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Liquid Crystalline Catalysis. 2.[1] Sulfonate Ester Rearrangements Induced in Solution by the Ordered Structure of a Smectic B Solvent

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Abstract: We have used a smectic B (Sm B) solvent to obtain experimental evidence of the catalytic effect of tightly ordered mesomorphic structures. To accomplish this we have selected two reactions with severe orientational demand in the transition state. The liquid crystalline catalysis is clearly displayed by the ability of the Sm B solvent to reproduce in solution the crystal phase quarternization reaction of methyl *p*-(dimethylamino)benzenesulfonate (MSE). It can also promote the corresponding rearrangement of the allyl sulfonate ester (ASE). The latter reaction was not previously observed and apparently is not attainable in any other conditions at the temperature and in the time scale of our experiments. The results are interpreted in terms of the ability of the mesomorphic solvent to drastically affect the free energy of activation of a reaction by exerting anisotropic restraints on the dynamic properties of the reactant molecules. The Sm B structure of the ZLI-1409 (E. Merck) solvent used in this investigation has been demonstrated by X-ray diffraction and differential scanning calorimetry (DSC). In support of the reactivity model previously suggested,[1] linear dichroism spectra provide some evidence of the preferred alignment of the long axes of the solute reactant and mesomorphic solvent molecules. However, solute expulsion processes from the rigid-core Sm layers should also be taken into account.

When a nonmesomorphic solute molecule is dissolved in a liquid crystal the correlations of the molecular orientations, and hence the ordering of the mesomorphic solvent, are locally disturbed.[2] The tendency of the solvent to keep its lowest energy state undisturbed provides a driving force which gives rise to constraints to the conformations of the solute molecules[2a,3] and induces an anisotropy in their orientation and translational diffusion.[4] If the molecular collisions inside the mesomorphic solution can promote a reaction of the solute molecules, the solvent ordering should be able to influence the stereochemistry and the rate of process. Rate accelerations can be expected if the critical orientation of the reactant molecules (required for bimolecular reactions to take place) is induced by the linear anisotropic restraints exerted by the mesomorphic solvent. In terms of the transition-state theory, such orientational effects exerted by a liquid crystalline solvent are expected to act mainly on the entropic part of the free energy of activation.[5] Reactions with low enthalpy of activation and high entropic demand to reach the transition state are thus expected to be particularly influenced by a mesomorphic solvent.

Despite high expectations and interest in the field, all the research so far reported on the influence of thermotropic liquid crystalline solvents on the rates and stereochemistry of thermal reaction has been rather frustrating and seems to discourage hopes of notable developments in this field.[5-7] More noticeable effects have been reported for some photochemical reactions.[8] On the other hand, the use of orientational effects, even if modest, provided by liquid crystalline solvents can be very useful as a tool in the elucidation of both reaction[8] and fluorescence quenching[9,10] mechanisms. However, apart from one exception[8b] (where the rate of a photochemical reaction was enhanced by a cholesteric (Ch) and not a Sm or a nematic (N) solvent) these results have all been obtained with only the easily handable N or Ch liquid crystalline solvents. In this latter case, the "microscopic matrix effect", determined by the short-range orientational order, is expected to be very similar to that of isotropic solvents.[2b,11] The anisotropic forces which can drive the reaction toward a decrease or increase of its free energy of activation are expected to be linked to the rigidity of the molecular packing of the mesomorphic solvent, and tightly ordered Sm mesophases will certainly be much more effective to this end than N and Ch solvents.

By using tightly ordered smectic solvents and by selecting reactions whose energies of activation were expected to be mainly determined by the entropy terms (i.e., with severe orientational demands in the transition states), we have recently[1] obtained first evidence of relevant catalytic effects due to the ordering of these mesomorphic solvents.

