Concealed Cyclotrimeric Polymorph of Lithium 2,2,6,6-Tetramethylpiperidide Unconcealed: X-ray Crystallographic and NMR Spectroscopic Studies

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Abstract: Lithium 2,2,6,6-tetramethylpiperidide (LiTMP), one of the most important polar organometallic reagents both in its own right and as a key component of ate compositions, has long been known for its classic cyclotetrameric $(LiTMP)_4$ solid state structure. Made by a new approach via transmetallation of $Zn(TMP)_2$ with *t*BuLi in hexane solution, a crystalline polymorph of LiTMP has been uncovered. X-ray crystallographic studies at 123(2) K reveal this polymorph crystallises in the hexagonal space group $P6_3/m$ and exhibits a discrete cyclotrimeric (C_{3h}) structure with a strictly planar $(LiN)_3$ ring containing three symmetrically equivalent TMP chair-shaped ligands. The molecular structure of $(LiTMP)_4$ was redetermined at 123(2) K as its original crystallographic characterisation was done at ambient temperature. This improved redetermination confirmed a monoclinic C2/c space group with the planar $(LiN)_4$ ring possessing pseudo (non-crystallographic) C_{4h} symmetry. Investigation of both metallation and transmetallation routes to LiTMP under different conditions established that polymorph formation did not depend on the route employed but rather the temperature of crystallisation. Low temperature (freezer at -35°C) cooling of the reaction solution favoured $(LiTMP)_3$; whereas high temperature (bench) storage favoured $(LiTMP)_4$. Routine ^1H and ^{13}C NMR spectroscopic studies in a variety of solvents showed that $(LiTMP)_3$ and $(LiTMP)_4$ exist in equilibrium while ^1H DOSY studies gave diffusion coefficient results consistent with their relative sizes.

Keywords: amide • crystal structures • DOSY • lithium • NMR spectroscopy • polymorphism

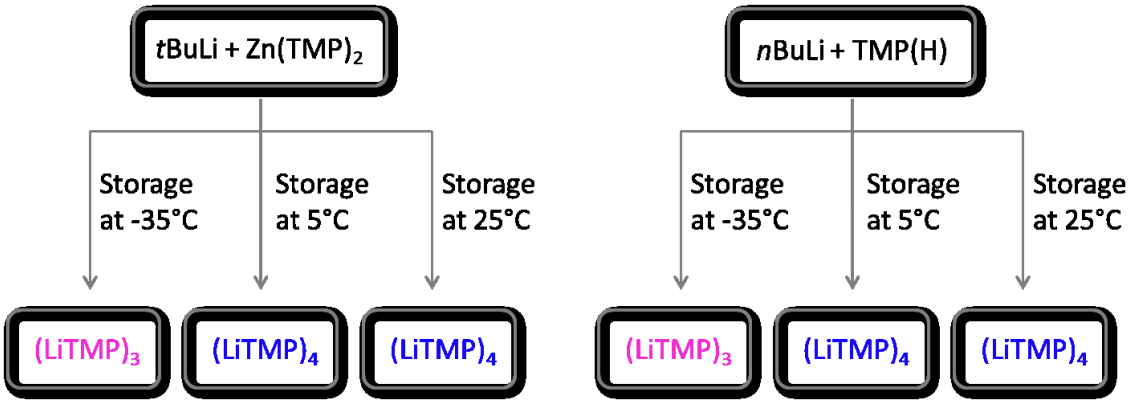
Introduction

A recent review[1] put the spotlight on lithium 2,2,6,6-tetramethylpiperidide, LiTMP, as one of a trio of utility lithium amides (along with diisopropylamide, LiDA and 1,1,1,3,3,3-hexamethyldisilazide, LiHMDS) derived from organic secondary amines that have been worked in synthesis for over 40 years.[2] Due to a combination of low nucleophilicity and high Brønsted basicity, LiTMP excels especially in the selective cleavage of C-H bonds (to more functionally pliable C-Li bonds).[3] This high reactivity reflects the special architecture of its cyclic anion TMP^- where electron releasing methyl branches dress both α-positions adjacent to nitrogen. In organolithium chemistry one's eyes must generally look beyond the steric profile of the anionic moiety as the large polarity of $Li^{\delta+}$ - $C^{\delta-}$ (here $Li^{\delta+}$ - $N^{\delta-}$) bonds often promotes aggregation phenomena that lead to the vast assortment of structures that gives organolithium structural chemistry its aesthetic beauty. Reported by Lappert and Atwood[4] 10 years after its embracing as a base by organic chemists,[5] the solid state structure of LiTMP is a classic within organolithium chemistry,[6] a discrete cyclotetramer with a planar $(LiN)_4$ ring comprising 2-coordinate Li and 4-coordinate N atoms within TMP chairs. This and related 2-dimensional structures of other lithium amides when contrasted with 3-dimensional lithium imide structures inspired Snaith to develop his seminal ring-laddering and ring-stacking principles in organolithium chemistry.[7] Surveying the well-studied solution structural behaviour of LiTMP as part of our ongoing mixed metal base investigations we were struck by its complexity and diversity in hydrocarbon media.[8] Collum detected high cyclic oligomers $(LiTMP)_n$ (n>2) in pentane from $^6Li/^{15}N$ NMR studies assigning them to tetramers and trimers and reasoning that in theory there would be six such oligomers altogether due to differently arranged TMP chair conformations.[9] Indirect evidence from a ^6Li-^{15}N HMQC (heteronuclear multiple quantum correlation) spectrum of LiPMP (PMP is 2,2,4,6,6-pentamethylpiperidide), where introducing a fifth Me substituent at the apex of the ring slows down conformational dynamics, enabled Collum to detect and assign five species, four cyclotetramers and one cyclotrimer. Since our subsequent DFT calculations predicted these oligomeric isomers had similar relative energies[10] and knowing that polymorphs exist in related alkali metal amides (e.g., trimeric and polymeric NaHMDS)[11], we pondered whether the solid state picture of LiTMP was complete given the multiplicity of species that co-exist in hydrocarbon solution, a medium more like the solid

