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# 1,8,1′,8′-Tetrakis(dimethylamino)-2,2′-dinaphthylmethanols: Double *In*/*Out* Proton Sponges with Low-Barrier Hydrogen-Bond Switching

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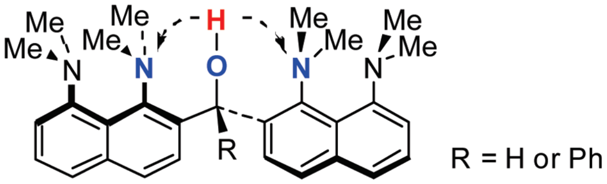

*Rechelation or formation of O–H...O–H...N dimers depending on R, aggregate state, and temperature*

Previously unknown bis[1,8-bis(dimethylamino)naphth-2-yl]phenylmethanol (**5**) and bis[1,8-bis-(dimethylamino)naphth-2-yl]methanol (**6**) have been obtained and studied by combination of X-ray, NMR, and IR techniques at variable temperature. It has been established that both proton sponge units in the solid tertiary alcohol **5** exist in nonconventional *in*/*out* form, one of which is fixed by intramolecular O−H···N hydrogen bonding. In solution, a fast interconversion of two isoenergetic hydrogen chelates occurs which can be frozen below 183 K. Unlike this, the secondary alcohol **6** in the solid at 100 K adopts the *in*/*out*−*in*/*in* conformation and at 293 K demonstrates a kind of dynamic behavior which can be described as temperature-driven *dimer-induced rechelation*. In solution under ambient conditions **6** exists as an equilibrating mixture of chelated and unchelated monomeric forms in a ~1:1.8 molar ratio.

## Introduction

It has been previously disclosed that placing almost any substituent in the *ortho*-positions of 1,8-bis(dimethylamino)-naphthalene (“proton sponge”, **1**) influences, often dramatically, its structure,[1−3] basicity,[1,2,4] and reactivity.[5,6] For example, whereas the parent compound **1** and the vast majority of its derivatives normally exist as *in*/*in* conformers with the free $NMe_2$ electron pairs pointing toward each other, for 2,7-bis(trimethylsilyl)derivative the nonconventional *in*/*out* form **2** becomes dominant.[2,7] Recently,[3] we have demonstrated that fixation of the *in*/*out* form can be organized via intramolecular hydrogen bonding (IHB) between the $NMe_2$ and tertiary α-hydroxymethyl groups as in **3**. Unlike this,

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(1) (a) Pozharskii, A. F.; Ozeryanskii, V. A. In *The Chemistry of Anilines*; Rappoport, Z., Ed.; J. Wiley & Sons: Chichester, 2007; Part 2, Chapter 17, pp 931−1026. (b) Pozharskii, A. F. *Russ. Chem. Rev.* **1998**, *67*, 1–24. (c) Alder, R. W. *Chem. Rev.* **1989**, *89*, 1215–1223.

(2) Pozharskii, A. F.; Ryabtsova, O. V.; Ozeryanskii, V. A.; Degtyarev, A. V.; Kazheva, O. N.; Alexandrov, G. G.; Dyachenko, O. A. *J. Org. Chem.* **2003**, *68*, 10109–10122.

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(7) For general survey on *in*/*out* isomerism and related questions, see: (a) Alder, R. W.; East, S. P. *Chem. Rev.* **1996**, *96*, 2097–2111. (b) Chambron, J.-C.; Meyer, M. *Chem. Soc. Rev.* **2009**, *38*, 1663–1676.

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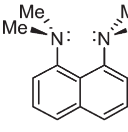
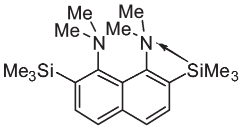
primary and secondary *o*- mono- and dialcohols prefer *in*/*in* conformation in which the OH groups participate in the formation of ···OH···OH··· associates[3,8] (cf. also ref 9).

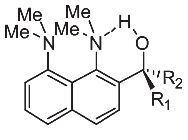
For tertiary 2,7-dialcohols, the situation is completely different. In crystals, they exist in the *in*/*out* form where one hydroxyl group is chelated while another is engaged in the intermolecular association. In solution, such dialcohols equilibrate between two isoenergetic *in*/*out*–*out*/*in* forms **4a** and **4b** that are accompanied by tandem nitrogen inversion of both $NMe_2$ groups.[3]



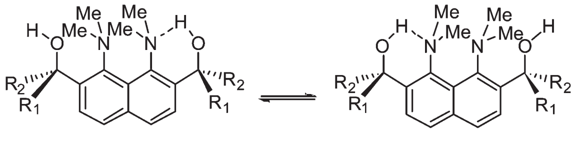
**1**



**2**

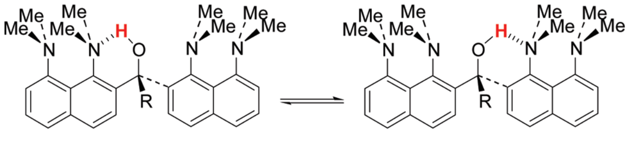


**3**



**4a** **4b**

These findings have inspired us to undertake investigation of still unknown proton sponge-based di(naphth-2-yl)-methanols **5** and **6**. We suggested that for these compounds another type of rechelation, namely **5a**(**6a**) ⇌ **5b**(**6b**), involving both proton sponge units, might operate. In such a case it could serve as a specific kind of switching device (see ref 10 as an example) or as a model for hydrogen transfer in enzymatic reactions.[11,12] In the present paper, we report on preparation of alcohols **5** and **6** and a study of their structure, stereodynamics, and spectroscopic properties.



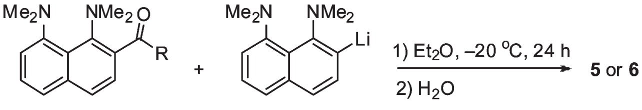
**5a** R = Ph
**6a** R = H

**5b** R = Ph
**6b** R = H

## Results and Discussion

**Synthesis.** New double proton sponges **5** and **6** were prepared in nearly 50% yield on treatment of 2-benzoyl- (**7**) or 2-formyl-1,8-bis(dimethylamino)naphthalene (**8**) with 2-lithium derivative **9** generated from the corresponding bromide (Scheme 1).[2,3,6] Their structures have been proved by X-ray and spectral measurements.

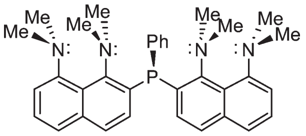
SCHEME 1



**7** R = Ph
**8** R = H

**9**

**X-ray Structure.** As expected, in the solid state the alcohol **5**, similarly to its tertiary analogues **3**, is chelated (Figure 1, Table 1). However, the most striking thing is that not only the hydrogen-bonded 1-$NMe_2$ group but also its nonchelated 1′-$NMe_2$ counterpart adopt the *out*-conformation. Such an *in*/*out*–*in*/*out* structure looks quite unusual, although recently it has been also observed for dinaphthylphosphine proton sponge **10**.[6,13]



**10**

Several differences in geometry of the two proton sponge moieties in molecule **5** deserve short comments. The first one deals with an extent of "out-ness" of the 1- and 1′-$NMe_2$ groups. Whereas for the chelated 1-$NMe_2$ group the nitrogen inversion [$\Sigma N(1) = 350°$], expressed as a sum of valence angles at the nitrogen atom, is typical for *in*/*out* proton sponges **2** and **3**,[2,3] for the nonchelated 1′-$NMe_2$ group it is considerably smaller [$\Sigma N(1') = 357°$]. The second difference is a nonequivalence of the two N···N distances. As was disclosed previously,[2,3] a transition from the *in*/*in* to the *in*/*out* form is always accompanied by a substantial elongation of the internitrogen distance. Normally, for *in*/*out* proton sponges it varies in limits of 2.92–2.94 Å against 2.79 Å for **1** and other *in*/*in* proton sponges.[1a,2,3] In the case of **5**, the N(1)···N(8) and N(1′)···N(8′) distances are equal to 2.97 and 2.87 Å, thus being at extremes of the above range. The difference in "out-ness" of the 1- and 1′-$NMe_2$ groups somewhat influences the geometry of the neighboring 8- and 8′-$NMe_2$ groups. As expected, the former is pyramidalized in a larger extent than the second one: $\Sigma N(8) = 335.2°$; $\Sigma N(8') = 339.0°$.

