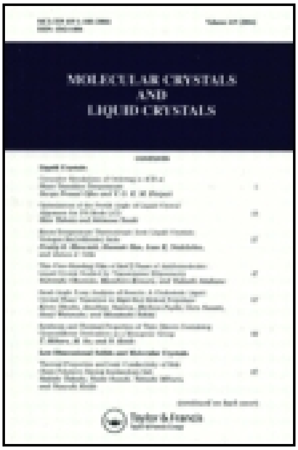

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Liquid Crystalline Properties of Mixtures Composed of *N*-[4-(Dimethylamino)phenyl]- and *N*-(4-Nitrophenyl)-α-(4-alkoxyphenyl)nitrones

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Nematic and smectic liquid crystals induced in binary mixtures of electron donors and acceptors of the type 4-X-C_6H_4-CH=NO-C_6H_4-Y-4 (nitrones) and those of the type 4-X-C_6H_4-CH=N-C_6H_4-Y-4 (Schiff's bases) were compared. The terminal substituent X is a dimethylamino group in the donors and is a nitro group in the acceptors. The other terminal substituent Y is a methoxyl, ethoxyl, propoxyl or butoxyl group. The nematic liquid crystals induced by the compounds of the former type are as stable as those by the compounds of the latter type. Even though a smectic liquid crystal is more often observable when the central linkage is —CH=NO—, its thermal stability is, in general, not much affected by the modification. The following mixtures are exceptional; the donor carrying a butoxyl group with the acceptor carrying a propoxyl or butoxyl group. In these two cases, the maximum temperatures of the smectic liquid crystals induced in the nitrones are lower as much as 35 to 40°C than those induced in the corresponding Schiff's bases.

Keywords: liquid crystals, mixtures, induced nematic phases, induced smectic phases, nitrones, Schiff's bases

INTRODUCTION

Young *et al.* have investigated the mesomorphic behavior of a homologous series of *N*-(4-alkoxyphenyl)-α-anisylnitrones and concluded that the thermal stability of the nematic phase of these compounds and analogous ones is enhanced by the central linkages in this order: —CH═N— < —N═N— < —CH═NO— < —N═NO—.[1] As the data of liquid crystals induced in mixtures of the 4-dimethylamino and 4-nitro derivatives of *N*-benzylideneaniline have been accumulated by the present authors,[2–4] it seemed worthwhile to examine the liquid crystalline properties of mixtures composed of the corresponding nitrones in order to find how large the effects of modification introduced to the central linkage on induced nematic and smectic liquid crystals are.

EXPERIMENTAL

p-Nitroanisole and *p*-nitrophenetole were commercially available. *p*-Propoxy- and *p*-butoxynitrobenzenes were obtained by the alkylation of *p*-nitrophenol following the procedure reported by Gray and Jones.[5] All the nitrones were prepared by the general method described by Young *et al.*[1] *p*-Alkoxynitrobenzene was reduced to the intermediate hydroxylamine with zinc dust and ammonium chloride in aqueous ethanol. To the filtered solution, *p*-(dimethylamino)- or *p*-nitrobenzaldehyde was added and the mixture was left overnight at room temperature. The precipitated nitrone was filtered and recrystallized several times from appropriate solvents. Hereafter, the compound 4-X-C_6H_4-CH═NO-C_6H_4-Y-4 will be denoted by the terminal substituents ⟨X, Y⟩. The following melting points were recorded: 133°C for ⟨Me_2N, MeO⟩, 145°C for ⟨Me_2N, EtO⟩, 120°C for ⟨Me_2N, PrO⟩, 112°C for ⟨Me_2N, BuO⟩, 134°C for ⟨NO_2, MeO⟩, 122°C for ⟨NO_2, EtO⟩, 102°C for ⟨NO_2, PrO⟩, and 72°C for ⟨NO_2, BuO⟩. The *N*-benzylideneanilines (Me_2N, BuO) and (NO_2, BuO) were made by a condensation between a *p*-X-benzaldehyde and *p*-butoxyaniline. The former Schiff's base melts at 113°C and the latter at 79°C. Calorimetric and microscopic studies were carried out as described in our previous papers.[2–4]

