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^{1}H-NMR Investigations of the Conformation of Aryl-(hydroxynaphthyl)-methylpiperidines. Intramolecular Interactions, IV** [1]

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Summary. The ^{1}H-NMR spectra of aryl-(hydroxynaphthyl)-methylpiperidines, which are model compounds for intramolecular hydrogen bonding, have been analyzed in order to investigate their conformations in solution. As dynamic phenomena can be assumed from line broadening, low temperature spectra have been measured to evaluate the coalescence temperatures and the energy barriers. The latter have been discussed with respect to the size and position of selected substituents. It can be shown that the molecules exist in one energetically favorable conformation with the aryl ring perpendicular to the plane of the naphthol ring system. The interaction between the naphthol ring and the aryl ring influences the conformation at the piperidine ring moiety. This effect leads to an increase of the inversion barrier of the piperidine residue.

Keywords. Conformational analysis; Intramolecular hydrogen bonding; Piperidines; Naphthols.

Konformationsuntersuchungen an Aryl-(hydroxynaphthyl)-methylpiperidinen. Intramolekulare Wechselwirkungen, Teil IV

Zusammenfassung. Die Konformation von Aryl-(hydroxynaphthyl)-methylpiperidinen wurde in Lösung mit Hilfe der ^{1}H-NMR-Spektroskopie untersucht, da diese Substanzen als Modellverbindungen für intramolekulare Wasserstoffbrückensysteme herangezogen werden. Zum Studium dynamischer Vorgänge wurden die Spektren bei verschiedenen Temperaturen vermessen und die entsprechenden Aktivierungsparameter bestimmt. Es konnte gezeigt werden, daß die erwähnten Moleküle in einer energetisch bevorzugten Konformation vorliegen, in der der Arylring senkrecht auf die Ebene des Naphtholringes steht. Die sterische Wechselwirkung zwischen Naphthol- und Arylring erhöht außerdem die Inversionsbarriere des Piperidinringes.

Introduction

Aminomethylnaphthols are covenient model systems for the study of hydrogen bonding and proton transfer. Various naphthols as proton donors and piperidine

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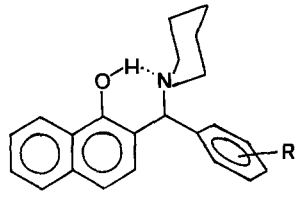
** Dedicated to Prof. Dr. K. Schlögl on the occasion of his 65th birthday
*** On Sabbatical Leave from Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan

or morpholine as proton acceptors are connected in these compounds by a methylene bridge. A favorable geometry leads to the formation of an intramolecular hydrogen bond. The properties of the hydrogen bond depend on the donor strength of the naphthol ring, which can be varied by different substituents, as well as on the basicity of the acceptor. Proton transfer equilibria and hydrogen bond strengths have been studied in detail by spectroscopic methods [2–9]. As the intramolecular hydrogen bond is not linear, careful analysis of the geometry of these systems has been done [1, 10]. Additional substitution at the methylene bridge which connects the naphthol moiety and the nitrogen base, has been performed here to change the electron density in the hydrogen bond. This class of compound shows interesting spectroscopic and thermodynamic properties [11].



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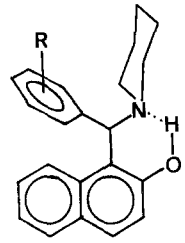

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Compound	*R*
1a	H
1b	*p*-Br
1c	*m*-Br
1d	*o*-Br
2a	H
2b	*p*-Br
2c	*m*-F
2d	*m*-Cl
2e	*m*-Br
2f	*o*-OCH_3
2g	*o*-F
2h	*o*-Cl
2i	*o*-Br

The NMR spectra of piperidine or N-methyl substituted piperidines are influenced by ring inversion as well as by nitrogen inversion. The formation of a hydrogen bond to the nitrogen increases the nitrogen inversion barrier and slows also down the rate of the ring inversion [12], therefore the NMR spectra have been recorded over a wide temperature range in order to obtain information regarding the dynamics of the phenyl and piperidine part of the molecule. An analysis of the ^{1}H-NMR spectra of compounds of type **1** and **2** at different temperatures has been performed; the assignment of various lines was done with the help of two-dimensional NMR-spectroscopic techniques [13, 14].

