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Investigations into Supramolecular Lyotropic Liquid Crystals Based on 1,3,5-Benzenetricarboxamides by NMR Spectroscopy

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In memory of Klaus Hafner

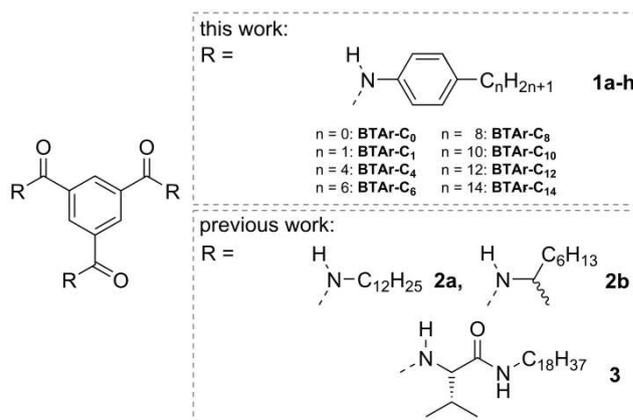
New supramolecular lyotropic liquid crystals (LLC) based on 1,3,5-benzenetricarboxamides (BTAs) with *n*-alkylaniline side-chains are described. Using NMR spectroscopy, we investigate the effects of different chain lengths along the homologous series and of non-BTA additives on liquid crystalline behaviour. From this, we attempt to answer two questions: First, how

aliphatic chain length and the addition of further aromatic rings affect the self-assembly process in general and compared to previously reported systems with purely aliphatic sidechains. Second, whether these modifications are suitable to increase the resulting LLC phases' resilience against disrupting effects of further, non-BTA additives.

Introduction

Supramolecular self-assembly is a fascinating concept in which complex structural features spontaneously arise from non-covalent interactions of often much smaller and simpler molecular building blocks.^[1] One type of supramolecular building block studied extensively are the 1,3,5-benzenetricarboxamides (BTA, Scheme 1).^[2] Under suitable conditions these structures self-assemble into long, helical stacks through tri-fold hydrogen bonding of the amide groups, aided by π - π -interactions of the central aromatic ring. This can give rise to liquid crystalline behaviour both in the bulk^[3,4] and suitable solvents,^[5-8] although hydro-^[9-14] and organogels^[15-18] are generally more common in the latter case. Through variation of their sidechain structure it has further been possible to – for example – enable BTA self-assembly even in polar solvents,^[10,19,20] dictate the handedness of resulting helical aggregates in mixtures,^[21-23] control their self-assembly mechanism^[24] and stabilize or weaken BTA-BTA interactions^[25-27] – results which have provided valuable insights into the general principles of supramolecular interactions.

Apart from these fundamental studies, BTA-based lyotropic mesophases have also been utilized as so called alignment media in NMR spectroscopy.^[8,18] In this application the inherent order of such lyotropic liquid crystalline (LLC) or gel phases is



Scheme 1. General BTA structure (left) and sidechains investigated in this work (**1 a–h**, in the following denoted **BTAr-C_n**) and those utilized for alignment media in earlier publications (**2**^[8] and **3**^[18]).

exploited to induce a preferential orientation (“alignment”) of dissolved analytes in relation to the external magnetic field (with the sample then composed of the analyte, the solvent and a component inducing orientation, here a BTA). This in turn makes anisotropic interactions^[28-32] observable even in solution. While BTA-based mesophases were found to be in principle suitable for this purpose, there were also challenges encountered regarding analyte compatibility – an issue also known for other supramolecular media.^[33] For the original systems with purely aliphatic sidechains^[8] (branched, linear and mixtures thereof, **2**) for example, even a single polar group within an analyte led to strong interactions with the BTAs and resulted in significant line broadening. This made the extraction of anisotropic observables impossible for this particular analyte. While we were able to provide remedy for these issues by doubling the number of hydrogen bond donor/acceptor functions per BTA molecule (**3**),^[18] this also caused the system

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to behave gel-like^[34] and necessitated a more complicated preparation.

