Self-organization of mesomeric–ionic hybrid heterocycles into liquid crystal phases: a new class of polar mesogens

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The first mesoionic nematic and smectic A mesogens derived from sydnones that are characterized by both covalent and ionic features have been synthesized and evidenced by optical, calorimetric and X-ray diffraction studies.

Self-organization or self-assembly of organic molecules results in a variety of noncovalent, reversible nanostructures that have great significance in biological and material sciences.[1] Thermotropic liquid crystal (LC) phases, generally obtained by the action of heat on shape-anisotropic organic molecules are well-known examples of such macroscopic structures.[2] The LC phases are characterized by both optical anisotropy (Δn) and dielectric anisotropy ($\Delta\varepsilon$) properties which have been well exploited in practical applications, especially in display device technology. The most popular examples are the covalent (apolar or polar) rod-like LCs formed by connecting rigid cores such as aliphatic or aromatic or heteroaromatic rings and flexible tails *via* linking groups. Such molecules self-organize into layer (smectic: Sm) and/or non-layered (nematic: N) fluid structures. On the other hand, ionic LCs that are comprised of oppositely charged species, are equally important materils[3,4] owing to their amphotropic nature and also their ability to act as model systems for the simulation of biomembranes.

The term "mesoionic" (mesomeric + ionic) has been conferred to a novel class of five-membered heterocycles such as sydnones **I** (Fig. 1), which cannot be represented satisfactorily by any one covalent or polar structure but only as hybrids of polar structures.[5a] In other words, for any particular polar structure that may be written for a mesoionic compound the charges cannot wholly neutralize one another to give a covalent structure. Sydnones are one of the most extensively studied mesoionic systems, mainly due to their potential value as biologically active substances found in their planar aromatic character[5b–d] and interesting physical and chemical properties[5,6] associated with them. Most importantly, their highly polarized yet net neutral electrical character and high dipole moments (μ = 5–6 D) are promising in the context of properties of liquid crystalline materials. For example, from the viewpoint of display devices, $\Delta\varepsilon$ that is a measure of the dipole moment (polarity) of the material is an important factor. In continuation of our investigations on technologically important thermotropic LCs,[7] we have embarked on realizing novel mesoionic nematic and smectic LCs that are derived from the sydnones. As a first step, we intended that sydnone ring be introduced in place of the cyano group of 4-*n*-alkylcyanobiphenyls (***n*-CBs**), materials known to form the N and SmA phases.[8] Thus, on the molecular or segmental level, the introduction of a sydnone ring could produce the structures with properties between those of covalent and ionic LCs. The target compounds, biphenylsydnones (***n*-BS**: n = 2 to 10), were prepared by Suzuki coupling[9a] of known 3-(4-bromophenyl)sydnone (**Ib**) with boronic acids[9b,c] (**IIa–i**). The final compounds thus obtained were characterized†.

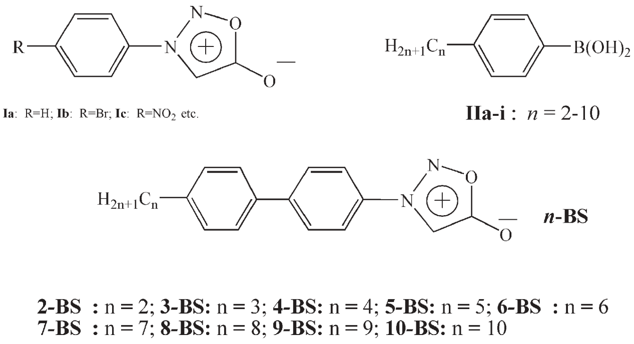

Fig. 1 Molecular structures of 3-arylsydnones (**Ia–c**), 4-*n*-alkylphenylboronic acids (**IIa–i**) and 3-(4′-*n*-alkylbiphenyl-4-yl)sydnones (***n*-BS**).

