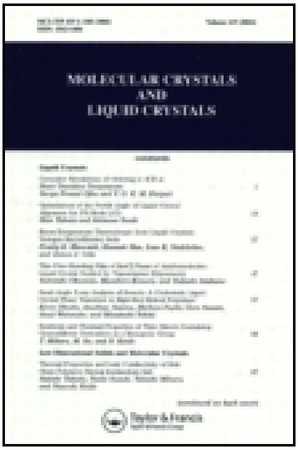

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Solid Phase Transitions of the Cyclohexane Derivatives and the Model of Energy States of Molecules in Plastic Crystals

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Solid Phase Transitions of the Cyclohexane Derivatives and the Model of Energy States of Molecules in Plastic Crystals

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The present paper summarizes the results of the measurements of thermodynamic properties of phase transitions of some cyclohexane derivatives in the condensed state and provides the analysis of the changes of dynamic behaviour of molecules during transitions from rigid crystal to plastic crystalline state. These results are discussed on the basis of the main trends of thermodynamic properties of solid state transitions in the series of the compounds having the similar structure. The analysis of the data obtained allows to develop new concept of energy states of molecules in plastic crystals. The combination of the results of calorimetric and spectral measurements with the data obtained by the method of statistical thermodynamics for the series of cyclohexane derivatives leads to the conclusion of the existence of internal rotation, ring inversion, and rotation of molecules as a whole in the nodes of the plastic crystal lattice.

Keywords: Cyclohexane derivatives; phase transitions; thermodynamic properties; plastic crystals; molecular state

INTRODUCTION

The prediction of thermodynamic properties of organic compounds based on classic theory of the structure of molecules is very complicated for the substances in the crystalline state [1, 2]. It is especially difficult to make

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a priory estimation of the solid-to-solid and solid-to-liquid transitions parameters (their temperatures and enthalpies) [3]. Thus, the entropies and the enthalpies of fusion may be more than 10 times different even in a series of the organic compounds of similar structure. Such a wide variation of $\Delta_{\rm fus}H^o_m$ and $\Delta_{\rm fus}S^o_m$ often occurs due to formation of plastic crystals (orientationally disordered crystals). The transitions into the plastic crystalline states are also difficult to predict for organic compounds and they are accompanied with simultaneous changes of mechanical, optical and dielectric properties and conformational composition of the substances [4–9].

The present paper summarizes the results of the measurements of thermodynamic properties of phase transitions of some cyclohexane derivatives in the condensed state and provides the analysis of the changes of dynamic behaviour of molecules during transitions from rigid crystal to plastic crystalline state. These results are discussed on the basis of the main trends of thermodynamic properties of solid state transitions in the series of the compounds having the similar structure. The analysis of the data obtained allows to develop new concept of energy states of molecules in plastic crystalline phase. The existence of plastic crystals is of crucial importance in explanation for possible reasons of the anomalous high rates of some reactions in the solid phase studied by Lishnevskii for the first time [10]. It was found that these reactions start spontaneously on frequent occasions on heating up to the temperatures closely approximating those of solid-to-solid transitions and fusion [11].

EXPERIMENTAL

The low-temperature heat capacities and enthalpies of phase transitions of the compounds in the condensed state between 5 and 320 K were measured in a Model TAU-1 vacuum adiabatic calorimeter fabricated by VNIIFTRI (Moscow) and described earlier [2]. The volumes of two calorimetric cells used were 0.6 and 1.0 cm^3. The temperature was measured by the iron-rhodium resistance thermometers ($R_{01} = 45.32\,\Omega$ and $R_{02} = 101.83\,\Omega$) located on the internal surface of the adiabatic shields and calibrated also in VNIIFTRI. The adiabaticity was maintained with the use of 4-junction differential thermocouple as an indicator of the temperature difference between the shield and calorimetric ampule. The accuracy of the calorimeter was verified by the measurements of the heat capacity of benzoic acid (K-1 grade, purity of not less than 0.99995 mass.) and of highly purified copper (purity of not less than 0.99995 mass.) The probable error of the molar heat capacity values $C_{s,m}$ is considered to be $\pm 4 \cdot 10^{-3} \cdot C_{s,m}$ over the temperature range 40 to 320 K. The final purity of the samples synthesized and purified by the authors was tested by gas chromatography.

The enthalpies of solid-to-solid and solid-to-liquid transitions (in general, transition from phase 1 to phase 2) were determined by the experiments in which each phase transition was initiated by a single impulse of the external energy. Thus, the values of $\Delta_{\mathrm{trs}}H_m^o$ were calculated as a difference between the total energy provided to the sample and the sum of the heats consumed to change the temperature of the phase 1 from the initial temperature to the T_{trs} and the temperature of phase 2 from T_{trs} to the final temperature of the experiment. For this purpose, the values of the heat capacity of both phases necessary were calculated by the extrapolation of the experimental data. 4 to 5 runs were conducted to determine $\Delta_{\mathrm{trs}}H_m^o$ of each phase transitions of compounds. The heat capacity changes during phase transitions $\Delta_{\mathrm{trs}}C_s$ were obtained as a difference between the values of C_s of phase 2 and phase 1 at T_{trs} estimated on the base of corresponding polinoms $C_s = f(T)$ at $T > T_{\mathrm{trs}}$ and $T < T_{\mathrm{trs}}$.

Thermodynamic parameters of phase transitions of the compounds under study in the condensed state are presented in Table I.

TABLE I Thermodynamic characteristics of phase transitions of cyclohexane derivatives measured under this study

Compound	*Transition*	$\frac{T_{trs}}{K}$	$\frac{\Delta_{trs}H_m^o}{kJ \cdot mol^{-1}}$	$\frac{\Delta_{trs}S_m^o}{J \cdot K^{-1} \cdot mol^{-1}}$
chlorocyclohexane [12]	crIII → crII	120.0	0.051 ± 0.001	0.43 ± 0.01
	crII → crI	220.4	8.010 ± 0.003	36.34 ± 0.01
	crII → l	229.34	2.043 ± 0.005	8.91 ± 0.02
1-chloro-1-methyl-cyclohexane	crII → crI	214.37	9.381 ± 0.028	43.76 ± 0.13
	crI → l	234.52	1.630 ± 0.004	6.95 ± 0.02
1-methylcyclohexanol	cr → l	299.40	14.322 ± 0.019	47.84 ± 0.06
1,1-dichlorocyclo-hexane	crII → crI	225.00	9.150 ± 0.018	40.67 ± 0.08
	crI → l	236.59	1.465 ± 0.005	6.19 ± 0.02
cyclohexyl formate	cr → l	201.33	10.490 ± 0.032	52.10 ± 0.16
cyclohexyl acetate	crII → crI	221.8	5.240 ± 0.030	23.62 ± 0.14
	crI → l	224.64	7.993 ± 0.030	35.58 ± 0.13
cyclohexyl butyrate	cr → l	219.60	16.574 ± 0.040	75.47 ± 0.18
cyclohexyl valerate	cr → l	222.40	18.315 ± 0.039	82.35 ± 0.18