Experimental

The synthesis of compounds was performed according to literature [1, 15, 16]. Since the NMR-spectral patterns of these compounds are highly dependent on moisture and protic solvent content, care was taken during the entire procedure of solution preparation; the compounds were recrystallized several times and finally dried for about twelve hours at reduced pressure and at temperatures 10 K below their melting points. Deuterated chloroform (99.5%) was purified on an alumina column and then stored over molecular sieves in a dry box. Preparation of sample solutions and their transfer into NMR-sample tubes was done in a glove box under an argon atmosphere. The concentration of the compounds was kept within the range 30–36 mg/ml solvent. It is worth mentioning that the chemical shifts of some of the compounds were measured at different concentrations and were found

to be invariant. The NMR-spectra were recorded on a Bruker WM-250 spectrometer equipped with an 80 K ASPECT-2000 computer running the DISNMRP-85 program release. The resonance frequency for protons was 250.13 MHz. The deuterium signal of the solvent provided the field-frequency stabilization. The temperature of the sample was regulated by the B-VT-100 Variable Temperature Unit. NMR-sample tubes of 5 mm diameter were used and sample heights range from 3 to 3.5 cm. For the proton spectra 32–64 accumulations were performed. The coalescence temperature (T_C) was estimated with an accurancy of ± 5 K, ΔG^*-values were calculated using the Eyring equation. Taking into account the error limit of T_C and the shift differences, ΔG^* is expected to be accurate to ± 2 kJ/mol.

Results

^{1}H-NMR Spectra

The ^{1}H-NMR spectrum of the piperidine ring hydrogens of 1-piperidinomethyl-2-naphthol (**3**) shows a similar pattern as other N-methyl substituted piperidine derivatives [17–22]. The ring reversal is slightly hindered ($\Delta G^* = 54.5$ kJ/mol at 280 K) in comparison to N-methylpiperidine ($\Delta G^* = 50.2$ kJ/mol, $T_C = 245$ K) and N-*tert*-butylpiperidine ($\Delta G^* = 46.9$ kJ/mol, $T_C = 233$ K), due to the hydrogen bond formation, which also prevents nitrogen inversion to a large extent [12]. Figure 1 shows the ^{1}H-NMR spectrum of **3** at 240 K, a temperature below the coalescence temperature.

A doublet at 3.1 ppm can be observed for the equatorial hydrogen atoms in positions 2 and 6. The corresponding axial hydrogen atoms are shielded by the axial unshared pair of electrons on the nitrogen atom and appear as a triplet at 2.1 ppm. The shift difference implies that there is a highly preferred conformation, where the substituent is bound equatorially to the nitrogen atom. Additional an