Choice of Reactant Probes for Liquid Crystalline Catalytic Effects

The rearrangement of crystalline methyl *p*-(dimethylamino)benzenesulfonate (methyl sulfonate ester (MSE)) to a zwitterionic product, *p*-(trimethylammonio)benzenesulfonate (MZWI), is reported to occur at room temperature.[12] On the other hand, anhydrous solutions of MSE in various isotropic organic solvents are indefinitely stable. This rearrangement is due to an intermolecular methyl migration not controlled by the normal reactivity of the functional groups but by stacking of the reactant molecules

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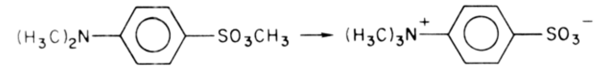


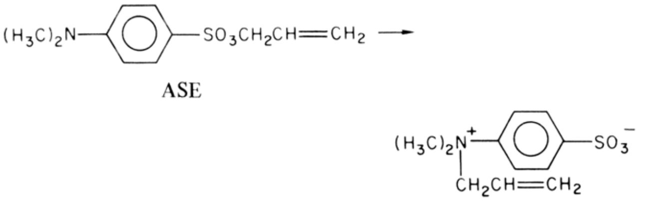
MSE MZWI

of MSE.[12] Both a chain and a dimeric intermolecular mechanism were in fact suggested for this reaction. The first mechanism proposed by Bergman et al.[12] on the basis of X-ray diffraction evidence of a chained orientation of the molecules of MSE in its crystals has been firmly supported by Raman phonon studies.[13] These results indicate the occurrence of a heterogenous transfer process predicting a long-range cooperative rearrangement. The potential energy surface calculations of the reaction recently computed by Gavezzotti and Simonetta[14] do not rule out the chain mechanism even if a dimeric two-step mechanism, involving an intermediate structure, has been preferred by the authors on the basis of the observed formation of a "metastable intermediate".[12] On the other hand, the X-ray powder observation of this intermediate does not seem to be confirmed by the more recent Raman phonon spectroscopy investigation[13] which is expected to be a safer technique for detecting such metastable species.

The high entropy demand of this reaction is clearly demonstrated by the abrupt decrease of the MSE conversion rate with rising temperature, on passing from the crystal phase to the melt where the chained stacking of the reactant molecules is partially destroyed.[12]

The rate data for the conversion to MZWI in the pure MSE crystal and melt phases at 81 and 98 °C, measured by NMR and reported in Figure 1 and Table II of ref 12, have been confirmed by our present spectrophotometric method of analysis of MZWI.

Besides this widely studied and already well-known solid-state MSE quaterization, the analogous reaction of the parent ester allyl *p*-(dimethylamino)benzenesulfonate (allyl sulfonate ester (ASE)) has been selected by us as a further and possibly better probe of the occurrence of liquid crystalline catalysis. In fact by replacing the small methyl group of the sulfonate ester with a bulky allyl group, the quaternization reaction is no longer attainable in the ASE crystals,[12] probably as a consequence of a different and unfavorable crystal lattice molecular stacking. Side contributions to the reactivity due to reagent microcrystal nucleations, i.e., to solid-phase conversion processes which are possible in the MSE case, are certainly impossible when the ASE probe is used.



ASE

AZWI

Choice of a Tightly Ordered Solvent. X-ray Diffraction and Calorimetric Studies of the Smectic Mesophase

ZLI-1409 liquid crystal (see Chart I) recently synthesized at E. Merck (Darmstadt) has been selected as a suitable solvent for our probing into the reactivity in Sm phases owing to its hydrocarbon structure and very wide smectic phase.

We report here the X-ray diffraction evidence of the very highly ordered B structure of the ZLI-1409 Sm phase. This is an ordered phase with molecular axes perpendicular to the Sm layers and a hexagonal order within the layers. The layered arrangement of this phase has a periodicity and rigidity similar to that of a two-dimensional solid.

From the single narrow diffraction ring usually observed in the Sm B phase[15,16] (Figure 1a) an intermolecular distance $d = 5.50 \pm 0.03$ Å is derived. This value is in satisfactory agreement with the $d = 5.52 \pm 0.06$ Å value obtained[17] from the N phase (Figure 1b). From the small-angle peaks the interplanar Sm distance proves to be $d = 21.4 \pm 0.2$ Å, which is in reasonably good agreement with the molecular length deduced from the model, $d = 23.5 \pm 0.5$ Å. Moreover, the low-angle-peak position does not change appreciably between the N and the Sm phase, thus confirming that the molecules are perpendicular to the layers.

