# *Mixed Liquid Crystals. Part II.* The Effect of Structure on the Transition Temperatures of Mixed Liquid Crystals.*

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Continuing an earlier investigation * we have studied additional binary systems in which one component can itself form liquid crystals. Conclusions are drawn concerning the relation between chemical structure and ability to form liquid crystals, and the shapes of the transition lines in the phase diagrams are discussed.

Earlier * we described a study of several binary systems in which one component (*p*-azoxyanisole) can exist in a nematic liquid-crystalline form. We have now examined a number of additional systems with the object of obtaining information about the factors that control liquid-crystal formation. As in the systems studied previously, the birefringent two-component liquids obtained invariably behaved as single phases, and the transitions to and from normal liquid were sharp. The phase diagrams were of the types previously reported.

## Experimental

*Preparation and Purification of Materials.*—p-*Bromo*-N-4-*methylbenzylideneaniline*. Equimolecular proportions of *p*-tolualdehyde and *p*-bromaniline were heated slowly in a little alcohol until the mixture boiled; the residue, on cooling, was crystallised several times from alcohol, forming colourless plates, m. p. 133° (Found: C, 61·5; H, 4·6; N, 5·2; Br, 28·9. $C_{14}H_{12}NBr$ requires C, 61·3; H, 4·4; N, 5·1; Br, 29·2%).

*N*-*p*-Anisylidene-*p*-dimethylaminoaniline (m. p. 146°), *N*-*p*-nitrobenzylidene-*p*-toluidine (m. p. 124°), *N*-4-nitrobenzylidene-*p*-anisidine (m. p. 136°), *p*-dimethylamino-*N*-4-nitrobenzylideneaniline (m. p. 220°), *N*-4-chlorobenzylidene-*p*-toluidine (m. p. 128°), *p*-chloro-*N*-4-chlorobenzylideneaniline (m. p. 112°), *p*-dimethylamino-*N*-4-methylbenzylideneaniline (m. p. 146°), *N*-4-methylbenzylidene-*p*-toluidine (m. p. 93·5°), *N*-4-methylbenzylideneaniline (m. p. 45°), *N*-benzylidene-*p*-anisidine (m. p. 71°), *N*-benzylidene-*p*-dimethylaminoaniline (m. p. 101°),

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* Part I, *J.*, 1954, 4616.

and *N*-benzylideneaniline (m. p. 53°) were prepared and purified likewise; their m. p.s agree with those recorded in the literature. The purification of the remaining materials was described in Part I.

*Phase Diagrams.*—These were studied as described previously; the optical method was used throughout, but the regions of special interest, in particular those near the solid–liquid–liquid-crystal triple point, were also studied in detail by the thermal method. The system *p*-azoxyanisole–*p*-dimethylamino-*N*-4-nitrobenzylideneaniline could not be studied by our optical method at high concentrations of the latter since it is so highly coloured.

The results are shown in Tables 1, 2, and 3.

TABLE 1. *Systems studied (component A stated first).*

| System no. | Components |
|---|---|
| 1 | *p*-Anisic acid (A) with : |
| | Cinnamic acid |
| 2 | *p*-MeO·C$_6$H$_4$·CH:N·C$_6$H$_4$·OMe-*p* (A) with : |
| | *p*-MeO·C$_6$H$_4$·CH:N·C$_6$H$_4$Me-*p* |
| | *p*-Azoxyphenetole (A) with : |
| 4 | 4 : 4′-Dichloroazoxybenzene |
| 28 | *β*-Naphthylamine |
| | *p*-Azoxyanisole (A) with : |
| 3 | 4 : 4′-Dichloroazoxybenzene |
| 5 | *p*-MeO·C$_6$H$_4$·CH:N·C$_6$H$_4$·NMe$_2$-*p* |
| 6 | 4-NO$_2$·C$_6$H$_4$·CH:N·C$_6$H$_4$Me-*p* |
| 7 | 4-NO$_2$·C$_6$H$_4$·CH:N·C$_6$H$_4$·OMe-*p* |
| 8 | 4-Me·C$_6$H$_4$·CH:N·C$_6$H$_4$·NMe$_2$-*p* |
| 9 | 4-Me·C$_6$H$_4$·CH:N·C$_6$H$_4$·OMe-*p* |
| 10 | *p*-MeO·C$_6$H$_4$·CH:N·C$_6$H$_4$Me-*p* |

