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THERMODYNAMIC STUDIES OF *p*-POLYPHENYLS: HEAT CAPACITY OF *p*,*p*′-BIPHENOL *

KAZUYA SAITO [1], TOORU ATAKE [2] and HIDEAKI CHIHARA [1]

[1] *Department of Chemistry and Chemical Thermodynamics Laboratory, Faculty of Science, Osaka University, Toyonaka, Osaka 560 (Japan)*
[2] *Research Laboratory of Engineering Materials, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 227 (Japan)*

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ABSTRACT

The heat capacity of *p*,*p*′-biphenol was measured by adiabatic calorimetry between 3 and 315 K. No anomaly in heat capacity was observed. The property is compared with that of 4,4′-difluorobiphenyl and qualitative deductions are made as to the potential hindering molecular twisting in the crystal. A slow process was observed on the approach to thermal equilibrium below 10 K. Thermodynamic functions derived from the measured heat capacities are tabulated.

INTRODUCTION

The crystals of the first three members of *p*-polyphenylene undergo phase transitions associated with a molecular conformation change [1,2], which is closely related to the subtle balance between intra- and intermolecular interactions. The potential energy for the twisting motion in the isolated state is considered as a resultant of two opposing contributions, π-conjugation and steric repulsion. In the case of biphenyl, the stable conformation is the twisted form in the isolated state. Experimental results, indeed, have revealed that the biphenyl molecule is twisted by about $2\pi/9$ rad in the gaseous state [3,4] and by about $\pi/6$ rad in the liquid state [4–8]. On the other hand, the molecule is planar in the crystalline state at room temperature [9–16]. When the temperature is lowered, the molecule resumes the twisted conformation [17–19] below a phase transition at 40.4 K [20,21]. Similar phase transitions (twist transitions) have also been found in *p*-terphenyl at 193.5 K [22–26] and in *p*-quaterphenyl at 233.0 K [26–28].

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However, their behaviour at the twist transition is very different. Biphenyl shows a displacive-type phase transition associated with soft-modes [29–32], while *p*-terphenyl and *p*-quaterphenyl crystals undergo an order–disorder type of transition [25,33] at much higher temperatures compared with biphenyl. Furthermore, the heat capacity anomalies of biphenyl [20,21] and *p*-quaterphenyl [26] are very broad but that of *p*-terphenyl is sharper [34,35]. In a previous paper [26], we showed that it is possible to understand the behaviours of the three compounds qualitatively by taking into account molecular symmetry and potential curves for the twisting modes in the isolated state.

If one introduces any substituents into the biphenyl molecule, the intramolecular potential curve for the twisting motion will be affected and the twist transition, if present, would reflect its contribution. Hence, studies on substituted biphenyls will help to substantiate our understanding of the twist transitions experimentally. An inspection of available data about crystal structures of symmetrically substituted biphenyls [36] revealed that there might be a twist transition in the crystals of two of the compounds, 4,4′-difluorobiphenyl and *p*,*p*′-biphenol (4,4′-dihydroxybiphenyl), on cooling because their crystal structures were similar to that of biphenyl at room temperature [37–40]. The search for the twist transition in crystalline 4,4′-difluorobiphenyl was carried out by the present authors using adiabatic calorimetry [36]. No thermal anomaly, however, was observed, and it was deduced that the planar conformation of the 4,4′-difluorobiphenyl molecule in the crystalline state was not the result of a statistical average but was a fixed one. The study described in this paper is an extension of our thermodynamic investigations on twist transitions in crystalline *p*-polyphenylenes [20,21,26,36,41,42].

The molecular structure of *p*,*p*′-biphenol is planar in the crystalline state at room temperature [38–40]. The crystal consists of molecular layers parallel to the $(20\bar{1})$ plane, in which the molecules are connected to each other by hydrogen-bonds. The structure has been analysed using X-ray diffraction, but the hydrogen atoms have not been located. The reported space group $P2_1/a$ is compatible with a paraelectric or antiferroelectric order of hydrogen-bonds but incompatible with a ferroelectric order.

