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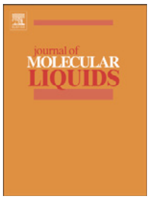

Effect of a structural modification of the bipyridinium core on the phase behaviour of viologen-based bistriflimide salts

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ABSTRACT

We report on the synthesis and characterization of novel viologen-based low-melting salts of bistriflimide, namely 1,1′-di-*n*-alkyl-2,2′,6,6′-tetramethyl-4,4′-bipyridinium, with lateral alkyl chains of 8, 10 and 12 carbon atoms. The thermotropic behaviour has been fully characterized by polarized optical microscopy, X-ray scattering and calorimetric measurements. Comparison with literature data shows that the increase of the effective volume of the rigid bipyridinium core, obtained by methylation, has a dramatic effect on the phase behaviour and on the transition temperature to the isotropic liquid. DFT calculations of the energy and structure of model clusters provide useful insights to interpret the experimental findings.

1. Introduction

Viologen salts, that is systems based on 1,1′-dialkyl-4,4′-bipyridinium, are continuously receiving a great deal of attention [1]. As examples of recent applications we mention here viologen-based molecular wires [2] and molecular machines [3], the production of hydrogen from water [4] and several kinds of chemosensors [5]. With the appropriate anions they may also exhibit low temperature melting points, giving rise to viologen-based ionic liquids and, in some cases, viologen-based ionic liquid crystals [6].

These latter materials, ionic liquid crystals (ILC), are attracting interest on their own because they have the potential of combining together the technological applications of liquid crystals (LC) and ionic liquids (IL) [7]. However, the details governing the stability of the liquid phase and of the low-order mesophases of ionic systems, and their relation with the molecular structure, are still not clear. The widespread appearance of smectic mesophases for typical amphipilic molecules made of a polar head and a long alkyl chain, suggests that the key factor responsible for their stability is the microphase segregation with ionic/polar layers alternating with hydrophobic layers. This is quite at variance with the general behaviour of dipolar LC where the subtle balance of anisotropic attractive and repulsive forces and entropy effects may favour nematic phases over smectic ones.

However, recently, microphase segregation has been observed, both from MD simulations [8,9] and experiments [10], also for the isotropic phase of common ILs. Also, liquid mixtures, e.g. the strongly non-ideal water/acetonitrile mixture, are known to have a complex structure, at a molecular level, with water domains microsegregated from the organic solvent [11]. Therefore, microsegregation alone cannot be invoked to explain the stability of ionic smectic phases. In fact, some rare examples of nematic ionic systems have been reported recently [7b]. Since nematic liquid crystals play such an important role in the realm of LC technology, for example in display devices, it is desirable to improve our understanding on the molecular features that influence the structure of ionic compounds and in particular identify those that may favour ionic nematic phases.

On the other hand, the structural and dynamical properties of room-temperature ionic liquids, which are simpler fluids, in the sense that they only exhibit crystalline and isotropic liquid phases, are also rather poorly understood. The regular dependence of the melting point on the radius of the ions (that is the larger the ions, the weaker the electrostatic interaction, the lower the melting point) does not hold for typical ionic liquids based on imidazolium. An even more unexpected behaviour is observed when 1-alkyl-3-methylimidazolium compounds are methylated on the 2 position. Generally the rather acidic H2 hydrogen is involved in strong hydrogen bonds with the anions. It might be expected that substituting H2 with a methyl group, therefore reducing the extent of hydrogen bonding in the system, would lower the melting point. In contrast, a higher melting point is found [12,13]. It appears, therefore, unlikely, that the limited understanding we have on the properties of ionic liquids could help in comprehend the relation between the molecular structure and the type and stability of ionic mesophases.

Based on intuitive grounds, it might be expected that smectic phases, that is layered phases, where rod-like molecules are aligned side-by-side, might be destabilized in favour of less ordered phases, if

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the steric hindrance in the middle of the rod is increased. Some preliminary computer simulation results on non-ionic, non-polar model mesogenic systems agree with this qualitative view [14].

