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NEMATIC ISOTROPIC TRANSITION TEMPERATURE OF BINARY NEMATIC LIQUID CRYSTAL MIXTURES

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Summary

*Using the pseudo potentials proposed by Humphries, James and Luckhurst in a Bethe-Peierls-Weiss cluster approach, the partition functions for a binary mixture of nematic liquid crystals are obtained. By taking the partial derivatives of the logarithms of the partition functions with respect to various parameters, a functional expression for the nematic-isotropic transition temperature is obtained and is used to reconstruct the nematic isotropic phase boundaries of *p*-azoxyanisole (PAA) and *p*-*p'*-di-*n*-hexyloxyazoxybenzene (PHAB) mixtures and of *p*-azoxyanisole and *p*-*p'*-di-*n*-pentyloxyazoxybenzene (PPAB) mixtures.*

Introduction

The thermodynamic properties of binary mixtures of nematic liquid crystals have been studied extensively¹⁻³. However, the development of a theory which could explain some of the observed properties of the binary mixtures has been relatively lacking. The first step in this direction was taken by Chandrasekhar and Madhusudana⁴ who proposed an empirically based relationship between the order parameter of the mixtures and the order parameters of the constituents in the mixtures. One

of the first attempts to formulate a theory was by Humphries, James and Luckhurst⁵. Using Maier-Saupe type dispersive potentials⁶ as the pseudo potentials acting on the different types of nematic molecules in the mixture, they were able to obtain an expression for the Helmholtz free energy. By numerically evaluating the Helmholtz free energy to find the temperature at which the free energy goes to zero, they obtained a set of values for the transition temperatures which appeared to obey the empirical relationship,

$$T_{\text{mix}} = xT_1 + (1 - x)T_2 \quad (1)$$

where x is the mole fraction of the constituent having a transition temperature T_1 and $(1-x)$ is the mole fraction of the constituent with transition temperature T_2 . To be able to obtain numerical values which would fit the above empirical relationship, a "geometric mean approximation" had to be assumed. However, to achieve a fit of some experimental data⁷ to the transition temperatures required for their Helmholtz free energy to go to zero, it was necessary for a derivation from the geometric mean approximation. In other words, the observed transition temperatures⁷ did not follow the linear compositional dependence predicted by Eqn. 1. The linear dependence is only valid when the geometric mean approximation holds.

The purpose of this paper is to derive the compositional dependence of the nematic-isotropic transition temperatures of binary mixtures. It should be pointed out that Humphries *et al.*⁵ were not able to derive any functional relationship between the mixtures' transition temperatures and the transitions of the constituents. The starting point of our approach will be the pseudo potentials proposed by Humphries *et al.*⁵ modified later by Humphries and Luckhurst.⁸ Our method differs from theirs in that we will be using the Bethe-Peierls-Weiss cluster approach⁹ used to investigate ferromagnetism. We will show that the partition functions for the two clusters required in our approach can be expressed in terms of the confluent hypergeometric functions. Then by differentiating the log of the partition functions with respect to certain parameters and imposing some self consistency conditions, we will be able to obtain an expression for the nematic isotropic transition temperature. The Bethe-Peierls-Weiss approach has previously been applied to pure nematic liquid crystals.¹⁰⁻¹² The self consistency conditions imposed by Krieger and James¹⁰ and by Madhusudana and Chandrasekhar¹¹ are different from the ones used in this paper. Our conditions are similar to those used by Ypma and Vertogen¹².

The Partition Functions

We begin by picking out a type 1 and a type 2 nematic crystal molecule located anywhere in the mixtures. These two molecules will now be considered to be the central molecules in two clusters of $z+1$ molecules each. By assuming that the mixture is homogeneous, all other clustering of $z+1$ molecules in the mixture must be the same as one of the two clusters we have just formed. This assumption of homogeneous mixing means that we have not allowed for any compositional fluctuations in our theory. As in the Bethe-Peierls-Weiss approach to magnetism, we shall

assume that the central molecule within each cluster interacts with the other z molecules in the cluster and with an applied external field (a stress field T_0 in our case) while the z surrounding molecules with a mean field which arises from the applied field, the other molecules in the cluster and from other clusters in the mixtures.