No reports have been published on the molecular structure of *p*,*p*′-biphenol in its isolated state. Substitution with hydroxyl groups probably lowers the potential barrier of the planar conformation owing to greater π-conjugation compared with biphenyl. Taking into account the barrier height in the biphenyl molecule of about 10 kJ mol^{-1} [7,8], however, the molecule of *p*,*p*′-biphenol will be twisted in the gaseous and liquid states. Therefore, the twist transition in the crystal might take place at a lower temperature. This paper describes the results of precision heat capacity measurements and the thermodynamic properties of crystalline *p*,*p*′-biphenol.

EXPERIMENTAL

A sample of *p*,*p*′-biphenol was purchased from Tokyo Kasei Kogyo Co., Ltd., and purified by fractional sublimation at about 450 K in vacuum. The mass percentages of C and H were 77.41 (calcd. 77.40) and 5.41 (5.41), respectively, for the purified sample as determined by chemical analysis. The powdered sample was loaded into a gold-plated copper calorimeter vessel without any further treatment, as Wallwork and Powell [38] reported that the specimen prepared by sublimation was the same as a specimen obtained by recrystallization from an alcohol–water solution. A small amount of helium gas (7 kPa at room temperature) was also put into the vessel to aid thermal equilibration within the vessel. The amount of sample used for heat capacity measurements was 13.5333 g (0.0726776 mol) after buoyancy correction. The sample contributed to the total heat capacity including the vessel by 52% at 10 K, 36% at 100 K, 43% at 200 K, and 51% at 300 K. The contribution of the helium gas in the vessel was smaller than the experimental error.

The working thermometers mounted on the vessel were a platinum resistance thermometer (model 8164, Leeds & Northrup Co.) above 13.81 K and a germanium resistance thermometer (model CR-1000, CryoCal Inc.) below 14 K. Their temperature scales are based on IPTS-68, helium gas thermometry, and the 1958 ^{4}He vapour-pressure scale [43,44]. The apparatus and the operation of the adiabatic calorimeter are described elsewhere [45].

RESULTS AND DISCUSSION

Measurements of the heat capacities were performed between 3 and 315 K. The primary data are shown in Fig. 1 and tabulated in Table 1 in chronological order. The temperature increment of each measurement may be deduced from the adjacent mean temperatures. After the energy input was over, thermal equilibrium within the calorimeter vessel was attained within 1 min between 10 and 30 K, 7 min at 50 K, 25 min at 100 K, and 15 min above 200 K. However, below 10 K the time needed for equilibration was abnormally long (see Fig. 4).

Some thermodynamic functions were obtained through manipulation of the measured heat capacity values and are given at rounded temperatures in Table 2, where the small contributions below 4 K were estimated by smooth extrapolation of the heat capacity curve from the higher temperature side.

Figure 1 shows no recognizable anomaly. The Debye characteristic temperatures corresponding to the measured heat capacities in the low temperature region are plotted in Fig. 2, because a small anomaly can, in general, be made more prominent by such a graph. It was assumed that there were 9 degrees of freedom per molecule when we converted the heat capacities into

TABLE 1

Measured molar heat capacities of p,p'-biphenol

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})
Series 1		21.865	12.699	23.077	14.116	194.561	146.98	309.279	232.52
90.126	73.610	23.219	14.285	24.174	15.421	196.730	148.50	311.517	234.07
91.474	74.643	24.608	15.929	25.279	16.726	198.883	150.17	313.762	235.76
93.191	75.806	*Series 10*		26.392	18.049	201.023	151.79	315.995	237.53
94.987	77.011	25.748	17.279	27.499	19.355	203.166	153.40	*Series 15*	
96.875	78.266	27.294	19.106	28.596	20.652	205.301	155.07	14.332	4.979
98.832	79.567	29.655	21.921	29.678	21.937	207.444	156.72	15.126	5.674
100.826	80.878	32.090	24.810	30.738	23.207	209.596	158.24	15.886	6.358
Series 2		33.765	26.748	*Series 12*		211.746	159.78	16.606	7.030
3.641	0.038	35.432	28.647	101.657	81.274	213.914	161.34	17.315	7.730
4.001	0.054	37.106	30.538	103.711	82.605	216.077	163.05	18.039	8.523
4.412	0.071	38.753	32.321	105.805	84.117	218.222	164.76	18.782	9.274
4.786	0.095	40.372	34.062	107.944	85.619	220.351	166.35	19.531	10.093
5.219	0.146	41.967	35.708	110.089	87.109	222.470	167.84	20.272	10.914
5.768	0.258	43.558	37.394	112.197	88.588	224.600	169.50	21.007	11.721
Series 3		45.107	38.901	114.293	90.000	226.735	171.09	21.739	12.554
7.249	0.584	46.622	40.358	116.384	91.422	228.858	172.76	22.479	13.413
8.077	0.890	48.151	41.877	118.464	92.885	230.988	174.40	23.232	14.293
Series 4		49.664	43.326	120.565	94.373	233.125	176.24	23.976	15.219
3.931	0.045	51.161	44.675	122.666	95.809	235.246	177.47	24.710	16.056
4.290	0.057	52.637	45.994	124.752	97.236	237.377	179.06	25.442	16.933
4.656	0.102	54.121	47.310	126.833	98.692	239.519	180.66	26.171	17.784
5.156	0.164	55.667	48.622	128.911	100.12	241.647	182.10	26.897	18.656
5.762	0.263	57.252	49.996	131.006	101.64	243.783	183.81	27.626	19.506
6.451	0.409	58.884	51.348	133.091	103.13	245.937	185.43	28.354	20.372
7.255	0.601	60.564	52.698	135.172	104.64	248.074	187.04	29.075	21.227
8.081	0.868	62.248	53.990	137.272	106.22	250.188	188.58	29.789	22.062

