

New polymorphism and structural sensitivity in triphenylmethylphosphonium trihalide salts

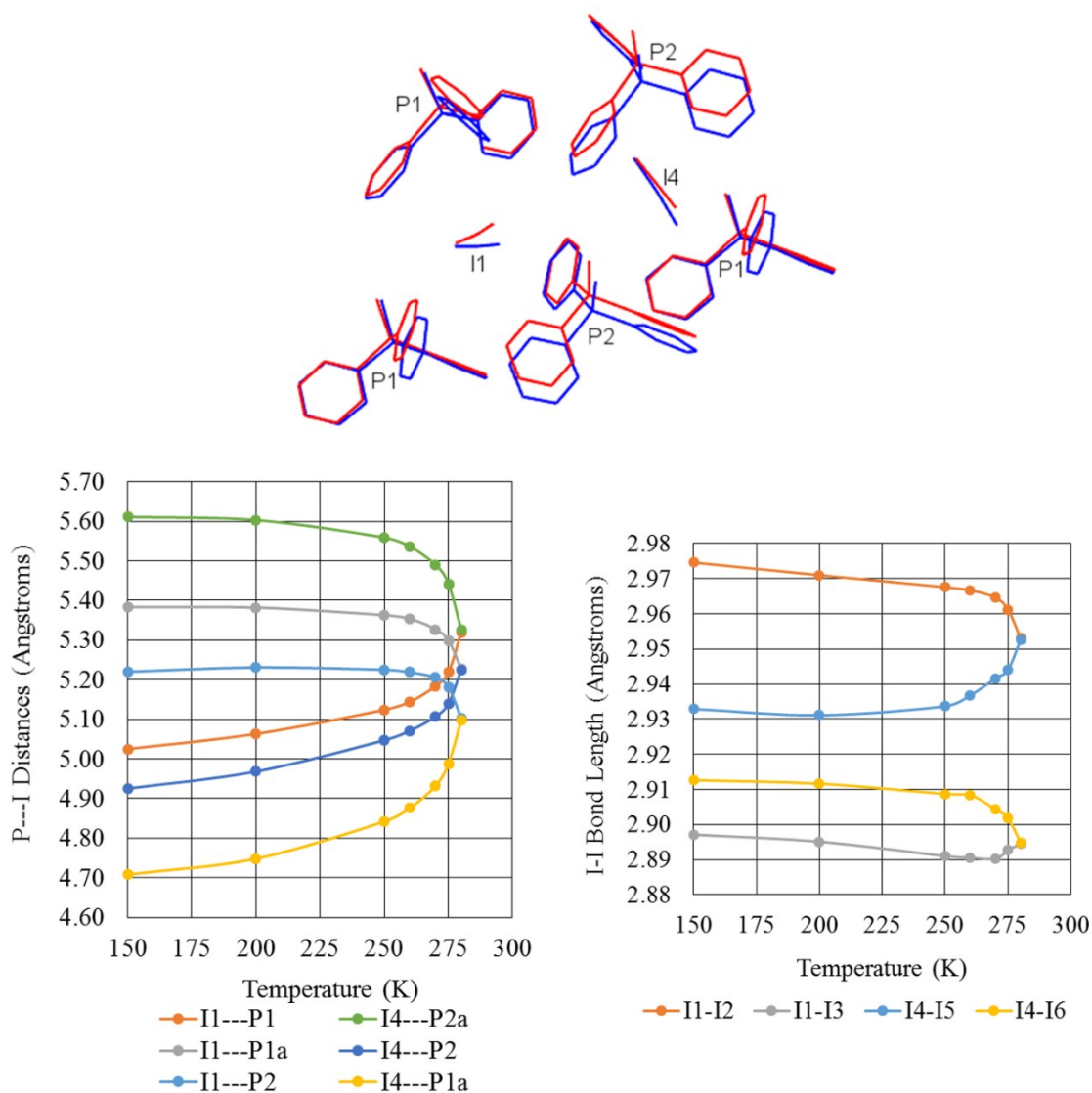