We now assume that a type 1 central molecule interacts with its z neighboring nematic molecules through pseudo potential

$$U_1 = (x \frac{\epsilon_{11}}{V} \langle P_2(\cos \theta_1) \rangle + (1-x) \frac{\epsilon_{12}}{V} \langle P_2(\cos \theta_2) \rangle) P_2(\cos \theta_1) \quad (2a)$$

while a type 2 central molecule interacts with its z neighbors through the pseudo potential

$$U_2 = (x \frac{\epsilon_{12}}{V} \langle P_2(\cos \theta_1) \rangle + (1+x) \frac{\epsilon_{22}}{V} \langle P_2(\cos \theta_2) \rangle) P_2(\cos \theta_2) \quad (2b)$$

In the above expressions, the subscripts refer to its being for a type 1 or 2 molecule and $\langle \rangle$ denotes an ensemble average, v is the molar volume of the mixture, and x is the mole fraction of constituent 1 in the mixture. The quantity, ϵ_{12} is proportional to the strength of the dispersive interaction between a type 1 and type 2 molecule. The two other constants ϵ_{11} and ϵ_{22} are proportional to the nematic isotropic transition temperatures of the pure constituent nematic liquid crystals. The development of the above pseudo potentials for the binary mixtures from a general type of interaction between two cylindrical molecules is given in references 5 and 8.

Having said the above, we now write down the partition functions for the two clusters.

$$Z_1 = \int_0^{+1} d(\cos \theta_0^1) \exp[-\beta(T_0 P_2(\cos \theta_0) + U_1)] \left\{ \int_0^{+1} d(\cos \theta_1) \exp[-\beta(B_1 S P_2(\cos \theta_1))] \right\}^{n_1} \\ \times \left\{ \int_0^{+1} d(\cos \theta_1) \exp[-\beta(B_2 S P_2(\cos \theta_1))] \right\}^{n_2} \quad (3a)$$

$$Z_2 = \int_0^{+1} d(\cos \theta_0^2) \exp[-\beta(T_0 P_2(\cos \theta_0) + U_2)] \left\{ \int_0^{+1} d(\cos \theta_1) \exp[-\beta(B_1 S P_2(\cos \theta_1))] \right\}^{n_1} \\ \times \left\{ \int_0^{+1} d(\cos \theta_2) \exp[-\beta(B_2 S P_2(\cos \theta_2))] \right\}^{n_2} \quad (3b)$$

In the above expressions, $\theta_0^{1(2)}$ is the angle between the long axis of the central molecule of the cluster 1 (2) and the applied stress field whose direction picks out the direction of the director of the liquid crystal. As in the Bethe-Peierls-Weiss approach, the applied (stress) field will be set to zero at a later point. S is the mean field (macroscopic order parameter) which will be determined by some self consistency requirements. B_1 and B_2 are constants which indicate how strongly the type 1 and 2 molecules interact with the mean field. n_1 and n_2 are the number of pairwise interaction a central type 1 (2) molecules make with a type 1 surrounding molecule or type 2 molecule.

The evaluation of the integral

$$\int_0^{+1} d(\cos \theta) \exp(-A (\frac{1}{2}(3 \cos^2 \theta - 1))) \tag{4}$$

is carried out by first noting that part of the above expression can be expressed as the probability function $A(x)^{13}$. The probability function $A(x)$ can in turn be expressed as a confluent hypergeometric function ${}_1F_1(\frac{1}{2}, \frac{3}{2}, -\frac{3A}{2})$. By making a Kummer transformation, the function ${}_1F_1(\frac{1}{2}, \frac{3}{2}, -\frac{3A}{2})$ can be expressed in terms of a different confluent hypergeometric function. By the above means, we get

$$\int_0^{+1} d(\cos \theta) \exp(-A (\frac{1}{2}(3 \cos^2 \theta - 1))) = e^{-A} {}_1F_1(1, \frac{3}{2}, \frac{3}{2} A) \tag{5}$$

