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Abstract

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HEAT CAPACITIES AT LOW TEMPERATURES

AND THERMODYNAMIC FUNCTIONS

OF ENDO- AND EXO-2-CYANO-BICYCLO-(2, 2, 1)-HEPTANE

(Presented by Academician B. A. Kazanskii, 24 IV 1962)

Of great interest in recent times is the study of organic compounds with highly symmetric molecules, close in shape to a sphere ([1], [2]). In particular, a number of works have been devoted to the investigation of heat capacities at low temperatures and phase transitions of such substances ([2-4]). Interest in these substances is due to the characteristic features of their crystalline structures, which permit, owing to the high symmetry of the molecules, rotation of the latter without destruction of the crystal lattice ("plastic crystals"). The realization of such a state, which is sometimes also called a rotational-crystalline state, is usually associated with a transformation in the solid phase (or with several transformations).

Fig. 1. A –endo isomer, **B** –exo isomer

As the objects of the present work, two stereoisomers from among bridged bicyclic compounds were chosen, namely endo-2-cyano-bicyclo-(2, 2, 1)-heptane and exo-2-cyano-bicyclo-(2, 2, 1)-heptane (for brevity we shall call them simply endo- and exo-isomers) (Fig. 1). Both these compounds, being derivatives of bicyclo-(2, 2, 1)-heptane, the molecules of which possess very high symmetry, form typical "plastic crystals." A comparison of the properties of these two isomers is of considerable interest, since they differ only in the direction of the –

C N group relative to the bicycle. We note that, in general, the measurement of the heat capacity of the endo- and exo-isomers at low temperatures has been carried out in the present work for the first time.

Both isomers were synthesized by condensation of cyclopentadiene with acrylonitrile, followed by hydrogenation of the condensation products over platinum black. Separation of the isomers was carried out by distillation on a column. The amounts of impurities found by us in the course of determining the heats of fusion of the substances are 0.12 mole % in the endo-isomer and 0.18 mole % in the exo-isomer.

Heat-capacity measurements were carried out in a small-volume vacuum adiabatic calorimeter (about 9 ml), described earlier ([5]). Only the method of filling the calorimeter was modified. To avoid losses of substance as a result of considerable overheating of the calorimeter when sealing the lid, the more volatile exo-isomer was loaded into a previously sealed calorimeter. For this purpose two copper capillaries were soldered in advance into the calorimeter lid, one of which was connected to a small copper funnel, and the other to a vacuum pump. The previously melted substance was drawn through the capillary into the calorimeter. After helium had been introduced into the calorimeter, both capillaries were pinched off, which ensured the tightness of the calorimeter.

The true heat capacity of the endo and exo isomers was measured in the interval from 12°K to a temperature 10-20° above the melting temperature. The values of the true heat capacities from the smoothed curves C_p—T for each isomer are given in Table 1. The deviations of the experimental points from the smoothed curve over the greater part of the temperature interval studied did not exceed 0.2% (only below 30°K did the deviations sometimes reach 0.5%). The thermodynamic functions S_T and $H_T - H_0$ of the endo and exo isomers (Table 1) were obtained by numerical integration of the curves

Table 1

T, °K	Endo-2-cyano-bicyclo-(2, 2, 1)-heptane: C_p^*, cal/(deg·mol)	Endo-2-cyano-bicyclo-(2, 2, 1)-heptane: S_T, e.u.	Endo-2-cyano-bicyclo-(2, 2, 1)-heptane: $H_T - H_0$, cal/mol	Exo-2-cyano-bicyclo-(2, 2, 1)-heptane: C_p^*, cal/(deg·mol)	Exo-2-cyano-bicyclo-(2, 2, 1)-heptane: S_T, e.u.	Exo-2-cyano-bicyclo-(2, 2, 1)-heptane: $H_T - H_0$, cal/mol
12	$1{,}40_0$	0,62	5,13			
16	$2{,}51_3$	1,17	12,88	$2{,}19_4$	0,70	8,97
20	$3{,}69_2$	1,86	25,28	$3{,}53_3$	1,34	20,45
24	$4{,}86_2$	2,64	42,39	$4{,}77_9$	2,09	37,10
28	$5{,}98_7$	3,47	64,10	$5{,}93_7$	2,92	58,56