| System no. | Components |
|---|---|
| | *p*-Azoxyanisole (A) with : |
| 11 | 4-Me·C$_6$H$_4$·CH:N·C$_6$H$_4$Me-*p* |
| 12 | 4-NO$_2$·C$_6$H$_4$·CH:N·C$_6$H$_4$·NMe$_2$-*p* |
| 13 | 4-Cl·C$_6$H$_4$·CH:N·C$_6$H$_4$·OMe-*p* |
| 14 | *p*-MeO·C$_6$H$_4$·CH:N·C$_6$H$_4$Cl-*p* |
| 15 | 4-Cl·C$_6$H$_4$·CH:N·C$_6$H$_4$Me-*p* |
| 16 | 4-Cl·C$_6$H$_4$·CH:N·C$_6$H$_4$Cl-*p* |
| 17 | 4-Me·C$_6$H$_4$·CH:N·C$_6$H$_4$Br-*p* |
| 18 | Ph·CH:N·C$_6$H$_4$·OMe-*p* |
| 19 | 4-Me·C$_6$H$_4$·CH:NPh |
| 20 | Ph·CH:N·C$_6$H$_4$·NMe$_2$-*p* |
| 21 | Ph·CH:NPh |
| 22 | Azobenzene |
| 23 | Azoxybenzene |
| 24 | Cinnamic acid |
| 25 | Acetanilide |
| 26 | *α*-Naphthylamine |
| 27 | *β*-Naphthylamine |

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 were read from the phase diagrams.*

