

First X-ray crystal structure and NMR spectroscopic analysis of a lithiated 1,2-diazapentadiene

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Deprotonation of 1,2-diazapentadienes in Et₂O leads to the respective lithium compounds which, in the case of [(η¹-PhNLiNCHCMeCHPh)·Et₂O]₃, consists of an almost planar (Li–N)₃ hexagon resulting in a tunnel-like arrangement of the W-shaped 1,2-diazapentadienyl chains; the X-ray structure, solution NMR spectra and reactions with electrophiles are reported.

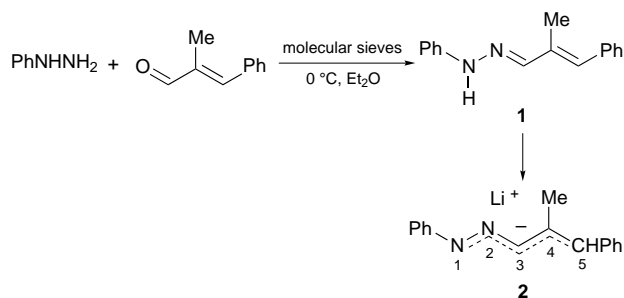
Nitrogen containing organolithium compounds¹ play a major role in synthetic organic chemistry. Therefore, much effort has been focused on the elucidation of the coordination chemistry of lithium bases,^{2,3} lithium hydrazides⁴ or azapolyenyl metal compounds.⁵ In spite of their widespread use in organic chemistry only rarely has evidence for solution or solid state structures of lithiated hydrazone intermediates been published.^{2,6,7}

We became interested in the theoretical, synthetic and structural aspects of aza- and diaza-polyenyl metal compounds. Our studies involve the dependence of the electronic and structural behaviour of the intermediates on the positions and nature of the heteroatoms within the conjugated lithiated polyenyl chain.⁵ Here we report on the single crystal X-ray structure and NMR spectroscopic analysis of the hitherto unknown 4-methyl-1,5-diphenyl-1,2-diazapentadienyllithium.

4-Methyl-1,5-diphenyl-1,2-diazapentadiene **1** was obtained by condensation of phenylhydrazine and 2-methylcinnamaldehyde following the method of Schantl and Hebeisen.⁸ Subsequent deprotonation with LDA or BuⁿLi in Et₂O or THF at –78 °C yielded a dark red solution of the respective lithium hydrazide **2** (Scheme 1).

¹H and ¹³C NMR spectra of **2** in [2H₈]THF were recorded in the temperature range –80 to 50 °C.‡ The spectra show two sets of signals which have been assigned to the W-shaped conformers **2a** and **2b** (Scheme 2) in a ratio 65:35 (**2a**:**2b**), which remains constant over the whole temperature range.

The equilibrium between the two isomers (Scheme 2) could not be frozen out. At 50 °C the spectra resulting from NOE experiments surprisingly show a negative NOE of one isomer upon saturation of the other. Although coalescence could not be achieved this NOE must be due to a transfer of saturation from **2a** to **2b** which can be observed beneath the coalescence temperature when the equilibration occurs faster than the relaxation of the spin system.⁹



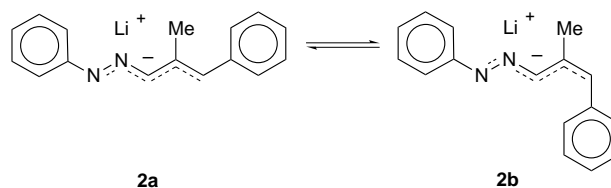
Scheme 1

In the ¹³C NMR spectra of **2** the resonance frequencies of C(5) and C(3) are shifted by about 11 ppm to higher field, while for C(4) a downfield shift of about 5 ppm relative to the resonances of **1** can be observed. This can be explained by delocalization of the negative charge in the diazapentadienyl unit producing large HOMO coefficients on atoms 1, 3 and 5 and approximately nodal positions on atoms 2 and 4. So, C(3) and C(5) are positioned on centres of high electron density while C(4) is deshielded. As indicated by the ¹³C NMR shifts, the phenyl substituents are also involved in the charge delocalization, which is additionally confirmed by the deep red colour of the reaction solution. The exact position of the lithium cation will be determined using Li NMR techniques in further experiments.

Crystallization from Et₂O–*n*-hexane leads to yellow single crystals of the trimeric compound **2a**‡ whose molecular structure is shown in Fig. 1.

