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## Molecular Structure and Melting: Implications for Phase Change Materials

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## Molecular Structure and Melting: Implications for Phase

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## Change Materials

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**14 Abstract**

15 Phase change materials (PCM) offer a promising technology for thermal energy storage, load  
16 leveling, and peak shifting applications. A desirable PCM has a melting temperature within the  
17 temperature boundaries of its application, and a high change in enthalpy on melting. Knowledge  
18 of the relationships between these thermodynamic properties and molecular structure would  
19 advance informed selection of PCM candidates for a given application. In the present  
20 investigation, the relationship between structure (length of alkyl chains) and properties has been  
21 investigated for isomeric esters, showing that esters containing longer individual alkyl chains  
22 have higher melting temperatures, and higher enthalpy changes on melting. The melting entropy  
23 changes, however, are relatively independent of the alkyl chain distribution.

24

**25 Keywords:**

26 Thermodynamics

27 Energy storage

28 Phase change materials

29

## 30 1. Introduction

31 One of the barriers to a large-scale shift to renewable energy is the inherent intermittency  
32 of renewable energy sources, especially wind and solar, leading to an imbalance between the  
33 supply of renewable energy and the demand from the grid. As such, storage technologies are  
34 required to make renewable energy available at times when its source is not. Furthermore, energy  
35 demand needs to be reduced through energy conservation and increased energy efficiency. While  
36 considerable focus is placed on electrical energy, there are gains to be made in terms of thermal  
37 energy too, especially when the end use is heat. Solar thermal energy can be used to heat homes  
38 and water, but requires energy storage for use when solar flux is low. Approximately 50 % of  
39 domestic energy use goes toward heating and cooling of buildings.<sup>1</sup> As such, reduction of  
40 heating and cooling requirements, and increase in insulation efficiency, are attractive targets.

41 Sensible heat storage materials, using the heat capacity of the material, have been used  
42 for millennia.<sup>2</sup> These are materials with high heat capacity and, once heated, they radiate heat for  
43 an extended period. Examples include rocks heated in the sun or with fire, and water. Sensible  
44 materials also can be used for cooling, as they absorb relatively large inputs of energy for a given  
45 increase in temperature. For example, this is the premise of cold cellars constructed of rock or  
46 concrete.

47 More recently, phase change materials (PCM) have been used for thermal energy  
48 storage.<sup>2,3,4</sup> PCMs store energy via the enthalpy change of a phase transition, typically melting,  
49 although solid-solid transitions are also possible.<sup>5</sup> Over moderate temperature ranges, PCMs can  
50 store much more energy per unit mass or volume than a sensible heat storage material. PCMs are  
51 used in heat storage applications such as solar thermal hot water<sup>6</sup> and peak shifting. In the latter  
52 case, the PCM is heated/charged using off-peak power, and the heat is recovered later. Similarly,

53 ice-based PCMs can be solidified using off-peak power and then used later for cooling, in place  
54 of conventional air conditioning, throughout the day.<sup>2</sup> Another important application of PCMs is  
55 in moderating temperature swings in a building,<sup>7</sup> thereby reducing heating and air conditioning  
56 requirements. PCMs can be placed within walls, floors, or ceilings<sup>8</sup> to absorb energy during the  
57 warmest parts of the day, before releasing it at night when the temperature has dropped. By  
58 doing so, extreme temperature swings can be vastly reduced.<sup>9</sup>

59 Many materials have been studied for use as PCMs, including salt hydrates, paraffins,  
60 fatty acids, and esters.<sup>10,11,12</sup> A number of materials properties are of concern in the selection of  
61 an appropriate PCM for a given application. These requirements include appropriate melting  
62 temperature, high enthalpy change of fusion, high heat capacity, high thermal conductivity,  
63 controllable hysteresis, low cost, high stability, and low toxicity.<sup>2</sup> Of these, melting temperature  
64 and enthalpy change of fusion are most important. The melting temperature of the PCM must fall  
65 within the temperature range of the application: if it does not, the PCM will not change phase,  
66 and will act solely as a sensible heat storage material. The enthalpy change of fusion (latent heat)  
67 of the material should be as high as possible in order to maximize the energy storage density.

68 An understanding of the connection between chemical structure and thermodynamic  
69 properties would allow for informed selection of potential PCMs. By determining which  
70 structural features contribute to high enthalpy change on melting, it would be possible to define  
71 which classes of materials hold the most promise for latent heat storage applications.  
72 Furthermore, knowledge of the link between molecular features and melting temperatures would  
73 allow PCMs within a class of materials to be tailored for specific applications at a variety of  
74 temperatures. The main question addressed here is: how does molecular structure influence  
75 thermodynamic properties associated with melting? Although the overarching question is

76 general, in this work we examine a specific example: the impact of carbon atom distribution in  
77 linear, saturated esters. For a linear, saturated ester containing 12 carbon atoms, it is possible to  
78 form 11 different esters, depending on how the carbon atoms are distributed between the alkyl  
79 chains on either side of the bridging oxygen atom. All have the same molecular mass, but their  
80 thermodynamic properties differ. Here, the influence of structure on melting temperature,  
81 enthalpy change, and entropy change are determined by examining three such esters: ethyl  
82 decanoate, butyl octanoate, and hexyl hexanoate. The 12-carbon fatty acid, dodecanoic acid, can  
83 be considered as a related case, in which all 12 carbon atoms are part of a single alkyl chain. It is  
84 a structural isomer of these esters, and is also included in this analysis.

## 85 2. The Thermodynamics of Melting

86 The melting temperature ( $T_{fus}$ ) and the enthalpy change on fusion ( $\Delta_{fus}H$ ) are intimately  
87 linked to the entropy change on fusion ( $\Delta_{fus}S$ ) by the equality of the Gibbs energy of the solid and  
88 liquid phases, whereby at the melting point equilibrium,

$$89 \quad T_{fus} = \frac{\Delta_{fus}H}{\Delta_{fus}S} \quad (1)$$

90 Immediately it can be seen that when two materials with equal entropy changes on melting are  
91 compared, the more stable solid, *i.e.* the one with the higher  $\Delta_{fus}H$ , will have a higher melting  
92 point.<sup>13</sup> Conversely, for two materials of equal  $\Delta_{fus}H$  and the same absolute entropy of the melt,  
93 the lower entropy solid, *i.e.* the material with higher  $\Delta_{fus}S$ , would melt at a lower temperature.  
94 Furthermore, for a given melting point, the enthalpy and entropy changes will be directly  
95 proportional, and so high  $\Delta_{fus}S$  leads to high  $\Delta_{fus}H$ . Therefore, by understanding how structure  
96 relates to the thermodynamic properties of a material as it melts, it could be possible to predict

97 which materials are the best candidates for use as PCMs. Note that the focus here is on molecular  
98 materials, as they are one of the common families of PCMs.

