Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Laterally substituted dimeric liquid crystals

C. T. Imrie[a]
[a] Department of Chemistry, The University, Southampton, England

To cite this Article Imrie, C. T.(1989) 'Laterally substituted dimeric liquid crystals', Liquid Crystals, 6: 4, 391 — 396
To link to this Article: DOI: 10.1080/02678298908034184
URL: http://dx.doi.org/10.1080/02678298908034184

LIQUID CRYSTALS, 1989, VOL. 6, NO. 4, 391–396

Laterally substituted dimeric liquid crystals

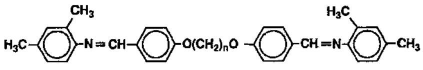
by C. T. IMRIE
Department of Chemistry, The University, Southampton SO9 5NH, England

(*Received 20 April 1989; accepted 25 May 1989*)

Ten members of the homologous series α,ω-bis(2,4-dimethylanilinebenzylidine-4′-oxy)alkanes and four members of the α-(4-cyanobiphenyl-4′-oxy)-ω-(2,4-dimethylanilinebenzylidine-4′-oxy)alkanes have been synthesized. Their transitional properties are compared to those of the analogous compounds not possessing the 2-methyl substituent. Lateral substitution results in a large decrease in the nematic–isotropic transition temperatures. In contrast, the reduction in the entropy change associated with the nematic–isotropic transition is only slight.

1. Introduction

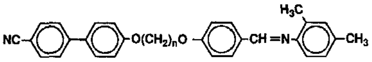
Dimeric liquid crystals are currently of great interest even though both their original discovery over sixty years ago by Vorländer [1] and their subsequent rediscovery some fifty years later by Rault *et al.* [2] were apparently overlooked. At the root of this recent interest in dimers is their role as model compounds for semi-flexible liquid-crystalline polymers as well as their quite different properties to conventional low molar mass mesogens having a semi-rigid core. This has prompted the synthesis of a great number of dimers. The majority of these investigations, however, have focused upon varying either the length of the flexible alkyl spacer (see, for example, [3]) or the nature of the terminal substituents (see, for example, [4]). In contrast, the effect of lateral substitution on the properties of dimers has been largely ignored. This is somewhat surprising because lateral substitution in main-chain polymers has been extensively investigated as a means of reducing high transition temperatures (see, for example, [5]). As part of an established programme to investigate the properties of dimeric liquid crystals and their relationship to molecular structure a homologous series of symmetric dimers possessing laterally substituted semi-rigid groups has been synthesised, namely the α,ω-bis(2,4-dimethylanilinebenzylidine-4′-oxy)alkanes,



the mnemonic used for this series is 1(Me).O*n*O.(Me)1 where *n* denotes the number of carbon atoms in the alkyl spacer. This series was chosen because the corresponding unsubstituted dimers, the α,ω-bis(4-methylanilinebenzylidine-4′-oxy)alkanes (1.O*n*O.1 series) have been synthesized and certain of their properties determined [6, 7]. In addition, the monomeric analogues the *N*-(4-*n*-alkyloxybenzylidine)-4′-*n*- alkylanilines (the *n*O.*m* series) [8] and the corresponding 2′-methyl substituted analogues [9] have been synthesized.

0267-8292/89 $3.00

In order to investigate the effect of a single lateral substituent several asymmetric dimers have been synthesized, namely the α-(4-cyanobiphenyl-4′-oxy)-ω-(2,4-dimethylanilinebenzylidine-4′-oxy)alkanes,



the mnemonic used for this series is CB . O*n*O . (Me)1 where *n* denotes the number of carbon atoms in the alkyl spacer. This series was chosen because the corresponding unsubstituted dimers, the CB . O*n*O . 1 series, are known [7, 10] and also, the analogous monomeric materials have been thoroughly investigated.

2. Experimental

The 1(Me) . O*n*O . (Me)1 series was prepared by the condensation of 2,4-dimethylaniline with an α,ω-bis(4-formylphenyl-4′-oxy)alkane; the final products having an odd-membered spacer were recrystallised twice from absolute ethanol while the even members were recrystallised twice from toluene. The CB . O*n*O . (Me)1 compounds were prepared and purified in an analogous manner; the synthesis of the α-(4-cyanobiphenyl-4′-oxy)-ω-(4-formylphenyl-4′-oxy)alkanes will be described elsewhere.