RESULTS AND DISCUSSION

The donor ⟨Me_2N, MeO⟩ and the acceptor ⟨NO_2, MeO⟩ form a solid complex possessing a congruent melting point at 135°C. The eutectic points are located at 123°C and 18 mol% and at 120°C and 87 mol% of the acceptor. This is the only system which induces no mesophase among the sixteen combinations composed of the nitrones.

a) Combinations of the methoxy and ethoxy derivatives

As is shown in Figure 1a, a solid complex melting at 112°C is formed when ⟨Me_2N, EtO⟩ is mixed with ⟨NO_2, MeO⟩. The freezing point curve covers only the range from 48 to 66 mol%. We cannot conclude whether the former point is eutectic or peritectic from the diagram. The induced nematic (*N*) phase is metastable and is observable in the range from 20 to 70 mol% of ⟨NO_2, MeO⟩. The transition temperature at the former composition is 104°C and that at the latter 101°C. A broad maximum of 108°C occurs around 50 mol%. It may be worthwhile to add that the phase diagram given by the corresponding Schiff's bases is of the eutectic type.[4]

The ⟨Me_2N, MeO⟩-⟨NO_2, EtO⟩ system forms a metastable *N* phase appearing in the composition range from 40 to 90 mol% (see Figure

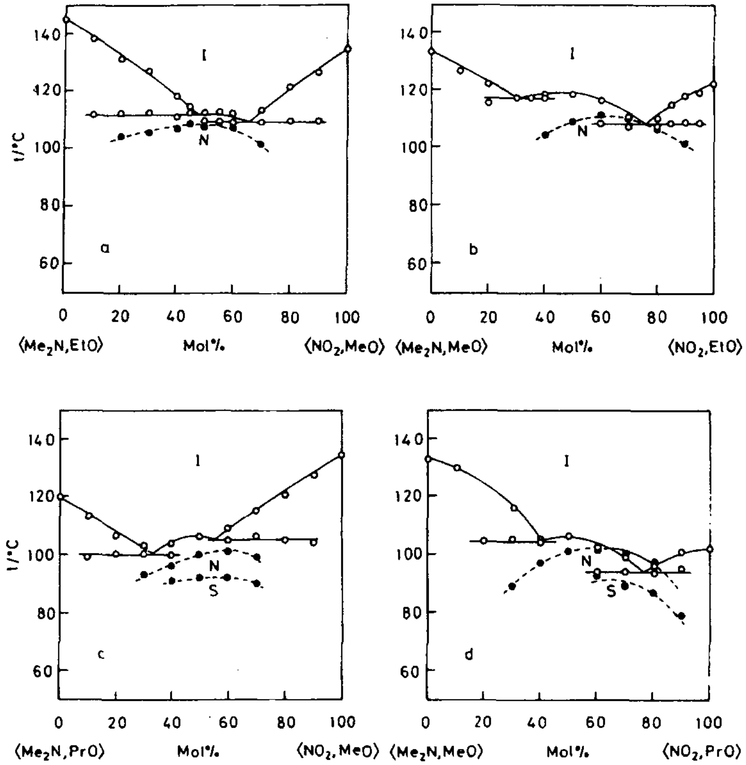

FIGURE 1 Phase diagrams of the nitrone systems, (a) ⟨Me_2N, EtO⟩ – ⟨NO_2, MeO⟩, (b) ⟨Me_2N, MeO⟩ – ⟨NO_2, EtO⟩, (c) ⟨Me_2N, PrO⟩ – ⟨NO_2, MeO⟩, (d) ⟨Me_2N, MeO⟩ – ⟨NO_2, PrO⟩. The open and shaded circles are transitions recorded in the processes of heating and cooling respectively.

