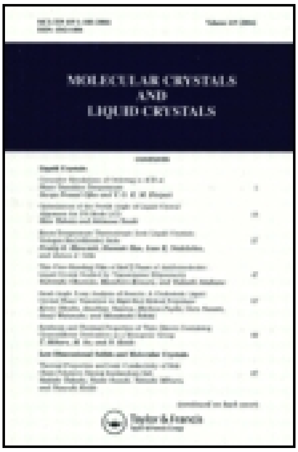


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

New Methods for Calculating the Temperatures and the Enthalpy Changes of Virtual Transitions and Predicting Phase Diagrams-Applied to the Tolans

M. Domon [a] & J. M. Buisine [a]

[a] Equipe de Dynamique des Cristaux Moléculaires Université des Sciences et Techniques de Lille Flandres Artois 59655 Villeneuve d'Ascq, Cédex, France

Version of record first published: 28 Mar 2007.

To cite this article: M. Domon & J. M. Buisine (1987): New Methods for Calculating the Temperatures and the Enthalpy Changes of Virtual Transitions and Predicting Phase Diagrams-Applied to the Tolans, Molecular Crystals and Liquid Crystals, 149:1, 347-358

To link to this article: http://dx.doi.org/10.1080/00268948708082990

Mol. Cryst. Liq. Cryst., 1987, Vol. 149, pp. 347–358
Photocopying permitted by license only

Printed in the United States of America

New Methods for Calculating the Temperatures and the Enthalpy Changes of Virtual Transitions and Predicting Phase Diagrams—Applied to the Tolans†

M. DOMON and J. M. BUISINE

Equipe de Dynamique des Cristaux Moléculaires‡
Université des Sciences et Techniques de Lille Flandres Artois
59655 Villeneuve d'Ascq Cédex—France

(*Received November 22, 1984; in final form June 9, 1986*)

For a mesogen which does not exhibit an enantiotropic nematic phase when pure, two new methods are proposed for the determination of the temperatures and enthalpy changes of the nematic-isotropic liquid virtual transitions. These calculations, based on Schröder-van Laar and van Laar equations, use the value of the liquid appearance temperature (the determination of which is easy and accurate) for mixtures of the compound with another mesogen which exhibits the enantiotropic mesophase when pure. Both methods are applied to the study of the first ten compounds in the series: 4-methoxy-4′-*n*-alkyl-tolan. The results are then used to determine the eutectic, liquid appearance and nematic disappearance temperatures of mixtures of two tolans that do not exhibit an enantiotropic nematic phase when pure. In seven cases, an enantiotropic nematic phase is predicted and observed; in one case, the phase diagram differs from that expected; for the remainder, there is a good agreement between calculated and experimental data.

Keywords: liquid crystals, nematic, phase diagram, virtual transition

INTRODUCTION

When two mesogens do not exhibit the same mesophase, the isobaric phase diagram for their mixtures can be explained in terms of virtual transitions. Knowledge of these virtual transitions permits us to pre-

---

†Paper presented at the 11th International Liquid Crystal Conference, Berkeley, CA, 30 June–4 July, 1986.

‡Unité associée au C.N.R.S. No. 801

dict the phase diagram.[1] Generally, at the nematic–liquid (N–I) transitions, the enthalpy changes are very small; so many authors have described the [N–I] equilibrium curves in binary diagrams as straight lines[2–6] or a slight curves,[7,9] and determined the temperature of the virtual [N–I] transition of pure compounds by extrapolation. Although this method generally gives good results, it does not permit the determination of enthalpy changes of virtual transitions. For two compounds, one of which exhibits an enantiotropic nematic phase, the phase diagram is given in Figure 1. In previous work, it has been shown that this diagram can be calculated, using the Schröder–van Laar equation[11] for the solubility curves,[1,12–19] and using the van Laar equations[20] for the [N–I] equilibrium curves.[1] Conversely, the use of the same equations allows us to calculate the temperature and enthalpy change at the virtual [N–I] transition from the temperatures of the triple points.[1] However, the latter method gives acceptable

