DISCUSSION

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A mesophase is a state intermediate between an ordered solid crystal on the one hand and an isotropic liquid on the other, exhibiting properties which are unique by themselves. Some notable properties of solid crystals and true liquids show a remarkable degree of coexistence in this intermediate state of the mesomorphic substances. This coexistence of crystalline and liquid properties in a mesophase is attributed to certain structural characteristics of the molecules and the significant play of internal forces arising therefrom. In a nematic liquid crystal the molecules are long and rod-shaped, having more or less translational freedom but only a restricted rotational freedom. It has a domain structure in which all the molecules in the given domain lie parallel to one another.

Any other substance, when dissolved in such a nematic liquid, will be in an anisotropic environment causing to more or less extent a kind of readjustment of the molecules in the given domain. It is not surprising that both its physical and chemical properties are considerably affected in such a medium, depending upon the structure of the molecules. In such cases mixed liquid crystals will be formed over a range of temperature and concentration. Binary mixtures of certain compounds which are non-liquid crystalline substances by themselves, also exhibit

mesomorphism over a range of temperature and concentration. Thus the binary systems exhibiting mixed liquid crystallinity are divided into three types :

1. Systems where both the components are liquid crystalline substances,
2. Systems where one component is a mesomorphic substance and the other a non-liquid crystal and
3. Systems where both the components are non-liquid crystalline substances.

A number of binary systems of the types mentioned above have been studied during the course of this investigation and these are listed in Table 70.

Table 70

Binary systems of the type 1, where both the components are liquid crystals by themselves.

1. p-Azoxyanisole : p-Acetoxybenzal-p-anisidine.
2. p-Azoxyanisole : p-Acetoxybenzal-p-phenetidine.
3. p-Acetoxybenzal-p-phenetidine : p-Acetoxybenzal-p-anisidine.

Binary systems of the type 2, where one component is a liquid crystal by itself and the other a non-liquid crystal.

Component A p-Azoxyanisole (a liquid crystal)

mixed with

Component B (A non-liquid crystal)

4. p-Dimethylaminobenzal-p-anisidine.
5. p-Chlorobenzal-p-phenetidine.
6. p-Dimethylaminobenzal-p-phenetidine.
7. p-Nitrobenzal-p-chloroaniline.
8. p-Anisal-p-phenetidine.
9. p-Nitrobenzal-p-phenetidine.
10. p-Nitrobenzal-p-dimethylaminoaniline.
11. p-Dimethylaminobenzal-p-nitroaniline.
12. p-Dimethylaminobenzal-p-dimethylaminoaniline.
13. p-Hydroxybenzal-p-toluidine.
14. p-Hydroxybenzal-p-anisidine.
15. p-Hydroxybenzal-p-phenetidine.
16. p-Dimethylaminobenzal-p-toluidine.
17. p-Dimethylaminobenzal-p-bromoaniline.
18. p-Chlorobenzal-p-dimethylaminoaniline.
19. Benzal-p-phenetidine.
20. p-Hydroxybenzal-aniline.
21. p-Hydroxybenzal-p-chloroaniline.
22. p-Hydroxybenzal-p-bromoaniline.
23. p-Nitrobenzal-aniline.
24. p-Anisal-aniline.
25. p-Anisal-p-iodoaniline.
26. p-Dimethylaminobenzal-p-iodoaniline.

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MIXED MESOMORPHISM

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NATIONAL ACADEMY OF SCIENCES, INDIA
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MIXED MESOMORPHISM

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ABSTRACT

A number of binary systems have been investigated with *p*-azoxyanisole as a liquid crystalline component and another arbitrary normal solute. It is observed that (i) mixed liquid crystals will always be formed over a certain minimum area irrespective of the shape, size and structure of the solute molecules, (ii) dissimilarity in the molecules of the two components causes a difficulty in the packing of the molecules together resulting into a concavity of the transition lines which increases to a minimum with increased mesomorphic tendency of the non-liquid crystalline component and (iii) contribution of the central group towards the mesomorphic tendency of the non-liquid crystalline component seems to be negligible.