state than strongly solvating/deaggregating donor solution (note that Fox reports a monomer-dimer equilibrium for LiTMP in d_8-THF at -50°C)[12]. Moreover, unless one deliberately looks for a polymorph of LiTMP it is unlikely to be discovered fortuitously as LiTMP is generally prepared in situ without isolation, increasingly in THF solution as part of mixed metal reagents where it will exist at least predominately in solvated form.[13] Here we report that changing the temperature at which LiTMP is crystallised does indeed uncover a new polymorph as elucidated by X-ray crystallography. We show also that NMR spectroscopic studies, both routine (^{1}H and ^{13}C) and DOSY (Diffusion Ordered SpectroscopY) can easily distinguish between this long concealed polymorph and its predecessor which exist in equilibrium.

Results and Discussion

Synthesis and Crystallisation: As following the original crystallisation method it has become standard practice to synthesise LiTMP by metallation of the parent amine with an alkyllithium reagent, we decided to investigate a new approach. Exploiting the superior carbophilicity of zinc,[14] we performed a transmetallation between $Zn(TMP)_2$ and *t*-butyllithium in hexane solution at ambient temperature (Scheme 1). Regardless of the stoichiometry employed, LiTMP was produced in crystalline form in yields of 90% or higher. An X-ray crystallographic study revealed these crystals to be predominately a cyclotrimeric polymorph, $(LiTMP)_3$, **1**, of the known cyclotetramer $(LiTMP)_4$, **2** (see below). Unit cell checks of several crystals from each of the stoichiometric variant reactions confirmed their identity as **1**. Significantly these crystals were grown from solutions in the freezer at -35°C. For comparison we reprepared LiTMP by metallation reacting *n*-butyllithium with TMP(H) in hexane at ambient temperature (Scheme 1) and storing the resulting solution at different temperatures. Freezer storage at -35°C afforded mainly crystals of cyclotrimer **1**, but raising the storage temperature to 5°C or 25°C gave mainly the other polymorph **2**. Returning to the alternative transmetallation approach but growing crystals on the bench at 25°C or in the refrigerator at 5°C also gave **2**. Therefore crystallisation at low temperature favours formation of **1**; whereas **2** is favoured at high temperature. While identities were confirmed by unit cell checks of several crystals from each reaction, as Figure 1 shows **1** and **2** could be distinguished qualitatively by the naked eye due to their contrasting habits [**1** forming prismatic (rod-like) crystals; whereas those of **2** are more anhedral].



Scheme 1. Alternative syntheses of LiTMP showing major lithium products obtained under different storage conditions. Note these reactions do not take into account stoichiometry.

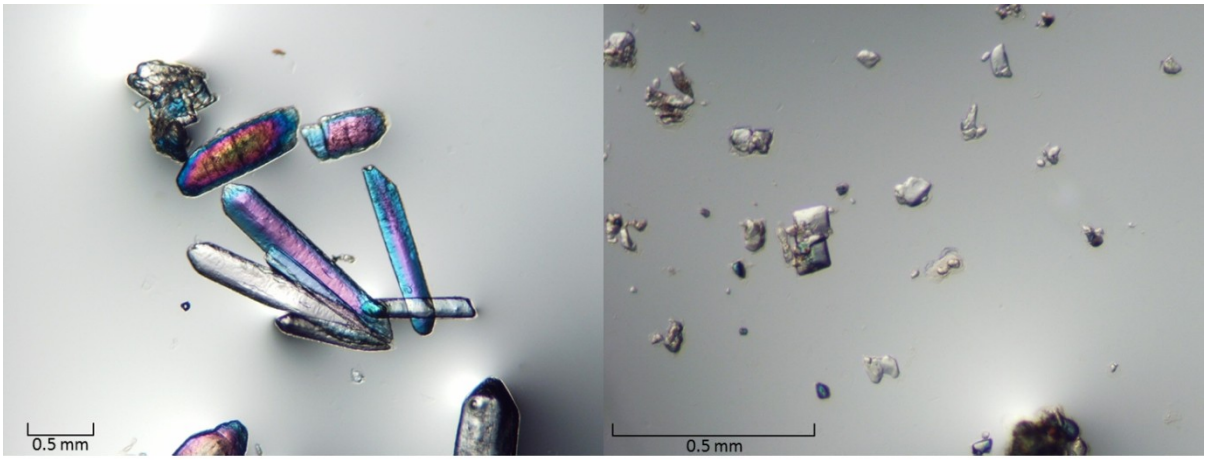


Figure 1. Microscope photographs of crystalline **1** (LHS) and **2** (RHS) showing approximate scale.