T, °K	Endo-2-cyano-bicyclo-(2, 2, 1)-heptane: C_p^*, cal/(deg·mol)	Endo-2-cyano-bicyclo-(2, 2, 1)-heptane: S_T, e.u.	Endo-2-cyano-bicyclo-(2, 2, 1)-heptane: $H_T - H_0$, cal/mol	Exo-2-cyano-bicyclo-(2, 2, 1)-heptane: C_p^*, cal/(deg·mol)	Exo-2-cyano-bicyclo-(2, 2, 1)-heptane: S_T, e.u.	Exo-2-cyano-bicyclo-(2, 2, 1)-heptane: $H_T - H_0$, cal/mol
32	$7{,}03_0$	4,34	90,16	$7{,}00_7$	3,78	84,47
36	$7{,}97_9$	5,22	120,2	$7{,}98_9$	4,66	114,5
40	$8{,}83_9$	6,11	153,9	$8{,}88_3$	5,55	148,2
44	$9{,}61_8$	6,99	190,8	$9{,}68_9$	6,43	185,4
48	10,34	7,86	230,7	10,41	7,31	225,6
52	11,02	8,71	273,5	11,07	8,17	268,6
56	11,67	9,55	318,9	11,66	9,01	314,0
60	12,29	10,38	366,8	12,20	9,83	361,7
70	13,69	12,38	496,9	13,48	11,81	490,1
80	14,93	14,29	640,1	14,63	13,69	630,6
90	16,09	16,12	795,2	15,66	15,47	782,1
100	17,24	17,87	961,9	16,62	17,17	943,5
110	18,43	19,57	1141	17,56	18,80	1115
120	19,66	21,23	1332	18,51	20,37	1295
130	20,89	22,85	1535	19,47	21,89	1485
140	22,12	24,44	1750	20,47	23,37	1685
150	23,45	26,01	1977	21,47	24,81	1895
160	24,97	27,57	2219	22,48	26,23	2115
170	26,70	29,14	2477	23,53	27,63	2345
180	(transition region)	(transition region)	(transition region)	24,62	29,00	2586
190	(transition region)	(transition region)	(transition region)	25,76	30,36	2837
200	35,78	37,27	3987	27,03	31,72	3100
210	36,73	39,04	4349	28,52	33,07	3378
220	37,72	40,77	4721	30,17	34,44	3672
230	38,76	42,47	5103	(transition region)	(transition region)	(transition region)
240	39,89	44,14	5496	39,93	45,25	6620
250	41,05	45,79	5901	41,83	46,92	6629
260	42,20	47,42	6317	43,72	48,59	7056
270	43,33	49,04	6744	45,65	50,28	7503
280	44,45	50,63	7183	47,81	51,98	7970
290	45,51	52,21	7633	(melting region)	(melting region)	(melting region)
298,15	46,34	53,49	8007	—	55,11	8873

Fig. 2. Heat capacity of 2-cyanobicyclo-(2, 2, 1)-heptane: 1 —endo isomer; 2 — exo isomer (2-c —stable modification, 2-m —metastable modification)

Figure 2: Fig. 2. Heat capacity of 2-cyanobicyclo-(2, 2, 1)-heptane: 1 —endo isomer; 2 —exo isomer (2-c —stable modification, 2-m —metastable modification)

T, °K	Endo-2-cyano-bicyclo-(2, 2, 1)-heptane: C_p^*, cal/(deg·mol)	Endo-2-cyano-bicyclo-(2, 2, 1)-heptane: S_T, e.u.	Endo-2-cyano-bicyclo-(2, 2, 1)-heptane: $H_T - H_0$, cal/mol	Exo-2-cyano-bicyclo-(2, 2, 1)-heptane: C_p^*, cal/(deg·mol)	Exo-2-cyano-bicyclo-(2, 2, 1)-heptane: S_T, e.u.	Exo-2-cyano-bicyclo-(2, 2, 1)-heptane: $H_T - H_0$, cal/mol
300	46,53	53,77	8093	47,55	57,77	9674
310	47,57	55,32	8563	48,61	59,35	10155
320	48,61	56,84	9044	49,66**	60,91	10646
330	(melting region)	(melting region)	(melting region)	50,71**	62,45	11148
340	51,97	62,54	10755	51,76**	63,98	11660
350	52,96	64,06	11280	52,81**	65,48	12183

* Adopted: 1 cal equals 4.1840 abs. J.
** Extrapolated values.

C_p—$\ln T$ and C_p—T. Extrapolation of the heat-capacity curves to 0°K was carried out graphically, since it turned out that the heat capacity of both isomers, down to the lowest temperatures reached in the experiments, does not obey Debye' s "cube law." The error of the graphical extrapolation did not exceed 0.15 e.u. The total error in the values of the absolute entropies of the endo and exo isomers under standard conditions is 0.2-0.3 entropy units.

It was found that both substances undergo transformations in the solid phase (apparently isothermal): the endo isomer at 177.37° K, and the exo isomer at 237.7° K (Fig. 2). However, a detailed study of the form of the $C_p - T$ curves in the region of the transformations is greatly complicated by the fact that in both cases

Fig. 2. Heat capacity of 2-cyanobicyclo-(2, 2, 1)-heptane: 1 —endo isomer; 2 —exo isomer (2-c —stable modification, 2-m —metastable modification)

equilibrium between the solid phases is established slowly (in heat-capacity measurements of the endo isomer in the anomalous region, several hours are required for thermal equilibrium to be reached in the calorimeter). The observed transformations, probably, as in other substances whose molecules have a shape close

to spherical, are associated with the onset of molecular rotation at the sites of the crystal lattice.