1b). The nematic-isotropic (*N-I*) transition point curve reaches its maximum at about 60 mol% and passes through the eutectic located at 108°C and 75 mol%. The solid complex melts at 118°C and shows the other eutectic at 117°C and about 30 mol%. In this case, the diagram is not much affected by the modification introduced to the —CH=N— linkage.

b) Combinations of the methoxy and propoxy derivatives

Figure 1c presents the phase diagram of the ⟨Me_2N, PrO⟩-⟨NO_2, MeO⟩ system. A solid complex melting at 106°C is formed. The freezing point curve starts from 100°C and 33 mol% and ends at 105°C and 56 mol%. An *N* phase is induced in the range from 30 to 70 mol%, the maximum temperature being 101°C. In addition, the smectic-nematic (*S-N*) transition appears in the range between 40 and 70 mol%. The temperatures at these compositions are about 90°C and a broad maximum of 92°C lies around 55 mol%. In contrast, the *S* phase in the Schiff's base mixtures (Me_2N, PrO)-(NO_2, MeO) is detectable only near 80 mol%.

The combination of ⟨Me_2N, MeO⟩ and ⟨NO_2, PrO⟩ yields both an *N* and an *S* phase (see Figure 1d). The eutectic points are at 104°C and 40 mol% and at 94°C and 77 mol%. The melting point of the solid complex is only 2°C higher than the former temperature. The *N-I* transition point curve meets the freezing point curve of the complex at 102°C and 62 mol% and that of the acceptor compound at 97°C and 82 mol%. Therefore, the *N* phase is enantiotropic in the area defined by these intersections and the eutectic on the acceptor-rich side. The *S-N* transition is detected in the range from 60 to 90 mol%. The former point is below the *N-I* transition point by 10°C. The general feature of the above-mentioned two diagrams given by the nitrones is in close resemblance to that by the corresponding Schiff's bases, but the solid complexes in the former diagrams are thermally less stable than those in the latter.

c) Combination of the ethoxy derivatives

The phase diagram illustrated in Figure 2a is very similar to that produced by the Schiff's bases, (Me_2N, EtO) and (NO_2, EtO). The melting point of the solid 1:1 complex is 126°C and essentially agrees with that given by the Schiff's bases. Although the region of the existence of this complex, 45 mol%, is narrower compared with 50 mol% found in the (Me_2N, EtO)-(NO_2, EtO) system, the thermal behavior of the induced *N* phase is almost identical. The *N-I* transition

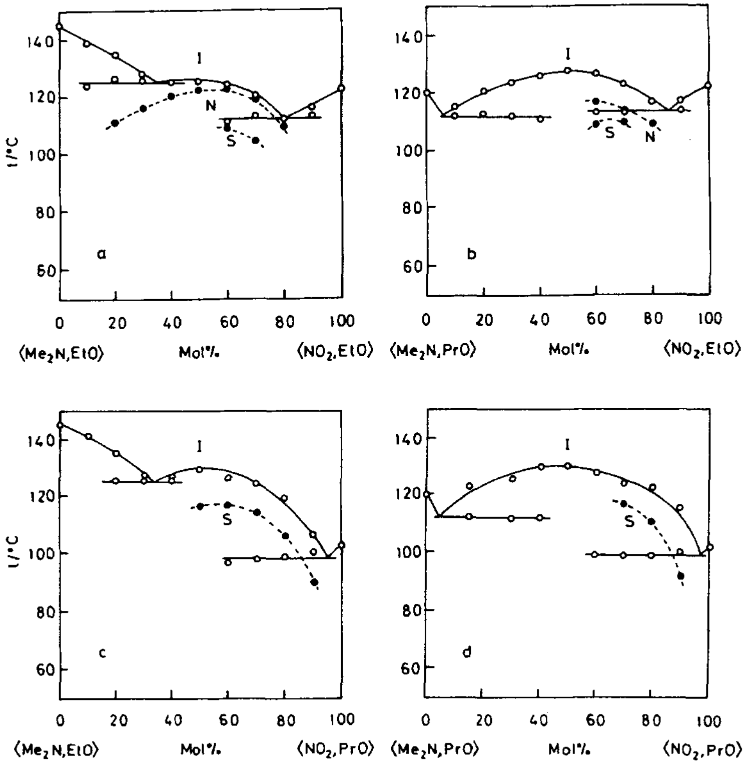

FIGURE 2 Phase diagrams of the nitrone systems, (a) ⟨Me_2N, EtO⟩ – ⟨NO_2, EtO⟩, (b) ⟨Me_2N, PrO⟩ – ⟨NO_2, EtO⟩, (c) ⟨Me_2N, EtO⟩ – ⟨NO_2, PrO⟩, (d) ⟨Me_2N, PrO⟩ – ⟨NO_2, PrO⟩. As to the open and shaded circles, see the caption of Figure 1.