| System no. | Mol. % of component A (see Table 1) | | | | | | | | | | | Eutectic | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 | A (mol. %) | Temp. |
| 1 | 133·0° | 128·2° | 120·6° | 117·7° | 132·8° | 143·8° | 153·0° | 161·3° | 169·0° | 176·5° | 183·8° | 27·8 | 113·0° |
| 2 | 91·7 | 90·0 | 91·0 | 104·2 | 113·2 | 120·4 | 126·5 | 132·0 | 137·2 | 142·2 | 147·0 | 17·8 | 86·5 |
| 3 | 157·5 | 150·5 | 143·5 | 136·2 | 128·8 | 121·0 | 112·7 | 103·5 | 108·3 | 113·0 | 118·0 | 70·0 | 103·5 |
| 4 | 157·5 | 150·6 | 143·6 | 136·5 | 129·1 | 121·0 | 112·5 | 119·0 | 125·1 | 131·2 | 137·0 | 60·0 | 112·5 |
| 5 | 145·5 | 140·0 | 134·1 | 128·0 | 121·8 | 115·5 | 108·5 | 100·8 | 102·3 | 111·0 | 118·0 | 74·5 | 97·0 |
| 6 | 124·0 | 118·3 | 112·3 | 106·0 | 99·0 | 91·0 | 94·5 | 101·2 | 107·2 | 112·8 | 118·0 | 52·5 | 89·0 |
| 7 | 135·7 | 130·0 | 123·8 | 117·1 | 109·5 | 100·8 | 95·0 | 101·2 | 107·2 | 112·8 | 118·0 | 57·0 | 93·0 |
| 8 | 146·3 | 140·5 | 134·5 | 128·5 | 121·8 | 114·0 | 105·2 | 104·3 | 110·0 | 113·3 | 118·0 | 66·5 | 97·5 |
| 9 | 87·5 | 82·5 | 75·8 | 77·1 | 86·4 | 93·7 | 99·0 | 103·2 | 108·0 | 112·8 | 118·0 | 25·0 | 72·0 |
| 10 | 92·0 | 89·2 | 83·8 | 76·8 | 86·0 | 93·6 | 99·0 | 103·0 | 107·4 | 112·4 | 118·0 | 29·8 | 76·5 |
| 11 | 92·8 | 87·8 | 81·8 | 75·0 | 86·3 | 94·0 | 99·7 | 104·5 | 109·0 | 113·2 | 118·0 | 30·0 | 75·0 |
| 12 | — | — | — | — | — | — | — | — | 112·5 | 113·0 | 118·0 | — | — |
| 13 | 124·0 | 118·7 | 112·5 | 105·8 | 98·7 | 91·5 | 98·5 | 103·0 | 107·6 | 112·5 | 118·0 | 50·0 | 91·5 |
| 14 | 93·0 | 89·3 | 85·5 | 81·5 | 83·3 | 90·7 | 97·8 | 102·7 | 107·5 | 112·5 | 118·0 | 35·0 | 79·5 |
| 15 | 128·0 | 121·5 | 115·0 | 108·5 | 101·5 | 93·8 | 100·3 | 106·3 | 99·7 | 113·2 | 118·0 | 52·5 | 91·5 |
| 16 | 112·0 | 106·5 | 100·8 | 94·8 | 88·3 | 89·6 | 98·2 | 104·8 | 109·0 | 113·2 | 118·0 | 44·7 | 85·0 |
| 17 | 133·0 | 126·8 | 120·5 | 113·8 | 106·8 | 98·8 | 98·5 | 116·5 | 110·9 | 113·9 | 118·0 | 56·0 | 93·0 |
| 18 | 71·0 | 66·5 | 61·0 | 77·0 | 86·4 | 93·7 | 99·9 | 105·0 | 110·0 | 114·5 | 118·0 | 19·2 | 58·0 |
| 19 | 45·0 | 47·0 | 66·2 | 78·5 | 87·7 | 95·0 | 101·0 | 106·0 | 110·4 | 114·2 | 118·0 | 7·8 | 40·0 |
| 20 | 100·5 | 95·0 | 88·0 | 79·2 | 86·8 | 94·0 | 100·3 | 105·5 | 110·2 | 114·3 | 118·0 | 31·3 | 78·0 |
| 21 | 52·0 | 45·0 | 66·1 | 79·0 | 88·9 | 96·2 | 102·1 | 107·0 | 111·2 | 114·9 | 118·0 | 10·0 | 45·0 |
| 22 | 68·0 | 64·0 | 68·2 | 78·0 | 87·5 | 95·8 | 102·9 | 108·7 | 112·8 | 115·0 | 118·0 | 13·3 | 61·5 |
| 23 | 36·0 | 43·2 | 65·3 | 78·6 | 88·0 | 95·6 | 101·5 | 106·7 | 111·0 | 115·0 | 118·0 | 7·5 | 32·5 |
| 24 | 133·0 | 128·2 | 122·0 | 114·8 | 106·7 | 99·3 | 107·0 | 111·5 | 119·3 | 116·3 | 118·0 | 49·3 | 98·5 |
| 25 | 114·0 | 109·7 | 105·0 | 99·8 | 99·5 | 104·1 | 107·8 | 110·6 | 112·8 | 114·5 | 118·0 | 35·3 | 97·0 |
| 26 | 50·0 | 40·2 | 59·4 | 72·0 | 82·8 | 91·5 | 100·0 | 103·0 | 110·4 | 112·7 | 118·0 | 11·5 | 37·5 |
| 27 | 110·0 | 105·1 | 99·4 | 92·7 | 84·0 | 92·9 | 99·8 | 105·5 | 110·5 | 115·0 | 118·0 | 40·0 | 84·0 |
| 28 | 110·0 | 105·5 | 99·1 | 94·2 | 103·9 | 112·7 | 120·3 | 126·7 | 131·5 | 134·6 | 137·0 | 28·3 | 92·5 |

TABLE 3. *Amorphous-liquid–liquid-crystal transition temperatures. The values were read from phase diagrams.*

