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Non-covalent Li···H interaction in the synthesis of *peri*-disubstituted naphthalene proton sponges.

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Abstract

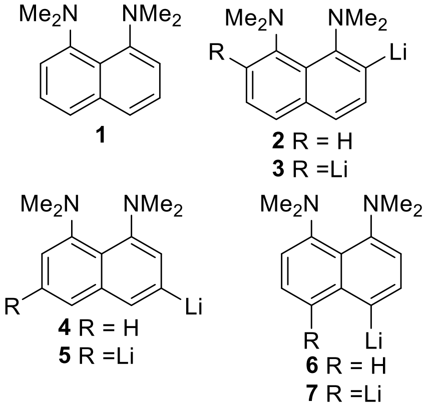
Non-covalent Li···H interaction was utilized as a tool for the second lithiation of 4-lithio-1,8-bis(dimethylamino)naphthalene with *n*-BuLi in the presence of TMEDA in hexane. Metallation proceeds with 100% selectivity in the second *peri*-position and with up to 90% yield. A series of 4,5-disubstituted derivatives of DMAN has been prepared in a good to excellent yield after quenching the reaction mass with different electrophiles.

Keywords

Agostic interaction; metallation; proton sponge; lithium

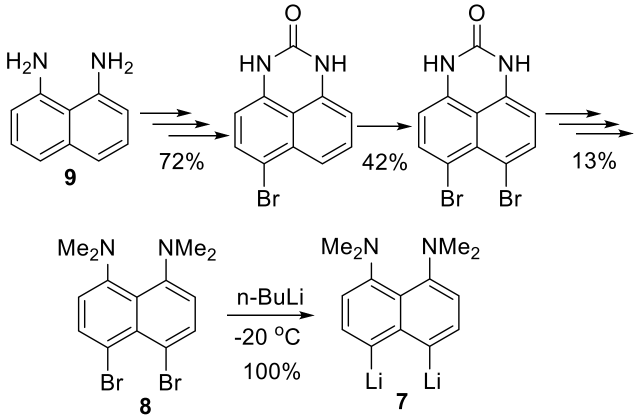
Introduction

Organometallic compounds are traditionally considered to be convenient tools for the modification of organic molecules. Thus, organolithium, organomagnesium and organozinc reagents are widely used to introduce a wide variety of functional groups via reactions with electrophilic agents [1,2]. It is not surprising that the discovery of the direct CH bond metallation made organometallics, especially organolithiums, indispensable agents for modern organic synthesis [3,4]. Organometallics play a key role in the preparation of naphthalene proton sponges, which are widely known for their outstanding basicity (pKa (**1**) = 12.1 in H_2O [5], 18.62 in MeCN [6], 7.5 in DMSO [7]). Dozens of *ortho*-, *para*- and even *meta*- derivatives of **1** were obtained from organolithiums **2**-**6** (Scheme 1) [8–10], which not only made it possible to establish the relation between structure and basicity of these interesting compounds [11,12], but also revealed their unusual reactivity leading to the formation of key heterocyclic systems, such as indoles [10,13], pyrazoles [14], isoxazoles [14], quinolines [15], quinasolines [16]. Moreover, in the past two decades, naphthalene proton sponges drew additional attention as a convenient core for the development of superbasic heterogeneous catalysts [17–21].



Scheme 1: 1,8-bis(dimethylamino)naphthalene **1** and its lithio derivatives.

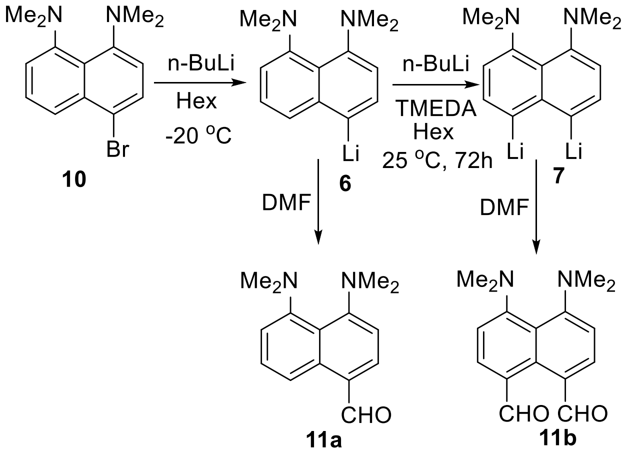
Nevertheless, *peri*-disubstituted naphthalene proton sponges are barely known, since the common approach to their generation is based on low-yielding electrophilic substitution [22–25]. As a result, known compounds of this group are limited to the products of nitration and acylation due to the low accessibility of proper organometallic precursors, such as *peri*-dilithio sponge **7**. This is indeed an unfortunate gap in the chemistry of naphthalene proton sponges: the influence of sterical interaction between two *peri*-substituents on basicity and reactivity remains unclear. So far, the only way to obtain **7** was the exchange of bromine in 4,5-dibromo-1,8-bis(dimethylamino)naphthalene **8**. Unfortunately, the latter could only be obtained via a multistage procedure starting from commercially available 1,8-diaminonaphthalene with very low yield (~4-5% in total, Scheme 2), since direct *peri*-dibromination of **1** is impossible [26]. Here we present a simple and effective procedure for the synthesis of different *peri*-disubstituded naphthalene proton sponges based on the selective second lithiation of 4-lithio-1,8-diaminonaphthalene **6**.