Table 2

	Endo isomer	Exo isomer
T_{tr}, °K	177.35 ± 0.08	237.7 ± 0.2
ΔH_{tr}, cal/mol	500.6 ± 0.3	1895 ± 11
ΔS_{tr}, e.u.	2.82	7.97
T_m, °K	$331.67 \pm 0.02^*$	$300.27 \pm 0.04^*$
ΔH_m, cal/mol	707.7 ± 3.2	703.4 ± 1.8
ΔS_m, e.u.	2.13	2.35
$S^0_{298.15}$, e.u.	53.49 ± 0.25	55.11 ± 0.26
$H^0_{298.15} - H_0$, cal/mol	8007 ± 16	8873 ± 29

* The melting temperatures of absolutely pure substances are given.

As can be seen from Table 2, the enthalpy change upon transition of the exo isomer to the high-temperature modification is more than three times greater than the corresponding enthalpy change for the endo isomer. Thus, the transition entropies also differ considerably, amounting to about 8 e.u. in the case of the exo isomer and about 3 e.u. in the case of the endo isomer. The values of ΔH of melting of both isomers are small and practically coincide. The melting entropies of both isomers only slightly exceed 2 e.u. This, apparently, may serve as additional confirmation that the transformations occurring below the melting point are associated with the appearance of the possibility of molecular rotation (such transformations may be regarded as "melting" with respect to molecular orientation). As noted earlier ([1]), in substances having transformations associated with molecular rotation in the crystal, a substantial contribution to the entropy of melting may

introduce only the translational motion of the molecules, and therefore the ΔS of melting of such substances should be close to 2 e.u.

It is interesting to note the existence of two modifications of exo-2-cyanobicyclo-(2, 2, 1)-heptane in the low-temperature region. One of them, metastable, is obtained by rapid cooling of the exo isomer from room temperature to the temperature of liquid nitrogen. Below 177°K this modification is quite stable; its heat capacity in the interval 12—177°K is indicated in Fig. 2 by the dashed line. On heating the metastable modification above 177°K, it spontaneously transforms into the stable one, which has a considerably lower heat capacity (solid line in Fig. 2). This transformation is irreversible and proceeds very slowly (several days). The heat capacities of the metastable and stable modifications differ at 177°K by 7%; with decreasing temperature this difference gradually diminishes, and in the interval 30—50°K the heat capacities of both modifications

coincide within the limits of experimental error. Below 30°K a difference in the heat capacities of these modifications again appears, which gradually increases with decreasing temperature and at 16°K amounts to about 10%. We note that both the stable and metastable modifications were obtained repeatedly in the course of the work (6–7 times), and the control measurements of heat capacity always led to results falling on the corresponding curve. The strict reproducibility of the properties permits the supposition that both these modifications are crystalline. The numerical data given in Tables 1 and 2 refer to the stable modification.

To determine the enthalpy of transformation from the metastable modification to the stable one, the exo isomer in the metastable modification was heated from 160 to 250°K (i.e., to a temperature lying in the region of existence of the high-temperature phase). The amount of heat expended in this heating proved to be 5335 cal/mole. On the other hand, heating the substance in the stable modification from 160 to 250°K requires 6150 cal/mole. Since the final state of the substance is the same in both cases (the heat capacity of the high-temperature phase at 250°K is reproduced exactly), the value of ΔH for the transition of the exo isomer from the metastable modification to the stable one at 160°K is about −815 cal/mole.

It is also interesting to note that the transformation temperature of the endo isomer practically coincides with the temperature at which the metastable modification of the exo isomer begins to transform into the stable one. Possibly this coincidence is not accidental and is due to the similarity of the corresponding crystal structures. To resolve this question it is necessary to study the crystal structures of the endo and exo isomers at low temperatures. From the data of Table 2 it is seen that the standard entropies of the solid compounds, $S_{298.15}$, are close to one another. The value of the absolute entropy of the exo isomer at 298.15°K is higher by approximately 1.5 entropy units; a difference of the same order is often observed in the absolute entropies of cis and trans isomers. However, the separate contributions to the values of $S_{298.15}$ differ more appreciably. Thus, over almost the entire temperature interval investigated, C_p of the exo isomer is lower than C_p of the endo isomer. On the other hand, as already noted, the values of ΔH and ΔS of transformation for the exo isomer are considerably higher than for the endo isomer. The higher values of the heat of transformation, as well as of the transformation temperature of the exo isomer, indicate that the stable low-temperature modification of the exo isomer has a stronger crystal lattice than the low-temperature modification of the endo isomer.

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Note: Figure translations are in progress. See original paper for figures.