Structure of 2,5-dimethylhexane-2,5-diol at 293 K and of its dimer

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Dedicated to Professor P. Kristian, DrSc., in honour of his 60th birthday

In the course of a photosynthesis of dimethylvinylmethanol two crystalline compounds were obtained as by-products and identified by X-ray crystallography as 2,5-dimethylhexane-2,5-diol and its dimer, 4,5-bis(2--hydroxy-2-propyl)-2,7-dimethyloctane-2,7-diol.
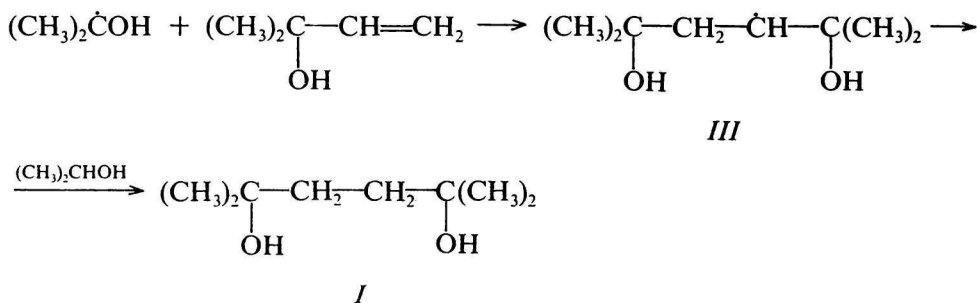
В ходе фотосинтеза диметилвинилметанола были получены в качестве побочных продуктов два кристаллических соединения, идентифицированные с помощью рентгеновской кристаллографии как 2,5--диметилгексан-2,5-диол и его димер, 4,5-бис(2-гидрокси-2-пропил)--2,7-диметилоктан-2,7-диол.

In the course of a photosynthesis of dimethylvinylmethanol [1], a number of by-products, mainly diols of varying length and structure, forms according to the reaction scheme

$$2\text{-propanol} + \text{acetone} + \text{acetylene} \rightarrow \text{products}$$
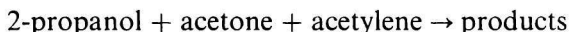
When the mother liquor (as obtained from the reaction mixture) was allowed to stand for a longer period of time, single crystals of the form of transparent thin plates appeared (compound *I*). After the mother liquor was extracted by ethanol and the solvent allowed to evaporate slowly at room temperature, other colourless prism-like crystals (compound *II*) were obtained. Elemental analyses were consistent with the formulae $C_8H_{18}O_2$ ($M_r = 146.2$) and $C_{16}H_{34}O_4$ ($M_r = 290.4$) for *I* and *II*, respectively. To identify and elucidate their crystal and molecular structures, crystals of both compounds were selected for X-ray single-crystal analysis, which confirmed the assumption that compound *I* is 2,5-dimethylhexane-2,5-diol and compound *II* 4,5-bis(2-hydroxy-2-propyl)-2,7-dimethyloctane-2,7-diol.

While the presence in the reaction mixture of compound *I* as arising from the 2-hydroxy-2-propyl radical and dimethylvinylmethanol by the reaction sequence

$$(CH_3)_2\dot{C}OH + (CH_3)_2\underset{\underset{OH}{|}}{C}-CH{=\!\!=}CH_2 \longrightarrow (CH_3)_2\underset{\underset{OH}{|}}{C}-CH_2-\dot{C}H-\underset{\underset{OH}{|}}{C}(CH_3)_2 \longrightarrow$$

III

$$\xrightarrow{(CH_3)_2CHOH} (CH_3)_2\underset{\underset{OH}{|}}{C}-CH_2-CH_2-\underset{\underset{OH}{|}}{C}(CH_3)_2$$

I

was expected, the presence of compound *II* was, to a certain extent, surprising and its formation can be explained by a recombination of radical *III*.