3. Characterization

The structures of all the final products were verified using I.R. and ^{1}H N.M.R. spectroscopy. Their thermal properties were investigated using a Perkin-Elmer DSC-2C differential scanning calorimeter as well as a Nikon polarizing microscope equipped with a Linkam hot stage. This was also employed to examine the optical textures of the liquid-crystalline phases.

4. Results and discussion

The transitional properties of the 1(Me) . O*n*O . (Me)1 series are given in table 1; the compounds are monotropic nematogens with the exceptions of those having spacer lengths of 6, 8, 9 and 10 which are enantiotropic and 1(Me) . O3O . (Me)1 for which no mesophase is observed. The nematic phases were assigned from their schlieren optical texture. The dependence of the transition temperatures upon the

Table 1. The transition temperatures and entropies of transition for the 1(Me) . O*n*O . (Me)1 homologous series; ( ) indicates a monotropic transition.

n	T_{CI}/°C † T_{CN}/°C	T_{NI}/°C	$\Delta S_c/R$	$\Delta S_{\mathrm{NI}}/R$
3	135	—	23·7	—
4	189	(164)	14·2	1·14
5	96	(71)	15·0	0·25
6	† 135	146	13·1	1·49
7	104	(74)	10·5	0·30
8	† 118	125	15·8	1·72
9	† 81	84	12·1	0·58
10	† 109	115	17·4	2·00
11	100	(90)	21·3	0·66
12	111	(105)	18·4	2·17

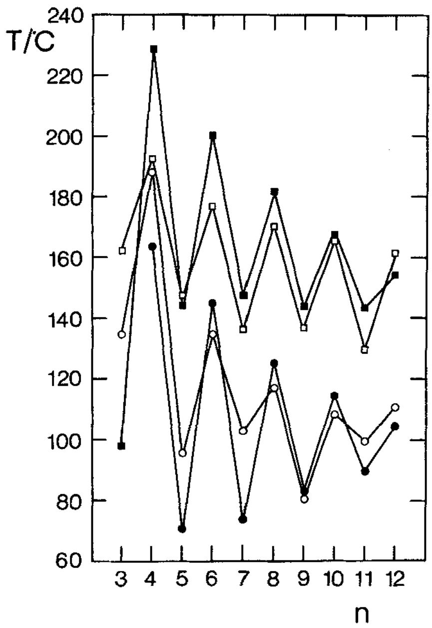


Figure 1. The dependence of the transition temperatures on the length of the flexible spacer, *n*, for the 1(Me).O*n*O.(Me)1 series; the melting point is denoted by ○ and ● indicates the nematic–isotropic transition. Also shown are the transition temperatures of the 1.O*n*O.1 series for which □ represents the melting point and ■ the nematic–isotropic transition.

length of the flexible spacer is shown in figure 1; both the melting temperatures and the nematic–isotropic transition temperatures show pronounced odd–even effects with the compounds possessing an even length spacer having the higher values; these alternations attenuate with increasing *n*. This behviour is very typical of that observed for dimeric liquid crystals [3]. Also shown in figure 1 are the transition temperatures for the 1.O*n*O.1 series; lateral substitution has reduced both the melting points and the T_{NI}s. In all but two examples the reduction of the melting point is smaller than that of the T_{NI}. It is interesting to note that the reduction in T_{NI} is larger for odd-membered compounds than for even-membered compounds and this results in an increased odd–even effect; this is more pronounced for short spacer lengths. The average reduction in T_{NI} on the addition of two lateral methyl groups is approximately 59°C whereas in the corresponding monomers the addition of a single methyl group reduces T_{NI} by 57°C [9].