What is the reason for the *out*-configuration of the 1′-$NMe_2$ group in **5**? The answer is best seen from the framework molecular model, but certain information can be gained from Figure 1b. Though the two naphthalene rings are almost perpendicular to each other, the hydroxyl group is in a convenient position for binding with either the 1- or the 1′-$NMe_2$ group. Both $NMe_2$ groups, being out-inverted, are also preorganized for such interactions. Several structural movements are needed for the interconversion **5a** ⇌ **5b**:

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(8) Degtyarev, A. V.; Pozharskii, A. F. *Chem. Heterocycl. Compd.* **2008**, *44*, 1138–1145.

(9) Al-Masri, H. T.; Sieler, J.; Lonnecke, P.; Blaurock, S.; Domasevitch, K.; Hey-Hawkins, E. *Tetrahedron* **2004**, *60*, 333–339.

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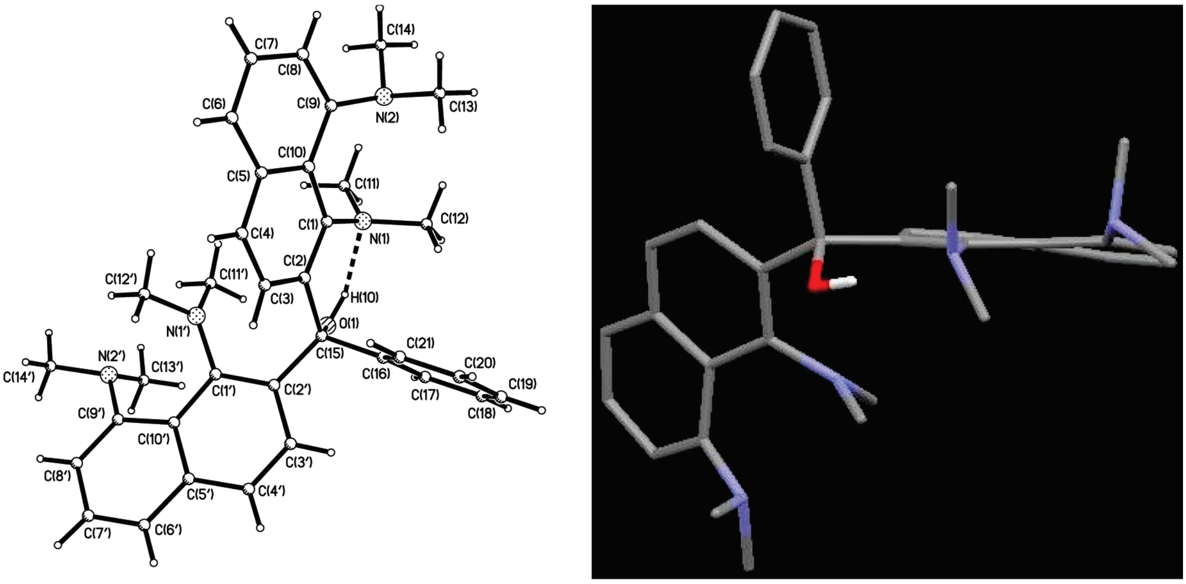
(12) (a) Min, D; Josephine, H. R.; Li, H.; Lakner, C.; MacPherson, I. S.; Naylor, G. J. P.; Swofford, D.; Hedstrom, L.; Yang, W. *PLoS Biol.* **2008**, DOI: 10.1371/journal.pbio.0060206. (b) Fang, C.; Frontiera, R. R.; Tran, R.; Mathies, R. A. *Nature* **2009**, *462*, 200–204.

(13) The authors[6] did not comment on the *in*/*out*-*in*/*out* structure of binaphthylphosphine **10**. We believe that, as in the case of **2**, it can be caused either by a purely steric pressure of the bulky *ortho*-substituent on the neighboring N–Me groups or by an n→d interaction of the amine nitrogens and the phosphorus atom. The former version seems to be more likely since of the two N···P distances for the less [$\Sigma N(1') = 359.5°$] and the more [$\Sigma N(1) = 356.2°$] inverted nitrogen atoms in **10**, the N(1′)···P one, contrary to expectation, is shorter [2.915 Å against 2.997 Å for N(1)···P].



(a) (b)

**FIGURE 1.** Two views of the molecular structure of tertiary alcohol **5** (100 K); in case (b), all hydrogen atoms, except OH, are omitted for clarity.

**TABLE 1. Selected X-ray Structural Characteristics for Alcohols 5 and 6**

| compd | N···N (*peri*) | O···N | N···H | ΣN(1)[a] ΣN(1′)[a] | ΣN(8)[a] ΣN(8′)[a] | O−H···N | *T* (K) |
|---|---|---|---|---|---|---|---|
| **5**[b] | 2.970(2) | 2.642(1) | 1.90 | 350.4(1) | 335.2(1) | 145 | 100 |
| | 2.865(2) | | | 357.1(1) | 339.0(1) | | |
| **6A**[b] | 2.867(6) | 2.850(7)[c] | 2.03[d] | 357.6(5) | 337.5(5) | 162[e] | 100 |
| | 2.766(5) | | | 357.3(5) | 341.2(5) | | |
| **6B**[b] | 2.879(6) | 2.727(5) | 2.01 | 353.6(5) | 334.8(5) | 141 | 100 |
| | 2.817(6) | | | 360.0(5) | 339.7(5) | | |
| **6C**[b,f] | 2.955(9) | 2.905(7) | 2.11 | 355.1(5) | 343.2(7) | 141 | 293 |
| | 2.799(2) | | | 358.8(2) | 341.9(2) | | |
| **6D**[g] | 2.821(9) | 3.126(7) | | 359.1(5) | 331.1(7) | | 293 |

[a] Sum of the CNC angles at the nitrogen atoms. [b] Upper values correspond to the unit with chelated or inverted NMe$_2$ group (*in*/*out* unit). [c] Distance O···O. [d] Intermolecular OH···O distance **6A**···**6B**. [e] Angle O−H···O. [f] Data for intramolecularly O−H···N bonded conformer. [g] *In*/*out* conformer without O−H···N bonding.

rotation of the hydroxyl group around the C−O bond and antiphase rotations of both naphthalene rings around the C$_{naph}$−C(O) bonds accompanied the naphthalene ring flipping. Such rotational barriers for alcohols (~1.5 kcal mol$^{-1}$)[14] and for sterically crowded naphthalenes like 1,8-di-*tert*-butylnaphthalenes (~6.5 kcal mol$^{-1}$)[15] are known to be rather small, and the flipping energy is only slightly larger (~7.5 kcal mol$^{-1}$).[16,17] Definitely, in the solid all types of the movements should be hindered due to the IHB and crystal lattice forces. Nevertheless, even in this state, the 1′-NMe$_2$ group appears to be ripe for the binding with the OH group.