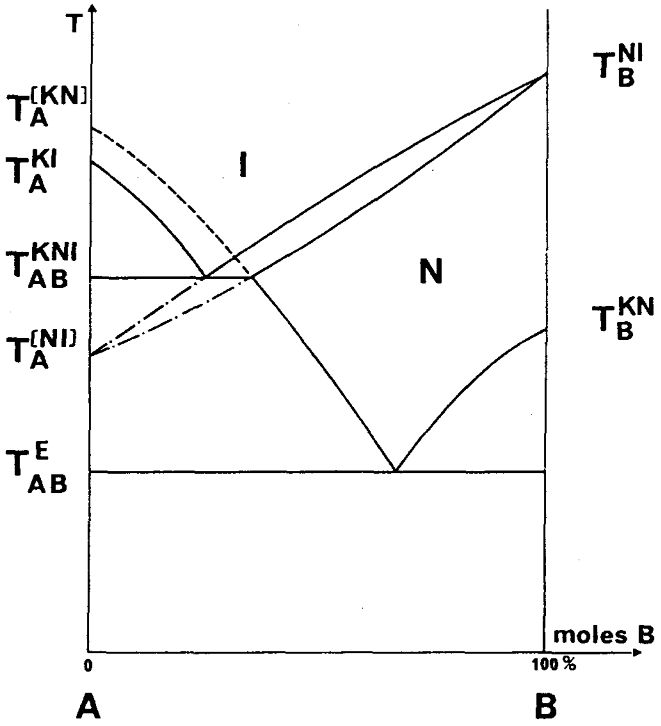


FIGURE 1 Isobaric phase diagram of a compound (*B*) exhibiting an enantiotropic nematic phase with a compound (*A*) which does not; brackets [ ] indicate the virtual transitions.

values for the parameters of the virtual transitions only if the measurements of the temperatures of the triple points are sufficiently accurate ($\pm 0.2°C$). Although the liquid appearance temperature can be easily determined with precision (about 0.2°C), fluctuations of some degrees are often observed for the eutectic temperature. This is why we propose two methods for the determination of the temperatures and enthalpy changes of virtual [N–I] transitions, based on the measurement of the liquid appearance temperature. These methods are then used in the study of a series of nematogens in order to predict the existence or non-existence, of an enantiotropic nematic phase in mixtures of two compounds that do not exhibit it when pure.

METHODS

The calculations involved in both approaches are described in reference [1].

One-diagram method

For a compound A, exhibiting a virtual nematic–liquid [N–I] transition, where the transition temperature $T_A^{[NI]}$ is known, the value of the corresponding enthalpy change $\Delta H_A^{[NI]}$ can be calculated from a measurement made on mixtures of A with a compound B exhibiting an enantiotropic (N–I) transition (Figure 1), of the liquid appearance temperature T_{AB}^{KNI}, and from the values of the temperatures and enthalpy changes at the crystal-isotropic liquid-(K–I) transition for A (respectively T_A^{KI} and ΔH_A^{KI}) and at the nematic–liquid (N–I) transition for B (respectively T_B^{NI} and ΔH_B^{NI}):

$$\Delta H_A^{[NI]} = \frac{R}{\dfrac{1}{T_A^{[NI]}} - \dfrac{1}{T_{AB}^{KNI}}} \times \frac{\exp\left\{\dfrac{\Delta H_A^{KI}}{R}\left(\dfrac{1}{T_A^{KI}} - \dfrac{1}{T_{AB}^{KNI}}\right)\right\} \exp\left\{\dfrac{\Delta H_B^{NI}}{R}\left(\dfrac{1}{T_B^{NI}} - \dfrac{1}{T_{AB}^{KNI}}\right)\right\}}{\exp\left\{\dfrac{\Delta H_A^{KI}}{R}\left(\dfrac{1}{T_A^{KI}} - \dfrac{1}{T_{AB}^{KNI}}\right)\right\} + \exp\left\{\dfrac{\Delta H_B^{NI}}{R}\left(\dfrac{1}{T_B^{NI}} - \dfrac{1}{T_{AB}^{KNI}}\right)\right\} - 1} \tag{1}$$

where R is the gas constant.

