

THERMODYNAMIC STUDIES OF (*R*)-BINOL-MENTHYL DICARBONATES

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The (*R*)-BINOL-menthyl dicarbonates, one of the most important compounds in catalytic asymmetric synthesis, was synthesized by a convenient method. The molar heat capacities $C_{p,m}$ of the compound were measured over the temperature range from 80 to 378 K with a small sample automated adiabatic calorimeter. Thermodynamic functions $[H_T-H_{298.15}]$ and $[S_T-S_{298.15}]$ were derived in the above temperature range with a temperature interval of 5 K. The thermal stability of the substance was investigated by differential scanning calorimeter (DSC) and a thermogravimetric (TG) technique.

Keywords: adiabatic calorimeter, low-temperature heat capacity, (*R*)-BINOL-menthyl dicarbonates, thermal analysis

Introduction

The chemical name of the compound, (*R*)-BINOL-menthyl dicarbonates (Beilstein registry no. 7471390) is carbonic acid 2-isopropyl-5-methyl-cyclohexyl ester and the autname is carbonic acid 2-isopropyl-5-methyl-cyclohexyl ester. The molecular formula of (*R*)-BINOL-menthyl dicarbonates is $C_{42}H_{50}O_6$ (the molar mass: $650.85 \text{ g mol}^{-1}$). The structure of the compound is shown in Fig. 1.

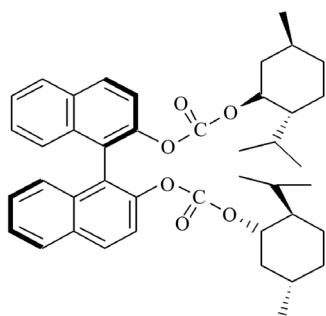


Fig. 1 Structure of (*R*)-BINOL-menthyl dicarbonates

Enantiopure 1,10-bi-2-naphthol (BINOL) is one of the most important C₂ symmetric chiral compounds [1]. It plays an important role in catalytic asymmetric synthesis [2–6]. It is widely used for the resolution of racemic compounds [7–9] and as a chiral source [10, 11]. Up to now several methods have successfully been developed for the resolution of BINOL and other diols, such as the classical crystallization of diastereomeric derivatives [12–23], enantioselective formation of inclusion crystals with chiral host molecules [24–32], and enzymatic hydrolysis of esters [33]. Re-

cently, Li *et al.* developed a convenient resolution method for BINOL with crude (–)-menthyl chloroformate in the presence of TBAB in aqueous NaOH/CH₂Cl₂ solution. The deprotection of the hydroxy group of the diastereomers can be smoothly performed at reflux in aqueous KOH/EtOH solution. (*R*)-BINOL menthyl dicarbonates is the intermediate for the resolution of BINOL. The *R*-(+)-BINOL can be resolved from (*R*)-BINOL-menthyl dicarbonates [34].

For the application of (*R*)-BINOL-menthyl dicarbonates, thermodynamic properties of this substance are urgently required. However, the thermodynamic properties of the compound have not been reported up to now. Heat capacities determinations of various compounds had attracted many researchers' attention [35–40]. In the present study, the heat capacities, which was one of the fundamental thermodynamic properties of substances, was measured by a precision automatic adiabatic calorimeter. The stability of the substance was investigated by a differential scanning calorimeter (DSC) and a thermogravimetric analyser (TG).

Experimental

Sample

The (*R*)-BINOL-menthyl dicarbonates used for the calorimetric study was prepared by using the procedures [41], which is shown in Fig. 2.

