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論 文

Heat Capacity and Thermodynamic Functions of Anhydrous 4,4'-Bipyridine

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Heat capacity of anhydrous 4,4'-bipyridine was measured by adiabatic calorimetry between 10 and 300 K. Thermodynamic functions are tabulated.

INTRODUCTION

Recently, much synthetic efforts have been devoted for constructing two- or three-dimensionally organized organometallic polymeric compounds.[1] One strategy to construct desired structure is the use of polydentate ligands as building blocks. Although 2,2'-bipyridine is a famous bidentate ligand, it is inadequate for such a purpose because its coordination sites locate close to each other. In contrast, the title compound, 4,4'-bipyridine, has its coordination sites at two ends of the molecule, and the electron clouds of the lone-pair electrons of the nitrogen atoms direct to the opposing directions. Indeed, many three-dimensional organometallic compounds have been successfully synthesized using 4,4'-bipyridine molecules as bridging rods.[2-5]

Thermodynamic data is required as basic information for rational design of synthetic process of new functional materials. Selection of the successful reaction is crucial especially for organometallic compounds, because the resulting structure is, with relative ease, predicted from the stereochemistry of the building blocks. Little is, however, known for properties of 4,4'-bipyridine.

There exists another motivation to study the properties of 4,4'-bipyridine. Crystal of a similar compound, biphenyl, has been known to undergo interesting phase transitions associated with the change in the molecular conformation at low temperatures.[6-8] The authors have revealed that the property of the "twist transition" can be controlled by shifting the delicate balance between the intra- and intermolecular potentials.[9] Since the molecular structures of biphenyl and 4,4'-bipyridine are similar, two compounds will possibly form solid solution. It is interesting to see how the twist transition, which is of displacive type in crystalline biphenyl, is affected by the existence of 4,4'-bipyridine molecules as the impurity, because reports are scarce concerning the impurity effect on the displacive phase transition. Before starting such experiments, the property of the pure substance should be established.

In this paper, the results of precise heat capacity measurement is described for crystalline 4,4'-bipyridine. Some thermodynamic functions are derived from the results.

CALCULATION

To obtain some information concerning the intramolecular potential for the twisting motion, quantum-chemical calculations were carried out for 4,4' bipyridine, biphenyl and 4,4'-difluorobiphenyl molecules using the GAUSSIAN90.[10] The basis set used was the 3-21G. The geometry was first optimized within the Hartree-Fock method while keeping D_2 (twisted conformation) or D_{2h} (planar conformation) symmetry. The

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energy differences between the stable twisted and planar conformations were then calculated using the MP2 method. As a measure of the curvature of the potential function at the planar conformation, harmonic frequencies for the twisting vibration, which were imaginary because of the unstable nature of the conformation to twist, were also estimated within the Hartree-Fock method.

EXPERIMENTAL

Nominally anhydrous 4,4'-bipyridine (Aldrich Chemicals, Inc.) was purified by fractional sublimation in vacuum at about 360 K. Since the compound is highly hygroscopic, the compound is handled under argon atmosphere for purification and heat capacity measurement. The purified sample was loaded into the gold-plated copper calorimeter vessel. The vessel was evacuated through a copper tubing (1 mm in outer diameter and 7 cm in length), and pinched off after introducing a small amount of helium gas (7 kPa at room temperature) for heat exchange. After the measurement was over, the gas inside the vessel was replaced with argon of atmospheric pressure. The vessel filled with argon was weighed in the air. The mass of the sample used for the measurement was, thus, determined as 1.8948 g (0.012132 mol) after the buoyancy correction. The absence of hydrated water was confirmed by the subsequent TG experiment.