point curve is found at 111°C and 20 mol%, passes through the maximum at 123°C and around 55 mol% and reaches 109°C at 80 mol%. Nonetheless, there is one remarkable difference between the two; namely, an *S* phase is detected at 109°C and 60 mol% and at 104°C and 70 mol% with the nitrones but not with the Schiff's bases.

d) Combinations of the ethoxy and propoxy derivatives

As is shown in Figure 2b, the ⟨Me_2N, PrO⟩ – ⟨NO_2, EtO⟩ system produces a solid complex melting at 128°C. Its range of the existence is as wide as 80 mol%. The appearance of a metastable *N* phase is noted in the range from 60 to 80 mol% and that of an *S* phase from 60 to 70 mol%. The upper limit of the former mesophase is at 117°C and 60 mol% and that of the latter at 110°C and around 65 mol%. The thermal behavior of these liquid crystals differs from that appearing in mixtures of the related Schiff's bases; that is, the *S* phase in the latter system is relatively more stabilized and the supercooled isotropic liquid at 60 mol% is directly transformed into the *S* phase.

The phase diagram of the system composed of ⟨Me_2N, EtO⟩ and ⟨NO_2, PrO⟩ in Figure 2c closely resembles the diagram of the corresponding Schiff's base system.[4] The *S* phase appears in the range from 50 to 90 mol% and the maximum temperature is 116°C.

e) Combination of the propoxy derivatives

As is shown in Figure 2d, a solid 1:1 complex dominates the phase diagram of this binary system. The freezing point curve covers a range over 90 mol%. The melting point is 130°C. An *S* phase is observable in the range from 70 to 90 mol%, the temperature at the former composition being 117°C. Contrary to the present system, no mesophase is detectable when the Schiff's bases, (Me_2N, PrO) and (NO_2, PrO) are employed.[2,3]

f) Combinations of the methoxy and butoxy derivatives

The donor compound ⟨Me_2N, BuO⟩ is monotropically nematogenic and gives a solid complex of low thermal stability when it is mixed with ⟨NO_2, MeO⟩ (see Figure 3a). The complex melts at 104°C and produces eutectic points at 18 and 58 mol%. The *N-I* transition point curve intersects the freezing point curve of the donor at 101°C and 13 mol% and that of the acceptor at 105°C and 60 mol%. The diagram of the Schiff's base system to be compared with this is presented in Figure 3c. The existence of the solid complex here is less significant and gives a peritectic near 50 mol%. The eutectic point on the donor-rich side is located at about 33 mol%; therefore, the region of stable existence of the induced *N* phase is reduced by a factor of about two.

The nitrones ⟨Me_2N, MeO⟩ and ⟨NO_2, BuO⟩ and the Schiff's bases (Me_2N, MeO) and (NO_2, BuO) yield the diagrams shown in Figures 3b and 3d respectively. The maximum temperature of the *N-I* transition point curve is about 110°C and that of the *S-N* transition point curve is 95°C in these systems; however, the stability of the solid complex is markedly affected by the change in the central linkage. The complex given by the nitrones melts at a temperature about 10°C lower than that by the Schiff's bases. Consequently, the induced *S* phase in the former system can be enantiotropic in some composition range, whereas the same phase in the latter is entirely monotropic. Furthermore, the stable *N* phase induced by the nitrones occupies a much larger area in the diagram. It may be added that the Schiff's base (Me_2N, BuO) exhibits an *N-I* transition at 97°C.