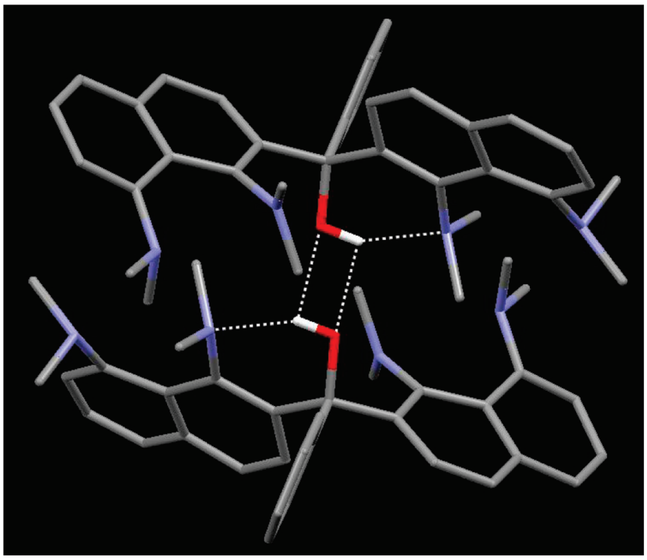


**FIGURE 2.** Dimer character of the solid **5** at 100 K.

Concerning the hydrogen bridge in **5**, it seems less strong than in the tertiary alcohols **3**. This follows from decreasing the N···H−O angle by ~10° and increasing the N···H distance by 0.16 Å.

The crystal structure of the double proton sponge **5** is also of interest due to the formation of the centrosymmetric H-bonded dimers. Within these dimers, the two OH groups already engaged in IHB are interconnected as shown in Figure 2. Judging from the rather large O···H (2.50 Å) and N···H distances (1.90 Å), the intermolecular interactions here are substantially weaker than IHB.

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(14) Anslyn, E. V.; Dougherty, D. A. *Modern Physical Organic Chemistry*; University Science Books: Sausalito, CA, 2006; p 97.

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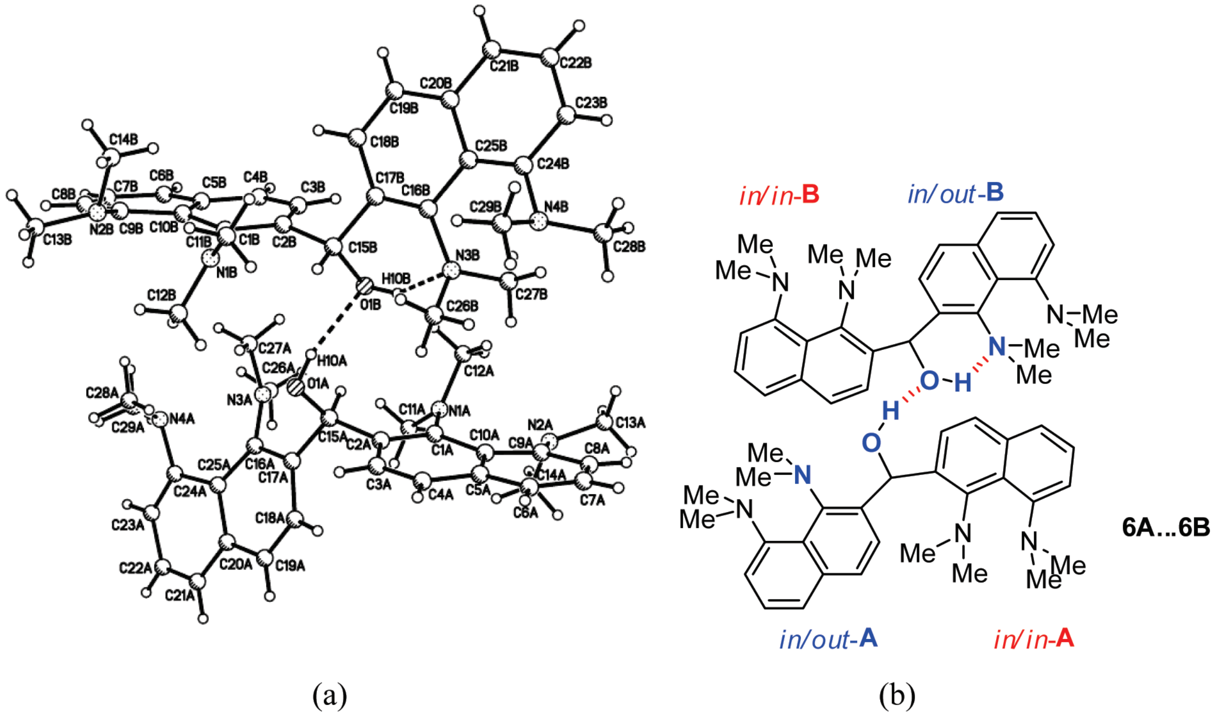
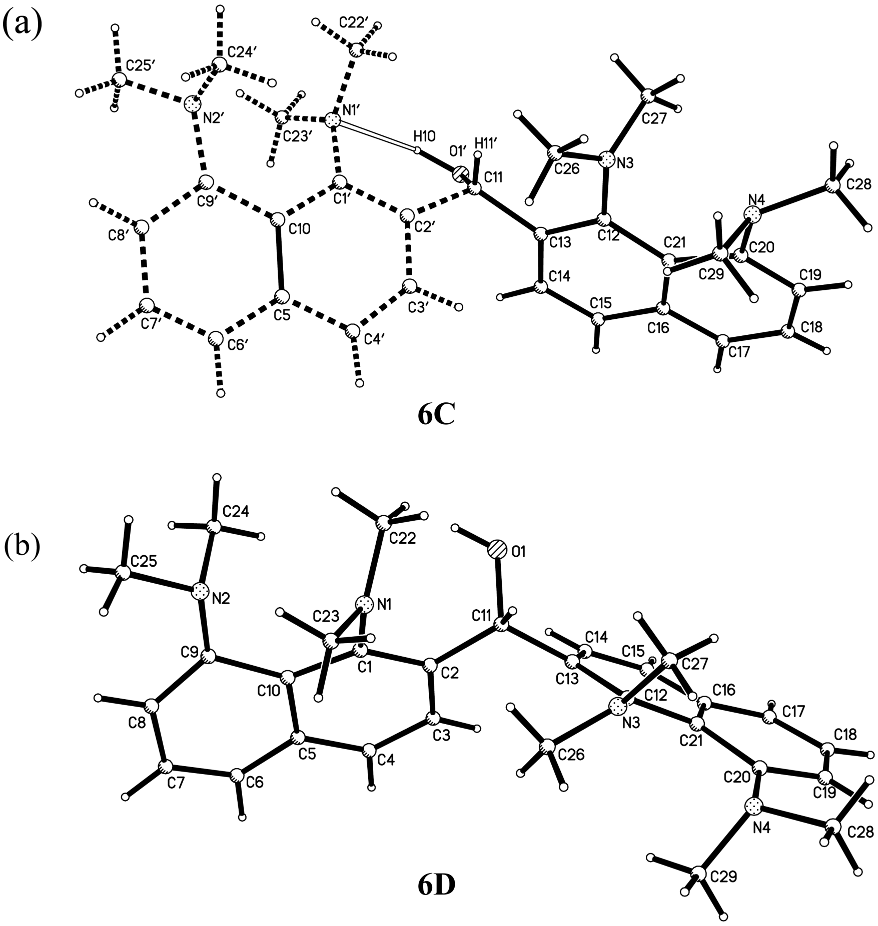
(16) Alder, R. W.; Anderson, J. E. *J. Chem. Soc., Perkin Trans 2* **1973**, 2086–2088.

(17) The flipping barrier was first estimated for the parent compound **1**. This type of movement appears to be very characteristic for all proton sponges but still remains little studied.[1a]



(a) (b)

**FIGURE 3.** Molecular structure of secondary alcohol **6** at 100 K (a) and its schematic representation (b) indicating different modes of coordination and inversion in dimeric **6A**···**6B**.