Figure 2 shows the dependence of the entropy associated with the nematic–isotropic transition on the length of the flexible spacer for both the 1.O*n*O.1 and 1(Me).O*n*O.(Me)1 series. The entropies of both series show a very pronounced odd–even effect on increasing *n* with the even membered compounds having the higher values. This alternation attenuates in a relative sense as *n* increases. Also both sets of data show an underlying increase in the value of $\Delta S_{NI}/R$ on increasing the spacer length. It should be noted that the entropy change measured for a 1(Me).O*n*O.(Me)1 compound is invariably less than that of the corresponding 1.O*n*O.1 member. However, this is a smaller effect than that observed in the nematic–isotropic transition temperatures. The reduction in $\Delta S_{NI}/R$ on lateral

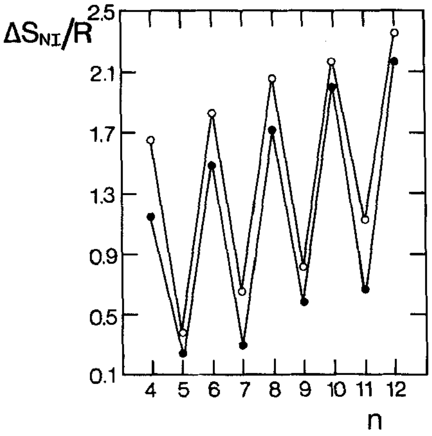


Figure 2. The dependence of the entropy change associated with the nematic–isotropic transition on the number of methylene groups, *n*, in the flexible spacers of the 1(Me).O*n*O.(Me)1 series denoted by ● and the 1.O*n*O.1 series indicated by ○.

substitution is a surprising result if compared to monomeric liquid crystals for which it is often found that a lateral substituent increases $\Delta S_{NI}/R$ [11]. Lateral substitution in polymeric liquid crystals also results in a decrease in T_{NI} but an increase in $\Delta S_{NI}/R$ [5]. The observed decrease in $\Delta S_{NI}/R$ on laterally substituting the 1.O*n*O.1 series is difficult to interpret unambiguously although presumably reflects in part, the increase in biaxiality of the mesogenic groups which results in the flexible spacer being less strongly anchored at its ends and thus, the conformational entropy decreases. Alternatively, this may simply reflect a decrease in the interaction strength parameter of the core resulting from a reduction in the degree of conjugation.

The transitional properties of four members of the CB.O*n*O.(Me)1 series are given in table 2; the compounds are all nematic although the third member is monotropic. It should be noted that the unsubstituted analogues exhibit smectic behaviour and the reduction in T_{SN} for the even membered compounds is over 60°C. This is readily explained by remembering that the smectic phases of CB.O*n*O.*m* compounds having even values of *n* and values of $m \lesssim n$ are thought to have an intercalated structure arising from the mixed core interaction [10]. Lateral substitution of the Schiff's base group reduces this interaction because the lateral spacing is increased resulting in the observed decrease in smectic phase stability.

The dependence of the transition temperatures on the length of the spacer is shown in figure 3; the melting points exhibit no regular dependence on *n* unlike the symmetric dimers whereas the nematic–isotropic transition temperatures show a very pronounced

Table 2. The transition temperatures and entropies of transition for the CB.O*n*O.(Me)1 homologous series; ( ) indicates a monotropic transition.

n	† T_{CI}/°C T_{CN}/°C	T_{NI}/°C	$\Delta S_{C-}/R$	$\Delta S_{NI}/R$
3	† 139	(71)	11·4	0·11
4	132	204	12·1	1·58
5	125	133	8·99	0·38
6	133	177	10·1	1·62

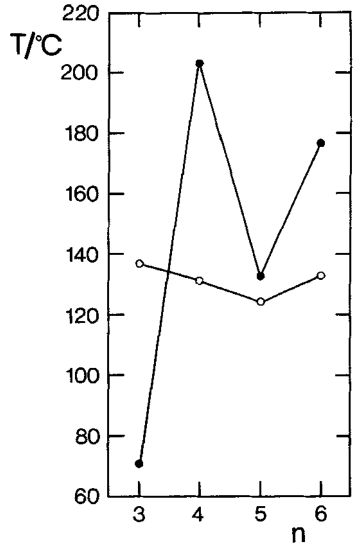


Figure 3. The dependence of the transition temperatures on the length of the flexible spacer, *n*, for the CB . O*n*O . (Me)1 series; the melting point is denoted by ○ and ● indicates the nematic–isotropic transition.

