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Heat capacity and thermodynamic functions of crystalline 4,4‴-difluoro-*p*-quaterphenyl

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Abstract

The heat capacity of crystalline 4,4‴-difluoro-*p*-quaterphenyl was measured between 8 and 303 K by adiabatic calorimetry. A broad heat-capacity anomaly was found at 200.5 ± 0.5 K and attributed to a phase transition associated with molecular twisting. Some thermodynamic properties including those concerning the phase transition are reported.

Keywords: *p*-polyphenyl; Heat capacity; Structural phase transition

1. Introduction

A molecule of *p*-quaterphenyl consists of four benzene rings connected linearly with each other and has twisting degrees of freedom around the C–C bonds. At room temperature, the molecules have a seemingly planar conformation and the room-temperature phase is disordered in nature [1]. On cooling, the disordered phase changes to the ordered phase at 233.0 K [2] and the four benzene rings are alternately twisted. A similar phase transition is also observed in crystalline *p*-terphenyl which consists of three benzene rings (at 193.5 K [3]). The transitions of *p*-quaterphenyl and *p*-terphenyl are of order–disorder type [4]. Crystals of biphenyl which have two benzene rings, are also isostructural with *p*-quaterphenyl and *p*-terphenyl at room temperature [4]. The molecules in the crystal have a planar conformation at room temperature and are twisted below 40.4 K [5]. The nature of the phase transition is,

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however, different from that of the phase transitions of *p*-quaterphenyl and *p*-terphenyl, i.e. the transition of biphenyl is of displacive type associated with soft modes [4, 6]. Thus, the crystalline *p*-polyphenyls differ in the property of the phase transition to one another as briefly summarized above.

In systems where phase transitions are mainly concerned with the intramolecular degree(s) of freedom, as in crystalline *p*-polyphenyl, the properties of the phase transition are determined by both intramolecular potential and intermolecular interaction. If the two factors are competing, a delicate balance between the two determines the property of the phase transition. In the present case of *p*-polyphenyls, the intramolecular potential prefers the twisted conformation, while the intermolecular interaction favors the planar conformation for dense molecular packing. It has been reported that the transition temperatures of the three compounds decrease and the phase transitions of *p*-terphenyl and *p*-quaterphenyl seem to become of displacive type, if the balance is shifted by some pressure [7–13]. Pressure mainly acts on the intermolecular interaction and shifts the balance in the direction to make the molecular conformation planar.

The change in the intramolecular potential should also shift the balance. The introduction of substituents into the molecule is one way to change the intramolecular potential. Substitution of two hydrogen atoms at the para positions of *p*-polyphenyls with two fluorine atoms is one way to do this because such a substitution will hardly change either the intermolecular interaction or the rotational moment of inertia about a figure axis of the molecules. Indeed, the first three fluorine-substituted members are isostructural to the corresponding hydrogen compounds [14–17]. In our previous studies, the nature of the phase transitions of biphenyl and *p*-terphenyl were found to be changed by the fluorine substitution, as follows. There is no structural phase transition in crystalline 4,4′-difluorobiphenyl (DFBP) [18] while in crystalline 4,4" -difluoro-*p*-terphenyl (DFTP), the transition temperature is lowered (127.05 K) and the twist transition lies in the transition region between the order–disorder and displacive types of structural phase transition [19]. Such changes in the nature of the phase transitions result from an enhanced stability of the planar conformation of the molecules.

The crystal of the title compound,4,4‴ -difluoro-*p*-quaterphenyl (DFQP), is also isostructural with crystalline *p*-quaterphenyl and has the disordered nature at room temperature [17]. It is, therefore, expected that in crystalline DFQP a twist transition with more displacive nature occurs at a lower transition temperature, similarly to DFTP. Indeed, the X-ray [20] and heat capacity [21] studies revealed such a situation. The relationship among the twist phase transitions in unsubstituted and fluorine-substituted *p*-polyphenyls has also been discussed [21]. In the present paper, the results of the precision heat-capacity measurements, preliminarily reported before [21], are described in detail, and the deduced thermodynamic functions are reported.