RESULTS AND DISCUSSION

An Ability to Form Plastic Crystals and the Sums $\Sigma\, \Delta_{trs} S_i$ in a Series of Cyclohexane Derivatives

A rather good criteria of formation of plastic crystals is the low entropy of fusion (in the order of *R*) [3]. On the basis of the data summarized in Table II (the temperatures and the molar entropies of phase transitions for some mono- and disubstituted cyclohexane derivatives in the condensed state) one can confirm that

1. It is quite difficult to predict the existence of plastic crystals in a series of cyclohexane derivatives based only on the simple structure analogies and group additivity. The following series of cyclohexane derivatives with regular varying structure (see also Fig. 1) can illustrate this conclusion ("rig. cr." designates the existence of regular rigid crystalline phase up to the T_{fus}; "pl. cr." designates plastic crystalline phase up to the T_{fus}):

1. Cyclohexane (pl.cr.) → Methylcyclohexane (rig.cr.) → 1,1-Dimethylcyclohexane (pl.cr.)

$$\begin{tikzcd}
 & \text{Methylcyclohexane (rig.cr.)} \arrow[dr] & \\
\text{2. Cyclohexane (pl.cr.)} \arrow[ur] \arrow[dr] & & \text{1-Chloro-1-methylcyclohexane (pl.cr.)} \\
 & \text{Chlorocyclohexane (pl.cr.)} \arrow[ur] &
\end{tikzcd}$$

The comparison of thermal behaviours of 1-methylcyclohexanol and 1-chloro-1-methylcyclohexane is of great interest. Some substitutes are combined in geminal pairs in the molecules of these compounds and it is known that thermal evolutions of the corresponding monosubstituted cyclohexane derivatives are essentially different. So, cyclohexanol [17] and chlorocyclohexane [12] form plastic crystals, but methylcyclohexane [14] does not. Only 1-chloro-1-methylcyclohexane generates the plastic crystalline state [13] from the pair of 1,1-disubstituted derivatives under study. Therefore, an ability to form orientationally disordered crystals are not additive in the series of cyclohexane derivatives (otherwise either both compounds form plastic crystals or they do not form such a phase). Non-additive character of this ability also manifests itself in the fact that, unlike methylcyclohexane, 1,1-dimethylcyclohexane exists in the plastic crystalline state [15].

2. The entropies of fusion can differ by the factor of 6 to 15 in a series of cyclohexane derivatives. This is principally because of the different characters of thermal behaviour of compounds under discussion at

$T < T_{\text{fus}}$. Furthermore, the ratio between the entropy of solid-to-solid transition and the entropy of fusion and the temperature range of plastic crystalline phase vary within wide limits for compounds forming plastic crystals.

3. Considerably more constancy is characteristic of the sums of the entropies of all solid-to-solid transitions and fusion ($\sum \Delta_{\text{trs}} S_m^o$). So, this sum is about 50 $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ on the average for the compounds represented in Table II. Significant departures from the constancy of the sum $\sum \Delta_{\text{trs}} S_m^o$ in a series of compounds having similar structure can be caused by a formation of essentially associated liquids at temperatures near T_{fus}. This is true, as an example, for cyclohexanol [17].

From the data summarized in the Tables I and II it will be also noted that the $\sum \Delta_{\text{trs}} S_m^o$ values depend on total numbers of the tops in molecules. However, it is difficult to express this dependence in numerical terms since the thermodynamic properties of cyclohexane derivatives having more than two tops in molecules have not been adequately investigated. Nevertheless this dependence is clearly evident for the series of monoalkylcyclohexanes (the sum $\sum \Delta_{\text{trs}} S_m^o$ is notably increasing while passing from cyclohexane to propylcyclohexane) and for the series of esters of cyclohexanol and carbonic acids (Tabs. I and II).

The Changes of Molecular States During Rigid Crystal-to-plastic Crystal Transition

The large values of the entropy changes $\Delta_{\text{trs}} S_m^o$ and the heat capacity changes $\Delta_{\text{trs}} C_s$ corresponding rigid crystal-to-plastic crystal transitions (Tab. II, "crII → crI" transition) results from total combination of some reasons.

Firstly, the transition into the plastic crystalline phase is accompanied by the changes of crystal structure and density (molar volume) of substance and these changes make a corresponding contribution ($\Delta_v S_m^o$) to the entropy change $\Delta_{\text{trs}} S_m^o$ [23–25].

Secondly, it was shown in our previous works [12, 13, 26] that the transition from rigid crystal to plastic crystal occurs with the abrupt complication of conformational composition of the compounds. So, only the C—Cl valence bands corresponding to thermodynamically most stable conformers of compounds remain in the infrared spectra of chlorocyclohexane [12] and 1-chloro-1-methylcyclohexane [13] at temperatures $T < T_{\text{trs}}$ (T_{trs} is the temperature of rigid crystal-to-plastic crystal transition). Consequently, the potential barriers of ring inversion are overcomed at transition of these

TABLE II Thermodynamic characteristics of the phase transitions in the condensed state for the series of cyclohexane derivatives. T_{trs}, $\Delta_{\mathrm{trs}}S_m^\circ$ and $\Delta_{\mathrm{trs}}C_s$ are the temperature, the entropy and the heat capacity changes during these transitions. $\sum \Delta_{\mathrm{trs}}S_m^\circ$ is a sum of entropies of all phase transitions between the low-temperature rigid crystal and the liquid

