially impact sensitive and explosive according to the Yoshida analysis. Despite

Table 8. Sealed cell DSC (scDSC) results for cubanes **10**–**17**, and explosives TATP (**48**) and TNT (**49**).

Compound		Q_{DSC} [J g^{-1}]	T_{DSC} [°C]
diester[a]	**10**	−3005	179.5
diacid	**11**	−2689	217.4
acid ester	**12**	−2298	176.8
ester[a]	**13**	−4078	124.3
acid	**14**	−4081	135.3
amide	**15**	−3839	126.6
amide ester	**16**	−2712	173.0
amide acid	**17**	−3247	162.5
TATP[47]	**48**	−3173	167.5
TNT[47]	**49**	−3099	281.4

[a] Cubanes **10** and **13** did not display exothermic transitions in open pan TGA/DSC due to complete mass loss, but did decompose exothermically in sealed crucibles.

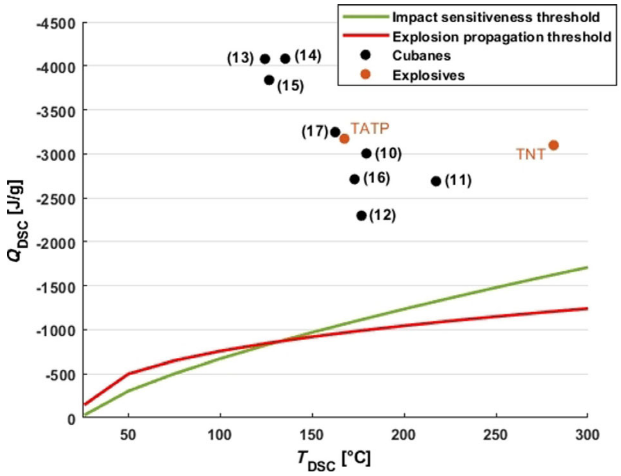


Figure 3. Yoshida Correlation results for cubanes **10**–**17**, and explosives TATP and TNT.[47] Data for TATP and TNT are literature values while all other values were collected as part of this work.

these predictions **10**–**17** have not displayed untoward handling issues in our laboratories, barring the hammer test result for diacid **11**. It should be kept in mind that the Yoshida correlation thresholds are designed for pilot plant and large-scale reactions, far beyond what is found in a normal research laboratory.

Conclusion

The cubane motif was investigated to determine whether it displayed promising scaffold attributes for the development of high energy pyrotechnic fuels. A model for predicting $\Delta_{sub}H^{\circ}$ values for cubanes substituted with a variety of functional groups (e.g., methyl ester, carboxylic acids, and amides) has been developed. An error of ± 21 kJ mol^{-1} for $\Delta_{sub}H^{\circ}$ predictions is acceptable and comparable to other applications of the ESP method. However, application of the model developed herein is limited by the compound classes found within the training set and it should only be used for predictions of structurally similar compounds.

The large strain energy of the cube scaffold resulted in large exothermic decomposition, despite some substituted cubanes having negative $\Delta_f H^{o}_{solid}$ values. Such energetic decomposition may assist in achieving sufficient spectral efficiency to decoy missiles away from platforms. It should be noted that the fuel is only one part of a pyrotechnic formulation, and there are many factors which contribute to spectral efficiency, combustion behaviour, and overall performance.[2b, 3a, 4a, 14, 49]

Although quantitative sensitiveness testing has indicated that diacid **11** and amide acid **17** are impact sensitive, it is not as high as predicted by Yoshida correlations. The investigated cubanes were found to undergo highly exothermic decomposition in scDSC measurements yet exhibit reduced sensitiveness to various ignition stimuli. Hammer test results herein when compared to previous reports highlight the subjectiveness of hammer testing, for example, diacid **11** reacted to hammer strikes both in our hands and as reported in the literature, whereas we were unable to illicit any reaction from diester **10** as was reported by Nesterenko et al.[10]

Despite their *F* of *I* values being in the secondary explosive range, diacid **11** and amide acid **17** are still potentially useful fuels for pyrotechnic IRCM formulations. RDX, which is slightly more impact sensitive than cubanes **11** and **17**, is used as a fuel in similar formulations.

In summary, utilisation of the cubane framework presents a promising approach to high energy molecule design, which can offer aspects of stability for use as high energy pyrotechnic fuels.

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Conflict of interest

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Keywords: cubane · energetic materials · infrared · pyrotechnics · Yoshida

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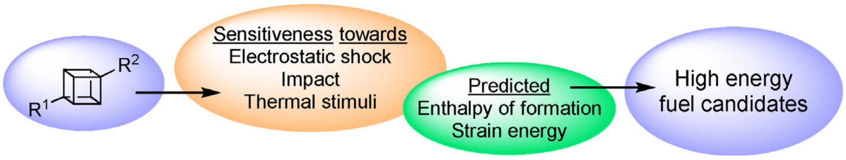
FULL PAPER

Energetic Materials

M. A. Dallaston, J. S. Brusnahan, C. Wall, C. M. Williams**

■■ – ■■

Thermal and Sensitiveness Determination of Cubanes: Towards Cubane-Based Fuels for Infrared Countermeasures



Feeling the strain: A series of cubanes were tested for thermal, impact, and electrostatic discharge sensitiveness. The results are discussed in the context of pyrotechnic fuels for spectrally matched flares.