Given these results, we were wondering whether the use of other, weaker supramolecular interactions might be more suitable to reduce BTA-analyte interactions and improve analyte compatibility. Particularly, our interest fell onto utilizing alkyl aramides (1) instead of aliphatic amides (2) as sidechains, which are expected to provide both additional steric shielding for the central, structure-defining core as well as further binding π - π -interactions. This general kind of structure has previously been investigated by Nagarajan and Pedireddi^[35] for chain lengths from zero to four carbons, yielding gels in both DMSO and DMSO/water mixtures – solvents which strongly affect hydrogen bonding – serving as an indication that the added aromatic moieties might have a stabilising effect.

We have thus synthesized and investigated the homologous series of 1,3,5-benzenetricarboxaramides (BTAr- C_n , 1a–h) to shed light on how this modification affects BTA-analyte interactions and whether it can reduce the effects resulting from them. Additionally, we seek to establish some insights into the effect of sidechain length, an aspect which is well known to be relevant in thermotropic liquid crystals of this type,^[34] but has to our knowledge only been investigated to a limited degree for dilute systems,^[34–37] and not at all for LLC phases. For this purpose, we have selected *n*-alkyl chain lengths to account for the range of sizes investigated in these previous studies.

Results and Discussion

In order to elucidate the synthesised BTAr building blocks' abilities to form LLC phases, we have investigated solutions thereof in deuterated solvents by ²H-NMR-imaging.^[38] Here, anisotropic behaviour is indicated by the splitting of the solvent's resonance line (solvent signal quadrupolar splitting, $\Delta\nu_Q$) into a doublet as a result of the solvent's alignment by the medium. Assuming the medium's liquid crystalline structure (and thus the induced orientation of the solvent) to be constant, the size of this splitting can serve as a measure of differences in alignment strength upon changes of e.g. temperature^[39] or concentration^[8,40] within a given system. Comparisons *between* systems on the other hand are more difficult and require phase morphologies and thus induced orientations to be the same or at least very similar in all cases – which we assume to be the case here for LLCs of different BTAr building blocks based on molecular similarity. The relations observed between residual dipolar couplings^[28] in the systems compared potentially support this assumption (see SI). To complement this information, we further examined samples between crossed polarizers, where a visual brightening (birefringence) is indicative of liquid crystalline behaviour (Figure 1, top).

Our first experiments were concerned with the gels in DMSO and DMSO/water mixtures originally described by Nagarajan and Pedireddi^[35] (although with deuterated solvents in our case). In accordance with their results, we obtained highly viscous, opaque gels with BTAr- C_0 and BTAr- C_1 , which

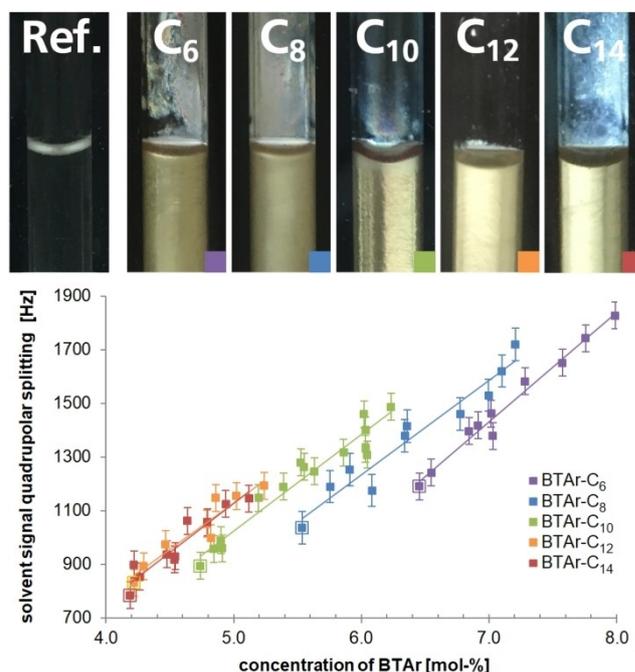


Figure 1. Top: Birefringent samples of BTAr- C_6 to BTAr- C_{14} in $CDCl_3$ and isotropic sample containing only solvent (Ref.) for reference. Differences in opacity for anisotropic samples are caused by concentration differences. Bottom: Plots of quadrupolar splittings vs. BTAr concentration (solvent: $CDCl_3$). Unfilled boxes around data points indicate first appearance of a residual isotropic signal and correspond to the approx. critical concentrations.

