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Full Miscibility of Disk- and Rod-Shaped Mesogens in the Nematic Phase

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Rod-shaped (prolate) and disk-shaped (oblate) liquid crystals can form a uniaxial (N_u) mesophase, characterized by long-range orientational order in one direction. Although the nematic phases for both type of molecules are fundamentally identical, mixing between disks and rods in the thermotropic nematic phase has so far never been observed. Those mixtures are of particular interest, as already 33 years ago the existence of the nematic biaxial (N_B) phase[1] has been predicted at certain ratios;[2] see Figure 1. The N_B phase is characterized by orientational order in *two* directions.

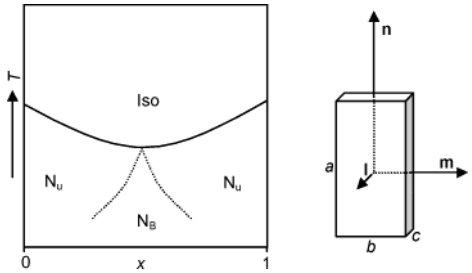


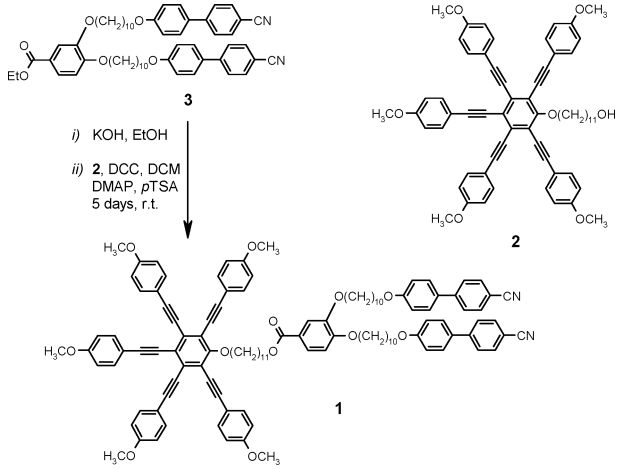
Figure 1. Schematic phase diagram containing the N_B phase. For board-shaped molecules, *x* scales with the ratio *b*/*a*; for mixtures of disks and rods, *x* represents the fraction of disks. The exact shape of the phase transitions between the N_B and the N_u phase depends on the model used.

Experimentally, the nematic biaxial phase has been accomplished for ternary lyotropic mixtures,[3] and also results for side-chain polymers indicate some phase biaxiallity.[4] Efforts to realize the N_B phase in thermotropic systems include two main routes of investigation. One approach combines the rod and disk shape of conventional mesogens to a more boardlike shape.[5] An alternative approach is based on mixtures of prolate and oblate mesogens[6−9] requiring the miscibility of both species over the entire phase diagram. To avoid phase separation between the two entities, molecules combining disk- and rod-shaped moieties have been prepared and studied;[10] however, no continuous rod−disk phase diagrams have been constructed. Mixtures of oblate and prolate mesogens have been subject to intensive computer simulations. Common for all models is the occurrence of the N_B phase around the minimum of the isotropization temperature in the disk−rod phase diagram (see Figure 1). Furthermore, the various models predict a strong decrease of the latent heat of the N_u to I transition upon approaching the tricritical point.

Encouraged by promising initial results for related materials,[11] we synthesized the novel mesogen **1** (see Scheme 1) bearing both calamitic and discotic mesogens. Compound **1** mixes without a miscibility gap with **3**, and the transitions of intermediate mixtures show a nearly linear dependence of the clearing temperature with the mol fraction of **1**. In addition, **1** mixes with the discotic mesogen **2** over the entire phase diagram. The characteristics of the phase diagram of **1** and **2** are presented, and the results of the miscibility studies are correlated with theoretical and simulation studies.

The synthesis of the investigated products is outlined in Scheme 1. The preparation of **2** has been published before.[12] The rod-

Scheme 1. Synthesis of the Disk−Rod Mesogens



containing moiety **3** was prepared by etherification of 4-hydroxy-4′-cyanobiphenyl and 1,10-dibromodecane under Williamson conditions. Subsequent etherification of the product with ethyl 3,4-dihydroxybenzoate yielded **3**. Deprotection of **3** and esterification with **2** afforded the linked disk−rod mesogen **1**.[13] The phase behavior of the pure components is summarized in Table 1. All materials exhibit a nematic mesophase, although the mesophase of **3** is monotropic.

Table 1. Phase Behavior of Mesogens **1**−**3**

material	phase behavior[a]				
1	G_N	31	N	77 (1.0)	I[b]
2	Cr	137 (37)	N	246 (0.2)	I
3[c]	Cr	118 (104)	N	106 (5.1)]	I

[a] Transition temperatures in °C (latent heat in kJ mol^{-1}), G_N = glassy, nematic phase frozen in, N = nematic, I = isotropic, Cr = crystalline. [b] Compound **1** shows a single melting transition (T_m = 113 °C, ΔH = 3.4 kJ mol^{-1}) during the first heating run that does not return in subsequent runs. [c] Monotropic phase transition.