The working thermometers attached to the calorimeter vessel were platinum (S1055, MINCO Products, Inc.) and germanium (GR-200B-500, Lake Shore Cryotronics, Inc.) resistance thermometers. Their temperature scales are based on the ITS-90. The details of the calorimeter and procedure of measurement have been described elsewhere.[11]

RESULTS AND DISCUSSION

The stable conformations predicted by the calculation are twisted for all molecules. The dihedral angles between two hexagons are 49.3°, 50.9° and 52.2° for 4,4'-bipyridine, biphenyl and 4,4'-difluorobiphenyl molecules, respectively. The angles for biphenyl and 4,4'-difluorobiphenyl are larger than those experimentally observed [$(45 \pm 10)°$ and $(44 \pm 5)°$].[12, 13] The energy difference, *i.e.*, the potential barrier height at the planar conformation becomes somewhat smaller on fluorine substitution for biphenyl molecule (18.52 $kJ \cdot mol^{-1}$ and 18.23 $kJ \cdot mol^{-1}$). The harmonic frequency also shows the enhanced planarity of 4,4'-difluorobiphenyl, *i.e.*, 95.0*i* cm^{-1} and 93.6*i* cm^{-1} for biphenyl and 4,4'-difluorobiphenyl, respectively. According to the authours' previous analysis,[9, 14, 15] the planarity of 4,4'-difluorobiphenyl molecule (the smallness of the barrier height) is beyond the threshold for the appearance of the twist transition. Namely, these small differences govern the appearance of the twist transition. 4,4'-Bipyridine molecule shows much enhanced planarity (14.92 $kJ \cdot mol^{-1}$ and 85.8*i* cm^{-1}). The optimized structure of the 4,4'-bipyridine molecule shows that this enhanced planarity is caused by the reduced repulsion between ortho hydrogen atoms which results from a larger deformation of the hexagon due to the shorter length of the carbon-nitrogen bonds.

The heat capacity measurement on anhydrous 4,4'-bipyridine was made between 10 and 303 K. The sample contributed 48 per cent at 20 K, 24 per cent at 100 K, and 34 per cent at 300 K to the total heat capacity including that of the calorimeter vessel. After each energy input, thermal equilibrium within the calorimeter vessel was attained within about 5 min below 50 K, 8 min around 80 K, and 10 min above 100 K.

The experimental heat capacities are tabulated in the chronological sequence in **Table 1**. A temperature increment by each energy input can be deduced from the adjacent mean temperatures. Since the temperature increment was small enough to be ignored, no curvature correction was applied in calculation of the heat capacities. Some thermodynamic functions at rounded temperatures were calculated and are given in **Table 2**. Small contributions below 10 K were estimated by smooth extrapolation that fits the Debye's law in the low temperature limit.

The measured heat capacities are plotted in **Fig. 1**. The temperature dependence of the heat capacity is smooth and resembles that of crystalline biphenyl except for the anomalies due to phase transitions.[16-18] The magnitude of the heat capacity is, however, smaller. This can be rationalized if considering of the decrease in the number of atoms (two hydrogen atoms) and the higher frequency for the twisting vibration due to the twisted conformation in the crystal.[19]

Table 1 Measured molar heat capacities of 4,4'-bipyridine.

