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A concealed anomaly at 117.5 K in the heat capacity of hexamethylbenzene^{a)}

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Heat capacities of solid hexamethylbenzene were measured in an adiabatic calorimeter between 3 and 300 K with particular attention to the phase transition at 117 K between phase III and phase II. The transition is very likely to be of first order with the temperature 117.5 ± 0.1 K, the heat of the transition 0.99 ± 0.02 kJ mol⁻¹, and the entropy of transition 8.3 ± 0.2 J K⁻¹ mol⁻¹. The reason why the transition has been referred to as a λ transition is because there is an additional thermal anomaly concealed behind the transition, which has a maximum as large as 50 J K⁻¹ mol⁻¹ at 128 K. This anomaly, or hump in the heat capacity curve, was interpreted in terms of rotatory oscillation/hindered rotation of the methyl groups in a potential barrier of the shape $V = V_3 \cos 3\theta + V_6 \cos 6\theta + V_9 \cos 9\theta$ with $V_3 = 4 \times 10^{-21}$ J, $V_6 = 1 \times 10^{-21}$ J, and $V_9 = 3 \times 10^{-21}$ J. The effect of the transition on the hump is merely to cause a small jump and the hump is otherwise continuous beginning in phase III through phase II. A term, excitation index, is proposed to characterize a first order portion of a phase transition.

I. INTRODUCTION

Because of its highly symmetric molecular shape, solid hexamethylbenzene has been studied extensively.¹⁻²² It is known to undergo two phase transitions at 117 and 383 K before melting at 438 K.

In spite of simple molecular structure, its thermodynamic properties show peculiar features. Thus, in phase I, which exists between 383 and 438 K, the molar volume has a maximum at 405 K and then contracts until it expands greatly at the melting point.^{4,5} The transition at 383 K is a structural phase transition from triclinic (phase II) to orthorhombic.⁶ The structure of phase III is not known completely⁷ but the transition at 117 K has been referred to as " λ type" since Frankosky and Aston² reported their heat capacity measurements. NMR studies¹³⁻¹⁹ revealed that the reorientation of molecules about their hexad axis is excited in phase II, and also that methyl group reorientation is seen in phase III with an activation energy of 7.9 kJ mol⁻¹. Below 30 K, even tunnel rotation of methyl groups has been observed directly by the field cycling technique of NMR.¹⁹ Optical spectroscopy provided evidence of considerable changes in the lattice modes that occur at the 117 K transition.^{8,9} A single crystal shatters when this transition is traversed^{7,22}; this fact suggests that the transition is of first order rather than λ type.

As the first of a series of calorimetric investigations on halogen-substituted hexamethylbenzene, we have remeasured the heat capacity of solid hexamethylbenzene with improved precision, with particular attention to the behavior near the 117 K transition. The results are interesting in that we discovered that this transition is of first order and is superimposed on top of a very broad hump of the heat capacity curve, which has hitherto been considered as pre- or post-transi-

tion contributions.

II. EXPERIMENTAL

A sample of hexamethylbenzene was purchased (the stated purity better than 99%) from Nakarai Chemicals Ltd. and purified by fractional sublimation in vacuum. The sublimed sample was melted by warming it up to the melting point under dry helium gas; this was done because organic substances often crystallize into a metastable modification by such sublimation-deposition processes.^{23,24} The melted sample was cooled down slowly to room temperature and then pulverized gently for calorimeter loading. The purity of the sample used for calorimetry was at least 99.99 mol%, as confirmed by gas-liquid chromatography.

The amount of the sample used for heat capacity measurements was 16.956 g (0.10449 mol), which contributed about 70% to the total heat capacity including that of the calorimeter vessel at 10 K, about 55% at 100 K, and about 60% above 200 K. A small amount of helium gas (6 kPa) was also put into the calorimeter vessel for heat exchange, and its contribution to the total heat capacity was ignored. After each heat input was over, the thermal equilibrium within the calorimeter vessel was attained in a few minutes at about 10 K, 10 min at about 50 K, 15 min or longer above 100 K, except for the phase transition region. At the transition point, it took several hours for the whole system to reach thermal equilibrium.

