

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Reduced odd-even effects in liquid crystalline carbonate dimers: molecular field analysis

Roberto Centore^a

^a Dipartimento di Chimica 'Paolo Corradini', Università degli Studi di Napoli 'Federico II', Napoli, Italy

To cite this Article Centore, Roberto(2009) 'Reduced odd-even effects in liquid crystalline carbonate dimers: molecular field analysis', *Liquid Crystals*, 36: 3, 239 – 245

To link to this Article: DOI: 10.1080/02678290902818800

URL: <http://dx.doi.org/10.1080/02678290902818800>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Reduced odd–even effects in liquid crystalline carbonate dimers: molecular field analysis

Roberto Centore*

Dipartimento di Chimica 'Paolo Corradini', Università degli Studi di Napoli 'Federico II', Via Cinthia, 80126 Napoli, Italy

(Received 30 March 2008; final form 12 February 2009)

Four liquid crystalline carbonate dimers DC_n containing the dimethylbenzalazine mesogen, bis(oxycarbonyloxy)alkane flexible spacers with three to six methylene units and acetate terminal groups were synthesised and their mesogenic behaviour investigated. As compared with the corresponding ester dimers a strong reduction of odd–even fluctuations of nematic–isotropic (N–I) transition entropy is observed. A theoretical analysis of the dimers within the rotational isomeric states (RIS) mean-field approach is also reported. A satisfying agreement between calculated and observed thermodynamic properties is obtained. In fact, the theoretical analysis correctly predicts a significant reduction of the odd–even fluctuations for the core order parameter *S* as well as for the nematic to isotropic transition entropy ΔS_{NI} . The calculated distributions of conformers also show reduced differences between even and odd members. In particular, for even dimers the calculated fraction of linear extended conformers in the nematic phase at the N–I transition is around 27%, which is far below that of the corresponding ester dimers (46%).

Keywords: dimers; molecular-field analysis; liquid crystals; carbonate

1. Introduction

Liquid-crystalline dimers are molecules containing two mesogenic units connected by a flexible spacer. Their mesogenic behaviour shows interesting features that have stimulated investigations both experimentally and theoretically; one of the most relevant features are odd–even effects. According to these effects, some properties related to the degree of order of the nematic phase (the molar entropy of transition from the nematic to isotropic phase, as an example) have an oscillatory behaviour depending on the flexible spacer (a polymethylenic chain in the most simple case) having an even or odd number of carbon atoms. In these oscillations, whose amplitude generally decreases by increasing the length of the spacer, the transition entropy of even members can be greater than that of the odd ones by a factor two or even more (1–5).

While odd–even effects are a typical feature of many classes of liquid-crystalline dimers and polymers, it is known experimentally that in some cases these effects are absent or greatly reduced. A relevant example is given by carbonate dimers and polymers, in which the mesogens are linked to the polymethylenic spacer through carbonate groups, see Scheme 1.

In fact, strong odd–even fluctuations of nematic (N) to isotropic (I) transition temperature (T_{NI}), entropy (ΔS_{NI}) and order parameter (*S*) are observed in nematogenic symmetric ester dimers containing the mesogenic groups of α -methylstilbene and dimethylbenzalazine (3–5), while by replacing the ester linkage between the spacer and mesogens by carbonate groups no significant odd–even effect is found for the

transition temperatures and only a small oscillation of the entropies is still retained (6, 7).

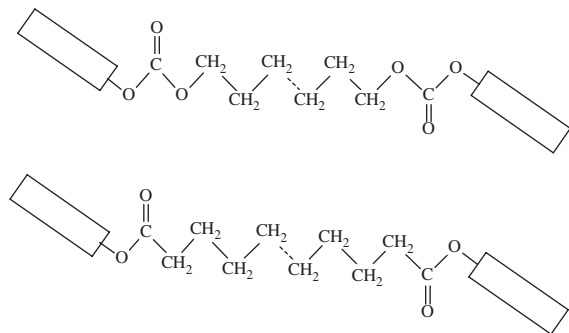
The strong attenuation of odd–even fluctuations in carbonate systems is found also in the corresponding classes of polymers (e.g. main-chain polycarbonates as compared with polyesters) (8), and it has also been observed for dimers containing the cyanobiphenyl mesogenic group (9), so it can be considered a stable feature of carbonate systems possibly related to structural and conformational features of this linkage.