however appeared isotropic – both in terms of lacking quadrupolar splitting and missing birefringence. These systems thus are not suitable as alignment media. Since further attempts to induce anisotropy through dilution or preparative variations were unsuccessful and BTAr- C_4 did not form a gel in DMSO/water mixtures as reported previously by the authors,^[35] we shifted our investigations towards other solvents.

Based on similarity of the BTAr investigated to building blocks used in previous BTA-based alignment media,^[8,18] we next tested them in the same solvent utilized there – deuterated chloroform ($CDCl_3$). Here, results turned out to be essentially the inversion of results above: While the shortest chains (BTAr- C_0 and BTAr- C_1) were barely soluble, BTAr- C_4 showed better solubility, but mixtures were also very turbid. Additionally, we have observed a crystalline shimmer (see SI) upon shaking or inducing flow, which however only persisted for a few minutes thereafter. This might be an indication for the presence of shape anisotropic aggregates which align as result of shear flow, but no quadrupolar splitting was detectable. We thus interpret these findings towards a limited stability of the phase at this chain length.

All higher homologues (BTAr- C_6 to BTAr- C_{14}) displayed both clear birefringence and quadrupolar splittings; hence further investigations were focused on these exclusively. Figure 1 shows plots of observable splittings *versus* concentration for these building blocks. As can be seen there, the critical concentration (that is, in our case, the lowest concentration at

which no residual isotropic signal is detectable via ^2H) shows a clear trend towards lower values with longer chains. In addition to this lower limit, an upper limit of preparability related to increasing viscosity is observable, beyond which samples were no longer reliably homogenizable – still, samples display birefringence even above it.

For lyotropic systems of long cylindrical mesogens it is generally expected that the critical concentration decreases with increasing aspect ratio/length.^[41–43] Thus one could interpret our findings in such a way, that BTAr with longer sidechains yield longer stacks for a given concentration. The most likely explanation for this behaviour are favourable changes in BTAr-BTAr interactions^[22] shifting the equilibrium further from individual molecules to longer aggregates as alkyl chains get longer. Since the lengths of BTA-stacks are notoriously difficult to determine already in dilute solution, we refrained from attempting to obtain these in the LLC state here (see estimation of a lower stack length limit of approximately 500 Å for 4.5×10^{-4} M solution of a BTA with *n*-alkyl sidechains (C_{16}) in methylcyclohexane^[44]). Similar behaviour was, however, also reported previously in other BTA-based systems: For thermotropic LCs based on *n*-alkyl-substituted BTAs the liquid crystalline temperature range becomes larger with sidechain length.^[4] More specifically were decreasing solid-LLC transition and higher clearing temperatures observed. Further evidence comes from computed dimerization free energies for BTA systems with different *n*-alkylchain lengths (in *n*-nonane and gas phase).^[37]

It is also noteworthy that the differences in critical concentration appear to both become smaller with increasing chain length and level off at C_{14} . Based on our argumentation above this would imply that the favourable changes in BTAr-BTAr interactions as result of increased chain length diminish along the homologous series. In order to confirm this observation as systematic, investigations into further sidechain lengths and actual stack sizes would be required, which we did, however, not undertake here.