The adiabatic calorimeter used for heat capacity measurements was the same as described previously,²⁵⁻²⁷ with an improved automated control and a system of data acquisition using a microcomputer.²⁸ The working thermometers were a platinum resistance thermometer (Leeds and Northrup Co., model 8164, $R_0 = 25 \Omega$) calibrated on IPTS-68 above 13.81 K and a germanium resistance thermometer (CryoCal Inc., model CR-1000) below 15 K. The germanium scale was fixed by calibrating it on a helium vapor pressure scale, helium gas thermometry, and the IPTS-68 scale.^{27,28}

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TABLE I. Measured molar heat capacities of hexamethylbenzene.

T (K)	C_p (J K ⁻¹ mol ⁻¹)	T (K)	C_p (J K ⁻¹ mol ⁻¹)
(Phase III)		Series VI	
Series I		6.684	0.653
82.624	99.68	7.225	0.849
84.503	102.13	7.851	1.106
86.410	104.60	8.533	1.431
88.386	107.20	9.272	1.857
90.399	110.00	10.010	2.339
92.504	112.75	10.780	2.896
94.657	115.69	11.750	3.672
96.824	118.62	12.853	4.666
98.946	121.25	13.997	5.829
100.959	123.59	Series VII	
103.020	127.25	Series VII	
105.128	130.37	4.071	0.148
107.195	133.47	4.463	0.204
109.225	136.69	4.871	0.269
111.218	139.84	5.282	0.341
113.170	143.34	5.688	0.421
115.081	147.33	6.154	0.518
Series II		6.717	0.674
55.734	63.57	7.379	0.906
57.856	66.50	8.104	1.229
59.673	69.00	8.830	1.602
61.568	71.56	9.683	2.116
63.425	74.08	10.682	2.821
65.325	76.54	11.807	3.729
67.294	79.22	13.204	4.969
69.243	81.77	Series VIII	
71.204	84.12	11.737	3.598
73.287	86.97	12.659	4.435
75.345	89.60	13.789	5.605
77.281	92.05	15.133	7.044
79.333	94.70	16.552	8.623
81.462	97.44	17.925	10.234
83.535	100.08	19.246	11.850
Series III		20.509	13.429
4.032	0.106	21.759	15.063
4.603	0.184	23.099	16.767
5.139	0.284	24.366	18.413
5.662	0.386	25.582	20.040
6.238	0.519	26.872	21.767
Series IV		28.248	23.630
3.879	0.099	29.610	25.511
4.240	0.160	31.052	27.554
4.589	0.192	32.580	30.373
4.965	0.250	34.152	32.241
5.358	0.316	35.765	34.414
5.788	0.412	37.392	36.817
Series V		39.082	39.290
3.818	0.242	40.870	41.901
4.080	0.221	42.729	44.659
4.585	0.177	44.684	47.542
4.979	0.237	46.657	50.480
5.370	0.316	48.591	53.314
5.782	0.411	50.564	56.162
6.240	0.529	52.634	59.148
6.787	0.697	54.775	62.912
7.502	0.956	(Phase II)	
		Series IX	
		136.600	169.80
		137.595	170.27
		139.622	170.78

TABLE I (Continued)

