액정 *p*-Azoxyanisole 의 열역학적 성질에 대한 이론적인 예측

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Theoretical Prediction of the Thermodynamic Properties of Liquid-Crystalline *p*-Azoxyanisole

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요 약. 액체에 대한 significant structure theory와 상의 전이에 대한 Bragg-Williams 근사를 사용하여 액정 화합물인 *p*-azoxyanisole의 열역학적 성질을 nematic phase와 isotropic phase의 온도범위에 걸쳐 계산하였다. Isotropic phase 는 일반적인 액체로 보았으며 nematic phase 는 액체적인 성질 외에도 분자쌍극자의 배열에 의한 영향도 고려하였다. *p*-Azoxyanisole의 액체적인 성질은 significant structure theory로 기술하였으며 분자쌍극자 배열에 의한 영향은 Bragg-Williams 근사로써 고려하였다. 부피, 증기압, 정압비열, 열팽창계수, nematic-isotropic 전이점에서의 엔트로피 엔탈피 변화, 절대엔트로피, Helmholtz free energy 등을 계산하여 실험치와 비교하였다.

ABSTRACT. The significant structure theory of liquids and the Bragg-Williams approximation of phase transition theory have been applied to the calculation of the thermodynamic properties of *p*-azoxyanisole which exhibits a liquid crystal phase of the nematic type. The isotropic phase was treated as a normal liquid; and for the nematic phase, in addition to its liquidity, the effect due to the arrangement of molecular-dipoles was considered. The liquidity of the *p*-azoxyanisole was described by the significant structure theory of liquids, and the Bragg-Williams approximation was used to consider the effect due to the arrangement of molecular-dipoles. The molar volume, vapor pressure, heat capacity at constant pressure, thermal expansion coefficient, compressibility, entropy and enthalpy change at the nematic-isotropic phase transition point, absolute entropy, and absolute Helmholtz free energy were calculated over the temperature range of the nematic and isotropic phases. The calculated results of the thermodynamic properties were compared with the experimental data.

1. INTRODUCTION

Liquid crystals have been an object of scientific curiosity because of its wide applicability[1~4] and its abnormal thermodynamic properties.[5~9] In line with the rapid increase in interest for liquid

crystals, a number of experimental studies about the structure and the properties of liquid crystals have been carried out extensively. But according to our historical survey about the theoretical works,[7~13] it has been left as an important problem to predict theoretically the background quantities of the thermodynamic properties(*Fig.* 1), the surface tension, and the transport properties of liquid crystals.

Maier and Saupe[7] and Alben[8] applied a general theory of phase transition described by a long–range order parameter to nematic *p*-azoxyanisole. Chandrasekhar *et al.*[10] obtained the contribution of the disorder part using the extended theory of the two-lattice model of Lennard-Jones and Devonshire. Imura and Okano[12] calculated the excess quantity of the heat capacity and the thermal expansion coefficient due to the order-parameter fluctuation by using the continuum fluctuation theory of de Gennes. Ma and Eyring[13] extended the significant structure theory of liquids to the mesophase system. In their calculations, a few properties were evaluated

Fig. 1. Schematic representation of the background (X_{bgd}) and configurational (X_{conf}) contributions to the thermodynamic properties X of *p*-azoxyanisole.

without introducing order-disorder concepts.

The *p*-azoxyanisole system was chosen in this research because better and sufficient experimental results can be found in the literature. The molecule of *p*-azoxyanisole (PAA; 4, 4′-dimethoxyazoxy-benzene) has a permanent dipole of 2.28 Debye unit[14] and the molecular weight of 258.28. The molecule of crystalline *p*-azoxyanisole consists in the C_{2h}^5 group with four molecules per unit cell.[15] The molecules are fixed in position with the long axes aligned approximately perpendicular to the (100) plane: they form an imbricated structure with the benzene rings of the two neighboring molecules either facing or perpendicular to each other. The CH_3O groups should then be in close contact with the N_2O groups. In the nematic phase, the molecules are no longer rigidly fixed in position. They are still well aligned, but they can rotate more or less freely about their own long axes.[16,17] The nematic range of *p*-azoxyanisole extends from about 391.4 to 408°K.[18~22] In the isotropic liquid phase, all long-range ordering breaks down including the ordering in the molecular alignment.