Considering the ubiquitous presence of smectic mesophases for ionic systems we decided to test whether increasing the effective volume in the center of a rod-like ionic mesogenic compound would result in a stabilization of a less ordered phase, hopefully a nematic one. In any case, investigating the changes in the phase behaviour as the molecular structure is modified would provide a first set of structure–properties relationships to guide in the design of novel ionic mesogens.

In this work we report on the effect of a structural modification of the bipyridinium core of viologen-based bistriflimide salts. These latter systems have been recently investigated by Bhowmik et al. and were found to exhibit smectic phases near room temperature and relatively high transition temperatures to the isotropic liquid [15]. We will show that increasing the steric hindrance of the central core destabilizes the smectic phases in favour of the isotropic liquid thus lowering significantly the melting point.

2. Experimental

Compounds **1a–c** and **2a–c** (see Scheme 1) were synthesized according to literature procedures, slightly modified as reported below.

2.1. 1,1′-di(n-C_nH_{2n+1})-2,2′,6,6′-tetramethyl-4,4′-bipyridinium diiodide, **1a–c**, $n=8$, 10, 12

Iodide salts were synthesized according to slightly modified literature protocols [15] by refluxing in acetonitrile the desired amount of 2,2′,6,6′-tetramethyl-4,4′-bipyridine (Synchem OHG) with the corresponding excess of iodoalkane (Sigma-Aldrich). Since the methyl groups in *ortho* position hinder the nucleophilic attack the reaction is rather slow, therefore long times (1 week) and very large excess of iodoalkane (1:35) was necessary. An attempt running the reaction under microwave irradiation did not afford the desired product. The orange precipitate was filtered, washed with cold acetone (0 °C), recrystallized twice from water/acetone 15:85 v/v, and dried in vacuum for several days. Yield 60%. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta=9.35$ (s, 4H, H3, H5, H3′, H5′), 4.70 (t br, $^3J_{HH}$ 8.4 Hz, 4H, N–CH_2–R), 3.19 (s, 12H, Ar–CH_3), 1.65 (m, 4H, N–CH_2–CH_2–R), 1.6–1.2 (m, 20H octyl, 28H decyl, 36H dodecyl), 0.90 (m, 6H, R–CH_3) ppm. UV/Vis (CH_2Cl_2, $2\cdot10^{-4}$ M): an intermolecular CT band is observed at 466 nm. Elemental analysis. $n=8$: found: C 52.08%; H 7.28%; N 3.96%; calcd. C 52.03%; H 7.28%; N 4.04%.

2.2. 1,1′-di(n-C_nH_{2n+1})-2,2′,6,6′-tetramethyl-4,4′-bipyridinium dibis (trifluoromethanesulfonyl)amide, **2a–c**, $n=8$, 10, 12