Experimental

As noted above, single crystals of *I* as obtained directly from the mother liquor were used for X-ray analysis. A crystal of the size $0.30 \times 0.25 \times 0.05$ mm was sealed in Lindemann glass capillary to avoid deterioration in air. Systematic absences of reflections $0k0$ for k odd and $h0l$ for l odd, as determined by Weissenberg and precession methods, were consistent with space group $P2_1/c$. Data were collected at ambient temperature (293 K) by using $P2_1$ diffractometer and graphite-monochromated $CuK\alpha$ radiation ($\lambda = 1.5418$ Å). 1488 reflections were measured, of which 823 with $I > 2\sigma(I)$ were considered observed. Intensities were not corrected for absorption ($\mu = 0.87$ mm^{-1}). Accurate unit-cell parameters were obtained by least-squares refinement of 15 precisely centred reflections, having $20° < \Theta < 45°$, namely: $a = 15.674(4)$ Å, $b = 10.175(3)$ Å, $c = 9.061(3)$ Å, $\beta = 91.22(2)°$ ($V = 1444.7(8)$ Å^3). The measured density (by flotation) $D_m = 1.01(1)$ Mg m^{-3}, agrees with the calculated density $D_x = 1.008$ Mg m^{-3} for $Z = 6$.

The structure was solved by direct methods using MULTAN 80 program [2] and refined by successive Fourier and block-diagonal least-squares methods. A difference Fourier map of partially refined structure revealed positions of all H atoms and the refinement continued on all positional parameters, anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms. In final cycle $R = 0.053$ and $wR = 0.049$ for 823 unique observed reflections. Maximal and minimal heights in the difference Fourier map were 0.18 and 0.21 e Å^{-3}, respectively. Atomic scattering factors for neutral atoms were obtained from International Tables for X-Ray Crystallography (1974). All calculations (except MULTAN) were performed by a local version of the NRC system [3].

Single crystals of *II* were obtained by crystallization from ethanol and were quite stable in air. The structure is monoclinic, space group $C2/c$ [4]. To determine the melting point, differential thermal analysis was undertaken by using DSC DuPont 1090 apparatus; weighed amount used 3.55 mg, rate 10(N2) (CER. 0.815); program Interactiv DSC V3.0.

4

Results and discussion

The asymmetric unit of the structure of *I* contains half molecule (A) occupying a centre of symmetry and the other molecule (B) lying in a general position. Both molecules, along with the atom numbering, are depicted in Fig. 1, atomic coordinates of non-H atoms are given in Table 1, their thermal parameters in Table 2, while Table 3 lists bond lengths and angles. The crystal structure is identical to that of 2,5-dimethylhexane-2,5-diol at 110 K [5], but their molecular structures differ significantly, the main difference being a shortening of the C(3)—C(3′) bond in molecule A (1.461(3) Å) and of the C(7)—C(8) bond in molecule B (1.442(4) Å) as compared to the corresponding values of 1.525(5)
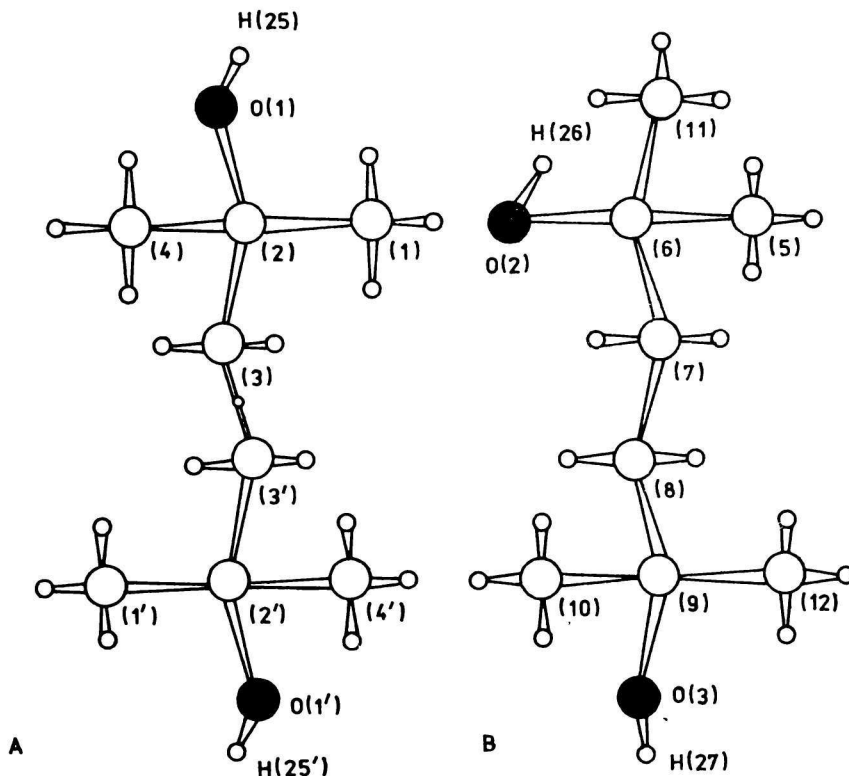

Fig. 1. A perspective drawing of both crystallographically independent molecules (A and B) of compound *I*.