Scheme 2: Existing way for the multistep synthesis of **7** from **9**

Results and Discussion

It is known that the presence of a lithium atom in aromatic molecules facilitates the second lithiation of the nearest CH-bond [27–29]. For example, 1-lithionaphthalene can be selectively converted into 1,8-dilithinaphthale after treatment with *n*-buthyllithium in the presence of *N,N,N,N*-tetramethylethylenediamine (TMEDA) [29]. Keeping this in mind, we have conducted a series of experiments in which 4-lithio-1,8-bis(dimethylamino)naphthalene **6** was subjected to the action of the mixture of *n*-butyllithium with TMEDA (LiTMEDA) in hexane (Table 1, Scheme 3). In order to simplify the process, **7** was prepared *in situ* and was not separated before the second metallation. To establish the ratio of lithium derivatives **6** and **7**, the crude reaction mixture was usually quenched with *N,N*-dimethylformamide (DMF) to give easily identified proton sponge aldehydes **11a** and **11b**. The reaction mixture components were first registered by ^{1}H NMR spectroscopy and then separated by TLC on alumina. The spectral yield of the aldehydes **11a** and **11b** and indirectly their lithium predecessors **6** and **7** was determined via intensities of aldehyde and aromatic proton signals characteristic for each compound (Figure 1).



Scheme 2: Preparation of **6** and its second lithiation.

Table 1: Results of control experiments on the metallation of **6** with LiTMEDA after quenching the reaction mixture with DMF.

Run	LiTMEDA, equiv,^{a}	Time, h	T, °C	Products yield (NMR), %		
				11a	**11b**	**1**
1	1.5	72	25	90	10	0
2	2	72	25	75	25	0
3	3	72	25	33	67	0
4	4	72	25	16	84	0
5	5	72	25	10	90	0

6	3	72	70	0	0	100
7	4	24	25	54	46	0
8	4	96	25	9	91	0

[a]Excluding the amount used for the generation of **6** from **10**

It was found that the reaction is best carried out at 25 °C in hexane using five (excluding the amount used for the generation of **6** from **10**) molar equivalents of LiTMEDA (run 5). The process proceeds slowly but selectively; thus, prolonged stirring (run 1-7) with subsequent quenching of the crude reaction mass with DMF results in the formation of 4,5-dialdehyde **11b** together with **11a** (originating from reaction of the leftovers of the starting material **6** with DMF), no isomeric dialdehydes are formed. A 72-hour metallation is considered to be optimal (run 5); decreasing and increasing the reaction time did not significantly change these results (runs 7,8). The attempt to increase the reaction temperature leads to the decomposition of organolithium species which in turn leads to the formation of diamine **1** (run 6).

The observed reactivity originates from a non-covalent, so called agostic [30], interaction between the lithium atom and the neighboring CH-bond, serving as a pseudo-ligand in hetero-dimer **12** [31]. The latter can be formed after the deaggregation of the dimeric complex (**6**·TMEDA)$_2$ in the presence of the excess of *n*-BuLi (Scheme 3).