The reaction gave (*R*)-BINOL-menthyl dicarbonates 90% yield. The purity of the substance was determined to be higher than 99.5% by HPLC. The structure of the compound was determined [34]

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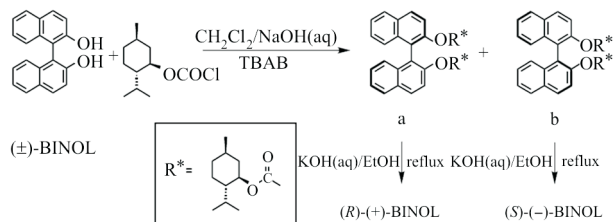


Fig. 2 Procedure of prepared (*R*)-BINOL-menthyl dicarbonates used for the calorimetric study

by infrared (IR model: Bruker TENSOR27), hydrogen-1 nuclear magnetic resonance (^1H NMR), carbon-13 nuclear magnetic resonance (^{13}C NMR) (model: Bruker DRX-400 spectrometer, 400 MHz), HRMS (model: Mariner-TOF 5303) and highly sensitive polarimeter (model: HORIBA SEPA-200). The results of IR analysis were as follows (KBr pellet, cm^{-1}): 2958, 2935, 1756, 1223, 1251, 962.

Methods

Adiabatic calorimetry

A precision automatic adiabatic calorimeter was used to measure the heat capacities of the compound over the temperature range between 78 and 360 K. The instrument was established in Thermochemistry Laboratory of Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

The structure and principle of the adiabatic calorimeter have been described in detail elsewhere [42–44]. The automatic adiabatic calorimeter mainly consisted of a sample cell made of gold-plated copper, a miniature platinum resistance thermometer (IPRT No. 2, produced by Shanghai Institute on Industrial Automatic Meters, 16 mm in length, 1.6 mm in diameter and a nominal resistance of 100 Ω), an electric heater, the inner and the outer adiabatic shields, two sets of six-junctions chromel-constantan thermopiles installed between the calorimetric cell and the inner shield and between the inner and the outer shields, respectively, and a high vacuum can [45–47].

The effective capacity of the sample cell was 6 cm^3 . Four gold-plated copper canes of 0.2 mm in thickness placed inside with an X-shape to promote heat distribution. A miniature platinum thermometer was inserted into a horizontal copper sheath soldered under the bottom. The thermometer was calibrated on the basis of ITS-90 by the Station of Low-temperature Metrology and Measurements, Academia Sinica. The resistance of the thermometer was measured by a 71/2 Digit Nano Volt/Micro Ohm Meter (Model 34420, Agilent, USA). The heater wire was bifilarly wound and fixed around outside the wall of the sample cell. After the sample was loaded, the cell was sealed and evacuated. A small amount of helium gas (0.1 MPa) was introduced into the cell so as to enhance the heat transfer.

The temperature difference between sample cell and inner shield, and between inner and outer shield were monitored by two sets of thermocouples. Both shields were heated under the control of Temperature Controller (Model 340, Lakeshore, USA) and kept at the same temperatures as that of the sample cell. The electrical energy introduced into the sample cell was automatically picked up by a Data Acquisition/Switch Unit (Model 34970A, Agilent, USA). The equilibrium temperature of the cell after the energy input was measured by the 71/2 digit Nano Volt/Micro Ohm Meter. The energy and the temperature data were processed on line by a computer.

The heat capacity measurements were conducted by the standard procedure of intermittently heating the sample and alternately measuring the temperature. The heating rate was (0.1 to 0.4) K min^{-1} ; the temperature increments of the experimental points were between 1 and 4 K; the heating duration was 10 min and the temperature drift rates of the sample cell, which was measured in an equilibrium period, were kept within (10^{-3} to 10^{-4}) K min^{-1} .

Prior to the heat capacity measurement of the sample, the molar heat capacities of $\alpha\text{-Al}_2\text{O}_3$, the standard reference material, were measured from 78 to 400 K to verify the reliability of the adiabatic calorimeter. The results showed that the deviation of our calibration data from those of NIST [48] was within $\pm 0.3\%$.

In the present paper, the mass of (*R*)-BINOL dicarbonates used for the heat capacity measurement was 1.1802 g, which was equivalent to 0.0018 mol on the base of its molar mass $M=650.85 \text{ g mol}^{-1}$.

DSC and TG technique

Thermal analysis of (*R*)-BINOL-menthyl dicarbonates was performed using a differential scanning calorimeter (DSC-141, Setaram, France) at the heating rate of 10 K min^{-1} under pure nitrogen with a flowing rate of 50 mL min^{-1} . The mass of the sample used in the experiment was (5.00 \pm 0.01) mg.