In this paper, using the basic concepts of the significant structure theory of liquids and the Bragg-Williams approximation of phase transition, the thermodynamic properties of *p*-azoxyanisole are evaluated and the calculated results are compared with the observed values.

2. THEORY

Partition Function of Nematic *p*-Azoxyanisole. According to the density measurement of *p*-azoxyanisole[7,20,22,23] the density change of the nematic-isotropic transition is about 0.36 % whereas the density change at the crystal-nematic phase transition is in the range of 7~11 %. This indicates that the nematic phase has many fluidized vacancies and also that the theory of
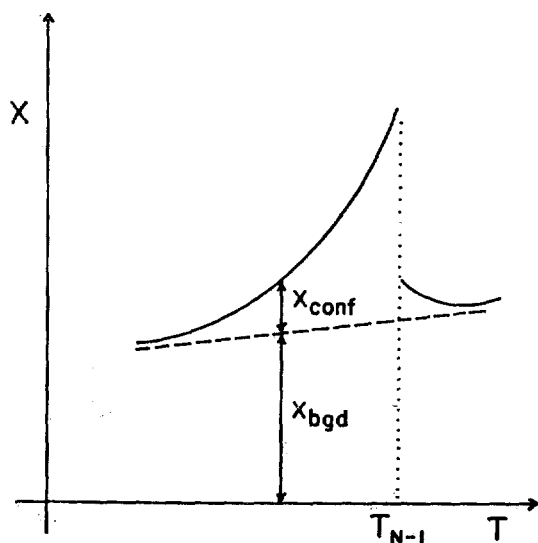
liquids such as the significant structure theory of liquids can be applied to nematic p-azoxyanisole to explain the liquidity of liquid crystal. In spite of increasing the fluidized vacancies, the molecules of nematic p-azoxyanisole are still well aligned along their long axes and have long-range ordering. Therefore, for sufficient understanding of the system of liquid crystal, it is necessary to have other partition function including the term of long-range ordering. So the partition function of nematic p-azoxyanisole can be written as

$$f_{L.C.} = f_{bgd} \cdot f_{conf} \qquad (1)$$

where $f_{L.C.}$ is the partition function of nematic p-azoxyanisole, f_{bgd} is the partition function which is introduced to take into account the aspects of the liquidity of nematic p-azoxyanisole, and f_{conf} is the partition function including the long-range ordering of nematic p-azoxyanisole.

As illustrated in *Fig.* 1, it is reasonable to think that any thermodynamic properties of nematic p-azoxyanisole, X, is given as the sum of two terms, X_{bgd} and X_{conf}. The term X_{bgd}, called background quantity, is the contribution due to the background partition function, f_{bgd}, and the configurational quantity, X_{conf}, is the contribution due to the configurational partition function, f_{conf}.

Using the basic concepts of the significant structure theory of liquids,[24, 26] the background partition function of nematic p-azoxyanisole can be written as:

$$f_{bgd} = \left[\frac{e^{E_s/RT}}{(1-e^{-\theta/T})^5} \left\{ 1 + n\left(\frac{V-V_s}{V_s}\right) \right. \right.$$
$$\left. \cdot \exp\left(-\frac{aE_s V_s}{RT(V-V_s)}\right) \right\}$$
$$\cdot \frac{2\pi(2\pi I_C kT)^{1/2}}{\sigma h} \cdot \frac{kT}{B}\sinh\left(\frac{B}{kT}\right)$$
$$\left. \cdot \prod_{i=1}^{93}(1-e^{-h\nu_i/kT})^{-1} \right]^{NV_s/V}$$

$$\times \left[\frac{(2\pi m kT)^{3/2}}{h^3} \cdot \frac{eV}{N} \right.$$
$$\cdot \frac{8\pi^2(8\pi^3 I_A I_B I_C)^{1/2}(kT)^{3/2}}{\sigma h^3}$$
$$\cdot \frac{kT}{B}\sinh\left(\frac{B}{kT}\right)$$
$$\left. \cdot \prod_{i=1}^{93}(1-e^{-h\nu_i/kT})^{-1} \right]^{N\frac{V-V_s}{V}} \qquad (2)$$

Here, m is the mass of a molecule; R is the gas constant; h is Plank's constant; k is Boltzmann's constant; N is Avogadro's number; e is the base of natural logarithm; σ is the symmetry number; a and n are the dimensionless parameters; B is the interaction parameter; I_A, I_B and I_C are the principal moments of inertia; E_s is the heat of sublimation; θ is the Einstein characteristic temperature; ν_i is the vibrational frequency; V_s is the molar volume of the solid like melecule at the phase transition point; and V is the molar volume of p-azoxyanisole at temperature T in Kelvin degree. In the case of p-azoxyanisole, σ is unity.