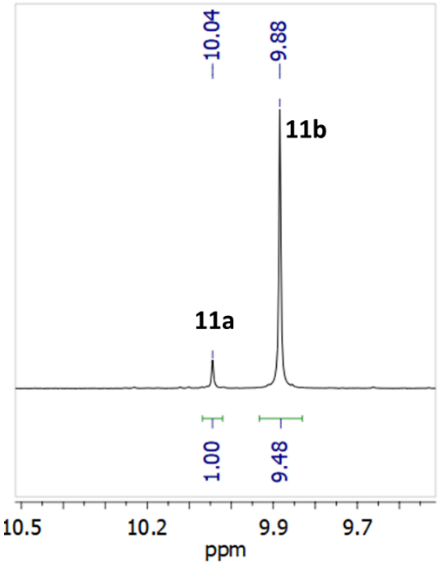
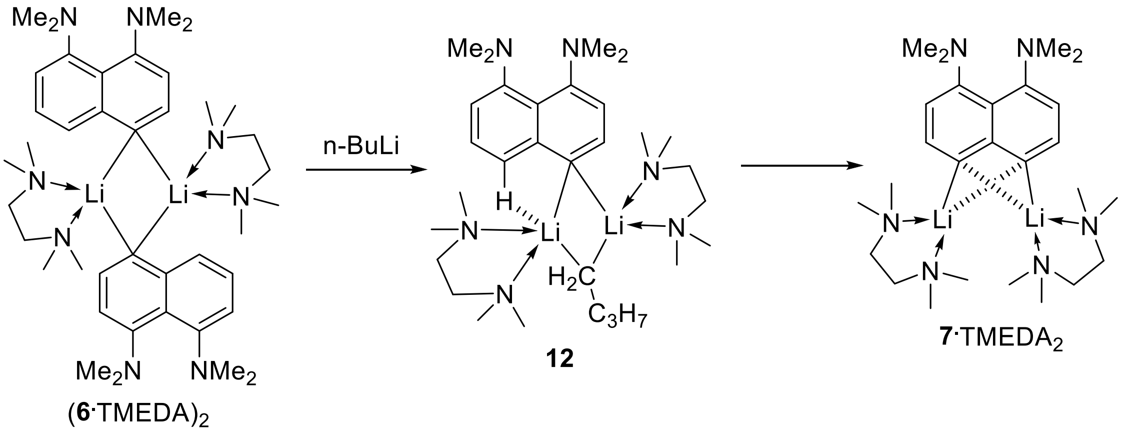


Figure 1: Aldehyde groups region in the ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the reaction mixture after its quenching with DMF (Table 1, run 5).

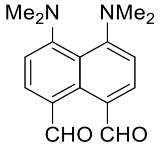
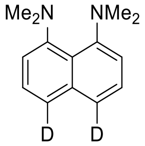
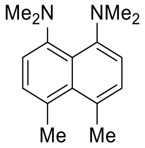
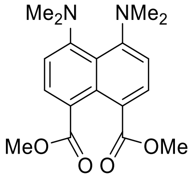
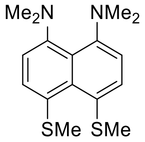
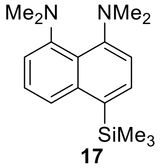


Scheme 3: Proposed mechanism of the formation of **7**

It has been shown, that **6** in comparison with 1-lithionaphthalene demonstrates much lower reactivity towards the second metallation. Thus, a great excess of LiTMEDA is required to reach a reasonable conversion. We believe that the strong electron-donor effect of two NMe_2 groups significantly suppresses CH-acidity of *para*-protons.

The optimized reaction conditions were further used to synthesize a series of proton sponges containing various functional groups in *peri*-positions via the reaction of **7** with different electrophilic reagents (Table 2). Noticeably, the treatment of **7** with chlorotrimethylsilane leads to the formation of the monosubstituted sponge **17**. Obviously, the extreme bulkiness of $SiMe_3$ groups prevents disubstitution.

Table 2: Application of the developed method for the synthesis of *peri*-disubstituted proton sponges.

Electrophilic reagent	Product	Yield (%)
DMF	 **11b**	88
CH_3OD	 **13**	80
MeI	 **14**	83
$CO(OMe)_2$	 **15**	89
Me_2S_2	 **16**	78
Me_3SiCl	 **17**	32

Conclusion

In summary, we have developed a new, highly efficient method for the synthesis of *peri*-disubstituted naphthalene proton sponges via the directed second metallation of a naphthalene core utilizing non-covalent Li···H interaction. It has been shown that, unlike 1-lithionaphthalene, the metallation of 4-lithio-1,8-diaminonaphthalene proceeds slower due to the strong +*M*-effect of NMe_2 groups. This method opened a way for the preparation of a wide range of 4,5-disubstituted derivatives of DMAN, by quenching the lithium intermediate with appropriate electrophiles.

Experimental

General Procedures. Liquid-state NMR experiments were performed at 400 MHz for ^1H and 100 MHz for ^{13}C (Centre for Magnetic Resonance, St. Petersburg State University). Chemical shifts are referred to TMS for ^1H and ^{13}C.