Two-diagram method

When the virtual transition temperature is unknown, $\mathrm{T}_A^{[\mathrm{NI}]}$ and $\Delta H_A^{[\mathrm{NI}]}$ can be calculated from a measurement, on two binary mixtures of A with two compounds B and B' exhibiting an enantiotropic (N–I) transition, of the liquid appearance temperatures $\mathrm{T}_{AB}^{\mathrm{KNI}}$ and $\mathrm{T}_{AB'}^{\mathrm{KNI}}$, and the values of the temperatures and enthalpy changes at the crystal–nematic (K–N) transitions for pure B and B' ($\mathrm{T}_B^{\mathrm{KN}}$; $\mathrm{T}_{B'}^{\mathrm{KN}}$; ΔH_B^{KN}; $\Delta H_{B'}^{\mathrm{KN}}$, respectively) and at the crystal–isotropic liquid (K–I) transition for A (respectively $\mathrm{T}_A^{\mathrm{KI}}$ and ΔH_A^{KI}):

$$\Delta H_A^{[\mathrm{NI}]} = \frac{R(\varepsilon - \varepsilon')}{\dfrac{1}{\mathrm{T}_{AB'}^{\mathrm{KNI}}} - \dfrac{1}{\mathrm{T}_{AB}^{\mathrm{KNI}}}} \tag{2-a}$$

$$\mathrm{T}_A^{[\mathrm{NI}]} = \frac{\varepsilon - \varepsilon'}{\dfrac{\varepsilon}{\mathrm{T}_{AB'}^{\mathrm{KNI}}} - \dfrac{\varepsilon'}{\mathrm{T}_{AB}^{\mathrm{KNI}}}} \tag{2-b}$$

where

$$\varepsilon = \ln \frac{1 - \exp\left\{\dfrac{\Delta H_A^{\mathrm{KI}}}{R}\left(\dfrac{1}{\mathrm{T}_A^{\mathrm{KI}}} - \dfrac{1}{\mathrm{T}_{AB}^{\mathrm{KNI}}}\right)\right\}}{1 - \exp\left\{\dfrac{\Delta H_B^{\mathrm{KN}}}{R}\left(\dfrac{1}{\mathrm{T}_B^{\mathrm{KN}}} - \dfrac{1}{\mathrm{T}_{AB}^{\mathrm{KNI}}}\right)\right\}}$$

and ε' is the similar expression corresponding to B'. Both expressions are valid only when $\mathrm{T}_{AB}^{\mathrm{KNI}}$ differs from $\mathrm{T}_{AB'}^{\mathrm{KNI}}$.

Exploitation of both methods

Using the data obtained with the one- or the two-diagram method, it is possible to determine, for two compounds A and A' which do not exhibit enantiotropic nematic phases when pure, but give an enantiotropic nematic perfect solution in their mixtures (Figure 2), the temperatures at the triple points limiting the nematic domain, i.e., the eutectic temperature $\mathrm{T}_{AA'}^{\mathrm{E}}$, the liquid appearance temperature $\mathrm{T}_{AA'}^{\mathrm{KNI}_1}$ and the nematic disappearance temperature $\mathrm{T}_{AA'}^{\mathrm{KNI}_2 1}$. There is an enantiotropic nematic solution in the mixtures of A and A' only

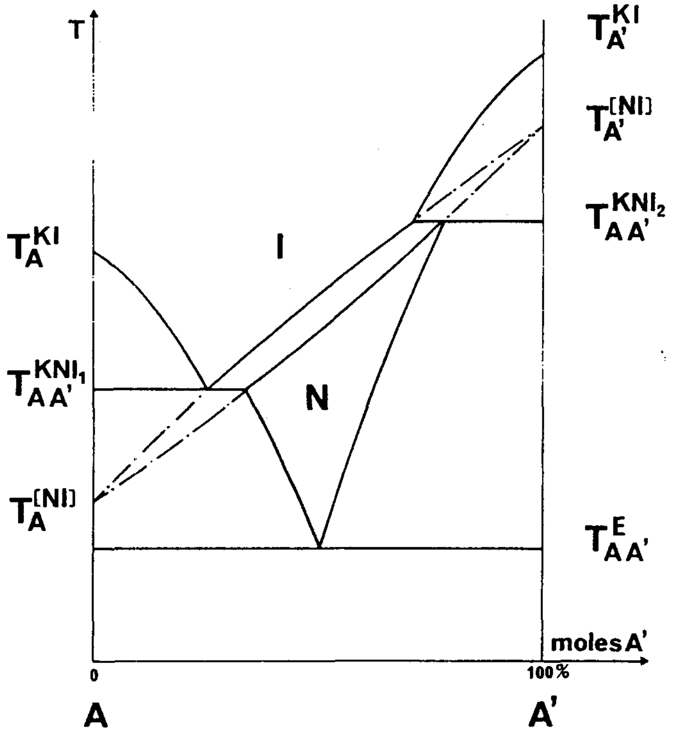


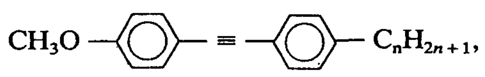
FIGURE 2 Isobaric phase diagram of two compounds which exhibit an enantiotropic nematic phase in their mixtures and not when pure; brackets [ ] indicate the virtual transitions.