A theoretical analysis of the reduced odd–even effects in carbonate dimers was proposed by Abe *et al.* (9) on the basis of their model of RIS fitting of ²H-NMR (nuclear magnetic resonance) quadrupolar splitting data (10). They found that while for ester and ether dimers the distributions of conformers are clearly different between odd and even members, in the case of carbonate dimers the distinction becomes obscure. In their analysis, they also point to some structural differences between the carbonate linkage as compared with ester and ether linkages, as a possible source of the observed different odd–even features.

We have recently reported a theoretical analysis of nematogenic liquid-crystalline dimers within the RIS mean-field approach. Fair results in the prediction of transitional properties (including the order parameter) of ester dimers showing strong odd–even fluctuations were obtained (11).

In this paper, we test our model on the analogous dimers of (5, 11), but with carbonate linkage between the mesogenic groups and the spacer, their chemical diagrams being shown in Scheme 2.

*Email: roberto.centore@unina.it



Scheme 1. Schematic diagram of carbonate type dimers (up) and ester type dimers (down).

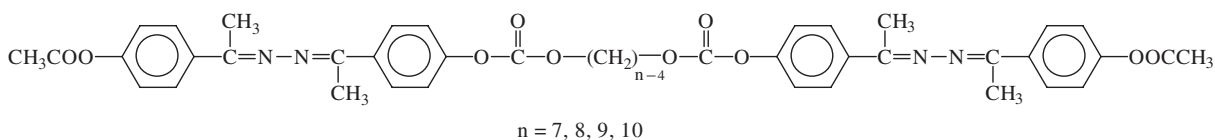
We note that several mean field theoretical analyses have been proposed for dimers showing strong odd–even effects (ether (12–16), alkane (12–16), ester dimers (11)), while the present analysis is the first for carbonate dimers in which those effects are strongly reduced.

2. Experimental

2.1 Synthesis

Carbonate dimers DC n were prepared according to Scheme 3, i.e. by reaction of the monoacetate ester of 4,4'-dihydroxy- α,α' -dimethylbenzalazine (5) with the appropriate alkyl-bis(chlorocarbonate), in stoichiometric ratio 2.2/1.0.

The reaction was performed at room temperature in anhydrous mixture of chloroform and pyridine. After 2 h reaction, the mixture was poured in excess ethanol and the carbonate dimer DC n collected by filtration. Further purification was achieved by column chromatography (silicagel plus chloroform as eluant). Final recrystallisation was from chloroform/ethanol. The alkyl-bis(chlorocarbonate)s were prepared by slow addition of the appropriate di-alcohol to a cold benzene/phosgene solution, under stirring (caution must be used in handling phosgene). Stirring at room temperature was continued for 24 h. Then, the excess benzene/phosgene solution was removed at reduced pressure and the resulting bis(chlorocarbonate) was used without further purification (17).



Scheme 2. Chemical diagram of the carbonate dimers DC n .

The identity and purity of dimers was confirmed by $^1\text{H-NMR}$. NMR assignments for DC8 and DC9 are reported as examples.

DC8. IUPAC name: 2, 7-dioxo-1,8-octanedioic acid, bis[4-[1-[[1-[4-[(1-acetyloxy)phenyl] ethylidene] hydrazono]ethyl]phenyl] ester. $^1\text{H-NMR}$. CD_2Cl_2 . δ (ppm): 1.921 (quintet, 4H), 2.305 (s+s, 18 H), 4.336 (tr, 4H), 7.146 (d, 4H), 7.249 (d, 4H), 7.930 (d, 4H), 7.967 (d, 4H).

DC9. IUPAC name: 2, 8-dioxo-1,9-nonanedioic acid, bis[4-[1-[[1-[4-[(1-acetyloxy)phenyl] ethylidene] hydrazono]ethyl]phenyl] ester. $^1\text{H-NMR}$. CD_2Cl_2 . δ (ppm): 1.549 (quintet, 2H), 1.842 (quintet, 4H), 2.304 (s+s, 18 H), 4.301 (tr, 4H), 7.146 (d, 4H), 7.244 (d, 4H), 7.938 (d, 4H), 7.963 (d, 4H).

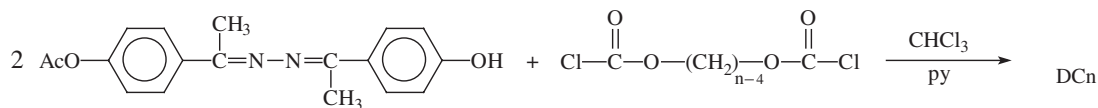
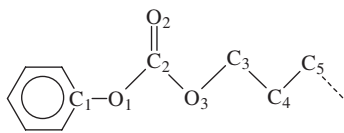
The liquid crystalline behaviour of DC n compounds was investigated by polarising microscopy (Zeiss polarising microscope equipped with Mettler hotstage) and differential scanning calorimetry (Perkin-Elmer Pyris DSC system accurately calibrated with high-purity indium standard, nitrogen atmosphere, scanning rate 10 K/min).