A thermogravimetric analyzer (model: DT-20B, Shimadzu, Japan) was used to carry out the TG measurement of the compound at the heating rate of 10 K min^{-1} under pure nitrogen with a flow rate of 30 mL min^{-1} . The mass of the sample used in the experiment was (8.10 \pm 0.01) mg.

Results and discussion

Molar heat capacity and thermodynamic functions

The experimental molar heat capacities, $C_{p,m}$, and temperature T from 80 to 378 K of (*R*)-BINOL-menthyl dicarbonates are listed in Table 1 and plotted in Fig. 3.

Table 1 Heat capacities of (*R*)-BINOL-menthyl dicarbonate

Temperature/K	$C_p/J\ K^{-1}\ mol^{-1}$	Temperature/K	$C_p/J\ K^{-1}\ mol^{-1}$	Temperature/K	$C_p/J\ K^{-1}\ mol^{-1}$
81.708	129.00	176.13	548.33	277.16	1072.9
83.708	137.50	178.03	558.35	279.84	1082.4
85.708	146.00	180.02	566.78	282.44	1097.7
87.716	161.34	181.83	574.17	285.04	1106.2
89.706	169.77	183.82	585.77	287.63	1118.8
91.696	178.21	185.73	594.20	290.23	1135.7
93.685	193.50	187.63	601.58	292.73	1143.4
95.675	202.46	189.53	608.96	295.16	1156.4
97.751	197.19	191.44	619.51	297.58	1167.8
99.740	212.48	193.34	626.89	298.79	1171.5
101.73	214.06	195.16	634.80	301.30	1184.7
103.72	229.35	196.97	645.34	303.81	1190.0
105.71	237.79	198.88	654.31	306.23	1207.9
107.70	246.22	200.78	665.38	308.74	1220.6
109.69	247.80	202.68	672.23	311.16	1234.3
111.68	256.77	204.50	680.14	313.58	1248.5
113.67	265.20	206.28	681.90	316.00	1265.9
115.75	273.64	208.13	704.92	318.34	1280.7
117.73	282.07	209.95	712.30	320.70	1299.5
119.72	290.51	211.77	720.21	323.13	1313.3
121.71	305.80	213.58	727.07	325.50	1325.7
123.70	314.24	215.31	736.56	327.83	1339.8
126.21	313.18	217.22	746.57	330.20	1351.3
128.55	330.05	219.03	753.95	332.54	1362.9
131.06	333.74	220.76	766.61	334.97	1376.8
133.39	350.09	222.58	776.10	337.40	1390.4
135.73	361.16	224.39	783.48	339.77	1404.7
138.06	370.65	226.13	795.61	342.11	1414.8
140.40	381.20	228.55	806.15	344.47	1426.8
142.65	391.21	231.49	819.86	346.75	1441.2
144.98	401.23	234.43	846.75	349.08	1452.3
147.23	414.94	237.37	864.15	351.45	1465.3
149.39	417.58	240.23	878.91	353.79	1478.7
151.56	428.65	243.08	896.31	356.15	1492.3
153.72	432.34	246.11	910.02	358.42	1501.5
155.97	448.68	248.96	929.00	360.69	1513.5
157.96	458.17	251.90	939.54	363.03	1524.5
160.04	468.19	254.59	951.14	365.30	1536.7
162.11	478.74	257.44	965.91	367.57	1548.9
164.19	489.81	260.29	981.20	369.84	1559.7
166.26	496.66	263.06	995.43	372.05	1571.9
168.17	504.57	265.83	1015.5	374.32	1581.1
170.16	514.06	268.60	1032.3	376.49	1591.6
172.15	528.82	271.54	1042.4	378.60	1603.4
174.05	540.42	274.57	1058.2		