A nematic liquid crystal is a system of domain structure in which rod-shaped molecules having translational freedom but restricted rotational freedom, lie parallel in a given domain. Another substance dissolved in such a liquid would be in an anisotropic environment and it would affect the properties of the mesomorphic substance in an interesting manner; the orientation of molecules in a mesomorphic substance will be affected to a more or less extent depending upon the similarity of structure of the dissolved solute. Similar to the depression in melting points by the presence of a foreign substance, the transition points also undergo a depression, the extent of which, depends upon the concentration of another substance mixed with the mesomorphic compound and differs from solute to solute. It is known that on dissolution of another substance in a mesomorphic substance, mixed liquid crystals are formed and as the phenomenon of liquid crystallinity is called mesomorphism, this may be called 'mixed mesomorphism'. Such binary systems of mixed mesomorphism may conveniently be divided into three types viz. (1) where both the components are mesomorphic substances, (2) where one component exhibits mesomorphism and the other is a non-liquid crystal and (3) where both the components are non-liquid crystalline compounds.

A number of binary systems of the types mentioned above were studied by Prins[1], Bogojawlensky and Winogradov[2], de Kock[3], Walter[4] and others. A more systematic study in recent times, of the second type of binary systems was done by Dave and Dewar[5,6] who observed very steep transition lines in such systems wherein *p*-azoxyanisole was mixed with substances which should have less tendency to form liquid crystals on fusion. It has also been observed that the transition lines of binary systems, the admixed molecules of which are of dissimilar shape and size have a tendency to show a concavity. During the course of our investigation we have studied the binary systems listed in table 1, comprising of *p*-azoxyanisole as a liquid crystalline component and another arbitrary non-liquid crystalline substance.

The melting points and the transition points alongwith the eutectics of these binary systems are recorded in tables 2 and 3. Values for the slopes of the transition lines of these systems are given in table 4.

TABLE 1

Component A.—*p*-azoxyanisole (a liquid crystal) Mixed with Component B	M. P. °C.
1. Succinic acid	184·0
2. α-Naphthol	94·0
3. β-Naphthol	123·0
4. Benzoic acid	122·0
5. *o*-Hydroxybenzoic acid	159·0
6. *p* Hydroxybenzoic acid	213·0
7. *p*-Chlorobenzoic acid	236·0
8. *p*-Toluic acid	179·0