2.2 Theoretical calculations

Conformations of DC n dimers were generated using the geometry of the mesogenic group taken from the crystal structure analysis reported in (5) and following the mathematical procedures described in (11).

Geometric parameters of the carbonate group (Scheme 4) are reported in Table 1; bond lengths were obtained by averaging data from well refined X-ray structures of alkyl-arylcarbonates found in the Cambridge Structural Database (Version 5.29) (18); the set of bond angles was taken from the work of Abe *et al.* on carbonate dimers of cyanobiphenyl (9).

The relative orientation of the two mesogenic groups in the dimer molecule is determined by the Lagrangian coordinates shown in Scheme 5: torsions around the bonds from the mesogen to the alkyloxy O atoms, indicated by ϕ_1 and ϕ_2 respectively; torsions around the bonds from the carbonyl C atom to the two adjacent oxygens, indicated by (χ_1, ψ_1) and (χ_2, ψ_2) ; torsions around the bonds from oxygen to the first CH_2 group of the spacer, indicated by ω_1 and ω_2 ; torsions around $\text{CH}_2\text{-CH}_2$ bonds internal to the polymethylene spacer,

Scheme 3. Synthesis of DC n dimers.

Scheme 4. Numbering scheme of the carbonate group.

Table 1. Bond lengths (Å) and bond angles (°) assumed for the carbonate group.

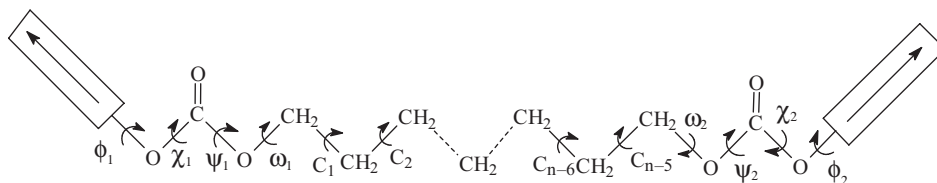
C1–O1 1.408	C2–O3 1.318	O3–C3 1.470
O1–C2 1.351	C2–O2 1.200	C3–C4 1.520
C1–O1–C2 122	O1–C2–O3 108	O1–C2–O2 124
O2–C2–O3 128	C2–O3–C3 118.3	O3–C3–C4 110
C3–C4–C5 112		

indicated by C_i ($i = 1, 2$ for DC7, $n = 1, \dots, 3$ for DC8, $n = 1, \dots, 4$ for DC9 and $n = 1, \dots, 5$ for DC10).

We have assumed a fourfold potential for ϕ_1 and ϕ_2 rotations (minima at $\pm 60^\circ$ and $\pm 120^\circ$) as for the corresponding ester dimers (11) and in agreement with several conformational studies of polycarbonate chains (19, 20); for (χ, ψ) rotations the minimum energy conformation is the (*trans, trans*). However, an old analysis by Williams and Flory (21) and more recent ones (20, 22) indicate that contributions from conformations (*trans, cis*) or (*cis, trans*), with energy higher by 6.74 kJ/mol (20), can also play a role, so we have retained these conformations; (*cis, cis*) conformations have been discarded for sterical reasons (20–22). The torsional potential for ω_1, ω_2 and C_i rotations is threefold (minimum at 180° , secondary minima at $\pm 120^\circ$ (G^\pm)); the energy difference is 0.84 kJ/mol for ω_1 and ω_2 and 2.09 kJ/mol for internal $\text{CH}_2\text{--CH}_2$ bonds (23); for $\text{CH}_2\text{--CH}_2$ bonds adjacent to

oxygens (i.e. C_1 and C_{n-5}), we have assumed the conventional model in which the torsional potential is threefold with T and G states having the same energy (23). This model was already used in theoretical studies of carbonate dimers (9) and ‘reversed ester’ liquid crystalline polymers (24). Conformations corresponding to sequences G^+G^- or G^-G^+ for consecutive bonds of the spacer have been discarded if the 1,5 contact is between C atoms (‘pentane’ effect) (14,23); if the contact is between C and O atoms the conformation has been retained with additional energy of 2.47 kJ/mol, while it has been retained with 2.09 kJ/mol additional energy if the contact is between O atoms (i.e. for DC7) (23). Finally, for each conformer, a direct check was performed on the distances between atoms of the two different mesogenic groups, discarding those conformers for which the minimum distance was less than 3.4 Å. The total number of conformations used in the calculations was 6467 for DC7, 19002 for DC8, 43507 for DC9 and 106352 for DC10.