2. Experimental

A powdered specimen of DFQP was synthesized as described previously [17]. The specimen was purified by means of fractional sublimation in vacuum at about 520 K.

The sublimed sample was used for the measurement without further treatment. The sample was loaded into a gold-plated copper calorimeter vessel. The mass of the loaded sample was 1.6296 g (0.0047560 mol) after the buoyancy correction. The calorimeter vessel was evacuated and sealed after introduction of a small amount of helium gas for heat exchange (7 kPa at room temperature). The contribution of the helium gas to the total heat capacity was negligibly small in the whole temperature region studied. The sample contributed 39% at 10 K, 19% at 100 K, and 29% at 300 K to the total heat capacity including that of the calorimeter vessel.

The apparatus and operation of the adiabatic calorimeter were described elsewhere [22]. The working thermometers were platinum (S1055, Minco Products, Inc.) and germanium (GR-200B-500, Lake Shore Cryotronics, Inc.) resistance thermometers above and below 13.8 K, respectively. Their temperature scales are based upon the ITS-90.

3. Results and discussion

The heat capacity measurement of crystalline DFQP was carried out between 8 and 303 K. After each energy input was over, thermal equilibrium within the calorimeter vessel was attained in about 2 min below 50 K, 4 min at 80 K and 7 min above 100 K. No anomalous behavior in the equilibration process was encountered even in the region of a phase transition around 200 K.

The measured molar heat capacities are plotted in Fig. 1 and tabulated in Table 1 in chronological sequence. The temperature dependence of the heat capacity of DFQP is similar to that of *p*-quaterphenyl [2], except for an anomaly in the heat capacity. It seems that the region between 140 and 250 K is related to this anomaly. In the region of the phase transition, the time for thermal equilibration within the calorimeter vessel did not show anomalous behavior, and no latent heat was observed. These results show that the phase transition is of higher order. The resemblance of the shape of the anomaly to that of *p*-quaterphenyl and the disordered nature of crystalline DFQP at room temperature naturally lead the assignment of the anomaly to the "twist" transition.

Separation of the excess heat capacities and the determination of thermodynamic quantities concerning the phase transition have already been reported [21] for the present data. The maximum of the excess heat capacity is found at 200.5 ± 0.5 K, which is regarded as a transition temperture. The enthalpy and entropy of transition are $322 \pm 20\ \mathrm{J\ K^{-1}\ mol^{-1}}$ and $1.65 \pm 0.10\ \mathrm{J\ K^{-1}\ mol^{-1}}$, respectively. These values are smaller than those of *p*-quaterphenyl. In crystalline *p*-quaterphenyl the transition temperature is 233.0 K, and the enthalpy and the entropy of transition are $414\ \mathrm{J\ mol^{-1}}$ and $1.82\ \mathrm{J\ K^{-1}\ mol^{-1}}$, respectively [2]. Although decreases in the temperature and entropy of transition in *p*-quaterphenyl and DFQP are smaller than that of *p*-terphenyl and DFTP, the decrease shows that the nature of the transition in DFQP approaches a displacive one compared with that of *p*-quaterphenyl, as in DFTP. The present authors reported previously in detail that phase transitions in *p*-polyphenyls and their fluorine-substituted compounds are described successfully in terms of the unified theory of structural phase transition proposed by Onodera [20, 21, 23, 24].