T/K	C_p/J·K^{-1}·mol^{-1}	T/K	C_p/J·K^{-1}·mol^{-1}	T/K	C_p/J·K^{-1}·mol^{-1}	T/K	C_p/J·K^{-1}·mol^{-1}	T/K	C_p/J·K^{-1}·mol^{-1}
Series 1		30.980	28.122	80.071	65.682	150.770	99.350	238.793	146.32
10.285	3.087	31.649	28.967	81.098	66.185	151.959	100.06	240.577	147.19
10.585	3.589	32.317	29.740	82.161	66.880	153.143	100.56	242.351	148.35
10.943	3.855	32.974	30.436	83.252	67.496	154.322	101.06	244.118	149.48
11.353	4.319	33.644	31.184	84.331	68.022	155.497	101.66	245.880	150.40
11.804	4.780	34.345	31.982	85.396	68.474	156.667	102.26	247.635	151.41
12.266	5.195	35.079	32.721	86.459	68.942	157.832	103.06	249.383	152.39
12.712	5.497	35.833	33.530	87.593	69.691	158.993	103.57	251.123	153.56
13.158	5.968	36.583	34.426	88.798	70.309	160.190	103.97	252.857	154.55
13.611	6.691	37.353	35.202	89.999	70.890	161.449	104.51	254.587	155.49
14.110	7.104	38.165	36.017	91.193	71.505	162.762	105.09	256.311	156.54
14.630	7.483	38.988	36.900	92.379	71.994	164.133	105.92	258.029	157.66
15.078	8.149	39.810	37.708	93.553	72.620	165.547	106.60	259.739	158.90
15.529	8.714	40.615	38.492	94.715	73.096	166.972	107.32	261.497	159.88
15.976	9.297	41.396	39.267	95.867	73.694	168.409	107.91	263.333	160.83
		42.153	39.987	97.006	74.300	169.857	108.61	265.218	162.02
Series 2		42.926	40.727	98.136	74.866	171.298	109.54	267.157	163.35
10.483	3.502	43.714	41.458	99.257	75.384	172.735	110.26	269.143	164.39
10.851	3.750	44.499	42.174	100.369	75.890	174.183	110.88	271.169	165.68
11.354	4.197	45.303	42.959	101.471	76.299	175.643	111.68	273.249	166.84
11.865	4.810	46.116	43.641	102.564	76.787	177.099	112.28	275.357	167.90
12.332	5.279	46.928	44.390	103.649	77.426	178.548	112.94	277.459	169.20
12.823	5.537	47.731	45.073	104.757	77.884	179.992	113.79	279.551	170.59
13.307	5.937	48.542	45.781	105.887	78.501	181.431	114.57	281.671	171.84
13.798	6.789	49.371	46.420	107.030	78.970	182.864	115.39	283.817	173.29
		50.197	47.094	108.187	79.441	184.310	116.15	285.991	174.69
Series 3		51.011	47.747	109.333	79.976	185.769	116.76	288.191	176.29
14.357	7.454	51.831	48.414	110.471	80.497	187.221	117.51	290.426	177.40
14.840	8.082	52.674	49.010	111.604	81.087	188.668	118.19	292.738	178.78
15.307	8.554	53.531	49.638	112.824	81.561	190.128	119.14	295.082	181.04
15.753	9.050	54.395	50.255	114.059	82.240	191.601	119.82	297.416	182.30
16.198	9.601	55.254	50.883	115.286	82.904	193.069	120.67	299.738	183.19
16.656	10.117	56.095	51.473	116.529	83.388	194.532	121.43	301.925	184.24
17.116	10.638	56.921	52.055	117.814	83.830	195.990	122.16		
17.580	11.193	57.743	52.643	119.146	84.614	197.443	123.00	Series 4	
18.037	11.837	58.564	53.129	120.497	85.238	198.930	123.84	141.082	94.670
18.492	12.314	59.390	53.694	121.841	86.003	200.449	124.67	142.429	95.384
18.975	12.967	60.221	54.205	123.176	86.526	201.962	125.49	143.770	96.004
19.491	13.674	61.038	54.779	124.503	87.072	203.470	126.32	146.449	97.334
20.022	14.296	61.842	55.268	125.822	87.772	204.973	127.26	147.790	98.006
20.563	15.035	62.633	55.728	127.133	88.324	206.472	128.01	149.127	98.637
21.112	15.700	63.446	56.295	128.436	88.937	208.003	128.81	150.463	99.256
21.595	16.284	64.294	56.867	129.730	89.455	209.570	129.69	151.800	99.875
22.016	16.929	65.157	57.363	131.017	90.157	211.132	130.56	153.142	100.50
22.489	17.522	66.049	57.903	132.298	90.719	212.689	131.35	154.490	101.25
23.014	18.153	66.963	58.432	133.571	91.295	214.283	132.25	155.840	101.79
23.555	18.889	67.880	59.032	134.837	91.928	215.916	133.10	157.194	102.50
24.105	19.579	68.783	59.471	136.099	92.580	217.565	134.05	158.554	103.10
24.658	20.274	69.672	60.070	137.353	92.960	219.255	135.11	159.914	103.69
25.211	20.991	70.549	60.587	138.602	93.635	220.963	135.95	161.275	104.42
25.759	21.714	71.373	61.012	139.844	94.222	222.689	136.97	162.635	105.07
26.305	22.420	72.180	61.457	141.079	94.860	224.434	137.97	163.996	105.77
26.842	23.083	73.068	62.038	142.309	95.425	226.171	138.89	165.365	106.34
27.359	23.708	74.007	62.530	143.534	95.958	227.954	139.94	166.740	107.16
27.897	24.467	74.978	63.059	144.753	96.359	229.779	140.74	168.120	107.95
28.497	25.102	75.990	63.572	145.965	97.164	231.597	142.07	169.502	108.65
29.108	25.910	77.008	64.128	147.174	97.903	233.405	143.40		
29.717	26.575	78.032	64.712	148.378	98.307	235.206	144.54		
30.339	27.388	79.053	65.202	149.577	98.733	237.003	145.23		