The background partition function given in Eq. (2) was formulated readily as follows. In nematic phase, p-azoxyanisole molecule rotates one-dimensionally about its long-axis. But the molecules have permanent dipoles and the dipoles of p-azoxyanisole are well aligned in the z axis. So in a macroscopic view, the molecule looks like as if it were in a field of potential $V(=-B\cos\theta)$ where θ is the angle between the z axis and the molecular dipole. This consideration was introduced to the one-dimensional rotational partition function of the solid-like molecule and to the three-dimensional rotational partition function of the gas-like molecule in the form of $\left(\frac{kT}{B}\right) \cdot \sinh\left(\frac{B}{kT}\right)$.[27] Furthermore, the entropy change of the solid-nematic phase transition is about 18 e.u.[16,18,21] Hence, the degrees of freedom of Einstein oscillators were taken as five.

Nematic p-azoxyanisole obtained from crystal-

line p-azoxyanisole by heating has well aligned molecular arrangement. The order of the arrangement is broken down gradually as the temperature is raised and at the nematic–isotropic transition point the complete disordered state appears. This order–disorder phenomenon can be explained quantitatively by the theory of phase transition such as the Bragg–Williams approximation.[28,29]

Assuming that the dipole of a p-azoxyanisole molecule has only two states of up and down directions, and that all short range order parameters are the same, and neglecting the local statistical fluctuation, the application of the Bragg–Williams approximation to the evaluation of the configurational partition function is straightforward. Then the configurational partition function of nematic p-azoxyanisole for a given Q can be given as following equations.

$$f_{conf} = W(Q) \cdot \exp(-E(Q)/kT) \qquad (3)$$

$$W(Q) = {}_N C_{Na} \cdot {}_N C_{Nb}$$

$$= \left[\frac{N!}{\left(N\frac{1+Q}{2}\right)! \ \left(N\frac{1-Q}{2}\right)!} \right]^2 \qquad (4)$$

$$E(Q) = N_a V_a + N_b V_b$$

$$= N\frac{1+Q}{2}V_a + N\frac{1-Q}{2}V_b$$

$$= \frac{N}{2}(U_0 - V_0 Q^2) \qquad (5)$$

$$Q = \frac{N_a - N_b}{N_a + N_b} \qquad (6)$$

Here Q is the long range order parameter; N_a N_b denote the number of dipoles in the up-direction and down-direction, respectively; W (Q) is the number of possible ways obtaining the $N_a \cdot N_b$ state of the dipoles; $E(Q)$ is the configurational internal energy of the system; V_a and V_b are the potential energy of the up and down directional dipoles, respectively; and U_0 is the energy of the complete disordered state $Q=0$. Equations (3) to (6) were obtained by assuming that there are $2N$ sites for N mo-

lecules and that the relation $V_b - V_a = V_0 Q$ holds where V_0 is a proportionality constant.

Partition Function of Isotropic p-Azoxyanisole. In the isotropic phase of p-azoxyanisole, the ordering in the molecular alignment and all long-range orderings are completely broken down. So there is no contribution from the configurational partition function, f_{conf}, and there is no field interaction effect. Thus the partition function of isotropic liquid of p-azoxyanisole, $f_{I \cdot L \cdot}$, is given by Eq. (7).

$$f_{I \cdot L \cdot} = f'_{bgd} = \left[\frac{e^{E_i/RT}}{(1-e^{-\theta/T})^5} \left\{1 + n\frac{V-V_s}{V_s} \cdot \right. \right.$$

$$\left. \cdot \exp\left(-\frac{aE_s V_s}{RT(V-V_s)}\right) \right\} \cdot \frac{2\pi(2\pi I_C kT)^{1/2}}{h}$$

$$\cdot \prod_{i=1}^{93} (1-e^{-h\nu_i/kT})^{-1} \right]^{NV_s/V}$$

$$\times \left[\frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{eV}{N} \right.$$

$$\cdot \frac{8\pi^2 (8\pi^3 I_A I_B I_C)^{1/2} (kT)^{3/2}}{h^3}$$

$$\left. \cdot \prod_{i=1}^{93} (1-e^{-h\nu_i/kT})^{-1} \right]^{N(V-V_s)/V} \qquad (7)$$

All notations in Eq. (7) have the same meaning as in Eq. (2).