if the eutectic temperature is lower than both liquid appearance and nematic disappearance temperatures:

$$T_{AA'}^{E} < T_{AA'}^{KNI_1} \quad \text{and} \quad T_{AA'}^{E} < T_{AA'}^{KNI_2} \tag{3}$$

EXPERIMENTS

The compounds used to verify the validity of both methods are 4-methoxy-4'-*n*-alkyl-tolans[21]:


, with $n = 1$ to 10

Previous studies[13,22,23] have established that compounds with $n = 3$ and 4 exhibit monotropic nematic phases, and for $n = 5$ to 7, 9 and 10 enantiotropic ones. Literature data for the temperatures and enthalpy changes at the phase transitions are reported in Table I [1, 22 to 26].

The temperatures of the transitions for pure compounds, and at the triple points for binary mixtures, were measured with a heating stage (Mettler, FP 52) equipping a polarizing microscope (Ortholux Leitz); the temperature calibration was verified with melting standards. The experimental values were averages of at least five measurements.

For pure compounds, the temperature of the monotropic (N–I) transition was determined by observation of the undercooled melt between glass slides, or by means of the droplet method[26] (accuracy: 0.2°C).

For binary mixtures, the contact method[10] has been used.

RESULTS

Experimental results

The experimental transition temperatures for pure compounds are shown in Table I; they agree with literature data.

All of the binary phase diagrams of compounds which exhibit an enantiotropic nematic phase ($n = 5, 6, 7, 9, 10$) with compounds which do not ($n = 1, 2, 3, 4, 8$) have the general appearance of Figure 1. The experimental liquid appearance temperatures are reported in Table II.

Among the ten binary diagrams of two compounds without enantiotropic nematic phases, seven (for $n = 8$ & 1, 8 & 2, 8 & 3, 8 & 4, 2 & 3, 2 & 4 and 3 & 4) exhibit an enantiotropic nematic phase. For the first six mixtures, the phase diagram has the general appearance of Figure 2; the temperatures at the triple points ($T^{E}_{AA'}$, $T^{KNI_1}_{AA'}$, $T^{KNI_2}_{AA'}$) limiting the nematic area are shown in Table III. For the seventh mixture ($n = 3$ & 4) the phase diagram is shown in Figure 3. In the other binary mixtures, no enantiotropic nematic phase appears; for $n = 1$ & 2, the compounds form a solid solution despite their belonging to different crystalline systems,[6] and for $n = 1$ & 3, 1 & 4 an undercooled nematic phase is observable.

Calculations

For compounds exhibiting a monotropic [N–I] transition ($n = 2, 3, 4, 8$) the corresponding enthalpy change has been calculated by means

TABLE I

Temperature (°C) and enthalpy changes (in italics) (k cal.mole^{-1}) of the crystal–nematic (K–N), nematic–isotropic liquid (N–I) and crystal—isotropic liquid (K–I) transitions in the 4-methoxy-4′-*n*-alkyl-tolan series.

n	K		N		I	Ref.
1	.	124.8[a]	—	[32.1 ± 4.5][c]	.	
		124.3				24
		6.8				26
				.13 ± .03[c]		
2	.	72.5[a]	.	[34.7][a]	.	
		72.8				24
				34.2 ± 2.9[c]		
		5.62				26
				.17 ± .04[b]		
				.19 ± .05[c]		
3	.	65.0[a]	.	[61.4][a]	.	
		66		61		22
				61.4 ± 0.8[c]		
		5.0		*.15*		22
				.17 ± 0.3[b]		
				.23 ± 0.4[c]		
4	.	50.4[a]	.	[40.2][a]	.	
		49.5		40.3		1
				40.3 ± .03[c]		
		4.10				22
				.16		1
				.21 ± .09[b]		
				.26 ± 11[c]		
5	.	45.6[a]	.	57.1[a]	.	
		43		55		22
		4.2		*.14*		22
6	.	39.1[a]	.	43.4[a]	.	
		39.1		42.2		25
		5.71		*.17*		25
7	.	40.9[a]	.	54.0[a]	.	
		39		54		13
		5.1		*.12*		13
8	.	48.4[a]	.	[47.9][a]	.	
		48.7				25
				47.9 ± .0[c]		
		8.37				25
				.13 ± .06[b]		
				.11 ± .03[c]		
9	.	43.4[a]	.	54.5[a]	.	
		41		53.5		13
		7.45		*.21*		13
10	.	50.5[a]	.	51.4[a]	.	
		49.5		50.0		26
		9.10		*.285*		26

[ ]: monotropic transition.
·:observable phase.
—not observable phase.