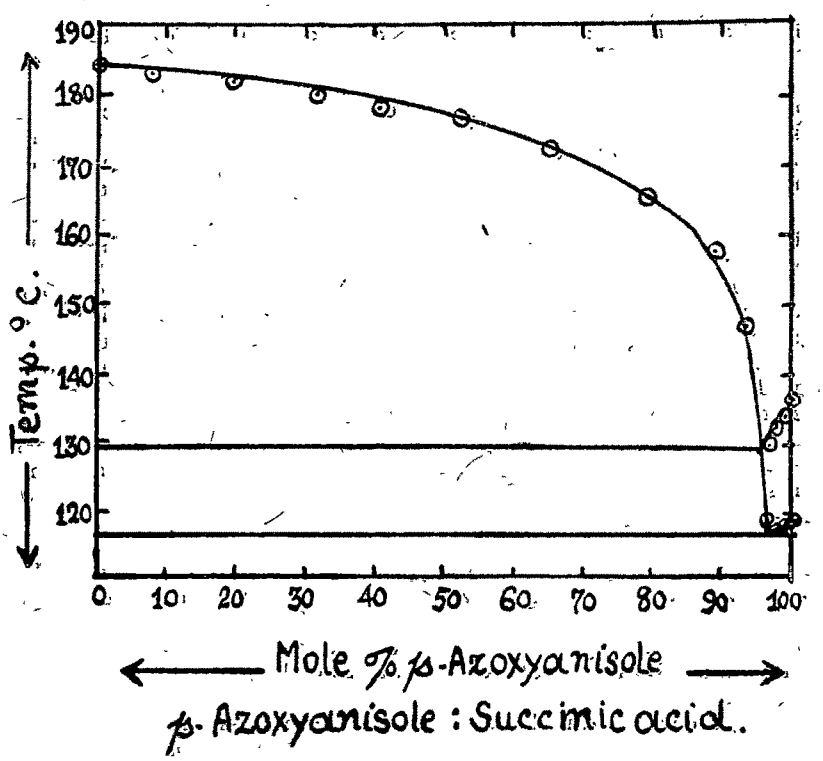

Fig. 1

It can be seen that in the case of system no. 1 (fig. 1), where the non-liquid crystalline component is succinic acid, mixed liquid crystals are certainly

TABLE 2

Solid-liquid transition temperatures for binary systems. The eutectic temperatures and m. p. s. of pure components are direct experimental values : the other temperatures are read from the phase diagrams

	Mole % of component A											Eutectics	
No.	0	10	20	30	40	50	60	70	80	90	100	Mole % A	Temp. °C
1.	184·0	183·1	182·4	181·2	179·5	177·5	174·7	170·8	165·2	154·6	118·0	97·0	116 5
2.	94·0	86·7	78·2	66·4	73·8	86·3	96·1	104·0	110·6	115·4	118·0	33·5	60·0
3.	123·0	115·3	106·4	95·5	80·7	89·7	98·0	105·2	111·0	115·5	118·0	39·0	79·8
4.	122·0	115·0	107·7	100·0	94·5	100·8	105·6	109·5	112·7	115·5	118·0	38·2	93·1
5.	159·0	152·5	145·6	138·3	130·5	121·7	111·3	107·4	112·2	115·6	118·0	65·5	104·0
6.	213·0	206·4	199·8	192·7	185·3	177·3	167·5	155·7	138·8	106·0	118·0	88·5	115·0
7.	236·0	228·2	220·2	212·0	203·3	194·2	184·0	171·6	154·2	127·5	118·0	91·5	115·0
8.	179·0	171·0	162·9	154·7	146·0	136·8	126·8	114·6	111·8	114·8	118·0	73·5	109·5

TABLE 3

Amorphous liquid-liquid crystal transition temperatures.
The values are read from phase diagrams

	Mole % of component A																Triple points	
No.	0	10	20	30	40	50	60	70	80	85	90	93	95	97	99	100	Mole % A	Temp. °C
1.	...	...	...	...	...	...	...	...	...	...	...	...	...	130·0	134·6	136·0	96·5	129·5
2.	...	...	...	...	...	...	...	...	...	...	...	...	120·5	126·7	133·2	136·0	93·5	116·5
3.	...	...	...	...	...	...	...	...	....	...	...	117·3	123·1	128·0	134·0	136·0	92·5	116·0
4.	...	...	...	...	...	...	...	...	...	..	...	120·4	124·8	129·7	134·1	136·0	91·0	115·8
5.	...	...	...	...	...	...	...	...	...	...	...	117·6	123·3	128·5	134·0	136·0	92·5	116·0
6.	...	..	...	...	...	...	...	...	...	...	117·7	123·0	126·6	130·4	134·0	136·0	88·5	115·5
7.	...	...	...	...	...	...	...	...	...	...	...	124·0	126·5	129·8	134·2	136·0	91·0	122·0
8.	...	...	...	...	...	...	...	...	113·5	116·3	120·7	124·4	126·9	130·5	133·3	136·0	72·5	110·5

formed, but only up to 3·5 mole per cent of succinic acid. Any further addition of succinic acid disturbs the specific orientation of molecules in the mesophase resulting in the complete disappearance of the birefringence. Succinic acid is an aliphatic compound and hence without any benzene rings, at least two of which are considered to be the minimum basic structural requirement of mesomorphism in most of the liquid crystalline substances. However, the disturbing effect caused by succinic acid is limited to a certain minimum. Similarly, α-naphthol and β-naphthol with two benzene rings but much dissimilar in shape and size to *p*-azoxyanisole, have less tendency to form liquid crystals, as is evident from the slopes of the transition lines given in table 4. Even then, mixed mesomorphism is observed up to 6·5 and 7·5 mole per cent of the two naphthols respectively. This indicates that whatever be the structure of the solute molecules and howsoever they may differ in shape and size in relation to the solvent mesomorphic substance, there is a certain mimimum limit of distrubance by the solute molecules resulting in a certain minimum area of mixed mesomorphism; in other words, there will always be a minimum certain limit over which mixed liquid crystals will be formed whatever be the shape, size and structure of the solute molecules.