Table 2 Molar thermodynamic quantities of 4,4'-bipyridine.

$\frac{T}{K}$	$\frac{C_p}{J \cdot K^{-1} \cdot mol^{-1}}$	$\frac{\{H(T)-H(0)\}/T}{J \cdot K^{-1} \cdot mol^{-1}}$	$\frac{S(T)-S(0)}{J \cdot K^{-1} \cdot mol^{-1}}$	$-\frac{\{G(T)-H(0)\}/T}{J \cdot K^{-1} \cdot mol^{-1}}$
15	8.17	2.35	3.19	0.835
20	14.30	4.56	6.36	1.80
30	26.97	9.94	14.58	4.64
40	37.89	15.61	23.89	8.28
50	46.94	21.00	33.35	12.35
60	54.11	25.94	42.57	16.62
70	60.25	30.41	51.38	20.96
80	65.71	34.49	59.79	25.29
90	70.90	38.25	67.83	29.58
100	75.63	41.75	75.54	33.79
110	80.32	45.05	82.98	37.93
120	84.98	48.18	90.16	41.98
130	89.65	51.19	97.15	45.96
140	94.30	54.11	103.96	49.86
150	99.03	56.94	110.63	53.69
160	103.86	59.72	117.18	57.45
170	108.74	62.46	123.62	61.16
180	113.75	65.17	129.97	64.80
190	119.00	67.87	136.26	68.40
200	124.47	70.56	142.51	71.95
210	129.92	73.26	148.71	75.46
220	135.41	75.96	154.88	78.93
230	141.14	78.66	161.03	82.36
240	146.96	81.39	167.16	85.77
250	152.82	84.13	173.27	89.15
260	158.83	86.89	179.38	92.50
270	164.90	89.66	185.49	95.83
280	170.96	92.46	191.60	99.14
290	177.10	95.27	197.70	102.43
300	183.32	98.10	203.81	105.71
298.15	182.17	97.57	202.68	105.11

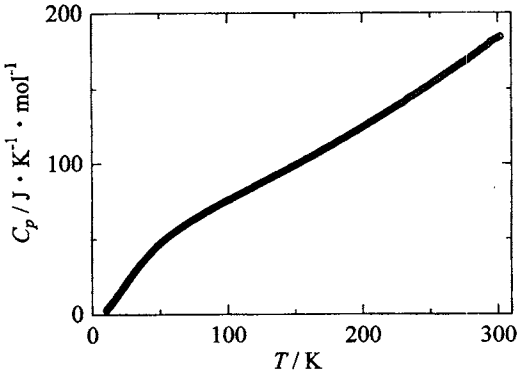

Fig. 1 Measured molar heat capacities of anhydrous 4,4'-bipyridine.

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要　旨

4,4'-ビピリジン結晶の熱容量を10 Kから300 Kの範囲で断熱型熱量計により測定し，熱力学関数を与えた。