The calculation of the thermodynamic properties of the dimers was performed following the molecular-field approach reported in detail in (11). For each conformer, the τ angle between the elongation axes of the two mesogenic groups was calculated (the axes are indicated by arrows in Scheme 4). The elongation axis of the mesogen was taken as the segment connecting the two phenyl-C atoms bonded to O atoms. The energy of each conformer was split in an internal part (conformation dependent) and in an external part (orientation dependent) (25). After proper averaging over all orientations and conformations, the orientation-conformation partition function was evaluated and, from that, the Helmholtz free energy and other related thermodynamic quantities (11). The experimental N–I transition temperatures of the dimers were used in the Boltzmann factors.

Scheme 5. Definition of torsional coordinates and of the angles between the mesogenic groups for DC n dimers. τ is the angle between the arrows; θ is the supplementer angle of τ ($\theta = 180^\circ - \tau$).

3. Results and discussion

DC n dimers show thermotropic mesomorphism (Table 2). The liquid-crystal phase was assigned as nematic, as suggested by the mobile schlieren texture observed by the polarising microscope. Concerning odd–even fluctuations, it is evident from Table 2 that they are absent for the transition temperatures, and still present, but greatly reduced, for transition enthalpies and entropies. This behaviour is similar to the few classes of carbonate dimers studied up to now (6,7,9) and may be considered as typical of carbonate dimers as compared with ester dimers.

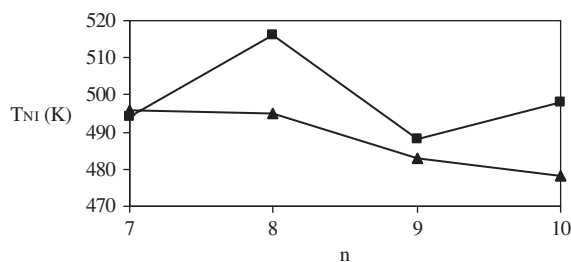
On the other hand, the corresponding D n ester dimers show strong odd–even fluctuations (5). The striking difference between DC n and D n dimers is graphically shown in Figure 1. We note that a comparison between the two classes of dimers is particularly significant in our case, since they have the same mesogenic group and the same terminal tails. Actually, D n and DC n dimers (same n) differ only for a CH₂ group being replaced by an O atom (see Scheme 1), so they are isoelectronic. Looking at Figure 1 it is also evident that between correspondent carbonate and ester dimers relevant differences are mainly observed for even members, the differences between odd members being smaller by far.

Now we discuss the results of the theoretical analysis.

The dependence of the calculated core order parameter S versus the scaled interaction parameter X_a^* is shown in Figure 2.

Table 2. Experimental thermodynamic data of DC n dimers.

	T_{C-N} (K)	T_{NI} (K)	ΔH_{NI} (kJ/mol)	$\Delta S_{NI}/R$
DC7	463	496	4.3	1.04
DC8	465	495	5.5	1.34
DC9	447	483	4.7	1.17
DC10	445	478	5.2	1.31



The shape of the curves is very similar to the theoretical curves reported by Ferrarini *et al.* in their theory of dimers as mixtures of the linear and the bent conformers (12) and to the curves we have evaluated for the corresponding D n ester dimers (11). We note the closeness of curves for dimers of the same parity when plotted against the scaled X_a^* parameter. However, the spanning between the curves for even and odd dimers is significantly reduced in DC n as compared with D n dimers.

The value of X_a^* at the N–I transition, X_a^{*NI} , is obtained by equating the Helmholtz free energy of the isotropic and nematic phases (11,12–16,25).

From the values of X_a^{*NI} we have estimated the core order parameter at the N–I transition, S^{NI} , as well as other thermodynamic properties of the dimers, such as ΔS_{NI} and T_{NI} (11).

The transition temperatures have been scaled with the transition temperature of the DC7 dimer and approximate molecular volumes have been estimated from the crystal structures of ester dimers D8 and D9 (5).

The calculated thermodynamic properties are summarised in Table 3. For easy comparison, they are also reported graphically in Figures 3 and 4 together with the calculated properties of the corresponding ester dimers (11).