T (K)	C_p (J K ⁻¹ mol ⁻¹)	T (K)	C_p (J K ⁻¹ mol ⁻¹)
(Phase II)		Series XIII	
Series IX		263.403	226.30
141.719	171.25	266.452	228.15
143.806	171.91	269.477	230.80
145.874	172.33	272.479	232.50
147.941	172.66	275.548	234.43
149.997	173.03	278.604	236.89
152.034	173.46	281.550	238.78
154.062	173.89	284.476	240.74
Series X		287.440	243.36
156.092	174.35	290.499	245.32
158.153	174.80	293.602	247.50
160.244	175.38	296.782	249.49
162.323	175.85	299.741	251.76
164.394	176.40	Series XIV	
166.457	176.91	112.241	151.10
168.511	177.46	114.058	153.34
Series XI		116.096	155.66
170.545	178.14	118.268	157.93
172.581	178.69	120.491	160.02
174.611	179.31	122.686	161.79
176.632	179.94	124.858	163.36
178.643	180.75	127.007	164.97
180.655	181.53	129.136	166.18
182.667	182.35	131.248	167.22
184.673	183.08	133.344	168.09
186.671	183.77	(Transition region)	
188.687	184.57	115.702	154.22
190.725	185.48	117.030	148.14
192.757	186.36	117.515	1802.9
194.778	187.12	117.701	1171.1
196.790	187.79	118.996	396.62
198.796	189.17	118.785	211.31
200.788	189.81	119.675	177.07
Series XII		120.627	167.86
202.769	190.95		
204.790	191.86		
206.922	192.93		
209.187	193.99		
211.509	195.35		
213.817	196.39		
216.042	197.19		
218.245	198.91		
220.519	200.15		
222.849	201.43		
225.236	202.70		
227.609	204.10		
229.967	205.45		
232.312	207.04		
234.643	208.06		
237.032	209.45		
239.472	210.73		
241.895	212.59		
244.302	214.26		
246.697	215.24		
249.081	216.66		
Series XIII			
251.571	218.47		
254.322	220.00		
257.251	221.94		
260.307	223.96		

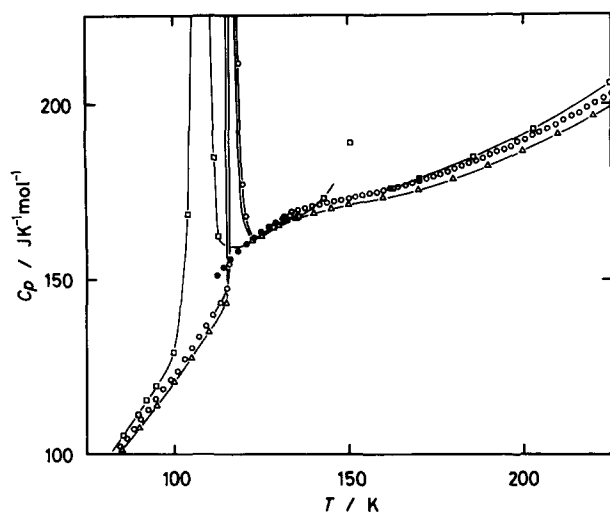


FIG. 1. The molar heat capacities of hexamethylbenzene in the transition region. \circ, \bullet , this research (\circ , the data for phases II and III; \bullet , the data obtained for undercooled phase II); \square , H. M. Huffman, *et al.* (Ref. 1); Δ , M. Frankosky and J. G. Aston (Ref. 2).

III. RESULTS AND DISCUSSION

A. Heat capacities

The heat capacity of crystalline hexamethylbenzene was measured from 3 to 300 K. The primary data of molar heat capacities are tabulated in Table I, and the values in the transition region are plotted in Fig. 1. As clearly seen in Fig. 1, the room temperature phase (phase II) can be undercooled and its heat capacity can be measured in the temperature region of about 10 K below the phase transition II \leftrightarrow III where phase II can exist as a metastable phase and phase III should be the most stable. In other words, the transition is of the first order. This point will be discussed in detail in the following section.

Some molar thermodynamic functions obtained through manipulation of the measured values are tabulated in Table II, where the small contribution below 3 K was estimated by smooth extrapolation from higher temperatures.

For the anomalous heat capacities in the phase tran-

TABLE II. Molar thermodynamic functions of hexamethylbenzene.

