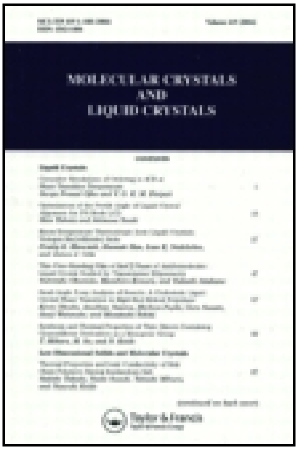

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# Heat Capacity of *p*-*n*-Hexyloxybenzylideneaniline (HBA)†

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The heat capacity of HBA has been measured between 16 and 385 K with an adiabatic calorimeter. A crystal–crystal phase transition was observed at about 73 K. The enthalpy and entropy of this transition were 0.192 kJ $mol^{-1}$ and 2.70 J $K^{-1}$ $mol^{-1}$, respectively. The crystal melted into the isotropic liquid at 321.63 K. The enthalpy and entropy of melting were 30.91 kJ $mol^{-1}$ and 96.1 J $K^{-1}$ $mol^{-1}$. The melting entropy of HBA agreed well with those of the homologous compounds in which the *p*-position of the aniline ring is substituted by CN, Cl, F and $CH_3$, respectively.

## 1 INTRODUCTION

Liquid crystalline states are usually realized by rather elongated molecules consisting of a rigid core and at least one long flexible end group. In addition, a special substituent group such as phenyl, nitro, halogen or nitrile-group at the opposite terminal position plays an important role for the appearance of a liquid crystalline state.[1] Therefore, a molecule lacking such a substituent group often remains non-mesogen even though a core and a flexible groups exist in the molecule.[2]

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† This paper is one of the series initiated from Ref. 13. Contribution No. 41 from Chemical Thermodynamics Laboratory.

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*p*-*n*-Hexyloxybenzylideneaniline (HBA) is one of such examples because, although it has a core part (—$C_6H_4$—CH=N—$C_6H_5$) and a long flexible part (*n*-$C_6H_{13}O$—) in the molecule, it does not exhibit any mesogenic states.[2,3] On the other hand, when *p*-position of the aniline ring in HBA is substituted by appropriate groups, those compounds generally exhibit mesomorphism.[3-8] In a homologous series represented by the chemical formula, $C_6H_{13}O$—$C_6H_4$—CH=N—$C_6H_4$—X, all the compounds have essentially the same degrees of freedom of molecular motion as far as the substituent group X is monatomic or quasi-monatomic. However, the kind of mesophase and phase sequence decisively depend on X. For instance, the compound with X=Cl, *p*-*n*-hexyloxybenzylideneamino-*p*′-chlorobenzene (HBAC), is known to show two smectic phases,[4,5] and one additional intermediate phase[9,10] though its phase has not yet been assigned.[11] *p*-*n*-Hexyloxybenzylideneamino-*p*′-fluorobenzene (HBAF) obtained by replacing Cl in HBAC by F exhibits two smectic and one nematic phases.[5,12] Although the sequence of mesophase of HBAF is different from that of HBAC, the cumulative transition entropy from the crystal to the isotropic liquid of HBAF (93.6 J $K^{-1}$ $mol^{-1}$)[12] agreed well with that of HBAC (95.1 J $K^{-1}$ $mol^{-1}$).[10] This kind of situation is also encountered between *p*-*n*-hexyloxybenzylideneamino-*p*′-benzonitrile (HBAB)[13] and *p*-*n*-hexyloxybenzylidene-*p*′-toluidine (HBT)[14] in spite of the fact that their substituent groups are not monatomic and have internal degrees of freedom. They exhibited a crystal–crystal phase transition accompanied by a considerable amount of the transition entropy. When the entropies of these crystal–crystal transitions are included, the total entropies of transitions for HBAB and HBT amounted to 91.1 and 94.7 J $K^{-1}$ $mol^{-1}$, respectively. These values are nearly identical with those for HBAC and HBAF.

These facts suggest that they acquire the same magnitude of degrees of freedom of molecular motions through their transitions from the crystalline solid to the isotropic liquid. In other words, the melting entropy of the present series of compounds can be regarded as being independent of both the substituent group and the sequence of mesomorphic states; the average value of the melting entropy is 93.6 J $K^{-1}$ $mol^{-1}$.