The results for the order parameter are satisfying. In fact, the predicted values are quite realistic for all dimers and the odd–even fluctuations are clearly reduced as compared with ester dimers. Actually, for all DC n dimers, the predicted order parameter at the N–I transition is close to 0.4 (in particular, $S^{NI} \cong 0.4$ for odd and $S^{NI} \cong 0.45$ for even members) which is intermediate between the predicted value of 0.35 for odd and 0.5 for even D n ester dimers (11).

This result is in agreement with experimental data available from the literature. For ester dimers containing the mesogenic groups of cyanobiphenyl or phenylbenzoate, Toriumi *et al.* (26) measured the order parameter with the ²H-NMR technique and found values, extrapolated at $T = T_{NI}$, of 0.38 for the odd

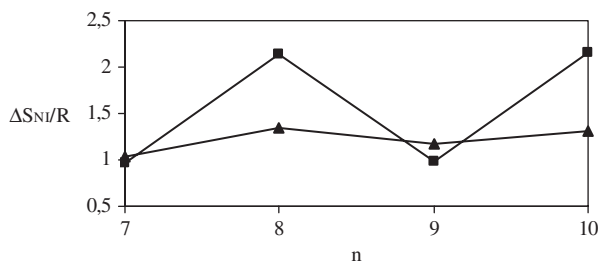


Figure 1. Experimental nematic–isotropic transition temperatures and entropies for ester D n dimers (squares) and carbonate DC n dimers (triangles). Data for D n dimers are taken from (5).

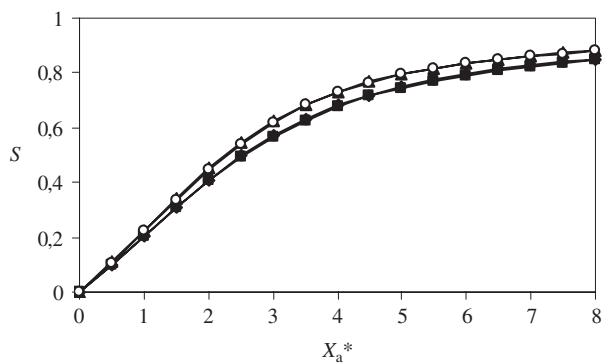


Figure 2. Plot of the orientational order parameter, S , versus X_a^* , for DC7 (squares), DC8 (triangles), DC9 (diamonds) and DC10 (circles).

members and 0.60 for the even members; for the carbonate dimers, on the other hand, the difference between odd and even members is scarcely significant and intermediate values close to 0.5 were found both for even and odd members (9). Analogously, for ester dimers containing the α -methylstilbene mesogen, the order parameter measured with the X-ray scattering technique was 0.45 for odd members and 0.58 for even ones (27); for the corresponding carbonate dimers the difference between even and odd members is not appreciable and values of the order parameter, measured with the same technique, were around 0.48 for all (7).

The calculated transition entropies are also substantially satisfying, showing a reduction of the odd–even fluctuations; moreover we note that, in

Table 3. Calculated thermodynamic properties of DCn dimers at the N–I transition.

DCn	X_a^{NI}	S^{NI}	$T_{NI}^c/T_{NI}^c(\text{DC7})$	$\Delta S_{NI}^c/R$
DC7	1.915	0.390	1	0.77
DC8	2.000	0.454	1.09	0.91
DC9	1.920	0.396	0.96	0.77
DC10	2.032	0.453	1.02	0.92

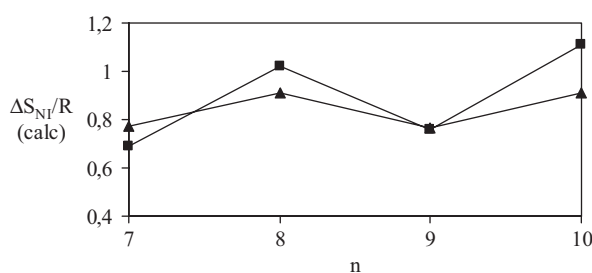
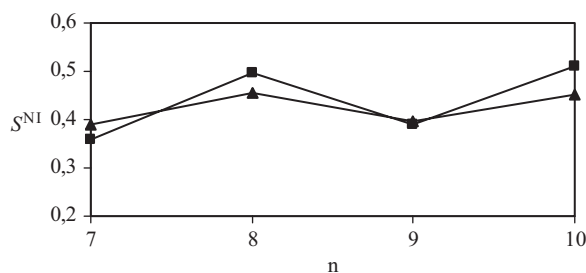


Figure 3. Calculated order parameter at $T = T_{NI}$ (left), and transition entropy (right) for DCn (triangles) and Dn (squares) dimers. Data for Dn dimers are taken from (11).

comparison with ester dimers, the transition entropies of the odd members are less varied than the even members, in agreement with the experimental data.