T (K)	C_p (J K ⁻¹ mol ⁻¹)	$H^0(T) - H^0(0)$ (J mol ⁻¹)	$S^0(T) - S^0(0)$ (J K ⁻¹ mol ⁻¹)	$-[G^0(T) - H^0(0)]/T$ (J K ⁻¹ mol ⁻¹)
(Phase III)				
5	0.254	0.309	0.0823	0.0205
10	2.33	5.66	0.744	0.179
20	12.80	76.61	5.243	1.413
30	26.04	269.71	12.893	3.903
40	40.64	602.69	22.371	7.304
50	55.37	1082.8	33.023	11.367
60	69.48	1708.3	44.388	15.917
70	82.79	2470.1	56.105	20.818
80	95.86	3363.3	68.013	25.972
90	109.15	4388.1	80.070	31.313
100	122.81	5547.3	92.270	36.797
110	137.88	6849.6	104.67	42.401
(Phase II)				
110.	148.17	7765.1	112.43	41.838
120	159.42	9306.9	125.84	48.283
130	166.61	10940.0	138.91	54.756
140	170.77	12629.0	151.42	61.214
150	173.07	14349.0	163.29	67.629
160	175.29	16091.0	174.53	73.964
170	177.90	17856.0	185.23	80.194
180	181.27	19651.0	195.49	86.317
190	185.13	21483.0	205.39	92.323
200	189.58	23356.0	215.00	98.221
210	194.51	25276.0	224.37	104.01
220	199.83	27247.0	233.54	109.69
230	205.49	29274.0	242.55	115.27
240	211.43	31358.0	251.42	120.76
250	217.55	33503.0	260.17	126.16
260	223.96	35710.0	268.83	131.48
270	230.70	37983.0	277.41	136.73
280	237.67	40325.0	285.93	141.91
290	244.82	42737.0	294.39	147.02
300	252.11	45222.0	302.81	152.07

sition region, a comparison is made in Fig. 1 with the previous results by Huffman *et al.*¹ and by Frankosky and Aston.² There are the discrepancies in the phase transition temperature: 108 K by Huffman *et al.*, 116.48 K by Frankosky and Aston, and 117.5 ± 0.1 K by the present authors. The discrepancy is probably due to the difference in the purity of the sample besides small difference in the temperature scales employed. In fact, Frankosky and Aston ascribed the discrepancy between their results and Huffman's to some impurity effect. A large hump of the heat capacity at about 151 K reported by Huffman *et al.* was observed neither by Frankosky and Aston nor by us. In spite of such large discrepancies in the transition region, the heat capacity values in the normal region are in good agreement with one another, and the results of the present investigation fall between the previous results.

B. The two overlapping anomalies

As described in the preceding section, the phase transition is of the first order, in contrast with the report by Frankosky and Aston.² They claimed it to be a second order phase transition and reported effects of thermal history concerning the reproducibility of the heat capacity values in the vicinity of the phase transition.

Our result is more straightforward (see Fig. 2). On cooling, phase II readily undercools without undergoing the phase transition II \leftrightarrow III (normally at 117.5 K). It was thus possible to measure the heat capacities of pure phase II above 110 K in the heating direction. When the temperature was close to 110 K, it sometimes so happened that phase II transformed spontaneously to the stable phase III. Since this monotropic change was not very rapid, however, quasiequilibrium heat capacities were obtainable by treating the warming drift caused by

