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Investigation of thermodynamic properties of trans-2-cyclohexylcyclohexanol

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A comprehensive study of thermodynamic properties of trans-2-cyclohexylcyclohexanol (t-2CCOL) was carried out in this work. The subject compound is a by-product from the synthesis of 2-phenylphenol. The standard molar enthalpy of combustion of t-2CCOL, found by the bomb calorimetry method, $\Delta_c H^\circ_m(\mathrm{cr}, 298.15\ \mathrm{K}) = -(7388.05 \pm 1.37)\ \mathrm{kJ \cdot mol^{-1}}$, and the standard molar enthalpy of formation $\Delta_f H^\circ_m(\mathrm{cr}, 298.5\ \mathrm{K}) = -(478.25 \pm 2.13)\ \mathrm{kJ \cdot mol^{-1}}$. The molar sublimation and vaporization enthalpies of t-2CCOL were measured with a heat-conduction differential microcalorimeter: $\Delta^g_{cr} H^\circ_m(319.5\ \mathrm{K}) = (98.56 \pm 0.52)\ \mathrm{kJ \cdot mol^{-1}}$; $\Delta^g_l H^\circ_m(345.8\ \mathrm{K}) = (80.31 \pm 0.34)\ \mathrm{kJ \cdot mol^{-1}}$. Vapour pressure of t-2CCOL was measured by the integral effusion Knudsen method in the temperature range 293 K to 325 K for crystal: $\ln(p/\mathrm{Pa}) = (37.30 \pm 0.22) - (11616 \pm 69) \cdot T^{-1}$, and in the temperature range 328 K to 364 K for liquid: $\ln(p/\mathrm{Pa}) = (34.41 \pm 0.44) - (10013 \pm 150) \cdot T^{-1}$. The heat capacity of t-2CCOL was measured by the vacuum adiabatic calorimetry ($T = 5$ K to $T = 338$ K). The fusion temperature of t-2CCOL is 325.8 K, and the molar enthalpy of fusion is $\Delta_{fus} H^\circ_m = (14.515 \pm 0.029)\ \mathrm{kJ \cdot mol^{-1}}$. Standard molar thermodynamic functions of t-2CCOL in the crystalline state at $T = 298.15$ K were obtained on the basis of these measurements: $C^\circ_{p,m} = (248.68 \pm 0.99)$; $\Delta^T_0 S^\circ_m = (263.85 \pm 1.18)$; $\Delta^T_0 H^\circ_m / T = (130.52 \pm 0.51)$; $\Phi^\circ_m = (133.33 \pm 1.29)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. © 1997 Academic Press Limited

KEYWORDS: trans-2-cyclohexylcyclohexanol; heat capacity; entropy; enthalpy of formation; saturated vapour pressure

1. Introduction

2-cyclohexylcyclohexanol is formed as a by-product of the industrial hydrogenation of phenol(1) to obtain cyclohexanol, and of oxidation of cyclohexanone.(2) In addition, 2-cyclohexylcyclohexanol is also a semi-product in the industrial synthesis of 2-phenylphenol.(3) All these facts necessitate a comprehensive study of the thermodynamic properties of 2-cyclohexylcyclohexanol, which is important to analyse the methods of its synthesis and processing.

It is known that cyclohexylcyclohexane(4) and cyclohexanol,(5) which have similar structures, are characterized by complex thermal behaviour in the crystalline state. Cyclohexanol forms a plastic crystal in the temperature range 265.5 K to 299.05 K and has a low fusion entropy typical for plastic crystals $\{\Delta_{fus} S^\circ_m(299.05\ \mathrm{K}) = 5.96\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}\}$. According to the results(4) of the d.s.c. investigations cyclohexylcyclohexane forms four crystalline phases at the temperatures from 256 K

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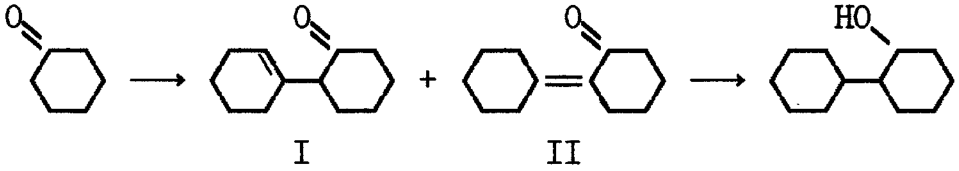
to 278 K, but it has a higher fusion entropy $\{\Delta_{\text{fus}}S^{\circ}(277.2\text{ K}) = 24.26\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}\}$ than the majority of plastic crystals. The investigation of i.r. and Raman spectra of cyclohexylcyclohexane at different temperatures(6) showed that solid-to-solid transformations are accompanied by considerable changes in conformational composition and molecular symmetry (C_{2h} to C_2). The study of low-temperature heat capacity and measurement of phase transition enthalpies in 2-cyclohexylcyclohexanol also permits estimation of to what extent crystal polymorphism of different compounds can be predicted from simple structure analogies for molecules.