Table 1

Final atomic coordinates ($\times 10^4$) with e.s.d.'s in parentheses and equivalent isotropic thermal parameters ($B_{eq}/\text{Å}^2$)

$$B_{eq} = 4/3 \sum_i \sum_j B_{ij} \bar{a}_i \bar{a}_j$$

Atom	x	y	z	B_{eq}
C(1)	813(2)	2893(3)	8798(4)	8.02
C(2)	963(1)	4364(3)	8828(2)	4.71
C(3)	464(1)	5073(3)	10017(3)	6.37
C(4)	786(2)	4922(3)	7297(3)	7.41
O(1)	1839(1)	4619(2)	9207(2)	5.77
C(5)	2127(2)	−1399(3)	8010(3)	7.74
C(6)	2854(2)	−475(2)	7634(3)	5.52
C(7)	3404(2)	−104(3)	8970(3)	6.43
C(8)	3013(2)	634(3)	10135(3)	6.45
C(9)	3577(1)	1101(2)	11462(2)	4.56
C(10)	4228(2)	2118(3)	11038(3)	6.72
C(11)	3433(2)	−1115(3)	6475(3)	8.14
C(12)	3992(2)	−37(3)	12302(3)	6.04
O(2)	2510(1)	722(1)	7012(2)	5.43
O(3)	3000(1)	1694(2)	12501(2)	5.26

Table 2

Coefficients of anisotropic temperature factors ($\times 10^4$). E.s.d.'s are given in parentheses. Temperature factor is of the form

$$T = \exp[-(B_{11}h^2 + \ldots + B_{12}hk + \ldots)]$$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	75(2)	129(4)	347(7)	3(4)	56(6)	−64(8)
C(2)	37(1)	122(3)	166(4)	15(3)	− 8(3)	−49(6)
C(3)	48(1)	171(4)	223(5)	25(5)	33(4)	−62(7)
C(4)	61(2)	215(5)	220(5)	39(5)	−30(4)	− 9(8)
O(1)	39(1)	181(3)	181(3)	11(3)	−15(2)	−80(5)
C(5)	86(2)	157(4)	249(6)	−41(5)	−57(5)	−13(8)
C(6)	69(1)	99(3)	171(4)	− 8(4)	−76(4)	6(6)
C(7)	68(2)	141(4)	205(5)	42(4)	−59(4)	−49(7)
C(8)	68(2)	157(4)	187(4)	39(4)	−12(4)	−37(7)
C(9)	50(1)	111(3)	128(4)	−12(3)	13(3)	−21(6)
C(10)	54(1)	182(4)	225(5)	−21(4)	53(4)	0(8)
C(11)	103(2)	157(5)	236(6)	85(5)	−32(5)	−84(8)
C(12)	70(1)	133(4)	173(4)	39(4) ·	−37(4)	30(7)
O(2)	67(1)	86(2)	184(3)	9(2)	−48(2)	15(4)
O(3)	59(1)	109(2)	170(2)	4(2)	44(2)	15(4)