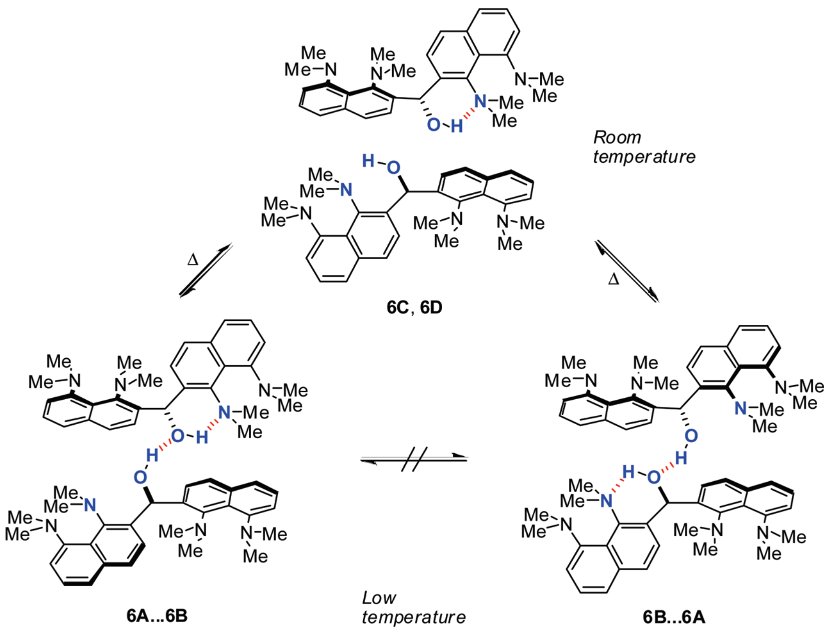


**6C**

**6D**

**FIGURE 4.** Molecular structure of secondary alcohol **6** at 293 K as represented by chelated (a) and nonchelated conformers (b); note that only the left unit undergoes structural changes in the solid.

SCHEME 2



For the secondary alcohol **6**, X-ray measurements have been conducted at 100 and 293 K and led to essentially different results. At the lower temperature, the crystal structure of **6** consists of two independent and almost identical molecules differing by location of the OH proton (Figure 3a). In one independent molecule, the hydroxyl hydrogen is chelated by the nearest 1-NMe$_2$ group (in accord with Figure 3a, this molecule is designated as **6B** in Table 1), while in the second one (marked as **6A**) it is engaged in the formation of O$-$H$\cdots$O intermolecular hydrogen bridge with molecule **6B**, thus forming a hydrogen-bonded dimer **6A**$\cdots$**6B**. Both independent molecules **6A** and **6B** adopt *in*/*out*-*in*/*in* conformation, and only their *in*/*out* units are involved in hydrogen bonding (Figure 3b). However, *out*-inversion of the 1-NMe$_2$ groups in **6A** [$\Sigma$N(1) = 358°] and **6B** (354°) is weaker than in tertiary alcohols **3** and **5**. In conjunction with the somewhat enlarged N$\cdots$H distance in **6** (2.0 Å versus 1.9 Å for **5**), one can conclude that the IHB in **6** is also weakened in comparison with **3** and **5**.

Compound **6** is the first example of a secondary proton sponge alcohol which is capable of inverting and chelating the adjacent NMe$_2$ group in the solid.[3] A possible reason for this might be the presence of two proton sponge residues which influence each other via steric and electrostatic stimuli. Their favorable disposition relatively the α-OH group obviously facilitates the formation of IHB (enthropy factor).

The increase in temperature sharply changes the crystal structure of **6** (Figure 4 and Figure S1, Supporting Information). First, it destroys the O$-$H$\cdots$O bonding so that the dimers of type **6A**$\cdots$**6B** do not exist any more at room temperature. Second, the structure with one disordered unit carrying the 1- and 8-NMe$_2$ groups is realized. It looks as if the alcohol **6** in the solid state at 293 K exists as a mixture of chelated, **6C** (Figure 4a), and nonchelated, **6D** (Figure 4b), forms nearly in a 50:50 ratio. Some geometrical parameters of these forms are given in Table 1.

It is seen that in the form **6C** the proton sponge moiety, involving IHB, adopts the *in*$-$*out* conformation with rather low "out-ness" of the N(1) atom [$\Sigma$N(1)) = 355.1°]. Along with some elongation of the O$\cdots$N and N$\cdots$H distances, this means that the IHB in **6C** is weakened on heating. In another proton sponge moiety of the form **6C**, the 1′- and 8′-NMe$_2$ groups adopt an *in*/*in*-conformation in which the N(1′) atom [N(3) in Figure 4a] is strongly flattened [$\Sigma$N(1′) = 358.8°] and the N(8′) nitrogen is substantially pyramidalized [$\Sigma$N(8′) = 341.9°] (Table 1).

The form **6D**, similar to **6C**, also belongs to the *in*/*out*-*in*/*in* type, but the *out*-inversion of the N(1) atom here is even smaller [$\Sigma$N(1) = 359.1°]. The geometrical parameters of the *in*/*in* moieties of both **6C** and **6D** are very close except those of atom N(8) in **6D** [N(2) in Figure 4b], whose hybridization is practically pure $sp^3$ [$\Sigma$N(8) = 331°].

What is the driving force for the observed disordering? We believe that this is caused by aspiration of the C$_\alpha$-hydrogen atom as the smallest substituent at C$_\alpha$ to eclipse the C$-$NMe$_2$ bond.[3b] Thus, the energy gain from the formation of IHB in molecule **6** opposes the minimization of steric repulsion between the *ortho*-substituent and the 1-NMe$_2$ group (see Figures 4A and 12 in ref 3b). To a certain extent, geometrical movements that cause disordering **6C** $\rightleftharpoons$ **6D** are quite similar to those discussed above for equilibrium **5a** $\rightleftharpoons$ **5b**.[18]

In general, structural changes observed for the solid **6** at different temperatures can be treated as a rather unusual hydrogen bond switching process. It involves two low-temperature isoenergetic supramolecular aggregates **6A**$\cdots$**6B** and **6B**$\cdots$**6A**, which may interconvert only[19] via the **6C**, **6D** tight pair (Scheme 2). This requires no substantial turning around the C$_{naph}$$-$C(O) bonds. Being strongly disordered at

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[18] Flipping in **6** might be considered as a new phenomenon in naphthalene proton sponges since it holds both conformers in the *in*/*out* form. Unlike this, in **1** and probably in majority of its derivatives two *in*/*in* forms usually interconvert.

[19] No disordering is observed for **6** at 100 K. Along with the noncentrosymmetric space group *P*1 and the fact that molecules **6A** and **6B** differ geometrically [e.g., the N(3A)$\cdots$O(1A) distance (3.306 Å) is much longer than the N(3B)$\cdots$O(1B) one (2.727 Å); see Figure 3a], this excludes any dynamic transitions between **6A**$\cdots$**6B** and **6B**$\cdots$**6A** at that temperature.