In relation to this, we were much interested in the melting entropy of the non-mesogenic homologue, HBA. In this paper we report the results of heat capacity measurements of HBA between 16 and 385 K. The melting entropy of HBA will be compared to the cumulative entropies of the four mesogenic compounds, and the melting phenomena will be accounted for in terms of successive phase transitions.

## 2 EXPERIMENTAL

HBA was synthesized by the dehydration reaction of *p-n*-hexyloxybenzyaldehyde (Tokyo Kasei Kogyo Co., Ltd.) and aniline (Wako Pure Chemicals Co., Ltd.). The details of synthesis and purification procedure were the same as those reported previously.[13] The elemental analyses for C, H and N were 81.23% (theoretical: 81.10%), 8.26% (8.24%) and 4.95% (4.98%), respectively.

For preliminary thermal study, differential thermal analysis (DTA)[15] was carried out. The heat capacity was measured between 16 and 385 K by using an adiabatic calorimeter reported previously.[13] The amount of the sample used was 18.9335 g.

## 3 RESULTS

### DTA

The purified sample was at first used for DTA to assess the purity and thermal behavior between 80 and 400 K. The results of DTA are shown in Figure 1. The heating curve (run 1) represented only one endothermic peak at 321.5 K, corresponding to the melting point of HBA.[2,3] The cooling curve (run 2) showed two monotropic phase transitions at about 308 and 293 K. The peak area at 293 K was approximately three times larger than that of the 308 K peak. As these two transition temperatures are located rather closely, the peak areas may roughly reflect the ratio of two transition enthalpies. Judging from these facts, the intermediate phase observed between 293 and 308 K might be a smectic phase.[16] Run 3 is the heating curve of the sample once cooled to about 80 K. A small endothermic and an exothermic hump were observed at about 280 and 300 K. After these two thermal anomalies were over, the specimen showed the same melting behavior as run 1. It was possible to obtain the same DTA curve as run 1 after the sample was annealed at 310 K for several hours.

### Heat capacity measurements

Figure 2 shows the heat capacity curve measured in the whole temperature range studied here. HBA is known to have no stable mesomorphic state.[2,3] Instead, however, a solid–solid phase transition was discovered below 100 K. Figure 3 shows the enlarged heat capacity curve around the phase transition region. This heat capacity anomaly seems to be composed of two parts. One is a sharp peak at low temperature side

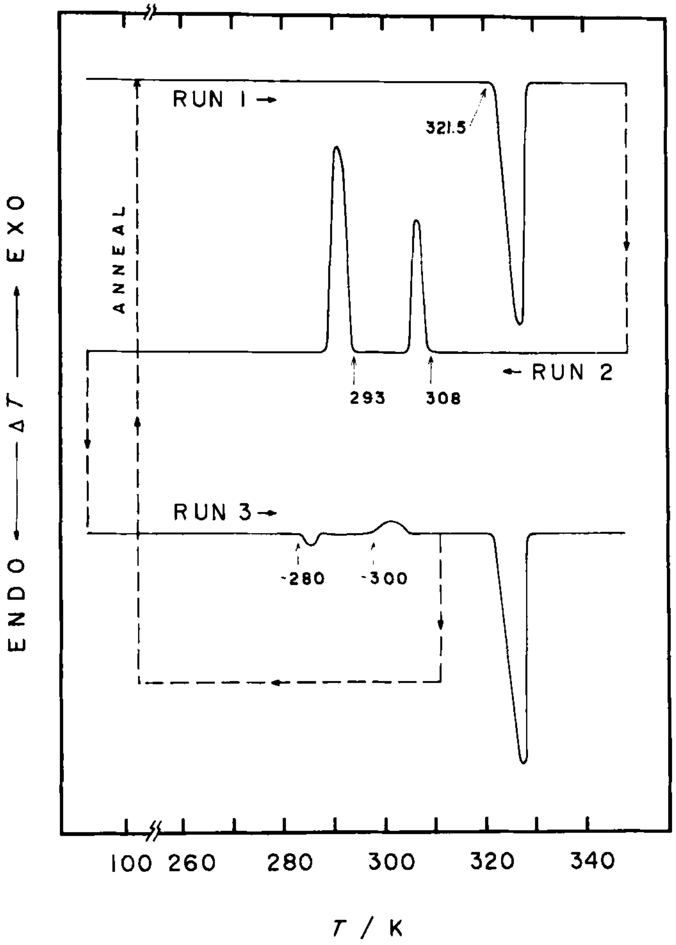

FIGURE 1 DTA curves of HBA.

