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Application of the Onsager Model to the LC–Isotropic Phase Transition of Binary Mixtures of a Nematic Liquid with Diluents

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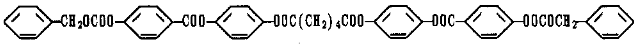
ABSTRACT: A model nematic compound, bis(4-(4′-benzyloxycarbonyloxybenzoyloxy)phenyl)adipate (1), has been dissolved in two different solvents (adipic acid dinitrile and hydroquinone dimethyl ether) which represent parts of the building blocks of the pure liquid crystalline compound 1 with two mesogen unit dipoles pointing in opposite directions and is obtained by a stepwise reaction using protective groups. The behavior of this LC model compound at the isotropic–nematic phase transition as a function of temperature at a given solvent volume fraction is in good agreement with the classical Onsager model for the entropic ordering of hard rods with increasing number density. The corresponding endotherms are also very sharp, indicating that intermolecular interactions (aside from excluded volume) are not dominant and that the system can respond effectively to rapid changes in number density resulting from changes in solvent density with temperature.

Introduction

Rigid, rodlike molecules interacting with each other mainly through steric, excluded volume interactions form an interesting model system which can be used to study the nematic–isotropic phase transition, and to test the validity of theoretical models. A well-known theory of the ordering of hard rods with a large aspect ratio L/d at sufficiently high density is due to Onsager.[1] In this picture the free energy of the system includes the entropy of long rigid rods, as well as the excluded volume interaction for a large aspect ratio (neglecting the effect of the shapes of the rod ends) based on a second-virial-coefficient approximation. The theoretical description can be used to numerically calculate the bulk isotropic–nematic phase transition, as well as properties of the equilibrium isotropic–nematic interface.[2] The question remains, however, as to how good this simple model is for a real system. Although the Onsager model is widely regarded as accounting for the formation of nematic ordering in liquid crystals,[3] it is useful to have an independent assessment of the theory based on observed properties at the phase transition. Other treatments applying the Flory–Huggins theory to nematic–isotropic phase equilibria have also been discussed.[4,5]

In this paper we present the results of experiments using a model nematic compound bis(4-(4′-benzyloxycarbonyloxybenzoyloxy)phenyl)adipate (1) dissolved in turn in two different solvents (adipic acid dinitrile [**A**] and hydroquinone dimethyl ether [**B**]) which themselves represent parts of the building blocks of the pure LC compound. The structural characteristics of these model compounds are that the dipoles of the oxyphenylcarbonyloxyphenyloxy mesogen are in opposite directions because the adipic ester linkage is exclusively formed through the hydroxy hydroquinone group. This intramolecular compensation of the two mesogen unit dipoles is advantageous for the experiments described below, since the mesogenic properties of the model compound predominately result only from its isotropic shape.



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Experimental Section

The LC model compound 1 was synthesized by reacting adipic acid dichloride with 4-(benzyloxycarbonyloxy)(4′-hydroxyphenyl)benzoate (1:2 mole ratio) in dichloromethane with pyridine as HCl scavenger; the 4-hydroxybenzoic acid hydroquinone ester derivative has been obtained by first reacting 4-(benzyloxycarbonyloxy)benzoyl chloride with 4-(*tert*-butyldimethylsilyloxy)phenol and subsequent removal of the silyl protecting group. Experimental details including the synthesis of the monofunctional mesogen starting material will be given elsewhere:[6] T_m = 155 °C; T_c = 200 °C. ^{1}H NMR (CDCl$_3$-d_1, 250 MHz, TMS, δ, ppm): 1.89 (m, 4H), 2.65 (m, 4H), 5.29 (s, 2H), 7.17 (d, 4H, J = 9.2 Hz), 7.24 (d, 4H, J = 9.2 Hz), 7.35 (d, 4H, J = 8.7 Hz), 7.43 (m, 10H), 8.23 (d, 4H, J = 8.7 Hz). ^{13}C NMR (CDCl$_3$-d_1, 62.5 MHz, TMS, δ, ppm): 24.21, 33.88, 70.67, 121.21, 122.49, 122.52, 127.04, 128.58, 128.74, 128.91, 131.87, 134.45, 148.15, 148.17, 152.82, 155.09, 164.07, 171.54.

The diluents adipic acid dinitrile (A) and hydroquinone dimethyl ether (B) were obtained from Fluka.