The mixing behavior was investigated by studying contact samples with optical microscopy and by preparation of discrete mixtures, which were studied by both OPM and DSC. The resulting binary phase diagrams are shown in Figure 2a and b. Contact studies of **1** and **2** and **1** and **3** showed a complete miscibility over the entire composition range.[14] Attempts to detect nonmiscible regions have failed. A nematic phase, characterized by a typical *schlieren* or marbled texture, is observed over the full width of the phase diagram of **1** and **2**.[13]

Destabilization due to the mixing process causes a minimum in the clearing temperature (~55 °C) at $\phi_2 \approx 0.56$. The latent heat of the clearing transition decreases strongly, going from high fractions of **1** to the center of the phase diagram (Figure 2c). A minimum is observed in the region of the lowest transition temperatures. Indeed, these mixtures have isotropization enthalpies below 0.1 J g^{-1},

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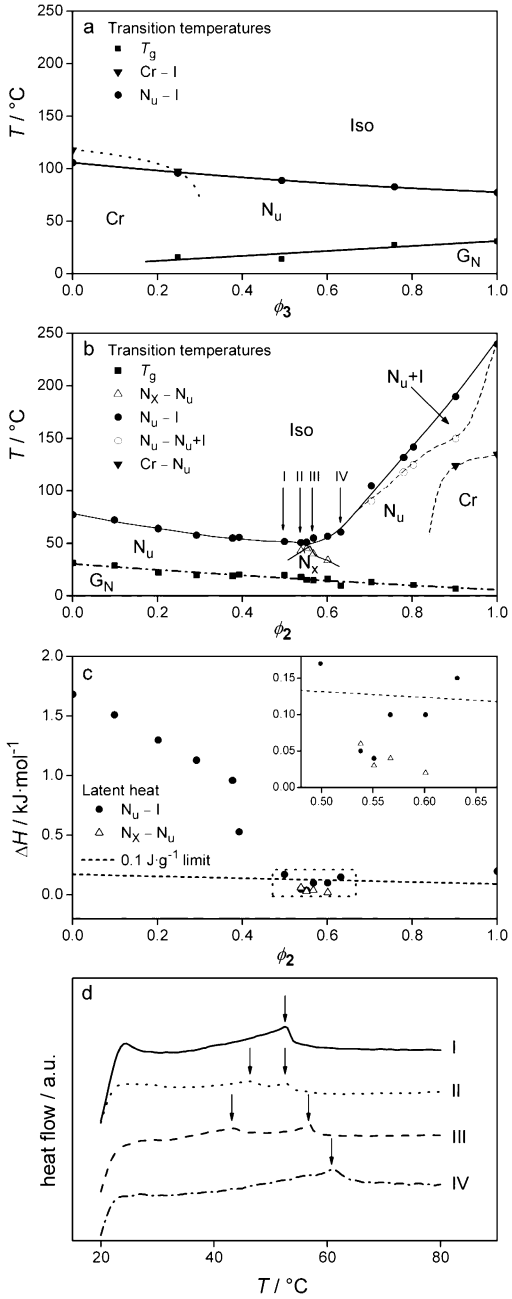

Figure 2. (a) Phase diagrams of **1** and **3**. (b) Phase diagrams of **1** and **2**. Experimental data (symbols) are obtained from DSC studies, apart from the mixtures showing the N_u+I biphasic area (data from OPM). The lines are a guide to the eye. DSC traces of mixtures I−IV are shown in diagram d. (c) Latent heat values for the N_u−I and N_X−N_u transitions of **1**:**2** mixtures. The dotted line represents the maximum resolution of the DSC for integrating phase transitions unambiguously. The inset shows a magnification from the data in the box. (d) Normalized DSC traces of mixtures **1**:**2** (at the N_X phase region) in ratios: (I) 0.50:0.50; (II) 0.46:0.54; (III) 0.43:0.57; and (IV) 0.37:0.63. The arrows indicate the maxima of the phase transitions.

estimated to be the maximum resolution for reliable quantitative evaluation of the instrument used. Further increasing the fraction of **2** results in a small increase in the latent heat. Smearing out the small transitions in the bistable N+I area hampered quantitative evaluation of the isotropization enthalpy in that region, approaching the limit of the sensitivity of the instrumentation used.

Mixtures of disk fractions $0.54 \leq \phi_2 \leq 0.60$ show a second transition in the DSC traces between the glass transition and the clearing temperature; see II and III in Figure 2d. The small transition is not associated with a change of the optical texture, even after prolonged annealing. Preliminary X-ray studies show only diffuse halos in the wide and the small angle region, indicating the absence of any positional order and, hence, excluding the assignment to smectic or columnar phase structures.[13]

As no demixing could be observed experimentally, the assignment of the extra N_X phase to a N_B phase correlates the achievements of theory and the experiment best. Demixing would have pointed toward a phase separation process into two uniaxial phases, predicted by theoretical models[8,15] to occur at temperatures below the N_B phase or instead of the N_B phase.

In conclusion, these results indicate that it is possible to synthesize molecules which are completely miscible in the nematic phase with rod-shaped and disk-shaped molecules. To the best of our knowledge, we presented the first experimentally obtained phase diagram of thermotropic discotic and calamitic mesogens. The construction of such a phase diagram is a major step forward in the design and development of future materials exhibiting a nematic biaxial phase. As theory for the N_B phase predicts, the mixtures exhibit a minimum in the transition enthalpies when approaching the minimum nematic to isotropic transition. Furthermore, a subsequent nematic−nematic transition can be observed, in line with theoretical predictions, thus requiring further investigations (e.g., solid state NMR on systematically deuterated samples) to confirm phase biaxiallity.

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Supporting Information Available: Experimental procedures, phase diagrams, OPM and XRD data of mixtures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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