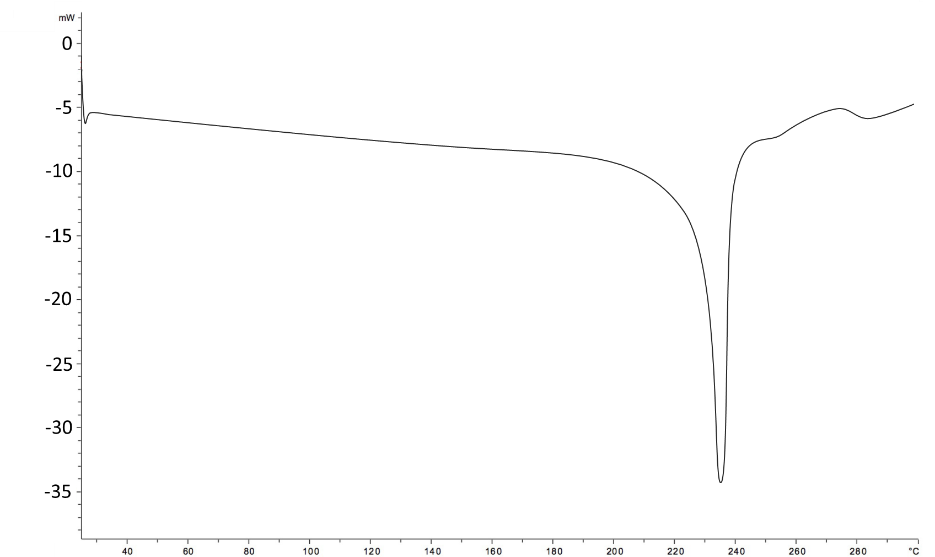
**Figure S1.** Differential scanning calorimetry of methscopolamine bromide.



**Table S1.** Summary of Rietveld structure refinement for methscopolamine bromide at *T*= 308 K and *T* = 458.

|  |  |  |
| --- | --- | --- |
|  | Methscopolamine | Methscopolamine |
| Temperature of data collection / K | 308 | 458 |
| Zero shift/ °2Theta | 0.0163(6) | -0.021(2) |
| Profile function | Pseudo Voigt | Pseudo Voigt |
| R (profile)/ % | 3.72081 | 4.18956 |
| R (weighted profile)/ % | 5.53854 | 5.95837 |
| Formula sum | C72.00N4.00O16.00Br4.00 | C72.00N4.00O16.00Br4.00 |
| Formula mass/ g/mol | 1496.42 | 1496.42 |
| Density (calculated)/ g/cm3 | 1.462 | 1.464 |
| Weight fraction/ % | 100.0 | 100.0 |
| Space group (No.) | P 21 21 21 (19) | P 21 21 21 (19) |
| Lattice parameters |  |  |
| a/ Å | 7.0550(3) | 7.1980(1) |
| b/ Å | 10.9396(4) | 10.825/(1) |
| c/ Å | 23.3869(1) | 23.7867(3) |
| alpha/ ° | 90 | 90 |
| beta/ ° | 90 | 90 |
| gamma/ ° | 90 | 90 |
| V/ 106 pm3 | 1804.9747 | 1853.4204 |
| U | 0.01(1) | 0.000000 |
| V | 0.015(5) | 0.059(8) |
| W | 0.0078(5) | 0.004(2) |
| Peak shape parameter 1 | 0.50(3) | 0.6(1) |
| Peak shape parameter 2 | -0.001(2) | -0.003(4) |