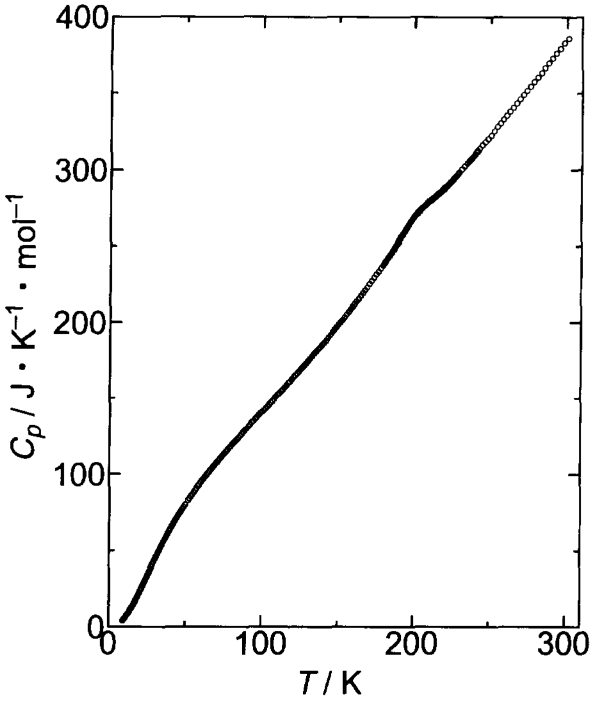

Fig. 1. Measured molar heat capacities of 4,4‴-difluoro-p-quaterphenyl.

A slight winding of the heat capacity curve can be seen at around 100 K. This is probably a due to a phase transition of DFTP (127.05 K) present in the sample as an impurity. DFTP is formed as a by-product in the synthesis of DFQP and cannot be removed completely by the method of purification described above. The DFTP content in the sample, however, was very small and could not be detected by gas-chromatography. In addition, the difference in the specific heats (heat capacity per unit mass) between DFQP and DFTP is within 10% in the whole temperature region studied. Consequently, the values of the experimental molar heat capacity of DFQP are hardly influenced by the presence of a small amount of DFTP. Some thermodynamic functions of crystalline DFQP at round temperatures were, therefore, calculated from the observed results tabulated in Table 1 without any correction, and are given in Table 2. Small contributions below 8 K were estimated by smooth extrapolation to fulfil Debye's law (T^3) at the low-temperature limit from the high-temperature side.

It is interesting to note that the difference between the heat capacity of DFQP and p-quaterphenyl at room temperature is about 20 J K^{-1} mol^{-1}, which is roughly the same as those between DFTP and p-terphenyl and between 4,4'-difluorobiphenyl and biphenyl. The difference results from the substitution with two fluorine atoms. Similarly, the difference between the heat capacities of DFQP and DFTP is about 80 J K^{-1} mol^{-1} at room temperature, roughly equal to that between DFTP and 4,4'-difluorobiphenyl. This also equals those among p-polyphenyls. The differences result