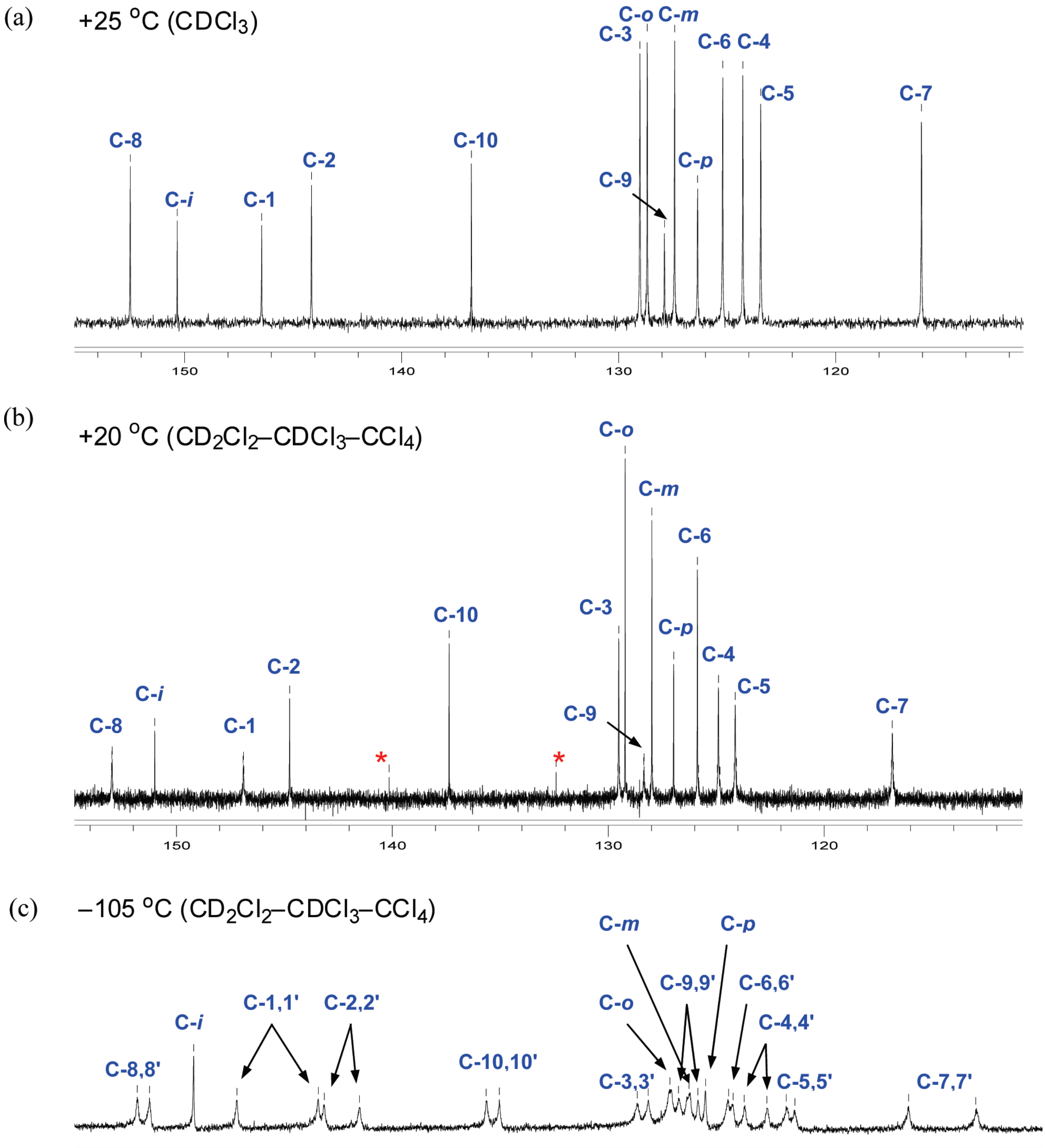


**FIGURE 5.** $^{13}$C NMR spectra of alcohol **5** at room (a,b) and low temperature (c) (aromatic region, 75 MHz, $c$ = 0.14 M; impurities in the solvent, freezing out on cooling, are marked by an asterisk).

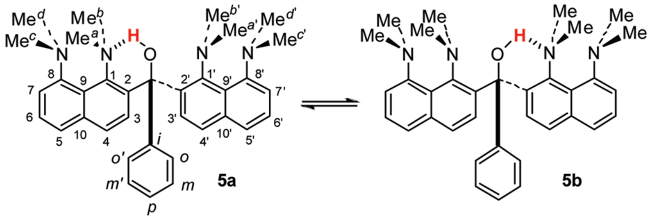
293 K, the **6C**, **6D** pair is frozen at 100 K into the **6A**···**6B** or **6B**···**6A** dimer with equal probability. Thus, here we deal with a new type of *out*-rechelation in proton sponge series, which can be called the temperature-driven *dimer-induced rechelation*.

Virtually, the process is realized through sequential cooling−heating steps and is accompanied by the $Me_2N$ $O{-}H\cdots O{-}H\cdots NMe_2 \rightleftharpoons Me_2N\cdots H{-}O\cdots H{-}O\,NMe_2$ rearrangement.

Finally, it should be pointed out that in the solid both alcohols **5** and **6** are in fact chiral with the asymmetrical center located at the $C_\alpha$ atom.

**NMR Spectra: Aromatic Region.** $^{13}$C NMR measurements unambiguously testify that tertiary alcohol **5** in solution equilibrates between conformers **5a** and **5b**. This follows from the observation that between +45 and −90 °C only 14 peaks of the aromatic C-atoms are registered in the carbon spectrum: 10 from the magnetically equivalent naphthalene

**TABLE 2.** $^{13}$C NMR Spectra of 2,2′-Dinaphthylmethanols 5 and 6 (in $CD_2Cl_2-CDCl_3-CCl_4$)[a]



| atom | 5 |  | 6 |  |
|---|---|---|---|---|
|  | 20 °C | −105 °C | 20 °C | −105 °C |
| C-1,1′ | 146.9 | 148.7, 144.9 | 147.2 | 147.6 |
| C-2,2′ | 144.8 | 144.7, 143.0 | 139.8 | very broad |
| C-3,3′ | 129.5 | 130.3, 129.8 | 126.9 | 126.6 |
| C-4,4′ | 124.9 | 125.4, 124.3 | 125.4 | 124.9 (br) |
| C-5,5′ | 124.1 | 123.4, 123.1 | 124.7 | 123.8 (br) |
| C-6,6′ | 125.9 | 126.1, 125.9 | 126.0 | 125.5 (br) |
| C-7,7′ | 116.9 | 117.9, 114.8 | 116.4 | 115.6 (br) |
| C-8,8′ | 153.0 | 153.2, 152.7 | 152.5 | 152.6 |
| C-9,9′ | 128.4 | 128.4, 127.5 | 126.4 | 126.2 |
| C-10,10′ | 137.4 | 137.2, 136.6 | 137.7 | 137.4 |
| C-*i* | 151.0 | 150.7 |  |  |
| C-*o*,*o*′ | 129.2 | 128.8 |  |  |
| C-*m*,*m*′ | 128.0 | 127.9 |  |  |
| C-*p*,*p*′ | 127.0 | 127.2 |  |  |
| $C_\alpha$ | 85.6 | 85.1 | 70.1 | 69.9 |
| $N-CH_3(a)$ | 44.8 | 44.3[b] | 44.4 | 44.0 |
| $N-CH_3(a')$ | 44.8 | 44.3[b] | 44.4 | 44.0 |
| $N-CH_3(b)$ | 44.8 | 44.6[b] | 44.4 | 44.4 |
| $N-CH_3(b')$ | 44.8 | 44.6[b] | 44.4 | 44.4 |
| $N-CH_3(c)$ | 48.7 | 51.0[b] | 45.8 | 45.3 |
| $N-CH_3(c')$ | 48.7 | 48.9[b] | 45.8 | 45.3 |
| $N-CH_3(d)$ | 46.2 | 45.4[b] | 48.2 | 49.6 |
| $N-CH_3(d')$ | 46.2 | 46.0[b] | 48.2 | 49.6 |

[a] A 60:27:13 (v/v/v) mixture of $CD_2Cl_2$, $CDCl_3$, and $CCl_4$ was used, which is liquid down to −110 °C; see also ref 20. [b] Assignment of peaks with $\delta_C$ 44.3 and 44.6 ppm can be interchanged; the same is true for the $N-CH_3(c,c')$ and $N-CH_3(d,d')$ peaks.

rings and 4 from the α-$C_6H_5$ group (Figure 5a,b, Table 2). Evidently, such symmetry can be well provided by the stereodynamics mentioned above for **5a** ⇌ **5b**. The energy required for rechelation should not be high, since the strength of IHB in the chelated alcohols **3** is about 7 kcal mol$^{-1}$.[3b]

On cooling to −90 °C, the naphthalene signals in the $^{13}$C NMR spectrum of **5** broaden markedly, and at −105 °C they split into reasonably defined doublets that increase the overall number of peaks of the aromatic carbon atoms up to 24 (Figure 5c). Obviously, below −100 °C the molecule **5** is frozen in unsymmetrical form with two nonequivalent proton sponge moieties, chelated and unchelated. The largest splitting is observed for the C-1(1′) pair ($\Delta\delta_C = 3.8$ ppm), followed by C-7(7′) and C-2(2′) (3.1 and 1.7 ppm, respectively) (Table 2). In fact, while the C-1(1′) carbons may response on the chelation as it is switched on and off, the other two pairs are sensitive to the resonance interaction of the *peri*-NMe$_2$ groups with the naphthalene π-system that is stronger in the unchelated half of **5**. The splitting of the C-1(1′) pair of carbons was used to estimate the rechelation barrier: $\Delta G^\ddagger$ ~9 kcal mol$^{-1}$ for $T_c$ being near −75 °C.