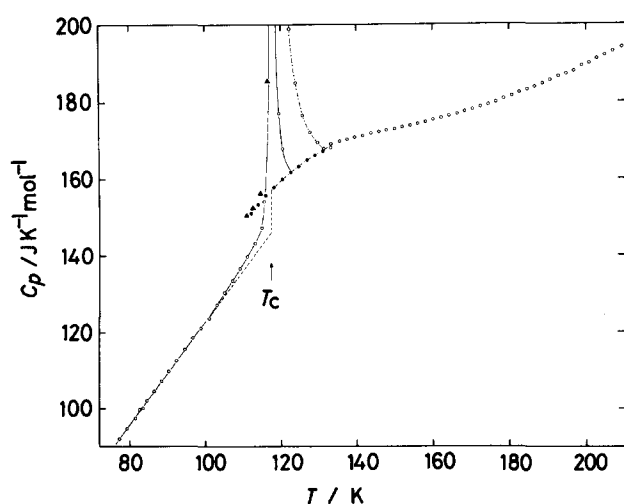


FIG. 2. The equilibrium and nonequilibrium heat capacities in the phase transition region. \circ , Phase II and/or phase III (dotted-dashed curve shows nonequilibrium measurements on mixtures of phases II and III for the temperature region of superheated phase III. Solid curve shows equilibrium heat capacities); \bullet , the data for undercooled phase II; \blacktriangle , nonequilibrium heat capacities of mixtures of phases II and III for the temperature region of undercooled phase II.

TABLE III. The data of the first order phase transition of hexamethylbenzene.

	Frankosky and Aston	This research
T_t	116.48	117.5 ± 0.1
$\Delta H_t / \text{kJ mol}^{-1}$	1.12 ± 0.02	0.99 ± 0.02
$\Delta S_t / \text{J K}^{-1} \text{mol}^{-1}$	10.1 ± 0.2	8.3 ± 0.2

the exothermic stabilization effect under the adiabatic conditions as if it were a heat leak due to poor adiabatic control. Thus, the points marked \blacktriangle in Fig. 2 are such nonequilibrium "heat capacities" of mixtures of phases II and III, where the composition of the solid is not constant but the fraction of phase III gradually increases with time and/or temperature increase. If a long enough time was not allowed for equilibration in the transition region, an analogous nonequilibrium heat capacity curve (dotted-dashed curve in Fig. 2) was obtained even when the measurements were made for the pure phase III to begin with. Because the rate of transition was very slow in either direction, it took more than three hours to obtain a single point on the solid curve in Fig. 2.

The interesting discovery in the present research is that behind the heat capacity anomaly due to the first order transition, there is another broad hump which continuously joins to the post-transition hump above 117 K. We were able to find this concealed hump by utilizing undercooling of phase II, which had not been previously possible probably because of insufficient purity.

An attempt has been made to separate the two anomalies. To obtain the first order portion, the concealed hump was included in the "normal" heat capacity, which is represented by the dashed curve in Fig. 2. The data of the first order phase transition thus separated are given in Table III, together with those of Frankosky and Aston² for the sake of reference. The difference in ΔH_t and ΔS_t are of course due to different estimates of the normal portion. In spite of such discrepancies in the transition region, the standard entropy values at room temperature are in good agreement; $S_{(\text{solid})}$ at 303.15 K is $304 \text{ J K}^{-1} \text{mol}^{-1}$ by Frankosky and Aston,² whereas it is $305 \pm 1 \text{ J K}^{-1} \text{mol}^{-1}$ in this research.

There is some problem in assuming additivity in the heat capacities, particularly in the region of the phase transition. However, in the present instance, the concealed hump portion does not show any hysteresis but persists even when the first order portion is quenched by undercooling or displaced by the effect of impurities. Such experimental facts assure us that we may treat the two anomalies separately. If the hump were part of the first order transition, one would view the latter a lambda type anomaly. This is what has been believed so far.

C. The concealed anomaly

For the reason discussed in the preceding section, we will treat the concealed anomaly, or the broad hump,