Table 1
Measured molar heat capacities of 4,4‴-difluoro-*p*-quaterphenyl

T/K	$C_{p,\mathrm{m}}$/ J K^{-1} mol^{-1}	T/K	$C_{p,\mathrm{m}}$/ J K^{-1} mol^{-1}	T/K	$C_{p,\mathrm{m}}$/ J K^{-1} mol^{-1}	T/K	$C_{p,\mathrm{m}}$/ J K^{-1} mol^{-1}
Series 1		181.548	240.76	9.254	4.327	74.672	112.53
126.714	170.85	182.669	242.43	9.623	4.858	75.680	113.52
127.768	171.96	183.684	243.79	10.105	5.291	76.690	114.77
128.966	173.04	184.695	245.19	10.691	6.035	77.687	115.87
130.274	174.72	185.705	246.91	11.371	7.290	78.671	117.13
131.575	176.24	186.710	248.25	12.076	8.075	79.641	118.16
132.881	177.84	187.716	250.11	12.710	8.929	80.621	119.48
134.193	179.63	188.725	251.51	13.302	9.850	81.612	120.46
135.498	180.94	189.734	252.56	13.887	11.350	82.618	121.60
136.801	182.45	190.741	255.46	14.443	11.827	83.655	122.65
138.101	183.77	191.748	256.83	Series 5		84.710	123.87
139.395	185.45	192.755	258.06	14.909	12.629	85.783	125.02
140.696	186.72	193.762	259.47	15.377	13.504	86.861	126.23
142.019	188.19	194.767	261.52	15.843	14.318	87.927	127.76
143.348	190.10	195.770	262.80	16.305	15.207	89.001	128.96
144.671	191.64	196.774	264.31	16.773	16.078	90.083	129.76
145.988	193.39	197.780	265.58	17.246	17.062	91.155	130.92
147.298	195.09	198.784	267.37	17.735	17.990	92.237	132.20
148.601	196.69	199.789	268.97	18.246	19.030	93.329	133.68
149.928	198.35	200.793	270.21	18.778	20.088	94.430	134.70
151.277	199.95	201.795	271.58	19.337	21.323	95.552	135.96
152.620	201.48	202.796	272.64	19.942	22.515	96.681	137.25
153.956	203.18	203.799	273.64	20.600	23.927	97.812	138.59
155.317	205.21	204.803	274.89	21.308	25.449	98.938	139.92
156.702	206.95	205.809	275.45	22.065	27.064	100.082	140.88
158.081	208.79	206.814	276.41	22.861	28.825	101.244	141.90
159.454	210.25	208.339	278.03	23.678	30.584	102.396	143.07
160.819	212.16	209.346	279.35	24.473	32.298	103.538	144.29
162.178	213.83	210.353	279.70	25.288	34.127	104.675	145.74
163.563	215.53	211.362	280.17	26.175	35.982	105.814	147.06
164.975	217.50	212.369	280.97	27.063	37.856	106.956	148.09
166.380	219.27	213.375	282.09	27.837	39.565	108.100	149.29
167.779	221.21	214.380	282.81	28.555	41.140	109.247	151.04
169.173	223.10	215.382	284.54	29.314	42.666	110.391	152.15
170.612	225.30	216.389	284.63	30.124	44.399	111.528	153.08
172.094	227.33	217.400	285.48	31.003	46.323	112.666	154.25
173.570	229.47	218.408	286.56	31.933	48.143	113.808	155.45
175.059	231.56	219.414	288.22	32.898	50.117	114.958	156.97
176.559	233.37	220.419	288.77	33.854	52.113	116.116	158.36
178.051	235.57	221.424	289.46	34.783	53.933	117.267	159.91
179.537	237.49	222.431	290.70	35.708	55.700	118.416	160.84
181.017	240.13	223.441	291.91	36.638	57.486	119.563	162.42
182.492	242.08	224.452	292.66	37.569	59.245	120.714	163.79
183.962	243.90	225.464	294.29	38.489	60.949	121.881	165.09
185.424	246.35	226.474	295.29	39.393	62.644	123.065	166.26
186.879	248.62	227.481	296.21	40.283	64.280	124.252	167.64
188.328	251.12	228.485	297.47	41.253	65.953	125.431	169.14

Table 1 (*Continued*)