The calculated N–I transition temperatures, on the other hand, show a less satisfying behaviour. In fact, though the predicted fluctuations are strongly reduced as compared with esters, we have to remember that odd–even fluctuations of transition temperatures are absent in DCn–carbonates.

As a general remark to the above data, we stress that just because odd–even fluctuations are absent or greatly reduced in carbonates, and the differences between the thermodynamic properties of consecutive members are small, it is clear that quantitative agreement between calculated and observed data is not expected for a simulation based on a simplified model, like our model. A better quantitative agreement could be reached perhaps by using more sophisticated mean-field approaches (13,14). However, it seems that the reduction of odd–even fluctuations in carbonate as compared with ester dimers, which is a quantitative rather than a qualitative effect, is within the target of our model.

Further insight into the difference between carbonate and ester dimers can be reached by comparing the calculated distributions of conformers in the liquid crystal phase. These are reported in Figure 5 for DC7 and DC8 (similar distributions are calculated for DC9 and DC10). For easy comparison with the work from previous literature on ester and carbonate dimers (28), we have reported in Figure 5 the integrated distribution curves as a function of the disorientation angle θ between the mesogenic groups, which is the supplement of the τ angle: $\theta = 180^\circ - \tau$ (see Scheme 5). In this way, for a given θ_m value, $P(\theta_m)$ in the curves of Figure 5 gives the probability of conformers with $0 \leq \theta \leq \theta_m$ (29). In Figure 5, are also reported the correspondent curves for the ester dimers D7 and D8 calculated from the data of (11).

For ester dimers the curves clearly have different shapes between even and odd members showing, in particular, the bimodal character first pointed out by

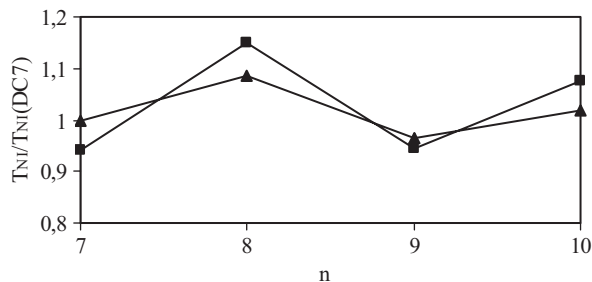


Figure 4. Calculated scaled transition temperatures for DC n (triangles) and D n (squares) dimers. Data for D n dimers are taken from (11).

Abe *et al.* (28, 29). Passing to carbonate dimers, the characteristic features of the curves become less marked by far, and the curves lose their identity assuming a shape not so easily distinguishable between even and odd members. It is noteworthy that the curves of Figure 5 are similar to those reported by Abe *et al.* in their RIS/ 2 H-NMR analysis (28).

A quantitative comparison between DC n and D n dimers shows that for odd members the changes are relatively minor. As an example, in the nematic phase at $T = T_{NI}$, the probabilities of linear extended conformers, say those with $150^\circ \leq \tau \leq 180^\circ$, i.e. $0^\circ \leq \theta \leq 30^\circ$, are 10.1% for DC7 and 9.9% for DC9; for D7 and D9 the

corresponding values are 2.3% and 2.2% respectively. On the other hand, for even dimers the change is more relevant. In fact, the probabilities of conformers with $150^\circ \leq \tau \leq 180^\circ$ ($0^\circ \leq \theta \leq 30^\circ$), in the nematic phase at $T = T_{NI}$, are 27.6% for DC8 and 27.0% for DC10, while for D8 and D10 the corresponding values are 44.7% and 46.9%. These conformational data are summarised in Table 4, in which the probability of linear extended conformers is also reported for the isotropic phase ($X_a^* = 0$).