99         The investigation of the relationship between molecular structure and melting has a long  
100 history. In 1882, after reviewing information for 15000 compounds, Carnelley,<sup>14,15</sup> showed that  
101 symmetrical molecules with compact and efficient crystal packing tend to have higher melting  
102 points. A similar conclusion was reached more recently by Boese *et al.*<sup>16</sup> who showed that the  
103 melting point of the symmetrical 1,4-dichlorobenzene (326 K) is significantly higher than the  
104 asymmetrical 1,2- and 1,3-isomers (256 K and 246 K, respectively). It is the efficient packing of  
105 symmetrical molecules that leads to a more stable solid, and therefore a high melting point.

106         Another general finding is that melting temperature increases with molar mass so long as  
107 the increase in mass does not significantly change the symmetry or packing. This trend can be  
108 observed in the even-numbered alkanes. The melting points of the alkanes increase with the  
109 addition of methylene units to the chain, forming two nearly linear trends, one for even number  
110 of carbons in the chains and one for odd, reflecting the two types of packing.<sup>17,18</sup> However,  
111 branched alkanes have significantly lower melting points than their corresponding structurally  
112 isomeric linear alkanes.

113         Gilson<sup>19</sup> compiled entropy changes of fusion for the 358 compounds with listed enthalpy  
114 changes of fusion available at that time in the *CRC Handbook of Chemistry and Physics*,<sup>20</sup> and  
115 found three groupings of materials. The recent compilation by Acree and Chickos<sup>21,22</sup> of  
116 thermodynamic properties for over 7000 organic and organometallic compounds allowed us the  
117 opportunity to extend Gilson's study to include >5000 organic compounds, and again we  
118 distinguished three groupings (Figure 1).

119 The small grouping at the low end,  $\Delta_{fus}S \sim 5$  to  $25 \text{ J mol}^{-1} \text{ K}^{-1}$ , typically includes  
120 compounds that are disordered crystals of rigid molecules. The disorder already present in the  
121 crystalline phase makes the additional entropy gain upon melting relatively small. An example in  
122 this category is cubane ( $\text{C}_8\text{H}_8$ ) for which  $\Delta_{fus}S$  is  $22 \text{ J mol}^{-1} \text{ K}^{-1}$ .<sup>23</sup> In the crystalline phase of  
123 cubane, just below the melting point, the cubane molecules rotate rapidly on their lattice sites,  
124 and the entropy of fusion is low because the rotational degrees of freedom are already active in  
125 the solid.

126 Figure 1 also shows a second, and large, grouping of compounds with  $\Delta_{fus}S$  centered at  
127 about  $58 \text{ J mol}^{-1} \text{ K}^{-1}$ . These compounds form ordered crystals of rigid molecules. Regardless of  
128 composition, materials in ordered crystals all tend to have the same entropy change on  
129 transforming from solid to liquid. This generalization was noted more than a century ago, and is  
130 known as Walden's rule.<sup>24</sup> (It is analogous to Trouton's rule,<sup>25</sup> in which the entropy change on  
131 evaporation is almost the same for most materials, due to the very similar increase in disorder on  
132 going from the liquid to the vapour.)

133 Finally, 1780 of these 7038 compounds were identified with high entropy changes of  
134 fusion ( $\Delta_{fus}S > 85 \text{ J mol}^{-1} \text{ K}^{-1}$ ). These are typically non-rigid molecules, including those with long  
135 alkyl chains. Upon melting, these materials gain considerable entropy as their non-rigid  
136 structures allow them to sample many configurations. From equation 1, it can be seen that these  
137 materials with high  $\Delta_{fus}S$  could also have high  $\Delta_{fus}H$ , which would make them attractive  
138 candidates for PCMs. Many of these compounds, including alkanes and fatty acids, are already  
139 being used in heat storage applications.

140 Special mention should be made of the values of  $\Delta_{fus}H$  and  $\Delta_{fus}S$  for solids in which  
141 hydrogen-bonding plays an important role. In this case, typically the melting point is higher than



142 usual due to the stabilizing influence of the hydrogen-bonding on the crystalline structure, so  
143 even if  $\Delta_{fus}S$  falls in the “normal” range, then  $\Delta_{fus}H$  can be exceptionally high (see equation 1).  
144 Sugar alcohols are one such example, with exceptional promise as phase change materials, if  
145 their inherent hysteresis is not an impediment.<sup>26</sup>

146 Saturated fatty acids are a promising family of PCMs.<sup>11,12,27</sup> They have high melting  
147 enthalpy changes, which increase nearly linearly (with a significant odd/even effect<sup>18</sup>) with the  
148 length of the carbon chain.<sup>21,22</sup> Their melting temperatures also increase with increasing chain  
149 length, although they plateau above a chain of about 20 methylene units.<sup>21,22</sup> Fatty acids can be  
150 used in energy storage applications at a variety of temperatures by selecting a molecule of the  
151 appropriate length. Saturated fatty acids also cycle well<sup>11,12</sup> and can be produced sustainably<sup>28</sup>.  
152 They can be extracted from a variety of renewable sources including plants, such as oil palm,  
153 algae, and animal fats. Saturated fatty acids typically have very low embodied energy, and that,  
154 coupled with their high energy storage density, means that their energy payback time can be very  
155 short when used in devices to store renewable energy.<sup>28</sup>

156 While pure materials often have excellent thermodynamic properties for use in heat  
157 storage applications, mixtures also can be extremely useful, especially to allow applications in  
158 temperature ranges where there is no suitable pure material. In a simple ideal eutectic system,  
159 addition of one material to another leads to depression of the melting point. The minimum  
160 melting temperature is found at the eutectic composition. In thermal storage applications,  
161 eutectics can be used to access melting temperatures lower than for pure materials. Using  
162 saturated fatty acids as an example, if one wished to store energy at 22 °C for a temperature  
163 moderating application say in residential buildings, the closest melting temperatures one could  
164 achieve using pure materials are 16.5 °C with octanoic acid, or 28.4 °C with undecanoic acid,

165 neither very useful. However, the eutectic mixture of undecanoic acid (~ 81.5 mol%) and  
166 tetradecanoic acid has a very useful melting temperature of 21.7 °C.<sup>29</sup> Without the use of  
167 eutectics, compromises such as more expensive materials, or materials with lower energy storage  
168 density might be required. Furthermore, some fatty acid eutectic mixtures are found in nature.<sup>30</sup>  
169 Such a mixture can be directly extracted and used in its natural proportions, avoiding energy-  
170 intensive separation processes which would then be followed by re-mixing.