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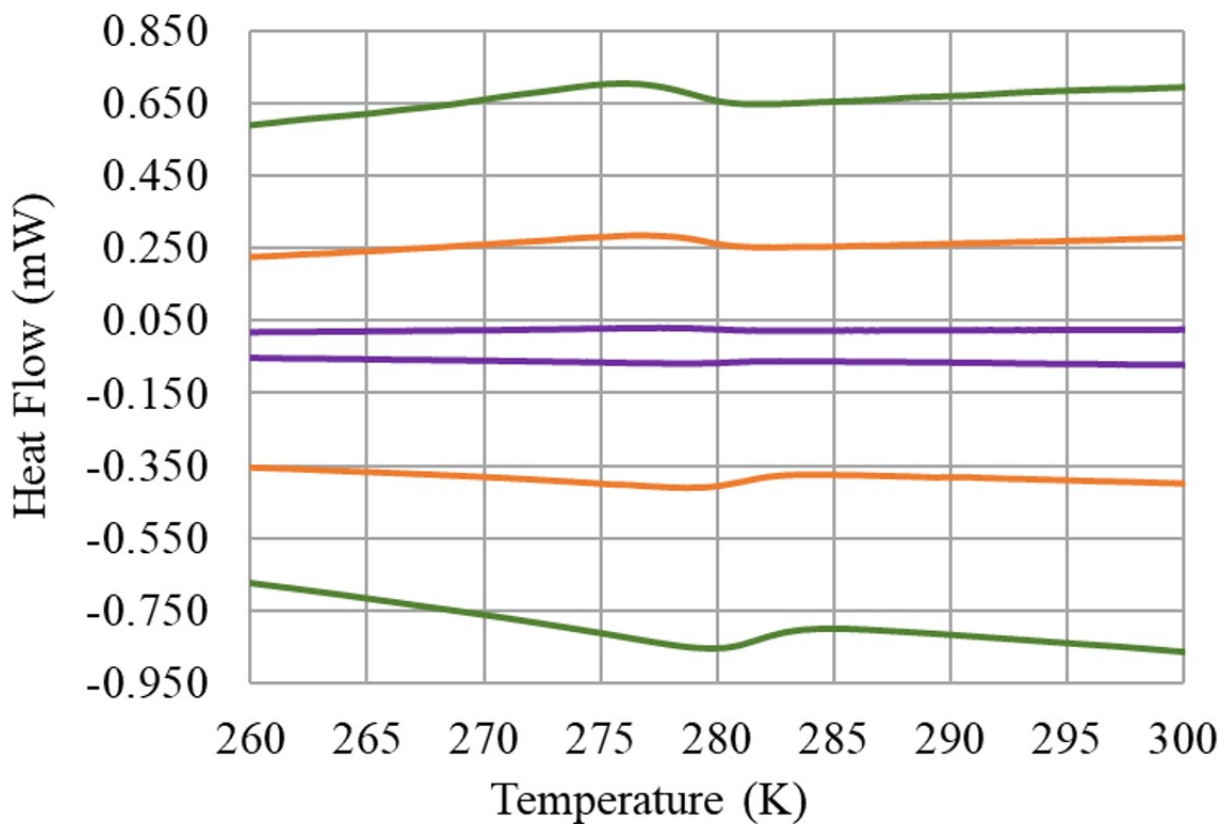
**Electronic Supplementary Information**