2. Experimental section

Trans-2-cyclohexylcyclohexanol was synthesized by the following manner:



The starting reactant cyclohexanone was condensed under atmospheric pressure at $T = 373$ K in 5 mass per cent NaOH solution.(7) The obtained mixture $\{0.9x\cdot$2-(1′-cyclohexenyl)cyclohexanone(I) + $0.1x\cdot$2-(1-cyclohexyliden)cyclohexanone(II)$\}$ was hydrogenated in the autoclave at $p = 11.15$ MPa and $T = 373$ K using 0.5 mass per cent Pt on the graphite as a catalyst. The hydrogenation products ($0.9x\cdot$trans-2-cyclohexylcyclohexanol + $0.06x\cdot$cis-2-cyclohexylcyclohexanol + $0.04x\cdot$impurities) were crystallized for a long time. The separation of the trans-isomer was made at consecutive seven-fold recrystallizations from petrol ether (fraction boiling in the temperature range from 313 K to 323 K). The final purification of sample was carried out in a sublimator at $p = 0.4$ kPa and $T = 350$ K. Vapour was condensed on the surface of a glass trap, forming crystals. The trap was cooled by water. The purest middle crystal fractions were taken for measurements.

The relative content of components in mixtures was determined by gas chromatograph CHROM-5 (carrier gas N_2) with a flame ionization detector. The condensation products were analysed using a glass column (1.7 m long, 4 mm i.d.), filled with polysorb W on 30 per cent PPMS. The 2-cyclohexylcyclohexanol diastereomers were separated in steel column (3 m long, 4 mm i.d.), containing 5 per cent polyethylene glycol-1500 on inerton AV-DMCS. The mass fraction purity of 2-cyclohexylcyclohexanol was 0.9948 of the trans-isomer and 0.0052 of the cis-isomer according to chromatographic analysis. We found, on the basis of gravimetric analysis of combustion products in a calorimetric bomb, that the total mass fraction of isomers was (0.9996 ± 0.0005). Prior to use, the samples were kept in a desiccator over P_2O_5. The density of crystalline sample $d = 0.987\ \text{g}\cdot\text{cm}^{-3}$ at $T = 293\ \text{K}$ was determined by the picnometric method using as a reference liquid the saturated solution of the studied sample in petrol ether.

The low-temperature heat capacity was measured in the vacuum adiabatic calorimeter TAU-1, fabricated by VNIIFTRI (National Scientific and Research Institute for Physical-technical and Radio-technical Measurements) in Moscow. The studied sample ($m = 0.46212\ \text{g}$) was put into a stainless steel container filled with heat-exchange helium gas and sealed with an indium gasket. The container was tightly inserted into the calorimetric sleeve and provided with a manganin heater. The sleeve was suspended by three nylon cords within the adiabatic shield, which was also provided with a manganin heater. The temperature difference between the adiabatic shield and the calorimetric sleeve was determined by a four-junction differential thermocouple: $\{(0.999\ \text{Cu} + 0.001\ \text{Fe})\text{-to-Chromel}\}$. The electric potential of the thermocouple after preliminary amplification went to the terminals of an analogue regulation block, which assured automatic adiabatic shield control with proportional integral/differential action. The thermometric measurements were made by a capsule type (iron + rhodium) resistance thermometer ($R_o = 45.32\ \Omega$) installed on the inner surface of the adiabatic shield. The thermometer was fabricated and calibrated by VNIIFTRI. The reliability of the calorimetric apparatus was established by measuring the heat capacities of standard benzoic acid K-1 and high-purity copper. The probable error of the heat capacity values is considered to be 0.4 per cent at the temperatures 40 K to 321 K; this error increases at $T < 40$ K and it is 2 per cent at the helium temperatures.

The sublimation and vaporization enthalpies were determined in a differential heat conducting microcalorimeter of Calvet type using special calorimetric cells. A detailed description of the cells appears elsewhere.(8) The investigated samples $\{m = (0.040\ \text{to}\ 0.075\ \text{g})\}$ were put into stainless steel hermetic ampoules supplied with an aluminium membrane. After preliminary thermostatting of the calorimeter the membrane was pierced by a special demountable rod and a heating flux needed for evaporation was recorded. The calorimeter was calibrated by sublimation of benzoic acid (trade mark K-1), naphthalene (twice sublimed from the sample "pure for analysis") and by vaporization of *n*-decane (sample "for chromatographic analysis"), twice-distilled water. As a result it was found that the evaporation enthalpy measurement error does not exceed 1.0 per cent.

The saturated vapour pressure over crystalline and liquid trans-2-cyclohexylcyclohexanol was determined by integral effusion Knudsen method. The sample was located in a stainless steel chamber, which was sealed with a Teflon gasket. The chamber was placed in a copper block, which was placed in a water thermostat. The thermostatting accuracy was within 0.005 K. The temperature was measured with accuracy of 0.01 K by a Pt-resistance thermometer using the potentiometric method. The copper block was filled with heat exchange gas helium to accelerate the establishment of thermal equilibrium. At the beginning of the experiment helium was pumped out, and the sample mass diminution during the non-steady evaporation period was determined by the method described earlier.(9) Membranes of nickel foil with thickness 0.05 mm and diameters of effusion orifices

0.8254 mm and 0.2453 mm were used in experiments with crystal and liquid, respectively. The correction coefficients k to calculate saturated vapour pressure p from Knudsen pressure data p_k, according to the equation $p = k \cdot p_k$, were found in preliminary experiments using membranes with different effusion orifice diameters.(10) Errors in measurements of saturated vapour pressure did not exceed 5 per cent, as it was established on the base of comparison of our result for urea and benzoic acid with reliable literature data.(11, 12) The saturated vapour pressure of trans-2-cyclohexylcyclohexanol in the studied temperature range 293 K to 364 K being rather low ($p < 130$ Pa), the equilibrium of reaction "monomer-associates" is almost completely displaced to the side of the monomer. That is why, from calculating the Knudsen vapour pressure, we supposed that the vapour has a monomolecular composition.