The binary mixture of 1 with diluents **A** or **B** was prepared by accurately weighing the diluent (0.1 up to 20 mg) in a small test tube; then the LC compound 1 was weighed until the total weight of the binary mixture was exactly 100 mg. For complete mixing of the two components, the test tube was sealed, heated about 10 K above the melting temperature T_m (about 165 °C), agitated at this temperature, and then cooled down to room temperature. The composition of the binary mixtures and the phase transition temperatures together with the heats of fusion are given in Tables I and II.

Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC II. The sample weight was 2–5 mg. The melting temperature T_m and the nematic–isotropic phase transition temperature T_c were taken as the corresponding endotherm peak maximum temperature. Gallium, indium, tin, azobenzene, and acetanilide were used as calibration standards.

^{1}H NMR and ^{13}C NMR spectra of the model compound were recorded at 250 or 62.5 MHz on a Bruker AC 250 MHz NMR in CDCl$_3$-d_1 referenced to a standard of Me$_4$Si (TMS) at 25 °C (~ 5% or ~ 40% w/v solutions; s = singlet, d = doublet, m = multiplet).

The optical micrographs were obtained with a Leitz microscope Laborlux R pol, which was equipped with a Linkam Scientific

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Table I. Melting Temperature T_m of the Crystalline–Nematic Phase Transition and Clearing Temperature T_c of the Nematic–Isotropic Phase Transition for LC Compound 1/Diluent A (Adipic Acid Dinitrile) Binary Mixtures with Diluent Volume Fraction ϕ, Corresponding Enthalpies ΔH_m and ΔH_i, and Density ρ_A of Diluent A and ρ_{LC} of 1 at T_c

concn of **A**, wt %	ϕ	T_m, K	ΔH_m, J/g	T_c, K	ΔH_i, J/g	ρ_A,[a] g/cm^3	ρ_{LC},[b] g/cm^3
0.1	0.00107	424.9	80.1	468.7	7.5	0.8361	0.871
0.5	0.0053	424.2	78.6	466.9	6.8	0.8374	0.873
1	0.0107	423.8	76.2	462.8	7.1	0.8403	0.876
2	0.0214	422.8	72.5	458.2	6.9	0.8436	0.881
5	0.053	421.8	70.9	452.2	7.0	0.8479	0.886
10	0.106	420.2	63.7	432.8	1.3	0.8619	0.904
20	0.211	407.4	65.8	–	–	–	–

[a] Approximate experimental error: ±0.0005. [b] Approximate experimental error: ±0.002.

Table II. Melting Temperature T_m of the Crystalline–Nematic Phase Transition and Clearing Temperature T_c of the Nematic–Isotropic Phase Transition for LC Compound 1/Diluent B (Hydroquinone Dimethyl Ether) Binary Mixtures with Diluent Volume Fraction ϕ, Corresponding Enthalpies ΔH_m and ΔH_i, and Density ρ_B of Diluent B and ρ_{LC} of 1 at T_c

concn of **B**, wt %	ϕ	T_m, K	ΔH_m, J/g	T_c, K	ΔH_i, J/g	ρ_B,[a] g/cm^3	ρ_{LC},[b] g/cm^3
0.5	0.0048	424.6	80.1	469.2	7.5	0.895	0.870
1	0.00955	423.9	79.1	468.5	7.5	0.896	0.871
2	0.0191	423.2	76.8	465.4	7.0	0.899	0.874
5	0.048	422.1	73.3	459.6	6.3	0.905	0.879
7.5	0.072	421.1	70.7	455.1	5.2	0.910	0.883
10	0.096	420.1	65.5	442.0	5.9	0.924	0.895
20	0.193	414.1	57.9	–	–	–	–

[a] Approximate experimental error: ±0.005. [b] Approximate experimental error: ±0.002.

Instrument hot stage Model THM 600. Ice, azobenzene, acetanilide, and benzanilide were used as calibration standards.