Table 2 $C_{p,m}$, enthalpy and entropy of (*R*)-BINOL-menthyl dicarbonate

Temperature/K	$C_{p,m}/\text{J mol}^{-1} \text{K}^{-1}$	$[H_T - H_{298.15}]/\text{kJ mol}^{-1}$	$[S_T - S_{298.15}]/\text{J mol}^{-1} \text{K}^{-1}$
85	152.19	-135.55	-68.871
90	171.08	-134.74	-62.837
95	190.34	-133.84	-57.056
100	209.95	-132.84	-51.524
105	229.90	-131.74	-46.24
110	250.19	-130.54	-41.199
115	270.81	-129.23	-36.399
120	291.75	-127.83	-31.838
125	313.00	-126.32	-27.511
130	334.55	-124.70	-23.417
135	356.40	-122.97	-19.551
140	378.53	-121.13	-15.912
145	400.94	-119.18	-12.495
150	423.61	-117.12	-9.299
155	446.55	-114.95	-6.320
160	469.74	-112.66	-3.555
165	493.18	-110.25	-1.001
170	516.85	-107.73	1.345
175	540.75	-105.08	3.486
180	564.86	-102.32	5.424
185	589.19	-99.433	7.164
190	613.72	-96.425	8.707
195	638.44	-93.295	10.058
200	663.35	-90.041	11.219
205	688.43	-86.661	12.192
210	713.68	-83.156	12.982
215	739.09	-79.524	13.591
220	764.65	-75.765	14.022
225	790.36	-71.878	14.279
230	816.20	-67.861	14.364
235	842.17	-63.715	14.280
240	868.25	-59.439	14.031
245	894.45	-55.033	13.619
250	920.74	-50.495	13.048
255	947.13	-45.825	12.320
260	973.60	-41.023	11.439
265	1000.1	-36.089	10.408
270	1026.8	-31.022	9.230
275	1053.4	-25.821	7.908
280	1080.2	-20.487	6.445
285	1106.9	-15.020	4.845
290	1133.7	-9.418	3.109
295	1160.6	-3.682	1.242
298.15	1177.5	0.000	0.000
300	1187.4	2.187	-0.753
305	1214.3	8.192	-2.874
310	1241.1	14.330	-5.117
315	1267.9	20.602	-7.479
320	1294.8	27.009	-9.957
325	1321.6	33.550	-12.547

Table 2 Continued

Temperature/K	$C_{p,m}/\text{J mol}^{-1} \text{K}^{-1}$	$[H_T - H_{298.15}]/\text{kJ mol}^{-1}$	$[S_T - S_{298.15}]/\text{J mol}^{-1} \text{K}^{-1}$
330	1348.4	40.225	-15.248
335	1375.1	47.033	-18.055
340	1401.8	53.975	-20.965
345	1428.4	61.050	-23.976
350	1454.9	68.259	-27.084
355	1481.4	75.599	-30.285
360	1507.8	83.072	-33.578
365	1534.1	90.677	-36.958
370	1560.3	98.413	-40.422
375	1586.4	106.28	-43.968

The curve indicates that the structure of the sample is stable: no phase change occurred in the solid phase from 80 to 378 K.

One polynomial equation was obtained by the least-squares fitting by using the experimental molar heat capacities ($C_{p,m}$) and the experimental temperatures (T).

From 82 to 378 K

$$C_{p,m} [\text{J K mol}^{-1}] = 816.2 + 766.79x + 55.313x^2 - 36.305x^3 \quad (1)$$

where x is the reduced temperature, $x = (T [\text{K}] - 230)/148$, T is the experimental temperature, 205 is obtained from polynomial $(T_{\max} + T_{\min})/2$, 148 is obtained from polynomial $(T_{\max} - T_{\min})/2$, T_{\max} is the upper limit (330 K) of the above temperature region, T_{\min} is the lower limit (80 K) of the above temperature region. Correlation coefficient R^2 of least square fitting is 0.9998. The relative deviations of the smoothed heat capacities from those obtained from the experiment were within $\pm 0.3\%$.

Thermodynamic functions $[H_T - H_{298.15}]$ and $[S_T - S_{298.15}]$ of the compound were calculated in the temperature range from 80 to 378 K with a temperature interval of 5 K in terms of the polynomials of heat capacity and the thermodynamic relationship and listed in Table 2.