The combustion enthalpy was determined in two bomb calorimeters with isothermal shields. Their temperatures were maintained constant within $\pm$ 0.0015 K. The measurements error for combustion energies is 0.02 per cent.(13) The calorimetric bomb was filled with purified oxygen under pressure 3.04 MPa. Thermometric measurements were carried out by the 100 Ω Pt-resistance thermometers with recording of amplified signal by digital voltmeter. The compound was burnt in the form of tablets pressed in the air without auxiliary substances. Samples were ignited by passing electrical current from a capacitor battery, (capacity = 0.01 F) through a platinum wire (diameter = 0.05 mm). Energy equivalents of calorimeters $(14954.2 \pm 5.6)\ \mathrm{J \cdot K^{-1}}$ and $(14938.6 \pm 5.3)\ \mathrm{J \cdot K^{-1}}$ were determined from a reference sample of benzoic acid (trade mark K-1) with combustion energy = $-(26434.6 \pm 4.5)\ \mathrm{J \cdot g^{-1}}$ based on weight in a vacuum. The sample masses were reduced to vacuum, taking into consideration the density value of crystalline trans-2-cyclohexylcyclohexanol. The completeness of combustion was checked by gravimetric analysis of combustion products using the Rossini method.(14) The Washburn corrections were calculated by the Prosen method and recommendations given in reference 15. The molar mass of trans-2-cyclohexylcyclohexanol ($M = 182.3052\ \mathrm{g \cdot mol^{-1}}$) was evaluated from the relative atomic masses of elements.(16)

3. Thermodynamic properties of trans-2-cyclohexylcyclohexanol

Experimental heat capacity $C_{s,\mathrm{m}}$ values of crystalline trans-2-cyclohexylcyclohexanol, measured in five experimental series in the temperature range from 5.10 K to 337.73 K are represented in table 1. To extrapolate the heat capacity to $T < 5$ K the Debye equation was used:

$$C_{s,\mathrm{m}} = 3 \cdot \mathrm{R} \cdot \mathrm{D} \cdot (\theta_\mathrm{D} \cdot T^{-1}), \tag{1}$$

where the characteristic temperature $\theta_\mathrm{D} = 68.2$ K was obtained from experimental measurements of $C_{s,\mathrm{m}}$ between $T = 5.10$ K and $T = 12.72$ K.

No anomaly was discovered on the $C_{s,\mathrm{m}} = f(T)$ curve (figure 1) in the whole temperature interval studied, excluding the fusion region.

TABLE 1. Experimental molar heat capacities $C_{s,\mathrm{m}}$ at vapour saturation pressure for trans-2-cyclohexylcyclohexanol in temperature range ΔT and at mean temperature $\langle T \rangle (R = 8.31451\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}})$

$\frac{\langle T \rangle}{\mathrm{K}}$	$\frac{C_{s,\mathrm{m}}}{R}$	$\frac{\Delta T}{\mathrm{K}}$	$\frac{\langle T \rangle}{\mathrm{K}}$	$\frac{C_{s,\mathrm{m}}}{R}$	$\frac{\Delta T}{\mathrm{K}}$
	Series 1		25.08	3.042	0.76
5.10	0.0971	0.18	25.92	3.163	0.90
5.45	0.121	0.16	26.81	3.270	0.85
5.64	0.131	0.21	27.64	3.426	0.80
5.84	0.151	0.20	28.44	3.531	0.77
6.09	0.170	0.29	29.19	3.668	0.73
6.37	0.195	0.27		Series 2	
6.63	0.217	0.25	31.41	4.024	0.95
6.88	0.238	0.24	32.45	4.186	1.13
7.18	0.261	0.22	33.55	4.375	1.06
7.34	0.273	0.21	34.59	4.553	1.01
7.59	0.315	0.28		Series 3	
7.86	0.333	0.25	23.27	2.755	0.88
8.10	0.362	0.23	24.13	2.894	0.82
8.33	0.390	0.22	27.23	3.351	1.08
8.58	0.418	0.27	28.28	3.518	1.01
8.84	0.449	0.26	29.33	3.703	1.06
9.14	0.490	0.32	32.73	4.227	1.33
9.76	0.563	0.28	34.02	4.445	1.24
10.04	0.602	0.27	35.36	4.624	1.42
10.30	0.633	0.25	36.75	4.838	1.33
10.55	0.691	0.24	38.18	5.002	1.51
10.79	0.712	0.23	39.65	5.196	1.42
11.08	0.750	0.34	41.04	5.393	1.34
11.42	0.806	0.32	42.52	5.534	1.61
11.75	0.843	0.31	44.08	5.667	1.52
12.06	0.901	0.30	45.71	5.926	1.73
12.35	0.933	0.29	47.41	6.107	1.63
12.72	0.984	0.43	49.00	6.311	1.54
13.13	1.079	0.39	50.71	6.498	1.86
13.51	1.149	0.36	52.54	6.752	1.79
13.88	1.176	0.36	54.51	6.968	2.14
14.29	1.263	0.45	56.60	7.212	2.02
14.73	1.327	0.42	58.79	7.419	2.35
15.15	1.390	0.41	61.11	7.690	2.27
15.55	1.457	0.39	63.72	7.955	2.93
15.94	1.508	0.38	66.57	8.255	2.77
16.31	1.564	0.36	69.28	8.561	2.63
16.75	1.647	0.50	74.33	9.093	2.41
17.25	1.704	0.48	76.93	9.344	2.80
17.72	1.805	0.46	79.68	9.602	2.69
18.17	1.902	0.44	82.22	9.854	2.39
18.61	1.947	0.42	84.59	10.10	2.33
19.02	2.024	0.41	87.35	10.35	3.19
19.43	2.103	0.39	90.48	10.64	3.07
19.82	2.167	0.38	93.50	10.97	2.97
20.30	2.260	0.56	96.72	11.28	3.45
20.85	2.331	0.54	100.12	11.56	3.34
21.38	2.446	0.51	103.82	11.93	4.06
22.00	2.550	0.70	107.81	12.32	3.92
22.69	2.680	0.66	111.68	12.69	3.80
23.46	2.781	0.85	115.43	13.04	3.70
24.29	2.916	0.80	119.08	13.37	3.60