The HR-ESI mass-spectra were obtained on a BRUKER maXis spectrometer equipped with an electrospray ionization (ESI) source; methanol was used as the solvent (Chemical Analysis and Materials Research Centre, St. Petersburg State University). The instrument was operated in positive mode using an m/z range of 50–1200. The capillary voltage of the ion source was set at 4000 V. The nebulizer gas pressure was 1.0 bar, and the drying gas flow was set to 4.0 L/min.

Melting points were determined in glass capillaries on a Stuart SMP30 device and are uncorrected.

Second metalation of 4-lithio-1,8-bis(dimethylamino)naphthalene. 4-Bromo-1,8-bis(dimethylamino)naphthalene [32] (200 mg, 0.75 mmol) was placed in a flame-dried, round-bottomed flask. 10 mL of freshly distillated over sodium *n*-hexane was added. The flask was filled with dry argon and closed with a serum cap. The mixture was cooled to −24 ℃ for 30 min and a 1.6 M solution of n-BuLi in hexanes (2.8 mL, 4.5 mmol) was added via syringe. The yellow mixture was kept at −24 ℃ for 1 hour in order to form 4-lithio-1,8-bis(dimethylamino)naphthalene. Freshly distillated TMEDA (0.7 mL, 4.5 mmol) was added via syringe to the formed yellow suspension. The dark orange solution was stirred at 25 ℃ for 72 h. The resulting grayish brown suspension (**A**) contained about 90% of 4,5-dilithio-1,8-bis(dimethylamino)naphthalene.

4,5-bis(dimethylamino)naphthalene-1,8-dicarbaldehyde (**11b**): The absolute *N,N*-dimethylformamide (0.36 mL, 4.5 mmol) was added via syringe to the cooled to −24 ℃ suspension **A**. The reaction mass was additionally stirred for 12 hours at −24 ℃ and treated with water (10 mL). The products were extracted with Et_2O (2 × 25 mL), the solvent was evaporated to dryness and the residue was chromatographed on aluminium oxide with an MeCN–benzene 1 : 10 mixture as the eluent. An orange fraction with Rf = 0.1 was collected. The product was isolated in the form of orange crystals with a yield of 88% (178 mg), mp 146–147 ℃ (*n*-octane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 2H), 7.95 (d, J = 8.3 Hz, 2H), 6.83 (d, J = 8.3 Hz, 2H), 2.96 (s, 12H). ^{13}C NMR (100 MHz, CDCl3) δ 188.58, 156.68, 135.77, 135.33, 122.21, 114.85, 108.74, 42.79. HRMS (ESI): found 303.1709 [M+MeOH+H$^+$]; calculated for $C_{17}H_{23}N_2O_3$ [M+MeOH+H$^+$] 303.1703.

1,8-Bis(dimethylamino)naphthalene-4,5-d_2 (**13**): Dry CH_3OD (0.43 mL, 10 mmol) was add-ed via syringe to the cooled to −24 ℃ suspension **A**. The reaction mass was additionally stirred for 12 hours at −24 ℃ and treated with water (10 mL). The product was extracted with hexane (2 × 25 mL), the solvent was evaporated to dryness. The residue was dissolved in Et_2O (5 mL) and 48% solution of HBF_4 in water (0.07 mL, 0.75 mmol) was added. The white precipitate was filtrated and recrystallized from water to form colourless needles, mp 271–272 ℃ (water). ^{1}H NMR (400 MHz, DMSO-d_6) δ 18.32 (s, 1H), 8.10 (d, J = 7.6 Hz, 2H), 7.75 (d, J = 7.6 Hz, 2H), 3.15 (d, J = 2.0 Hz, 12H). The obtained crystals were neutralized with aqueous ammonia and the product was extracted with n-hexane. The solvent was evaporated to dryness. The product was isolated as colourless crystals with a yield of 80% (130 mg), mp 45–47 ℃ (n-hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 7.4 Hz, 1H), 6.98 (d, J = 7.4 Hz, 1H), 2.84 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.79, 137.69, 125.29, 121.3 (m), 120.59, 44.41. HRMS (ESI): found 217.1741 [M+H$^+$]; calculated for $C_{14}H_{17}D_2N_2$ [M+H$^+$] 217.1668.