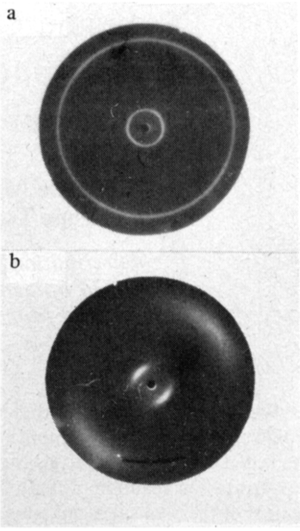
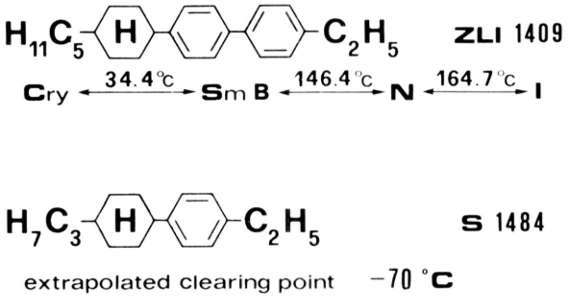


Figure 1. X-ray diffraction patterns from the smectic (a) and nematic (b) phases of ZLI-1409 at 50 and 145 °C, respectively. The nematic phase is aligned by a vertical magnetic field $H = 1.5$ kG.

Chart I



The hypothesis that the Sm phase is orthogonal was confirmed by conoscopic microscopy: the specimen is uniaxial positive. Moreover, a mosaic texture, compatible with a Sm B phase, was seen in optical microscopy.

The differential scanning calorimetry (DSC) thermogram of ZLI-1409 (Figure 2) clearly displays the differences in the heats associated with the phase transitions. The computed enthalpy and entropy of the Sm B phase isotropization (i.e., of the destruction of the ordering) are strictly comparable with those of the crystalline phase but at least one order of magnitude higher than those of the N phase (Figure 2).

The changes in the intermolecular forces and in the molecular packing, on passing from one phase to another, are reflected on the enthalpy and entropy of the transition, respectively.[18] Hence, the above values can be used to emphasize how low the solvent rigidity of the nematic phase is with respect to the Sm B and, further, how much more effectively the Sm solvents can affect the free energy of activation of a reaction. The rigidity of the solvent within the local environments of the reagent–solute molecules that is required to provide a desired catalytic effect will depend on the activation parameters of the investigated reaction. For this reason some correlation between isotropization heat and

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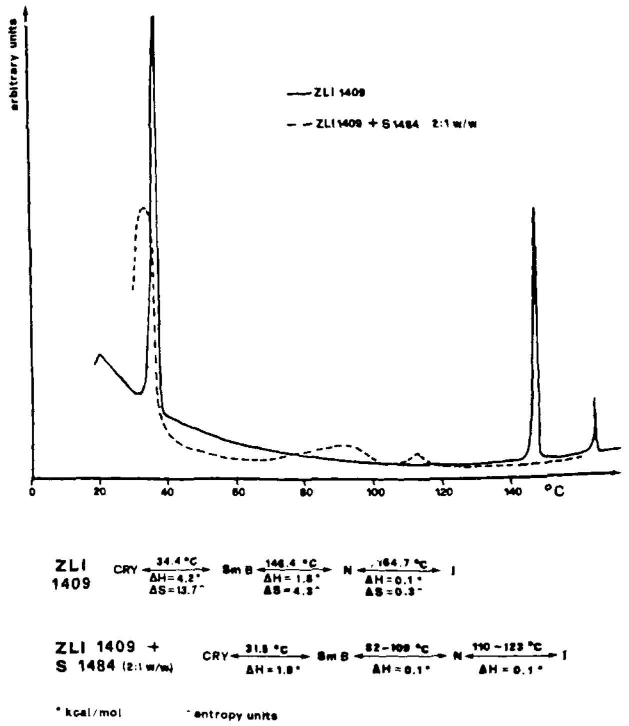

Figure 2. DSC thermogram and phase transition thermodynamic parameters of pure ZLI-1409 (solid line) and its mixture with S-1484 (dashed line).

entropy of the solvent phase and heat and entropy of activation on the solute reaction is expected and could probably be attempted in the future. In this context the drop of the isotropization heats of a ZLI-1409/S-1484 mixture (Figure 2), in which the MSE quaternization does not occur (see part 1 of this series), seems to be particularly meaningful and noteworthy.