TABLE 1—*continued*

$\frac{\langle T\rangle}{\mathrm{K}}$	$\frac{C_{s,\mathrm{m}}}{R}$	$\frac{\Delta T}{\mathrm{K}}$	$\frac{\langle T\rangle}{\mathrm{K}}$	$\frac{C_{s,\mathrm{m}}}{R}$	$\frac{\Delta T}{\mathrm{K}}$
	Series 4		212.20	21.52	3.69
122.30	13.58	3.50	215.92	21.89	3.66
125.76	13.91	3.42	219.62	22.23	3.62
129.15	14.27	3.36	223.63	22.63	4.26
132.47	14.55	3.29	227.94	23.01	4.22
133.95	14.63	3.26	232.22	23.39	4.19
135.74	14.82	3.21	236.47	23.87	4.15
138.92	15.15	3.15	240.70	24.29	4.11
142.06	15.32	3.11	244.91	24.64	4.08
148.19	15.96	3.07	249.09	25.08	4.05
151.19	16.29	2.96	253.25	25.50	4.02
154.08	16.50	2.84	257.39	25.93	3.98
157.22	16.79	3.43	261.51	26.32	3.95
	Series 5		265.71	26.74	3.92
159.68	17.11	3.55	269.71	27.15	3.90
163.22	17.40	3.51	273.79	27.61	3.86
166.71	17.67	3.47	277.86	27.91	3.84
173.57	18.39	3.39	281.92	28.34	3.82
177.29	18.67	4.94	285.97	28.71	3.79
181.31	18.98	3.98	290.01	29.12	3.77
185.29	19.29	3.94		Series 6	
189.23	19.51	3.91	328.26	50.89	3.05
193.14	19.81	3.86	330.95	51.39	3.60
197.02	20.14	3.83	332.35	51.65	3.61
200.86	20.47	3.79	334.83	52.11	3.58
208.44	21.18	3.72	337.74	52.65	3.56

Smoothing of experimental heat capacity values was realized with following polynomials:

$$C_{s,\mathrm{m}}(T) = \sum_{\mathrm{i}=0}^{n} a_{\mathrm{i}}\cdot T^{\mathrm{i}}. \tag{2}$$

To diminish the error at smoothing experimental results the whole temperature range was divided into six intervals. The coefficient values of a_{i}, calculated by the method of least squares for all temperature intervals, are given in table 2. In the overlapping regions of temperature intervals the $C_{s,\mathrm{m}}$ values, calculated from the coefficient of the polynomials for preceding and subsequent intervals coincided within $0.05\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. The linear extrapolation of heat capacity of solid and liquid phases in the heterogeneous region was carried out on the basis of heat capacity measurements at temperatures from 275 K to 290 K, and from 330 K to 340 K, respectively.

The thermodynamic fusion parameters were obtained by averaging three experimental determinations: $T_{\mathrm{fus}} = (325.80 \pm 0.05)\ \mathrm{K}$, $\Delta_{\mathrm{fus}}H^{\circ}_{\mathrm{m}} = (14515 \pm 29)\ \mathrm{J\cdot mol^{-1}}$, and $\Delta_{\mathrm{fus}}S^{\circ}_{\mathrm{m}} = (44.55 \pm 0.20)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$.

Thermodynamic functions of trans-2-cyclohexylcyclohexanol in the range from $T\rightarrow 0$ to $T = 335$ K (table 3) were calculated on the basis of smoothing polynomials