and the other is a small hump at high temperature side. The temperature of the peak was 73.41 K. The heat capacity maximum reached 162.12 J $K^{-1}$ $mol^{-1}$, but no latent heat was observed. The peak had a long tail at its low temperature side extending to as low as 55 K. On the other hand, the hump was located between 80 and 90 K. The total temperature range was as wide as 35 K. To determine the enthalpy and entropy of transition, we assumed a normal heat capacity as shown by a broken line in Figure 3. The evaluated enthalpy and entropy of transition amounted to 192.5 J $mol^{-1}$ and 2.70 J $K^{-1}$ $mol^{-1}$, respectively.

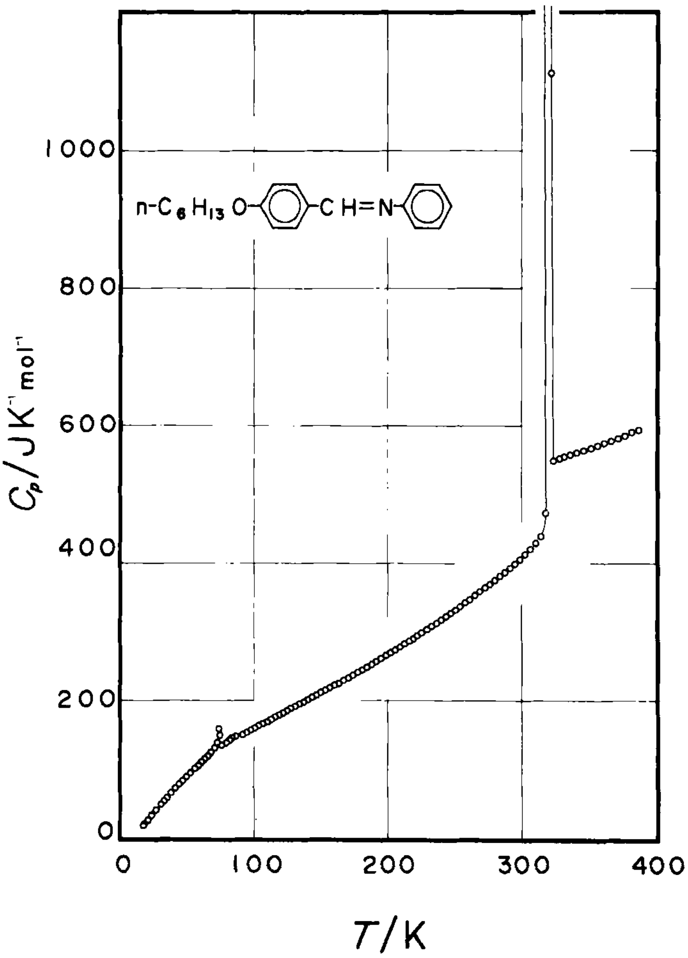

FIGURE 2 Molar heat capacity curve of HBA.

The high temperature crystalline phase was transformed into the isotropic liquid at about 231 K. No obvious pre- and post-melting effects were observed in the heat capacity curve. The melting was accompanied by a heat capacity jump of about 120 J $K^{-1}$ $mol^{-1}$. The heat capacity of the isotropic liquid was increased almost linearly with temperature. From the analysis of the melting process (Table I), the purity, the melting point of the present specimen and the triple point of pure HBA were determined to be 99.86%, 321.63 K and 321.66 K, respectively. Thermodynamic quantities associated with the melting are listed in