Value for the slope of the transition line in the case of β-naphthol is rather less than that in the case of α-naphthol, indicating a slightly greater tendency of β-naphthol towards mesomorphism than α-naphthol.

Systems 4 to 8 consist of benzoic acids as non-liquid crystalline components. These acids on dimerisation, form linear molecules with two benzene rings, a condition contributory to liquid crystal formation. In a binary system of mixed liquid crystals the nematic-isotropic transition line is a criterion of the liquid crystalline tendency of the non-liquid crystal component. The values of the slopes of the transition lines given in table 4 decrease with the increasing polarity of the end

TABLE 4

No.	Substance	Slope of the transition lines (°C/mole %) ×10
1.	Succinic acid	20·5
2.	α-Naphthol	31·0
3.	β-Naphthol	26·5
4.	Benzoic acid	22·5
5.	*o*-Hydroxybenzoic acid	27·0
6.	*p*-Hydroxybenzoic acid	18·0
7.	*p*-Chlorobenzoic acid	15·5
8.	*p*-Toluic acid	15·0

groups. Higher the polarity of the end groups, greater is the tendency for liquid crystal formation of the non-liquid crystal component. It can be seen that the value of the ortho-hydroxy substituted acid departs a good deal from that of the

corresponding *p*-hydroxy compound. Gray and Jones[7] have observed that in a linear nematic liquid crystal, increase in the breadth of a molecule tends to decrease or even destroy mesomorphism. OH group in the ortho position will increase the breadth of the acid molecule and hence will show a lesser tendency towards liquid crystallinity compared to the *p*-hydroxy benzoic acid.