T/K	$C_{p,\mathrm{m}}$/ J K^{-1} mol^{-1}	T/K	$C_{p,\mathrm{m}}$/ J K^{-1} mol^{-1}	T/K	$C_{p,\mathrm{m}}$/ J K^{-1} mol^{-1}	T/K	$C_{p,\mathrm{m}}$/ J K^{-1} mol^{-1}
189.771	253.67	Series 3		42.249	67.753	126.617	170.46
191.208	255.72	235.645	305.86	43.181	69.325	127.808	171.68
192.696	257.99	237.416	307.67	44.108	70.903	128.992	173.16
194.233	260.49	239.204	309.78	45.037	72.457	130.1691	174.61
195.803	263.09	241.009	312.08	45.973	73.984	Series 7	
197.429	265.65	242.834	314.42	46.918	75.489	180.984	239.46
199.069	268.18	244.679	316.73	47.869	76.988	182.437	242.01
200.703	269.93	246.546	318.62	48.819	78.510	183.885	244.02
202.331	271.90	248.436	320.66	49.769	79.957	185.328	246.01
203.954	273.20	250.376	322.72	Series 6		186.767	247.89
205.569	275.32	252.351	325.46	51.666	82.822	188.202	250.70
207.179	276.84	254.348	328.19	52.610	84.012	189.632	252.82
208.784	278.43	256.353	330.59	53.519	85.388	191.055	255.18
210.407	279.46	258.367	333.22	54.405	86.644	192.478	257.31
212.068	281.44	260.424	335.67	55.314	87.945	193.901	259.81
213.747	282.70	262.539	338.31	56.255	89.280	195.328	262.03
215.422	284.00	264.714	340.83	57.224	90.552	196.759	264.45
217.092	285.40	266.915	343.63	58.186	92.012	198.183	266.69
218.757	286.77	269.107	346.35	59.151	93.141	199.611	268.54
220.438	289.03	271.290	349.14	60.137	94.484	201.043	270.26
222.137	290.51	273.499	351.75	61.132	95.921	202.474	271.47
223.879	292.31	275.773	354.50	62.088	97.019	203.914	273.36
225.664	294.04	278.116	357.60	63.016	98.210	205.367	275.11
227.442	296.41	280.531	360.43	63.958	99.340	206.818	276.60
229.215	298.50	282.997	363.35	64.911	100.55	208.266	277.71
230.980	300.56	285.496	366.71	65.872	101.89	209.708	279.23
232.737	302.57	288.028	369.89	66.840	103.07	211.146	280.64
234.489	304.51	290.581	373.03	67.817	104.20	212.583	281.29
236.260	306.70	293.144	376.40	68.791	105.37	214.017	282.31
238.050	308.65	295.715	379.35	69.768	106.62	215.445	283.97
239.834	310.72	298.282	383.01	70.765	107.67	216.871	285.41
241.613	312.82	301.101	386.00	71.745	108.82	218.292	286.71
Series 2		Series 4		72.706	110.17	219.710	287.31
180.323	239.04	9.005	4.033	73.682	111.30		

from the increase in the number of benzene rings. These facts imply that the localized scheme of intramolecular vibration applies to these compounds.

4. Conclusions

The nature of the phase transitions associated with the intramolecular degree (s) of freedom in a series of *p*-polyphenyls can be changed by changing the interamolecular potential. In this series of compounds, it is possible to see that the phase transition depends on the property of the molecule comprising the crystal. This series should be

Table 2
Molar thermodynamics quantities of 4,4‴-difluoro-*p*-quaterphenyl

T/K	$C^0_{p,m}$/ J K^{-1} mol^{-1}	$\{H^0_m(T)-H^0_m(0)\}/T$/ J K^{-1} mol^{-1}	$S^0_m(T)-S^0_m(0)$/ J K^{-1} mol^{-1}	$-\{G^0_m(T)-H^0_m(0)\}/T$/ J K^{-1} mol^{-1}
10.0	5.19	1.46	1.96	0.50
20.0	22.64	7.31	10.39	3.08
30.0	44.12	16.01	23.64	7.63
40.0	63.75	25.56	39.10	13.54
50.0	80.29	34.90	55.15	20.25
60.0	94.31	43.65	71.05	27.40
70.0	106.87	51.80	86.55	34.75
80.0	118.57	59.42	101.59	42.17
90.0	129.67	66.61	116.20	49.59
100.0	140.79	73.48	130.45	56.96
110.0	151.43	80.08	144.36	64.28
120.0	162.94	86.50	158.02	71.52
130.0	174.42	92.82	171.52	78.70
140.0	186.14	99.07	184.87	85.80
150.0	198.35	105.28	198.13	92.85
160.0	211.03	111.49	211.33	99.84
170.0	224.33	117.73	224.52	106.79
180.0	238.58	124.05	237.74	113.70
190.0	253.59	130.46	251.03	120.58
200.0	269.23	137.01	264.45	127.43
210.0	279.47	143.57	277.84	134.28
220.0	288.37	149.94	291.04	141.10
230.0	299.41	156.19	304.10	147.91
240.0	310.93	162.39	317.08	154.69
250.0	322.66	168.57	330.01	161.44
260.0	335.15	174.73	342.91	168.17
270.0	347.44	180.90	355.78	174.88
280.0	359.74	187.07	368.64	181.57
290.0	372.41	193.24	381.48	188.24
300.0	384.69	199.42	394.32	194.90
298.15	382.51	198.28	391.95	193.67

regarded as one in which the nature of the phase transition in molecular crystals is successfully controlled.

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