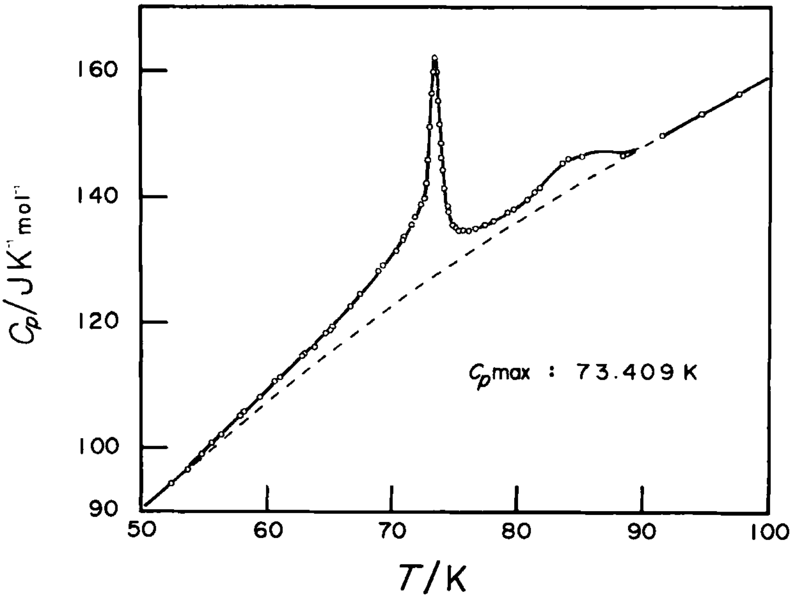

FIGURE 3 Molar heat capacity curve of HBA around its crystal–crystal transition region. Broken line means the normal lattice heat capacity.

TABLE I

Determination of the purity of HBA.

| $\frac{T}{\mathrm{K}}$ | $\frac{1}{f}$ | | |
|---|---|---|---|
| 321.552 | 6.15 | Enthalpy of melting | 30.91 kJ mol$^{-1}$ |
| 321.584 | 3.72 | | |
| 321.608 | 2.50 | Melting point of sample | 321.631 K |
| 321.611 | 1.93 | | |
| 321.617 | 1.57 | Triple point of pure material | 321.663 K |
| 321.621 | 1.32 | | |
| 321.626 | 1.15 | Purity of sample | 99.86% |
| 321.633 | 1.02 | | |

TABLE II

Transition temperatures, enthalpies and entropies of transitions of HBA.

| | Crystal–crystal | Crystal–isotropic |
|---|---|---|
| $T$/K | 73.41 | 321.63 |
| $\Delta H_t$/kJ mol$^{-1}$ | 0.192 | 30.91 |
| $\Delta S_t$/J K$^{-1}$ mol$^{-1}$ | 2.70 | 96.1 |

Table II together with the values relevant to the crystal–crystal transition.

Numerical data of the heat capacity are listed in Table III. The standard thermodynamic functions are listed in Table IV at selected temperatures.

TABLE III

Molar heat capacities of HBA.

| $T_{av}$/K | $C_p$/J K$^{-1}$ mol$^{-1}$ | $T_{av}$/K | $C_p$/J K$^{-1}$ mol$^{-1}$ | $T_{av}$/K | $C_p$/J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|---|
| 80.246 | 137.43 | 291.283 | 393.00 | 28.045 | 44.913 |
| 85.158 | 146.53 | 295.100 | 399.65 | 30.034 | 49.457 |
| 88.383 | 146.70 | 298.908 | 405.70 | 32.132 | 53.992 |
| 91.540 | 149.82 | 302.710 | 413.22 | 34.322 | 58.849 |
| 94.621 | 153.23 | 306.522 | 420.23 | 37.551 | 66.147 |
| 97.634 | 156.42 | 310.355 | 428.84 | 38.742 | 68.269 |
| 100.578 | 159.52 | 314.203 | 438.72 | 41.078 | 72.962 |
| 103.510 | 162.67 | 317.995 | 472.89 | 43.675 | 78.215 |
| 106.479 | 165.99 | 320.652 | 1637.6 | 46.590 | 83.568 |
| 109.474 | 169.09 | 321.498 | 29252 | 49.484 | 89.185 |
| 112.464 | 172.16 | 321.568 | 102715 | 52.262 | 94.349 |
| 115.491 | 175.55 | 321.593 | 227324 | | |
| 118.556 | 178.56 | 321.606 | 434076 | 52.932 | 95.280 |
| 121.623 | 181.74 | 321.614 | 557468 | 55.580 | 100.81 |
| 124.704 | 185.04 | 321.619 | 957233 | 58.141 | 105.79 |
| 127.784 | 188.22 | 321.624 | 727455 | 60.636 | 110.65 |
| 130.860 | 191.39 | 321.630 | 497434 | 63.011 | 115.01 |
| 133.902 | 194.65 | 322.221 | 1112.9 | 65.282 | 119.44 |
| 136.927 | 197.63 | 323.825 | 548.75 | 67.461 | 124.61 |
| 139.997 | 200.85 | 325.899 | 550.08 | 69.315 | 129.16 |
| 143.125 | 204.14 | 328.484 | 551.98 | 70.407 | 131.51 |
| 146.436 | 207.57 | 332.040 | 554.38 | 71.015 | 133.80 |
| 149.903 | 211.22 | 336.400 | 557.04 | 71.616 | 135.70 |
| 153.355 | 214.70 | 341.232 | 560.25 | 72.209 | 139.01 |
| 156.803 | 218.57 | 346.315 | 563.94 | 72.791 | 146.17 |
| 160.252 | 222.15 | 351.491 | 567.41 | 73.353 | 159.03 |
| 163.696 | 225.88 | 356.221 | 570.43 | 73.909 | 148.60 |
| 167.142 | 229.49 | 361.354 | 574.21 | 74.480 | 138.64 |
| 170.607 | 233.42 | 366.363 | 577.62 | 75.060 | 135.25 |
| 174.086 | 237.05 | 371.513 | 581.47 | 75.692 | 134.78 |
| 177.576 | 241.15 | 376.601 | 585.15 | 76.710 | 135.09 |
| 181.082 | 245.07 | 381.643 | 590.36 | 78.141 | 136.26 |
| 184.599 | 249.08 | 386.663 | 593.71 | 79.722 | 138.14 |
| 188.119 | 253.03 | | | 81.790 | 141.57 |
| 191.639 | 257.27 | 53.624 | 96.552 | | |
| 195.169 | 261.15 | 54.770 | 99.052 | 70.930 | 133.21 |
| 198.686 | 265.49 | 56.336 | 102.12 | 71.893 | 136.88 |
| 202.190 | 269.63 | 57.885 | 105.19 | 72.389 | 138.84 |
| 205.699 | 273.71 | 59.450 | 108.11 | 72.611 | 139.83 |