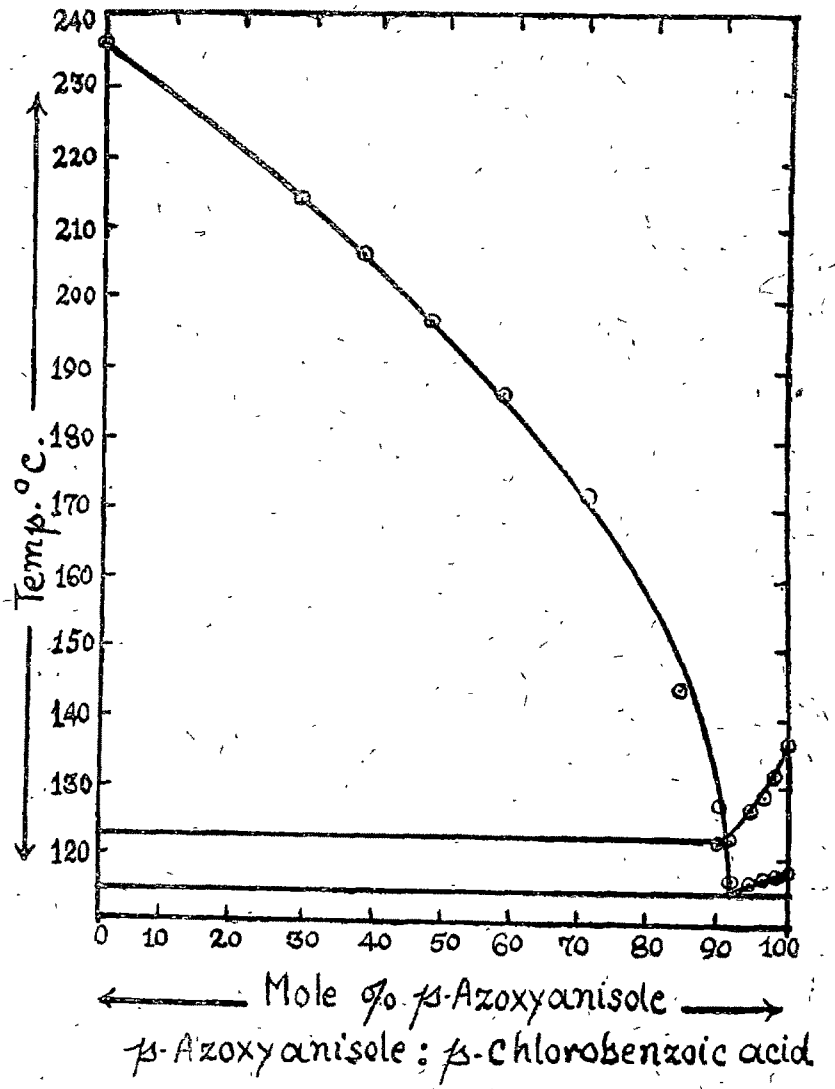

Fig. 2.

A reference to the graphs (figs. 2 and 3) shows that *p*-chloro and *p*-methyl substituted benzoic acids exhibit a concavity in their transition lines. This should

be expected when the molecules of the two components differ in shape and size, due to the difficulty in packing together of the molecules. This concavity should increase and exhibit a minimum in the transition line with the increased mesomorphic tendency of the non-liquid crystal component, which increases with increased polarity of the end groups. Such a minimum in transition line has been observed by Dave and Dewar[6] in the case of the system *p*-azoxyanisole: anisic acid and by de Kock[3] in the system *p*-azoxyanisole: *p*-methoxy cinnamic acid. Our observation in the case of the system *p*-azoxyanisole: *p*-ethoxybenzoic acid is a similar one. This behaviour should be attributed to the dissimilarity in the shapes of the molecules of the two components.

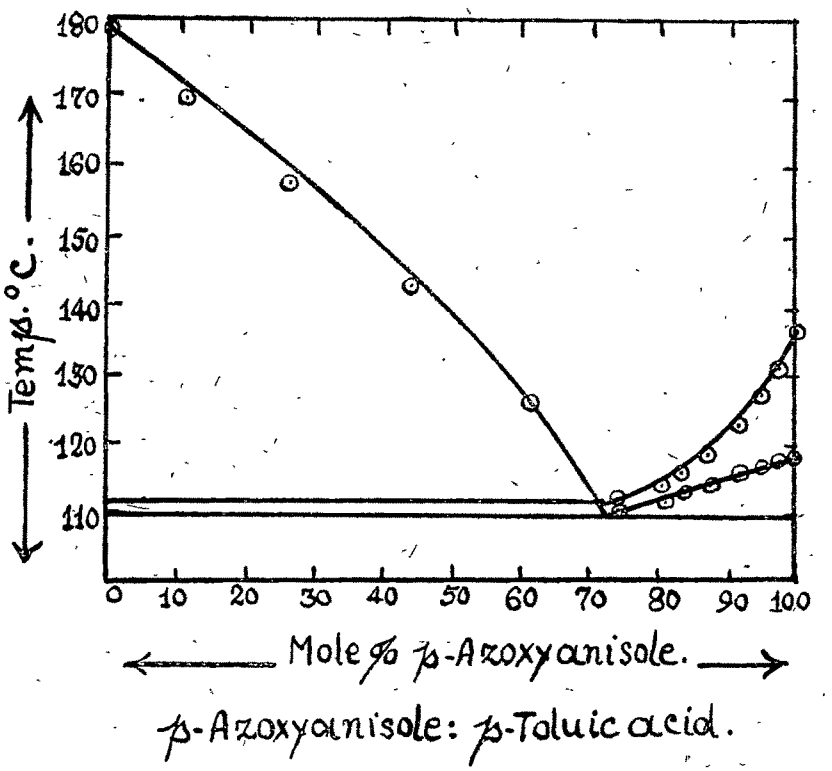

Fig. 3

p-Chlorobenzoic acid and *p*-toluic acid on dimerisation will possess Cl, Cl and CH_3, CH_3 as terminal groups and —C(=O..H–O)(O–H..O=)C— as the central group. Dave and Dewar[6] studied the systems *p*-azoxyanisole: *p*-chlorobenzal-*p*-chloroaniline and *p*-azoxyanisole: *p*-tolual-*p*-toluidine, where the schiff's bases have the same Cl, Cl and CH_3, CH_3 end groups but a different central -CH:N-group; they obtained the