X-ray Crystallographic Studies: Since we determined the molecular structure of **1** (Figure 2) at low temperature [123(2) K][15] whereas that of **2** was determined originally at ambient temperature, we redetermined the structure of **2** (Figure 3) at 123(2) K[16] both to confirm its cyclotetrameric arrangement and for a more direct comparison. Data discussed here for **2** will be restricted to those of this new improved low temperature structure. Table 1 compares selected bond parameters for **1** and **2**. Trimer **1** crystallises in the hexagonal space group $P6_3/m$ in contrast to the monoclinic space group C2/c of tetramer **2**. Strictly planar, the $(LiN)_3$ ring of **1** exhibits C_{3h} symmetry, while the $(LiN)_4$ ring of **2** exhibits pseudo (non-crystallographic) C_{4h} symmetry. These symmetries (easily seen in ChemDraw representations in Figure 4) are dictated by the number and conformations of TMP ligands. Exclusively chair shaped, the TMP ligands are all strictly equivalent in **1** and approximately equivalent in **2**.

Since the TMP ligand in **1** presents a different steric profile to the Li atoms either side of the N atom adjacent Li-N bond lengths are inequivalent, so that short [1.988(3) Å] and long [2.066(3) Å] bonds alternate around the ring with a mean length of 2.027 Å. Endocyclic bond angles at Li [150.22(16)°] and N [89.78(16)°] show marked distortions from linear and tetrahedral geometries respectively, with the widest angle at N being 116.24(7) for C(1)-N(1)-Li(1). The reduced (crystallographic) symmetry in the larger ring of **2** means there are two distinct Li and two distinct N atoms present. Mean endocyclic bond angles [at Li, 168.9°; at N, 101.01°] suggest a slight relief of ring strain compared to that in **1**. Because of its lower symmetry **2** displays four distinct Li-N bond lengths which as in **1** alternate in a short-long pattern (mean short, 1.983 Å; mean long, 2.020 Å) and have an overall mean length (2.002 Å) marginally less than that in **1** (2.027 Å).

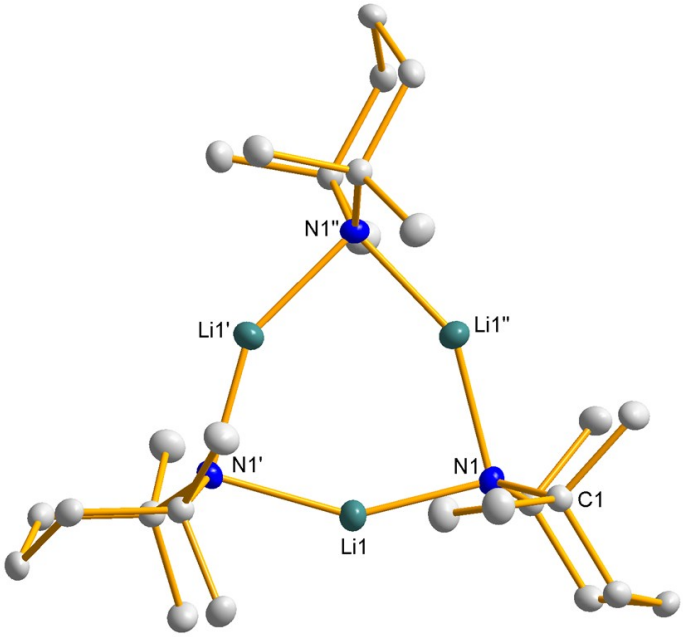


Figure 2. Molecular structure of **1**. Hydrogen atoms are omitted for clarity. The symmetry operation to generate the equivalent atoms labelled ' is 1-*y*, *x*-*y*, *z* and '' is 1-*x*+*y*, 1-*x*, *z*.