Table 3

Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

Atoms	Distances	Atoms	Angles
		Molecule A	
C(1)—C(2)	1.516(4)	C(1)—C(2)—C(3)	113.4(2)
C(2)—C(3)	1.526(3)	C(1)—C(2)—C(4)	109.1(2)
C(3)—C(3')	1.461(3)	C(3)—C(2)—C(4)	112.4(2)
C(4)—C(2)	1.520(4)	C(3)—C(2)—C(1)	104.4(2)
C(2)—O(1)	1.431(3)	C(1)—C(2)—O(1)	109.3(2)
		C(4)—C(2)—O(1)	107.9(2)
		C(2)—C(3)—C(3')	117.6(2)
		Molecule B	
C(5)—C(6)	1.522(4)	C(5)—C(6)—C(7)	112.9(2)
C(6)—C(7)	1.519(3)	C(6)—C(7)—C(8)	118.0(2)
C(7)—C(8)	1.442(4)	C(7)—C(8)—C(9)	117.9(2)
C(8)—C(9)	1.552(3)	C(8)—C(9)—C(10)	112.9(2)
C(9)—C(10)	1.510(4)	C(5)—C(6)—C(11)	110.2(2)
C(6)—C(11)	1.546(4)	C(10)—C(9)—C(12)	111.4(2)
C(9)—C(12)	1.524(3)	C(5)—C(6)—O(2)	109.5(2)
C(6)—O(2)	1.442(3)	C(7)—C(6)—O(2)	107.6(2)
C(9)—O(3)	1.450(3)	C(11)—C(6)—O(2)	108.1(2)
		C(8)—C(9)—O(3)	106.1(2)
		C(10)—C(9)—O(3)	108.3(2)
		C(12)—C(9)—O(3)	104.9(2)

and 1.533(5) Å in the low-temperature structure. Coincident with this is a widening of the C(2)—C(3)—C(3') (117.6(2)°), C(6)—C(7)—C(8) (118.0(2)°), and C(7)—C(8)—C(9) (117.9(2)°) bond angles *vs.* the corresponding values of 115.0(3)°, 115.6(3)°, 115.5(3)° in the structure at 110 K.

An explanation of the above facts is at present rather difficult. As mentioned above, compound *I* is extremely unstable at room temperature and, for this reason, *Helmholdt* and *Reynaers* [5] elucidated its structure at 110 K. Based on the analysis of the thermal parameters, the latter authors came to the conclusion that the molecules of *I* cannot be regarded as rigid bodies, implying that the compound is thermally unstable even at relatively lower temperatures. A similar behaviour exhibits 2,5-dimethyl-3-hexene-2,5-diol at 113 K as reported by *Ruysink* and *Vos* [6]. The latter compound crystallizes as a *trans* form in Pbcn and as a mixture of *cis* and *trans* forms in P1̄. The lengths of the unsaturated bonds, which are of interest here, are 1.326 Å in the orthorhombic structure and 1.338 and 1.344 Å in the triclinic structure for *trans*, resp. *cis* forms, all values being consistent with a pure $C(sp^2){=}C(sp^2)$ double bond [7]. The bond angles about

the double bond are 127.4° and 134.9° in the *trans* isomer and 132.5° and 132.1° in the *cis* isomer.

In contrast, the structure of a tetrahydrate of *I* with monoclinic symmetry, space group P2$_1$/c, has been reported to be stable even at room temperature [8]. The length of the central bond in this structure is 1.534(3) Å, a value typical for a C(sp^3)—C(sp^3) single bond.