Thus the partition functions, Eqns. (4a) and (4b), become

$$Z_1 = \exp(-\beta y_1) {}_1F_1(1, \frac{3}{2}, \frac{3}{2} \beta y_1) \left\{ \exp(-\beta B_1 s) {}_1F_1(1, \frac{3}{2}, \frac{3}{2} \beta B_1 s) \right\}^{n_1} \\ \times \left\{ \exp(-\beta B_2 s) {}_1F_1(1, \frac{3}{2}, \frac{3}{2} \beta B_2 s) \right\}^{n_2} \tag{6a}$$

and

$$Z_2 = \exp(-\beta y_2) {}_1F_1(1, \frac{3}{2}, \frac{3}{2} \beta y_2) \left\{ \exp(-\beta B_1 s) {}_1F_1(1, \frac{3}{2}, \frac{3}{2} \beta B_1 s) \right\}^{n_1} \\ \times \left\{ \exp(-\beta B_2 s) {}_1F_1(1, \frac{3}{2}, \frac{3}{2} \beta B_2 s) \right\}^{n_1} \tag{6b}$$

where

$$y_1 = T_0 + x \frac{\epsilon_{11}}{V} \langle P_2(\cos \theta_1) \rangle + (1-x) \frac{\epsilon_{12}}{V} \langle P_2(\cos \theta_2) \rangle \tag{7a}$$

and

$$y_2 = T_0 + x \frac{\epsilon_{12}}{V} \langle P_2(\cos \theta_2) \rangle + (1-x) \frac{\epsilon_{22}}{V} \langle P_2(\cos \theta_2) \rangle \tag{7b}$$

Nematic Isotropic Transition Temperature

The order parameter or degree of ordering in a liquid crystal is defined as the ensemble average of the second Legendre polynomial $P_2(\cos \theta)$ where θ is the angle between the long axis of the molecule and the director which is the average direction of all the molecules. The degree of ordering of a central type 1 molecule in the cluster can be obtained by differentiating the log of the partition function Z_1 with respect to T_0 and then setting $T_0 = 0$, i.e.,

$$S_1 = \langle P_2(\cos \theta_0^1) \rangle = \lim_{T_0 \rightarrow 0} (-kT \frac{\partial \ln Z_1}{\partial T_0}) \tag{8}$$

while the degree of a central type 2 molecule in its cluster can be obtained by differentiating $\ln Z_2$ w.r.t. T_0 and again set $T_0 = 0$ i.e.,

$$S_2 = \langle P_2(\cos \theta_0^2) \rangle = \lim_{T_0 \rightarrow 0} (-kT \frac{\partial \ln Z_2}{\partial T_0}) \quad (9)$$

The self consistency conditions are that the order parameters of the central molecules be the same as the order parameters of the molecules when they are found among the surrounding sites, i.e.,

$$S_1 = \langle P_2(\cos \theta_0^1) \rangle = \langle P_2(\cos \theta_1) \rangle \quad (10)$$

and

$$S_2 = \langle P_2(\cos \theta_0^2) \rangle = \langle P_2(\cos \theta_2) \rangle \quad (11)$$

Eqns. 10 and 11 arise since a surrounding site type 1(2) molecule is the central molecule in a different but identical cluster. As was pointed out in the Introduction, these self consistency conditions are equivalent to those employed by Ypma and Vertogen¹² in their Bethe-Peierls-Weiss treatment of the single constituent liquid crystal.

Performing the differentiation, we get

$$S_1 = 1 - \frac{3}{2} \frac{{}_1F_1^1(1, \frac{3}{2}, X_1)}{{}_1F_1(1, \frac{3}{2}, X_1)} = 1 - \frac{{}_1F_1(2, \frac{5}{2}, X_1)}{{}_1F_1(1, \frac{3}{2}, X_1)} \quad (12)$$

and

$$S_2 = 1 - \frac{3}{2} \frac{{}_1F_1^1(1, \frac{3}{2}, X_2)}{{}_1F_1(1, \frac{3}{2}, X_2)} = 1 - \frac{{}_1F_1(2, \frac{5}{2}, X_1)}{{}_1F_1(1, \frac{3}{2}, X_1)} \quad (13)$$

where

$${}_1F_1^1(a, b, x) = \frac{\partial}{\partial x} {}_1F_1(a, b, x) = \frac{a}{b} {}_1F_1(a+1, b+1, x) \quad (14)$$

and

$$X_1 = \frac{3}{2} \beta (x \frac{\epsilon_{11}}{V} S_1 + (1-x) \frac{\epsilon_{12}}{V} S_2) \quad (15)$$

$$X_2 = \frac{3}{2} \beta (x \frac{\epsilon_{12}}{V} S_1 + (1-x) \frac{\epsilon_{22}}{V} S_2) \quad (16)$$

It should be noted that Eqns. 15 and (16) are just eqns. (7a) and (7b) with $T_0 = 0$ and the self consistency conditions, eqns. (10) and (11), employed. By numerically solving the two simultaneous non linear equations, eqns. (12) and (13), at different temperatures, we would obtain the temperature dependence of the order parameters of a type 1 and type 2 molecule when they are in the mixture.