171 The entropy change for melting eutectic mixtures is greater than for a mixture of the pure  
172 compounds, raised by the mixing entropy. For the eutectic mixture of decanoic acid (82 mol%)  
173 and tetradecanoic acid, the measured  $\Delta_{fus}S$  is 96 J mol<sup>-1</sup> K<sup>-1</sup>,<sup>31</sup> *i.e.*, at the high end in Figure 1.  
174 However, if  $\Delta_{fus}S$  were to be calculated based on the linear proportionality of the amounts of the  
175 pure components and their entropy changes on fusion,<sup>31</sup> excluding mixing, the expected entropy  
176 change would be only 87 J mol<sup>-1</sup> K<sup>-1</sup>. The  $\Delta_{fus}H$  of the same eutectic, however, is 28.2 kJ mol<sup>-1</sup>,  
177 <sup>31</sup> which is very close to the value (28.4 kJ mol<sup>-1</sup>) calculated from the molar percentages of each  
178 compound (*i.e.*, rule of mixtures). In this case,  $\Delta_{fus}S$  is higher for the mixture but  $\Delta_{fus}H$  is in  
179 proportion to the composition, and therefore (Equation 1),  $T_{fus}$  is depressed, as observed. The rule  
180 of mixtures does not always predict  $\Delta_{fus}H$  accurately for eutectics, especially if there are strong  
181 interactions between the components of the eutectic in the liquid phase. For example, the  
182 succinonitrile-phenanthrene eutectic system shows<sup>32</sup>  $\Delta_{fus}H$  much larger than would be expected  
183 based on the rule of mixtures, likely due to non-ideal behaviour as exemplified by liquid-liquid  
184 phase separation.

185 Inagaki and Ishida<sup>33</sup> have examined the four six-carbon sugar alcohols: galactitol,  
186 mannitol, sorbitol and iditol, both computationally and experimentally, for potential use as  
187 PCMs. All four alcohols have the same chemical formulae, and identical, linear carbon

188 backbones. They differ only in stereochemistry, with the hydroxyl groups on the four chiral  
189 centers arranged differently. Galactitol and mannitol were found to have high values of  $\Delta_{fus}H$  (60  
190  $\text{kJ mol}^{-1}$ ,  $52 \text{ kJ mol}^{-1}$ ) and  $T_{fus}$  (460 K, 439 K), while sorbitol and iditol were found to have lower  
191 values ( $34 \text{ kJ mol}^{-1}$ , 372 K,  $31 \text{ kJ mol}^{-1}$ , 353 K).<sup>33</sup> The authors ascribe the differences to the  
192 distribution of the hydroxyl groups. Sorbitol and iditol have adjacent hydroxyl groups which  
193 have large electrostatic repulsions that destabilize the crystalline phase. The decreased stability  
194 (increase in enthalpy) of the solid phase produces a smaller change in enthalpy upon melting.  
195 Based on additional data for sugar alcohols with carbon backbones of 4 to 8 carbons, three  
196 suggestions have been made for selection of sugar alcohols for thermal energy storage  
197 applications:<sup>33</sup> longer backbones provide higher  $\Delta_{fus}H$ ; the hydroxyl groups should be well  
198 separated in their distribution; and backbones with even numbers of carbons provide higher  
199 values of  $T_{fus}$  and thereby higher  $\Delta_{fus}H$ .

200 Stamatiou *et al.*<sup>34</sup> examined linear fatty esters for use as PCMs. They showed that both  
201  $T_{fus}$  and  $\Delta_{fus}H$  had strong positive correlations with the molar mass of the ester. In the present  
202 work, three linear, 12-carbon esters, and also dodecanoic acid have been examined. These  
203 compounds are isomers with linear alkyl chains totalling 12 carbons, differing in their  
204 distribution of their 12 carbon atoms between the alkyl chains. The influence of this distribution  
205 on  $T_{fus}$ ,  $\Delta_{fus}H$ , and  $\Delta_{fus}S$  was determined, and provides deeper insight concerning how molecular  
206 structure can be used to predict PCM properties, and aid in PCM selection.

### 207 3. Materials and Methods

208 Experimental values of  $T_{fus}$  and  $\Delta_{fus}H$  were determined using a TA Instruments Q200  
209 differential scanning calorimeter (DSC). The DSC was calibrated for  $T_{fus}$  and  $\Delta_{fus}H$  at 2 and 10 K  
210  $\text{min}^{-1}$  scan rates with both mercury and indium standards<sup>35</sup> before the measurements were taken.

211 Samples of dodecanoic acid (Aldrich, 98%), ethyl decanoate (Sigma-Aldrich, > 98%), butyl  
212 octanoate (Aldrich), and hexyl hexanoate (Sigma-Aldrich, >97%) were each analysed three times  
213 successively with 2 and then 10 K min<sup>-1</sup> scan rates. Measurements were made in crimped  
214 aluminum pans, under a flow of helium at a rate of 25 mL min<sup>-1</sup>. The sample masses were  
215 between 8.5 and 10 mg. The values of  $T_{fus}$  were determined from onset temperatures from the 2  
216 K min<sup>-1</sup> scans. A slow heating rate was used for melting point determination to minimize  
217 ‘thermal lag’ in the sample.<sup>36</sup> Melting temperatures determined by this method typically have  
218 uncertainties within 1 K. The values of  $\Delta_{fus}H$  were determined from the 10 K min<sup>-1</sup> scans. A  
219 faster heating rate was used for  $\Delta_{fus}H$  measurement because it results in sharper peaks, reducing  
220 the contribution of  $\Delta_{fus}H$  swept into the baseline. A well-calibrated DSC with excellent thermal  
221 contact between the sample and pan (as is the case for samples melted into the pan) can give  
222 transition enthalpy change values with as little as ~5 % uncertainty.

## 223 4. Results and Discussion

224 The four compounds analysed all have the molecular formula C<sub>12</sub>H<sub>24</sub>O<sub>2</sub>, and the chemical  
225 structure R<sub>1</sub>-O-C(O)-R<sub>2</sub>. They differ only in their distribution of methylene units between R<sub>1</sub> and  
226 R<sub>2</sub>. At one extreme is dodecanoic acid, in which R<sub>1</sub> is a proton and all carbon atoms belong to R<sub>2</sub>.  
227 The other extreme is hexyl hexadecanoate, in which the carbon backbones are distributed evenly  
228 on either side of the bridging oxygen.

### 229 4.1 Melting Temperature

230 DSC was used to determine  $T_{fus}$ , using a 2 K min<sup>-1</sup> scan rate (Figure 2). The results are  
231 summarized in Table 1. (No solid-solid phase transitions were found in the temperature ranges  
232 examined.) Over three melting cycles, there was no observable change in the melting

233 temperature. In all cases the standard deviation in  $T_{fus}$  was less than 0.1 K. The melting points of  
234 these compounds increased with increasing length of  $R_2$ , from 217 K (hexyl hexanoate) to 316 K  
235 (dodecanoic acid). Despite the fact that these molecules are isomers and that all their alkyl  
236 chains are linear, it is the longest uninterrupted alkyl chains that produced the highest melting  
237 points, likely due to their stability due to maximized van der Waals interactions between the  
238 chains. Stamatiou and coworkers<sup>34</sup> examined the melting points of eight linear fatty ester PCMs,  
239 including two structural isomers: ethyl tetradecanoate and butyl dodecanoate. Again, in this case,  
240 the ester with the longer uninterrupted alkyl chain, ethyl tetradecanoate, was found to have the  
241 highest melting temperature.<sup>34</sup> From the melting points for 53 linear, saturated esters as compiled  
242 by Acree and Chickos,<sup>21,22</sup> it can be seen that this is, in fact, a general phenomenon. As shown in  
243 Figure 3, the plot of  $T_{fus}$  vs. number of carbons has a trend of increasing melting temperature  
244 with increasing number of carbons. This is expected given that the molar masses of the esters  
245 increase with increasing carbon number, and the number of favourable chain-chain interactions  
246 in the solid phase increases as well, thereby increasing the stability of the solid phase and  
247 increasing the melting point. At each number of carbon atoms ( $x$ -axis in Figure 3), however,  
248 there is a spread of values for  $T_{fus}$ . These different values correspond to different structural  
249 isomers of linear esters. As also found here, the highest melting temperatures correspond to the  
250 esters with the longest uninterrupted alkyl chains. For example, among the esters for which data  
251 are available for 32 carbons, ethyl triacontanoate (341.5 K) has a significantly higher  $T_{fus}$  than  
252 either of tetradecyl octadecanoate (322.8 K) or octadecyl tetradecanoate (324.4 K). Similarly, at  
253 26 carbons, methyl pentacosanoate (332.2 K) has a higher  $T_{fus}$  than hexadecyl decanoate (302.6  
254 K).<sup>22</sup>