From the above it follows that the central bond (C(3)—C(3') in A and C(7) —C(8) in B) in the title compound *I* at ambient temperature is intermediate between C(sp^3)—C(sp^3) single and C(sp^2)═C(sp^2) double bonds. Other features characterizing the crystal and molecular structures of *I* are very similar to those in the related structures cited above. This, of course, holds for both the hydrogen-bonding pattern and molecular packing, the latter being the closest one according to *Kitaigorodskii* [9].
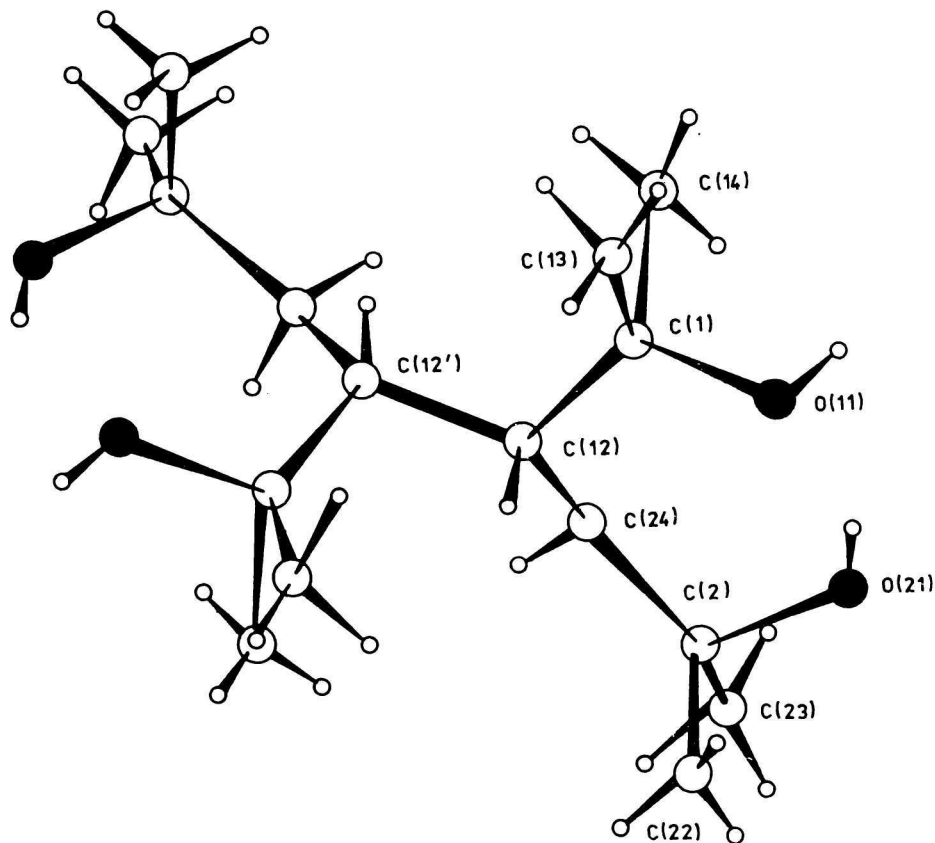

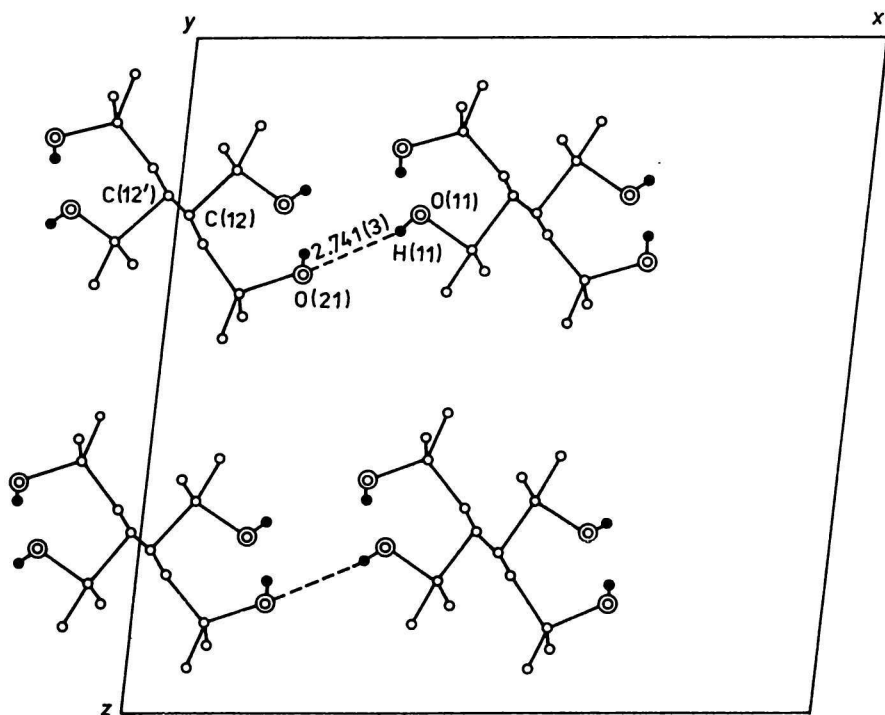*Fig. 2.* A perspective view of the molecular structure of *II*, showing the atom-numbering scheme.

Fig. 3. A projection of the crystal structure of *II* along the *y* axis.
○ C, ◎ O, ● H.

Molecular structure of *II* with the atom numbering is shown in Fig. 2. The molecule lies on a twofold axis of symmetry, the axis passing through the mid-point of the C(12)—C(12′) bond. Apparently the compound is a dimer of *I*. Projection of the structure onto (010) is shown in Fig. 3, the H-bonding interactions being indicated by broken lines. Bond lengths and angles are listed in Table 4.