With effects of chain lengths established we were next interested in investigating whether we can detect interactions of the sidechains' aromatic rings. For this purpose, we have utilized $^1\text{H-NMR}$ spectroscopy in dilute solution. Here, changes in line shapes and chemical shifts are expected upon association of BTA-building blocks. We have thus measured spectra both in pure CDCl_3 (as used for LLC phases above) and after addition of $\text{THF-}d_8$ (Figure 2). The latter is expected to strongly disrupt hydrogen bonding and therefore provide a point of reference for molecularly dissolved BTA molecules. As can be seen, both signals of the amidic N–H and aromatic protons of the central ring appear significantly broadened in pure CDCl_3 , a broadening which immediately disappears after $\text{THF-}d_8$ is added. Additionally, the resonances shift to lower (aramidic protons), and higher (aromatic core) ppm values, respectively. This indicates a more electron rich environment in the former and a less electron rich one in the latter case upon disassembly – an effect previously reported for similar BTAs (in this case induced by dilution).^[45]

Looking at the aromatic sidechain protons on the other hand, differences are much less pronounced: There is barely

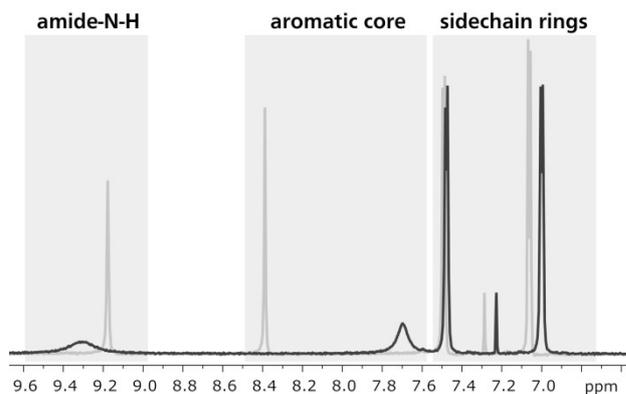


Figure 2. $^1\text{H-NMR}$ spectrum for BTAr- C_{14} in dilute CDCl_3 solution (black line) indicating significant supramolecular interactions even in dilution and the disappearance thereof upon addition of THF (grey). Only aromatic region shown, referenced to $\text{DMSO-}d_6$ capillary. Comparable behaviour was observed for lower homologues.

any broadening and only a small shift, pointing to weaker interactions between these aromatic rings. An explanation for this might be found in the solid state structures (XRD) obtained by Nagarajan and Peddiredi^[35] for BTAr- C_4 : Here, the sidechains' aromatic rings are tilted with respect to the central one. This might limit their ability to interact if this conformation persists in CDCl_3 solution and for higher homologues.

In order to answer the question how the obtained LLC phases react to the addition of further components, we have prepared mixtures containing the same two analytes (Figure 3) used in earlier studies:^[8,18] (–)- β -pinene and (–)-isopinocampheol (IPC). Of these, the latter was previously shown to interact strongly with the BTA LLC phase.^[8] This was attributed to its

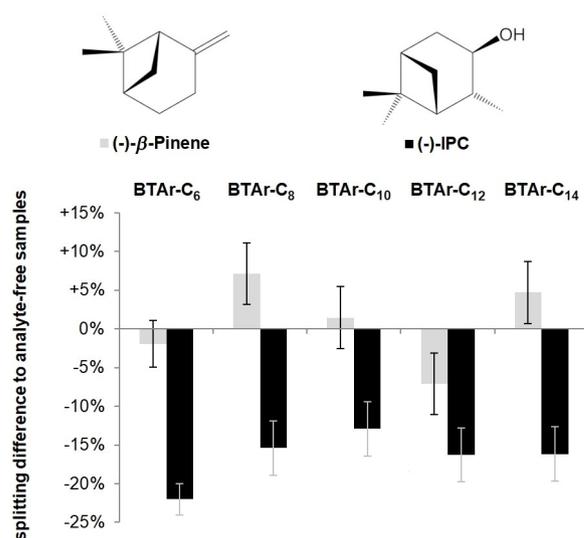


Figure 3. Effects of added β -pinene (grey) and IPC (black) on solvent signal quadrupolar splittings ($\Delta\nu_Q$) of LLC phases in deuterated chloroform (CDCl_3). See SI for full data. Error bars shown are the standard errors of regression used for calculation of splittings expected in analyte-free samples and the uncertainties of observable splittings in analyte containing samples.

ability to form hydrogen bonds, while the former displayed no such behaviour. Stable LLC phases were obtained with both analytes. As a measure for the respective effects of these additives we used the observable ^2H -quadrupolar splittings and compared their sizes with those for the analyte-free phases calculated based on the slopes in plots shown above (Figure 3, see also SI).