255 From the present results, while the melting points of hexyl hexanoate and butyl octanoate  
256 are separated by only 13 K, and those of butyl octanoate and ethyl decanoate by 22 K, there is a  
257 much larger jump of 64 K between ethyl decanoate and dodecanoic acid. This difference could  
258 be due, in part, to the fact that dodecanoic acid forms dimers, hydrogen-bonded through the  
259 carboxyl head groups of the molecules.<sup>37</sup> The dimers are found in the crystalline phase, and  
260 persist into the liquid phase.<sup>37</sup> As such, when dodecanoic acid melts, the dimer is similar to a 24-  
261 carbon molecule (*i.e.*, to tetracosanoic acid), rather than a single 12-carbon molecule, and  
262 therefore melts at a rather high temperature. However, the 24 carbon atoms of the dodecanoic  
263 acid dimer are distributed between two alkyl chains, and thus dodecanoic acid still has a lower  
264 melting point and enthalpy of fusion (Table 1) than tetracosanoic acid (356.5 K, 229.22 J g<sup>-1</sup>).<sup>22</sup>

265 On crystallization, all the three esters investigated here exhibited moderate supercooling.  
266 The amount of supercooling ranged from 9 to 10 K, 12 to 13 K, and 8 to 10 K for ethyl  
267 decanoate, butyl octanoate, and hexyl hexanoate, respectively. This, in itself, is an important  
268 consideration if fatty esters are to be used as PCMs, as the application must have a minimum  
269 temperature sufficiently low to nucleate the crystalline phase. Without crystallization, the latent  
270 heat which was input in melting cannot be recovered. However, to their benefit, crystallization in  
271 these esters occurs at relatively consistent temperatures over several cycles (standard deviation ~  
272 1 K). This predictable behaviour would be beneficial should they be employed in a PCM  
273 capacity.

#### 274 4.2. Melting Enthalpy Change

275 Using a 10 K min<sup>-1</sup> scan rate, the enthalpies of fusion also were determined using DSC,  
276 with high reproducibility (standard deviation <1 J g<sup>-1</sup>). The  $\Delta_{fus}H$  values for the three esters and  
277 the fatty acid follow the same trend as  $T_{fus}$ , decreasing with decreasing maximum individual

278 alkyl chain length. This finding would seem to indicate that more energy is required to separate  
279 single long chains than to separate multiple shorter chains with the same additive length, and that  
280 the rankings of  $\Delta_{fus}H$  and  $T_{fus}$  among linear isomers of esters are the same.

281         The picture becomes slightly less clear when considering the data compiled by Acree and  
282 Chickos<sup>21,22</sup> for 53 linear esters, as presented in Figure 4. The molar melting enthalpy change  
283 increases more or less linearly with the overall number of carbon atoms in the ester. This is  
284 logical given that each addition of a methylene unit increases the number of chain-to-chain  
285 intermolecular interactions which must be separated on melting, each requiring an input of  
286 energy. Again, the spread in values at a given number of carbon atoms is due to the different  
287 enthalpy changes on fusion for the different isomers. While in many cases the highest enthalpy  
288 change on fusion for esters of a given length belongs to the ester with the longest uninterrupted  
289 alkyl chain (methyl pentacosanoate, methyl heneicosanoate, methyl tetradecanoate, *etc.*), this is  
290 not always the case. And, in several cases, within esters of a given length, the ordering of the  
291 enthalpy values does not match the ordering of the longest individual alkyl chains or melting  
292 temperature. Ethyl triacontanoate is the 32-carbon ester with the longest individual alkyl chain  
293 for which data are available. It had the highest melting temperature of the 32-carbon esters, but  
294 the lowest  $\Delta_{fus}H$  value. Instead, for 32 carbons, it is the ester with the shortest maximum  
295 individual alkyl chain and the lowest melting point – tetradecyl octadecanoate – that has the  
296 highest  $\Delta_{fus}H$ . Among the 26-carbon esters, the highest melting isomer and isomer with the  
297 longest single alkyl chain, methyl pentacosanoate, also has the highest  $\Delta_{fus}H$ . However,  
298 hexadecyl decanoate, the lowest melting isomer, does not have the lowest  $\Delta_{fus}H$ . Instead, the  
299 lowest  $\Delta_{fus}H$  belongs to ethyl tetracosanoate. Ethyl tetracosanoate had the second highest melting

300 point, and the second longest individual alkyl chain, and so would have been expected to have  
301 had the second highest  $\Delta_{fus}H$ .

302 Note that the data from Acree and Chickos<sup>21,22</sup> are thoroughly tabulated but not assessed  
303 for accuracy. As we have indicated elsewhere,<sup>2</sup> for some PCMs, widely varying values of  
304 physical properties have been reported, and some of the reports are not accurate. For example,  
305 Acree and Chickos<sup>22</sup> present 16 values of  $\Delta_{fus}H$  for dodecanoic acid, ranging from 25.4 kJ mol<sup>-1</sup>  
306 to 44.9 kJ mol<sup>-1</sup>. (We take some comfort that the present value,  $36 \pm 1$  kJ mol<sup>-1</sup>, agrees well with  
307 our own previously published values of  $37 \pm 2$  kJ mol<sup>-1</sup> and  $35 \pm 3$  kJ mol<sup>-1</sup>.<sup>11,12</sup>) In principle,  
308 different polymorphs can have different melting properties so that could account for some of the  
309 spread of reported properties, but for dodecanoic acid, which has three polymorphs, the other  
310 two, A and B, convert to the C-form and only the C-form melts.<sup>38</sup> Especially when only a single  
311 data source is given, only general trends should be concluded from the Acree and Chickos<sup>21,22</sup>  
312 data, and specific details would require further experimental investigation.