The density ρ of diluents **A** and **B** at the temperature (T_c) of the nematic–isotropic phase transition of the binary mixtures has been calculated from the linear least-squares fit plot of density values given in the literature for the temperature range 15–85 °C (**A**[7,8]) and 55–184 °C (**B**[9-11]); the resulting expressions for the temperature dependency of the density are $\rho_T = -0.0007177T + 0.976\,58$ for diluent **A** and $\rho_T = -0.00105T + 1.1022$ for diluent **B** (ρ in g·cm^{-3}, temperature in °C). The density of the bimesogen model compound **1** at the nematic–isotropic phase transition temperatures T_c of the binary mixtures 1/diluent has been calculated from the relationship $\rho_T = -0.0009114T + 1.0498$ (ρ in g·cm^{-3}, temperature in °C). This result was established by using the density calculated from the mass/volume ratio of a cylindrical object of the LC-network of cured bis(4-(4′-methacryloyloxybenzoyloxy)phenyl)adipate at 25 °C (ρ_{25} = 1.027 g·cm^{-3}) and the density of the diluents **A** and **B** at T = 378 °C (ρ_{378} = 0.705 g·cm^{-3}), given by the intersection of the straight lines of the individual density–temperature relationships of **A** and **B**. The calculated densities of the diluents **A** and **B** and of the LC compound **1**, which were used for the calculation of the number density C_n of the binary mixture at the nematic–isotropic melt transition temperature, are listed in Tables I and II.

Results and Discussion

The bimesogen model compound **1** forms a thermotropic nematic liquid crystal with a crystalline–nematic transition temperature of T_m = 155 °C (ΔH_m = 80.3 J/g) and a nematic–isotropic transition temperature of T_c = 200 °C (ΔH_i = 7.5 J/g) (Figure 1). Upon cooling from the isotropic melt, the isotropic–nematic transition occurs at 194 °C, and crystallization, at 125 °C. In a second heating cycle, both T_m and T_c are shifted to lower temperatures by about 3 K. The nematic mesophase is evident from the marbled texture shown in the picture Figure 2a. The clearing temperature is clearly identified with the occurrence of the nematic-isotropic phase transition, as shown from the optical micrographs taken at the onset of the isotropization endotherm (Figure 2b).

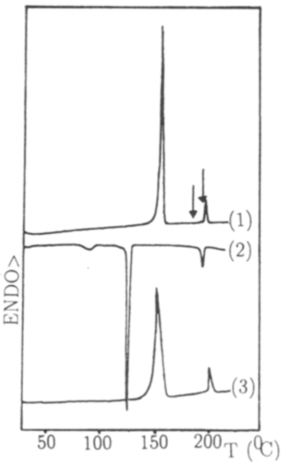

Figure 1. DSC traces of the model bimesogen **1** (heating/cooling rate: 20 K/min): (1) heating of the sample crystallized from ethanol; (2) cooling from the isotropic melt; (3) heating of the sample crystallized from the melt. The arrows in trace 1 denote the two temperatures at which pictures were taken using the polarizing microscope (see Figure 2).

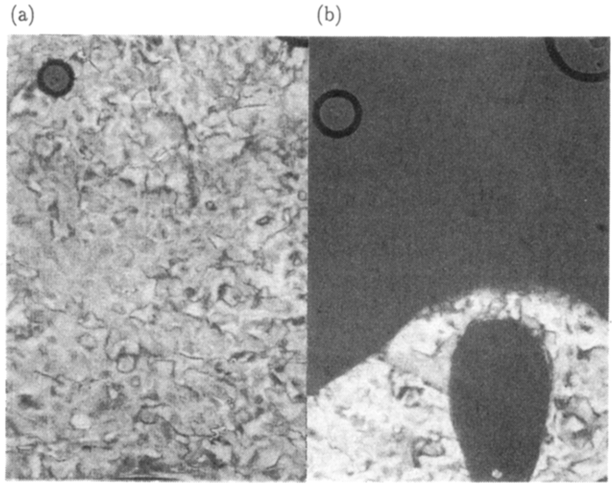
(a) (b)

Figure 2. Nematic marble texture of **1** in the mesophase at 189 °C (a) and a partial marble texture at 199 °C (b) close to the nematic–isotropic transition. Conditions: magnification, 90×; crossed polarizers; heating rate, 20 K/min.