ASE and MSE Conversion Yields in ZLI-1409 Sm B Solvent

The conversion yields of the ASE quaternization at 37 °C (below its melting point, 40.5 °C) are reported in Figure 3. The ability of the Sm B solvent to *catalyze a reaction which, at that temperature and in a comparable time scale, is apparently not attainable by any other means is clearly displayed.* A very sluggish ASE quaternization has been observed in the ASE melt where the crystal lattice stacking is destroyed: after 38 days at 51 °C only a 30% conversion was measured while in the Sm B solvent under the same conditions the reaction was already completed.

The MSE experiments (Figure 3) can be interpreted in terms of the solvent's ability to induce the required orientation of the colliding molecules. However, this interpretation is only valid if side contributions to the reactivity due to reagent microcrystal nucleations are ruled out by rate measurements at different reactant concentrations and temperatures (above and below 91 °C, the MSE melting point). The quantitative determination of the zwitterion products MZWI and AZWI by NMR[12] is not sensitive enough for our purposes, and a spectrophotometric analysis of the products, extracted with water from an organic solution of the reaction mixture, has been set up.

The MSE conversion-yield measurements at *different temperatures* (81 and 98 °C) reported in Figure 3 show that MSE, while stable when dissolved in a N or isotropic (I) solvent, in a Sm B phase does rearrange to MZWI (even if more slowly than it does in its crystals). Rate data in the Sm B solvent (see Figure 3), when fitted into the integrated form of the second-order rate law, lie in a straight line and give apparent rate constants $k(81\ ^\circ\mathrm{C}) = (1.4 \pm 0.1) \times 10^{-4}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ and $k(98\ ^\circ\mathrm{C}) = (5.3 \pm 0.5) \times 10^{-4}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ with an Arrhenius activation energy $E_A = 20.5 \pm 1$ kcal mol^{-1}. The "normal" dependence of the rate of the reaction above and below the MSE melting point *rules out any local microcrystallization or reagent self-aggregation process.*

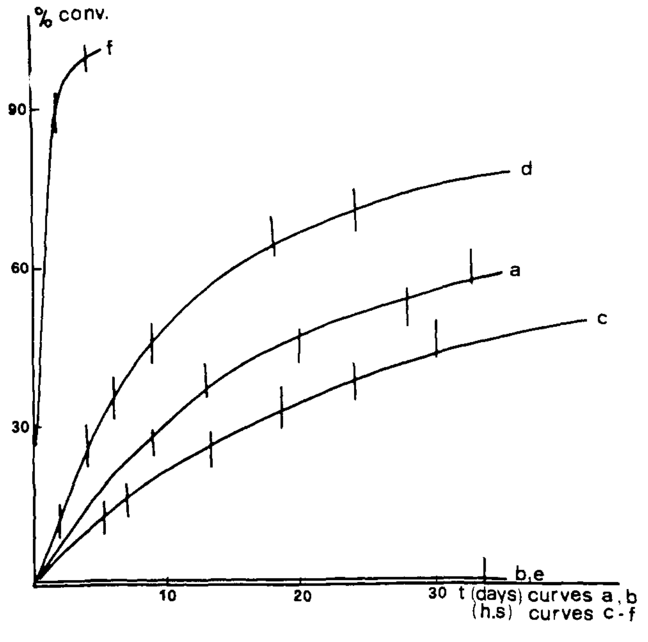

Figure 3. Conversion yields of the ASE quaternization at 37 °C in solutions of ZLI-1409 Sm B solvent (curve a) and S-1484 + ZLI-1409 nematic mixtures or S-1484 isotropic solvent (curve b). Conversion yields of the MSE quaternization in ZLI-1409 at 81 °C (curve c) and 98 °C (curve *d*), in isotropic or nematic solvents[1] at both temperatures (curve e). Curve f refers to MSE reactivity in its crystal phase at 81 °C.