### 313 *4.3. Melting Entropy Change*

314 The entropies of fusion of the examined isomers (Table 1) are all high in the context of  
315 values presented in Figure 1. Hexyl hexanoate has the lowest value of  $\Delta_{fus}S$  (and  $T_{fus}$  and  $\Delta_{fus}H$ ).  
316 The entropy changes for the other three compounds show a slightly different order from the  $T_{fus}$   
317 and  $\Delta_{fus}H$  order, with the highest  $\Delta_{fus}S$  belonging to butyl octanoate, and dodecanoic acid and  
318 ethyl decanoate having equal values of  $\Delta_{fus}S$ . When also considering the 53 esters from Acree  
319 and Chickos (Figure 5),<sup>21,22</sup> the general trends in  $\Delta_{fus}S$  mirror that of  $\Delta_{fus}H$ : there is a strong linear  
320 correlation between  $\Delta_{fus}S$  and the number of carbons, and in most cases, among esters of equal  
321 carbon number, the one with the longest unbroken alkyl chain has the highest  $\Delta_{fus}S$ . The



322 exceptions to this rule are largely the same compounds which deviated from the general trend for  
323  $\Delta_{fus}H$ .

324 Considering equation 1, for a constant  $T_{fus}$ , a high value of  $\Delta_{fus}S$  should give a high  $\Delta_{fus}H$ ,  
325 and so it is logical for  $\Delta_{fus}S$  and  $\Delta_{fus}H$  to correlate well. A plot of  $\Delta_{fus}S$  as a function of  $\Delta_{fus}H$  for  
326 the esters studied here, and the 53 esters from Acree and Chickos,<sup>21,22</sup> results in a linear  
327 relationship with  $R^2=0.991$  (Figure 6). Long alkyl chains provide the opportunity for many  
328 chain-chain interactions, stabilizing the solid phase (high  $\Delta_{fus}H$ ), but also increase the entropy  
329 gain upon melting as they gain many degrees of freedom in the liquid phase.

#### 330 4.4. PCM Selection

331 As described earlier, if  $T_{fus}$  is unchanged, high  $\Delta_{fus}S$  leads to high  $\Delta_{fus}H$ . Therefore, when  
332 selecting a material for use as a PCM for thermal energy storage, increasing the linear alkyl  
333 chain length of the material can lead to higher energy storage density. (Although the theoretically  
334 more meaningful quantities are the molar enthalpy or entropy changes, in practical terms the  
335 gravimetric enthalpy change is more meaningful. This is why comparisons of isomers is  
336 particularly instructive.) While molar mass generally has a direct correlation with melting  
337 temperature, the distribution of the atoms is important. Within a series of materials with equal  
338 total linear alkyl chain length, materials with longer uninterrupted alkyl chains have higher  $T_{fus}$ ,  
339 which means that if  $\Delta_{fus}S$  is unchanged, then  $\Delta_{fus}H$  will be higher, and the material will have a  
340 higher thermal energy storage density. From Figure 3, the 26-carbon hexadecyl decanoate melts  
341 at a ~20 K lower temperature, and has lower  $\Delta_{fus}H$ , than the shorter and lighter 24-carbon ethyl  
342 docosanoate. The presence of the 22-carbon chain in the lighter compound results in the high  
343 melting point relative to the heavier compound containing only 10 and 16 carbon alkyl chains,  
344 despite having nearly equal  $\Delta_{fus}S$  (242 vs. 244 J mol<sup>-1</sup> K<sup>-1</sup>).<sup>21,22</sup>

## 345 5. Conclusions

346 The interplay between molecular structure and thermodynamic properties is a valuable  
347 tool for PCM selection, and prediction of PCM properties. Increased molar mass leads to higher  
348 melting temperature, which in turn give rise to higher enthalpy change on fusion. Compact,  
349 symmetrical structures stabilize the solid phase and also give higher enthalpy changes. Materials  
350 with long alkyl chains have a high entropy change upon melting, and thereby also have high  
351 enthalpies of fusion.

352 In this study, the effect of carbon atom distribution in linear molecules of formula  
353  $C_{12}H_{24}O_2$  on  $T_{fus}$ ,  $\Delta_{fus}H$ , and  $\Delta_{fus}S$  was determined. Dodecanoic acid and three esters (hexyl  
354 hexanoate, butyl octanoate, and ethyl decanoate) were analyzed by DSC. It was determined that  
355 the highest melting temperatures and enthalpies of fusion could be achieved in the molecules  
356 with the longest individual alkyl chains. As such, hexyl hexanoate had the lowest melting  
357 temperature and enthalpy change, followed by butyl octanoate, ethyl decanoate, and finally  
358 dodecanoic acid had the highest. Comparing with data compiled by Acree and Chickos<sup>21,22</sup>, this  
359 seems to be a general trend amongst the unbranched, saturated fatty esters.

360 The compounds analyzed in this study follow many general trends for  $\Delta_{fus}S$  exhibited by  
361 the ester data compiled from Acree and Chickos,<sup>21,22</sup> with the highest values for  $\Delta_{fus}S$  typically  
362 found for the isomers with the longest alkyl chains. The high entropy change gives rise to a high  
363 enthalpy change on melting.

364 When selecting a PCM from long-chain organic molecules, longer chains, *i.e.*, higher  
365 molar mass, will give higher melting points, and higher enthalpy changes and entropy changes  
366 on fusion. With regard to the main question asked here, namely “how does molecular structure  
367 influence thermodynamic properties?”, it was found that amongst isomeric ester PCMs, the

368 highest  $T_{fus}$ ,  $\Delta_{fus}H$ , and  $\Delta_{fus}S$  will be found for the ester with the longest individual alkyl chain.  
369 Furthermore, fatty acids have higher melting temperatures and higher enthalpy changes than a  
370 corresponding ester isomer. However, even the low-melting esters with evenly distributed carbon  
371 atoms, such as hexyl hexanoate, have appreciable values of  $\Delta_{fus}H$  and could find use in  
372 refrigeration and cooling applications.

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**Table 1.** Thermodynamic properties of three esters and a fatty acid, each with chemical formula

$C_{12}H_{24}O_2$ .\*

<b>Compound</b>	$T_{fus} / \text{K}$	$\Delta_{fus}H /$ <b>kJ mol<sup>-1</sup></b>	$\Delta_{fus}H /$ <b>J g<sup>-1</sup></b>	$\Delta_{fus}S /$ <b>J mol<sup>-1</sup> K<sup>-1</sup></b>	$\Delta_{fus}S /$ <b>J g<sup>-1</sup> K<sup>-1</sup></b>
Hexyl Hexanoate	217 ± 1	22 ± 1	108 ± 5	100 ± 5	0.50 ± 0.03
Butyl Octanoate	230 ± 1	28 ± 1	140 ± 7	122 ± 6	0.61 ± 0.03
Ethyl Decanoate	252 ± 1	29 ± 1	143 ± 7	114 ± 6	0.57 ± 0.03
Dodecanoic Acid	316 ± 1	36 ± 2	180 ± 9	114 ± 6	0.57 ± 0.03

\*Errors represent overall experimental uncertainties.

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**Figure 1.** Entropies of fusion of 7038 organic compounds. Values from the data taken from Acree and Chickos.<sup>21,22</sup>



**Figure 2.** DSC traces showing melting for three 12-carbon linear esters and dodecanoic acid, taken at  $2 \text{ K min}^{-1}$ . Endothermic peaks point down, and curves are displaced vertically for ease of viewing.