Compound	*Transition*	$\frac{T_{trs}}{K}$	$\frac{\Delta_{trs}S_m^\circ}{J \cdot K^{-1} \cdot mol^{-1}}$	$\frac{\Delta_{trs}C_s}{J \cdot K^{-1} \cdot mol^{-1}}$	$\frac{\sum \Delta_{trs}S_m^\circ}{J \cdot K^{-1} \cdot mol^{-1}}$
cyclohexane* [14]	crII → crI	186.09	36.2	13.9	45.8
	crI → l	279.69	9.6	14.3	
methylcyclohexane [14]	cr → l	146.57	46.1	48.4	46.1
ethylcyclohexane[14]	cr → l	161.83	51.5	51.4	51.5
propylcyclohexane [14]	cr → l	178.28	58.2	54.0	58.2
1,1-dimethylcyclohexane* [14]	crII → crI	153.15	39.1	32.2	47.5
	crI → l	239.81	8.4	9.8	
cis-1,2-dimethylcyclohexane* [16]	crII → crI	172.50	47.9	37.7	55.3
	crI → l	223.28	7.4	9.8	
trans-1,2-dimethylcyclohexane [15]	cr → l	184.99	56.7	41.7	56.7
cis-1,3-dimethylcyclohexane [15]	cr → l	197.59	54.8	36.2	54.8
trans-1,3-dimethylcyclohexane [15]	cr → l	183.06	53.9	46.4	53.9
cis-1,4-dimethylcyclohexane [15]	cr → l	185.73	50.1	49.5	50.1
trans-1,4-dimethylcyclohexane [15]	cr → l	236.22	52.2	19.7	52.2
cyclohexanol* [17]	crII → crI	265.50	33.2	22.7	39.2
	crI → l	299.09	6.0	19.6	
cyclohexanethiol [18]	cr → l	189.64	52.7	58.1	52.7
cyclohexanone* [19]	crII → crI	220.83	39.2	25.1	44.6
	crI → l	245.22	5.4	8.2	
cyclohexyl amine [20]	cr → l	255.4	58.4	53.2	58.4
cyclohexanone oxime [21]	crIII → crII	240.8	0.1	0	35.4
	crII → crI	273.4	0.3	0	
	crI → l	362.5	35.0	52.2	

chlorocyclohexane* [12]	crIII → crII	120.0	0.4	−6.5	45.7
	crII → crI	220.4	36.3	17.6	
	crI → l	229.34	8.9	−8.6	
bromocyclohexane [22]	cr → l	216.87	49.8	41.9	49.8
1-methylcyclohexanol [13]	cr → l	299.40	47.8	87.6	47.8
1-chloro-1-methylcyclohexane* [13]	crII → crI	214.37	43.8	34.7	50.8
	crI → l	234.52	7.0	9.6	
1,1-dichlorocyclohexane*	crII → crI	225.00	40.7	37.9	46.9
	crI → l	236.59	6.2	5.1	
cyclohexyl formate	cr → l	201.33	52.1	67.8	52.1
cyclohexyl acetate	crII → crI	221.8	23.6	0	59.2
	crI → l	224.64	35.6	55.3	

* The compounds forming plastic crystals (transitions crII → crI).

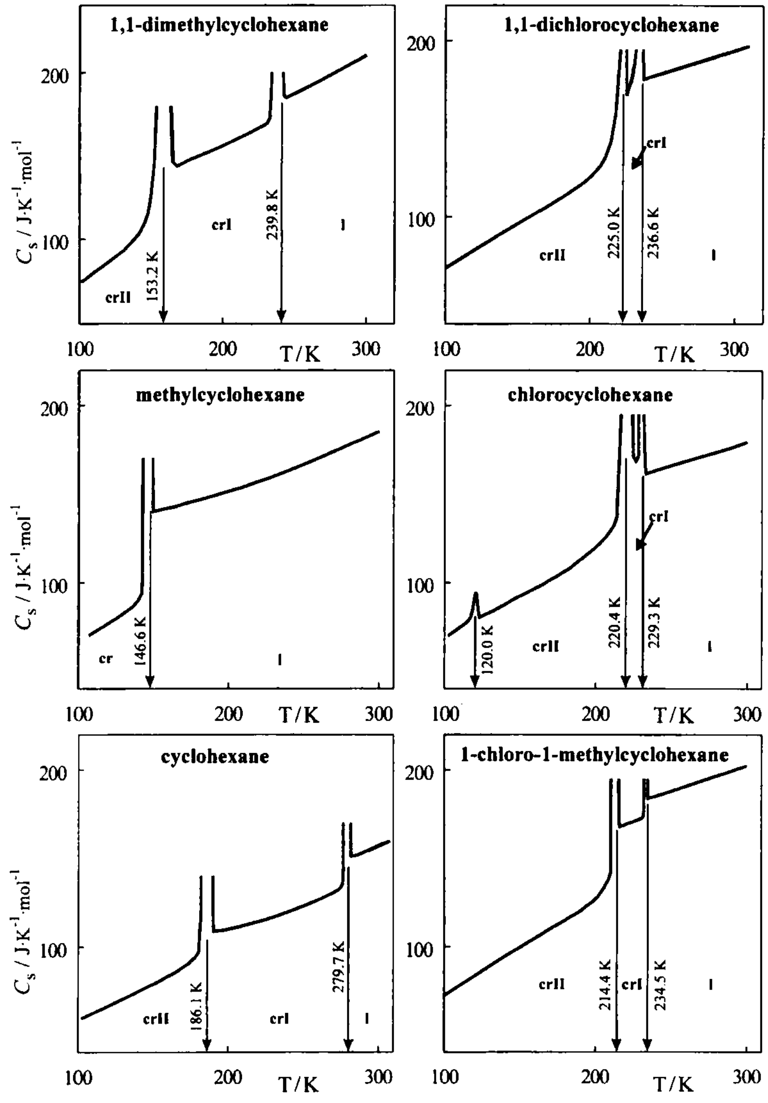

FIGURE 1 The temperature dependence of the heat capacity and the phase transitions of cyclohexane and some its derivatives in the condensed state between 100 and 300 K (crI is the plastic crystalline phase).

compounds from rigid crystal to plastic phase. Since the potential barrier for the 6-member ring inversion does not vary substantially for mono- and disubstituted cyclohexane derivatives, it is reasonable to assume that similar situation might occur for other cyclohexane derivatives forming plastic crystals as well.

Potential barriers of the internal rotation of the CH_3-, OH-, HS- tops are significantly lower than the barriers of the inversion of the cyclohexane ring for molecules in crystals and liquids. Therefore it is very likely that internal rotation of these groups are also excited at transition into the plastic crystalline state.

The contributions to the values of $\Delta_{\mathrm{trs}}S^o_m$ and $\Delta_{\mathrm{trs}}C_s$ caused by overcoming the potential barriers of ring inversion and internal rotation are designated, respectively, by $\Delta_{\mathrm{inv.}}S^o_m$, $\Delta_{\mathrm{inv.}}C_s$, $\Delta_{\mathrm{int.rot.}}S^o_m$, $\Delta_{\mathrm{int.rot.}}C_s$.

Thirdly, there are numerous experimental proofs that the total (over-all) rotation of the molecules or at least changing their orientations is possible in the plastic crystalline phase [4, 5]. The corresponding changes of thermodynamic properties are denoted by $\Delta_{\mathrm{orient.}}S^o_m$ and $\Delta_{\mathrm{orient.}}C_s$ (it means "orientational" contributions).