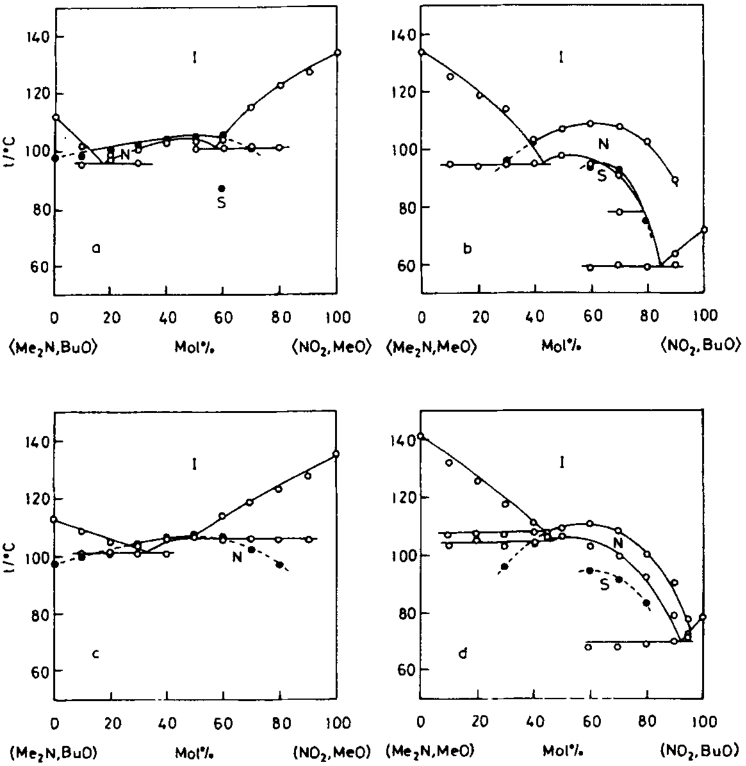

FIGURE 3 Phase diagrams of the nitrone systems, (a) ⟨Me_2N, BuO⟩ – ⟨NO_2, MeO⟩, (b) ⟨Me_2N, MeO⟩ – ⟨NO_2, BuO⟩, and of the Schiff's base systems, (c) (Me_2N, BuO) – (NO_2, MeO), (d) (Me_2N, MeO) – (NO_2, BuO). As to the open and shaded circles, see the caption of Figure 1.

g) Combinations of the ethoxy and butoxy derivatives

Figure 4a presents the phase diagram of the ⟨Me_2N, BuO⟩ – ⟨NO_2, EtO⟩ system. Both the induced *N* and *S* phases are monotropic. The maximum temperature of the former phase is 120°C and that of the latter is 118°C. The Schiff's bases carrying the same terminal groups give the diagram shown in Figure 4c. The solid complex, the *N* phase and the *S* phase in this diagram are thermally more stable, but only by a few degrees, than those in Figure 4a.

When the alkoxyl groups on the component molecules are exchanged, the diagrams presented in Figures 4b and 4d are obtained. While the eutectic temperatures and the melting points of solid complexes in these two systems differ by 6 to 7°C from each other, the stabilities of the mesophases are almost the same. As a result, the *N* phase induced in the nitrone system can be stable over a composition