**Figure 3.** Melting temperatures for the linear, saturated esters as compiled by Acree and Chickos<sup>21,22</sup> and the present data. Among the esters for which data are available, at each carbon number, the ester with the longest individual alkyl chain has the highest  $T_{fus}$ .

**Figure 4.**  $\Delta_{fus}H$  for the linear, saturated esters as compiled by Acree and Chickos<sup>21,22</sup> and present data.

**Figure 5.**  $\Delta_{fus}S$  for the linear, saturated esters as calculated from Acree and Chickos<sup>21,22</sup> and present data.

**Figure 6.** Relationship between  $\Delta_{fus}S$  and  $\Delta_{fus}H$  for the linear, saturated esters as compiled from Acree and Chickos<sup>21,22</sup> and present data. The line is a linear fit to the data.

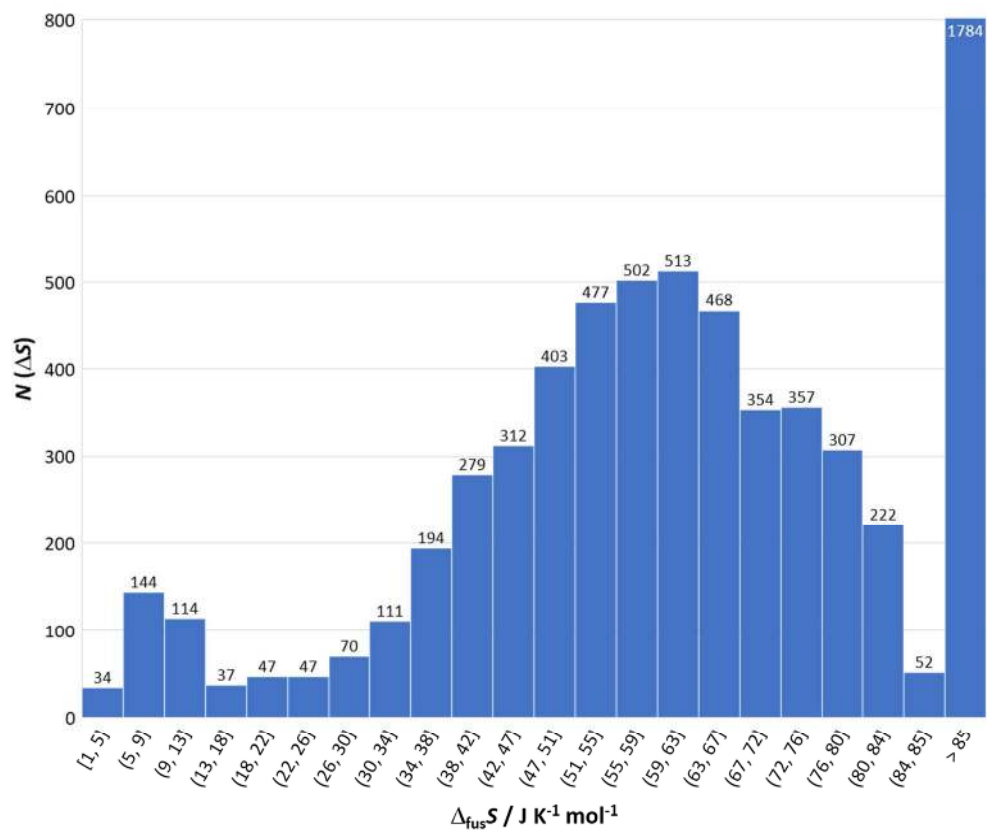


Figure 1. Entropies of fusion of 7038 organic compounds. Values from the data taken from Acree and Chickos.<sup>21,22</sup>

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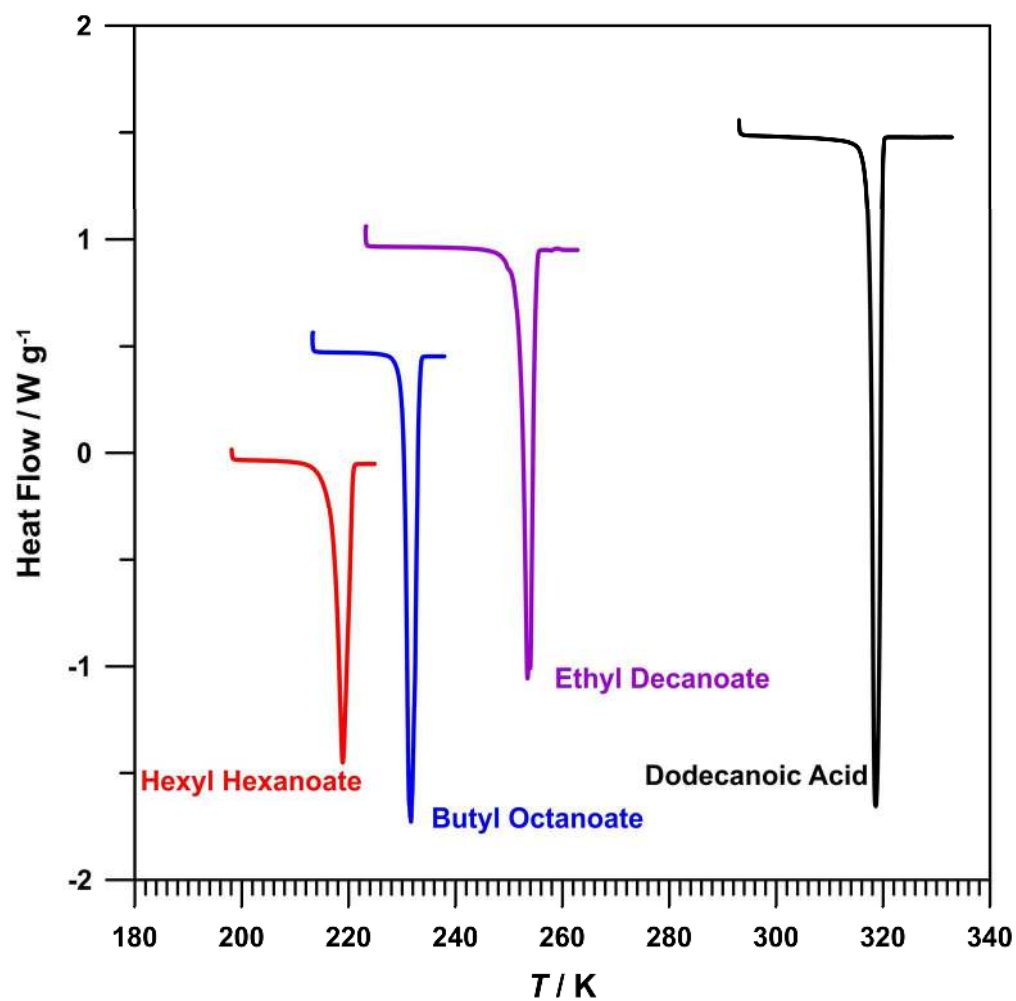


Figure 2. DSC traces showing melting for three 12-carbon linear esters and dodecanoic acid, taken at 2 K min<sup>-1</sup>. Endothermic peaks point down, and curves are displaced vertically for ease of viewing.