values for the slopes of the transition lines as 14·5 for both the systems. A reference to table 4 shows that the systems *p*-azoxyanisole: *p*-chlorobenzoic acid and *p*-azoxyanisole: *p*-toluic acid give comparable values for the slopes of the transition lines. This indicates that in mixed liquid crystal formation, compared to the effect of the end groxps, the effect of the central group is either very small or negligible.

EXPERIMENTAL

Purification of the substances :

p-Azoxyonisole was purified by repeated crystallization from alcohol to fine yellow needles. The other non-liquid crystalline substances also wero purified by repeated crystallization from suitable solvents like water or dilute alcohol to very fine crystals which melted sharply at their melting points given in literature.

Method of study :

The phase diagrams are studied by the optical method[5].

SUMMARY

1. Mixed liquid crystals will always be formed over a certain minimum area whatever be the shape, size and structure of the admixed non-liquid crystalline molecules.
2. In mixed liquid crystal formation, whenever the molecules of the components depart from similarity, the transition lines exhibit a concavity which increases to a minimum with increased liquid crystalline tendency of the non-liquid crystalline component.
3. In mixed mesomorphism the effect of the central group of the non-liquid crystalline component seems to be small or negligible.

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LIQUID CRYSTALLINITY IN SCHIFF'S BASES

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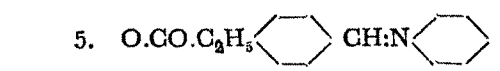
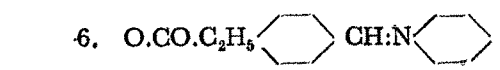
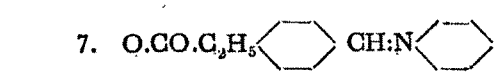
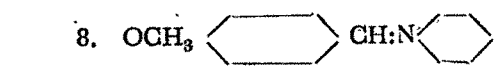
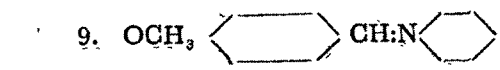
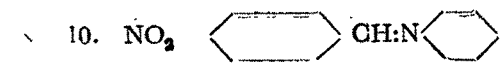
No.	Schiff's base	M.P.°C	T.P.°C
5.		101·5	(66·4)
6.		94·4	(78·3)
7.		95·0	106·4
8.		128·3	(121·5)
9.		147·0	..
10.		123·5	..

A study of Table 1 clearly shows that Nos. 1, 2, 9, and 10 are non-liquid crystalline Schiff's bases ; Nos. 5, 6 and 8 are monotropic liquid crystalline Schiff's bases, the isotropic-nematic transition points of which are shown in brackets while Nos. 3, 4 and 7 are enantiotropic liquid crystalline Schiff's bases. In the case of No. 3 the transition pionts given in the literature[3] are 112°-128°C, but we find that it definitely melts to a nematic liquid at 112°C, and on further heating it transforms to an isotrpic liquid at 119°C; the change from isotropic to nematic (anisotropic) liquid on cooling is also sharp and takes place at 119°C exactly. In the case of compound No. 4 not only there is a higher transition point, but it also possesses a longer phase length. The compound No. 7, *viz.* p-propionoxybenzal-p-anisidine also posssesses a greater phase length than the corresponding acetoxy compound No. 3. This can be attributed to the polarity of the groups present in these compounds. It is interesting to note that the p-acetoxybenzal-p-toluidine and p-acetoxybenzal-p-chloroaniline (Nos. 1 and 2) are not only non-liquidcrystalline, but do not exhibit even mono-tropic liquid crystallinity, while the p-propionoxybenzal-p-toluidine and p-propionoxybenzal-p-chloroaniline (Nos. 5 and 6) are both monotropic liquid crystals. This may probably be ascribed to the length and polarity of the propionoxy group compared to that of the acetoxy group.