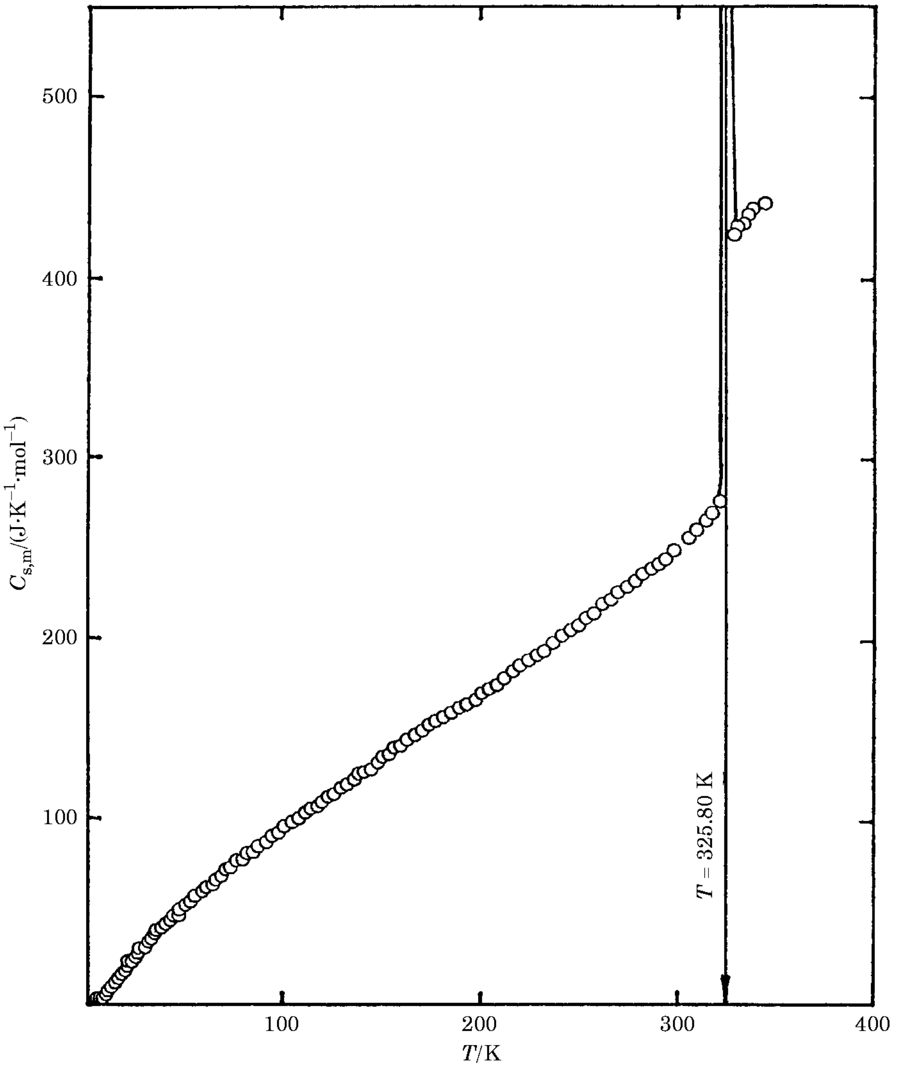


FIGURE 1. Experimental molar heat capacity $C_{s,\mathrm{m}}$ of trans-2-cyclohexylcyclohexanol in condensed state.

for the heat capacity. At temperature 298.15 K molar heat capacity $C^{\circ}_{p,\mathrm{m}}$, entropy $\Delta_0^{\mathrm{T}}S^{\circ}_{\mathrm{m}}$, enthalpy $\Delta_0^{\mathrm{T}}H^{\circ}_{\mathrm{m}}{\cdot}T^{-1}$, and molar Gibbs free energy function $\Phi^{\circ}_{\mathrm{m}} = \Delta_0^{\mathrm{T}}S^{\circ}_{\mathrm{m}} - \Delta_0^{\mathrm{T}}H^{\circ}_{\mathrm{m}}{\cdot}T^{-1}$ for crystalline trans-2-cyclohexylcyclohexanol are: $(248.68 \pm 0.99)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, $(263.85 \pm 1.18)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, $(130.52 \pm 0.51)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, and $(133.33 \pm 1.29)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, respectively.

Calorimetric measurements of sublimation and vaporization enthalpies of trans-2-cyclohexylcyclohexanol are given in table 4. The average values of sublimation and vaporization enthalpies, determined from six experiments, are: $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(319.5\ \mathrm{K}) = (98.56 \pm 0.52)\ \mathrm{kJ{\cdot}mol^{-1}}$ and $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(345.8\ \mathrm{K}) = (80.31 \pm 0.34)\ \mathrm{kJ{\cdot}mol^{-1}}$. Conversion of these values to fusion temperature $T_{\mathrm{fus}} = 325.8\ \mathrm{K}$ gives: $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(325.80\ \mathrm{K}) = (98.47 \pm 0.52)\ \mathrm{kJ{\cdot}mol^{-1}}$ and $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(325.80\ \mathrm{K}) = (83.73 \pm 0.34)\ \mathrm{kJ{\cdot}mol^{-1}}$. The fusion enthalpy $\Delta_{\mathrm{fus}}H_{\mathrm{m}}^{\circ}(325.80\ \mathrm{K}) = (14.74 \pm 0.62)\ \mathrm{kJ{\cdot}mol^{-1}}$ was obtained on the basis of Hess's law. This value, determined indirectly is in satisfactory agreement with the result of direct measurements: $\Delta_{\mathrm{fus}}H_{\mathrm{m}}^{\circ}(325.80\ \mathrm{K}) = (14.515 \pm 0.029)\ \mathrm{kJ{\cdot}mol^{-1}}$.

The experimental values of saturated vapour pressure over crystalline and liquid trans-2-cyclohexylcyclohexanol at temperatures from 293 K to 325 K and from 328 K to 364 K, respectively, are represented in table 5. The experimental results fitted by the least-squares method can be approximated for crystal by the equation:

$$\ln(p/\mathrm{Pa}) = (37.30 \pm 0.22) - (11616 \pm 69){\cdot}(T/\mathrm{K})^{-1}, \qquad (3)$$

and for liquid:

$$\ln(p/\mathrm{Pa}) = (34.41 \pm 0.44) - (10013 \pm 150){\cdot}(T/\mathrm{K})^{-1}. \qquad (4)$$

The thermodynamic parameters of sublimation and vaporization at the average temperatures of the measurements, obtained from equations (3) and (4) respectively, are: $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(309.1\ \mathrm{K}) = (96.58 \pm 0.57)\ \mathrm{kJ{\cdot}mol^{-1}}$ $\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}^{\circ}(309.1\ \mathrm{K}) = (214.3 \pm 1.9)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(346.1\ \mathrm{K}) = (83.25 \pm 1.25)\ \mathrm{kJ{\cdot}mol^{-1}}$, and $\Delta_{\mathrm{l}}^{\mathrm{g}}S_{\mathrm{m}}^{\circ}(346.1\ \mathrm{K}) = (156.3 \pm 3.6)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$. Conversion of the sublimation enthalpy, found by calorimetric method, to the temperature $T = 309\ \mathrm{K}$ with allowance for the temperature dependence of the heat capacities of crystalline and gaseous phases gives the value: $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(309\ \mathrm{K}) = (98.78 \pm 0.52)\ \mathrm{kJ{\cdot}mol^{-1}}$.