If we approach the transition from the isotropic side, we can expand the confluent hypergeometric function to get

$$S_1 = -\frac{x}{5k_B T} \frac{\epsilon_{11}}{V} S_1 - \frac{(1-x)}{5k_B T} \frac{\epsilon_{12}}{V} S_2 \tag{17a}$$

$$S_2 = -\frac{x}{5k_B T} \frac{\epsilon_{12}}{V} S_1 - \frac{(1-x)}{5k_B T} \frac{\epsilon_{22}}{V} S_2 \tag{17b}$$

where only the lowest order terms in the expansions were kept. Eqns. (17a) and (17b) yield non zero solutions for S_1 and S_2 only if

$$\det \begin{vmatrix} 5k_B T_m + x \frac{\epsilon_{11}}{V} & (1-x) \frac{\epsilon_{12}}{V} \\ x \frac{\epsilon_{12}}{V} & 5k_B T_m + (1-x) \frac{\epsilon_{22}}{V} \end{vmatrix} = 0 \tag{18}$$

Evaluating the determinant, we get

$$25 T_m^2 + 5 T_m \left(x \frac{\epsilon_{11}}{V} + (1-x) \frac{\epsilon_{22}}{V} \right) + (x(1-x)) \frac{\epsilon_{11}\epsilon_{22} - \epsilon_{12}^2}{V^2} = 0 \tag{19}$$

If T does not satisfy Eqn. 19, then $S_1 = S_2 = 0$ and so the mixture would be in the isotropic phase. At $T = T_m$, non zero values for S_1 and S_2 would be possible and so T_m can be considered as the minimum temperature at which the isotropic phase can exist. To establish the connection between the interaction constants, ϵ_{11} and ϵ_{22} , and the minimum temperatures, T_1 and T_2 , at which the isotropic phase of the two constituents can exist, we note that $T_m = T_1$ for $x = 1$ and $T_m = T_2$ for $x = 0$. This yields

$$\frac{\epsilon_{11}}{k_B T_1 V_1} = 5 \tag{20a}$$

and

$$\frac{\epsilon_{22}}{k_B T_2 V_2} = 5 \tag{20b}$$

Where V_1 and V_2 are the molar volumes of the pure constituent liquid crystals. A similar ratio between the interaction constant and the transition temperature was obtained by Maier and Saupe except for an inverse dependence of the square of the molar volume. Substituting (20a) and (20b) into equation (19), we get for the transition temperature (which we define as the minimum temperature for which the isotropic phase of the liquid crystal can exist)

$$T_m = x \left(\frac{V_1}{V_m} \right) T_1 + (1-x) \left(\frac{V_2}{V_m} \right) T_2 - \frac{x(1-x) T_1 T_2 \left(\frac{V_1 V_2}{V_m^2} \right) - \frac{\epsilon_{12}'}{V_m^2}}{x \left(\frac{V_1}{V_m} \right) T_1 + (1-x) \left(\frac{V_2}{V_m} \right) T_2} \tag{21}$$

where $\epsilon_{12}' = \epsilon_{12}/5$ and V_m is the molar volume of the mixture and for the purpose of a later analysis is taken to be the *measured* molar volume. In Humphries and Luckhurst⁸ expression for the transition temperature, it was assumed that the binary liquid crystals mixtures could be treated as an ideal mixture, i.e., $V_m = xV_1 + (1-x)V_2$. However, recent measurements¹⁴ of the molar volumes of mixtures of p-azoxyanisole

(PAA) and p-p'-di-n-pentyloxyazoxybenzene (PPAB) indicate that these mixtures exhibit a slight excess volume of mixing. Finally we wish to point out that when the geometric mean approximation is valid, Eqn. 12 reduces to the expression obtained by Humphries and Luckhurst⁸.

