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Abstract

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PHYSICAL CHEMISTRY

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HEAT CAPACITY AT LOW TEMPERATURES AND THERMODYNAMIC FUNCTIONS OF ENDO- AND EXO-2-METHYL-BICYCLO-(2,2,1)-HEPTANES

Previously performed measurements (^{1}) of the heat capacity at low temperatures of the endo- and exo-isomers of 2-cyano-bicyclo-(2,2,1)-heptane showed that the different spatial arrangement of the substituent (CN group) in the bicycle leads to a noticeable difference in the course of the heat-capacity curve, in particular in the temperature region of phase transitions.

The objects of the present study were the methyl stereoisomers: endo-2-methyl-bicyclo-(2,2,1)-heptane and exo-2-methyl-bicyclo-(2,2,1)-heptane (for brevity, in what follows we shall call them simply the endo- and exo-isomers). The molecules of both compounds are highly symmetric and close in shape to a sphere. For such substances, as is known, formation below the melting point of a rotational-crystalline phase (so-called plastic crystals) is characteristic.

Since these compounds differ from those studied in work (^{1}) only in the nature of the substituent in the endo- and exo-position, their study made it possible to identify characteristic features in the thermal properties inherent in the endo- and exo-isomers.

Methyl-bicyclo-(2,2,1)-heptanes were obtained as a result of a multistage synthesis based on individual endo- and exo-cyano-bicyclo-(2,2,1)-heptenes-5 through the stages of obtaining the methyl ester of 2-bicyclo-(2,2,1)-heptylcarboxylic acid and 2-bicyclo-(2,2,1)-heptylcarbinol (^{2}). Both preparations were purified by distillation on a rectification column. The amount of impurities in the endo-isomer, determined by us in the course of measuring the heat of melting of the substance, was 0.26 mole %. It proved impossible to use the same method for determining the purity of the exo-isomer because of the closeness of the melting temperature and the temperature of transformation of the substance in the

Fig. 1

Figure 1: Fig. 1

solid phase. But since both isomers studied were synthesized by a completely analogous route from endo- and exo-2-cyano-bicyclo-(2,2,1)-heptenes-5, whose purities are approximately identical, one should expect that these substances cannot differ greatly in impurity content.

Heat-capacity measurements were carried out in a small-volume adiabatic calorimeter described earlier ([3]). The calorimeter was filled with the substance through a copper capillary in the same manner as in work ([1]). The amount of sample in the calorimeter in both cases was about 6 g.

The true heat capacity of the endo- and exo-isomers was measured in the temperature interval 12–310° K; the heat-capacity values from the smoothed curve C_p—T for each isomer are given in Table 1. The root-mean-square deviation of the experimental points from the smoothed curve was, for both isomers, about 0.15% over the greater part of the temperature interval. Below 30° K, owing to the sharp decrease in the sensitivity of the thermometer, it reached 0.8%. 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 C_p—$\ln T$ and C_p—T. Extrapolation of the heat-capacity curves to 0° K was carried out graphically, since the temperature dependence of the heat capacity of both isomers at the lowest temperatures reached in the experiments could not yet be described by the Debye equation. The error of such extrapolation in calcu-

determination of the absolute entropy of the isomers at the standard temperature did not exceed 0.15 e.u.

Analysis of the C_p–T curves of the isomers (Fig. 1) showed that both substances exhibit transformations in the solid phase: the endo-isomer at 152.42° K, the exo-isomer at 164.10° K. Precise measurements of the heat capacity and, consequently, a careful study of the shape of the curve in the region of phase transformations are hampered by the very slow character of the transformations. A low rate is in general typical of transformations in crystals of organic substances (4). This, naturally, leads to an increase in the scatter of the experimental points in the temperature regions bordering on the anomalous one. Thus, for the exo-isomer in the interval 140—155° K the root-mean-square deviation of individual heat-capacity values from the smoothed curve increased to 0.5%. The observed transformations, probably, as in the case of the nitrile isomers of bicyclo-(2,2,1)-heptane (1), are associated with the onset of rotation of molecules at the sites of the crystal lattice.

Fig. 1

From the data given in Table 2 it is seen that the enthalpy and entropy of transformation of the endo-isomer are fairly large and considerably exceed the enthalpy and entropy of fusion of this isomer. It is interesting to note that the entropy of fusion of the endo-isomer is noticeably below 2 e.u. It has previously been noted (5) that in substances forming a rotational-crystalline phase below the melting temperature, the main contribution to the entropy of fusion is made by the translational motion of the molecules, and therefore ΔS_{fus} of such substances should be close to R, i.e., to 2 e.u. In those cases where $\Delta S_{\text{fus}} < 2$ e.u. (as, for example, in the case of the endo-isomer we studied), one may assume (5) that, as a result of the transformation in the solid phase, along with rotational degrees of freedom the molecules may also acquire a certain freedom of translation (so-called self-diffusion in the crystal).