The MSE rate constant calculated at 37 °C, $k(37\ ^\circ\mathrm{C}) = 2.2 \times 10^{-6}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$, is lower than that found for the corresponding ASE quaternization, $k_*'(37\ ^\circ\mathrm{C}) = 1.1 \pm 0.1 \times 10^{-5}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$, and rate measurements on both MSE and ASE reactions performed at 60 °C show that the latter reacts three times more rapidly than the former. This is as one might have predicted for a relatively unhindered S_N2'-like process.[12]

Fractional lives for some reactions both at 81 and 98 °C with an initial concentration of MSE $\leq 6.8 \times 10^{-2}$ M were as expected for a second-order reaction.[19] By solving the Noyes equation[19] for pairs of runs with *different initial concentrations* of MSE, a value very close to 2 for the reaction order was obtained. We also made sure that total conversion of MSE into MZWI can be achieved after 5 days at 98 °C. On the other hand, MZWI can be recovered unchanged after 5 days at 98 °C if set aside in the reaction conditions. These data indicate that the reaction under investigation is an irreversible process. Initial additions of MZWI to MSE do not show any autocatalytic effect for this reaction. In the light of the above results we conclude that the reaction under examination is kinetically a second order and, most likely, also a simple bimolecular process under the present conditions. The crystal field potential energy calculations by Gavezzotti and Simonetta[14] show that the activation energies for a dimeric and a chain mechanism are similar. Different restraints on the dynamic properties of the reactant molecules can thus easily drive the reaction to either mechanism. While the stacking of sheets of MSE molecules in a head-to-tail chain orientation in the crystalline phase is expected to favor the chain mechanism,[12] the dilute Sm solution seems more able to drive the reaction toward a dimeric mechanism, i.e., toward a *bimolecular process*, as suggested by our rate measurements.

Conversion yield measurements at *high initial MSE concentration* showed significant rate depressions for initial concentrations higher than about 6.8×10^{-2} M. For example, reaction rates with MSE concentrations of 3.4×10^{-1} and 6.8×10^{-1} M are about 40–50% slower than those predicted for diluted solutions, respectively. This behavior, besides displaying the importance of the gradual disturbance of the peculiar Sm B ordering by the solute molecules, clearly rules out crystallization effects which should

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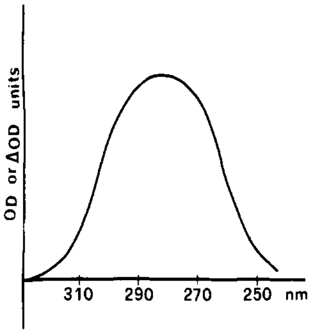

Figure 4. Shape of the LC–LD and UV spectra of ASE and MSE dissolved in a nematic- or smectic-oriented sample of ZLI-1167. ΔOD = ($OD_{\parallel}$ - $OD_{\perp}$) where parallel (||) and perpendicular ($\perp$) refer to the electric field, i.e., to the N or Sm director.

otherwise overcome and reverse the observed decrease in rate as the MSE concentration increases.

Liquid Crystal–Linear Dichroism (LC-LD) Spectra

By inspection the LD spectra of guest molecules macroscopically oriented by LC solvents,[20] information about the electronic states involved can be obtained if the main orientation of the guest molecule is known.[20,21] Conversely, if the polarization of the transitions is known, information about the guest molecule orientation can be obtained.[3b,20] The preferred orientation of the solute MSE molecules with respect to the directors of the ZLI-1409 mesophases cannot be directly obtained by the LC-LD technique owing to the nontransparency of the solvent to the UV light. However, LC-LD information on the orientational properties of the MSE molecules within a Sm solvent can be obtained by using the cyanobicyclohexyl mesomorphic derivatives,[22] commercialized by E. Merck as the ZLI-1167 mixture. The orientational properties of ASE and MSE with respect to the molecules of N and Sm mesophases can be displayed by recording LD spectra of oriented samples. The orientation is achieved by applying an alternating electric field to the samples in their N range[23] and then slowly (about 0.05°C $\min^{-1}$) cooling them to their Sm range. An electric field of 1 kHz up to 10 kV mm^{-1} has been used at temperatures from 40 down to 20 °C. The shapes of both UV and LD spectra of ASE and MSE bands centered at about 280 nm are practically coincident in Sm or N solutions (Figure 4). The intensity of the LD signals depends in nematic solutions on the electric field intensity and in Sm solutions on the annealing history of the sample around the N–Sm transition temperature. The band centered at 280 nm is due to a transition which can be safely assigned to a charge transfer (CT) from the donor dimethylamino group to the sulfonate acceptor. This can be inferred from the high maximum molar extinction coefficient ($\epsilon_{\max}$(MSE) = 24 750 and $\epsilon_{\max}$(ASE) = 25 850 in aqueous ethanol 3:2 v/v) and the strong sensitivity of band energetic location to solvent polarity ($\lambda_{\max}$ 276 nm in cyclohexane and $\lambda_{\max}$ 288 nm in aqueous ethanol 3:2 v/v). On the basis of this long-axis-polarization assignment, the positive sign of all the LD signals detected for this band clearly displays the preferred alignment of the long axes of the nonmesomorphic solute and mesomorphic solvent molecules. The molecular orientation proposed in Figure 1 of part 1[1] of this series is thus confirmed by the present spectroscopic data. It must also be pointed out that, on the basis of their expected tight packing in Sm phases, the cyclohexyl molecular residues of ZLI-1409 should be considered as taking part in the rigid core, which is not only aromatic as suggested in the ref 1 model. The model of Figure 1 of ref 1 is probably oversimplified as it does not take into account the fact that the anisotropy of the translational diffusion processes in the Sm A and B phses is apparently coupled to an expulsion process from the rigid-core layers to the more flexible aliphatic regions (at least in the case of small aliphatic solute molecules such as $CHCl_3$ and CH_4). Equilibria between solute locations in different sites[4c] could also be relevant in this context. The expulsion processes, if effective, are certainly able to play a relevant role in reactions performed in Sm A phases owing to the liquid-like high mobility within the aliphatic chains region experienced by the "expelled" solute–reactant molecules. On the other hand, the abrupt and drastic decrease "in the flexibility experienced by the aliphatic tails as the material is frozen into the crystalline Sm B phase"[4c] (see in particular Figures 12 and 14 of ref 4c) will provide a tightly ordered environment to any possible location of the solute molecule in this phase and very strong restrictions to a diffusion perpendicular to the smetic layers.[4c]