Unlike **5**, the ring carbon signals of the secondary alcohol **6** do not split on cooling (Figure S2, Supporting Information). Instead, some peaks, especially C-2(2′) and C-7(7′), are strongly broadened at −105 °C. This may be caused by the slow interconversion of the 1- and 1′-NMe$_2$ groups between the *in* and *out* conformations. It is likely, that further temperature lowering would also result in doubling of signals for **6** due to arising of the captured chelates, but this possibility could not be tested owing to solubility problems.

The $^1$H NMR spectra of **5** and **6** in the aromatic region are of little significance (Figures S3 and S4, Supporting Information). As expected, at ambient temperature they contain only five kinds of naphthalene hydrogen atoms, confirming the symmetry of the two aromatic moieties. On lowering the temperature, no substantial changes occur except small broadening of all peaks. Perhaps the only point to mention is the pronounced shielding of the $C_3$-H and $C_3$-H′ protons in the spectra of **5** ($\delta_H$ = 6.8 ppm) that can be caused by anisotropy of the $C_6H_5$ ring (Figures 1b and Figure S3, Supporting Information).

**NMR and IR Spectra: OH Group Appearance.** The behavior of the OH groups in the $^1$H NMR and IR spectra of **5** and **6** is very informative especially in comparison with diphenylmethanol and triphenylmethanol. In the $^1$H NMR spectrum of benzhydrol, the OH proton in $CDCl_3$ at a concentration range $3.6 \times 10^{-3}-1.8 \times 10^{-2}$ M resonates as a doublet ($J \sim 3$ Hz) near $\delta$ = 2.2 ppm (Figure S5, Supporting Information). Though the $\delta_{OH}$ value is practically insensitive to concentration, the CH(OH) coupling disappears at higher concentrations (>$5 \times 10^{-2}$ M), indicating the beginning of association. This agrees with the IR data, which demonstrate an appearance of the broad absorption from "polymeric" structures centered at 3468 cm$^{-1}$ at a concentration close to $10^{-1}$ M; the sharp "free" OH group absorbs strongly at 3617 cm$^{-1}$ (Figure S6, Supporting Information). Triphenylmethanol behaves similarly, although its association is considerably weaker (Figure S7, Supporting Information).

An appearance of the OH groups in alcohols **5** and **6** due to the chelation phenomenon strongly differs from that of diphenylmethanol and triphenylmethanol. In the $^1$H NMR spectrum of **5** ($CDCl_3$, 25 °C) (Figure S3a, Supporting Information), the peak of the chelated OH group (disappears with $D_2O$) is observed at $\delta$ 10.78 ppm.[21] At 45 °C, the signal shifts to 10.52 ppm, while at −105 °C it moves to 11.30 ppm, reflecting weakening/strengthening of the O−H···N chelation, respectively. On the contrary, the $^1$H NMR spectrum of the secondary alcohol **6** in $CDCl_3$ allows us to observe the OH proton at a much higher field ($\delta_H$ 5.35 ppm) as a broad and $D_2O$-exchangable singlet (Figure S4a, Supporting Information); a sharp peak at $\delta_H$ 6.74 ppm belongs to the C*H*(OH) methyne hydrogen. In DMSO-$d_6$, the OH- and C*H*(OH) protons give doublets at $\delta_H$ 5.65 and 6.55 ppm, respectively. The position of the OH signal in the $^1$H NMR spectrum of **6** gives a possibility for interesting speculations. On the first sight, the above $\delta_{OH}$ value can be hardly attributed to the formation of IHB. At the same time, the

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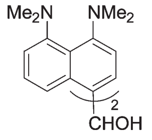
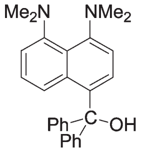
[20] Preliminary studies had shown that there is no significant difference in the NMR spectra of **5** in $CDCl_3$ and in the above solvent system under ambient conditions (see Figure 5). Somewhat lowered intensity of peaks at −105 °C is caused by decreased solubility of **5** at this temperature.

[21] There is a principal difference in the OH chemical shifts for systems **4a** ⇌ **4b** and **5a** ⇌ **5b**. Since in the former each OH group interchanges between chelated ($\delta$ = 10.6) and unchelated ($\delta$ = 3.4 ppm) states its $^1$H chemical shift ($\delta$ = 6.95 ppm) represents an average value.[3] Unlike this, the OH-proton in **5** remains chelated in both forms and appears at 10.8 ppm.

hydroxyl proton in **6** is substantially deshielded in comparison with diphenylmethanol ($\delta_{OH}$ = 2.2), triphenylmethanol ($\delta_{OH}$ = 2.8 ppm) and the related alcohols **11**[22] and **12**.[23] This discrepancy becomes understandable at considering IR spectra of **5** and **6** in $CCl_4$ solution.



**11** ($\delta_{OH}$ = 2.2 ppm)



**12** ($\delta_{OH}$ = 3.4 ppm)

In the IR spectra of tertiary alcohol **5**, no stretching band of the free OH group is observed. Instead, only very broad continuum between 3500−2500 cm$^{-1}$ is seen, independent of concentration (Figure S8, Supporting Information). This is very characteristic for many IHBs[11,24] and is in line with the above NMR data. Unlike **5**, the secondary alcohol **6** displays a more diverse picture. Along with the similar continuum, its IR spectra at concentrations of $1.2 \times 10^{-2}$−$2.5 \times 10^{-2}$ M contain the free OH group band with small splitting (3608, 3599 cm$^{-1}$; nature of this splitting is unclear) (Figure S9, Supporting Information). We think that the alcohol **6** exists in solution as an equilibrating mixture of chelated and unchelated forms. FT IR spectroscopy as a faster method allows these states to be distinguished, while a slower NMR technique gives an average picture. Fortunately, from the NMR data one can deduce the ratio of both forms in $CDCl_3$ solution of **6** as equal to 1:1.8 in favor of the monomeric unchelated form (Supporting Information, Appendix S1). It is easily seen that the dual behavior of the alcohol **6** in solution correlates well with that in the solid state.

Thus, the principal difference between alcohols **5** and **6** is that the former spends most of the time in the chelated state, whereas in the case of **6** the forms with the free OH group prevail. The situation can be conveniently presented by the overall energetic diagram shown in Figure S10 (Supporting Information). It should be especially stressed that both alcohols **5** and **6** are not associated in solution at common concentrations. Thus, in accordance with the $^{1}$H NMR measurements (600 MHz, $CDCl_3$, 30 °C) the signal of the OH group for **5** ($\delta$ = 10.7 ppm) remains unchanged at concentrations of $3.1 \times 10^{-4}$−$1.4 \times 10^{-1}$ M (Figures S3 and S11, Supporting Information). The same is true for **6**: $\delta_{OH}$ is near 5.3 ppm at concentrations of $3.7 \times 10^{-4}$−$1.7 \times 10^{-1}$ M (Figures S4 and S12, Supporting Information).