The liquid crystalline behavior of these compounds was studied with the help of polarizing optical microscope (POM) and differential scanning calorimeter (DSC) at a rate of 5 °C min^{-1}. The phase sequence, transition temperatures and associated enthalpies have been summarized in Table 1.

Compound **2-BS**, the first member of the series is non-mesomorphic whereas **3-BS** displays a supercooled monotropic nematic phase over a short thermal range. The next homologue **4-BS** was found to be crystalline while **5-BS** exhibits monotropic nematic and smectic A phases. The behavior of the successive homologues demonstrates the effect of odd–even parity of terminal tail on the mesomorphic property. The existence of the N phase was identified from the observation of a characteristic marble texture when slides treated for planar orientation were used (Fig. 2a). In a homeotropically-aligned sample, the N phase shows a pseudoisotropic texture, which flashed when subjected to shearing stress. Thus the compounds **3-BS** and **5-BS** represent the first examples of mesoionic nematic LCs. The presence of SmA phase was confirmed based on the microscopic observation of the characteristic focal-conic texture in slides treated for planar orientation (Fig. 2b) and a dark field of view in slides treated for homeotropic orientation. When untreated slides were employed, both the focal-conic as well as psuedoisotropic textures were observed. In the conoscopic view a Maltese cross was observed (see SI) confirming the orthogonal arrangement of the molecules in

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Table 1 Phase sequence, transition temperature (°C) and enthalpies (J g^{-1}) of 3-(4′-*n*-alkylbiphenyl-4-yl)sydnones (***n*-BS**)

Compds.	Heating	Cooling
2-BS	Cr 146 (80.3) I	—
3-BS	Cr 124.6 (73.4) I	I 92 (0.2) N 88.3 (30.5) Cr
4-BS	Cr 120.4 (70.2) I	—
5-BS	Cr 114.4 (64) I	I 110 (0.4) N 104.4 (0.1) SmA 71.3 (17.9) Cr
6-BS	Cr 106.8 (73.9) SmA 117.8 (2.5) I	I 116 (2.4) SmA 59.8 (29.5) Cr
7-BS	Cr 100.9 (66.7) SmA 135.2 (5.7) I	I 134.7 (5.3) SmA 59.8 (29.5) Cr
8-BS	Cr 98.5 (60.7) SmA 145.3 (7.1) I	I 144.5 (7) SmA 66.4 (57.5) Cr
9-BS	Cr 96 (57.3) SmA 156.1 (8.7) I	I 152 (8.4) SmA 59.9 (45.6) Cr
10-BS	Cr 98 (62.4) SmA 159.3 (9.1) I	I 158.5 (9) SmA 58.7 (31.1) Cr

[a] Peak temperatures in the DSC thermograms obtained during the first heating and cooling cycles at a rate of 5 °C min^{-1}. Cr = crystal; SmA = smectic A; N = nematic and I = isotropic.

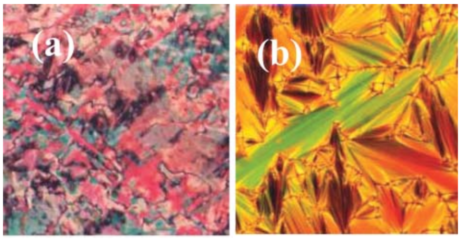

Fig. 2 POM textures observed (magnification 320 ×) while cooling from the I phase in slides treated for planar orientation for (a) the N phase of **5-BS** at 108 °C and (b) the SmA phase of **7-BS** at 130 °C.

the smectic phase. The birefringence measured using a tilting compensator was found to be 0.14 in the N phase at 107 °C for the mesoionic mesogen **5-BS**. Subsequent biphenylsydnones **6-BS**, **7-BS**, **8-BS**, **9-BS**, and **10-BS**, exhibit the SmA phase over a wide thermal range[10] (see Fig. 3).