Series 5		63.913	55.315	139.392	107.73	252.314	190.03	*Series 16*	
4.104	0.052	65.581	56.600	141.521	109.27	254.450	191.72	14.258	4.919
4.519	0.101	67.265	57.847	143.651	110.76	256.591	193.38	14.885	5.469
Series 6		68.969	59.125	145.803	112.37	258.738	195.06	15.504	6.005
5.241	0.130	70.677	60.372	147.960	113.89	260.874	196.70	16.097	6.547
5.693	0.226	72.403	61.638	150.119	115.40	262.946	198.29	16.671	7.084
6.248	0.352	74.156	62.871	152.269	117.02	265.025	199.89	17.243	7.630
6.943	0.519	75.921	64.118	154.402	118.32	267.168	201.48	17.832	8.251
7.716	0.748	77.702	65.367	156.515	119.92	269.299	202.93	18.424	8.874
8.514	1.041	79.486	66.600	158.597	121.47	*Series 14*		19.006	9.493
9.332	1.409	81.261	67.788	160.690	122.96	271.476	204.36	19.580	10.120
10.180	1.896	83.026	69.025	162.817	124.50	273.634	206.13	20.145	10.742
Series 7		84.785	70.212	164.944	126.06	275.818	207.51	20.703	11.378
10.659	2.179	86.540	71.371	167.051	127.58	278.034	209.67	21.253	11.967
12.112	3.185	88.292	72.575	169.168	129.08	280.258	211.28	21.797	12.617
13.359	4.145	90.048	73.780	171.285	130.52	282.488	212.94	22.337	13.249
Series 8		*Series 11*		173.384	132.00	284.727	213.98	22.873	13.880
14.987	5.562	12.733	3.576	175.496	133.44	286.957	216.53	23.412	14.522
16.827	7.253	13.698	4.385	177.613	135.06	289.194	218.42	23.955	15.175
18.453	8.935	14.594	5.169	*Series 13*		291.440	219.77	24.504	15.815
20.018	10.631	15.497	5.994	179.581	135.56	293.677	221.00	25.059	16.475
Series 9		16.456	6.863	181.681	137.21	295.904	222.64	25.622	17.138
14.455	5.083	17.469	7.877	183.808	139.03	298.140	224.33	26.177	17.803
16.120	6.578	18.559	9.031	185.955	140.55	300.383	225.97	26.727	18.449
17.721	8.151	19.710	10.279	188.103	142.16	302.616	227.59	27.292	19.131
19.163	9.693	20.858	11.553	190.251	143.75	304.832	229.23	27.866	19.797
20.527	11.187	21.976	12.826	192.401	145.30	307.051	230.89	28.447	20.485
								29.036	21.209
								29.628	21.898
								30.208	22.576