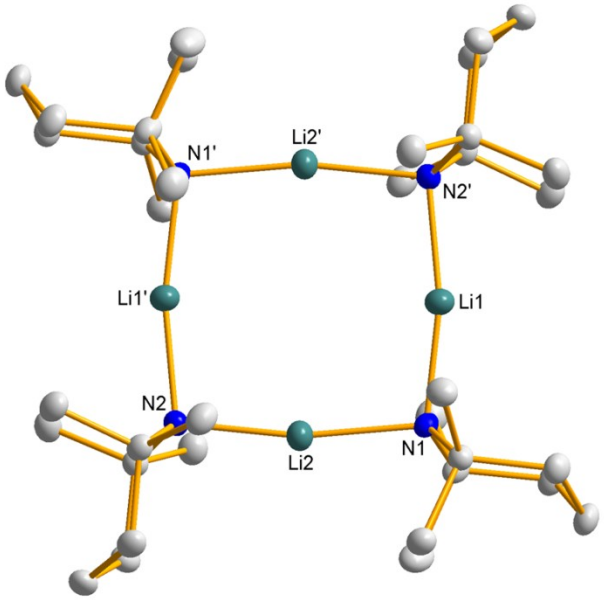


Figure 3. Redetermined molecular structure of **2**. Hydrogen atoms are omitted for clarity. The symmetry operation to generate the equivalent atoms labelled ’ is -*x*+0.5, -*y*-0.5, -*z*.

Table 1. Key bond lengths (Å) and bond angles (°) within the structures of **1** and **2**.

For **1**			
Li1-N1	1.988(3)	N1’-Li1-N1	150.22(16)
Li1-N1’	2.066(3)	Li1-N1-Li1’	89.78(16)
For **2**			
Li1-N1	1.981(3)	N1-Li1-N2’	168.51(14)
Li1-N2’	2.017(3)	N2-Li2-N1	169.29(14)
Li2-N1	2.023(3)	Li1-N1-Li2	100.97(10)
Li2-N2	1.985(3)	Li1’-N2-Li2	101.05(10)

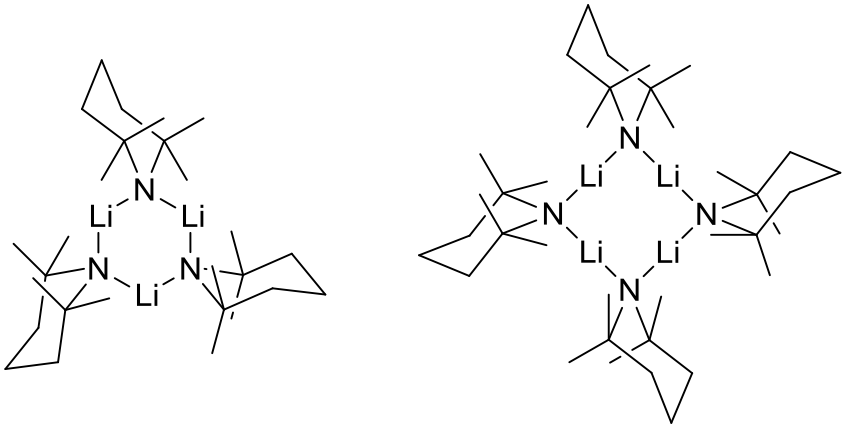


Figure 4. ChemDraw representations of **1** (LHS) and **2** (RHS).

NMR Spectroscopic Studies: Cyclotrimer **1** and cyclotetramer **2** were both observed and surprisingly easy to distinguish from routine ^{1}H and ^{13}C NMR spectra recorded in d_6-benzene solution. As alluded to earlier Collum utilised ^{6}Li, ^{15}N, and ^{6}Li-^{15}N HMQC NMR spectra in pentane to observe at -40°C a trimer:tetramer ratio of approximately 1:4 and at -120°C a decoalescence of the tetramer resonance into several overlapping resonances indicative of several tetrameric conformers.[9] These elegant studies of Collum required the special preparation of isotopically labelled compounds. To the best of our knowledge, the same observation of these two aggregation isomers **1** and **2** has not been noted previously in routine NMR studies using ordinary unlabelled samples. Resonances associated with the α-Me groups provide excellent diagnostic markers for recognising chemically distinct TMP ligands.[17] From ^{1}H NMR spectra recorded in d_6-benzene solution at ambient temperature we assign resonances at 1.36 and 1.30 ppm to **2** and **1** respectively. These species co-exist in solution irrespective of which crystals are used to make up the solution. Dissolving $(LiTMP)_3$ crystals (obtained at -35°C) produced integration values amounting to a 1.00:0.79 molar ratio of **1**:**2**, that is with the cyclotrimer in a small excess. This ratio reverses to 1.00:1.59 in favour of cyclotetramer **2** when $(LiTMP)_4$ crystals (grown either on the bench at ambient temperature or in the refrigerator at 5°C) are used for the same spectrum. A variable temperature study performed in d_8-toluene solution established that as the temperature is lowered from 300 K to 200 K the molar ratio of **1**:**2** increased from approximately 1.00:1.08 to 1.00:0.28. This is consistent with the two cycloaggregates being in equilibrium with the smaller trimer predominant at lower temperature. Three solutions of $(LiTMP)_3$ crystals prepared at different concentrations (6, 18, and 54 mg mL^{-1}) in d_{12}-cyclohexane solvent show a modest decrease in the smaller cyclotrimer species (**1**:**2** ratio from 1.00:0.24 to 1.00:0.16) as

the concentration is decreased. Probing a d_6-benzene solution of $(LiTMP)_3$ crystals at ambient temperature over time revealed the equilibrium favours the cyclotetramer as the **1**:**2** molar ratio drops from 1.0:0.8 initially to a minimum of 1.0:1.9 (after 3 hours) after which it levels off. Moving to a d_{12}-cyclohexane (C_6D_{12}) solution and monitoring the behaviour of **1** over 7 days (Figure 5) disclosed that $(LiTMP)_3$ is significantly more stable in the non-arene solvent only reaching a minimum **1**:**2** molar ratio of 1:1.35 after 1 week.