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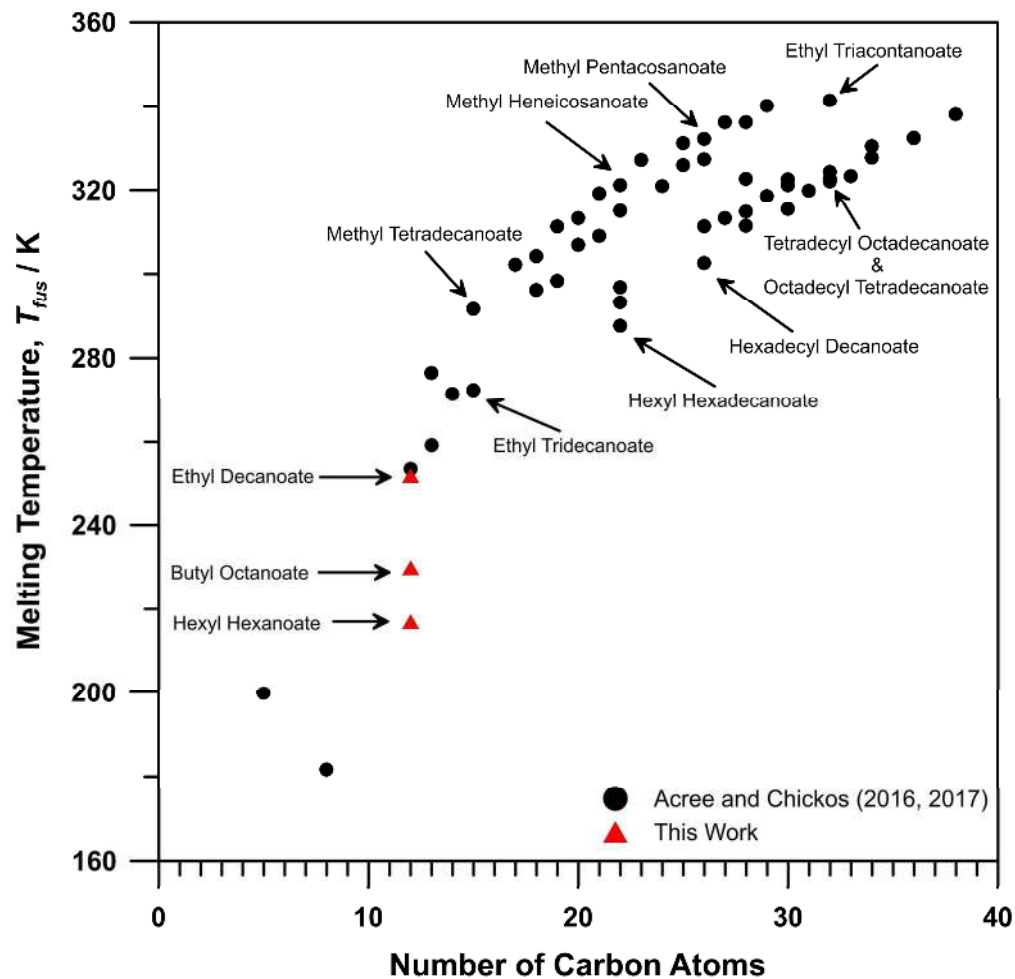


Figure 3. Melting temperatures for the linear, saturated esters as compiled by Acree and Chickos<sup>21,22</sup> and the present data. Among the esters for which data are available, at each carbon number, the ester with the longest individual alkyl chain has the highest  $T_{fus}$ .

177x172mm (300 x 300 DPI)

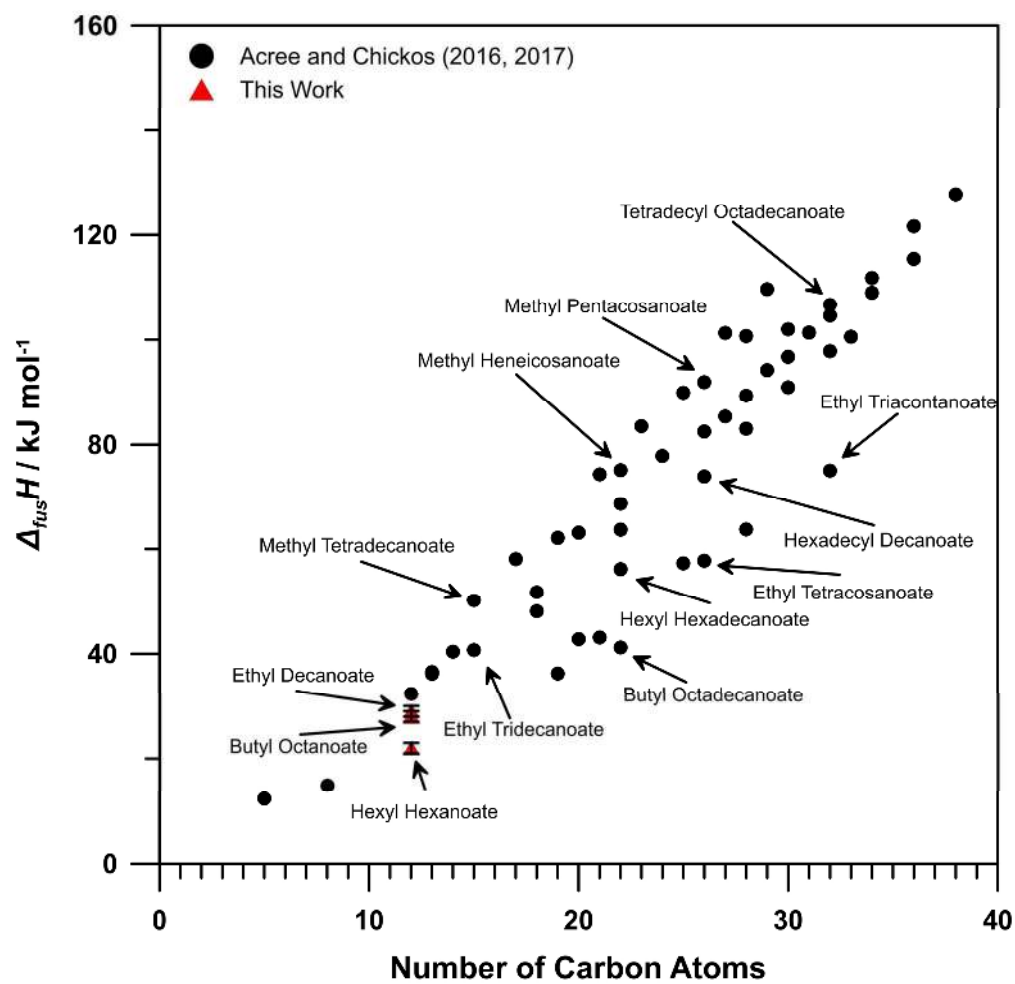


Figure 4.  $\Delta_{fus}H$  for the linear, saturated esters as compiled by Acree and Chickos<sup>21,22</sup> and present data.