4,5-Dimethyl-1,8-bis(dimethylamino)naphthalene (**14**): Dry MeI (0.61 mL, 10 mmol) was added via syringe to the cooled to −24 ℃ suspension **A**. The reaction mass was additionally stirred for 12 hours at −24 ℃ and treated with water (10 mL). The product was extracted with hexane (2 × 25 mL), the solvent was evaporated to dryness. The residue was dissolved in Et_2O (5 mL) and 48% solution of HBF_4 in water (0.07 mL, 0.75 mmol) was added. The pale-yellow precipitate was filtrated and recrystallized from water to form pale yellow needles, mp 279–280 ℃ (water). ^{1}H NMR (400 MHz, DMSO-d_6) δ 19.27 (s, 1H), 7.93 (d, J = 7.9 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 3.08 (d, J = 2.5 Hz, 12H), 2.93 (s, 6H). The obtained crystals were neutralized with aqueous ammonia and the product was extracted with n-hexane. The solvent was evaporated to dryness. The product was isolated as pale-yellow oil with a yield of 83% (149 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, J = 7.6 Hz, 2H), 6.78 (d, J = 7.6 Hz, 2H), 2.81 (s, 6H), 2.78 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.24, 137.20, 128.84, 127.28, 121.24, 110.88, 43.83, 25.29. HRMS (ESI): found 243.1904 [M+H$^+$]; calculated for $C_{16}H_{23}N_2$ [M+H$^+$] 243.1856.

Dimethyl 4,5-bis(dimethylamino)naphthalene-1,8-dicarboxylate (**15**): Dry dimethyl carbonate (0.84 mL, 10 mmol) was added via syringe to the cooled to −24 ℃ suspension **A**. The reaction mass was additionally stirred for 12 hours at −24 ℃ and treated with water (10 mL). The products were extracted with Et_2O (2 × 25 mL), the solvent was evaporated to dryness and the residue was chromato-graphed on aluminium oxide with an MeCN–benzene 1 : 20 mixture as the eluent. Yellow fraction with Rf = 0.5 was collected. The product was isolated as yellow crystals with a yield of 89% (220 mg), mp 179–181 ℃ (benzene). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.1 Hz, 2H), 6.79 (d, J = 8.1 Hz, 2H), 3.85 (s, 6H), 2.87 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.58, 154.00, 133.28, 131.15, 119.96, 118.35, 109.13, 51.49, 43.22. HRMS (ESI): found 331,1652 [M+H$^+$]; calculated for $C_{18}H_{23}N_2O_4$ [M+H$^+$] 331,1662.

4,5-Bis(methylthio)-1,8-bis(dimethylamino)naphthalene (**16**): Dry Me_2S_2 (0.5 mL, 5 mmol) was added via syringe to the cooled to −24 ℃ suspension **A**. The reaction mass was additionally stirred for 12 hours at −24 ℃ and treated with water (10 mL). The product was extracted with Et_2O (2 × 25 mL), the solvent was evaporated to dryness the residue was chromatographed on aluminium oxide with an EtOAc–n-hexane 1 : 15 mixture as the eluent. Yellow fraction with Rf = 0.6 was collected. The product was isolated as dark yellow oil with a yield of 78% (179 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.0 Hz, 2H), 6.79 (d, J = 8.0 Hz, 2H), 2.80 (s, 12H), 2.46 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.80, 137.86, 130.67, 125.85, 121.20, 111.05, 43.57, 21.76. HRMS (ESI): found 306,1259 [M$^+$]; calculated for $C_{16}H_{23}N_2S_2$ [M$^+$] 306,1219.

4-Trimethylsilyl-1,8-bis(dimethylamino)naphthalene (**17**): Me_3SiCl (0.7 mL, 5 mmol) was added via syringe to the cooled to −24 °C suspension **A**. The reaction mass was additionally stirred for 12 hours at −24 °C and treated with water (10 mL). The residue was dissolved in Et_2O (5 mL) and 48% solution of HBF_4 in water (0.07 mL, 0.75 mmol) was added. The pale-green precipitate was filtrated and recrystallized from water to form colourless plates. ^1H NMR (400 MHz, DMSO-d_6) δ 18.69 (s, 1H), 8.22 (d, J = 8.4 Hz, 1H), 8.12 (d, J = 7.6 Hz, 1H), 8.04 (d, J = 7.6 Hz, 1H), 7.86 (d, J = 7.5 Hz, 1H), 7.81 (t, J = 8.0 Hz, 1H), 3.15 (d, J = 2.3 Hz, 6H), 3.13 (d, J = 2.0 Hz, 6H), 0.47 (s, 9H). The obtained crystals were neutralized with aqueous ammonia and the product was extracted with *n*-hexane. The solvent was evaporated to dryness. The product was isolated as colourless oil with a yield of 32% (69 mg). Characterization data were consistent with those reported in the literature [33].

Supporting Information

Supporting Information File 1:

Copies of ^1H and ^{13}C NMR spectra confirming structure of new compounds

Acknowledgements

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