For β -pinene only small differences in quadrupolar splittings were obtained. Additional experiments (see SI) found this to be also the case at different analyte/BTA-ratios and BTA concentrations from those shown. 2D spectra displayed sharp lines and were generally suitable for extraction of RDCs, despite line shape distortions due to high alignment strength. Based on the single RDC available for all phases (C1–H1, see SI), different BTA chain lengths further seem not to lead to differences in induced orientation. This interpretation has to be viewed with caution, however, as it is based on a single RDC (see SI for more detailed discussion).

IPC on the other hand caused LLC phases to collapse beyond a certain amount added, which was significantly lower than quantities well tolerated with (–)- β -pinene. Even in cases where this did not occur, a significant reduction of quadrupolar splittings was observable (Figure 3) and strong line broadening prevented extraction of RDCs with no noticeable differences between chain lengths. Surprisingly, the reduction of splittings was also of comparable size for all BTAs tested, indicating sidechain length to be much less important in analyte-BTA interactions than for the self-assembly process itself – at least in this case.

While investigations towards the effects of additional non-BTA components on BTA-self-assembly in solution are scarce, much work has been done elucidating processes in mixtures of different building blocks.^[44,46] Specifically, the addition of BTAs with additional hydrogen bonding moieties or methylated amide groups has been shown to significantly affect stack lengths by inactivating individual building blocks (sequestration)^[47,48] or inhibiting chain growth (chain capping)^[49] at stack ends. It is reasonable to assume that similar processes are involved in analyte-BTA interactions as well.^[44]

When comparing our BTA-based systems to the one^[8,50] previously reported (**2a** in CDCl_3), it further seems as if there is also only a limited effect of the added aromatic rings on stability: Disruptive effects of IPC persist, leading to reduced quadrupolar splittings and strong line broadening. As a result, RDCs of IPC are still unavailable. Additionally, quadrupolar splitting vs. concentration plots for **BTA-C₈** (the most similar BTA in terms of total sidechain length) and its aliphatic, straight chain analogue **2a** (see SI) are also very similar, both in regard to slope and critical concentration. It thus appears as if the added aromatic rings do not have a significant effect and act essentially the same as *n*-alkyl chains of comparable length. This might be related to the limited interactions between them as indicated by ^1H -NMR spectra shown above.

Conclusion

In summary, we have presented a new type of supramolecular lyotropic liquid crystal based on 1,3,5-benzetricarboxamide-building blocks with *n*-alkylaniline sidechains in deuterated chloroform (CDCl_3). By investigating the homologous series thereof using NMR spectroscopy, we were able to obtain some insights into the constituting self-assembly process: Our results show a clear positive correlation between the minimum concentration for LLC behaviour and aliphatic chain length, indicating stronger self-assembly behaviour with longer sidechains. Interactions between the BTA stacks and additional components disrupting the LLC phase on the other hand seem to be independent of chain length. When comparing the systems further to previously reported BTA building blocks bearing *n*-alkyl sidechains^[8,50] of similar total length, there appears to be no significant effect of the aromatic rings added. Critical concentration, concentration dependent quadrupolar splittings and response to disrupting additives are all comparable. This appears to be a result of only limited interactions between side chain aromatic rings. It seems from this, that a more detailed understanding of specific interactions between BTA building blocks and non-BTA additives is needed to improve corresponding BTA-based LLC phase's resilience against disruption in the future.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: ^2H -NMR · BTAs · Lyotropic liquid crystals · Self-assembly · Supramolecular chemistry

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