The SmA phase has a layered structure (with a layer thickness *d*) in which the director is perpendicular to the plane of the layers giving rise to a 1-D mass density wave along the layer normal direction. A variety of SmA phases such as monolayer, partial bilayer and bilayer, are possible as a result of combination of polar and steric dipoles together with conformational flexibility of the tails. The magnitude of the wave vector $q = 2\pi/d$ of the mass density wave can be conveniently measured by X-ray diffraction (XRD) studies. Generally, polar LCs, for example ***n*-CBs**, have a tendency to form partially bilayered structure ($d/l \sim 1.4$ where l is the length of a molecule) in which antiparallel dimers form to account for the minimization of dipolar energy.[11] In order to ascertain the nature of the SmA phase exhibited by *n*-BS compounds, powder XRD experiment was carried out for **10-BS** as a representative case and the diffractogram obtained at 140 °C is shown in Fig. 4.

A sharp peak at small angle and a diffuse peak at wide angle were obtained. The broad peak at 4.6 Å is characteristic of liquid-like order within the smectic planes while the peak at 35.9 Å represents the layer thickness *d*, with a value greater than the estimated extended molecular length of 24.8 Å. Thus the layer thickness is about 1.4 times the molecular length and hence the molecular arrangements corresponding to the partial bilayer SmA phase (SmA$_d$) as shown in Fig. 5. It is interesting to note that this value (1.4) is in close agreement to that for ***n*-CBs**. In fact, the partial bilayer nature of the SmA phase clearly demonstrates the polar nature of these new mesogens. The partial bilayer arrangement in the ***n*-CBs** is known[11] to be due to the strongly polar terminal cyano dipole. The free energy of the system is minimized by having an antiparallel arrangement of the neighbouring molecules.

An evidence of this antiparallel arrangement of the molecules in this system is obtained through measurements of the dielectric constant.[12] The anisotropic average dielectric constant $\bar{\varepsilon}(= \frac{\varepsilon_{\parallel} + 2\varepsilon_{\perp}}{3}$,

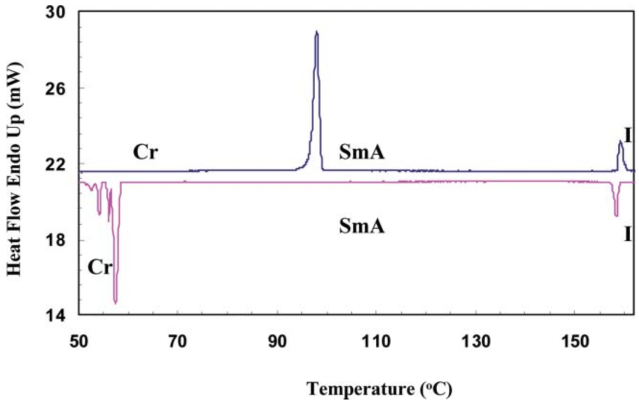

Fig. 3 DSC thermograms obtained in the heating (upper profile) and cooling (lower profile) modes for the **10-BS** at a rate of 5 °C min^{-1}. As can be seen, the SmA phase exists over a wide thermal range.

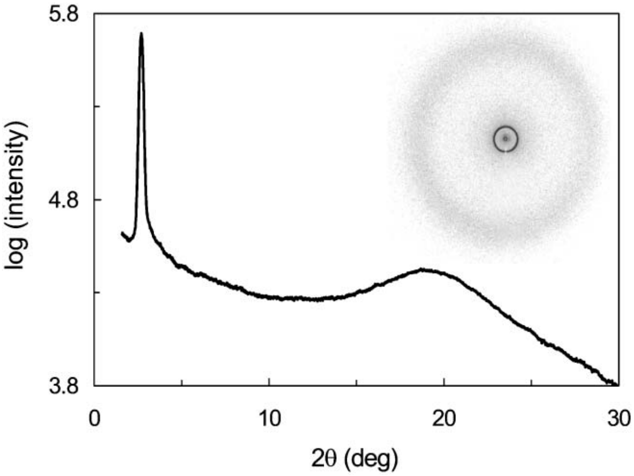

Fig. 4 One-dimensional intensity *vs.* 2θ profile derived from 2D-XRD pattern (see inset) obtained at 140 °C for compound **10-BS**.