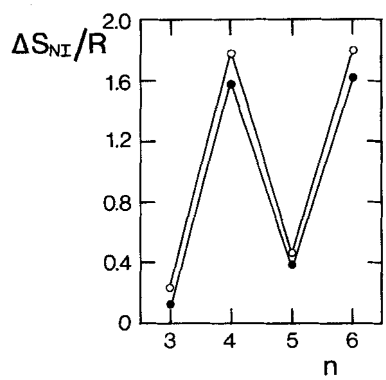


Figure 4. The dependence of the entropy change associated with the nematic–isotropic transition on the length of the flexible spacer, *n*, for the CB . O*n*O . (Me)1 series. Also shown are the entropy changes for the CB . O*n*O . 1 series denoted by ○.

odd–even effect on increasing *n*. The melting points of the CB . O*n*O . (Me)1 compounds are lower than those of the corresponding CB . O*n*O . 1 series with the exception of CB . O5O . (Me)1 whose melting point is actually slightly higher than that of the unsubstituted analogue. The nematic–isotropic transition temperatures of all four substituted compounds are significantly lower than those of the unsubstituted analogues. Figure 4 shows the dependence of the entropy change associated with the nematic–isotropic transition on *n* for both the CB . O*n*O . (Me)1 and CB . O*n*O . 1 series. Lateral substitution has again reduced $\Delta S_{NI}/R$ and again, this may reflect either the increased biaxility of the semi-rigid group or the reduction in conjugation.

5. Conclusions

The effect of laterally substituting the mesogenic units in dimeric liquid crystals is to reduce both the nematic–isotropic transition temperatures and, to a much lesser extent, the entropies associated with the nematic-isotropic transition. It is difficult to interpret these observations unambiguously and model calculations are required which include the flexible nature of the molecules.

I wish to thank the Royal Commission for the Exhibition of 1851 for the award of a postdoctoral fellowship.

References

[1] Vorländer, D., 1927, *Z. phys. Chem.*, **126**, 449.
[2] Rault, J., Liebert, L., and Strzelecki, L., 1975, *Bull. Soc. chem. Fr.*, 1175.
[3] Emsley, J. W., Luckhurst, G. R., Shilstone, G. N., and Sage, I., 1984, *Molec. Crystals liq. Crystals Lett.*, **102**, 223. Jin, J.-I., Kang, J.-S., Jo, B.-W., and Lenz, R. W., 1983, *Bull. Korean chem. Soc.*, **4**, 176. Griffin, A. C., Vaidya, S. R., Hung, R. S. L., and Gorman, S., 1985, *Molec. Crystals liq. Crystals Lett.*, **1**, 131. Buglione, J. A., Roviello, A., and Sirigu, A., 1984, *Molec. Crystals liq. Crystals*, **106**, 169.
[4] Griffin, A. C., and Britt, T. R., 1981, *J. Am. chem. Soc.*, **103**, 4957, Jin, J.-I., Chung, Y.-S., Lenz, R. W., and Ober, C., 1983, *Bull. Korean chem. Soc.*, **4**, 143. Jin, J.-I., and Park, J.-H., 1984, *Molec. Crystals liq. Crystals*, **110**, 293.
[5] Lenz, R. W., 1985, *Polym. J.*, **17**, 105.
[6] Date, R. W., Imrie, C. T., and Luckhurst, G. R. (in preparation).
[7] Imrie, C. T., 1988, Ph.D. Thesis, University of Southampton.
[8] Smith, G. W., Gardlund, Z. G., and Curtis, R. J., 1973, *Molec. Crystals liq. Crystals*, **19**, 327.
[9] Smith, G. W., Gardlund, Z. G., and Curtis, R. J., 1973, *J. chem. Soc. Chem. Commun.*, 202.
[10] Hogan, J. L., Imrie, C. T., and Luckhurst, G. R., 1988, *Liq. Crystals*, **3**, 645.
[11] See, for example: Gray, G. W., 1979, *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic Press), Chap. 1.