3. CALCULATIONS

All thermodynamic properties of p-azoxyanisole were calculated over the temperature range of anisotropic and isotropic phases using NOVA 840 computer. The partition function is closely related to the Helmholtz free energy, A, such as

$$A = -kT \ln f \qquad (8)$$

The thermodynamic properties of p-azoxyanisole can be deduced with the use of Eq. (8).

In *Table* 1 and 2, the parametric values and other input values for p-azoxyanisole, which are used in the calculation of the background partition function, are given. The parametric values

Table 1. Parametric values for *p*-azoxyanisole used in the calculation of the background partition function.

Phase of PAA	$E,$ (cal/mole)	θ (°K)	$V,$ (cc/mole)	n	$a \times 10^5$	$B \times 10^{13}$ (ergs)
Namatic	22226.2	78.40	218.38	11.840	6.6106	1.4967
Isotropic	22226.2	62.17	222.53	11.831	7.6162	—

Table 2. Vibrational frequencies and the moments of inertia used for *p*-azoxyanisole.

Vibrational frequencies (cm^{-1}) [17]			
210	756	1114	1333
234	797	1143	1370
317	832	1157	1410
360	848	1165	1425
417	911	1171	1438
474	943	1186	1454
494	959	1203	1465
536	1006	1220	1473
611	1013	1246	1501
629	1020	1252	1570
670	1028	1261	1582
717	1078	1276	1596
725	1095	1301	1604
753	1109	1319	1648

Monents of inertia $(g \cdot cm^2)$ [32]
$I_A = 7.50 \times 10^{-37}$
$I_B = 7.06 \times 10^{-37}$
$I_C = 4.71 \times 10^{-38}$

were determined by the Seoul technique;[30,31] and a suitable value which gives good results in the thermodynamic calculations was selected for the interaction parameter, *B*. The order parameter, *Q*, which is used to calculate the configurational partition function of *p*-azoxyanisole is presented in *Table* 3. The equilibrium values of *Q* as a function of temperature were obtained by minimizing the Helmholtz free energy A_{conf} with respect to *Q*, i.e., $(-kT \, \partial \ln f_{conf}/\partial Q) = 0$. This condition can be represented by the following equations:

$$Q = \tanh \left(\frac{V_0 Q}{2kT} \right) \qquad (9)$$

Table 3. Order parameter Q for *p*-azoxyanisole used in the calculation of the configurational partition function.

T(°K)	Q
391.4	1.0000
393.2	0.9476
395.2	0.8853
397.2	0.8177
399.2	0.7433
401.2	0.6598
403.2	0.5633
405.2	0.4454
407.2	0.2801
408.5	0.0000

$$V_0 = 2kT_{N-I} \qquad (10)$$

where $T_{N-I}(=408.5\,°K)$ is the nematic-isotropic transition temperature, and in deriving Eq. (9), the equation (12) which will be given shortly was utilized.

Molar Volume and Vapor Pressure. If the Helmholtz free energy is plotted as a function of volume at constant temperature, and a common tangent to the points corresponding to the liquid and vapor phases is drawn, the vapor pressure is given by the slope of the common tangent, and the abscissas of the two points indicate the respective volume of the liquid and vapor. The resulting values for the molar volume are given in *Table* 4 and those for the vapor pressure are shown in *Fig.* 2. The calculated results give good agreement with the observed values.

Thermal Expansion Coefficient and Compressibility. The thermal expansion coefficient α and compressibility β were calculated by using

Table 4.　Molar volumes of p-azoxyanisole.