TABLE III (*Continued*)

| $T_{av}$<br>K | $C_p$<br>J K$^{-1}$ mol$^{-1}$ | $T_{av}$<br>K | $C_p$<br>J K$^{-1}$ mol$^{-1}$ | $T_{av}$<br>K | $C_p$<br>J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|---|
| 209.201 | 278.05 | 61.094 | 111.27 | 72.758 | 144.27 |
| 212.697 | 282.42 | 62.865 | 114.73 | 72.896 | 145.98 |
| 216.194 | 286.60 | 64.733 | 118.34 | 73.027 | 151.23 |
| 219.234 | 289.98 | 66.684 | 122.68 | 73.156 | 156.54 |
| 222.311 | 294.42 | 68.957 | 128.24 | 73.283 | 159.95 |
| 225.826 | 298.94 | 71.482 | 135.78 | 73.409 | 162.12 |
| 229.343 | 303.67 | 73.594 | 147.66 | 73.535 | 159.90 |
| 232.864 | 308.13 | 75.024 | 135.37 | 73.662 | 155.37 |
| 236.389 | 312.97 | 76.167 | 134.70 | 73.791 | 151.65 |
| 239.904 | 317.70 | 77.464 | 135.61 | 73.921 | 146.28 |
| 243.417 | 322.47 | 79.244 | 137.68 | 74.052 | 144.38 |
| 246.938 | 327.31 | 81.364 | 140.89 | 74.187 | 141.43 |
| 250.474 | 332.16 | 84.073 | 146.12 | 74.326 | 134.39 |
| 253.806 | 336.69 | | | 74.546 | 137.74 |
| 257.478 | 342.20 | 16.486 | 18.942 | 74.876 | 135.62 |
| 261.171 | 347.30 | 17.226 | 20.406 | 75.331 | 134.69 |
| 264.877 | 352.76 | 18.009 | 22.128 | 76.167 | 134.70 |
| 268.593 | 358.38 | 18.904 | 24.105 | 78.101 | 136.16 |
| 272.326 | 363.99 | 20.042 | 26.648 | 80.800 | 139.63 |
| 276.077 | 369.49 | 21.362 | 29.650 | 83.594 | 145.43 |
| 279.853 | 375.26 | 22.816 | 33.054 | 86.773 | 147.35 |
| 283.655 | 381.18 | 24.430 | 36.594 | | |
| 287.462 | 386.18 | 26.169 | 40.549 | | |