So the different mesogenic behaviour of carbonates seems related mainly to a strong absolute reduction of the probability of linear extended conformers in the nematic phase for even members. This diminution, with reference to the corresponding ester dimers, can be due to various factors: the geometry of the carbonate linkage, as pointed out by Abe *et al.* (9), and also the different conformational features of the linkage (in particular, the torsional coordinates ψ_1 and ψ_2 for which *gauche* states are allowed in esters and forbidden in carbonates, and the torsional coordinates ω_1, ω_2, C_1 and C_{n-5} that make less energetically penalising, in carbonates, *gauche* conformations in the spacer (including G^+G^- or G^-G^+ sequences)). It can also be understood why the effects of this different conformational freedom are more relevant for even members; in fact, for the odd members the number of linear extended

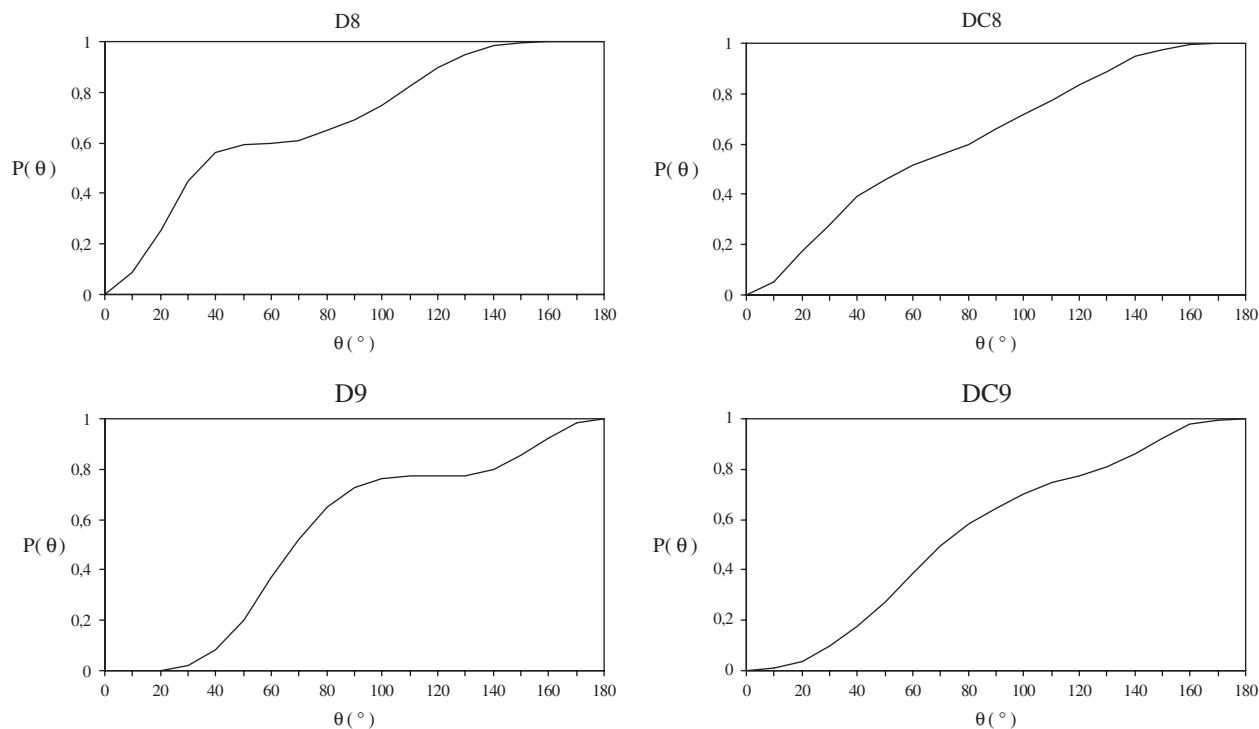


Figure 5. Integrated distribution curves for the disorientation angle θ between the mesogenic groups (see Scheme 5). The curves have been evaluated from the calculated distribution of conformers in the nematic phase at $T = T_{NI}$ with $X_a^* = 2.00$ for DC8 and $X_a^* = 1.92$ for DC9. Also reported are the correspondent curves for D7 and D8 calculated from data of (11).

Table 4. Calculated probability of linear extended conformers ($150^\circ \leq \tau \leq 180^\circ$) for DC n and D n dimers at $T = T_{NI}$ in the isotropic and nematic phase. Data for D n dimers are taken from (11).

	Isotropic	Nematic
DC7	5.4%	10.1%
DC8	14.9%	27.6%
DC9	5.3%	9.9%
DC10	14.3%	27%
D7	1.6%	3.5%
D8	26.2%	46.6%
D9	1.2%	2.2%
D10	24.9%	46.9%

conformers is in any case very small. As an example, for DC7 and DC9 the number fraction of conformers with $150^\circ \leq \tau \leq 180^\circ$ is 4.0% and 4.5% respectively, while it is 13.1% and 12.0% for DC8 and DC10.

Acknowledgement

I thank Professor A. Abe for sending me a preprint version of his and Professor Furuya's most recent paper entitled 'Spatial configuration and thermodynamic characteristics of main chain liquid crystals'.