T (°K)	V_{obs}[7] (cc/mole)	V_{calc} (cc/mole)	% error
	Nematic	phase	
391. 4	221. 34	221. 34	0
393. 2	221. 72	221. 61	−0. 05
395. 2	222. 08	221. 92	−0. 07
397. 2	222. 44	222. 23	−0. 09
399. 2	222. 81	222. 54	−0. 12
401. 2	223. 19	222. 85	−0. 15
403. 2	223. 60	223. 17	−0. 19
405. 2	224. 05	223. 48	−0. 25
407. 2	224. 51	223. 81	−0. 31
408. 5	224. 91	224. 02	−0. 40
	Isotropic	phase	
408. 5	225. 68	225. 68	0
410. 2	226. 01	225. 93	−0. 04
411. 2	226. 19	226. 08	−0. 05
413. 2	226. 55	226. 37	−0. 08
415. 2	226. 90	226. 67	−0. 10
417. 2	227. 24	226. 96	−0. 12

Table 5. Thermal expansion coefficients of p-azoxyanisole.

T (°K)	α_{obs}[7] $\times 10^4$ (°K⁻¹)	$\alpha_{calc} \times 10^4$ (°K⁻¹)	% error
	nematic	phase	
391. 4	7. 56	7. 24	−4. 23
393. 2	7. 70	7. 09	−7. 92
398. 7	8. 31	··	··
399. 2	··	6. 99	··
401. 2	8. 90	7. 02	−21. 12
403. 2	9. 33	7. 07	−24. 22
405. 2	9. 96	7. 13	−28. 41
407. 2	11. 65	7. 20	−38. 20
408. 5	14	7. 25	−48. 21
	isotropic	phase	
403. 5	··	6. 74	··
410. 2	8. 57	6. 60	−22. 99
411. 2	8. 13	6. 54	−19. 56
413. 2	7. 97	6. 48	−18. 70
415. 2	7. 63	6. 46	−15. 33
417. 2	7. 51	6. 46	−13. 98

Other observed[23] α of p-azoxyanisole.

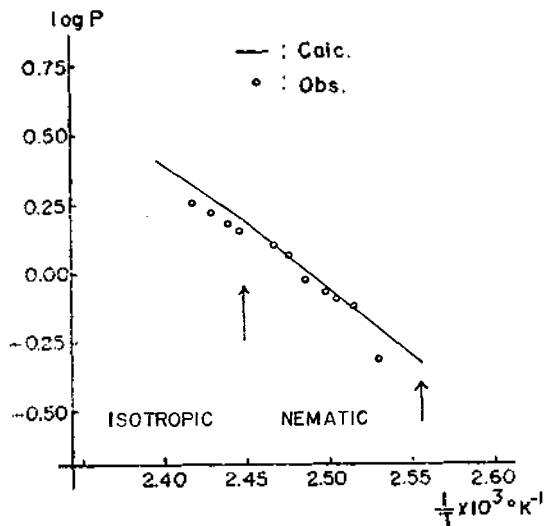|	
Nematic region	: 9. 4×10⁻⁴ °K⁻¹
Isotropic region	: 8. 4×10⁻⁴ °K⁻¹

Fig. 2. Logarithm of p-azoxyanisole vapor pressures vs. reciprocal temperatures. Observed pressures in mmHg were obtained from ref. (33).

the partition function and the equations,

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{V}\ \frac{(\partial P/\partial T)_V}{(\partial P/\partial V)_T}$$

and

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V(\partial P/\partial V)_T}$$

Comparisons between the calculated results with observed values of α and β were given in *Tables* 5 and 6, respectively. There are two different experimental results about the thermal expansion coefficient: one is the λ-type temperature dependence by Maier and Saupe,[7] the other is the linear temperature dependence by Price and Wendorff.[23] Both experimental results were given in *Table* 5 for comparison with the calculated results. The experimental compressibility was obtained from a graph by Alben[8] whose result agreed with that of Hoyer and Nolle.[9] Because the experimental transition temperature from nematic to isotropic phase is 405. 2 °K,

the compressibility was given as a function of $(T-Tr)°K$ where $T_r(\equiv T_{N-I})$ is the nematic-isotropic transition temperature.

Heat Capacity at Constant Pressure. The specific heat of p-azoxyanisole was also calculated by using the partition function and the equations

$$C_P = C_V + (TV\alpha^2)/\beta$$

and

$$C_V = (\partial E/\partial T)_V.$$

The calculated results are summarized in *Table* 7. And the λ-type temperature dependence of p-azoxyanisole is illustrated in *Fig.* 3.