Using different solvent concentrations (ranging from 0.1 to 20% by weight) for the LC compound, the different clearing points of the concentrated solutions were recorded as the temperature was raised (Figure 3a,b). All DSC traces show a large endotherm for the crystalline–nematic phase transition, followed by the smaller endotherm for the nematic–isotropic phase transition. In the case of the LC compound **1**/**B** diluent mixture, an additional melting endotherm appears at lower temperatures for **B** concentrations ≥5 wt %; this is associated with the melting of the **B** phase, which is formed after this concentration is exceeded. Both the crystalline–nematic (T_m) and the nematic–isotropic phase transition temperature (T_c) of the LC compound decrease with increasing diluent concentration. The temperature range of the mesophase and the enthalpy for the nematic–isotropic phase transition decrease as well (see Tables I and II), corresponding to the decrease of mesomorphic order. Above a diluent concentration of about 20 wt %, a mesophase does not appear,

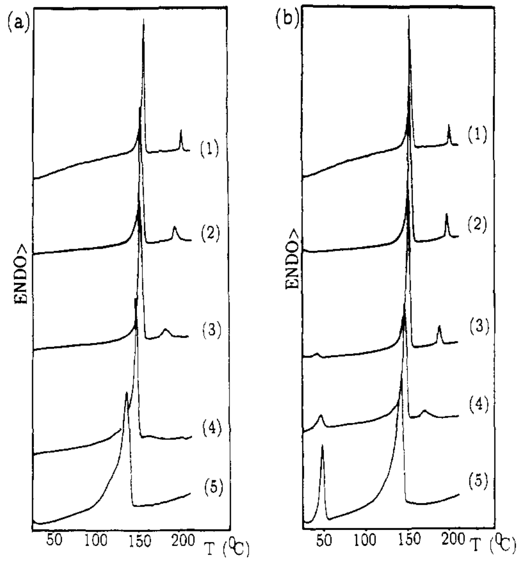

Figure 3. DSC traces of the pure bimesogen 1 and of binary mixtures bimesogen 1/diluent A (a) and bimesogen 1/diluent B (b) for different diluent concentrations. Conditions: heating rate, 20 K/min; (1) pure bimesogen 1; (2) 1 wt % diluent; (3) 5 wt % diluent; (4) 10 wt % diluent; (5) 20 wt % diluent.

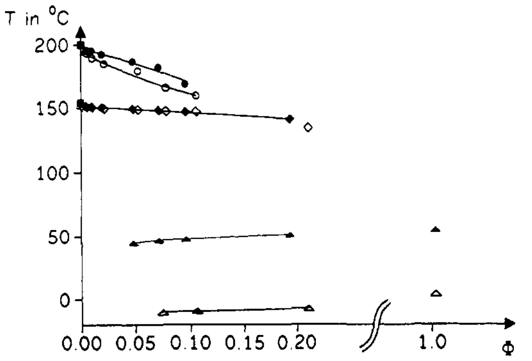

Figure 4. Phase diagram for the binary mixture bimesogen 1/diluent A and bimesogen 1/diluent B: dependency of the melting temperature T_m and clearing temperature T_c on the volume fraction ϕ of the diluent in the composition range $0 \leq \phi \leq 0.2$: system 1/diluent A, T_m (△) of diluent and T_m (◇)[12] and T_c (○) of bimesogen 1; system 1/diluent B, T_m (▲) of diluent and T_m (◆)[12] and T_c (●) of bimesogen 1.

and only the crystalline–isotropic phase transition is observed in the thermograms as well as under the microscope under crossed polarizers. The isotropization endotherm is sharper for the **B** diluent than the **A** diluent, implying a better order in the nematic phase for the system with the **B** diluent. It has to be emphasized that the sharpness of these endotherms indicates the distinct response of the system to rapid changes in the number density, which results from changes in solvent density with temperature; this reflects the primarily entropy driven nematic–isotropic phase transition and that intermolecular interactions are only a secondary factor for the phase transition.

The phase diagrams of the two binary mixtures as derived from the DSC traces (Figure 3a,b) are given in Figure 4. The decrease in the crystalline–nematic phase transition temperature with increasing diluent concentration is nearly identical for both diluents **A** and **B**. The effect of the diluent on the melting temperature depression is especially pronounced for very low diluent concentrations. The variation of the melting temperature T_m with diluent concentration (see Tables I and II) follows to a first approximation the relationship for an ideal solution; if we take the expression for the melting point depression in terms of the heat of mixing parameter **B** characteristic for a given polymer–diluent pair as developed by Flory,[13] we find $B \simeq 2$ cal/cm^3 for both adipic acid dinitrile (diluent **A**) and hydroquinone dimethylether (diluent **B**), which is in the range of values found earlier for similar diluents.[14]