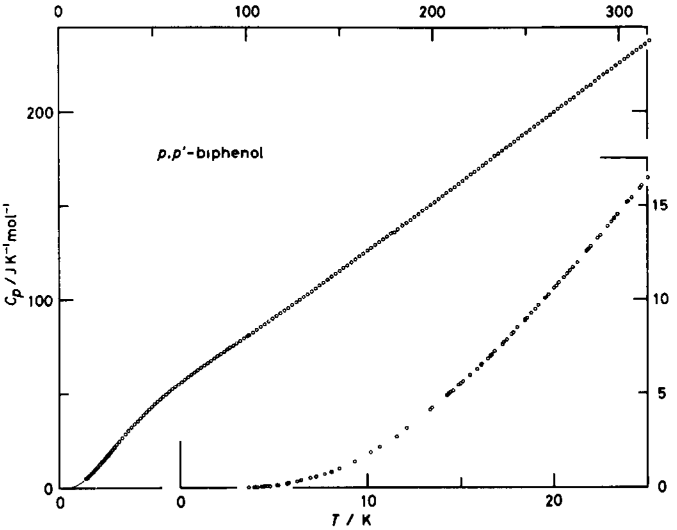

Fig. 1. Measured molar heat capacities of *p*,*p*′-biphenol.

Debye temperatures. Since no anomaly is recognized in Fig. 2 either, we now conclude that there is no phase transition in crystalline *p*,*p*′-biphenol between 4 and 315 K. If there were any, its entropy of transition must be smaller than about 0.005 J K^{-1} mol^{-1}, the value ascribed to the precision of measurements.

A similar situation has also been found in 4,4′-difluorobiphenyl [36], which may be rationalized from the following reasoning. First, the intramolecular potential of *p*,*p*′-biphenol is expected to be similar to that of 4,4′-difluorobiphenyl. In order to confirm this, the potential curves were estimated by using the simple Hückel method for the contribution from the π-delocalization and the atom–atom potential method for the contribution from steric repulsion. The resonance integrals of C–C (hexagon bond), C–F and C–O were β, 0.7β and 0.8β, respectively. The resonance integral of the central C–C depended on the twisting angle θ as $\beta \cos \theta$ [46]. The Coulomb integrals of C, F and O were α, $\alpha + 3\beta$ and $\alpha + 2\beta$, respectively. By comparing the result of the Hückel method with those of experiments on benzene, the value of β was derived to be -89 kJ mol^{-1} [47]. The bond lengths were 0.140 nm (hexagon C–C bond), 0.150 nm (central C–C bond), and 0.110 nm (C–H bond). The parameters of atom–atom potentials of Buckingham type (6-exp type) were taken from the literature [48]. The atom–atom potential was summed over all atom pairs within a molecule. The calculated potential curves are shown in Fig. 3. The barrier height and the location of the minimum for biphenyl and 4,4′-difluorobiphenyl are in reasonable agreement with the experimental results [3,4,7,8,49]. As is clearly seen in Fig. 3, the intramolecular potential curves of 4,4′-difluorobiphenyl

TABLE 2

Molar thermodynamic functions of p,p'-biphenol

T (K)	$C_{p,\mathrm{m}}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$\{H_\mathrm{m}(T)-H_\mathrm{m}(0)\}/T$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$S_\mathrm{m}(T)-S_\mathrm{m}(0)$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$-\{G_\mathrm{m}(T)-H_\mathrm{m}(0)\}/T$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)
5	0.134	0.026	0.032	0.006
10	1.78	0.403	0.507	0.104
20	10.60	3.09	4.15	1.07
30	22.32	7.53	10.65	3.12
40	33.66	12.68	18.65	5.98
50	43.62	17.89	27.26	9.37
60	52.24	22.92	35.99	13.08
70	59.87	27.66	44.63	16.97
80	66.93	32.13	53.09	20.96
90	73.70	36.38	61.36	24.99
100	80.31	40.44	69.47	29.03
110	87.03	44.36	77.44	33.07
120	93.95	48.21	85.31	37.10
130	100.93	51.99	93.10	41.11
140	108.13	55.75	100.85	45.10
150	115.29	59.48	108.55	49.07
160	122.37	63.19	116.22	53.03
170	129.45	66.88	123.85	56.97
180	136.32	70.54	131.44	60.90
190	143.56	74.19	139.01	64.81
200	151.03	77.85	146.56	68.71
210	158.53	81.51	154.11	72.60
220	166.03	85.19	161.66	76.47
230	173.61	88.87	169.20	80.34
240	181.02	92.55	176.75	84.20
250	188.44	96.24	184.29	88.05
260	196.02	99.93	191.83	91.90
270	203.46	103.63	199.37	95.74
280	211.09	107.33	206.90	99.58
290	218.33	111.03	214.44	103.41
300	225.68	114.73	221.96	107.23
310	233.02	118.43	229.40	111.05
298.15	224.31	114.05	220.57	106.52