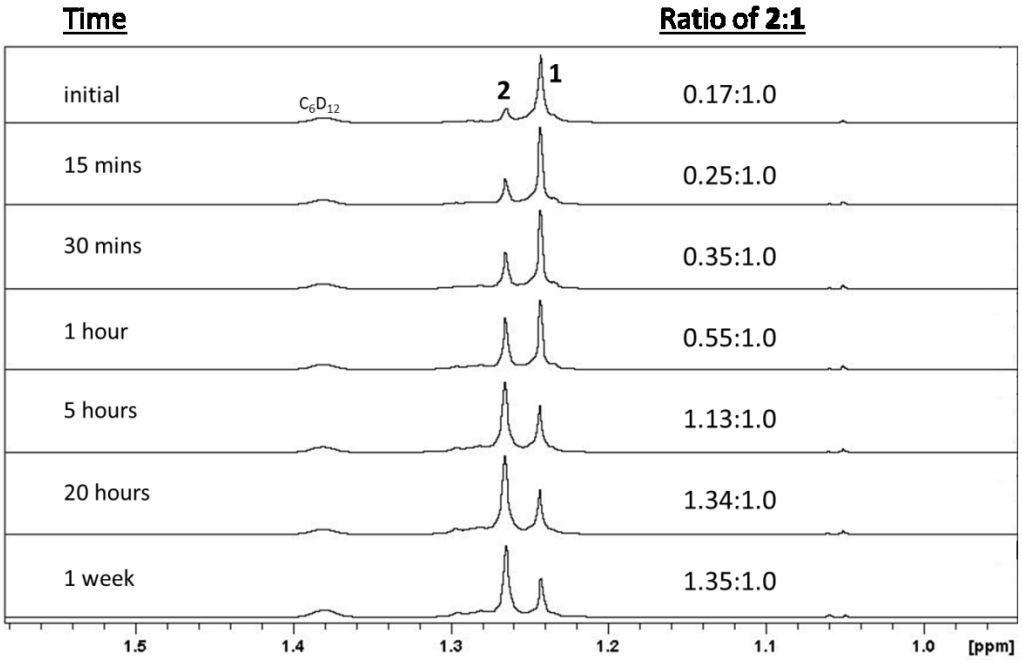


Figure 5. Variable time NMR study of **1** in C_6D_{12} solution showing the diagnostic Me resonances and the approximate **2**:**1** integration ratios.

DOSY ^{1}H NMR studies performed on $(LiTMP)_3$ crystals in both d_6-benzene (Figure 6) and d_{12}-cyclohexane solution add good support to the above ^{1}H assignments of **1** to the cyclotrimer and **2** to the cyclotetramer. Distinct species in solution can be separated due to their diffusion coefficients (d), from which molecular weights (MW_{DOSY}) can be estimated if internal inert standards of known molecular weight are employed for calibration purposes.[18] This study used tetramethylsilane, 1-phenylnaphthalene and tetraphenylnaphthalene (MW = 88, 204 and 433 g mol^{-1} respectively) as standards. Estimated molecular weights in both solvents were consistent with the expected relative size order with those of cyclotrimer **1** smaller than those of cyclotetramer **2** though reflecting the limitation of the method these values fall short of those expected theoretically. In d_6-benzene MW_{DOSY} is 348 g mol^{-1} for **1** and 420 gmol^{-1} for **2** equating to errors of -27% and -40% respectively compared against the

theoretical MWs (441 g mol^{-1} for **1**; 588 g mol^{-1} for **2**). Corresponding MW_{DOSY} values in d_{12}-cyclohexane are closer to the theoretical MWs (382 g mol^{-1}, -15% error for **1**; 554 g mol^{-1}, -6% error for **2**). Cyclooligomers **1** and **2** could also be distinguished in ^{13}C NMR spectra recorded in d_6-benzene solution at 300 K though the chemical shift separations were diminutive (e.g., CH_3: 37.1 ppm for **1**; 37.0 ppm for **2**). On moving to ^{7}Li NMR studies the two species became indistinguishable with a single resonance observed in d_6-benzene, d_{12}-cyclohexane and d_{14}-hexane solutions at 300 K with only broadening of it observed at temperatures down to 200 K (in d_{14}-hexane). Confirmation that the single ^{7}Li resonance was associated with both **1** and **2** was provided by a ^{1}H-^{7}Li HOESY experiment. The fact that ^{7}Li NMR spectroscopy on its own is not a good probe for separating **1** and **2** can be attributed to the two-coordinate equivalency of all the lithium atoms within each $(LiN)_n$ ring.