References

- (1) Emsley, J.W.; Luckhurst, G.R.; Shilstone, G.N.; Sage, I. *Molec. Cryst. Liq. Cryst. Lett.* **1984**, *102*, 223–233.
- (2) Emsley, J.W.; Luckhurst, G.R.; Shilstone, G.N. *Mol. Phys.* **1984**, *53*, 1023–1028.
- (3) Buglione, J.A.; Roviello, A.; Sirigu, A. *Molec. Cryst. Liq. Cryst.* **1984**, *106*, 169–185.
- (4) Centore, R.; Roviello, A.; Sirigu, A. *Liq. Cryst.* **1988**, *3*, 1525–1534.
- (5) Centore, R.; Roviello, A.; Sirigu, A.; Tuzi, A. *Liq. Cryst.* **2006**, *33*, 929–933.
- (6) Carfagna, C.; Iannelli, P.; Roviello, A.; Sirigu, A. *J. Therm. Anal.* **1985**, *30*, 1317–1324.
- (7) Centore, R. Thesis for Graduate Degree in Chemistry, University of Naples, 1986.
- (8) Roviello, A.; Sirigu, A. *Makromol. Chem.* **1982**, *183*, 895–904.
- (9) Abe, A.; Furuya, H.; Nam, S.Y.; Okamoto, S. *Acta Polym.* **1995**, *46*, 437–444.
- (10) Abe, A.; Furuya, H.; Shimizu, R.N.; Nam, S.Y. *Macromolecules* **1995**, *28*, 96–103.
- (11) Centore, R. *Liq. Cryst.* **2007**, *34*, 729–736.
- (12) Ferrarini, A.; Luckhurst, G.R.; Nordio, P.L.; Roskilly, S.J. *Chem. Phys. Lett.* **1993**, *214*, 409–417.
- (13) Ferrarini, A.; Luckhurst, G.R.; Nordio, P.L.; Roskilly, S.J. *J. Chem. Phys.* **1994**, *100*, 1460–1469.
- (14) Ferrarini, A.; Luckhurst, G.R.; Nordio, P.L. *Mol. Phys.* **1995**, *85*, 131–143.
- (15) Ferrarini, A.; Luckhurst, G.R.; Nordio, P.L.; Roskilly, S.J. *Liq. Cryst.* **1996**, *21*, 373–382.
- (16) Stocchero, M.; Ferrarini, A.; Moro, G.J.; Dunmur, D.A.; Luckhurst, G.R. *J. Chem. Phys.* **2004**, *121*, 8079–8097.
- (17) Roviello, A.; Sirigu, A. *Eur. Polymer J.* **1979**, *15*, 423–430.
- (18) Allen, F.H. *Acta Crystallogr. B* **2002**, *58*, 380–388.
- (19) Hutnik, M.; Argon, A.S.; Suter, U.W. *Macromolecules* **1991**, *24*, 5956–5961.
- (20) Sulata, M.S.; Natarajan, U.; Sivaram, S. *Macromol. Theory Simul.* **2002**, *11*, 655–668.
- (21) Williams, A.D.; Flory, P.J. *J. Polymer Sci.: Part A-2* **1968**, *6*, 1945–1952.
- (22) Bohets, H.; van der Veken, J. *Phys. Chem. Chem. Phys.* **1999**, *1*, 1817–1826.
- (23) Flory, P.J. *Statistical Mechanics of Chain Molecules*; Wiley Interscience Publishers: New York, 1969; Chap. V.
- (24) Yoon, D.Y.; Brückner, S. *Macromolecules* **1985**, *18*, 651–657.
- (25) Luckhurst, G.R. *Recent Advances in Liquid Crystalline Polymers*; Chapoy, L.L., Ed.; Elsevier Applied Science: London, 1985; Chap. 7, 105–127.
- (26) Toriumi, H.; Furuya, H.; Abe, A. *Polym. J.* **1985**, *7*, 895–898.
- (27) Capasso, R.; Iannelli, P.; Roviello, A.; Sirigu, A. *Macromolecules* **1985**, *18*, 2773–2775.
- (28) Abe, A.; Furuya, H. *Kobunshi Ronbunshu* **1986**, *43*, 247; *Ekisho Kobunshi*; Iimura, K.; Asada, T.; Abe, A., Eds.; Shiguma: Tokyo, 1988; Ch. 2, pp. 247–252.
- (29) Abe, A. *Macromolecules* **1984**, *17*, 2280–2287.