Conclusion

The Sm B phase of ZLI-1409 is able to reproduce in solution, even if by a different mechanism, the solid-state MSE quaternization reaction. This same solvent also promotes the corresponding ASE rearrangement which, at the temperature and in the time scale of our experiments, is apparently not attainable in any other conditions. In turn, the ASE quaternization reaction could be used as a useful probe of local solvation and orientational properties of different Sm solvents and phases.

Experimental

The syntheses of MSE and ASE were carried out according to ref 12. In order to avoid any solid-state reactivity, the MSE was always dissolved in the ZLI-1409 solvent (1-g samples) at about 160 °C by quick injections of samples of its diethyl ether solution of known concentration. The absence of any MSE reactivity during the preparation of its mesomorphic solutions has been checked. The N solutions of MSE have been rapidly cooled down into their Sm range by immersion in a bath thermostatted at the temperatures of the experiments. The ASE Sm solutions were prepared by the same injection procedure at room temperature. The complete homogeneity of these samples was promoted by further addition of small amounts of diethyl ether and then evaporation under vacuum of all the volatile solvent traces. Each reaction mixture was partitioned by a continuous liquid–liquid extractor for 60 h between a constant volume of water (which dissolves only the ionic products) and ether (which dissolves MSE or ASE and the mesomorphic solvent). The spectrophotometric analyses of the two zwitterions were performed on the aqueous extracts previously washed by spectrograde *n*-hexane. The well-resolved vibronic structures and the intensity of the lowest energy band of MZWI and AZWI were almost coincidental ($\epsilon_{\max}$ = 1170 and 1250 cm^{-1} mol^{-1} dm^{-3} at λ 270 nm, respectively). The liquid crystal was almost completely recovered by washing the ether phase from the liquid–liquid extractor with aqeuous HCl (10% w/w) and further solvent evaporation. ZLI-1409 was twice recrystallized from ethanol, and its purity was checked by DSC analysis.

The *LD* and *UV spectra* have been recorded on a JASCO-J 500 dichrograph and a Cary 15 spectrophotometer, respectively. The setup of the LC-LD technique and the required corrections of the experimental data are described in ref 20. An Elliot toroidal camera and nickel-filtered Cu Kα radiation (λ 1.54 Å) from a Rigaku-Denki rotating anode generator assembled with a conventional X-ray powder diffractometer were used for the X-ray diffraction measurements. The sample holder was described in ref 24.

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Registry No. ZLI-1409, 77702-36-4; S-1484, 87901-26-6; methyl *p*-(dimethylamino)benzenesulfonate, 57270-54-9; allyl *p*-(dimethylamino)benzenesulfonate, 62305-73-1.

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