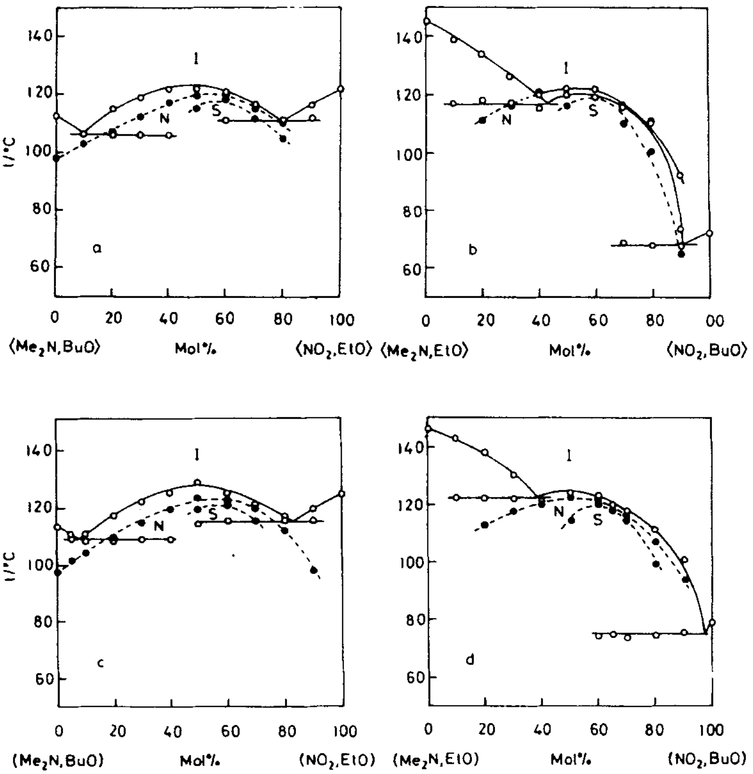

FIGURE 4 Phase diagrams of the nitrone systems, (a) ⟨Me_2N, BuO⟩ – ⟨NO_2, EtO⟩, (b) ⟨Me_2N, EtO⟩ – ⟨NO_2, BuO⟩, and of the Schiff's base systems, (c) (Me_2N, BuO) – (NO_2, EtO), (d) (Me_2N, EtO) – (NO_2, BuO). As to the open and shaded circles, see the caption of Figure 1.

range as wide as 50 mol% but merely in a temperature range of several degrees. On the other hand, the *N-I* transition point curve given by the Schiff's bases is located wholly beneath the freezing point curve of the solid complex. It must be noted that the maximum of the *S-N* transition point curve is within a few degrees of the *N-I* transition point curve in all the systems presented in Figure 4.

h) Combinations of the propoxy and butoxy derivatives

An *N* phase originates at 0 mol% and reaches 90 mol% in the ⟨Me_2N, BuO⟩ – ⟨NO_2, PrO⟩ system and seems to be enantiotropic around 60 mol%, at this composition the transition temperature being 123°C (see Figure 5a). The induced *S* phase observed only at 70 and 80

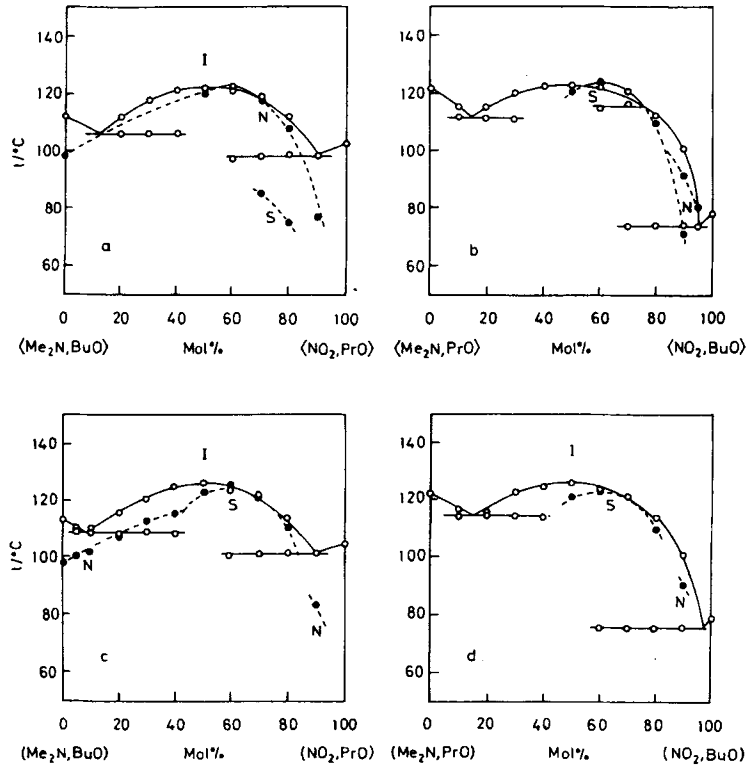

FIGURE 5 Phase diagrams of the nitrone systems, (a) ⟨Me$_2$N, BuO⟩ – ⟨NO$_2$, PrO⟩, (b) ⟨Me$_2$N, PrO⟩ – ⟨NO$_2$, BuO⟩, and of the Schiff's base systems, (c) (Me$_2$N, BuO) – (NO$_2$, PrO), (d) (Me$_2$N, PrO) – (NO$_2$, BuO). As to the open and shaded circles, see the caption of Figure 1.

mol% is located far below the *N-I* transition temperature. The corresponding Schiff's bases produce a diagram strikingly different from that given by the nitrones. The induced *S* phase is more stabilized than the *N* phase in the composition range from 43 to 88 mol%. The *N* phase is found on the both sides of this range. The maximum of the *S-I* transition point curve lies at 125°C and 60 mol% and that of the *N-I* transition point curve at 116°C and the intersection with the former curve.