[a] experimental
[b] calculated by the one-diagram method.
[c] calculated by the two-diagram method.

TABLE II

Experimental data for the liquid appearance temperature of mixtures of two 4-methoxy-4'-*n*-alkyl tolans, which exhibit (n = 5, 6, 7, 9, 10) and do not exhibit (n = 1, 2, 3, 4, 8) one enantiotropic nematic phase when pure.

n	1	2	3	4	8
5	54.2	45.2	60.9	41.9	48.0
6	41.9	38.9	56.2	40.8	47.7
7	51.5	43.0	59.3	42.2	48.0
9	52.7	45.7	58.0	42.2	48.2
10	49.6	44.8	57.0	41.7	48.0

of the "one-diagram method" (equation (1)). The results are shown in Table I and labelled (b). For 4-methoxy-4'-methyl-tolan, the [N–I] transition is unobservable; so the temperature and enthalpy change for this transition have been calculated by the "two-diagram method" (equation (2)). To compare the results of both methods, this calculation has also been applied to compounds exhibiting a monotropic transition (n = 2, 3, 4, 8). The results are indicated as (c) on Table I.

For mixtures of two compounds neither of which shows an enantiotropic nematic phase (n = 1, 2, 3, 4, 8) the temperatures $T^{E}_{AA'}$, $T^{KNI_1}_{AA'}$, $T^{KNI_2}_{AA'}$ limiting the nematic area have been calculated with the method of reference [1], first using the monotropic [N–I] temperatures and the data labelled (b) in Table I, and, secondly, using the data (c) in the same table. The results are shown on Table III and labelled (b) and (c) respectively. Equation (3) predicts the existence

TABLE III

Experimental data (a) and calculated values for the eutectic, liquid appearance and nematic disappearance temperatures limiting the extent of an enantiotropic nematic phase for the mixtures of two 4-methoxy-4'-*n*-alkyl-tolans that do not exhibit this phase when pure; (b) refers to the one-diagram method, (c) to the two-diagram method.

	Eutectic			Liquid appearance			Nematic disappearance		
n	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)
1.8	44.9	45.3	45.4	45.9	45.9	45.6	47.5	47.0	46.4
2.3	42.4	40.7	40.4	50.4	47.0	47.7	57.0	56.4	57.7
2.4	29.3	31.0	30.9	37.3	38.2	38.2	39.2	39.2	39.3
2.8	33.9	36.7	36.7	41.0	41.1	40.0	46.8	46.8	45.0
4.8	30.2	26.7	26.5	41.2	41.0	40.9	47.3	47.2	46.9
8.3	29.6	33.2	33.1	47.3	48.1	48.1	56.3	60.3	60.3

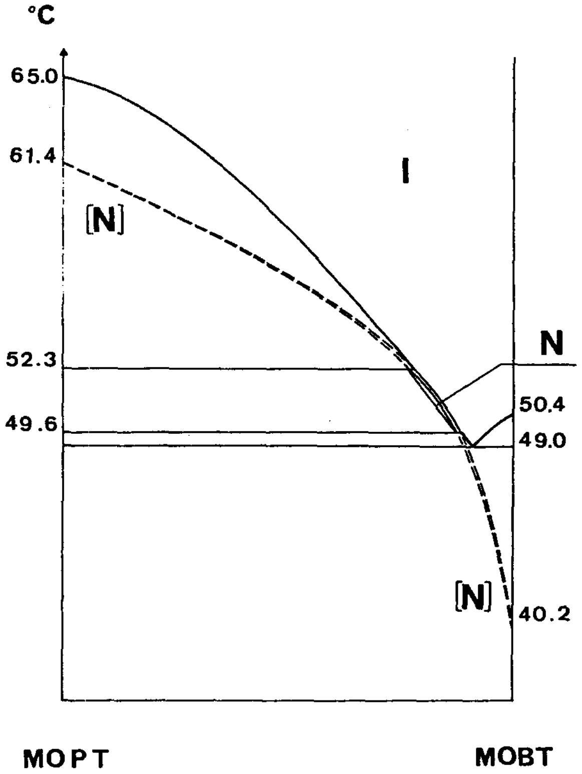


FIGURE 3 Experimental isobaric phase diagram of: 4-methoxy-4'-*n*-propyl-tolan (M-OP-T) and 4-methoxy-4'-*n*-butyl-tolan (M-OB-T).