The relationships among all above-mentioned contributions will be different in every specific case. If other possible changes at rigid crystal-to-plastic crystal transitions, namely, variations in vibration frequencies in crystal lattice and molecules, changes of the concentration of positional defects and so on, are ignored, the thermodynamic parameters corresponding the transitions under study can be represented as the following sums:

$$\Delta_{\mathrm{trs}}S^o_m = \Delta_V S^o_m + \Delta_{\mathrm{inv.}}S^o_m + \Delta_{\mathrm{int.rot.}}S^o_m + \Delta_{\mathrm{orient.}}S^o_m, \tag{1}$$

$$\Delta_{\mathrm{trs}}C_s = \Delta_{\mathrm{inv.}}C_s + \Delta_{\mathrm{int.rot.}}C_s + \Delta_{\mathrm{orient.}}C_s. \tag{2}$$

The methods of calculation of each specific terms of $\Delta_{\mathrm{trs}}S^o_m$ and $\Delta_{\mathrm{trs}}C_s$ represented in relations (1) and (2) are given below.

The Contributions of Volume Changes to the Values of $\Delta_{\mathrm{trs}}S^o_m$ and $\Delta_{\mathrm{trs}}C_s$ Corresponding Rigid Crystal-to-plastic Crystal Transition

It has been claimed [23–25] that the solid-to-solid transition of the compound can be conceived of as the sum of two consecutive processes. The former is the transition of the compound from low-temperature phase to high-temperature phase at constant volume and temperature. The latter is the isothermal expansion of high-temperature phase up to its equilibrium volume at given pressure and temperature. The volume-changes contributions to the entropy and the heat capacity changes during solid phase transition are due to the latter process.

The volume-changes contribution to the entropy of rigid crystal-to-plastic crystal transition can be calculated by the following equation

$$\Delta_v S_m^o = \int_{V_1}^{V_2} \left(\frac{\partial p}{\partial T}\right)_V dV = \int_{V_1}^{V_2} \beta_v(V) dV, \tag{3}$$

where V_1 and V_2 are the molar volumes of rigid crystal and plastic crystal, respectively, at the temperature T_{trs}. This equation can be simplified [23, 24] if it is assumed that the mean pressure coefficient $\beta_V = (\partial p/\partial T)_V$ is constant in the range from V_1 to V_2 at different pressures. Then

$$\Delta_v S_m^o = \beta_V \cdot \Delta_{trs} V, \tag{4}$$

where $\Delta_{trs} V = V_2 - V_1$.

By this means the calculations of the volume-dependent terms $\Delta_v S_m^o$ for solid phase transitions are possible on the basis of the (p, V_m, T)-data of the compounds at temperatures close to the solid-to-solid transition curve. The (p, V_m, T)-data for some compounds under study were obtained by Wurflinger [27–29]. The calculated values of $\Delta_v S_m^o$ for cyclohexane derivatives forming plastic crystals are given in the Table III. But, since (p, V_m, T)-data for some compounds represented in the Table III are not available, it was assumed that $\Delta_v S_m^o / \Delta_{trs} S_m^o \cong 0.42$ for these substances.

The volume-changes contribution to the heat capacity change during rigid crystal-to-plastic crystal transition can be estimated on the basis of the following relationship [30]:

$$\left(\frac{\partial (C_p/T)}{\partial p}\right)_T = -\left(\frac{\partial^2 V}{\partial T^2}\right)_p. \tag{5}$$

TABLE III The results of calculation of the volume-dependent contributions to the entropy changes during rigid crystal-to-plastic crystal transitions for some cyclohexane derivatives

Compound	$\frac{T_{trs}}{K}$	$\frac{10^6 \cdot \Delta_{trs} V}{m^3 \cdot mol^{-1}}$	$\frac{(\frac{\partial p}{\partial T})_V}{MPa \cdot K^{-1}}$	$\frac{\Delta_v S_m^o}{J \cdot K^{-1} \cdot mol^{-1}}$	$\frac{\Delta_{trs} S_m^o}{J \cdot K^{-1} \cdot mol^{-1}}$	$\frac{\Delta_v S_m^o}{\Delta_{trs} S_m^o}$
cyclohexane (CH) [27]	186.09	9.7	1.94	18.8	36.2	0.52
chlorocyclohexane [29]	220.4	6.53	1.81	11.8	36.3	0.32
cyclohexanone [27]	220.8	7.7	2.12	16.3	39.2	0.42
cyclohexanol [28]	265.50	7.95	1.76	14.0	33.2	0.42
				The average value:		0.42
1,1-dimethylCH*				16.4	39.1	
cis-1,2-dimethylCH*				20.1	47.9	
1-chloro-1-methylCH*				18.4	43.8	
1,1-dichloroCH*				17.1	40.7	

* It was assumed for these compounds that $\Delta_v S_m^o / \Delta_{trs} S_m^o = 0.42$ (the average value of this ratio for the compounds for which (p, V_m, T)-data are available).

Since the (V_m, T)-isobars of organic crystals are usually linear or nearly linear within the experimental errors [24, 29, 30], it may be considered that the heat capacities of the compounds depend almost not at all on the pressure during solid-to-solid transition. Therefore, it may be thought that the volume-change contribution to the heat capacity change $\Delta_{\text{trs}}C_s$ is equal to zero.

The Contributions of the Ring Inversion and the Internal Rotation of the Tops to the Values of $\Delta_{\text{trs}}S_m^o$ and $\Delta_{\text{trs}}C_s$ Corresponding Rigid Crystal-to-plastic Crystal Transition

These contributions were obtained using the procedures described in [31, 32] at the temperatures of corresponding solid-to-solid transitions of compounds and they are represented in the Tables IV and V. The parameters of the potential functions of the ring inversion and of the rotation of the tops were determined by the methods of molecular mechanics assuming no interations between the molecules [33]. The contributions $\Delta_{\text{inv.}}S_m^o$ were calculated based on the value of the frequency of the corresponding vibration under provision that this frequency was substantially different in the rigid crystal causing much smaller contribution into the entropy of the rigid crystal.

The analysis of the values given in the Tables II, III, IV, V shows that the sums $[\Delta_v S_m^o + \Delta_{\text{inv.}}S_m^o + \Delta_{\text{int.rot.}}S_m^o]$ and $[\Delta_{\text{inv.}}C_s + \Delta_{\text{int.rot.}}C_s]$ are less than the values of $\Delta_{\text{trs}}S_m^o$ and $\Delta_{\text{trs}}C_s$ for the compounds existing as plastic crystals. Thus, admittedly, the contributions caused by the total (over-all) rotation of the molecules or by the existence of different molecular orientations into thermodynamic properties of plastic crystals can be reasonably large.