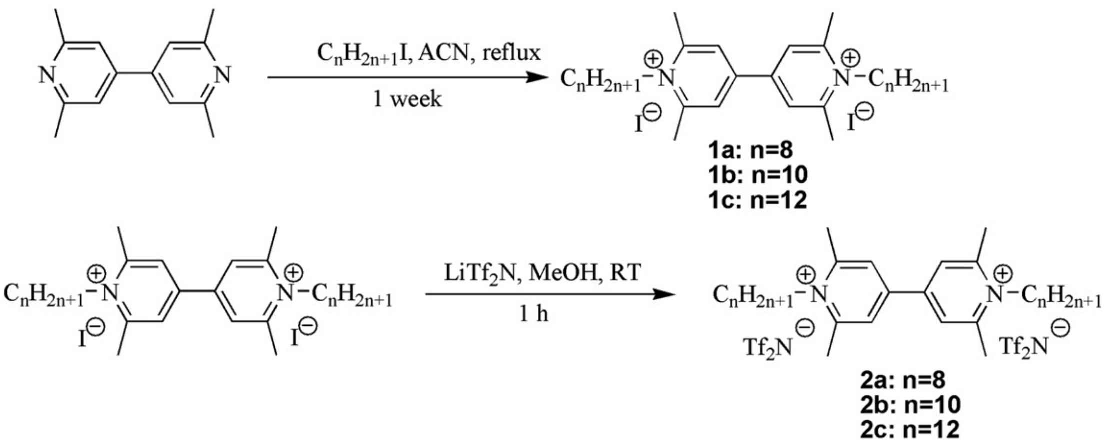
Bistriflimide (*bis*(trifluoromethanesulfonyl)amide, $(CF_3SO_2)_2N^-$, Tf_2N) salts were prepared by metathesis with $LiTf_2N$ (Sigma-Aldrich) in methanol. Since solutions of the iodide salts were found to be unstable (turning to a brown colour after 24 h) the literature procedure was slightly modified: a methanol solution of the iodide salt with an excess of $LiTf_2N$ was stirred for ca. 30 min. After removing methanol in a rotary evaporator water was added and the precipitate washed with water. The metathesis was then repeated with a fresh $LiTf_2N$ methanol solution. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta=8.09$ (s, 4H, H3, H5, H3′, H5′), 4.42 (t br, $^3J_{HH}$ 8.4 Hz, 4H, N–CH_2–R), 2.96 (s, 12H, Ar–CH_3), 1.89 (m, 4H, N–CH_2–CH_2–R), 1.6–1.2 (m, 20H octyl, 28H decyl, 36H dodecyl), 0.90 (m, 6H, R–CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) $\delta=156.5$ (C4, C4′), 149.7 (C2, C6, C2′, C6′); 127.9 (C3, C5, C3′, C5′); 120.3 (q, $^1J_{CF}$ 322 Hz, $((CF_3SO_2)_2N^-)$, 54.0 (N–CH$_2$–R), 29.4, 29.2, 28.7, 27.2, 23.0, 21.9, 14.4 ppm. ^{19}F (376.5 MHz, $CDCl_3$)–83.8 $((CF_3SO_2)_2N^-)$ ppm. ESI-MS $m/z=219$ [M^{2+}, $n=8$], 247 [M^{2+}, $n=10$], 275 [M^{2+}, $n=12$], −280 [Tf_2N^-]. Elemental analysis. $n=8$: found: C 40.73%; H 5.19%; N 5.59%; S 13.06%; calcd. C 40.88%; H 5.04%; N 5.61%; S 12.84%. $n=10$: found: C 43.21%; H 5.74%; N 5.18%; S 12.43%; calcd. C 43.26%; H 5.54%; N 5.31%; S 12.16%. $n=12$: found: C 45.60%; H 6.09%; N 4.96%; S 11.64%; calcd. C 45.40%; H 5.99%; N 5.04%; S 11.54%.

2.3. POM (polarized-light optical microscopy)

The textures of the samples were studied with a Leica DM4000M polarized light microscope. The samples were placed between a glass slide and a cover slip. A Mettler FP82HT hot stage was used to control the temperature. The samples were heated at 10 °C/min beyond the melting temperature determined by DSC experiments, and subsequently cooled at 10 °C/min to room temperature. The photomicrographs were taken between cross-polarizers with a Leica DFC280 digital camera.

2.4. DSC

All the measurements were carried out with a TA Instruments mod. 2920 calorimeter operating under N_2 atmosphere. Samples weighing about 5 mg closed in aluminum pans were used throughout the experiments. Indium of high purity was used for calibrating the DSC temperature and enthalpy scales. Four ramps were included in the temperature program: one heating from room temperature to 160 °C at 10 °C/min, followed by a cooling step to room temperature at 10 °C/min and by another analogous heating/cooling cycle. The



Scheme 1. Synthetic protocols of the compunds investigated.