

## Molar heat capacities of some derivatives of uracil and theophylline

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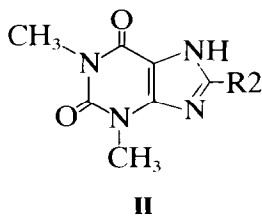
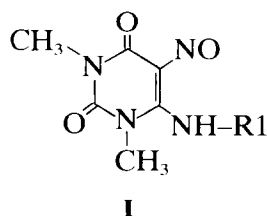
### Abstract

The molar heat capacities ( $C_{p,m}$ ) of 15 derivatives of 1,3-dimethyl-4-alkylamino-5-nitrosouracil and of the corresponding 8-substituted theophyllines were determined by DSC.

Empirical equations of the form  $C_{p,m} = a + bT$  were derived for the heat capacities of individual compounds.

### INTRODUCTION

Chemicals that are important for human health are currently the centre of scientific investigations. In our preceding publications [1–3] we studied the exothermic conversion of 1,3-dimethyl-4-alkylamino-5-nitrosouracils (**I**) to theophylline or its 8-substituted derivatives (**II**) (see the Formula).



The DSC method was most suitable for the complex description of this reaction in the solid phase, from the thermodynamic (determination of enthalpy of reaction or fusion) as well as the kinetic point of view.

The determination of molar heat capacities of the parent materials and of the products formed in this reaction are the subject of this paper.

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## EXPERIMENTAL

The 1,3-dimethyl-4-alkylamino-5-nitrosouracils and the 8-substituted theophyllines were prepared by a modification of the literature method [4]. After repeated crystallization in methanol, the structure of the synthesized compounds was confirmed by elemental analysis as well as by IR, UV,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and mass spectroscopy. The samples used in this work were the same as those used for the earlier determination of the enthalpies of reaction and fusion [3]. The heat capacities were determined with a DSC-2C differential scanning calorimeter (Perkin-Elmer) in a dynamic nitrogen atmosphere ( $20\text{ cm}^3\text{ min}^{-1}$ ), according to ref. 5. The rate of heating (cooling) was  $10\text{ K min}^{-1}$ . The temperature scale was calibrated with melting-point standards. The weighed amounts of samples were approx. 10 mg.

The heat capacities of the 1,3-dimethyl-4-alkylamino-5-nitrosouracils were measured in the narrow temperature interval from 290 K to the start of the cyclocondensation reaction, while the heat capacities of the 8-alkyltheophyllines were measured in the 290–415 K region, depending on the nature of the sample.

Each of these temperature regions was divided into overlapping intervals, spanning 25–30 K. The measurements were performed in these intervals as follows. Firstly, a series of curves for the individual temperature intervals was recorded with an empty sample pan. Then curves with a standard material in the same sample pan were recorded, followed by curves measured with the same sample pan containing weighed samples. All these measurements were carried out on the same day under the same conditions. An ice–water mixture was used for cooling.

Synthetic sapphire was used as a standard for the determination of  $C_{p,m}$ , and the values of the specific heat capacities of sapphire were taken from the literature [6].

## RESULTS AND DISCUSSION

The experimental molar heat capacity values obtained were treated by the least-squares method. The temperature dependence of  $C_{p,m}$  was linear in all cases (Figs. 1, 2). Thus the heat capacities may be expressed as a function of temperature by the equation  $C_{p,m} = a + bT$ . The values of the coefficients  $a$  and  $b$  of this equation are listed in Tables 1 and 2.

In the case of some of the derivatives of theophylline, for example those with longer chain alkyl groups, problems appeared during the experiments owing to the existence of s–s transitions in the investigated region before fusion [3]. Therefore, a shorter temperature interval was used, or else the heat capacity values of some theophylline derivatives are not given.

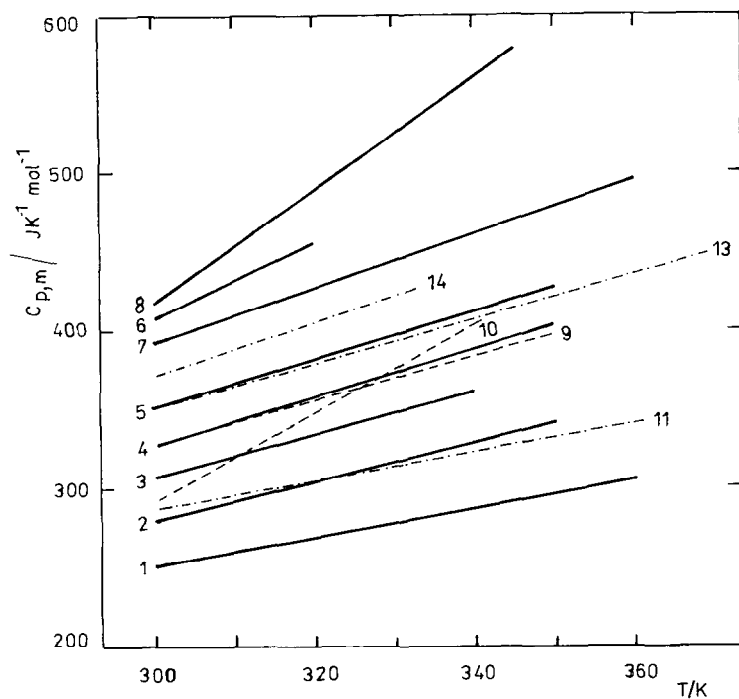


Fig. 1. Molar heat capacity of some 1,3-dimethyl-4-alkylamino-5-nitrosouracils as a function of temperature.