It should, however, be mentioned that p-anisal-p-phenetidine (No. 8) is a monotropic liquid crystal[4] while both p-anisal-p-anisidine (No. 9) and p-nitrobenzal-p-phentidine (No. 10) are non-liquid crystalline Schiff's bases[5-7], although p-nitrobenzal-p-phenetidine has a lower melting point and possesses a more polar NO_2 group. It seems, therefore, that the liquid crystallinity in monotropic systems may also depend on other factors like the supercooling and the cryslallising tendencies of the compounds.

Binary mixtures of some of the schiff's bases with another liquid crystalline substance *viz.* p-azoxyanisole have been studied, and in tables 2 and 3 are recorded the graphical observations of the study.

The slope of the curve of the transition lines in the case of schiff's bases listed above are given in Table No. 4.

TABLE 2

Solid-liquid transition temperature for the binary system. The eutectic temperatures and m. p. s. of pure components are direct experimental values ; the other temperatures are read from the phase diagrams

S. No.	Mole % p-Azoxyanisole (A)											Eutectic	
	0	10	20	30	40	50	60	70	80	90	100	Mole % A	Temp.
1	99·0	94·5	89·5	83·8	85·2	92·5	99·5	105·5	110·3	114·5	118.0	34·5	80·8
2	110·0	106·2	101·2	94·5	87·5	91·7	98·6	105·0	110·5	115·0	118·0	42·0	86·2
5	101·5	97·0	92·2	86·7	86·1	93·8	99·7	105·1	109·5	113·7	118·0	36·0	83·0
6	94·5	90·1	85·5	80·0	84·0	91·1	97·6	103·5	108·8	113·8	118·0	33·2	77·8
8	128·3	123·5	118·5	112·9	106·5	99·0	98·5	104·5	109·5	114·5	118·0	54·5	95·0
9	147·0	143·0	138·5	132·8	126·5	120·0	112·0	105·8	109·5	114·1	118·0	70·5	105·0[8]
10	123·5	117·5	112·5	107·0	102·0	96·1	95·0	101·5	107·6	113·4	118·0	57·0	93·5

TABLE 3

Isottopic-liquid-nematic liquid transition temperatures. The values are read from phase diagrams

S. No.	Mole % p-Azoxyanisole (A)													Triple-point	
	0	10	20	30	40	50	60	70	75	80	85	90	95	100	Mole %A	Temp.
1	..	..	(69 0)	(74·2)	(80·2)	(87·7)	(96·0)	(105·3)	110·0	115·1	120·3	125·5	130·6	136·0	70·5	105·7
2	..	..	..	..	..	..	(98·3)	107·0	111·7	117·0	121·2	126·0	131·0	136·0	63·0	100·7
5	(66·4)	(68·0)	(70·8)	(75·0)	(81·5)	(98·8)	(96·5)	(104·0)	109·0	114·5	120·0	125·5	130·7	136·0	72·1	106·5
6	(78·3)	(78·5)	(79·8)	82·8	87·0	92·5	99·5	107·7	112·2	117·0	121·5	126·0	131·0	136·0	27·0	81·6
8	(121·5)	(120·4)	120·7	121·5	122·5	123·6	125·0	127·1	128·0	129·5	131·0	132·5	134·1	136·0	16·0	102·5
9	..	..	..	..	..	..	119·9	124·0	125·6	128·4	130·0	131·5	133·2	136·0	55·5	116·5[8]
10	..	..	..	115·2	121·0	125·4	128·6	131·0	132·2	133·1	134·0	134·5	135·4	136·0	23·3	110·5