For the exo-isomer, unfortunately, it proved impossible to determine the entropy of fusion. The transformation temperature and the melting temperature of this isomer are apparently very close, which did not allow the enthalpy of transformation and the enthalpy of fusion of this isomer to be determined separately. For this reason the values ΔH and ΔS of the transformation of the exo-isomer given in Table 2 should be regarded as total values of the enthalpies and entropies of transformation and fusion.

For the exo-isomer (as also for exo-2-cyano-bicyclo-(2,2,1)-heptane (1)) the existence of two modifications in the low-temperature region is characteristic. The strict reproducibility of the heat capacity (both modifications were obtained repeatedly in the course of the work) permits the assumption that both modifications are crystalline. The metastable modification was obtained by rapid cooling of the exo-isomer from room temperatures to the temperature of liquid nitrogen. Below 127° K this modification is quite stable; in Fig. 1 its heat capacity in the interval 12—127° K is denoted by a dashed line. On heating the metastable modification above 127° K it spontaneously transforms into the stable one, which has a considerably lower heat capacity (solid line in Fig. 1). The transformation is irreversible and proceeds very slowly. (In the temperature interval 130—150° K it is completed in 180—200 h.) The heat capacities of the metastable and stable modifications differ at 127° K by 10%; at temperatures

Table 1

T, °K	C_p^*, cal/deg·mol Endo-2-methylbicyclo-(2,2,1)-heptane	S_T, e.u. Endo-2-methylbicyclo-(2,2,1)-heptane	H_T-H_0, cal/mol Endo-2-methylbicyclo-(2,2,1)-heptane	C_p^*, cal/deg·mol Exo-2-methylbicyclo-(2,2,1)-heptane	S_T, e.u. Exo-2-methylbicyclo-(2,2,1)-heptane	H_T-H_0, cal/mol Exo-2-methylbicyclo-(2,2,1)-heptane	T, °K	C_p^*, cal/deg·mol Endo-2-methylbicyclo-(2,2,1)-heptane	S_T, e.u. Endo-2-methylbicyclo-(2,2,1)-heptane	H_T-H_0, cal/mol Endo-2-methylbicyclo-(2,2,1)-heptane	C_p^*, cal/deg·mol Exo-2-methylbicyclo-(2,2,1)-heptane	S_T, e.u. Exo-2-methylbicyclo-(2,2,1)-heptane	H_T-H_0, cal/mol Exo-2-methylbicyclo-(2,2,1)-heptane
12	1.11_1	0.28	2.83	0.83_8	0.23	2.23	140	24.07	23.18	1702	19.90	21.12	1557
16	2.22_5	0.75	9.00	1.75_1	0.59	7.28	150	(transition region)	(transition region)	(transition region)	21.01	22.53	1762

T, °K	C_p^*, cal/deg mol Endo-2-methylbicyclo-(2,2,1)-heptane	S_T, e.u. Endo-2-methylbicyclo-(2,2,1)-heptane	H_T-H_0, cal/mol Endo-2-methylbicyclo-(2,2,1)-heptane	C_p^*, cal/deg mol Exo-2-methylbicyclo-(2,2,1)-heptane	S_T, e.u. Exo-2-methylbicyclo-(2,2,1)-heptane	H_T-H_0, cal/mol Exo-2-methylbicyclo-(2,2,1)-heptane	T, °K	C_p^*, cal/deg mol Endo-2-methylbicyclo-(2,2,1)-heptane	S_T, e.u. Endo-2-methylbicyclo-(2,2,1)-heptane	H_T-H_0, cal/mol Endo-2-methylbicyclo-(2,2,1)-heptane	C_p^*, cal/deg mol Exo-2-methylbicyclo-(2,2,1)-heptane	S_T, e.u. Exo-2-methylbicyclo-(2,2,1)-heptane	H_T-H_0, cal/mol Exo-2-methylbicyclo-(2,2,1)-heptane
20	3.40_6	1.38	20.24	2.87_2	1.09	16.44	160	30.45	34.20	3373	(transition and melting region)	(transition and melting region)	(transition and melting region)
24	4.63_5	2.11	36.33	3.98_5	1.71	30.02	170	30.66	36.05	3679	33.01	37.86	4266
28	5.74_5	2.91	57.12	5.04_7	2.40	47.98	180	31.02	37.82	3987	33.53	39.76	4599
32	6.73_1	3.74	82.10	6.04_4	3.14	70.13	190	31.41	39.50	4299	34.12	41.58	4937
36	7.62_9	4.58	110.8	6.95_6	3.91	96.15	200	31.52	41.12	4614	34.78	43.35	5281
40	8.45_2	5.43	143.0	7.78_1	4.68	125.7	210	31.93	42.66	4931	35.48	45.07	5633
44	9.19_2	6.27	178.3	8.52_4	5.46	158.3	220	32.62	44.16	5253	36.25	46.73	5991
48	9.85_5	7.10	216.4	9.20_4	6.23	193.8	230	33.45	45.63	5584	37.10	48.36	6358
52	10.46	7.91	257.0	9.83_3	6.99	231.9	240	34.43	47.08	5923	38.03	49.96	6734
56	11.02	8.71	300.0	10.42	7.74	272.4	250	35.72	48.51	6273	39.02	51.53	7119
60	11.55	9.49	345.1	10.96	8.48	315.1	260	(melting region)	(melting region)	(melting region)	40.07	53.09	7514
70	12.80	11.36	466.8	12.25	10.27	431.2	270				41.15	54.62	7920
80	14.04	13.15	601.1	13.43	11.98	559.6	280	42.04	54.23	7806	42.28	56.13	8338
90	15.31	14.88	747.9	14.50	13.63	699.3	290	43.14	55.72	8232	43.44	57.64	8766
100	16.62	16.56	907.5	15.53	15.21	849.4	298.15	44.04	56.93	8588	44.42	58.85	9124
110	18.04	18.21	1081	16.59	16.74	1010	300	44.24	57.20	8669	44.64	59.13	9207
120	19.60	19.85	1269	17.69	18.23	1181	310	45.34	58.67	9117	45.87	60.61	9659
130	21.56	21.49	1474	18.79	19.69	1364							