**NMR Spectra: Region of NMe$_2$ Groups.** An appearance of the $NMe_2$ groups in the $^{13}$C and $^{1}$H spectra of compounds **5** and **6** is complex and highly temperature dependent (Table 3, Figure 6 and Figures S3, S4, and S13, Supporting Information). Remarkably, in this region, the NMR spectra for both alcohols are quite similar, especially within +20 to −80 °C. Thus, the proton spectrum of **5** measured in the $CD_2Cl_2$−$CDCl_3$−$CCl_4$ mixture at 20 °C gave three singlets of the $CH_3$ groups at $\delta$ 2.77, 2.60, and 2.56 ppm with relative intensities 6H, 12H, and 6H, respectively (Figure 6a and Figure S3a, Supporting Information). The middle signal can be ascribed to the 1- and 1′-$NMe_2$ groups, while the $\delta$ 2.77 and 2.56 peaks belong to the Me$^{d,d'}$ and Me$^{c,c'}$ groups (see the Supporting Information, Appendix S2 for details). On heating, the signals at $\delta$ 2.77 and 2.56 ppm broaden and coalesce near 45 °C (Figure S3b,c, Supporting Information). The same is observed for the secondary alcohol **6**, but in this case, the 12-proton Me$^{a,a',b,b'}$ peak is the most deshielded (3.04 ppm) (Figure S4, Supporting Information).

**TABLE 3. Me Group Absorbances in $^{1}$H NMR Spectra of Alcohols 5 and 6 (300 MHz, $CD_2Cl_2$−$CDCl_3$−$CCl_4$)**

| | 5 | | 6 | |
|---|---|---|---|---|
| Me group | 20 °C | −105 °C$^{a}$ | 20 °C | −105 °C$^{b}$ |
| Me$^{a}$ | 2.60 | 1.98 | 3.03 | 3.04 |
| Me$^{a'}$ | 2.60 | (2.47) | 3.03 | 3.04 |
| Me$^{b}$ | 2.60 | 2.68 | 3.03 | 2.87 |
| Me$^{b'}$ | 2.60 | 2.68 | 3.03 | 2.87 |
| Me$^{c}$ | 2.56 | 2.23 | 2.69 | 2.52 |
| Me$^{c'}$ | 2.56 | (2.36) | 2.69 | 2.52 |
| Me$^{d}$ | 2.77 | 2.78 | 2.89 | 2.83 |
| Me$^{d'}$ | 2.77 | 2.78 | 2.89 | 2.83 |

$^{a}$The signals in parentheses are arbitrarily assigned. $^{b}$Assignment of pairs of signals at $\delta_H$ 3.04 and 2.87 as well as at 2.83 and 2.52 ppm can be interchanged.

On cooling, in contrast to the heating picture, the peak from the 1- and 1′-$NMe_2$ undergoes changes first. As one can see from Figure 6b, it first broadens and between −30 to −60 °C splits into a doublet (obviously, the right part of the doublet in Figure 6c,d overlaps with the Me$^{c,c'}$ peak). An appearance of six types of *N*-methyl groups at −90 to −105 °C is rather spectacular (Figure 6e,f). Perhaps the most striking observation is an unusual paratropic chemical shift of one methyl group ($\delta$ 1.98 ppm) lying on a level of $Me_3N$ and $Me_2NH$ absorption (~2 ppm).[25] We assign this peak to the Me$^{a}$ group (see the Supporting Information) judging from the fact that on cooling this group is fixed next to the centroid of the $C_6H_5$ ring plane and therefore sustains especially strong shielding (Figure 1 and Figure S14, Supporting Information). This phenomenon is not observed for **6**, though on the whole the NMR spectra of **5** and **6** between +20 and −80 °C look very similar (see, e.g., Figure S13, Supporting Information).

The carbon spectra of alcohols **5** and **6**, like $^{1}$H NMR, demonstrate the presence of three types of the N-Me groups at 20 °C (Figure S13, Supporting Information). On cooling, the signals broaden and split: for example, in the case of **5** into six peaks at −105 °C. Such broadening is especially

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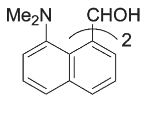
(22) Ryabtsova, O. V.; Pozharskii, A. F.; Ozeryanskii, V. A.; Vistorobskii, N. V. *Russ. Chem. Bull.* **2001**, *50*, 854–859.

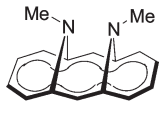
(23) Pozharskii, A. F.; Ryabtsova, O. V.; Vistorobskii, N. V.; Starikova, Z. A. *Russ. Chem. Bull.* **2000**, *49*, 1097–1102.

(24) (a) Pawlukojc, A.; Natkaniec, I.; Grech, E.; Baran, J.; Malarski, Z.; Sobczyk, L. *Spectrochim. Acta* **1998**, *A54*, 439–448. (b) Ozeryanskii, V. A.; Pozharskii, A. F.; Schilf, W.; Kamieński, B.; Sawka-Dobrowolska, W.; Sobczyk, L.; Grech, E. *Eur. J. Org. Chem.* **2006**, 782–790.

(25) To our knowledge, two extreme cases of this phenomenon were reported for 8,8′-bis(dimethylamino)-1,1′-dinaphthylcarbinol (E) and *N,N*′-dimethyl-*syn*-1,6:8,13-diimino[14]annulene (F), where methyls resonate at $\delta_H$ 1.56 and 0.55 ppm, respectively: Schiemenz, G. P.; Schiemenz, B.; Petersen, S.; Wolff, C. *Chirality* **1998**, *10*, 180–189. Gerson, F.; Gescheidt, G.; Knöbel, J.; Martin, W. B., Jr.; Neumann, L.; Vogel, E. *J. Am. Chem. Soc.* **1992**, *114*, 7107–7115.