Entropy and Enthalpy Changes at the Nematic-Isotropic Transition The entropy, Helmholtz free energy, internal energy and enthalpy of p-azoxyanisole were calculated by using Eq. (8) in addition with the equations,

$$S = -(\partial A/\partial T)_V$$

and

$$E = A + TS.$$

In the case of nematic p-azoxyanisole, the configurational entropy and Helmholtz free energy are simply given as

$$\begin{aligned} S_{conf} &= k \ln W(Q) \\ &= Nk\{2\ln2 - (1+Q)\ln(1+Q) \\ &\quad - (1-Q)\ln(1-Q)\} \end{aligned} \tag{11}$$

and

$$\begin{aligned} A_{conf} &= \frac{N}{2}\cdot(U_0 - V_0Q^2) \\ &\quad - NkT\{2\ln2 - (1+Q)\ln(1+Q) \\ &\quad - (1-Q)\ln(1-Q)\}. \end{aligned} \tag{12}$$

U_0 was obtained as 1.5×10^{-3} ergs by using the relation of $\Delta H = T\Delta S$ at the namatic-isotropic

Table 6. Compressibilities of p-azoxyanisole.

$T-T_r$ (°K)	$\beta_{obs.}[8] \times 10^{11}$ (cm²/dyne)	$\beta_{calc.} \times 10^{11}$ (cm²/dyne)	% error
−16	‥	7.29	‥
−14	‥	7.26	‥
−12	‥	7.27	‥
−10	‥	7.32	‥
−8	6.82	7.40	+8.50
−7	6.98	7.47	+7.02
−6	7.14	7.52	+5.3
−5	7.34	7.59	+3.41
−4	7.59	7.65	+0.79
−3	7.86	7.72	−1.78
−2	8.27	7.80	−5.68
−1	8.96	7.88	−12.05
−0	9.86	7.95	−19.37
+0	‥	7.35	‥
1	7.25	7.28	+0.41
2	7.11	7.24	+1.83
3	7.05	7.23	+2.55
4	7.00	7.22	+3.14
5	7.00	7.22	+3.14
6	‥	7.23	‥

Table 7. Heat capacities of p-azoxyanisole at constant pressure.

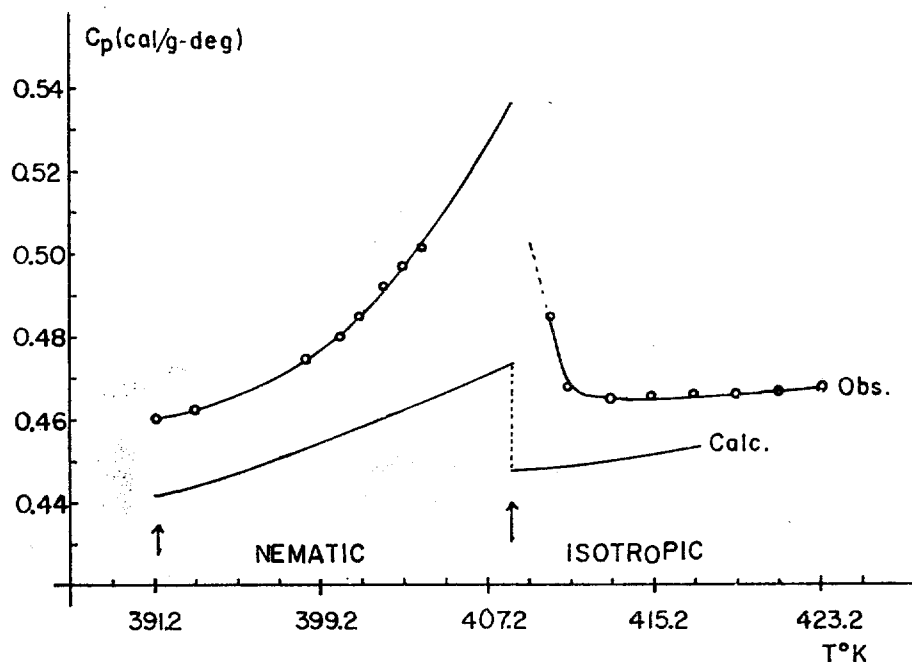| T (°K)	C_p(obs)[5,6] (cal/g-deg)	C_p (calc) (cal/g-deg)	% error
Nematic phase			
391.4	0.4600	0.4420	−3.91
393.2	0.4620	0.4441	−3.87
395.2	‥	0.4471	‥
397.2	‥	0.4506	‥
398.7	0.4740	‥	‥
399.2	‥	0.4543	‥
401.2	0.4842	0.4582	−5.37
403.2	0.4970	0.4622	−7.00
404.2	0.5120	‥	‥
405.2	‥	0.4663	‥
407.2	‥	0.4703	‥
408.5	‥	0.4732	‥
Isotropic phase			
408.5	‥	0.4475	‥
410.2	0.4850	0.4479	−7.65
411.2	0.4680	0.4483	−4.21
413.2	0.4650	0.4495	−3.33
415.2	0.4658	0.4510	−3.18
417.2	0.4660	0.4528	−2.83

