Structure determination of liquid biofuels via in situ cryocrystallisation and single crystal X-ray diffraction

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Supplementary Information

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A. *In-Situ* Cryocrystallization via OHCD technique:

Single crystals of the liquid FAMEs were grown via *in-situ* crystallization in a 0.3 mm diameter Lindemann (X-ray transparent glass) capillary using an Optical Heating and Crystallization Device (OHCD III). In this technique samples are loaded into a capillary, sealed on both sides is mounted vertically in the diffractometer (D8 VENTURE) then cooled down to crystallization temperature (just below the melting temperature) using a cold stream of liquid nitrogen. Diffraction quality crystals are created using a zone-melting technique where a small region of the capillary is heated with a CO$_2$ IR laser to create a molten zone. The laser intensity was increased from zero in 3 minutes to create the molten zone which is sample dependent (Table S1). Then the molten zone is slowly moved along the length of the capillary at about 3cm/30min by adjusting the position of the laser, allowing recrystallization of the molten zone.$^{1,2}$ After each cycle intensity was reduced back to zero in 3 minutes. This cycle is repeated several times until a single crystal amenable for diffraction is obtained. Crystals successfully grown this way are then analysed at the atomic level by X-ray diffraction. The number of cycles, cycle time and laser intensity required to obtain a good quality single crystal is sample dependant, and the whole process, which is labour intensive, can take several days. (For a few compounds several attempts have been required resulting in weeks of work). Since the samples are sensitive to temperature and melt easily, the whole experiment is carried out in the measurement device (a diffractometer) hence the term *in situ*.

**Table S1.** Values of Zone-Melting temperature and the corresponding laser intensity used in the method of *In-Situ* Cryocrystallization of FAMEs.

<table>
<thead>
<tr>
<th>FAMEs</th>
<th>Zone-Melting Temperature ($^\circ$)</th>
<th>Laser Intensity</th>
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<tbody>
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<td>C$_5$</td>
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<td>C$_6$</td>
<td>-77</td>
<td>19</td>
</tr>
<tr>
<td>C$_7$</td>
<td>-70</td>
<td>20</td>
</tr>
<tr>
<td>C$_8$</td>
<td>-46</td>
<td>18</td>
</tr>
<tr>
<td>C$_9$</td>
<td>-44.5</td>
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<tr>
<td>C$_{12}$</td>
<td>-5</td>
<td>24</td>
</tr>
<tr>
<td>C$_{13}$</td>
<td>-8</td>
<td>22</td>
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Figure S1. Experimental set up of In-Situ Cryocrystallization via OHCD technique on BRUKER D8 VENTURE X-ray diffractometer.
B. **ORTEP and Packing Diagrams of FAMEs**

B.1 **ORTEP and Packing Diagrams for C₅ Methyl Ester:**

**Figure S2.** The ORTEP diagram of C₅ methyl ester with displacement ellipsoids drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

**Figure S3.** Packing diagram of C₅ methyl ester down the c-axis, showing the head-to-head arrangement.
Figure S4. Hydrogen bonding and short contact packing diagram of C$_5$ methyl ester, showing the C2-H2A⋯O1 hydrogen bond and C6⋯O2 short contact.
B.2 ORTEP and Packing Diagrams for C₆ Methyl Ester:

**Figure S5.** The ORTEP diagram of C₆ methyl ester with displacement ellipsoids drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

**Figure S6.** Crystal packing diagram of C₆ methyl ester viewed along the b-axis, showing the C(2)-H(2B)⋯O(2) hydrogen bond and C(7)⋯C(7) short contact.
B.3 *ORTEP* and Packing Diagrams for C\textsubscript{7} Methyl Ester:

**Figure S7.** The *ORTEP* diagram of C\textsubscript{7} methyl ester with displacement ellipsoids drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

**Figure S8.** Packing diagram of C\textsubscript{7} methyl ester down the c-axis, showing the head-to-tail arrangement.
Figure S9. Hydrogen bonding diagram of C7 methyl ester, showing the C8-H8A⋯O2 and C8-H8B⋯O2 hydrogen bonds.
B.4 ORTEP and Packing Diagrams for C₈ Methyl Ester:

Figure S10. The ORTEP diagram of C₈ methyl ester with displacement ellipsoids drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Figure S11. Crystal packing diagram of C₈ methyl ester viewed down b-axis, showing the herringbone packing arrangement and the head-to-head arrangement. H atoms omitted for clarity.