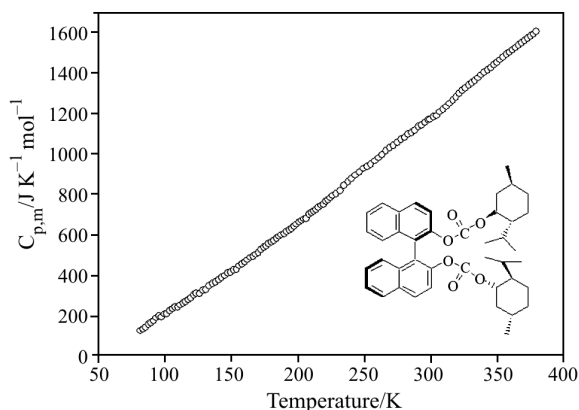


Fig. 3 Experimental molar heat capacity plotted vs. temperature for the sample (*R*)-BINOL-menthyl dicarbonate

DSC and TG analysis

The DSC curve (Fig. 4) indicated that the (*R*)-BINOL-menthyl dicarbonates was stable before 463.7 K. The curve had a heat flowing peak from 463.7 to 470.7 K. Based on the properties of the compound and the shape of the heat flow peak, this process was deduced to be melting instead of other phase behavior and the melting temperature was determined to be 469 K. The second peak of the curve was due to boiling other than decomposing based on the TG curve and the collected product.

The TG curve (Fig. 5) showed that the sample began to loss mass from about 488 K and ended at about 567 K. It lost mass at the fastest rate at 538 K. Combined with the DSC curve, the conclusion can be drawn that the compound melted from 463 to 471 K. The product collected during the heating until 567 K proved to be the same substance as the original sample judging from its color, melting point and morphology. Thus we can deduce that (*R*)-BINOL-menthyl dicarbonates evaporated other than decomposed following melting. It boiled at about 553 K and completely changed into vapor in the range of 553 to 567 K.

Based on the fact that it melted at 463.7 K, boiled at about 553 K and had no decomposing after 553 K. It can be concluded that the chemical bond be-

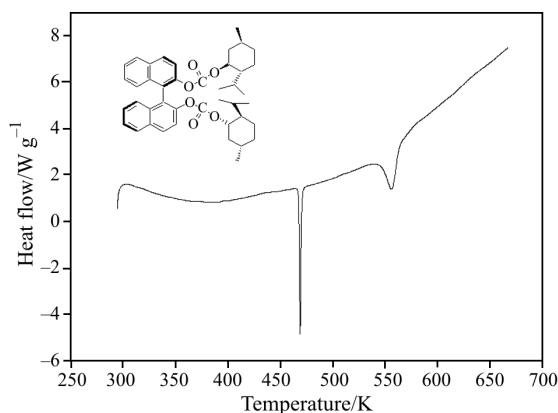


Fig. 4 DSC curve of (*R*)-BINOL-menthyl dicarbonate

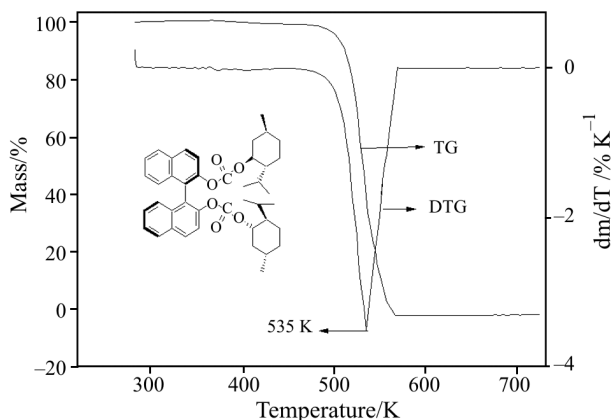


Fig. 5 TG-DTG curve of (*R*)-BINOL-menthyl dicarbonate

tween the two benzenes of BINOL did not rotate and the structure of the compound was stable in the studied temperature range.

Acknowledgements

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