Fig. 3.　Heat capacities of p-azoxyanisole at constant pressure as a function of temperature.

Table 8. Calculated absolute values of the entropy, Helmholtz free energy, internal energy, and enthalpy of p-azoxyanisole.

T (°K)	S (cal/mole-°K)	A (cal/mole)	$E \approx H$ (cal/mole)
Nematic phase			
391.4	81.726	−38617.2	−6628.2
393.2	82.739	−38870.9	−6341.4
395.2	83.700	−39098.6	−6020.6
397.2	84.619	−39308.9	−5697.1
399.2	85.507	−39506.8	−5372.9
401.2	86.359	−39698.5	−5052.1
403.2	87.227	−39888.1	−4718.0
405.2	88.065	−40072.4	−4388.4
407.2	88.894	−40247.1	−4049.6
408.5	89.429	−40369.8	−3838.4
Isotropic phase			
408.5	89.758	−40370	−3704
410.2	90.237	−40523	−3508
411.2	90.519	−40613	−3392
413.2	91.080	−40795	−3161
415.2	91.643	−40978	−2928
417.2	92.204	−41162	−2695

Table 9. Entropy and enthalpy changes of p-azoxy-anisole at the nematic-isotropic transition point.

	Calc.	Obs. [16,18]	% error
ΔS(cal/mole-°K)	0.329	0.335	1.79
ΔH(cal/mole)	134.4	137	1.90

transition point (see Discussions). Absolute values of the entropy (S), Helmholtz free energy (A), internal energy (E), and enthalpy (H) of p-azoxyanisole are summarized in *Table* 8. The calculated values of ΔS and ΔH at the nematic-isotropic transition point are compared with the experimental values in *Table* 9. Since the vapor pressure of p-azoxyanisole are very small, E and H have almost same values.

4. DISCUSSIONS

Vibrational Normal Modes. For p-azoxy-

anisole, there are ninety-three vibrational normal modes. Although the observed lines in the Raman Spectra[17] are assumed to be normal modes, there are many missing normal terms. These terms were taken into account as follows:

$$\ln\left(f_{vib}^{M}\right) = -\sum_{i=1}^{m} \ln(1 - e^{-h\nu_i/kT})$$
$$\simeq -m \cdot \ln(1 - e^{-h\nu/kT})$$

where f_{vib}^{M} is the vibrational partition function for the missing terms and m is the number of the missing normal modes. The essence of this consideration is that the missing vibrational frequencies are replaced by the parametric equivalent vibrational frequency. The calculated value of the parametric equivalent vibrational frequency which was determined from the experimental value of C_p at 391.4 °K is 674.4 cm^{-1}.

Parameters used in Calculations. According to the complete Raman spectra[17] of p-azoxyanisole in the three phases, the intermolecular interaction energy in the substance is about 10^{-13} ergs.

We consider why a nematic molecule of p-azoxyanisole has the potential energy of $V = -B \cos \theta$. The interaction energy of the dipole aligned in the Z direction with a dipole in any point is given by[34]

$$V = \frac{\mu_a \mu_b}{r_{ab}^3} \{ -2 \cos \theta_a \cos \theta_b + \sin \theta_a \sin \theta_b \cos(\phi_b - \phi_a) \}$$

where the subscript a indicates the dipole aligned in the z axis, and b expresses the dipole in a point in the space. Thus, the following equation results

$$V = \frac{\mu_a \mu_b}{r_{ab}^3} (-2 \cos \theta_b) = -B \cos \theta$$

According to our results, the value of $B(\simeq 10^{-13})$ is the dipole-dipole interaction energy, and it is about equal to the interaction energy of

oscillators mentioned previously.