The "Orientational" Contributions to the Entropy and the Heat Capacity Changes During Rigid Crystal-to-plastic Crystal Transition

It is not difficult to show (to verify) that the rotation of the molecules is hindered significantly in plastic crystals. The entropies of free rotation of non-interacted molecules as a whole of some cyclohexane derivatives at temperatures of their rigid crystal-to-plastic crystal transition are represented in the Table VI. These values ($S^o_{\text{free rot.}}$) were calculated on the basis of equation [31]:

$$S^o_{\text{free rot.}}(T) = R\left[\ln\frac{8\pi^2}{\sigma}\frac{(2\pi kT)^{3/2}}{h^3}(I_A I_B I_C)^{1/2} + \frac{3}{2}\right] \tag{6}$$

TABLE IV Entropy and heat capacity contributions of internal rotation in isolated molecules of cyclohexane derivatives at temperatures of rigid-to-plastic transition. V is value of potential barrier to internal rotation, σ is symmetry number, and I_{red} is reduced moment of inertia of internal rotation

Compound	$\frac{T_{trs}}{K}$	*Top*	$\frac{V}{kJ \cdot mol^{-1}}$	σ	$\frac{I_{red}}{10^{47} \cdot kg \cdot m^2}$	$\frac{\Delta_{int.rot.} S^\circ_m}{J \cdot K^{-1} \cdot mol^{-1}}$	$\frac{\Delta_{int.rot.} C_s}{JK^{-1} \cdot mol^{-1}}$	*Ref.*
1,1-dimethylcyclohexane	153.74	*e*-CH_3	14.8	3	5.31	3.5	6.1	(31)
		a-CH_3	16.8	3	5.31	3.1	5.7	(31)
cis-1,2-dimethylcyclohexane	172.50	*e*-CH_3	14.0	3	5.31	4.4	6.8	(31)
		a-CH_3	16.1	3	5.31	3.9	6.4	(31)
1-chloro-1-methylcyclohexane	214.37	*e*-CH_3	19.2	3	5.33	4.8	6.9	(13)
cyclohexanol	265.50	*e*-OH	8.2	1	1.39	5.8	7.3	(31)

TABLE V The entropy and heat capacity contributions of ring inversion in isolated molecules of some cyclohexane derivatives at the temperatures of rigid-to-plastic transitions. $\Delta_{\mathrm{conf}}H$ is the energy difference between "chair"-conformers of compounds

Compound	$\frac{T_{trs}}{K}$	$\frac{\Delta_{conf}H}{kJ \cdot mol^{-1}}$	$\frac{\nu}{cm^{-1}}$	$\frac{\Delta_{inv.}S^{o}_{m}}{J \cdot K^{-1} \cdot mol^{-1}}$	$\frac{\Delta_{inv.}C_{s}}{J \cdot K^{-1} \cdot mol^{-1}}$	*Ref.*
cyclohexane	186.09	–	241	4.3	6.3	(31)
1,1-dimethylcyclohexane	153.74	–	125	7.5	7.4	(31)
cis-1,2-dimethylcyclohexane	172.50	–	140	7.5	7.4	(31)
cyclohexanol	265.50	3.37	180	12.7	10.5	(31)
cyclohexanone	220.83	–	112	13.0	14.8	(31)
chlorocyclohexane	220.40	1.64	148	13.9	9.1	(12)
1-chloro-1-methylcyclohexane	214.37	2.04	125	14.6	9.8	(13)
1,1-dichlorocyclohexane	225.00	–	179	7.6	7.5	this work

TABLE VI Entropies of free total rotation of molecules and "orientational" contributions into entropy changes during rigid-to-plastic transition of cyclohexane and some of its derivatives at corresponding temperatures T_{trs}.$I_xI_yI_z$ is a product of principal moments of inertia; σ is a symmetry number of total rotation

Compound	$\frac{T_{trs}}{K}$	$\frac{I_xI_yI_z}{10^{135} \cdot kg^3 \cdot m^3}$	σ	$\frac{S_{free\,rot.}}{J \cdot K^{-1} \cdot mol^{-1}}$	$\frac{\Delta_{orient.}S^{o}_{m}}{J \cdot K^{-1} \cdot mol^{-1}}$	*Ref.*
cyclohexane	186.09	13.35	6	89.6	13.1	(31)
1,1-dimethylcyclohexane	153.74	81.07	1	109.6	8.6	(31)
cis-1,2-dimethylcyclohexane	172.50	87.93	1	111.1	12.0	(31)
cyclohexanol	265.50	37.42	1	113.2	6.5	(31)
cyclohexanone	220.83	32.09	1	110.3	9.9	(31)
chlorocyclohexane	220.40	88.47	1	114.5	10.6	(12)
1-chloro-1-methylcyclohexane	214.37	144.39	1	116.2	6.0	(13)
1,1-dichlorocyclohexane	225.00	268.78	1	119.4	16.0	this work

where I_A, I_B, I_C are the central principal moments of inertia of molecules; σ is a symmetry number of molecules; h is the Planck constant; k is the Boltzmann constant; R is the gas constant. The moments of inertia were obtained using structural parameters determined by the methods of molecular mechanics [33].

The values of $S^o_{\text{free rot.}}(T_{\text{trs}})$ far exceed the entropy changes $\Delta_{\text{trs}}S^o_m$ and the contributions $\Delta_{\text{orient.}}S^o_m$ calculated by relation (1). If it is granted that the total rotation of molecules arises instead of their torsional vibrations in the crystal lattice, the entropy changes should be equal to $[S^o_{\text{free rot.}} - S_{\text{tors. vibr.}}] \approx [S^o_{\text{free rot.}} - 3R]$. Since $[S^o_{\text{free rot.}} - 3R] > \Delta_{\text{orient.}}S^o_m$, it should be taken that the total (over-all) rotation of molecules in the nodes of crystal lattice is hindered significantly in the plastic crystals. Moreover, it is very probable that this rotation can occur only along one rotational axis, as suggested also in [34].

The simple Guthrie-McCullough model [35] is often used in order to interpret the entropy changes during solid phase transitions. In accordance to this model the value of $\Delta_{\text{trs}}S^o_m$ is determined by the mole fractions n_i of non-identical orientations of the molecules in the plastic crystal: $\Delta_{\text{trs}}S^o_m \approx -R \cdot \sum_i n_i \ln n_i$. It is commonly assumed for the applications of this model (the compounds with tetrahedral molecules, bicyclo[2.2.1]heptane [35]) that all the existing orientations in the plastic crystal are energy equivalent.