As a test of our theory, we attempted to fit the experimental data on mixtures of p-azoxyanisole (PAA) and p-p'-di-n-hexyloxyazoxybenzene (PHAB) and mixtures of PPAB and PAA. The nematic isotropic transition temperatures of the PAA-PHAB and the PAA-PPAB mixtures were observed by means of a Reichert heating stage microscope. The molar volumes of the PAA-PHAB mixtures were determined by the standard dilatometric method¹⁵ while the molar volumes of the PAA-PPAB were obtained with the use of an Anton Paar Precision Density Meter, Model DMA 20 D¹⁴. The details of the measurements of the PAA-PHAB will be reported elsewhere¹⁶. The nematic isotropic transition temperatures and molar volumes of the PAA-PHAB mixtures are listed in Table 1, while the relevant data for the PAA-PPAB mixtures are listed in Table 2.

TABLE 1 MOLAR VOLUMES AND NEMATIC ISOTROPIC TRANSITION TEMPERATURE OF PAA-PHAB MIXTURES

Mole Fraction of PAA	Molar Volume (ml/mole)	Transition Temperature (°K)
Pure PAA	224.66	408.3
0.9	243.25	403.5
0.8	260.67	401.5
0.7	278.28	399.3
0.6	295.99	398.8
0.5	314.11	399.0
0.4	332.00	399.8
0.3	350.31	400.0
0.2	368.21	401.5
0.1	386.09	403.5
Pure PHAB	403.98	403.5

TABLE 2 MOLAR VOLUMES AND NEMATIC-ISOTROPIC TRANSITION TEMPERATURE OF PAA PPAB MIXTURES

Mole Fraction of PAA	Molar Volume (ml/mole)	Transition Temperature (°K)
PAA	224.66	408.3
0.9	238.46	402.8
0.82	249.46	397.9
0.20	266.46	394.9
0.58	283.58	393.2
0.50	294.99	397.6
0.42	309.72	392.2
0.30	324.11	392.4
0.20	338.82	393.1
0.10	353.25	394.5
PPAB	368.14	395.9

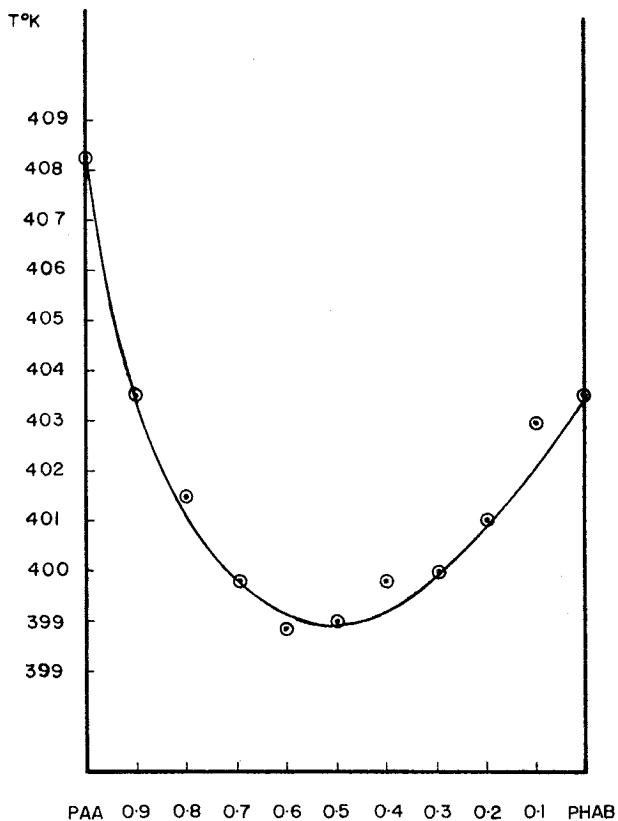


Fig. 1. Nematic-Isotropic phase boundary of PAA-PHAB mixtures. The line indicates the boundary determined by Eqn. (20) using the numerical value $\epsilon_{12}' = 117,648$. The dots are the observed nematic isotropic transition temperature for the PAA-PHAB systems.