of an enantiotropic nematic domain for seven mixtures: $n = 8$ & 1, 8 & 2, 8 & 3, 8 & 4, 2 & 3, 2 & 4, 3 & 4.

DISCUSSION

Considering the enthalpy change of the virtual [N–I] transitions of the compounds studied (Table I), there is a good agreement between the values calculated from one diagram, labelled (b), and those calculated from two diagrams, labelled (c), with a better accuracy for the one diagram method for most cases. In addition, for the [N–I] transition temperatures of compounds with a monotropic nematic phase, the experimental data (labelled (a) in Table I) are within the uncertainty range of the calculated values (labelled (c) in Table I).

The enthalpy changes at virtual transitions have the same order of magnitude as those of corresponding real transitions.

When shown on the same graph (Figure 4), real and virtual transitions can not be distinguished; as for many series of homologous compounds,[27] an odd-even effect appears, for $n \leq 2$, for both the T^{NI} values and for the difference ΔT between the melting and clearing temperatures.

Regarding the triple point temperatures in binary diagrams of compounds without enantiotropic nematic (see Table III), the data calculated using the one-diagram or the two-diagram method are generally very close together, or do not differ significantly. In most cases there is a good agreement between the calculated and experimental values. Except for the one mixture (n = 3 & 4) the shape of the experimental diagram is, as predicted, by Figure 2.

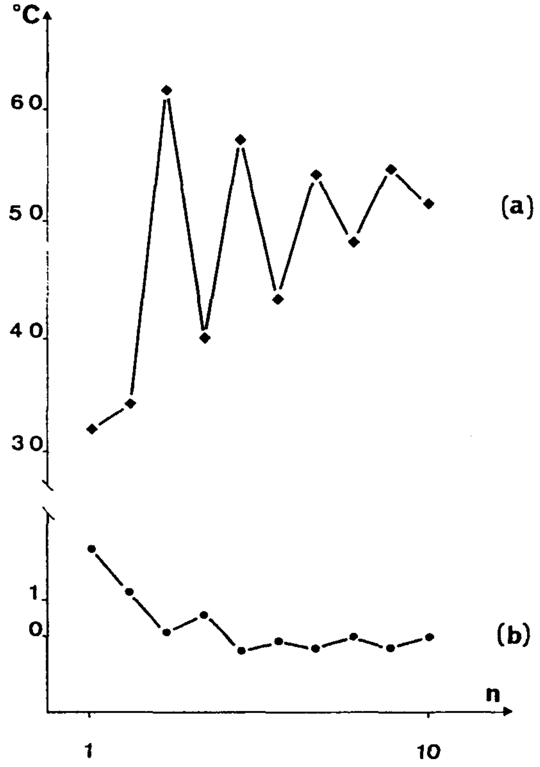


FIGURE 4 Nematic–isotropic liquid transition temperature (a) and difference between the melting and clearing temperatures (b) versus the number of carbons, n in the alkyl chain for the 4-methoxy-4′-n-alkyl-tolan series.

CONCLUSION

The concept of virtual transitions has been applied to the study of the first ten compounds of the 4-methoxy-4′-*n*-alkyl-tolan series, pure or in binary mixtures. By two different methods, according to whether a monotropic [N–I] transition is observable or not (and using the measurement of liquid appearance temperatures in binary mixtures of two compounds one only of which exhibits an enantiotropic nematic), the unknown temperatures and enthalpy changes at both virtual nematic–isotropic liquid and crystal–nematic transitions have been calculated. There is a good agreement between the results of the two methods. Furthermore, for the nematic–isotropic liquid transition, the calculated temperature coincides with the experimental monotropic one. The enthalpy changes of virtual transitions are comparable with those of corresponding real transitions; real and virtual transition temperatures vary in the same way with the length of the alkyl chain. The existence of an enantiotropic nematic phase is predicted for the mixture of two compounds neither of which exhibit it when pure; there is a good agreement between the calculated and experimental values for the temperatures of the triple points limiting the nematic region. To predict the existence of a mesophase in binary mixtures, these results extend the mesogenic character to all terms of the series, allow selection of the most interesting mixtures, and restrict the observations to these.