| System no. | Mol. % of component A (see Table 1) | | | | | | | | | | | Triple point | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 40 | 50 | 60 | 70 | 80 | 85 | 90 | 92·5 | 95 | 97·5 | 100 | A (mol. %) | Temp. |
| 3 | — | — | — | 105·3° | 115·8° | 120·8° | 125·8° | 128·3° | 130·8° | 133·0° | 135·5° | 69·0 | 104·5° |
| 4 | — | — | 127·4° | 135·6 | 148·6 | 153·5 | 158·5 | 161·0 | 163·5 | 165·7 | 168·0 | 52·5 | 119·0 |
| 5 | — | — | — | 112·7 | 120·8 | 124·7 | 128·5 | 130·3 | 132·0 | 133·8 | 135·5 | 62·5 | 106·5 |
| 6 | — | 96·5° | 104·3 | 112·4 | 120·3 | 124·3 | 128·3 | 130·2 | 132·1 | 134·0 | 135·5 | 46·5 | 94·0 |
| 7 | 115·4° | 120·0 | 124·0 | 127·5 | 130·6 | 132·0 | 133·4 | 134·0 | 134·6 | 135·2 | 135·5 | 35·5 | 113·0 |
| 8 | — | — | — | — | 110·0 | 116·3 | 122·7 | 126·0 | 129·2 | 132·5 | 135·5 | 80·0 | 110·0 |
| 9 | — | — | — | 107·8 | 117·5 | 122·2 | 126·6 | 128·9 | 131·0 | 133·2 | 135·5 | 62·5 | 100·0 |
| 10 | — | — | — | 107·7 | 117·8 | 122·5 | 127·2 | 129·2 | 131·4 | 133·5 | 135·5 | 63·0 | 100·0 |
| 11 | — | — | — | — | — | 113·5 | 120·9 | 124·6 | 128·3 | 132·0 | 135·5 | 82·5 | 110·0 |
| 12 | — | — | — | — | 126·7 | 127·7 | 129·4 | 130·4 | 132·3 | 133·5 | 135·5 | — | — |
| 13 | — | — | 98·5 | 108·8 | 118·0 | 122·5 | 126·8 | 129·0 | 131·1 | 133·3 | 135·5 | 60·0 | 98·5 |
| 14 | — | — | — | 107·3 | 117·2 | 121·8 | 126·4 | 128·6 | 131·0 | 133·3 | 135·5 | 62·0 | 99·0 |
| 15 | — | — | — | — | — | 113·8 | 121·3 | 125·0 | 128·6 | 132·3 | 135·5 | 83·0 | 110·5 |
| 16 | — | — | — | — | — | 114·5 | 121·8 | 125·4 | 129·0 | 132·3 | 135·5 | 81·5 | 109·5 |
| 17 | — | — | — | — | — | — | 120·0 | 123·8 | 127·7 | 131·5 | 135·5 | 85·5 | 112·5 |
| 18 | — | — | — | — | — | — | 114·5 | 120·0 | 125·3 | 130·4 | 135·5 | 90·0 | 114·5 |
| 19 | — | — | — | — | — | — | — | 116·8 | 123·8 | 130·1 | 135·5 | 92·0 | 115·0 |
| 20 | — | — | — | — | — | — | — | 119·0 | 124·5 | 130·0 | 135·5 | 90·5 | 114·5 |
| 21 | — | — | — | — | — | — | — | — | 121·2 | 128·7 | 135·5 | 93·2 | 115·8 |
| 22 | — | — | — | — | — | — | — | 115·5 | 122·2 | 129·2 | 135·5 | 92·5 | 115·5 |
| 23 | — | — | — | — | — | — | — | 116·5 | 123·0 | 129·7 | 135·5 | 92·5 | 116·5 |
| 24 | — | — | — | — | — | — | — | 119·8 | 125·4 | 130·6 | 135·5 | 91·0 | 116·5 |
| 25 | — | — | — | — | — | — | — | — | 121·0 | 128·3 | 135·5 | 93·0 | 115·0 |
| 26 | — | — | — | — | — | — | — | — | 122·2 | 129·0 | 135·5 | 93·0 | 116·8 |
| 27 | — | — | — | — | — | — | — | 116·0 | 123·0 | 129·3 | 135·5 | 92·5 | 116·0 |
| 28 | — | — | — | — | — | 136·5 | 147·7 | 152·7 | 157·8 | 162·7 | 167·5 | 83·5 | 133·0 |

## DISCUSSION

Bogojawlensky and Winogradoff (*Z. phys. Chem.*, 1907, **60**, 433; 1908, **64**, 229) studied a number of binary systems in which one or both components could form liquid crystals. In the latter cases they found that the liquid-crystal–normal-liquid transition lines were straight, representing the transition temperatures of a range of " ideal " mixed liquid crystals of varying composition. Since the transition lines were also straight in cases where one component, but not the other, formed liquid crystals, they deduced that in such cases the second component would form a liquid crystal if the liquid could be supercooled sufficiently, and that the corresponding virtual transition temperature could be determined by extrapolation. They confirmed this hypothesis by showing that similar values for the virtual transition temperatures could be obtained by extrapolation in different binary systems (the first component being varied); and also, more dramatically, by studying binary systems in which neither component itself formed liquid crystals, but where the depression of melting point in mixtures should allow them to show mesomorphism. The phase diagrams in such cases had the form predicted from the values for the virtual transition temperatures found by extrapolation in other systems. Similar cases have been reported by Walter (*Ber.*, 1925, **58**, 2303).