TABLE 4

S. No.	Schiff's bases	Slope of the curve
1	$O.CO.CH_3.C_6H_4.CH : N.C_6H_4.CH_3$	10·4
2	$O.CO.CH_3.C_6H_4.CH : N.C_6H_4.Cl$	10·1
5	$O.CO.C_2H_5.C_6H_4.CH : N.C_6H_4CH_3$	9·8
6	$O.CO.C_2H_5.C_6H_4.CH : N.C_6H_4.Cl$	9·5
8	$OCH_3\ C_6H_4.CH : N.C_6H_4.OC_2H_5$	3·2
9	$OCH_3.C_6H_4.CH : N.C_6H_4.OCH_3$	4·0
10	$NO_2.C_6H_4.CH : N.C_6H_4,OC_2H_5$	1·5

The slope of the curve of the transition line stands as a measure[7] of the tendency for liquid crystal formation. Further, it has been shown that the group values of the slope of the transition lines are approximately additive and that the values for different end groups can be deduced therefrom. The effect of the central group is either very small or negligible. The table No. 5 gives the values of the end groups arranged in the order of their magnitude.

TABLE 5

OC_2H_5	>	OCH_3	>	$OCO.C_2H_5$	>	$OCO.CH_3$	>	CH_3	=	Cl
1·0		2·0		2·4		3·05		7·2		7·2

It should be mentioned here that while the slopes of the curve for the groups OCH_3,$OCO.CH_3$ and $OCO.C_2H_5$ are almost near each other, the p-anisal-p-anisidine (No. 9) is not a liquid crystal[7] while both p-acetoxybenzal-p-anisidine (No. 3) and p-propionoxybenzal-p-anisidine (No. 7) are genuine enantiotropic liquid crystals This may probably be due to the lower melting points and the length of the corresponding p-acetoxy and p-propionoxy derivatives as compared to the p-anisal derivative.

EXPERIMENTAL

Preparation and purification of the schiff's bases.—The schiff's bases are prepared by heating equimolar quantities of the corresponding aromatic aldehydes and amines for an hour or two, and recrystallizing the crude product from ethyl-alcohol nto fine crystals which melt sharply. The acetoxy and propionoxy derivatievs were prepared from the corresponding aldehydes which in turn were prepared from p-hydroxybenzaldehyde by condensing with the respective acid anhydride for two three hours,and distilling the product under vacuum.[9]

p-Acetoxybenzal-p-anisidine, Found N-5·295 %, requires 5·204%, $C_{16}H_{15}O_3N$.

Method of study.—The phase diagrams areu stdiede by the optical method.[8]

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RMATION OF MIXED LIQUID CRYSTALS MIXTURES OF SCHIFF'S BASES: AN EXPLANATION

By J. S. Dave and J. M. Lohar

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Byron and Gray[1] studied the isotropic-nematic ısition temperatures for four mixtures of the two iff's bases, *p*-anisal-*p*-phenetidine and *p*-nitro-zal-*p*-phenetidine, over the range of mole per .. composition from 67·5 to 100 of the *p*-nitrobenzal ivative by supercooling the melts and thus suggest wer extrapolated value than indicated by our ata[2] for the "ısotropic-nematic" transition for the ure *p*-nitrobenzal-*p*-phenetidine. We did not study his as we were only interested in the range over which ntiotropic mixed liquid crystals were formed. We have now examined six different mixtures of the two Schiff's bases beyond 67·5 mole per cent. composition of the *p*-nitrobenzal derivative for their isotropic-nematic transitions and thus the extrapolated value for the "isotropic-nematic" transition for the pure *p*-nitrobenzal-*p*-phenetidine now comes to about 84°C.; however it should be noted that the melts of the mixtures beyond 89 mole per cent. composition of *p*-nitrobenzal-*p*-phenetidine crystallised before the monotropic mesophase could be observed. Evidently in agreement with Byron and Gray,[1] *p*-nitrobenzal-*p*-phenetidine is not liquid crystalline in either a monotropic or an enantiotropic sense.

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2 *ibid.*, 1959, 597

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