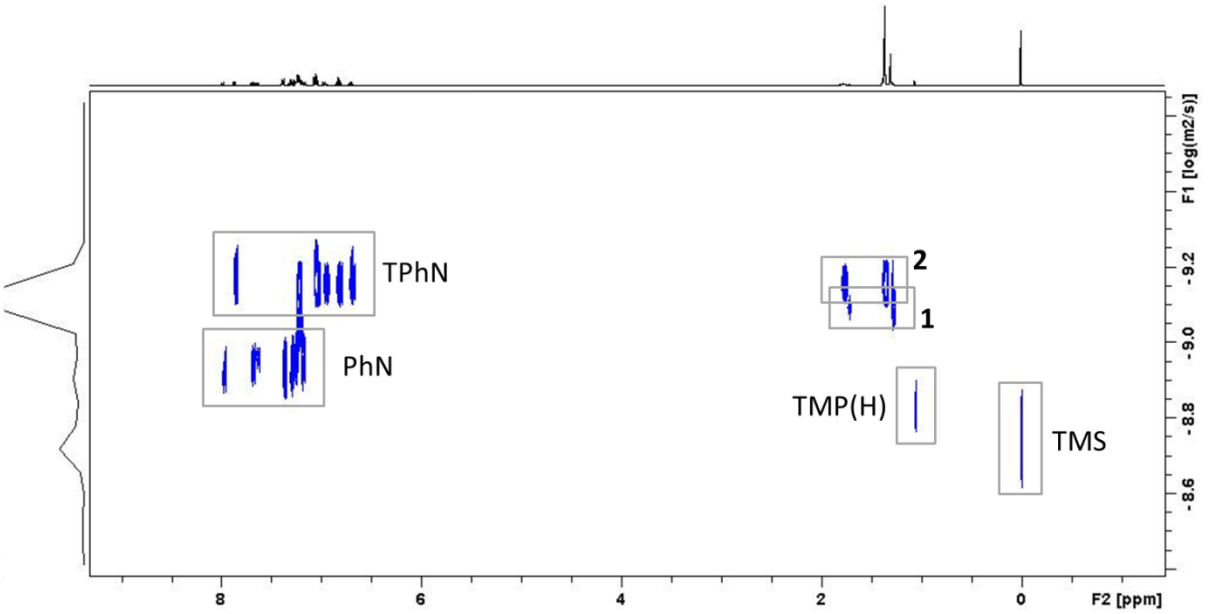


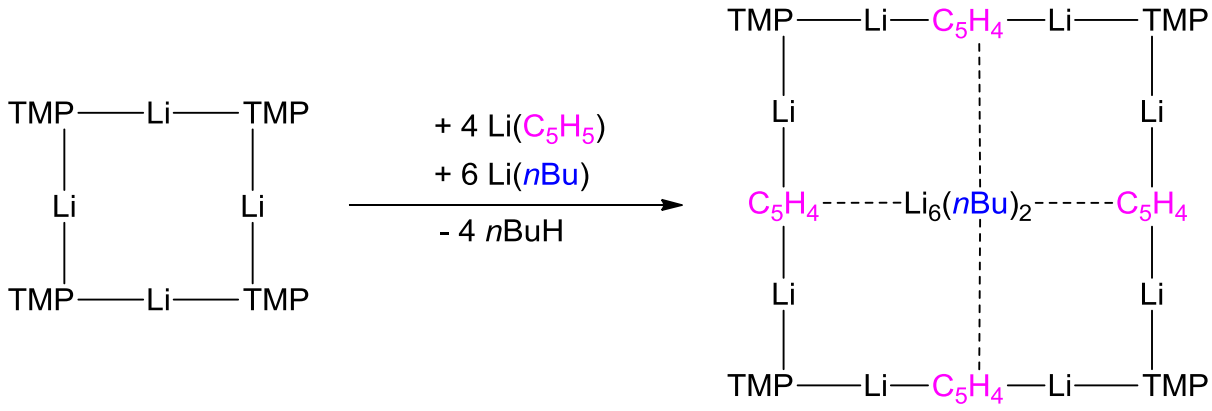
Figure 6. ^{1}H DOSY NMR spectrum of crystals of **1** in d_6-benzene solution at 300 K in the presence of inert standards 1,2,3,4-tetraphenylnaphthalene (TPhN), 1-phenylnaphthalene (PhN) and tetramethylsilane (TMS). Due to unavoidable hydrolysis a small amount of TMP(H) is also present.