* Adopted: 1 cal equals 4.1840 abs. J.

Table 2

	Endo isomer	Exo isomer
T_{tr}, °K	$152.42 \pm 0.01^\circ$	$164.10 \pm 0.01^\circ$
ΔH_{tr}, cal/mol	1125.0 ± 0.8	$2003.3^* \pm 36.0$
ΔS_{tr}, e.u.	7.38	12.21*
T_{m}, °K	$278.25^{**} \pm 0.09$	[~ 164.10]
ΔH_{m}, cal/mol	387.3 ± 2.1	
ΔS_{m}, e.u.	1.40	

	Endo isomer	Exo isomer
$S_{298.15}$, e.u.	56.93 ± 0.29	58.85 ± 0.49
$H_{298.15} - H_0$, cal/mol	8588 ± 19	9124 ± 54

* Total quantities relating to the transition in the solid phase with subsequent melting of the substance.
** Melting temperature of the absolutely pure substance.

At 12-15° K this difference reaches 50%. The data presented in Tables 1 and 2 refer to the stable modification. It should be noted that, upon slow cooling, the exo isomer can be obtained as a supercooled liquid; in Fig. 1, in the interval 140-164° K, its heat capacity is indicated by a dashed line.

The enthalpy of transition of the exo isomer from the metastable modification to the stable one was determined by comparing the amounts of heat required to heat the substance in each of these modifications from 112 to 170° K. Since in both cases the final state of the substance is the same (at a temperature of 170° K the isomer is liquid), the difference between these two quantities is the enthalpy of transition of the exo isomer from the metastable modification to the stable one at 112° K. According to the data of two experiments, this value is 850.9 ± 0.3 cal/mol.

Of definite interest is a comparison of the data obtained in the present work for the methyl endo and exo isomers of bicyclo-(2,2,1)-heptane with the results of a study of the corresponding nitrile endo and exo isomers (^{1}).

The C_p–T curves, both for the endo isomers and for the exo isomers, despite the different nature of the substituent, have much in common. Over a considerable part of the temperature interval studied, the heat capacity of the endo isomers is appreciably higher than the heat capacity of the corresponding exo isomers. On the other hand, in the exo isomers the values of ΔH and ΔS of the transformations in the solid phase are much larger, and the transformation and melting temperatures are appreciably higher. All this probably indicates a more compact structure of the crystal lattice of the exo isomers at low temperatures. The C_p–T curves in the region of transitions in the solid phase, both for the endo and for the exo isomers, have a characteristic form. In the case of the exo isomers the anomalous region is much more diffuse. The exo isomers are characterized by polymorphism in the low-temperature region, apparently associated with the greater orientational possibilities of the substituent in the exo position. It is interesting to note that the ΔH of the transition from the metastable modification to the stable one in the case of the nitrile and methyl exo isomers is very close. This is probably the result of the similarity of the corresponding crystal structures. The difference in the values of the absolute entropies $S_{298.15}$ of the endo and exo isomers is fairly appreciable: in both cases $S_{298.15}$ of the exo isomer is higher by 1.5-2 e.u. This somewhat exceeds the difference in absolute entropies at 298.15° K usually observed in the case of cis-trans isomerism.

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