For the following thermodynamic calculations the weighted average sublimation enthalpy value at $T = 309\ \mathrm{K}$ was used: $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(309\ \mathrm{K} = (97.78 \pm 0.77)\ \mathrm{kJ{\cdot}mol^{-1}}$, found from both these results. This value was converted to the temperature 298.15 K, $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(298.15\ \mathrm{K}) = (98.01 \pm 0.77)\ \mathrm{kJ{\cdot}mol^{-1}}$.

The standard molar entropy of $C_{12}H_{22}O(g)$ at $T = 309\ \mathrm{K}$: $S_{\mathrm{m}}^{\circ}(\mathrm{g}, 309\ \mathrm{K}) = (491.1 \pm 2.8)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ was derived from the entropy of the crystalline phase at $T = 309\ \mathrm{K}$, the weighted average sublimation enthalpy value and the vapour pressure at $T = 309\ \mathrm{K}$.

TABLE 2. Values of polynomials coefficients (a_i) to describe the temperature dependence of heat capacity of trans-2-cyclohexylcyclohexanol

	Temperature interval					
a_i	(5 to 25) K	(20 to 80) K	(75 to 180) K	(180 to 275) K	(275 to 290) K	(330 to 340) K
a_0	−1.0214	9.0698	−260.42	548.24	6.4738	−84.118
a_1	0.6130	−1.1698	18.630	−7.5204	0.8124	1.5453
a_2	−0.1728	0.1351	−0.4872	0.04783		
$a_3{\cdot}10^2$	3.4885	−0.3321	0.7248	−0.01215		
$a_4{\cdot}10^4$	−24.760	0.3626	−0.6302	0.00115		
$a_5{\cdot}10^6$	80.334	−0.1481	0.3190			
$a_6{\cdot}10^9$	−997.85		−0.8692			
$a_7{\cdot}10^{12}$			0.9839			

TABLE 3. Standard molar thermodynamic functions $C_{p,\mathrm{m}}$, $\Delta_0^{\mathrm{T}}H_{\mathrm{m}}^{\circ}$, $\Delta_0^{\mathrm{T}}S_{\mathrm{m}}^{\circ}$, $\Phi_{\mathrm{m}}^{\circ}$ for crystalline and liquid trans-2-cyclohexylcyclohexanol ($R = 8.31451\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)

$\frac{T}{\mathrm{K}}$	$\frac{C_{p,\mathrm{m}}^{\circ}}{R}$	$\frac{\Delta_0^{\mathrm{T}}H_{\mathrm{m}}^{\circ}}{RT}$	$\frac{\Delta_0^{\mathrm{T}}S_{\mathrm{m}}^{\circ}}{R}$	$\frac{\Phi_{\mathrm{m}}^{\circ}}{R}$ [a]
0	0.0000	0.0000	0.0000	0.0000
5	0.0930	0.0231	0.0308	0.0077
10	0.6005	0.1684	0.2283	0.0598
15	1.363	0.4362	0.6119	0.1757
20	2.196	0.7707	1.117	0.3459
25	3.019	1.140	1.697	0.5572
30	3.811	1.519	2.318	0.7984
35	4.558	1.901	2.962	1.061
40	5.242	2.276	3.616	1.340
45	5.867	2.641	4.270	1.629
50	6.447	2.993	4.919	1.926
60	7.549	3.661	6.192	2.531
70	8.650	4.295	7.438	3.143
80	9.635	4.903	8.660	3.757
90	10.62	5.484	9.852	4.368
100	11.58	6.046	11.02	4.975
110	12.51	6.592	12.17	5.577
120	13.42	7.124	13.30	6.174
130	14.31	7.642	14.41	6.764
140	15.22	8.151	15.50	7.349
150	16.15	8.653	16.58	7.929
160	17.09	9.151	17.65	8.503
170	18.01	9.645	18.72	9.073
180	18.84	10.13	19.77	9.638
190	19.58	10.61	20.81	10.20
200	20.42	11.08	21.84	10.76
210	21.31	11.55	22.85	11.31
220	22.25	12.01	23.87	11.85
230	23.22	12.48	24.88	12.40
240	24.20	12.95	25.89	12.94
250	25.19	13.42	26.89	13.48
260	26.17	13.89	27.90	14.01
270	27.15	14.36	28.91	14.55
280	28.14	14.83	29.91	15.08
290	29.11	15.31	30.92	15.61
298.15	29.91	15.70	31.73	16.04
300	30.09	15.79	31.92	16.13
310	31.07	16.26	32.92	16.66
320	32.04	16.74	33.92	17.18
325.80(cr)	32.61	17.02	34.50	17.49
325.80(l)	50.48	22.38	39.86	17.49
330	51.22	22.74	40.52	17.77
335	52.14	23.17	41.29	18.12

[a] $\Phi_{\mathrm{m}}^{\circ} = \Delta_0^{\mathrm{T}}S_{\mathrm{m}}^{\circ} - \Delta_0^{\mathrm{T}}H_{\mathrm{m}}^{\circ}{\cdot}T^{-1}$.