Table S1: Variable temperature single crystal X-ray diffraction measurements on PPh<sub>3</sub>MeI<sub>3</sub>.

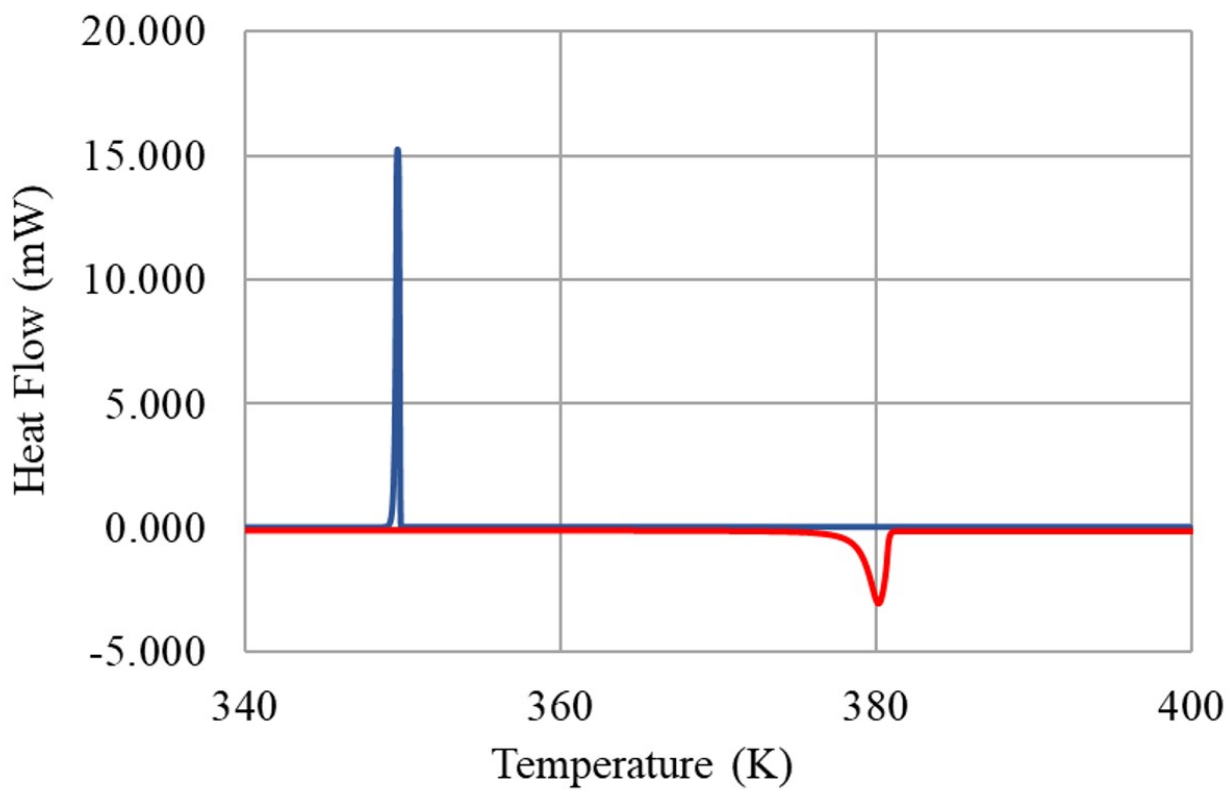
| Temp. (K)                      | 150         | 200         | 250         | 260         | 270         | 275         | 280        |
|--------------------------------|-------------|-------------|-------------|-------------|-------------|-------------|------------|
| a (Å)                          | 17.9211(5)  | 17.9647(5)  | 18.0237(5)  | 18.041(5)   | 18.0612(5)  | 18.0772(5)  | 14.676(4)  |
| b (Å)                          | 14.6131(4)  | 14.6361(4)  | 14.6603(4)  | 14.6663(4)  | 14.6723(4)  | 14.6727(4)  | 16.4963(4) |
| c (Å)                          | 16.2764(4)  | 16.3646(4)  | 16.4569(4)  | 16.4742(4)  | 16.4888(4)  | 16.4930(4)  | 18.0943(5) |
| $\alpha$ (°)                   | 90          | 90          | 90          | 90          | 90          | 90          | 90         |
| $\beta$ (°)                    | 95.0800(10) | 94.5631(10) | 93.4964(10) | 93.0780(10) | 92.3768(10) | 91.7019(11) | 90         |
| $\gamma$ (°)                   | 90          | 90          | 90          | 90          | 90          | 90          | 90         |
| V (Å <sup>3</sup> )            | 4245.8(2)   | 4289.2(2)   | 4340.4(2)   | 4352.7(2)   | 4365.8(2)   | 4372.7(2)   | 4380.6(2)  |
| D (g/cm <sup>3</sup> )         | 2.059       | 2.038       | 2.014       | 2.008       | 2.002       | 1.999       | 1.995      |
| tot. reflns.                   | 27921       | 26901       | 27546       | 27628       | 27661       | 27322       | 26587      |
| unique reflns.                 | 7876        | 7945        | 8048        | 8064        | 8080        | 8098        | 4068       |
| obs. reflns.                   | 6668        | 6137        | 5507        | 5274        | 5063        | 4799        | 2629       |
| R <sub>int</sub>               | 0.0379      | 0.042       | 0.05        | 0.0517      | 0.0555      | 0.0587      | 0.0653     |
| R <sub>1</sub><br>(obs. data)  | 0.0298      | 0.0345      | 0.044       | 0.0453      | 0.049       | 0.0488      | 0.0474     |
| wR <sub>2</sub><br>(obs. data) | 0.0854      | 0.0861      | 0.1115      | 0.1096      | 0.1126      | 0.1123      | 0.0879     |



**Figure S1:** The distances between unique pairs of anions and cations are highly asymmetric at low temperature in space group  $P2_1/c$ , and converge to become symmetry equivalents (and only moderately asymmetric) above 280 K in space group  $Pbca$ . Similarly, there are two unique triiodide anions in  $P2_1/c$  versus one unique triiodide anion in  $Pbca$ . In  $P2_1/c$ , one of the triiodides is highly asymmetric (I2-I1-I3), and the second is slightly asymmetric (I5-I4-I6). In  $Pbca$ , the one unique triiodide is moderately asymmetric.



**Figure S2:** Variable ramp rate DSC study of the monoclinic-orthorhombic phase transition of  $\text{PPh}_3\text{MeI}_3$ . Ramp rates of 1 degree per minute (purple), 5 degrees per minute (orange), and 10 degrees per minute (green) were studied. The bottom three lines correspond to second heat cycles while the top three lines correspond to cooling cycles.



**Figure S3:** Melting (red, upon heating) and crystallization (blue, upon cooling) behavior of orthorhombic  $\text{PPh}_3\text{MeI}_3$ .