The combination of ⟨Me$_2$N, PrO⟩ and ⟨NO$_2$, BuO⟩ yields an *S* phase more stable than the *N* phase (see Figure 5b). The latter phase can be seen in the acceptor-rich region only. The *S* phase is enantiotropic in the range from 55 to 75 mol% of ⟨NO$_2$, BuO⟩. The intersection between the *S-I* transition point curve and the freezing point curve of the solid complex is clearly evidenced by the horizontal line at 116°C. This is the only nitrone system which shows such a remarkable thermal enhancement of the induced *S* phase. The solid complex formed by the Schiff's bases shown in Figure 5d melts at 127°C. This temperature is a little higher than the melting point of the nitrone complex and the *S* phase induced in this system is entirely metastable. Otherwise, the diagram resembles that given by the nitrones. The *N*-*I* transition is observable at 90 mol%.

i) Combination of the butoxy derivatives

As is shown in Figure 6a, the thermal stability of the *S* phase formed by the nitrones is much lower than that of the *N* phase. Nevertheless, not only the *N* phase but also the *S* phase can exist stably. The *N*-*I* transition point curve meets the freezing point curve of the solid complex near the melting point of 124°C and then reaches its maximum of 127°C at 60 mol%. The *S*-*N* transition point curve intersects the freezing point curve of the solid complex at 85°C and 78 mol% and that of the acceptor compound at 72°C and 90 mol%. The eutectic located between these intersections lies at 70°C and 80 mol%. On the other hand, the *S* phase given by the corresponding Schiff's bases is more stabilized than the *N* phase in the range from 45 to 72 mol% as is presented in Figure 6b. The difference in the thermal enhancement of the *N* phase is insignificant between these two mixtures.

j) General remarks

The mesophases induced in the nitrone systems are summarized in Table I together with those in the corresponding Schiff's base systems. The parentheses mean that the phase is metastable. The symbol *N* for the nematic phase and *S* for the smectic phase are followed by the maximum temperatures when they are observable. The following tendencies may be noted:

1. The maximum temperatures of the *N* phases induced in the nitrone systems are close to those induced in the Schiff's base systems. When the donor is ⟨Me_2N, BuO⟩, the temperature increases monotonously with an increase of the alkoxyl chain length in the acceptor. However, such a tendency is not observed with the donor carrying a shorter alkoxyl group.

2. The maximum temperatures of the *S* phases induced in the nitrone systems are also similar to those induced in the Schiff's base