The X-ray diffraction analysis¶ reveals the trimeric structure [(PhNLiNCHCMeCHPh)·Et₂O]₃ of **2a** (containing one hexane molecule per unit cell) in which the lithium cations are η¹-coordinated to the nitrogen atoms N(1) of two W-shaped diazapentadienyl moieties and to one Et₂O molecule. Each metal cation is involved in one shorter Li...N link of 1.995(7) Å [2.022(6) and 2.020(6) Å, respectively] and one longer metal–nitrogen contact of 2.066(7) Å [2.085(6) and 2.051(6) Å, respectively]. Such values are typical for end-on bound lithium hydrazides.¹⁰ The resulting (Li–N)₃ hexagon with a diameter of 4.05 Å shows a slight boat-shaped distortion. The average Li...Li distance of 3.35 Å implicates a weaker intermetal contact than reported by Nöth *et al.*¹⁰ which can be explained by the steric hindrance caused by the ligands. The lithium centres exhibit a trigonal planar coordination formed by two N(1) nitrogen atoms and one Et₂O molecule.

The nitrogen atoms N(1) in the (Li–N)₃ hexagon show a trigonal pyramidal distorted tetrahedral geometry. The average N–Li angle of 109.3 Å and the Ph–N–N angle of 111.5 Å indicate sp³ hybridization of the hydrazide nitrogen atom N(1). The short N–N distance of 1.38 Å is in remarkable contrast to the N(1)–N(2) distances of 1.55 Å reported for bis-silylhydrazides by Klingebiel¹¹ or 1.47 Å of Nöth *et al.*¹⁰ in Li–diethylhydrazides and corresponds to non-negotiable double bond character. The N(2)–C(3) bond length of 1.29 Å correlates with the value of 1.305(5) Å found by Collum¹² in the dimeric lithiated 2-methoxycarbonylcyclohexanone dimethylhydrazone for which they postulate the contribution of C–N single and C=N double bond character. The C–C bond distances implicate a localized bond structure containing alternating single and double bonds with delocalization to a small extent. The solid



Scheme 2

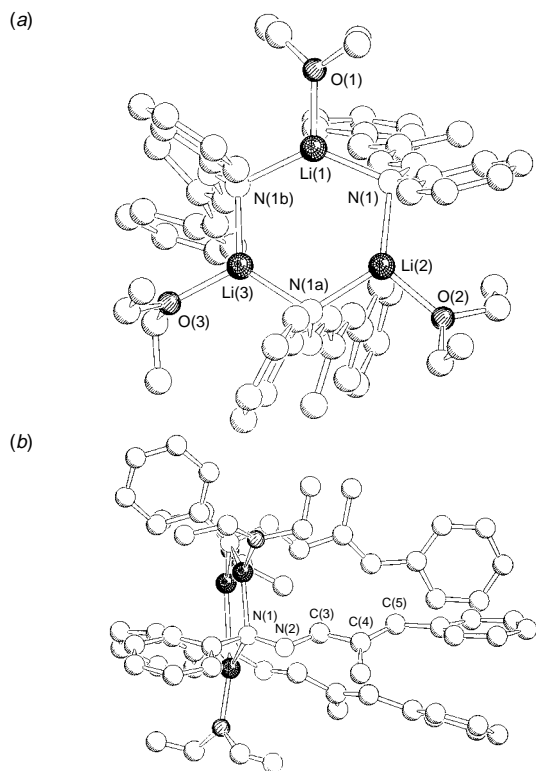


Fig. 1 Molecular structure of **2a**: (a) top view and (b) side view (hydrogen atoms omitted for clarity)

state structure can best be described as an end-on lithiated hydrazide with some contribution of a 1,2-diazallyllithium resonance structure.

According to semiempirical calculations using PM3¹³ the trimer of **2a** corresponds to a minimum on the potential energy hyperface in the gas phase, which indicates that the tunnel-like structure of the diazapentadienyl chains is not due to crystal packing forces. The W-shaped geometry of the unsubstituted 1,2-diazapentadienyl anion has also been obtained as the energetically most favoured conformer in *ab initio* calculations using the MP2/6-31+G*/RHF/6-31+G*¹⁴ basis set.¹⁵

Reaction of the intermediate **2** with several alkyl or acyl electrophiles leads regioselectively to the N(1)-substituted *E,E*-hydrazones. *Ab initio* calculations indicate that the 1,2-diazapentadienyl anion bears the highest electron density on N(1)—as expected—and so, structure **2** implicates an electrophilic attack on N(1) which may also be the result of thermodynamic control. Regarding the solid state structure of **2a** the regioselectivity can be explained by a metal controlled nucleophilic substitution at the attacking electrophile.