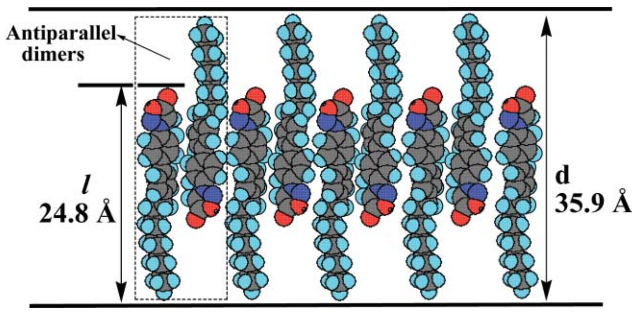

Fig. 5 Schematic representation of a self-assembly of mesogens **10-BS** into a partial bilayer SmA phase.

where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are the dielectric constants measured parallel and perpendicular to the director, *n*, the mean direction of the molecules), should then be smaller than ε_{iso}, the value in the isotropic phase. To find out whether this is true also in the present sydnone case, dielectric measurements were done using an impedance analyser (HP 4284 A) for the sample **5-BS**. The sample contained in a 30 μm thick parallel plate ITO-coated glass cell was oriented by a strong (2.1T) magnetic field. The orientations obtained parallel and perpendicular to the probing electric field directions yielded $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, respectively. The values of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ obtained at a frequency of 10 KHz, 5 °C below the transition to the isotropic phase, are 15.8 and 10.4 respectively. The calculated value of 12.2 for $\bar{\varepsilon}$ is thus below that of $\varepsilon_{iso} = 13.5$, confirming the antiparallel nature of the packing of molecules in both mesophases.

In conclusion, we have designed and synthesized the first examples of mesoionic nematic and smectic A liquid crystals derived from sydnones. Because of their highly polarized yet net neutral electrical character and high dipole moment, they are attractive candidates from the perspective of properties of liquid crystalline materials and deserve extensive investigation. Most importantly, these can be regarded as a novel hybrid structure of covalent and ionic LCs. We are continuing our synthetic work on sydnones to form new mesoionic mesogens.

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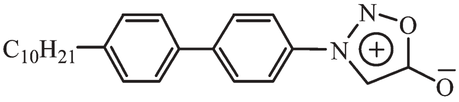
Notes and references

† The target molecules, 3-(4′-*n*-alkylbiphenyl-4-yl)sydnones, exhibited spectral data consistent with their molecular structure. Selected data for

10-BS:



R_f = 0.55 (50% EtOAc-hexanes); Yield: 64%; UV–Vis: λ_{max} = 298 nm, $\varepsilon = 2.35 \times 10^4$ L mol^{-1}cm^{-1}; IR (KBr pellet): ν_{max} 2921, 2850, 1741, 1601, 1501 and 1455 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.80 (*d*, *J* = 8.8 Hz, 2H, Ar), 7.78(*d*, *J* = 8.8 Hz, 2H, Ar), 7.54 (*d*, *J* = 8.1 Hz, 2H, Ar), 7.31 (*d*, *J* = 8.1 Hz, 2H, Ar), 6.74 (*s*, 1H, sydnone-H), 2.69 (*t*, *J* = 7.5 Hz, 2H, Ar–CH$_2$), 1.67–1.27 (*m*, 16H, 8 × CH$_2$) and .87 (*t*, *J* = 6.4 Hz, 3H, 1 × CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 168.96, 145.71, 144.01, 136.01, 133.51, 129.30, 128.54, 127.09, 121.58, 93.37, 35.66, 31.91, 31.37, 29.60, 29.51, 29.33, 22.68, 14.07; MS (FAB+): *m/z* for $C_{24}H_{31}N_2O_2$ (M + 1), Calcd.: 379. Found: 379; Elemental analysis: Calculated (Found): C 76.14 (76.38)%; H 7.99 (7.97)%; N 7.4 (7.24)%.

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