## 4 DISCUSSION

### Crystal-crystal phase transition

Instead of appearance of a mesophase, HBA exhibited the crystal-crystal phase transition at around 73 K. As the entropy of transition, 2.70 J K$^{-1}$ mol$^{-1}$, is relatively small, this transition may be due to a slight deformation of the crystal lattice. Such a transition accompaning small entropy change was reported at 99 K for terephthal-*bis*-4-butylaniline (TBBA) by Kobayashi *et al.*[17] Since two X-ray patterns of TBBA taken at 93 and 104 K were slightly different from each other, the transition was concluded to be due to a change in the crystal structure. The entropy of transition determined by DSC was 2.8 J K$^{-1}$ mol$^{-1}$, which was comparable with that of HBA. Therefore, the transition of HBA at 73 K may be the same kind of transition as that observed in TBBA.

TABLE IV

Standard thermodynamic functions of HBA.

| $\frac{T}{\mathrm{K}}$ | $\frac{C_p^\circ}{\mathrm{J\,K^{-1}\,mol^{-1}}}$ | $\frac{S^\circ}{\mathrm{J\,K^{-1}\,mol^{-1}}}$ | $\frac{(H^\circ - H_0^\circ)/T}{\mathrm{J\,K^{-1}\,mol^{-1}}}$ | $\frac{-(G^\circ - H_0^\circ)/T}{\mathrm{J\,K^{-1}\,mol^{-1}}}$ |
|---|---|---|---|---|
| 10 | (5.96) | (2.42) | (1.69) | (0.73) |
| 20 | 26.50 | 12.60 | 8.78 | 3.82 |
| 30 | 49.19 | 27.65 | 18.48 | 9.17 |
| 40 | 70.74 | 44.80 | 28.89 | 15.91 |
| 50 | 90.01 | 62.67 | 39.20 | 23.47 |
| 60 | 109.13 | 80.75 | 49.24 | 31.51 |
| 70 | 130.42 | 99.10 | 59.25 | 39.85 |
| 80 | 138.50 | 117.56 | 69.12 | 48.44 |
| 90 | 148.01 | 134.64 | 77.57 | 57.07 |
| 100 | 158.92 | 150.81 | 85.17 | 65.64 |
| 110 | 169.61 | 166.46 | 92.36 | 74.10 |
| 120 | 180.03 | 181.66 | 99.23 | 82.43 |
| 130 | 190.43 | 196.49 | 105.85 | 90.64 |
| 140 | 200.85 | 210.98 | 112.26 | 98.72 |
| 150 | 211.24 | 225.19 | 118.51 | 106.68 |
| 160 | 221.82 | 239.16 | 124.64 | 114.52 |
| 170 | 232.57 | 252.93 | 130.67 | 122.26 |
| 180 | 243.74 | 266.54 | 136.64 | 129.90 |
| 190 | 255.26 | 280.02 | 142.58 | 137.44 |
| 200 | 266.97 | 293.41 | 148.51 | 144.90 |
| 210 | 278.97 | 306.73 | 154.43 | 152.30 |
| 220 | 291.36 | 319.99 | 160.37 | 159.62 |
| 230 | 304.47 | 333.23 | 166.35 | 166.88 |
| 240 | 317.76 | 346.47 | 172.38 | 174.09 |
| 250 | 331.43 | 359.72 | 178.47 | 181.25 |
| 260 | 345.67 | 372.99 | 184.63 | 188.36 |
| 270 | 360.43 | 386.31 | 190.86 | 195.45 |
| 280 | 375.53 | 399.69 | 197.20 | 202.49 |
| 290 | 390.84 | 413.13 | 203.60 | 209.53 |
| 300 | 407.81 | 426.67 | 210.12 | 216.55 |
| 310 | 427.86 | 440.36 | 216.82 | 223.54 |
| 320 | transition | 455.15 | 224.61 | 230.54 |
| 330 | 552.76 | 567.90 | 327.85 | 240.05 |
| 340 | 559.38 | 584.50 | 334.57 | 249.93 |
| 350 | 566.21 | 600.82 | 341.09 | 259.73 |
| 360 | 573.26 | 616.86 | 347.44 | 269.42 |
| 370 | 580.38 | 632.66 | 353.65 | 279.01 |
| 380 | 587.49 | 648.24 | 359.71 | 288.53 |
| 385 | 590.96 | 655.97 | 362.71 | 293.26 |
| 273.15 | 365.20 | 390.52 | 192.85 | 197.67 |
| 298.15 | 404.52 | 424.16 | 208.91 | 215.25 |
| 373.15 | 582.64 | 637.59 | 355.57 | 282.02 |