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Notes and References

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‡ *Synthesis and ¹H and ¹³C NMR analysis of 2*. The lithium compound **2** was prepared by use of the syringe technique directly in the NMR tube. To a white slurry of LDA (0.5 mmol; from 0.3 ml BuⁿLi in *n*-hexane and 0.075 ml Pr₂NH) in 0.3 ml [2H₈]THF was added a solution of **1** (85 mg, 0.36 mmol) in 0.3 ml [2H₈]THF at -78 °C with shaking. The NMR tube was

sealed with Parafilm and analysed *via* NMR spectroscopy. δ_H(599.77 MHz, 223 K, [2H₈]THF): **2a** 2.34 (s, 3 H, 10-H), 6.02 (s, 1 H, 5-H), 6.20 (dd, ³J 7.7, 7.1, 1 H, H_{arom}), 6.85 (t, ³J 7.3, 2 H, H_{arom}), 6.98 (t, ³J 7.2, 2 H, H_{arom}), 7.22 (m, 3 H, H_{arom}), 7.29 (d, ³J 8.2, 2 H, 7'-H), 7.47 (s, 1 H, 3-H); **2b** 2.17 (s, 3 H, 10-H), 5.94 (s, 1 H, 5-H), 6.21 (t, ³J 7.3, 1 H, H_{arom}), 6.85 (t, ³J 7.3, 2 H, 7-H), 7.00 (t, ³J 7.2, 2 H, H_{arom}), 7.19 (m, 3 H, H_{arom}), 7.26 (d, ³J 8.2, 2 H, 7'-H), 8.02 (s, 1 H, 3-H). δ_C(150.85 MHz, 223 K, [2H₈]THF): **2a** 14.9 (C-10), 113.2 (C_{arom}), 115.2 (C_{arom}), 121.2 (C-5), 124.5 (C_{arom}), 128.5 (C_{arom}), 128.7 (C_{arom}), 128.9 (C-3), 129.7 (C_{arom}), 140.8 (C-4), 140.8 (C-6'), 160.8 (C-6); **2b** 14.2 (C-10), 113.7 (C_{arom}), 115.2 (C_{arom}), 118.0 (C-5), 124.8 (C_{arom}), 128.4 (C_{arom}), 128.8 (C_{arom}), 129.4 (C_{arom}), 135.1 (C-3), 139.4 (C-4), 140.9 (C-6'), 160.7 (C-6).

§ *Synthesis of [(PhNLiNCHCMeCHPh)-Et₂O]₃ 2a*. To a solution of BuⁿLi (2.8 ml, 4.5 mmol in *n*-hexane) in 15 ml Et₂O was added dropwise a solution of **1** (0.74 g, 3.1 mmol) in 25 ml Et₂O at -78 °C. After stirring the red solution for 30 min, the mixture was warmed to -20 °C. Recrystallization of the yellow precipitate from Et₂O-*n*-hexane yielded yellow crystals.

¶ *Crystal data for [(PhNLiNCHCMeCHPh)-Et₂O]₃*, monoclinic, space group P2₁/c (No. 14), with unit cell parameters *a* = 12.013(1), *b* = 17.608(3), *c* = 28.633(2) Å, β = 97.69° (1), *V* = 6002.1(12) Å³, ρ_{calc} = 1.098 g cm⁻³. The crystals were analyzed using an Enraf Nonius automatic CAD4 Diffractometer with Cu-Kα radiation (λ = 1.54178 Å) utilizing a graphite monochromator. The yellow single crystal of (C₂₀H₂₅N₂OLi·1/6C₆H₁₄)₃ (*M* = 992.16, crystal size: 0.50 × 0.30 × 0.30 mm³) was measured at -50 °C. 10391 reflections were collected (±*h*, +*k*, +*l*) leading to 10170 independent and 6106 observed [(sinθ)/λ]_{max} = 0.59 Å⁻¹. An empirical absorption correction *via* ψ-scan data (0.914 ≤ *C* ≤ 0.999) was carried out, absorption coefficient μ = 5.12 cm⁻¹. 672 refined parameters. *R* = 0.085, *R*_w² = 0.259, max. residual electron density ρ = 0.53 (-0.35) e Å⁻³. The structure was solved and refined using SHELXS-86 and SHELXL-93 with hydrogens calculated and refined as riding model, graphics SCHAKAL92. The unit cell contains one totally disordered hexane molecule which has been refined isotropically. CCDC 182/774.

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