The results of the combustion experiments are summarized in table 6. The standard molar energy of combustion $\Delta_{\mathrm{c}}U_{\mathrm{m}}^{\circ}$ and standard molar enthalpy of combustion $\Delta_{\mathrm{c}}H_{\mathrm{m}}^{\circ}$ were calculated, according to the reaction:

$$\mathrm{C_{12}H_{22}O(cr)} + 17\mathrm{O_2(g)} = 12\mathrm{CO_2(g)} + 11\ \mathrm{H_2O}, \qquad (5)$$

where $\Delta_c U^\circ_m = -(7375.65 \pm 1.37)\ \text{kJ}\cdot\text{mol}^{-1}$ and $\Delta_c H^\circ_m = -(7388.05 \pm 1.37)\ \text{kJ}\cdot\text{mol}^{-1}$.

As a result, the standard molar enthalpy of formation of crystalline trans-2-cyclohexylcyclohexanol was determined: $\Delta_f H^\circ_m(\text{cr}, 298.15\ \text{K}) = -(478.25 \pm 2.13)\ \text{kJ}\cdot\text{mol}^{-1}$. The standard molar enthalpies of formation $CO_2(g)$ and $H_2O(1)$ taken from reference 17 were used for the calculation. Taking into account the entropy of crystalline trans-2-cyclohexylcyclohexanol, its sublimation enthalpy and literature data for entropies of elements,(17) it was found that $\Delta_f G^\circ_m(\text{cr}, 298.15\ \text{K}) = -(77.59 \pm 2.83)\ \text{kJ}\cdot\text{mol}^{-1}$, and $\Delta_f H^\circ_m(\text{g}, 298.15\ \text{K}) = -(380.24 \pm 2.27)\ \text{kJ}\cdot\text{mol}^{-1}$.

4. Some regularities in entropies of phase transitions of cyclohexylcyclohexane derivatives

Thermodynamic functions of solid-to-solid transitions and fusion for compounds with a similar structure are represented in table 7. Trans-2-cyclohexylcyclohexanol, in contrast to cyclohexanol and cyclohexylcyclohexane, does not possess solid-to-solid transitions.

TABLE 4. Calorimetric results for the sublimation and evaporation of trans-2-cyclohexylcyclohexanol. The sublimation and evaporation enthalpy ΔH of a specimen and the molar enthalpies $\Delta^g_{cr} H^\circ_m$ and $\Delta^g_l H^\circ_m$ were calculated from the expression:

$$\Delta H = K^{-1} \cdot \int_{\tau=0}^{\tau=\tau_2} \Delta E \mathrm{d}\tau; \quad \Delta H^\circ_m = \Delta H \cdot M \cdot m^{-1}$$

where m is the specimen mass corrected to vacuum; M is the molar mass; K is the calorimeter constant; ΔE is the thermocouple potential difference corresponding to the temperature imbalance between cell and calorimeter thermostat at the time τ; τ_2 is the experiment duration; T is the temperature of the calorimeter

N	m/g	T/K	τ_2/s	$K\cdot\Delta H$/mV·s	Type of cell	ΔH/J	$\Delta^g_{cr,l} H^\circ_m$/kJ·mol^{-1}
1	0.07461	319.4	10175	7728.9	B	39.948	97.61
2	0.03972	319.4	7945	4158.2	B	21.492	98.64
3	0.04081	319.5	7230	4285.5	B	22.149	98.94
4	0.05064	319.3	8445	5152.4	A	27.427	98.74
5	0.04360	319.4	7055	4444.9	A	23.661	98.93
6	0.05195	319.6	7840	5273.9	A	28.073	98.52
$\Delta^g_{cr} H^\circ_m(319.5\ \text{K})\rangle = (98.56 \pm 0.52)\ \text{kJ}\cdot\text{mol}^{-1}$							
1	0.06536	346.5	5915	5363.6	A′	28.934	80.71
2	0.06857	345.2	5165	5587.0	A′	30.140	80.13
3	0.06593	346.0	5580	5379.4	A′	29.020	80.24
4	0.06535	346.3	4985	5271.2	B′	28.922	80.68
5	0.05381	344.9	4225	4297.0	B′	23.576	79.87
6	0.07458	345.9	4800	5981.2	B′	32.817	80.22
$\Delta^g_l H^\circ_m(345.8\ \text{K})\rangle = (80.31 \pm 0.34)\ \text{kJ}\cdot\text{mol}^{-1}$							

The K values for cells A, B, A′, and B′ were: (187.86, 193.48, 185.37, and 182.26) mV·s: J^{-1}, respectively. Uncertainties of the enthalpies were estimated with allowances for the Student coefficient $t = 2.571$ for 95 per cent confidence interval.