TABLE V

Sequences of phases, entropies of transitions and cumulative entropies of HBA and its four derivatives.

| | Sequences of transitions | $\Delta S_t$ J $K^{-1}$ $mol^{-1}$ | | | | $\Sigma S_t$ J $K^{-1}$ $mol^{-1}$ |
|---|---|---|---|---|---|---|
| HBA | C-IL | 96.1 | | | | 96.1 |
| HBAB | $C_{II}$—$C_I$—N—IL | 16.7 | 71.2 | 3.2 | | 91.1 |
| HBAC | C—$S_3$—$S_B$—$S_A$—IL | 33.2 | 37.0 | 9.3 | 15.6 | 95.1 |
| HBAF | C—$S_B$—$S_A$—N—IL | 70.7 | 9.2 | 10.2 | 3.5 | 93.6 |
| HBT | $C_{II}$—$C_I$—N—IL | 15.9 | 74.9 | 3.9 | | 94.7 |
| | | | | average | | 93.6 |

## Entropy of melting: Comparison with its derivatives

In the previous section, the entropy of melting of HBA was obtained to be 96.1 J $K^{-1}$ $mol^{-1}$. This value is very close to that we have predicted. For comparison, the entropies of transitions of the compounds so far reported by us[10,12–14] are listed in Table V. In the last column the cumulative transition entropies corresponding to the melting entropy of HBA are given.

Since HBA has no liquid crystalline phase, melting of the crystal lattice and the excitation of molecular motions take place simultaneously at its melting transition. On the contrary, the other compounds show crystalline and/or mesomorphic polymorphism before they melt into the isotropic liquid. Each time a phase transition takes place, they seem to acquire successively a part of their melting entropies. The magnitude of the entropy increment gained by each transition depends on the nature of the phase transition. However, the cumulative transition entropies are independent of the substituent groups as well as of the kinds of the polymorphism. The average value of them amounts to 93.6 J $K^{-1}$ $mol^{-1}$ as shown in Table V. The situation is drawn diagrammatically in Figure 4. The agreement between the melting entropy of HBA and this average value seems to be satisfactory. We have pointed out that a unified interpretation is possible concerning the transition from the crystal to the isotropic liquid from the entropic viewpoint. This prediction is more strenghthened by combining the present result with the previous papers.[10,12–14]

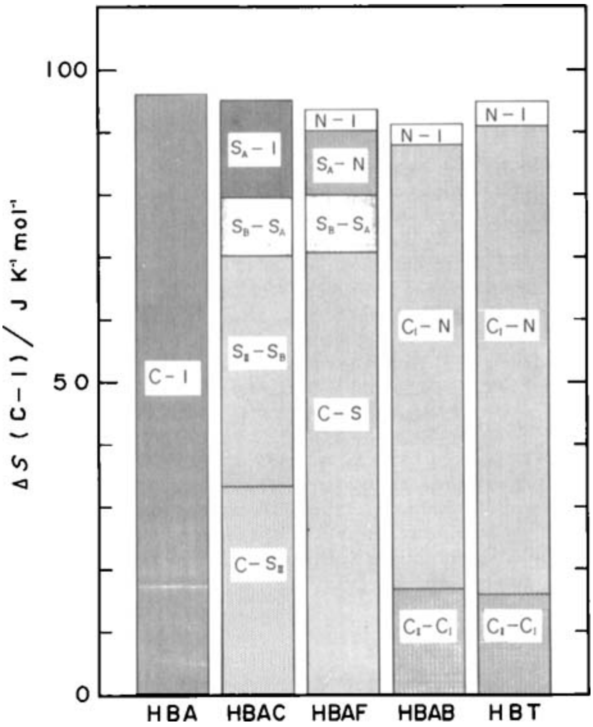

FIGURE 4 Histogram of cumulative transition entropies of five compounds.

## Concluding remarks

We have measured the entropy of melting of HBA and the entropies of transitions of four homologues of HBA. These five compounds have been selected so that they may have nearly the same magnitude of degrees of freedom of molecule. Therefore, the obtained cumulative entropies of transitions can be interpreted on the same level in terms of the successive melting phenomenon from the crystal to the isotropic liquid even though different kind of mesophase appears from compound to compound.

## Acknowledgments

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