However this simple model does not allow to explain the large values of the heat capacity changes $\Delta_{\text{trs}}C_s$ corresponding to rigid crystal-to-plastic crystal transition for cyclohexane derivatives ($\Delta_{\text{trs}}C_s$ is variable from 14 to 38 $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, see Tab. II). Such an increase of the heat capacity may occur only if the distinguishable orientation states of molecules with different energies exist in the plastic crystal. The heat capacity change ($\Delta_{\text{orient.}}C_s$) related to the existence of the variety of orientations might be expressed as a function of the energy differences ΔE_{ij} between the orientation i and orientation j for each pair of the orientations [36]:

$$\Delta_{\text{orient.}}C_s = -\frac{1}{RT^2}\sum_{i=1}^{n} x_i \sum_{j>i}^{n} x_j(\Delta E_{ij})^2 \tag{7}$$

where x_i, x_j are the molar fractions of the orientations i and j; n is the total number of the orientations. It is evident from Eq. (7) that $\Delta_{\text{orient.}}C_s \neq 0$ only if at least some $\Delta E_{ij} \neq 0$.

On this basis the following modification of the model of the orientation disorder in the plastic crystals by Guthrie-McCullough [35] is of interest.

1. The molecules in the plastic crystalline phases undergo hindered total rotation from one preferable orientation to another orientation having the local minima of energy.
2. The frequencies of the lattice vibrations (vibrations of the centers of gravity of the molecules) are close enough for the rigid and plastic

crystals to cause practically no difference in their contributions to thermodynamic properties of these two crystalline phases. The normal vibrations frequencies of molecules are also practically the same in the rigid and plastic crystalline phases.

3. The lowest energy (basic) orientation in the plastic crystal is the one existing in the rigid crystal (corresponding energy levels is E_{bas}). All other orientations of the molecules ("plastic" orientations) have higher energy. The diagram of the energy levels due to the orientation disorder in the plastic crystals is given on the Figure 2.

Consistently with this diagram, it might be assumed that the frequencies of torsional vibrations in the plastic crystals are close to those in the rigid crystals. However their amplitudes are substantially higher. Therefore molecules may turn through sufficiently large angle φ (in the limit of 2π) in the plastic crystal lattice forming a variety of relatively stable orientations having the energy levels $E_{\mathrm{pl.},i}$.

There is no detailed information available about the values of $E_{\mathrm{pl.},i}$ and the molar fraction n_i different orientations corresponding the minima of energy of hindered total rotation of molecules in the plastic crystalline phases of the cyclohexane derivatives. The following assumptions are used

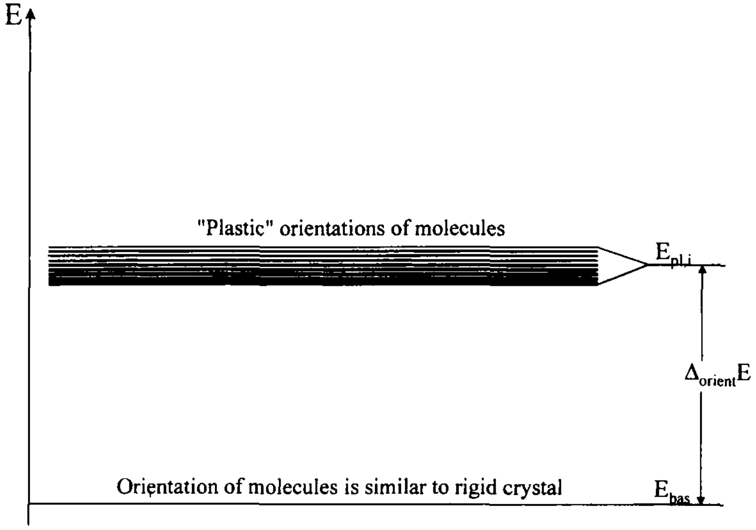

FIGURE 2 The model of energy states of molecules in the plastic crystalline phase.

here in order to make numerical estimates related to the model of plastic crystals discussed:

1. It is assumed that all $E_{\text{pl.},i}$ are very closed to each other. Therefore the energy levels of all "plastic" orientations might be characterized by a single (mean) value $(E_{\text{pl.}})_{\text{mean}}$.
2. The entropies of all plastic orientations are the same.
3. The mole fractions of the "plastic" orientations in the crystalline phase may be estimated from:

$$K_{\text{pl.}} = \exp(-\Delta_{\text{orient.}}G/RT), \tag{8}$$

$$\Delta_{\text{orient.}}G \approx \Delta_{\text{orient.}}E = (E_{\text{pl.}})_{\text{mean}} - E_{\text{bas}}, \tag{9}$$

where $\Delta_{\text{orient.}}G$ is the Gibbs energy change due to the change of the orientation of molecule in the plastic crystal; $K_{\text{pl.}}$ is the equilibrium constant:

$$K_{\text{pl.}} = \left(\sum_{i=1}^{n} x_{\text{pl.},i}\right)/x_{\text{bas}}. \tag{10}$$

4. The changes of the thermodynamic properties due to the occurrence of orientational disorder during rigid crystal-to-plastic crystal transition can be calculated from the relations which are analogous to the relations obtained for the calculation of the contributions of conformational conversions [36]:

$$\Delta_{\text{orient.}}S_m^o = -R\sum_{i=1}^{n} n_i \ln n_i, \tag{11}$$

$$\Delta_{\text{orient.}}C_s = -\frac{1}{RT^2}\sum_{i=1}^{n} n_i \sum_{j>i}^{n} n_j(\Delta_{\text{orient.}}E)^2, \tag{12}$$

$$\Delta_{\text{orient.}}H_m^o = \sum_{i=2}^{n} n_i(\Delta_{\text{orient.}}E), \tag{13}$$

where n_i, n_j are the mole fractions of molecules in *i,j*-"plastic" orientations (n_i = const for all $i = (2, 3, \ldots, n)$ for each plastic crystal accordingly accepted assumptions); $\Delta_{\text{orient.}}E$ is the mean energy difference between the plastic and basic orientations; T is the temperature; $\Delta_{\text{orient.}}S^o_m$, $\Delta_{\text{orient.}}H^o_m$, $\Delta_{\text{orient.}}C_s$ are the entropy, enthalpy and heat capacity changes, respectively, due to the changes of the orientations of molecules in the plastic crystalline phase.