TABLE 5. The experimental values of saturated vapour pressure p for trans-2-cyclohexylcyclohexanol. Δm and t are the decrease in specimen mass and the duration of each experiment, respectively

$\frac{T}{\text{K}}$	$\frac{p}{\text{Pa}}$	$\frac{10^6 \cdot \Delta m}{\text{Kg}}$	$\frac{t}{\text{s}}$
	Crystal		
293.27	0.091	7.46	47334
298.16	0.175	8.73	28854
302.91	0.316	7.81	14454
308.40	0.639	12.75	11754
313.19	1.12	13.65	7264
318.44	2.07	25.09	7269
322.45	3.28	19.90	3654
324.87	4.28	17.36	2454
	Liquid		
328.29	6.58	8.09	9354
333.21	10.7	10.12	7254
338.18	16.3	11.53	5454
343.61	26.3	14.38	4254
348.39	39.4	16.85	3354
353.35	59.7	18.54	2454
358.23	86.1	27.45	2534
363.87	130	29.97	1854

It should be noted that the values of fusion entropy for cyclohexylcyclohexane derivatives are very different, and lie within the bounds of 24.45 $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ and 65.02 $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. A considerably greater constancy is observed for Σ (the sum of the entropies of all the phase transitions between low-temperature crystal and liquid). The lower value of the above-mentioned sum for trans-2-cyclohexylcyclohexanol is a characteristic of cyclic alcohols. It is confirmed by the values of Σ for cyclohexane and its derivatives, given in table 7. Probably, the transition from "rigid"

TABLE 6. Experimental determination of the standard massic energy of combustion $\Delta_c u_m^\circ$ of crystalline trans-2-cyclohexylcyclohexanol at $T = 298.15$ K, where m is the mass of the substance; δ is the correction for the heat exchange between the calorimeter vessel and surroundings; K is the cooling constant of the calorimeter; ΔT is the corrected temperature rise; q_i is the correction for ignition; $q(\text{HNO}_3)$ is the correction for nitric acid formation; Σq is the sum of the Washburn corrections

N	$\frac{m}{\text{g}}$	$-\frac{\delta}{\text{K}}$	$\frac{K \cdot 10^3}{\text{A}^{-1}}$	$\frac{\Delta T}{\text{K}}$	$\frac{q_i}{\text{J}}$	$\frac{q(\text{HNO}_3)}{\text{J}}$	$\frac{\Sigma q}{\text{J}}$	$\frac{-\Delta_c u_m^\circ}{\text{J} \cdot \text{g}^{-1}}$
1	0.42601	0.048	1.05	1.1543	2.0	7.2	5.4	40441.9
2	0.42399	0.056	1.07	1.1483	2.0	6.6	5.3	40466.4
3	0.43069	0.050	1.06	1.1673	2.0	7.3	5.4	40452.9
4	0.46400	0.034	1.11	1.1673	2.0	8.1	6.0	40468.6
5	0.41427	0.040	1.08	1.1227	2.0	7.5	5.2	40449.7
6	0.45487	0.037	1.09	1.2331	2.0	8.7	5.8	40460.6
7	0.56027	0.023	1.07	1.5175	2.0	13.7	7.5	40461.0
8	0.46418	0.043	1.10	1.2572	2.0	11.2	6.0	40460.8
				40457.7 $\text{J} \cdot \text{g}^{-1}$				

The average square deviation of the average arithmetic value = 3.2 $\text{J} \cdot \text{g}^{-1}$.

TABLE 7. Thermodynamic properties of solid-to-solid transitions and fusion of cyclohexane and some of its derivatives ($R = 8.31451\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$). Σ is the sum of entropies of all phase transitions between low-temperature crystal and liquid

Compound	Property	Phase transitions				$\frac{\Sigma}{R}$	References
		crIV–crIII	crIII–crII	crII–crI	crI–liq		
cyclohexylcyclohexane	T/K	256.1	267.5	273.5	277.2		
	$\Delta H_\mathrm{m}/R$	185.2	89.0	851.5	815.4		4
	$\Delta S_\mathrm{m}/R$	0.72	0.33	3.11	2.94	7.11	
trans-2-cyclohexylcyclohexanol	T/K				325.8		
	$\Delta H_\mathrm{m}/R$				1746		this work
	$\Delta S_\mathrm{m}/R$				5.36	5.36	
2-cyclohexylcyclohexanone	T/K				277.0		
	$\Delta H_\mathrm{m}/R$				2165		18
	$\Delta S_\mathrm{m}/R$				7.82	7.82	
2-(1′-cyclohexenyl)cyclohexanone	T/K				278.8		
	$\Delta H_\mathrm{m}/R$				2076		18
	$\Delta S_\mathrm{m}/R$				7.45 [a]	7.45	
cyclohexane	T/K			186.09	279.694		
	$\Delta H_\mathrm{m}/R$			810.6	322.0		19
	$\Delta S_\mathrm{m}/R$			4.36	1.15	5.51	
cyclohexanol	T/K			265.50	299.05		
	$\Delta H_\mathrm{m}/R$			1062	214.4		5
	$\Delta S_\mathrm{m}/R$			4.00	0.72	4.72	
cyclohexanone	T/K			220.83	245.21		
	$\Delta H_\mathrm{m}/R$			1042	159.7		20
	$\Delta S_\mathrm{m}/R$			4.72	0.65	5.37	

[a] $\Delta_\mathrm{trs}S_\mathrm{m} + \Delta_\mathrm{fus}S_\mathrm{m}$.

crystal to liquid in cyclohexanol and in trans-2-cyclohexylcyclohexanol is accompanied by the formation of associated species in a liquid phase, leading to a significant reduction in entropy of liquid cyclic alcohols at a temperature near T_fus. An additive diminution of the liquid entropy for trans-2-cyclohexylcyclohexanol, in comparison with cyclohexanol, is probably caused by the restriction of internal rotation of the C_6H_{11}-tops in association, or by the formation of intramolecular H-bonds.

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