We studied the systems *p*-anisic acid–cinnamic acid (no. 1), and *N*-*p*-anisylidene-*p*-anisidine–*N*-*p*-anisylidene-*p*-toluidine (no. 2), in the hope that mixtures of these substances, neither of which itself forms liquid crystals, might show anisotropic behaviour, but this was not observed in either case.

Bogojawlensky and Winogradoff oversimplified the situation since the transition lines are not invariably straight. This will be evident, not only from the examples given in this paper, but also from systems studied previously in other investigations, *e.g.*, the system *p*-azoxyanisole–*p*-methoxycinnamic acid where the transition line shows a strong minimum (Kock, *Z. phys. Chem.*, 1904, **48**, 129). Moreover, we find different values (34° and 71°) for the virtual transition temperature of 4 : 4′-dichloroazoxybenzene depending on whether the second component in the binary system is *p*-azoxyanisole or *p*-azoxyphenetole (nos. 3, 4); this observation can be reconciled with Bogojawlensky and Winogradoff's views only if the unobserved parts of the transition lines bend appreciably—and in that case reliable extrapolation is impossible.

Nevertheless it is probably true that any substance with anisotropic molecules would form a liquid crystal if it could be obtained in liquid form at a sufficiently low temperature. For if the molecules are asymmetric, or if the force fields round them are asymmetric, the internal energy of the liquid would be less if the molecules were all oriented parallel to one another, in an appropriate mutual relationship. In other words, a nematic form of the substance must have a lower energy than the normal amorphous liquid, and this in turn implies that the normal liquid will undergo transition to a nematic form if it is cooled sufficiently. Whether this nematic form can be observed in practice will depend on the melting point of the solid; in most cases the transition will be virtual since it will lie below the melting point.

Consider now a mixture of two different substances, both with asymmetric molecules. In this case two factors will influence the ease of liquid-crystal formation; first, the ability of the molecules to pack into a single liquid-crystal " lattice," and, secondly, the mean orientational cohesive energy density of the mixture (*i.e.*, the decrease in energy on orientation of the liquid). If the two components are of similar size and shape, the steric factors will be uniform for mixtures of all compositions; since the orientational cohesive energy density will vary more or less linearly with composition, the transition line in the phase diagram should be more or less straight. This is certainly the case for mixture of compounds of the type *p*-$A{\cdot}C_6H_4{\cdot}B{\cdot}C_6H_4{\cdot}C$-*p*, where B is azo, azoxy, or –CH=N–; all these molecules, for given terminal groups A and C, should be similar in size and shape.

If, however, the molecules of the two components differ, there will be more difficulty in packing them together. The transition temperature should then be less than that predicted for the " ideal " behaviour considered above; the transition line in the phase diagram should then be concave upwards, and when the components differ markedly it should show a minimum. Such behaviour has been observed by Kock (*loc. cit.*) for *p*-azoxyanisole–*p*-methoxycinnamic acid, and clearly the system *p*-azoxyanisole–*p*-anisic acid (Part I, *loc. cit.*) is similar in type.

Our final group of compounds include examples which should have extremely little tendency to form liquid crystals, so that their virtual transition temperatures should be very low indeed. In the binary systems formed by such substances with a liquid crystal (*e.g.*, *p*-azoxyanisole), the transition line should on any basis be very steep. This is what we observe (cf. nos. 24—28); it is not possible here to distinguish between energetic and stereochemical factors since the transition lines can only be observed over a short range of composition.

We have studied a number of systems in which *p*-azoxyanisole is mixed with a second component similar in shape. The argument given above suggests that the slope of the transition line should in such cases be a measure of the virtual transition temperature of the second component, the virtual transition temperature being higher, the lower the slope.