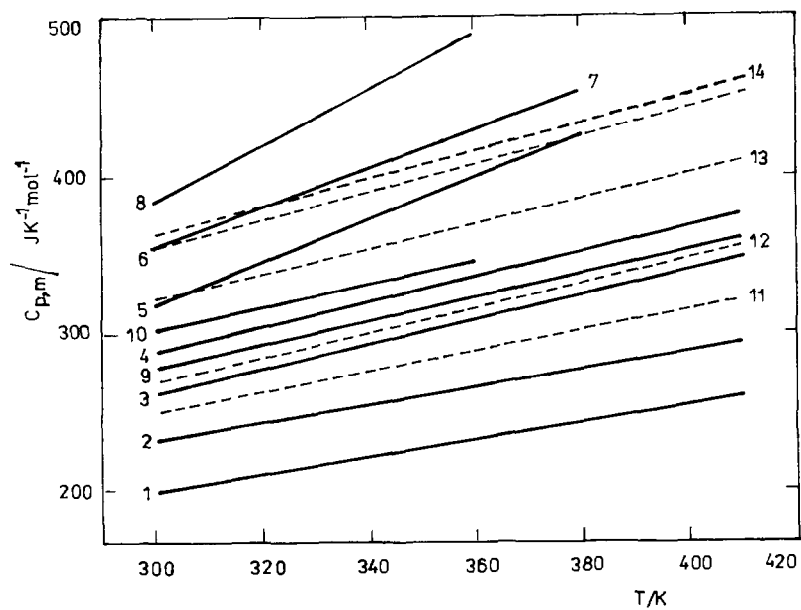


Fig. 2. Temperature dependence of the molar heat capacities of some 8-alkyltheophyllines.

TABLE 1

Molar heat capacities of 1,3-dimethyl-4-alkylamino-5-nitrosouracils (I)

R <sup>1</sup>	Constants of the equation $C_{p,m} = a + bT$		Temperature interval/K
	$a/(\text{J K}^{-1} \text{mol}^{-1})$	$b/(\text{J K}^{-2} \text{mol}^{-1})$	
1 CH <sub>3</sub>	-23.447	0.913	300–360
2 C <sub>2</sub> H <sub>5</sub>	-86.224	1.221	300–350
3 C <sub>3</sub> H <sub>7</sub>	-74.962	1.276	300–340
4 C <sub>4</sub> H <sub>9</sub>	-121.364	1.500	300–350
5 C <sub>5</sub> H <sub>11</sub>	-100.559	1.506	300–350
6 C <sub>6</sub> H <sub>13</sub>	-334.467	2.471	300–320
7 C <sub>7</sub> H <sub>15</sub>	-130.391	1.741	300–360
8 C <sub>8</sub> H <sub>17</sub>	-643.321	3.539	300–350
9 CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	-101.912	1.430	300–350
10 CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub>	-525.528	2.732	300–340
11 (CH <sub>2</sub> ) <sub>2</sub> OH	21.492	0.887	300–360
12 (CH <sub>2</sub> ) <sub>3</sub> OH	-182.807	1.688	300–350
13 (CH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	-81.866	1.440	300–370
14 (CH <sub>2</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	-133.274	1.685	300–330
15 CH <sub>2</sub> CH(OH)C <sub>6</sub> H <sub>5</sub>	-56.768	1.555	300–340

TABLE 2

Molar heat capacities of 8-alkyltheophyllines (II)

R <sup>2</sup>	Constants of the equation $C_{p,m} = a + bT$		Temperature interval/K
	$a/(\text{J K}^{-1} \text{mol}^{-1})$	$b/(\text{J K}^{-2} \text{mol}^{-1})$	
1 H	32.231	0.552	300–410
2 CH <sub>3</sub>	65.172	0.557	300–410
3 C <sub>2</sub> H <sub>5</sub>	27.324	0.780	300–410
4 C <sub>3</sub> H <sub>7</sub>	58.204	0.768	300–410
5 C <sub>4</sub> H <sub>9</sub>	-79.146	1.328	300–380
6 C <sub>5</sub> H <sub>11</sub>	95.704	0.867	300–410
7 C <sub>6</sub> H <sub>13</sub>	-18.291	1.240	300–380
8 C <sub>7</sub> H <sub>15</sub>	-148.042	1.772	300–360
9 CH(CH <sub>3</sub> ) <sub>2</sub>	55.362	0.739	300–410
10 C(CH <sub>3</sub> ) <sub>3</sub>	85.503	0.723	300–360
11 CH <sub>2</sub> OH	58.414	0.640	300–410
12 (CH <sub>2</sub> ) <sub>2</sub> OH	39.712	0.766	300–410
13 CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	80.149	0.802	300–410
14 (CH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	101.758	0.873	300–410
15 CH(OH)C <sub>6</sub> H <sub>5</sub>	29.382	1.107	300–380

The precision of a parallel series of determinations (at least three) of  $C_{p,m}$  of the investigated compounds was  $\pm 2\%$ , in all cases.

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