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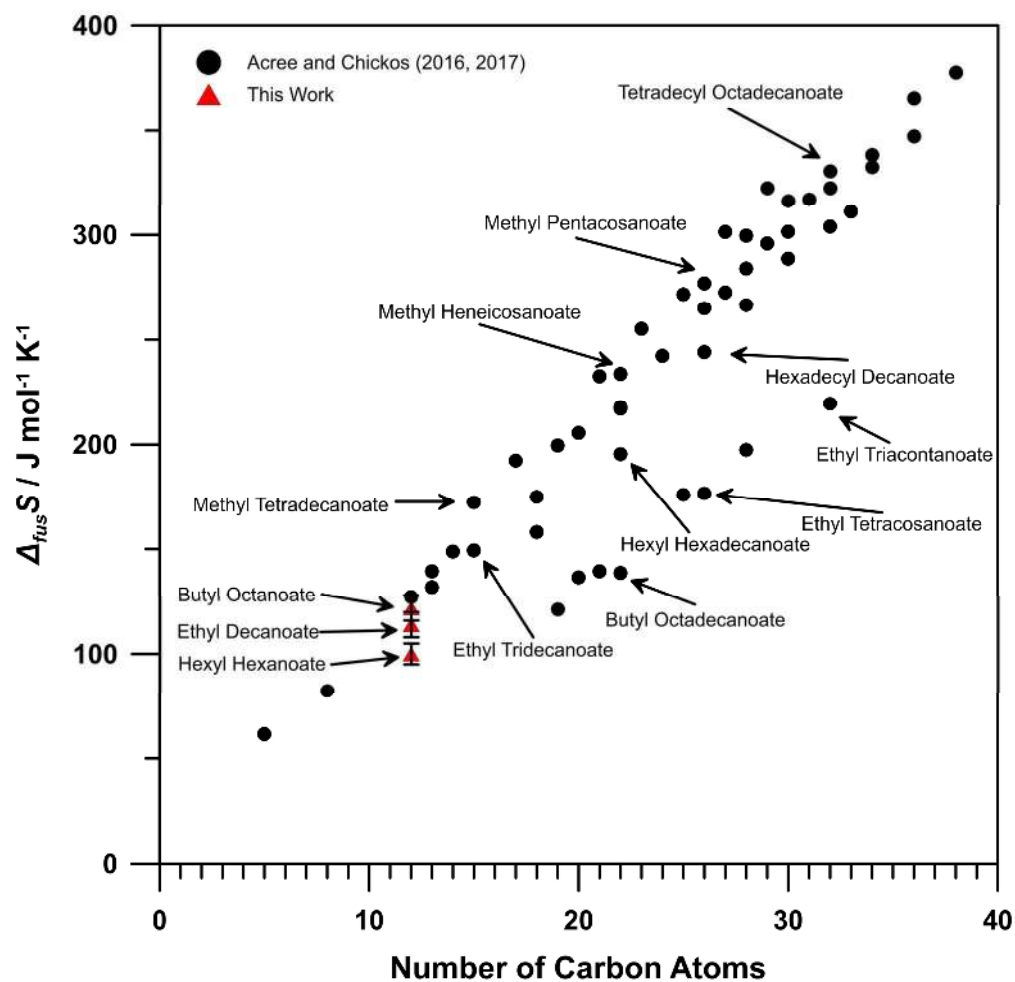


Figure 5.  $\Delta_{fus}S$  for the linear, saturated esters as calculated from Acree and Chickos<sup>21,22</sup> and present data.

177x172mm (300 x 300 DPI)

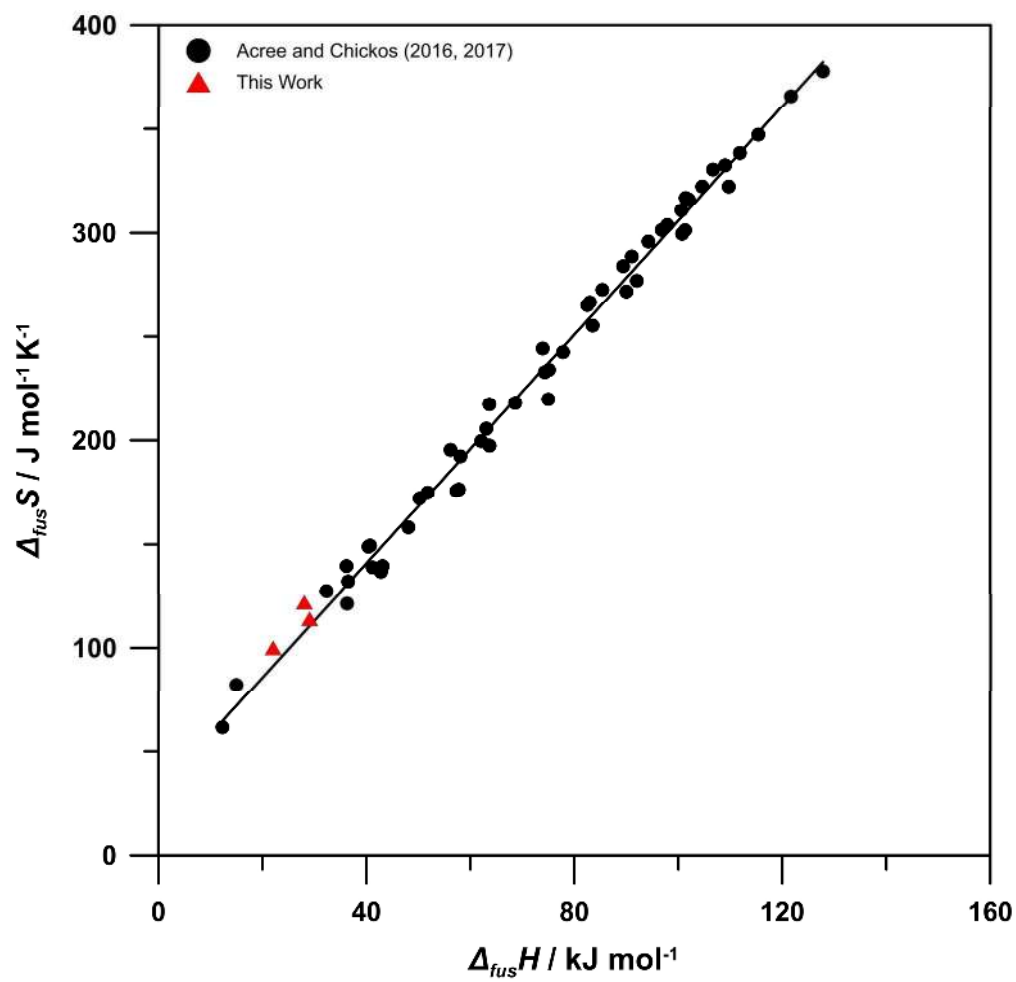


Figure 6. Relationship between  $\Delta_{fus}S$  and  $\Delta_{fus}H$  for the linear, saturated esters as compiled from Acree and Chickos<sup>21,22</sup> and present data. The line is a linear fit to the data.

178x173mm (300 x 300 DPI)