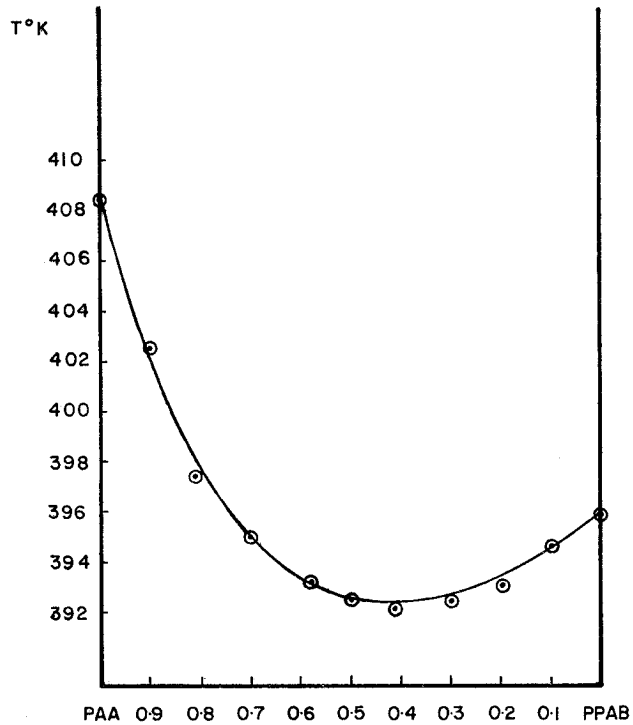


Fig. 2. Nematic-Isotropic phase boundary of PAA-PPAB mixtures. The line indicates the boundary determined by Eqn. (20) using the value $\epsilon_{12}' = 109,451$. The dots are the observed nematic isotropic transition temperatures for the PAA-PPAB mixtures.

A best least square fit of the PAA-PHAB data to Eqn. 21 was achieved with a value $\epsilon_{12}' = 117,648 k_B \text{ ml/mole}$. This represented a deviation of 4% from the geometric mean approximation. This value for ϵ_{12}' was then resubstituted into eqn. (21) to obtain the nematic-isotropic phase boundary for the PAA-PHAB mixtures shown in Figure 1. A similar best least square fit of PAA-PPAB data was achieved with $\epsilon_{12}' = 109,451 k_B \text{ ml/mole}$ which represented a deviation of 5.3% from the geometric mean approximation value for ϵ_{12}' . Using $\epsilon_{12}' = 109,451 k_B \text{ ml/mole}$ in eqn. (21), the nematic isotropic phase boundary for the PAA-PPAB mixtures shown in Figure 2 was obtained. The claimed best least square fit of these same systems by Humphries and Luckhurst⁸ using their approach is misleading since the molar volumes for PPAB and PHAB were calculated on the assumption that the densities for PPAB and PHAB are the same as the density of PAA. Measurements of the densities of PPAB¹⁴ and of PHAB¹⁵ shows that this assumption is wrong.

Conclusion

Our method for determining the minimum temperature at which the isotropic phase can exist by expanding the partition functions in the isotropic side of the nematic-isotropic transition and seeing at what temperature it is possible for non zero values of the two order parameter to exist, is preferable to the method employed by Humphries *et al.*^{5,8}. They defined the transition temperature as being the temperature at which the free energy goes to zero. It has been pointed out in ref. 6, that the nematic isotropic transition in liquid crystal is a first order transition and not a second order transition as would be implied by the free energy being equal to zero at the transition. Our method can also be extended to determine the compositional dependence of the mixtures' order parameter. However, the various hypergeometric functions can not be as easily expanded since the system would have to be on the nematic side of the transition. It would be easy to calculate numerically the resulting equation and will be the subject of a later paper.

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บทคัดย่อ

ใช้วิธีการจับกลุ่มของ Bethe-Peierls-Weiss ที่เสนอแนะโดย Humphries, James และ Luckhurst ในการคิด partition functions สำหรับผลึกเหลวผสมชนิดเนมาติก จำนวนอนุกรมเปลี่ยนแปลงจากเนมาติกเป็นไอโซโทรปิกของระบบ p-azoxyanisole (PAA) + p-p'-di-n-hexyloxyazoxybenzene (PHAB) และระบบ p-azoxyanisole (PAA) + p-p'-di-n-pentyloxyazoxybenzene (PPAB) เปรียบเทียบกับผลงานทดลอง