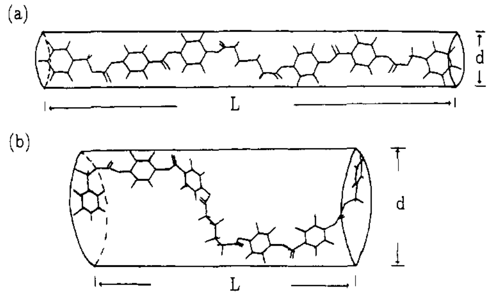

Figure 5. Schematic representation of the bimesogen model compound 1 in the fully extended conformation (a)[16] and the energy minimized conformation as obtained from molecular mechanics calculation for a single molecule in the gas phase (b).[15] The cylinders of length *L* and diameter *d* illustrate the size and volume of 1 in the mesophase for two different conformations: (a) $L \sim 44$ Å and $d \sim 5$ Å ($L/d = 8.8$); (b) $L \sim 30$ Å and $d \sim 11$ Å ($L/d = 2.7$).

The widening of the nematic–isotropic phase transition endotherm with increasing diluent concentration might be caused by larger density fluctuations of the LC phase. This is coupled with the formation of a two-phase system with variation of the diluent volume fraction (diluent rich and LC model compound rich phases) as revealed from the increase and sharpening of a diluent melting endotherm at lower temperature; simultaneously, the melting of the LC compound 1 reflects the usual melting temperature suppression effect caused by diluents in crystalline systems.

The temperature of the nematic–isotropic melt transition T_c decreases faster for the **A** diluent than for the **B** diluent system; this dependence is almost linear for the **B** diluent. As expected, the clearing points for diluents **A** and **B** converge to a common value as the concentration of diluent is decreased. Several reasons for the different behaviour of the binary LC systems can be suggested. The thermal expansion coefficient for adipic acid dinitrile (diluent **A**) is less than for hydroquinone dimethylether (diluent **B**). Nevertheless, as can be seen from Figure 5b, showing the conformation of the bimesogen according to a molecular mechanics calculation,[15] the hydroquinone dimethyl ether molecules can readily fit into this corkscrew conformation, resulting in an effectively shorter and thicker cylindrical shape, particularly when one takes into account the interaction of the π electrons of the aromatic rings of the mesogen and diluent **B**. Hence this conformation, the probability of which increases with increasing temperature above the crystalline–mesophase transition temperature T_m, is expected to be more stable for diluent **B** than for diluent **A**, resulting in a higher transition temperature for the clearing point T_c. It is also evident from Figure 5 that the relatively long and thin diluent **A** molecules cannot easily accommodate themselves to the corkscrew shape, resulting in a lower transition temperature for the clearing point.

The Onsager prediction for the value of $\bar{C}_n$ in the nematic phase at the phase transition point is $\bar{C}_n = C_n L^2 d = 5.341 \pm 0.005$.[2] The value determined from experiment is about 10% higher (Table III). This is reasonable because the number density at the phase transition increases with decreasing diluent concentration; also the aspect ratio of the molecule studied is $L/d \sim 8.8$ for the conformation shown in Figure 5a (with $L \sim 44$ Å, $d \sim 5$ Å[16]) and L/d

Table III. Number Density $C_n = (m_{LC}/M_{LC})(N_A/V)^a$ of the Nematic Phase at the Phase Transition Point T_c and Onsager Value $\bar{C}_n = C_nL^2d^b$ at the Phase Transition Point for Different Concentrations of Diluent A (Adipic Acid Dinitrile) and Diluent B (Hydroquinone Dimethyl Ether) in Binary Mixtures 1/Diluent

	$10^{-26}C_n$/m^{-3}		$\bar{C}_n$			
concn, of **A** or **B**, wt %	with **A** diluent	with **B** diluent	with **A** diluent		with **B** diluent	
			c	*d*	*c*	*d*
0.1	6.256	–	6.056	6.193	–	–
0.5	6.241	6.227	6.041	6.179	6.028	6.165
1	6.236	6.203	6.036	6.174	6.0005	6.141
2	6.198	6.162	5.999	6.136	5.965	6.100
5	6.038	6.014	5.845	5.978	5.822	5.954
7.5	–	5.888	–	–	5.699	5.829
10	5.819	5.811	5.633	5.753	5.625	5.753