The heat of sublimation for benzene is about 11 kcal per mole. On the other side, the sum of the enthalpy changes at the phase transitions of p-azoxyanisole is in the range of 21~26 kcal/mole [cf. ΔH (crystal→nematic)[16,18] = 7.067 kcal/mole; ΔH (nematic→isotropic)[18] = 0.137 kcal/mole; ΔH (isotropic→vapor)[33] = 13.8~18.8 kcal/mole]. From these facts the value of E_s = 2226.2 cal per mole is justified.

The value of n is usually between 10 and 12. Thus, the values of $n = 11.840$ and 11.831 are satisfactory. Although for normal simple liquids, the value of $a \cong 0.0052$[25] is usually found, for water which has composite structure the value of a is 1.653×10^{-5}.[31] Thus, the values of a in *Table* 1 are acceptable.

Usually the θ (Einstein) values for solid-like structures in liquids have been found smaller than the values for the solids. It is, of course, an oversimplification to take the librational frequency equal to the lattice vibrational frequency since the latter frequency is expected to be smaller than the former. According to the Raman spectrum for lattice vibrations of p-azoxyanisole single crystal,[32] the θ value for lattice vibration is running from about 46 to 95 °K. The values of θ in *Table* 1 lie within this range. The tendency that θ for the nematic phase is higher than that for the isotropic phase is justified by the fact that the molecules in the nematic phase have less rotational freedom than those in the isotropic phase.

The values of V_s are to be compared with the experimental values of the molar volume of solid at the crystal-nematic transition point of about 199 to 220 cc/mole.[7,22,23]

Calculations of Configurational Partition Function. The order parameter, Q, at the crystal-nematic transition point was scaled up to unity. According to the original Bragg-Williams approximation, the complete ordered state ($Q =$

1) is occurred at the absolute temperature of zero. But in the case of p-azoxyanisole system, it is reasonable that the order parameter Q, which considers only the orientational order, is scaled up to unity at the crystal-nematic transition point because the orientational order is broken down gradually for the first time only after the crystal-nematic phase transition is occurred.

U_0 in Eqs. (5) and (12), which is necessary to calculate the absolute thermodynamic properties such as the Helmholtz free energy, internal energy and enthalpy, was determined as follows. The entropy, vapor pressure and molar volume can be obtained without the U_0 value [cf. Eq. (11)]. Thus using the relation of $T\Delta S = \Delta H$ all the input values except E_N in Eq. (13),

$$\Delta H(N \to I) = (E_I + P_I V_I) - (E_N + P_N V_N),$$
(13)

can be calculated without U_0. The reasons are as follows: the quantities E_I, P_I and V_I for the isotropic phase can be calculated from Eq. (7), and P_N and V_N for the nematic phase also can be directly obtained from Eq. (2) because Eq. (12) is not a function of volume. Equation (13) is reduced to Eq. (14) using $E_N = E_{bgd} + E_{conf}$ (cf. Fig. 1) and Eq. (5) with $Q=0$.

$$E_{conf} = \frac{R}{2k} \cdot U_0 = E_I + P_I V_I - E_{bgd}$$
$$- P_N V_N - \Delta H(N \to I)$$
(14)

Considerations of the Results. Fig. 2 shows that a little change in the slope of the line (pressure-temperature relation) occurs at the nematic-isotropic transition point. This may be due to the difference between the heat of vaporization of the nematic phase and that of the isotropic phase.

The calculated values of the thermodynamic properties are in good agreement with experimental results. The discrepancy between theoretical

and experimental values is most significant in the vicinity of the anisotropic-isotropic phase transition point. The discrepancies in the molar volume, expansion coefficient and compressibility may arise from the fact that the Bragg-Williams approximation has no volume term which is a function of the order parameter. So the more advanced theory of order-disorder, which considers explicitly the volume term in the order parametric function, is necessary to obtain better predictions at the phase transition. But the discrepancy in the heat capacity may be improved by the application of the other theory of order-disorder such as Kirkwood's method[35] although this method does not also contain the volume term.

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