**Table S2.** Atomic coordinates and isotropic displacement parameters of methscopolamine at 308 K. Hydrogen atoms were not refined.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Atom |  | *x* | *y* | *z* | *B*iso/ 104 pm2 |
| C1 | 4a | 0.2941(6) | 0.0262(5) | 0.6613(8) | 5.6(1) |
| C2 | 4a | 0.1512(9) | 0.1013(6) | 0.6313(7) | 6.1(3) |
| C3 | 4a | 0.1442(8) | 0.0612(9) | 0.1115(6) | 5.5(1) |
| C4 | 4a | 0.1513(7) | 0.0624(9) | 0.5737(5) | 5.7(1) |
| C5 | 4a | 0.0418(6) | 0.5014(9) | 0.4104(7) | 5.9(2) |
| C6 | 4a | 0.3013(9) | 0.1422(7) | 0.5363(7) | 6.3(1) |
| C7 | 4a | 0.5042(9) | 0.1221(8) | 0.5613(7) | 5.2(2) |
| C8 | 4a | 0.1822(8) | 0.2319(6) | 0.3914(9) | 5.8(2) |
| C9 | 4a | 0.1632(7) | 0.1324(7) | 0.3421(5) | 4.7(3) |
| C10 | 4a | 0.3516(8) | 0.0617(7) | 0.3327(5) | 5.9(2) |
| C11 | 4a | 0.0951(9) | 0.1931(6) | 0.2914(5) | 5.5(2) |
| C12 | 4a | 0.1067(7) | 0.6716(6) | 0.2333(8) | 6.7(1) |
| C13 | 4a | 0.1716(8) | 0.7331(8) | 0.2815(9) | 8.9(4) |
| C14 | 4a | 0.0614(7) | 0.8121(5) | 0.3114(9) | 9.3(6) |
| C15 | 4a | 0.1243(6) | 0.3312(6) | 0.2145(6) | 8.4(6) |
| C16 | 4a | 0.2033(9) | 0.2735(6) | 0.2553(6) | 6.3(3) |
| C17 | 4a | 0.2215(6) | 0.1213(8) | 0.0132(7) | 6.2(4) |
| C18 | 4a | 0.4511(8) | 0.1516(9) | 0.0856(5) | 6.1(4) |
| N1 | 4a | 0.2913(8) | 0.0715(6) | 0.0691(9) | 4.7(2) |
| O1 | 4a | 0.0834(8) | 0.0221(6) | 0.6705(5) | 8.2(5) |
| O2 | 4a | 0.0116(8) | 0.2834(9) | 0.3954(7) | 5.4(3) |
| O3 | 4a | 0.3211(9) | 0.2636(9) | 0.4104(6) | 6.2(2) |
| O4 | 4a | 0.6212(7) | 0.4832(7) | 0.1212(6) | 7.2(3) |
| Br1 | 4a | 0.2109(6) | 0.4751(6) | 0.0556(8) | 5.1(3) |

**Table S3.** Atomic coordinates and isotropic displacement parameters of methscopolamine at 458 K. Hydrogen atoms were not refined.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Atom |  | *x* | *y* | *z* | *B*iso/ 104 pm2 |
| C1 | 4a | 0.2923(9) | 0.0267(9) | 0.6589(9) | 6.2(4) |
| C2 | 4a | 0.1515(8) | 0.1033(8) | 0.6299(8) | 6.4(3) |
| C3 | 4a | 0.1489(9) | 0.0638(6) | 0.1141(5) | 5.9(4) |
| C4 | 4a | 0.1517(9) | 0.0635(7) | 0.5669(7) | 5.5(2) |
| C5 | 4a | 0.0409(8) | 0.5017(8) | 0.4111(6) | 5.0(3) |
| C6 | 4a | 0.3017(7) | 0.1369(7) | 0.5351(9) | 6.1(3) |
| C7 | 4a | 0.5039(8) | 0.1230(7) | 0.5614(7) | 5.8(1) |
| C8 | 4a | 0.1826(9) | 0.2320(8) | 0.3854(7) | 5.8(3) |
| C9 | 4a | 0.1648(7) | 0.1329(8) | 0.3401(7) | 4.5(2) |
| C10 | 4a | 0.3519(8) | 0.0641(6) | 0.3324(6) | 5.7(2) |
| C11 | 4a | 0.0956(7) | 0.1945(7) | 0.2866(6) | 4.7(4) |
| C12 | 4a | 0.1077(8) | 0.6681(8) | 0.2329(6) | 6.2(5) |
| C13 | 4a | 0.1706(9) | 0.7399(8) | 0.2813(7) | 8.9(6) |
| C14 | 4a | 0.0681(9) | 0.8171(8) | 0.3115(8) | 9.9(4) |
| C15 | 4a | 0.1259(8) | 0.3279(9) | 0.2066(6) | 8.4(3) |
| C16 | 4a | 0.2043(7) | 0.2756(7) | 0.2558(6) | 6.3(4) |
| C17 | 4a | 0.2213(8) | 0.1180(6) | 0.0129(5) | 5.1(4) |
| C18 | 4a | 0.4517(7) | 0.1559(7) | 0.0857(9) | 6.2(4) |
| N1 | 4a | 0.2933(9) | 0.0699(5) | 0.0688(7) | 4.4(2) |
| O1 | 4a | 0.0847(7) | 0.0189(6) | 0.6713(9) | 8.8(6) |
| O2 | 4a | 0.0089(8) | 0.2808(8) | 0.3959(6) | 5.2(3) |
| O3 | 4a | 0.3231(7) | 0.2598(8) | 0.4108(8) | 6.5(2) |
| O4 | 4a | 0.6217(7) | 0.4833(9) | 0.1215(8) | 7.7(4) |
| Br1 | 4a | 0.2101(9) | 0.4747(7) | 0.0556(7) | 5.8(4) |

**Video S1**: heating of methscopolamine bromide starting at 320 K (heating rate 10 K/min).

**Video S2**: heating of methscopolamine bromide starting at 320 K (heating rate 20 K/min).

**Video S3**: cooling of methscopolamine bromide starting at 315 K (cooling rate 10 K/min).

**Video S4**: cooling of methscopolamine bromide starting at 315 K (cooling rate 20 K/min).

**Video S5**: heating of methscopolamine bromide starting at 310 K (cooling rate 10 K/min)