The values of $\Delta_{\text{orient.}}S^o_m$ and $\Delta_{\text{orient.}}C_s$ are calculated by the relations (1) and (2) on the basis of the experimental values of $\Delta_{\text{trs}}S^o_m$ and $\Delta_{\text{trs}}C_s$. In the case of the rigid crystal-to-plastic crystal transition of cyclohexane these terms are

$$\begin{aligned}\Delta_{\text{orient.}}S^o_m(186\,\text{K}) &= \Delta_{\text{trs}}S^o_m - \Delta_{\text{inv.}}S^o_m - \Delta_v S^o_m\\ &\cong 36.2 - 4.3 - 18.8 = 13.1\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1},\\ \Delta_{\text{orient.}}C_s(186\,\text{K}) &= \Delta_{\text{trs}}C_s - \Delta_{\text{inv.}}C_s - \Delta_v C_s\\ &\cong 13.9 - 6.3 - 0 = 7.6\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.\end{aligned}$$

The values obtained allow to estimate the mean energy difference $\Delta_{\text{orient.}}E$ and the number of non-equivalent orientations of molecules $n_{\text{orient.}}$ in the plastic crystal of cyclohexane. The values of $\Delta_{\text{orient.}}S^o_m$ and $\Delta_{\text{orient.}}C_s$ determined by the Eqs. (11) and (12) at the temperature $T_{\text{trs}} = 186\,\text{K}$ are represented as a function of $n_{\text{orient.}}$ and $\Delta_{\text{orient.}}E$ in Figures 3 and 4. Incorporating the lines corresponding $\Delta_{\text{orient.}}S^o_m = 13.1\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $\Delta_{\text{orient.}}C_s = 7.6\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ into Figures 3 and 4, respectively, the inter-depended values of $n_{\text{orient.}}$ and $\Delta_{\text{orient.}}E$ can be obtained. The region of common solutions marked by the black rhombs into Figures 3, 4, 5 is significantly less and corresponds to $\Delta_{\text{orient.}}E \approx 2.9\,\text{kJ}\cdot\text{mol}^{-1}$ and $n_{\text{orient.}} = 7$. In this region both the values of $\Delta_{\text{orient.}}S^o_m$ determined by the Eqs. (1) and (11) and the values of $\Delta_{\text{orient.}}C_s$ obtained by the Eqs. (2) and (12) are in a good agreements.

The values of $\Delta_{\text{orient.}}E$ and $n_{\text{orient.}}$ were calculated for all other compounds studied by the same procedure (Tab. VII). One can see from the data in this Table that the values of $\Delta_{\text{orient.}}E$ are less than the changes of enthalpy during rigid crystal-to-plastic crystal transition. The differences between $\Delta_{\text{orient.}}E$ and $\Delta_{\text{trs}}H^o_m$ may be explained by the fact that some energy changes occurring the solid phase transition under investigation are not related to the changes of orientations of molecules in the crystal lattice.

Clearly that the question concerning the physical interpretation of sufficiently large numbers of non-equivalent orientations of molecules in the plastic crystals ($n_{\text{orient.}}$ is variable from 6 to 32) is of interest. The large values $n_{\text{orient.}}$ may be interpreted by mutual coordination of the rotations of different molecules in the nodes of the crystalline lattice. Indeed, if there are

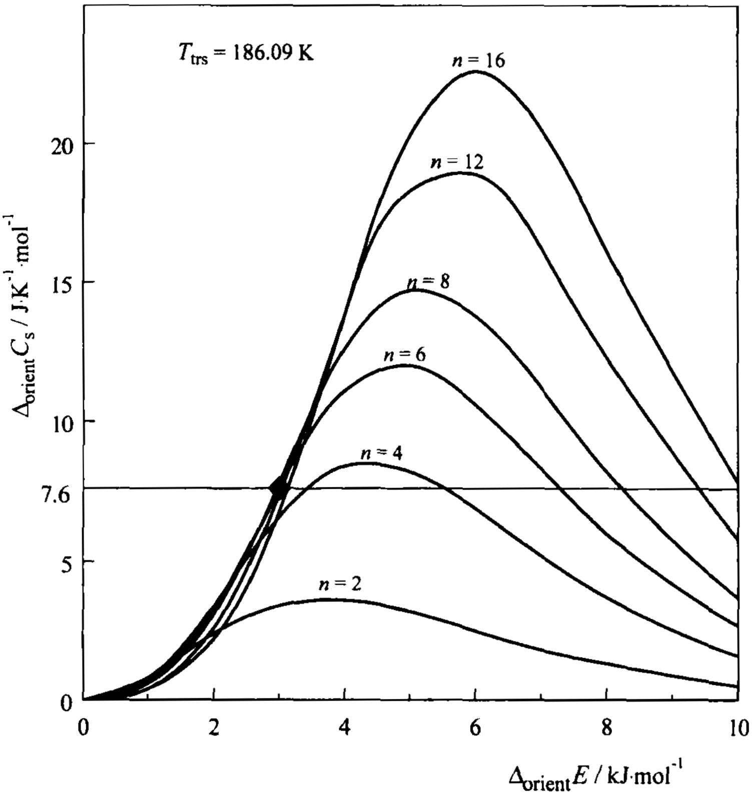

FIGURE 3 Orientational heat capacity $\Delta_{orient.}C_s$ as a function of the mean energy difference between plastic and basic orientations $\Delta_{orient.}E$ and the number of non-equivalent orientations of molecules $n_{orient.}$ for cyclohexane at T_{trs} = 186.09 K. ◆ is the region of general agreement between the experimental and calculated values $\Delta_{orient.}S^o_m$ and $\Delta_{orient.}C_s$.

m positions corresponding to the minima of the potential energy during the rotation of each molecule and *k* is the coordination number for each molecule in the crystal, then the total number of non-identical orientations of the ensemble of *k*-coordinated molecules is $n = m^{(k+1)}$. This fact indicates the possibility of the existence of large numbers of $n_{orient.}$.

The model of the plastic crystalline phase by Amzel and Becka [37] make allowance for two interpenetrating lattices of plastic crystal. According to this supposition the molecules can take any of *D* orientations on either of the sites of these lattices. The number of molecular orientations *D* can be also sufficiently large for this model (from 6 to 144).

It should be noted that cyclohexanol has anamalous low value of $\sum \Delta_{trs}S^o_m$ in comparison with other compounds represented in the Table II.