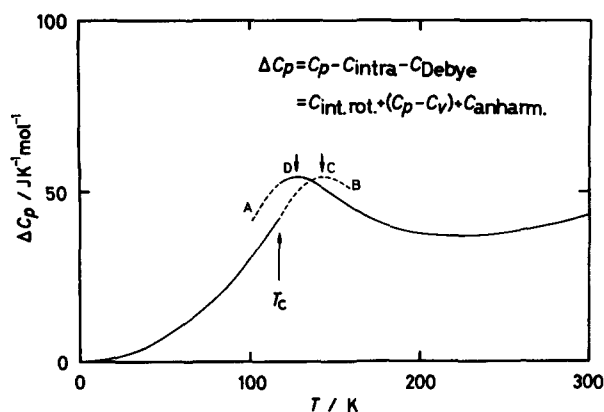


FIG. 3. The hump portion obtained by subtracting both the intramolecular vibrational heat capacity and the lattice heat capacity from the experimental heat capacities, $C_p - C_{\text{intra}} - C_{\text{Debye}} = C_{\text{int.rot.}} + (C_p - C_v) + C_{\text{anharm.}}$. C_{intra} is the intramolecular vibrational heat capacity approximated by Einstein functions for all the known fundamental frequencies except for the internal rotation of methyl groups. C_{Debye} is the lattice heat capacity approximated by a Debye function with $\theta_D = 135$ K for 6N degrees of freedom.

around 130 K as if it were unrelated to the first order transition at 117.5 K.

We will now separate the hump portion further from the rest of contributions to the heat capacity. Thus, the lattice heat capacity was approximated by a Debye function with $\theta_D = 135$ K for 6N degrees of freedom, and the intramolecular vibrational heat capacity by Einstein functions for all the known fundamental frequencies.² When these contributions, which do not include those arising from internal rotational degrees of methyl groups, have been subtracted from the experimental heat capacities, one obtains the excess portion as in Fig. 3. The maximum of this hump amounts to about $50 \text{ J K}^{-1} \text{ mol}^{-1}$ at 128 K. Judging from the temperature at which the maximum appears, the frequency or frequencies, whatever origin they may be, cannot be very high. Also, the maximum value ($50 \text{ J K}^{-1} \text{ mol}^{-1}$) implies that about six degrees of freedom are involved in the anomaly ($50/R \approx 6$). We assume then that internal rotation (including rotatory oscillation) of methyl groups is the most probable candidate which gives rise to this hump.

The general shape of the hump conforms to the heat capacity of a system in which rotational oscillation gradually changes to hindered rotation. We shall attempt to find an average potential energy hindering rotation of methyl groups by parameter fitting of the heat capacity. However, before doing that, let us explore the nature of the anomaly in more detail in connection with the transition between phases II and III.

As pointed out in the preceding section, the hump portion is not undercooled even when the transition is quenched. In other words, when phase II can be made to exist below 117.5 K, the hump continues on the portion A of the curve in Fig. 3. The other fact of interest is that the two portions of the hump, i.e., below and above the transition, can be made to join smoothly

if the jump at the transition point is ignored. This is shown by the portion B of the curve in Fig. 3. These facts lead to two important notions. (1) What is occurring in phase III continues to proceed in phase II. That is, what has been depicted in Fig. 3 corresponds to one and the same phenomenon that takes place in continuation from phase III to phase II. (2) The influence of the first order transition on this phenomenon is such that it displaces the maximum of the hump from where it would be located if there were no phase transition (the point C, 143 K) to where it is actually found (the point D, 128 K). This fictitious displacement of the maximum amounts to about 15 K. This means that the transition is equivalent to thermal excitation of 15 K with regard to internal rotation of methyl groups. The same interpretation is applicable to other properties such as molar volume, total enthalpy, and spin-lattice relaxation time which usually show a jump at a first order transition point. It is probably more meaningful to express the extra thermal excitation in terms of fractional lateral displacement $143/128 = 1.12$, which we now call "excitation index" of the transition. The excitation index may be different depending on what property one is observing.