and p,p'-biphenol for the twisting motion show strong similarity in spite of the different substituents. Second, the intermolecular interactions that determine a planar conformation in a crystal are insensitive to atoms at the 4 and 4′ positions, because the interatomic distance between the 4(4′) position of one molecule and the atom of the other molecule barely changes upon twisting of the latter molecule. Thus, intermolecular interactions are similar in the two compounds. Therefore, it is concluded that the potential hindering of the twisting has a single minimum at the planar conformation in

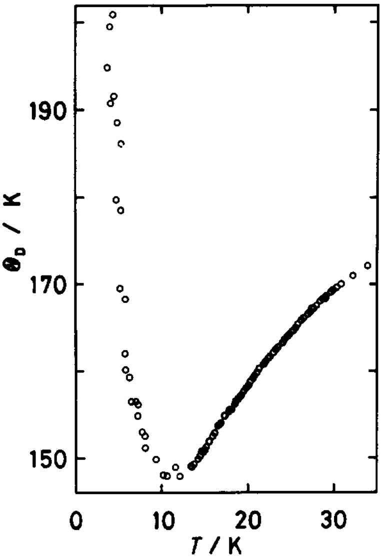

Fig. 2. Debye characteristic temperatures corresponding to the measured heat capacities of p,p'-biphenol assuming 9 degrees of freedom per molecule.

crystalline p,p'-biphenol as in the case of 4,4'-difluorobiphenyl and that the planar conformation is not the result of a statistical average but a fixed one.

Slow thermal relaxation was encountered below 10 K. The approach of

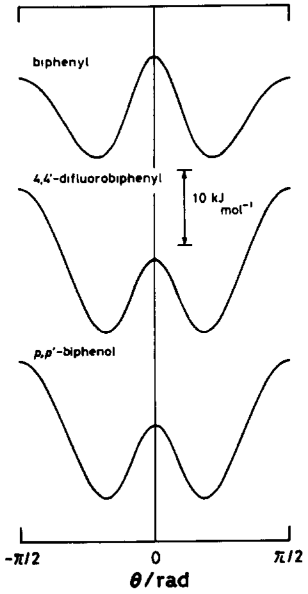

Fig. 3. Calculated intramolecular potential curves for biphenyl, 4,4'-difluorobiphenyl [42] and p,p'-biphenol based on the simple Hückel and the atom–atom potential methods.

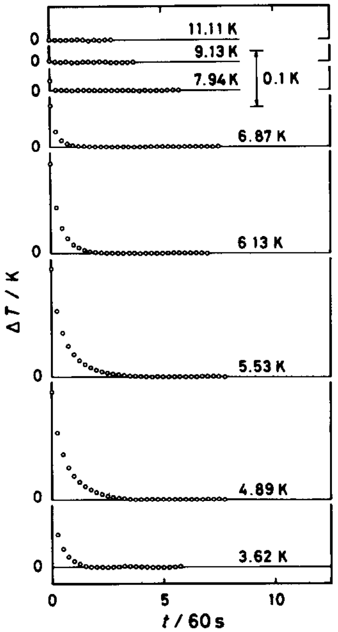

Fig. 4. Temperature drift under adiabatic conditions after each energy input in p,p'-biphenol.

the thermometer reading to a steady drift rate is shown in Fig. 4. Since thermal equilibrium is usually attained within a few tens of seconds in this temperature region, it seems that there is some slow mechanism of heat flow in the crystal. It can be considered that the crystal consists of sub-systems, such as the lattice and the other system(s). A few minutes are needed for heat flow between the lattice and the other sub-system(s) or for thermal equilibration within a sub-system. It is interesting that the Debye temperature increases rapidly in this temperature region as temperature decreases. Such a steep increase is due to large differences from the standard Debye-type densities of states in the low frequency end of the lattice vibration. This may be related to the properties of hydrogen-bond chains; a similar effect of slow equilibrium was also reported in p-phenylphenol [50]. Spectroscopic investigations, such as IR and NMR, will be of interest in order to clarify the phenomenon.

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