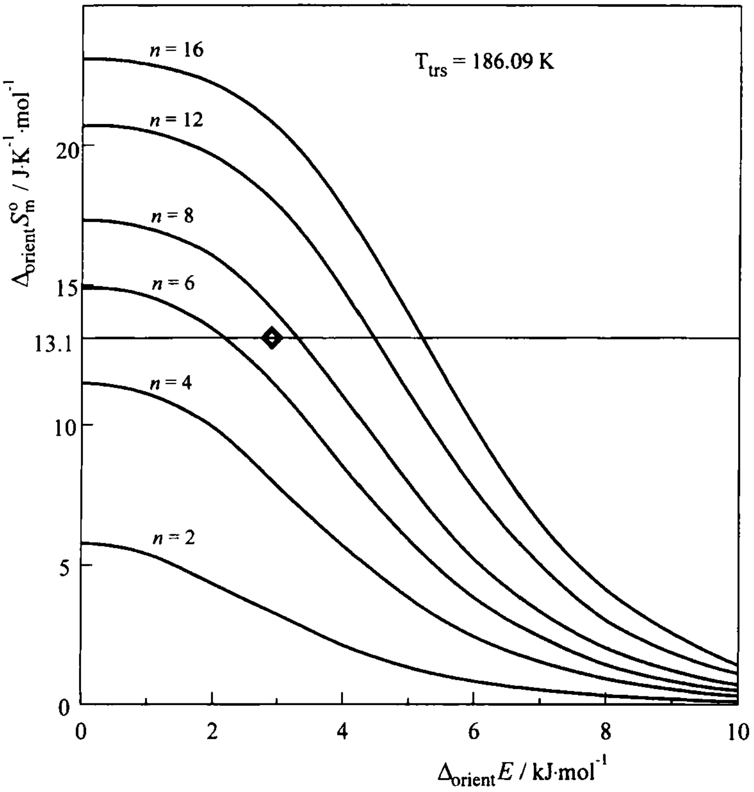

FIGURE 4 Orientational entropy $\Delta_{\text{orient.}}S^o_m$ as a function of the mean energy difference between plastic and basic orientations $\Delta_{\text{orient.}}E$ and the number of non-equivalent orientations of molecules $n_{\text{orient.}}$ for cyclohexane at $T_{trs} = 186.09$ K. ◆ is the region of general agreement between the experimental and calculated values $\Delta_{\text{orient.}}S^o_m$ and $\Delta_{\text{orient.}}C_s$.

It is caused by the fact that the molecules of cyclohexanol obtain an additional possibility to form hydrogen bonds since the transition from rigid crystal to plastic crystal has been occurred. Therefore the rotation of OH-groups is significantly hindered in the plastic crystal of cyclohexanol and do not contribute appreciably to the entropy and heat capacity changes at solid-to-solid phase transition under study. There are two kinds of molecular motion in the orientationally disordered crystal of cyclohexanol, namely: the over-all rotation of molecules and the ring inversion. The last supposition is confirmed by the results of NMR study of molecular motions in the cyclohexanol plastic crystal [38]. Taking into account this fact, the contributions of the internal rotation of OH-top (Tab. IV) were ignored at

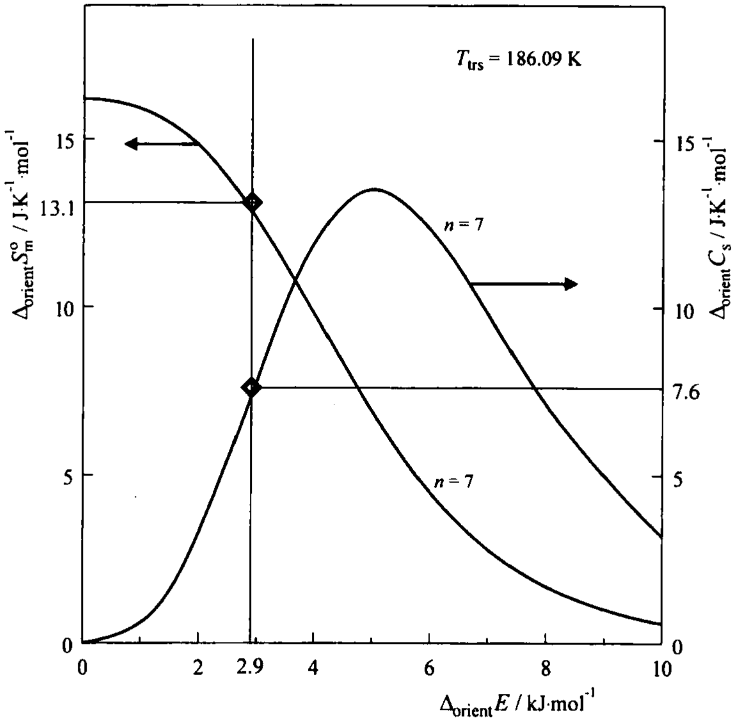

FIGURE 5 Orientational heat capacity $\Delta_{\text{orient.}}C_s$ and entropy $\Delta_{\text{orient.}}S^{\circ}_m$ as a function of the mean energy difference between plastic and basic orientations $\Delta_{\text{orient.}}E$ at the number of non-equivalent orientations of molecules $n_{\text{orient.}} = 7$ for cyclohexane at $T_{\text{trs}} = 186.09$ K. ◆ is the region of general agreement between the experimental and calculated values $\Delta_{\text{orient.}}S^{\circ}_m$ and $\Delta_{\text{orient.}}C_s$.

calculation of the "orientational" entropy and heat capacity of cyclohexanol (Tab. VII).

CONCLUSION

The model of energy states of molecules in plastic crystals suggested in this work gives an opportunity to determine the most important parameters of the plastic crystalline phase – the mean energy difference between the "plastic" and basic orientations and the number of non-equivalent orientations of molecules. It will be contribute into creation of the methods to predict the formation of plastic crystals by substances and the temperature region of the existence of the plastic phase and also into

TABLE VII The entropy and heat capacity changes during transition from rigid crystal to plastic crystal caused by hindered total rotation of molecules ("orientational" entropies and heat capacities) and corresponding parameters of the model of energy states of molecules in the plastic crystals for some cyclohexane derivatives. $n_{\mathrm{orient.}}$ is a number of non-equivalent molecular orientations; $\Delta_{\mathrm{orient.}}E$ is the mean energy difference between plastic and basic molecular orientations. $\Delta_{\mathrm{trs}}H_m^o$ is the enthalpy of rigid crystal-to-plastic crystal transition

Compound	$\frac{T_{trs}}{K}$	$\frac{\Delta_{orient.}S_m^o}{J \cdot K^{-1} \cdot mol^{-1}}$	$\frac{\Delta_{orient.}C_s}{J \cdot K^{-1} \cdot mol^{-1}}$	$n_{orient.}$	$\frac{\Delta_{orient.}E}{kJ \cdot mol^{-1}}$	$\frac{\Delta_{trs}H_m^o}{kJ \cdot mol^{-1}}$
cyclohexane	186.09	13.1	7.6	7	2.9	6.74
1,1-dimethylcyclohexane	153.74	8.6	13.0	7	3.7	5.99
cis-1,2-dimethylcyclohexane	172.50	12.0	17.1	12	4.4	8.26
cyclohexanol	265.50	6.5	12.2	6	6.8	8.82
cyclohexanone	220.83	9.9	10.3	6	4.3	8.66
chlorocyclohexane	220.40	10.6	8.5	6	3.8	8.01
1-chloro-1-methylcyclohexane	214.37	6.0	18.0	12	7.5	9.15
1,1-dichlorocyclohexane	225.00	16.0	30.4	32	7.4	9.38

collaboration of the methods to estimate possible differences of physical quantities of substances during rigid crystal-to-plastic crystal transition.

Another important problem is the search of technical application of plastic crystals.

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