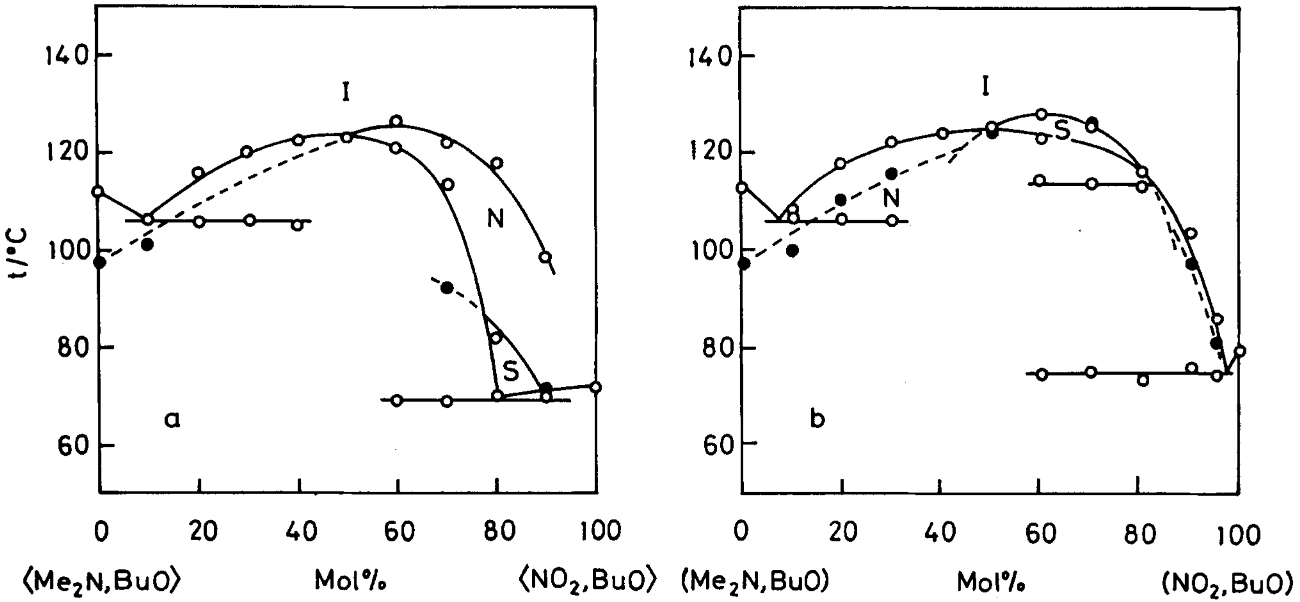

FIGURE 6 Phase diagrams of (a) the nitrone system, ⟨Me_2N, BuO⟩ – ⟨NO_2, BuO⟩, and of (b) the Schiff's base system, (Me_2N, BuO) – (NO_2, BuO). As to the open and shaded circles, see the caption of Figure 1.

TABLE I

Liquid crystals induced in the donor-acceptor systems and their maximum temperatures in °C

a. Nitrones

Donor Acceptor	⟨Me$_2$N, MeO⟩		⟨Me$_2$N, EtO⟩		⟨Me$_2$N, PrO⟩		⟨Me$_2$N, BuO⟩	
⟨NO$_2$, MeO⟩			(*N*)^a	108	(*N*)	101	*N*	105
					(*S*)	92	(*S*)	—
⟨NO$_2$, EtO⟩	(*N*)	111	(*N*)	123	(*N*)	117	(*N*)	120
			(*S*)	—	(*S*)	110	(*S*)	118
⟨NO$_2$, PrO⟩	*N*	102					*N*	123
	(*S*)	93	(*S*)	116	(*S*)	—	(*S*)	—
⟨NO$_2$, BuO⟩	*N*	110	*N*	122	(*N*)	—	*N*	127
	S	95	(*S*)	119	*S*	124	*S*	—

b. Schiff's bases

Donor Acceptor	(Me$_2$N, MeO)		(Me$_2$N, EtO)		(Me$_2$N, PrO)		(Me$_2$N, BuO)	
(NO$_2$, MeO)			(*N*)	108	(*N*)	102	*N*	107
					(*S*)	93		
(NO$_2$, EtO)	(*N*)	110	(*N*)	123	(*N*)	—	(*N*)	123
					(*S*)	118	(*S*)	120
(NO$_2$, PrO)	(*N*)	101					(*N*)	—
	(*S*)	92	(*S*)	119			(*S*)	124
(NO$_2$, BuO)	*N*	111	(*N*)	123	(*N*)	—	(*N*)	—
	(*S*)	95	(*S*)	120	(*S*)	125	(*S*)	128

^{a}Phases in parentheses are metastable.

systems, but the following three systems are exceptional: ⟨Me$_2$N, PrO⟩ – ⟨NO$_2$, EtO⟩, ⟨Me$_2$N, BuO⟩ – ⟨NO$_2$, PrO⟩, and ⟨Me$_2$N, BuO⟩ – ⟨NO$_2$, BuO⟩. The *S* phases induced in these mixtures are significantly less stable than those induced in the Schiff's base mixtures.

3. Nonetheless, the modification of the central linkage gives rise to the appearance of an *S* phase in the three systems; namely, ⟨Me$_2$N, EtO⟩ – ⟨NO$_2$, EtO⟩, ⟨Me$_2$N, PrO⟩ – ⟨NO$_2$, PrO⟩, and ⟨Me$_2$N, BuO⟩ – ⟨NO$_2$, MeO⟩.

In summary, the effects of central linkage on induced liquid crystals in binary mixtures are not straightforward and no simple conclusion can be reached from our results concerning the order of induction efficiency of the present central linkages, —CH=N— and —CH=NO—.

Acknowledgment

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