Figure S12. Hydrogen bonding and short contact packing diagram of C₈ methyl ester, showing the C2-H2A⋯O2 hydrogen bond and C9⋯C9 short contact.
B.5 ORTEP and Packing Diagrams for C₉ Methyl Ester:

**Figure S13.** The ORTEP diagram of C₉ methyl ester with displacement ellipsoids drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

**Figure S14.** Crystal packing diagram of C₉ methyl ester viewed down b-axis, showing the head-to-head parallel stacking.
Figure S15. Hydrogen bonding and short contact packing diagram of C₉ methyl ester, showing the C12-H12B⋯O4 and C20-H20A⋯O2 hydrogen bond.
B.6 ORTEP and Packing Diagrams for C$_{10}$ Methyl Ester:

**Figure S16.** The ORTEP diagram of C$_{10}$ methyl ester with displacement ellipsoids drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

**Figure S17.** Crystal packing diagram of C$_{10}$ methyl ester viewed down $b$-axis, showing the herringbone packing arrangement and the head-to-head arrangement. H atoms omitted for clarity.
Figure S18. Hydrogen bonding and short contact packing diagram of C\textsubscript{10} methyl ester, showing the C2-H2B⋯O2 hydrogen bond and C11⋯C11 short contact.
B.7 ORTEP and Packing Diagrams for C\textsubscript{11} Methyl Ester:

Figure S19. The ORTEP diagram of C\textsubscript{11} methyl ester with displacement ellipsoids drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Figure S20. Crystal packing diagram of C\textsubscript{11} methyl ester viewed down b-axis, showing the head-to-head parallel stacking.
Figure S21. Hydrogen bonding and short contact packing diagram of C$_{11}$ methyl ester, showing the C14-H14A⋯O4 and C24-H24A⋯O2 hydrogen bond.
B.8 ORTEP and Packing Diagrams for C\textsubscript{12} Methyl Ester:

**Figure S22.** The ORTEP diagram of C\textsubscript{12} methyl ester with displacement ellipsoids drawn at the 50\% probability level and H atoms are shown as small spheres of arbitrary radii.

**Figure S23.** Crystal packing diagram of C\textsubscript{12} methyl ester viewed down \textit{b}-axis, showing the herringbone packing arrangement and the head-to-head arrangement. H atoms omitted for clarity.

**Figure S24.** Hydrogen bonding diagram of C\textsubscript{12} methyl ester, showing the C2-H2B⋯O2 hydrogen bond.
B.9 ORTEP and Packing Diagrams for C\textsubscript{13} Methyl Ester:

**Figure S25.** The ORTEP diagram of C\textsubscript{13} methyl ester with displacement ellipsoids drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

**Figure S26.** Crystal packing diagram of C\textsubscript{13} methyl ester viewed down \( b \)-axis, showing the head-to-head parallel stacking.
Figure S27. Hydrogen bonding and short contact packing diagram of C$_{13}$ methyl ester, showing the C16-H16B⋯O4 and C28-H28B⋯O2 hydrogen bond.
C. DSC Scans for FAME

Table S2 Literature and experimental melting point determined by DSC

<table>
<thead>
<tr>
<th>Methyl ester</th>
<th>CAS</th>
<th>Melting Point Literature(^1) / °C</th>
<th>Melting Point (DSC) / °C</th>
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<tbody>
<tr>
<td>C(_5)</td>
<td>624-24-8</td>
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<td>C(_6)</td>
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C.1 C₈ Methyl Ester
C.2 C₉ Methyl Ester
C.3 C\textsubscript{10} Methyl Ester
C.4 C_{11} Methyl Ester
C.5 C_{12} Methyl Ester
C.6 C_{13} Methyl Ester

Lab: METTLER

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D.1 Hirshfeld surfaces analysis – Fingerprint plots

**Figure S20.** Fingerprint plots for the C$_5$ to C$_7$ FAMEs, resolved into O···H (left) and H···H contacts (right), with the full fingerprint plot as a grey shadow beneath each decomposed plot.

**Figure S21.** Fingerprint plots for the even- (left) and odd-numbered members (right) of the C$_8$ to C$_{13}$ FAMEs, resolved into O···H (left) and H···H contacts (right), with the full fingerprint plot as a grey shadow beneath each decomposed plot.