[a] m_{LC} = mass of 1 in the binary mixture; M_{LC} = molar mass of 1; N_A = Avogadro number; total volume $V = (m_{LC}/\rho_{LC}) + (m_{diluent}/\rho_{diluent})$ of the binary mixture with the mass *m* of the two components and their densities at the nematic–isotropic phase transition temperature T_c. [b] *L* and *d* are the length and diameter of the rigid rod (cylinder) in the Onsager model. [c] Calculated with L = 44 Å and d = 5 Å (L/d = 8.8) as tube dimensions to accommodate 1 in the extended conformation (see Figure 5a and text). [d] Calculated with L = 30 Å and d = 11 Å (L/d = 2.7) as tube dimensions to accommodate 1 in a corkscrew conformation (see Figure 5b and text).

$\sim$ 2.7 ($L \sim$ 30 Å, $d \sim$ 11 Å[15]) for the conformation shown in Figure 5b, sufficiently small enough to question the validity of neglecting end effects in the theoretical treatment of the excluded volume interaction. Furthermore, the solvents used in the experiments were not perfectly athermal for the LC molecules, and there is undoubtedly some residual van der Waals interaction in addition to the dipole–dipole interaction between the LC molecules in the ordered phase, in addition to the steric excluded volume interaction. Although this work focusses on the applicability and importance of the excluded volume effect and its main contribution to the nematic–isotropic phase transition, the mean field theory,[17,18] i.e., dipole–dipole interactions, might also be considered and is not ruled out. While there may be some compensation of different effects pushing the deviations from the theoretical value for the number density $\bar{C}_n$ at the phase transition point in different directions, it is seen that the Onsager prediction for the system studied is reasonably good, considering the simplicity of the model.

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References and Notes

(1) Onsager, L. *Ann. N.Y. Acad. Sci.* **1949**, *51*, 627.
(2) Chen, Z. Y.; Noolandi, J. *Phys. Rev. A* **1992**, *45*, 2389.
(3) See, for example: Lasher, G. *J. Chem. Phys.* **1970**, *53*, 4141. Cotter, M. A. *Phys. Rev. A* **1974**, *10*, 625. Frenkel, D.; Malder, B. M.; McTague, J. P. *Phys. Rev. Lett.* **1984**, *52*, 287.
(4) Kronberg, B.; Patterson, D. *J. Chem. Soc., Faraday Trans. 2*, **1976**, *72*, 1686.
(5) Orendi, H.; Ballauf, M. *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 96.
(6) Birkel, S.; Eisenbach, C. D. *Makromol. Chem.*, manuscript in preparation.
(7) Grzeskowiak, R.; Jeffrey, G. H.; Vogel, A. I. *J. Chem. Soc.* **1960**, 428.
(8) Woodman, R.; et al. *J. Phys. Chem.* **1960**, *64*, 658.
(9) Friend, S. *Hargreaves Philos. Mag.* **1947**, *7*, 37.
(10) Luzkii, P. *Zh. Obshch. Khim.* **1954**, *24*, 440.
(11) Jaeger, H. *Z. Anorg. Allg. Chem.* **1917**, *101*, 135.
(12) The data points of T_m (symbols ◇ and ◆) are superimposed for diluent concentrations up to $\phi \approx 0.1$.
(13) Flory, P. J. *J. Chem. Phys.* **1949**, *17*, 223.
(14) Mandelkern, L.; Flory, P. J. *J. Am. Chem. Soc.* **1951**, *73*, 3206.
(15) The energy-minimized conformation of the single molecule in the gas phase was calculated by using the Biosym Technologies software program, Insight II, Reference Guide, 1991, Version 2.0.0. The length *L* and thickness *d* of the molecule correspond to the dimensions of the cylinder required to accommodate the molecule in this conformation.
(16) The maximum possible chain length L was calculated using the bond length and angles between the carbon and ether elements as given in: *Handbook of Chemistry and Physics*, 62nd ed.; West, R. C., Ed.; CRC Press, Inc.: Boca Raton, FL, 1981; p F176. The length (*L*) and diameter (*d*) of the cylinder accommodate the extended conformation and correspond to the van der Waals diameter of the phenyl ring.
(17) Maier, W.; Saupe, A. *Z. Naturforsch.* **1959**, *14A*, 882.
(18) Maier, W.; Saupe, A. *Z. Naturforsch.* **1960**, *15A*, 287.