Acknowledgements

The authors thank J. Jacques and J. Malthete for the synthesis and purification of most of the compounds used, P. Le Barny for some calorimetric studies, and particularly Professor J. Billard, instigator of this study.

References

1. M. Domon and J. Billard, *Pramana, Suppl. No. 1*, pp. 131–154 (1975).
2. W. H. De Jeu, *Physical Properties of Liquid Crystalline Materials*, p. 13, Gordon and Breach, London (1980).
3. C. Fouquet and J. Jacques, *Bull. Soc. Chim. de France*, **1**, 165 (1966).
4. G. W. Gray and A. Mosley, *J.C.S. Perkin*, **11**, 97 (1976).
5 G. A. Oweimreen and D. E. Martire, *J. Chem. Phys.*, **72**, 2500 (1980); G. A. Oweimreen and M. Hasan, *Mol. Cryst. Liq. Cryst.*, **100**, 357 (1983).
6. J. M. Buisine and J. Billard, *Mol. Cryst. Liq. Cryst.*, **127**, 353 (1985).
7. A. C. De Kock, *Z. f. Phys. Chem.*, A **48**, 129 (1904).

8. A. Bogojawlensky and N. Winogradow, *Z. f. Phys. Chem.*, **A 60**, 433 (1907); **64**, 229 (1908).
9. A. V. Galanti and R. S. Porter, *J. Phys. Chem.*, **76**, 3089 (1972).
10. L. Kofler and A. Kofler, Thermomicromethoden zur Kennzeichnung organischer Stoffe und Stoffgemische, *Verlag Chemie*, Weinheim (1954).
11. I. Schroeder, *Z. f. Phys. Chem.*, **11**, 449 (1893); J. J. van Laar, *Arch. Néerl.*, **11.8**, 264 (1903).
12. J. Johnston, *J. Phys. Chem.*, **29**, 882 (1925).
13. J. Malthete, M. Leclercq, J. Gabard, J. Billard and J. Jacques, *C.R.A.S. Série C*, **273**, 265 (1971).
14. E. C. H. Hsu and J. F. Johnson, *Mol. Cryst. Liq. Cryst.*, **20**, 177 (1973); **27**, 95 (1974).
15. D. Demus, Ch. Fietkau, R. Schubert and H. Kehlen, *Mol. Cryst. Liq. Cryst.*, **25**, 215 (1974).
16. D. S. Hulme, E. P. Raynes and K. J. Harrison, *J.C.S. Chem. Comm.*, **98** (1974).
17. Zs. Szabo and I. Kosa-Somogyi, *Mol. Cryst. Liq. Cryst.*, **31**, 161 (1975).
18. A. V. Ivaschenko, V. V. Titov and E. I. Koshev, *Mol. Cryst. Liq. Cryst.*, **33**, 195 (1976).
19. V. A. Molochko, O. P. Chernova and G. M. Kurdyumov, *Zh. Prikhl, Khim.*, **50**, 45 (1977).
20. J. J. van Laar, *Z. f. Phys. Chem.*, **63**, 216 (1908).
21. M. Leclercq, J. Gabard, J. Billard and J. Jacques, French Patent No. 2234-261, U.S. Patent P. 210.125.72136.
22. J. Malthete, M. Leclercq, M. Dvolaitzky, J. Gabard, J. Billard, V. Pontikis and J. Jacques, *Mol. Cryst. Liq. Cryst.*, **23**, 233 (1973).
23. M. Cotrait, C. Destrade and H. Gasparoux, *Mol. Cryst. Liq. Cryst.*, **39**, 159 (1977).
24. P. Le Barny, Private communication.
25. J. Berthault, Unpublished results.
26. J. Malthete and J. Billard, *Mol. Cryst. Liq. Cryst.*, **54**, 45 (1979).
27. See for example: J. S. Dave and R. A. Vora, *Mol. Cryst. Liq. Cryst.*, **14**, 319 (1971); W. Elser, J. L. W. Pohlmann and P. R. Boyel, *Mol. Cryst. Liq. Cryst.*, **15**, 175 (1971).