Reflections on Previous Theoretical Calculations: Another factor that helped spark our interest in searching for a new solid state polymorph of LiTMP came from an earlier DFT investigation at the B3LYP/6-311G** level performed by our group.[10] We voiced the prospect of polymorphism on revealing that the C_{3h} cyclotrimer now verified here as **1** was computed to be actually 0.04 kcal mol^{-1} more stable than the C_{4h} cyclotetramer seen here in **2**,

previously reported by Lappert and Atwood,[4] and implicated in solution by Collum.[9] Though these calculations strictly model the gas phase only and therefore disregard crystal packing forces in solids and solvent effects in solution, the relative energy differences between this trimer and the four cyclotetramers studied in solution by Collum are so trivially small (the cyclotetramers cover a narrow range of 0.88 kcal mol^{-1}) it is unsurprising that **1** and **2** exist side by side and easily interconvert in apolar aromatic and aliphatic solvents devoid of lone pairs of electrons.

Relevance to Reactivity and Structural Design: Synthetic organic chemistry has long recognised the importance of oligomer size in organolithium-mediated reactions with in general small oligomers, usually solvated, being more kinetically labile than large oligomers.[2b, 14] For this reason donor solvents such as HMPA, THF, and TMEDA often accompany organolithium reagents in their bond breaking (Brønsted basic) or bond making (nucleophilic addition) adventures.[19] However less attention has been paid to exploiting organolithium oligomers in structural design though their propensity for aggregating and bridge bonding makes them ideal construction tools. The potential of LiTMP in structure building was recently demonstrated by Klett and us in the shape selective synthesis of the ring-cage hybrid compound $[\{Li(\mu\text{-}TMP)Li(\mu\text{-}C_5H_4)\}_4Li_6(n\text{Bu})_2]$ (Scheme 2).[20] This astonishing structure was prepared by crossing LiTMP with LiCp then tri-crossing with *n*BuLi. Notice however that LiTMP must exist in its cyclotetrameric architecture to facilitate the insertion of four LiCp molecules to construct the 5x5 molecular square arrangement of $[\{Li(\mu\text{-}TMP)Li(\mu\text{-}Cp)\}_4]$. If the smaller cyclotrimeric polymorph **1** was the starting point for this LiTMP/LiCp di-crossing then the same architecture could not be realised (ignoring any equilibria processes). Significantly $[\{Li(\mu\text{-}TMP)Li(\mu\text{-}C_5H_4)\}_4Li_6(n\text{Bu})_2]$ was prepared in methylcyclohexane solution heated to 110°C for 2.5 hours, conditions which as implied here would favour the formation of the cyclotetramer **2** primed for executing the tri-crossing reaction. This prompts the intriguing thought that it may be possible to construct a series of unusual architectures/hybrid structures and by doing so create novel chemistry (note the unusual deprotonation of Cp $[(C_5H_5)^-]$ to $C_5H_4^{2-}$ in the formation of the ring-cage hybrid) by crossing organolithium compounds (alkyls, aryls, amides, cyclopentadienyls etc.) at different temperatures in a range of solvents. The tactics of changing the conditions to tune the reactivity of organolithium reagents may be common in the context of synthetic organic chemistry but to the best of our knowledge they have been relatively unexplored in this area

of novel structure building. Of course, in reality organolithium and lithium amide compounds exhibit complicated equilibria in solution, as this study, and most pertinently those aforementioned studies by Collum,[9] have established for LiTMP. Therefore any possible shape selective reactions will be strongly influenced by such equilibria. At this stage with little knowledge of the mechanisms of such reactions, the best approach to extending this idea would seemingly be through trial and error. Further work in this regard is currently underway in our laboratory.



Scheme 2. Shape selective synthesis of [{Li(μ-TMP)Li(μ-C_5H_4)}$_4$$Li_6$(*n*Bu)$_2$].

Conclusions

A new synthesis of the popular utility amide LiTMP involving transmetallation between the zinc congener Zn(TMP)$_2$ and *t*BuLi in hexane solution has led to the discovery of a new crystalline polymorph in the cyclotrimer (LiTMP)$_3$ as established by X-ray crystallography. Repeating this reaction under different conditions and reinvestigating the original metallation synthesis revealed that polymorph formation was independent of the synthetic method employed but was dictated by the crystallisation temperature with low temperature favouring the smaller cyclic oligomer (LiTMP)$_3$ and high temperature favouring (LiTMP)$_4$. For completeness an improved low temperature X-ray crystallographic study of previously reported (LiTMP)$_4$ has also been carried out. The two polymorphs were surprisingly easy to distinguish by routine ^{1}H and ^{13}C NMR studies with the results of DOSY experiments consistent with their relative sizes. Given the inordinately long wait for this new LiTMP polymorph to be unearthed – 40 years since LiTMP was first introduced to synthesis and 30

years after crystallographic characterisation of $(LiTMP)_4$ – the intriguing question to be asked is "how many other polymorphs of important organolithium compounds may have been overlooked?"