D. The potential barrier hindering rotation of methyl groups

The average height of potential barrier hindering internal rotation of methyl groups in phase III of hexamethylbenzene has been determined from nuclear magnetic resonance to be 7.9 kJ mol^{-1} . We now try to find a potential function which would best reproduce the extra heat capacity curve as given in Fig. 3. The most widely used function for this purpose is a sinusoidal function having the threefold symmetry. The Mathieu function table calculated by Pitzer and Gwinn,²⁰ however, gives a maximum above room temperature for this height of barrier. We therefore used a trial function of the form

$$V(\theta) = V_3 \cos 3\theta + V_6 \cos 6\theta + V_9 \cos 9\theta$$

and searched for the best set of parameters V_3 , V_6 , and V_9 in the range $(0-11.0) \times 10^{-21} \text{ J}$ in steps of $1 \times 10^{-21} \text{ J}$. The basis function used was a series of free rotor wave functions

$$\Psi(\theta) = \sum_{i=1}^{50} \{a_i \cos(i-1)\theta\} + \sum_{i=1}^{50} \{b_i \sin(i\theta)\}$$

and the value of the moment of inertia of a methyl group was taken as $5.3 \times 10^{-47} \text{ kg m}^2$.

The energy levels were calculated by diagonalization of the energy matrix, from which the heat capacities were evaluated for six independent methyl groups as a function of temperature. The criteria of fitting were to reproduce the temperature at which the maximum of the hump appears, the maximum value of the hump, and the barrier height as measured from "average" torsional level occupied at that temperature.

The best set of parameter values which gives the heat capacity, as given in Fig. 4, was

$$V_3 = 4 \times 10^{-21} \text{ J}, \quad V_6 = 1 \times 10^{-21} \text{ J}, \quad V_9 = 3 \times 10^{-21} \text{ J}.$$

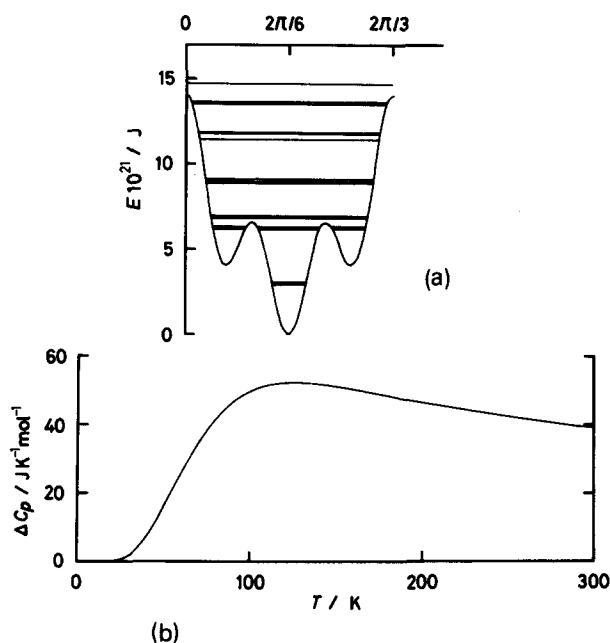


FIG. 4. (a) The effective potential energy curve for an isolated methyl group including ninefold term in the potential function. (b) The heat capacity due to internal rotation of six methyl groups calculated for the effective potential shown above.

This potential function has shoulders on either side of a potential minimum, which gives rise to a large number of low-lying levels in spite of the high barrier, which in turn bring the heat capacity hump to a much lower temperature.

The calculated shape of ΔC_p only reproduces the maximum value of the hump and the temperature at which the maximum appears besides the barrier height. Agreement with experimentally derived ΔC_p is poor on the low-temperature side of the maximum; this probably comes from approximations involved in the fitting, e.g., it was assumed that the six methyl groups oscillate or rotate independent of one another. Our recent NMR studies indicated that it is not the case.¹⁹ In fact, Hamilton *et al.*²² discussed the possible normal modes of rotation of the six methyl groups in hexamethylbenzene. If we could treat the methyl groups collectively, the ΔC_p fitting would be improved.

Nevertheless, it has been semiquantitatively substantiated that (1) the broad hump in C_p is due to rotatory

oscillation/hindered rotation of the methyl groups, and (2) excitation of this mode of motion begins in phase III and continues on in phase II.

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