**E**



**F**

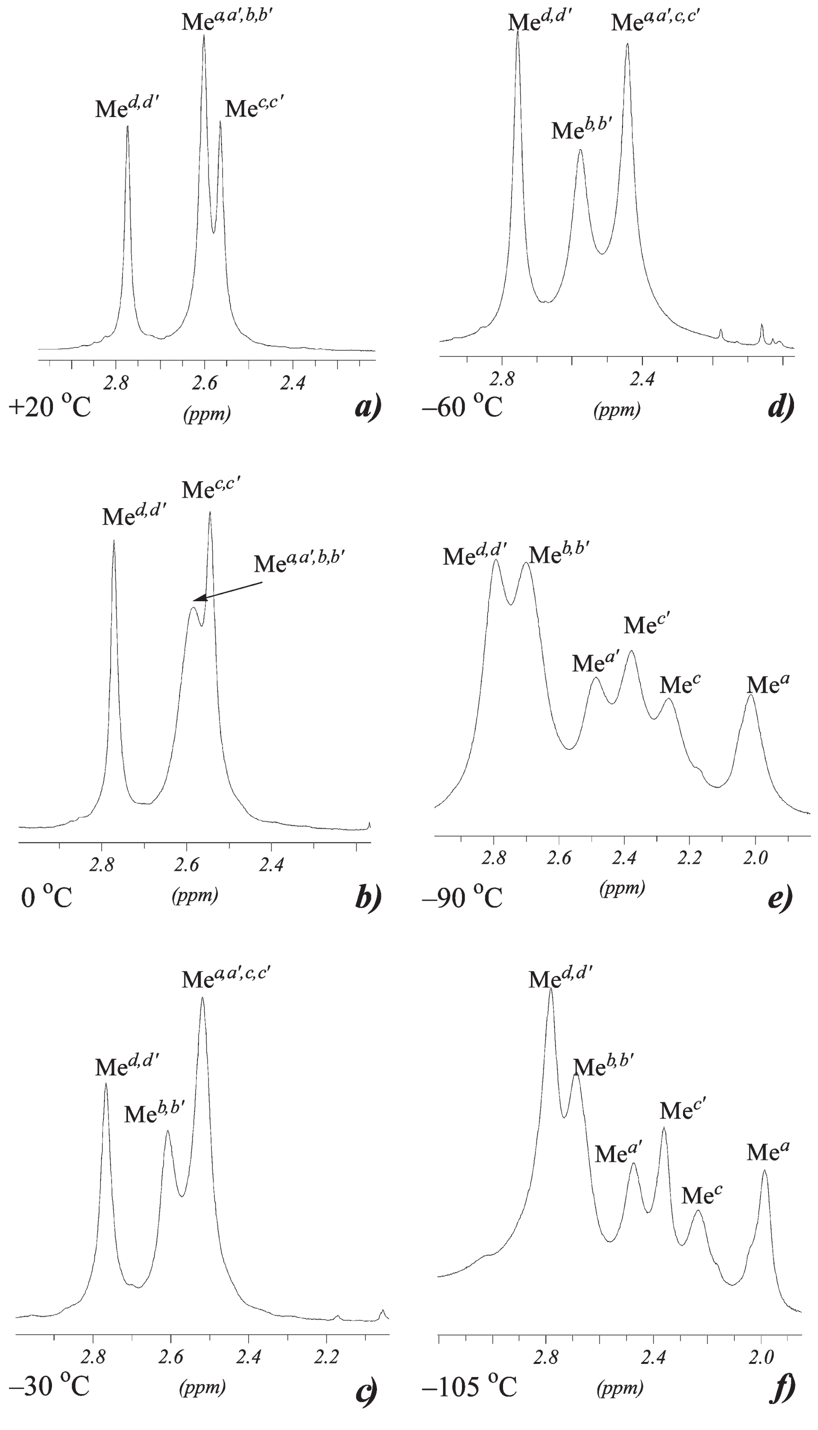


**FIGURE 6.** Temperature dependence of the *N*-methyl group region in the $^1$H NMR spectra of **5** (300 MHz, $CD_2Cl_2-CDCl_3-CCl_4$, $c$ = 0.14 M).

pronounced for **6**, in accord with its X-ray behavior (see above).

## Conclusions

In summary, we have prepared two representatives of earlier unknown proton sponge-based 2,2′-binaphthylmethanols **5** and **6** and have studied their ability to form and switch intramolecular hydrogen bonding of O−H···N type. It has been shown that in solution at temperatures from ambient to −80 °C the tertiary alcohol **5** rapidly undergoes rechelation, but near −100 °C this process stops and the molecule adopts an unsymmetrical form with the fixed intramolecular hydrogen bridge. A similar structure with the *in*/*out*-*in*/*out* conformation of four $NMe_2$ groups is realized in crystals. The secondary alcohol **6** in solution at temperatures up to −100 °C represents a mixture of chelated and monomeric unchelated forms with the greater prevalence of the latter. However, in the solid, as shown by X-ray measurements at 100 K, it adopts dimeric structure with two *in*/*out*-*in*/*in* proton sponge units. In half of the dimer the OH proton chelates the *in*/*out* unit of the same molecule, while the half forms an O−H···O intermolecular hydrogen bond with the second molecule of **6**. This supramolecular aggregate has been demonstrated to disassemble at 293 K into tight pair of two highly disordered molecules. The character of disordering, involving fast flipping of two *in*/*out* conformers, allows us to conclude that the temperature-driven *dimer-induced rechelation* with the $\mathrm{Me_2N\ O{-}H\cdots O{-}H\cdots NMe_2 \rightleftharpoons Me_2N\cdots H{-}O\cdots H{-}O\ NMe_2}$ switching mode is realized.

## Experimental Section

For general indications on reagents and methods, see ref 3b.

**Bis[1,8-bis(dimethylamino)naphth-2-yl]phenylmethanol (5).** To a solution of 1,8-bis(dimethylamino)-2-lithionaphthalene (**9**), prepared from 2-bromo-1,8-bis(dimethylamino)naphthalene (300 mg, 1.02 mmol) as previously described,[2,3] was added a solution of ketone **7**[3b] (247 mg, 1.02 mmol) in $Et_2O$ (2 mL) under argon at −20 °C. The resulting dark-yellow mixture was kept at −20 °C for 24 h, allowed to warm to rt, and poured into water (10 mL). The ethereal layer was separated, and the aqueous layer was extracted with $Et_2O$ (3 × 5 mL). The combined organic extracts were evaporated, and the residue was purified by PTLC ($Al_2O_3$, eluent $CHCl_3$, $R_f$ 0.38): yield 277 mg (51%); yellow crystals with mp 207−208 °C (*n*-hexane); $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 2.52 (6H, s), 2.54 (12H, s), 2.74 (6H, s), 6.77 (2H, d), 7.19−7.51 (13H, m), 10.78 (1H, br s, OH); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 44.4, 45.7, 48.4, 85.2, 116.1, 123.5, 124.3, 125.2, 126.4, 127.4, 127.9, 128.7, 129.0, 136.8, 144.2, 146.5, 150.4, 152.5. Anal. Calcd for $C_{35}H_{40}N_4O$: C, 78.91; H, 7.57; N, 10.52. Found: C, 78.94; H, 7.53; N, 10.49.

**Bis[1,8-bis(dimethylamino)naphth-2-yl]methanol (6).** Compound **6** was prepared similarly to **5** from lithionaphthalene (**9**) (1.02 mmol) and aldehyde **8**[3b] (247 mg, 1.02 mmol). The product was purified by PTLC ($Al_2O_3$, eluent MeCN; $R_f$ 0.05 in $CHCl_3$): yield 224 mg (48%); yellowish crystals with mp 178−179 °C (*n*-hexane)y $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 2.67 (6H, c), 2.90 (6H, c), 3.04 (12H, c), 5.36 (1H, br s, OH), 6.74 (1H, c, C*H*(OH)), 7.18−7.60 (10H, m); $^1H$ NMR (300 MHz, DMSO-$d_6$) $\delta$ 2.60 (6H, c), 2.75 (6H, c), 2.87 (12H, c), 5.65 (1H, d, $J$ = 5.9 Hz, OH), 6.55 (1H, d, $J$ = 5.9 Hz, C*H*(OH)), 7.02−7.73 (10H, m); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 43.9, 45.2, 48.0, 69.9, 115.5, 124.0, 124.8, 125.3, 126.0, 126.2, 137.2, 139.0, 146.8, 152.1. Anal. Calcd for $C_{29}H_{36}N_4O$: C, 76.28; H, 7.95; N, 12.27. Found: C, 76.21; H, 7.97; N, 12.24.

**X-ray Measurements.** X-ray measurements were carried out with Bruker APEX II (for **5**) and Bruker SMART 1000 (for **6**) CCD area detectors using graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å, $\omega$-scans with a 0.3° step in $\omega$ and 10 s per frame exposure). The crystals of suitable quality were obtained from *n*-hexane (both **5** and **6**). The structures were solved by direct methods and refined by the full-matrix least-squares against $F^2$ in anisotropic (for non-hydrogen atoms) approximation. The hydrogen atom of OH group of **5** and **6** was found in difference Fourier synthesis. The H(C) atom positions were calculated. All hydrogen atoms were refined in isotropic approximation in the riding model with the $U_{iso}(H)$ parameters equal to $1.2U_{eq}(C_i)$ (for Me groups the $U_{iso}(H)$ parameters are equal to $1.5U_{eq}(C_i)$), where $U_{eq}(C_i)$ is the equivalent thermal parameter of the atoms to which corresponding H atoms are bonded. The main crystallographic data and some experimental details are given in Table S1 (Supporting Information). Atomic coordinates, bond lengths, bond angles, and thermal parameters for **5** and **6** have been deposited at the Cambridge Crystallographic Data Centre (CCDC, deposit nos. 767928−767930). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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**Supporting Information Available:** Molecular structure of disordered compound **6**; dynamic $^1H$ and $^{13}C$ NMR spectra of **5** and **6**; $^1H$ NMR and IR spectra of **5**, **6**, and diphenyl- and triphenylmethanols at different concentrations; NMR peak assignments for **5** and **6**; COSY (HSQC and HMBC) data and 2D NMR plots for a set of 2-α-hydroxymethyl-1,8-bis(dimethylamino)naphthalenes; and crystal data and structure refinement for compounds **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.