TABLE 4. *Transition-line slopes for compounds of type p*-$A{\cdot}C_6H_4{\cdot}B{\cdot}C_6H_4{\cdot}C$-*p, admixed with* p-*azoxyanisole* (*in* °C *per* 10% *change in molar composition*).

| A | B | C | Slope | A | B | C | Slope |
|---|---|---|---|---|---|---|---|
| H | CH:N | H | 29·5 | OMe | CH:N | Br | 11·0 |
| H | N:N | H | 28·0 | Cl | N:NO | Cl | 10·0 |
| Me | CH:N | H | 26·0 | OMe | CH:N | Cl | 9·5 |
| H | N:NO | H | 25·0 | Cl | CH:N | OMe | 9·0 |
| H | CH:N | $NMe_2$ | 23·0 | Me | CH:N | OMe | 9·0 |
| H | CH:N | OMe | 22·0 | OMe | CH:N | Me | 8·5 |
| Me | CH:N | Br | 16·0 | $NO_2$ | CH:N | Me | 8·0 |
| Me | CH:N | Me | 14·5 | OMe | CH:N | $NMe_2$ | 7·5 |
| Cl | CH:N | Cl | 14·5 | OMe | CH:N | OMe | 4·0 |
| Cl | CH:N | Me | 14·5 | $NO_2$ | CH:N | OMe | 2·5 |
| Me | CH:N | $NMe_2$ | 13·0 | | | | |

Therefore the lower the slope, the greater the tendency of the second component to form a liquid crystal. Table 4 gives values of the slopes for the cases studied by us. First, it will be observed that the slopes are similar for isomeric pairs of Schiff's bases; *e.g.*, *n*-*p*-anisylidene-*p*-chloroaniline, and *N*-4-chlorobenzylidene-*p*-anisidine; that is not surprising, since such pairs of molecules are clearly very similar. Secondly, the presence of two polar terminal groups is essential for a low value of the slope; the differences between different monosubstituted Schiff's bases are small compared with the differences between any monosubstituted base and any disubstituted base. Thirdly, Table 5 shows that the effects of terminal groups are approximately additive; one can deduce the order of group efficiency as $NO_2 > OMe > Me_2N > Me > Cl > Br > H$; and one can even ascribe "group slopes," such that the slope for a given compound is expressed closely by a sum of the slope for the terminal groups present (Table 6). This order is the order of decreasing polarity of the groups regardless of sign; and so evidently the main factor is the magnitude of the group dipole, and not its direction. The similarity of Me and Cl is interesting; this may be partly a reflection of their similar size. The very large effect of $NO_2$ is surprising since very few liquid-crystalline nitro-compounds are known; this apparent discrepancy can probably be ascribed to the high melting points of nitro-compounds, their ability to form liquid crystals consequently remaining latent.

TABLE 5. *Slopes for various Schiff's bases.*

| A = | $NO_2$ | OMe | $Me_2N$ | Me | Cl | Br | H |
|---|---|---|---|---|---|---|---|
| C = MeO ......... | 2·5 | 4·0 | 7·5 | 9·0 | 9·0 | 11·0 | 22·0 |
| C = Me ......... | 8·0 | 9·0 | 13·0 | 14·5 | 14·5 | 16·0 | 26·0 |
| Difference ......... | 5·5 | 5·0 | 5·5 | 6·0 | 5·5 | 5·0 | 4·0 |

TABLE 6. *Group slopes for Schiff's bases.*

| $NO_2$ | OMe | $NMe_2$ | Me | Cl | Br | H |
|---|---|---|---|---|---|---|
| 0·5 | 2·0 | 5·6 | 7·2 | 7·2 | 8·9 | 19·0 |

One final point emerges. It was suggested by Kock (*loc. cit.*) that depression of liquid-crystal transition temperature by solutes might be used as a method of determining molecular weights. This would be correct in principle only if the solute were almost insoluble in the liquid crystal, the two-component liquid being a mixture of two phases, one containing only the liquid-crystalline component, and the other being a normal liquid containing both components. We showed, however, in our previous paper (*loc. cit.*) that the birefringent two-component liquids are composed of single liquid-crystalline phases. Depression of transition temperature cannot therefore be used as a reliable method of molecular-weight determination, and indeed the systems studied by us show that the molar depression varies from compound to compound.

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