Bond lengths are comparable to those generally found in other hexane- and hexenediols with the average values of 1.441, 1.540, and 1.517 Å for C—O, C—C (backbone), and C—CH$_3$ (terminal) bonds, respectively. The C—C—O bond angles range from 103.5(3)° to 110.9(3)° being on average lower than the C—C—C bond angles (108.8(3)°—121.2(2)°) in accordance with the structures of hexanediols. The angular expansions over a normal tetrahedral value may be ascribed to steric effects resulting from the linkage of two monomeric units of *I*.

In contrast to the structure of 2,7-dimethyl-2,7-octanediol tetrahydrate [10], compound *II* utilizes only one hydrogen-bonding interaction for the packing,

Table 4

Bond distances (Å) and angles (°) with e.s.d.'s in parentheses for compound *II*

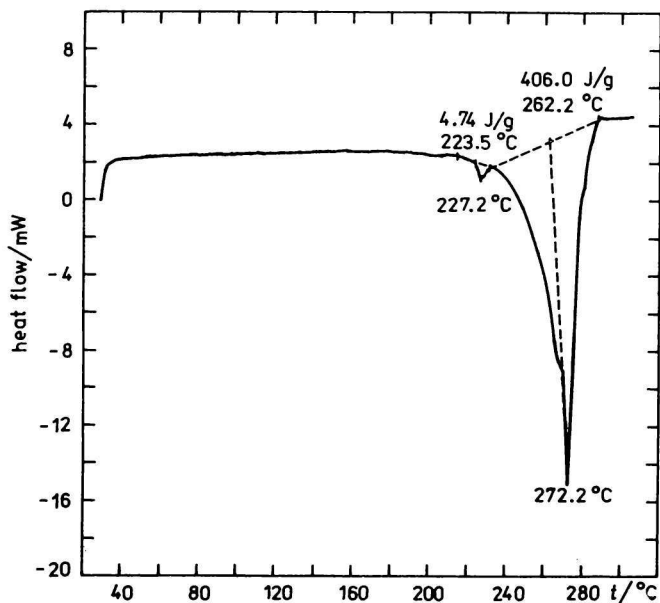| Atoms	Distances	Atoms	Angles
C(1)—O(11)	1.438(4)	C(13)—C(1)—C(14)	110.2(3)
C(1)—C(12)	1.560(5)	C(13)—C(1)—C(12)	112.3(3)
C(1)—C(13)	1.533(5)	C(13)—C(1)—O(11)	106.0(3)
C(1)—C(14)	1.502(6)	C(12)—C(1)—C(14)	115.1(3)
C(12)—C(24)	1.548(4)	C(12)—C(1)—O(11)	104.2(3)
C(2)—O(21)	1.444(4)	O(11)—C(1)—C(14)	108.6(3)
C(2)—C(22)	1.516(6)	C(1)—C(12)—C(24)	114.7(3)
C(2)—C(23)	1.519(6)	O(21)—C(2)—C(22)	108.0(3)
C(2)—C(24)	1.534(5)	O(21)—C(2)—C(23)	103.5(3)
		O(21)—C(2)—C(24)	110.9(3)
		C(22)—C(2)—C(23)	112.7(3)
		C(22)—C(2)—C(24)	112.6(3)
		C(23)—C(2)—C(24)	108.8(3)
		C(12)—C(24)—C(2)	121.2(2)

Fig. 4. DSC diagram of compound *II*.

namely the length of O(11)$\cdots$O(21) is 2.741(3) Å and the angle of O(11)—H(11)$\cdots$O(21) is 173(3)°, thus producing zigzag chains parallel to [100].

As mentioned above, the crystals of compound *II* are quite stable and well soluble in polar solvents, such as ethanol and water. To examine its thermal behaviour, differential thermal analysis was undertaken (Fig. 4). As evident, a solid-state phase transition occurs at 227.2 °C (the transition is visualized by a change of prism-like to plate-like crystals); on further heating, the compound melts at 272.2 °C and decomposes at 282.2 °C. A relatively small endothermal effect associated with the solid-state transition (9.5 J K^{-1} kg^{-1}) is consistent with a lowering of symmetry due to the formation of the high-temperature structure. The combined thermal effect associated with melting and decomposition is 117.9 kJ mol^{-1}.

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Translated by V. Kettmann