Experimental Section

General methods: All reactions and manipulations were carried out under a protective dry pure argon atmosphere using standard Schlenk techniques. Products were isolated and NMR samples prepared within an argon-filled glovebox. Hexane was dried by heating to reflux over sodium-benzophenone and distilled under nitrogen prior to use. *n*BuLi (1.6 M in hexanes) and *t*BuLi (1.7 M in pentane) were purchased from Aldrich and used as received. TMP(H) was obtained from Aldrich and dried over 4 Å molecular sieves prior to use. $ZnCl_2$ was purchased from Aldrich and dried under vacuum prior to use. $Zn(TMP)_2$ was prepared according to a modified literature method (see supporting information).[21] NMR spectra were recorded on a Bruker AVANCE 400 NMR spectrometer, operating at 400.13 MHZ for ^{1}H, 155.50 MHz for ^{7}Li and 100.62 MHz for ^{13}C. All ^{13}C NMR spectra were proton decoupled. ^{1}H and ^{13}C spectra were referenced to the appropriate solvent signal and ^{7}Li NMR spectra were referenced against LiCl in D_2O at 0.00 ppm.

Crystal structure determinations: Crystallographic data were collected at 123(2) K on Oxford Diffraction Diffractometers with $Mo_{K\alpha}$ (λ=0.71073 Å) radiation. Structures were solved using SHELXS-97,[22] and refined to convergence on F^2 against all independent reflections by the full-matrix least-squares method using the SHELXL-97 program.[22] CCDC-946875 and CCDC-946876 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of $(LiTMP)_3$: Transmetallation approach - $Zn(TMP)_2$ (0.35 g, 1 mmol) was dissolved in hexane (10 mL) and *t*BuLi (0.59 mL, 1.7 M in pentane, 1 mmol) added dropwise by syringe resulting in a pale yellow solution. After 10 min stirring the flask was placed in the freezer (-35°C) overnight to yield a crop of colourless crystals (0.132 g, 90%). The same procedure was repeated using 2 and 3 equivalents of *t*BuLi, resulting in the same product and similar yields. Deprotometallation approach - *n*BuLi (0.63 mL, 1.6 M in hexanes, 1 mmol) was added dropwise by syringe to a stirring mixture of TMPH (0.17 mL, 1 mmol) and hexane

(10 mL). The resulting pale yellow solution was then stored in the freezer (-35°C) overnight where a crop of colourless crystals formed (0.09 g, 20%). ^{1}H NMR (C_6D_6, 300 K): δ=1.73 (m, 6H, TMP γ), 1.30 ppm (s, 48H, TMP CH_3 and β); ^{13}C NMR (C_6D_6, 300 K): δ=52.3 (TMP α), 43.2 (TMP β), 37.1 (TMP CH_3), 20.1 ppm (TMP γ) [note that these resonances are for the pure $(LiTMP)_3$ however as seen in the supporting information resonances for the other polymorph $(LiTMP)_4$ are also present]; ^{7}Li NMR (C_6D_6, 300 K): δ=2.47 ppm; elemental analysis of monomer calcd (%) for $C_9H_{18}N_1Li_1$: C 73.44; H 12.33; N 9.52; found: C 73.97; H 12.05; N 9.03.

Synthesis of $(LiTMP)_4$: Transmetallation approach - $Zn(TMP)_2$ (0.35 g, 1 mmol) was dissolved in hexane (10 mL) and *t*BuLi (0.59 mL, 1.7 M in pentane, 1 mmol) added dropwise by syringe resulting in a pale yellow solution. A small amount of solvent was removed *in vacuo* and upon standing overnight (either on the bench or in the refrigerator) a crop of colourless crystals formed (typical yield = 0.06 g, 41%). Deprotometallation approach - *n*BuLi (0.63 mL, 1.6 M in hexanes, 1 mmol) was added dropwise by syringe to a stirring mixture of TMPH (0.17 mL, 1 mmol) and hexane (10 mL) resulting in a pale yellow solution. Some solvent was removed *in vacuo* and the flask was then stored either in the refrigerator or on the bench overnight to yield a crop of colourless crystals (0.03 g, 20%). ^{1}H NMR (C_6D_6, 300 K): δ=1.78 (m, 8H, TMP γ), 1.36 ppm (s, 64H, TMP CH_3 and β); ^{13}C NMR (C_6D_6, 300 K): δ=52.4 (TMP α), 42.8 (TMP β), 37.0 (TMP CH_3), 19.9 ppm (TMP γ) [note that these resonances are for the pure $(LiTMP)_3$ however as seen in the supporting information resonances for the other polymorph $(LiTMP)_4$ are also present].

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[16] Crystal data for **2**: $C_{36}H_{72}Li_4N_4$, M=588.74, monoclinic, space group C 2/c, a=16.6334(9), b=16.4942(5), c=15.7332(9) Å, α=90, β=117.372(7), γ=90°, V=3833.2(3) Å^3, Z=4, ρ=1.020 Mg m^{-3}, T=123(2) K, 9738 reflections collected, 3940 unique (R_{int}=0.0277), R_1=0.0474, based on F for 3026 reflections with I>2(σ)I, wR_2=0.1148 based on F^2 for all reflections, min/max residual electron density 0.233/-0.192 e Å^{-3}.

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