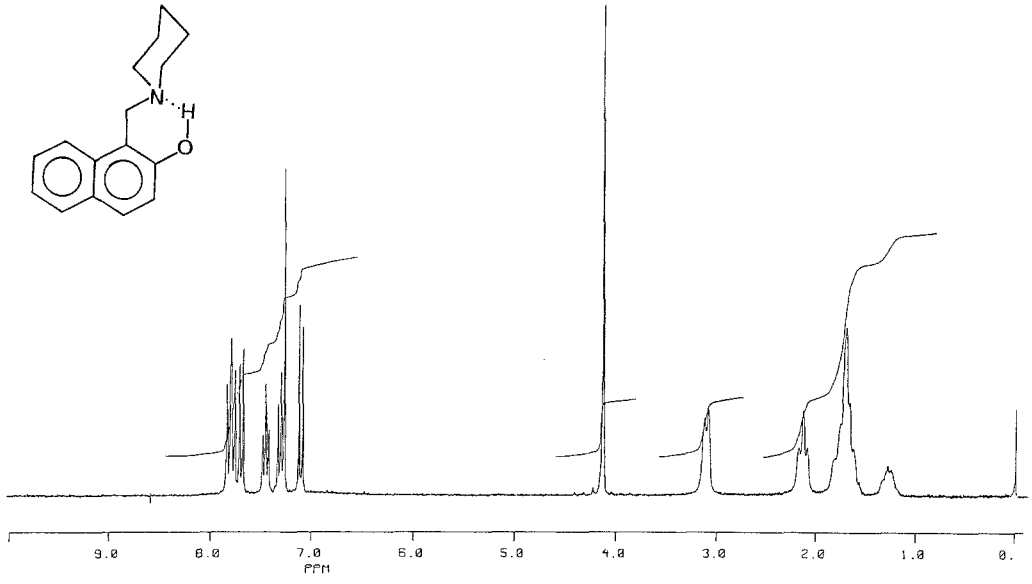


Fig. 1. ^{1}H-NMR spectrum of **3** at 240 K

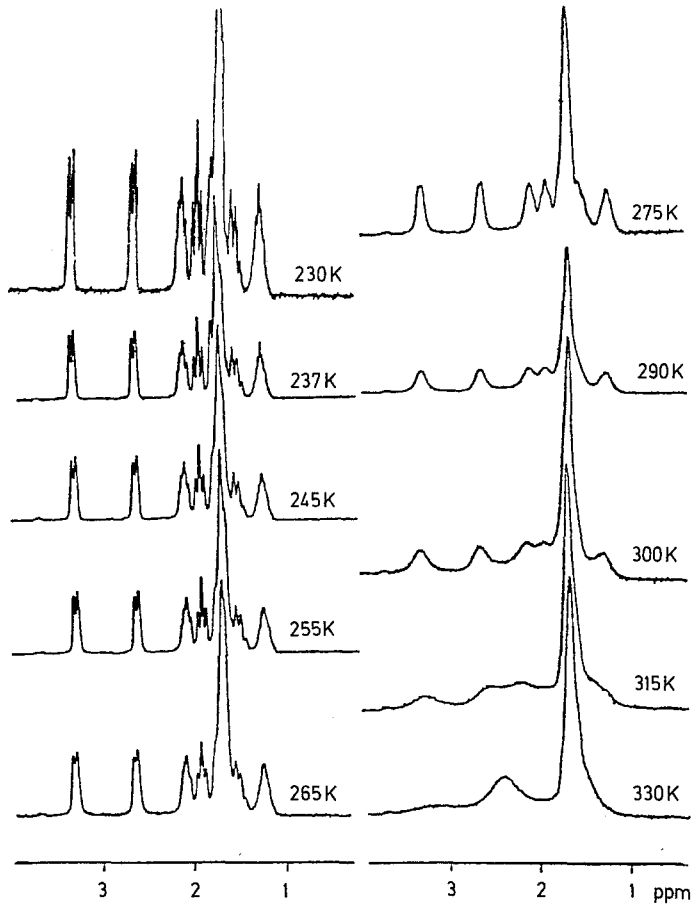
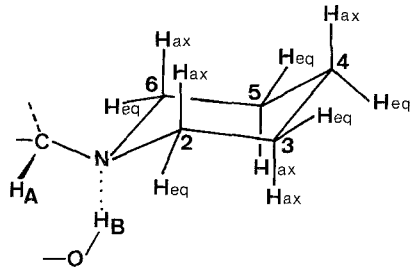


Fig. 2. Piperidine part of the ^{1}H-NMR spectrum of **2a** in the temperature range from 230 K to 330 K

intramolecular hydrogen bond is formed in axial position of the nitrogen atom, leading to a six-membered ring, which is nonplanar for steric reasons. The chemical shift value of 13.1 ppm for the hydroxyl proton supports the assumption of a relatively strong hydrogen bond. As no additional splitting of the piperidine ring protons is found, the inversion of the ring including the hydrogen bond is fast on the NMR-time-scale.

The substitution of one hydrogen atom of the methylene bridge between the naphthol and the piperidine ring by an aryl ring changes the room temperature ^{1}H-NMR-spectrum drastically. The NMR-lines of the piperidine protons are still broadened but separate signals for the different protons at positions 2 and 6 can be observed. In Fig. 2 the ^{1}H-NMR spectrum of the piperidine part of **2a** is given at different temperatures. It can be clearly seen that the coalescence temperature is increased in comparison to compound **3**, because in addition to the influence of the hydrogen bond the dynamics of the piperidine ring is restricted by the steric interaction with the aryl ring. The dynamic behaviour and the chemical shift values are dependent on the substituents on the aryl ring. To evaluate the influence of substituents on the chemical shift values of the piperidine protons, compounds of type **1** and **2** have been prepared. Their shifts are given in Table 1, together with the corresponding absorptions of the methine- and hydroxyl protons.

Table 1. Chemical shift values of the piperidine protons together with the methine and hydroxyl protons of compounds of types **1** and **2** at 297 K; all values are given in ppm with respect to internal *TMS*



Compound	ppm								
	2-equ	6-equ	2-ax	6-ax	3,5,4-ax		4-equ	H_A	H_B
1a		2.46			1.67		1.49	4.55	13.42
1b		2.44			1.67		1.50	4.50	13.22
1c		2.44			1.67		1.50	4.48	13.15
1d	3.36	2.69	2.30	2.30	1.68		1.33	5.39	13.55
2a	3.31	2.65	2.10	1.91	1.67		1.26	5.07	13.98
2b	3.31	2.65	2.10	1.92	1.67		1.29	5.03	13.81
2c	3.29	2.64	2.07	1.94	1.68		1.27	5.02	13.74
2d	3.28	2.63	2.10	1.94	1.68		1.26	5.03	13.73
2e	3.29	2.64	2.07	1.94	1.68		1.27	5.02	13.74
2f	3.34	2.67	2.25	2.10	1.68	1.52	1.21	5.81	14.37
2g	3.32	2.71	2.17	2.12	1.69	1.52	1.25	5.62	13.97
2h	3.31	2.62	2.28	2.32	1.70	1.49	1.26	5.83	14.28
2i	3.32	2.61	2.33	2.43	1.70	1.49	1.28	5.81	14.37
3		2.61			1.68		1.53	4.10	12.91
4	2.92		1.15		1.50		1.65	(4-equ: 0.86)	
5	3.69		2.63		1.04–2.34		1.80	(4-equ: 1.04)	

The piperidine ring protons of compounds of type **1** give broad signals at room temperature similar to those of compound **3**, whereas in compounds of type **2** the signals are broadened too, but they are split up, because the steric interaction in compounds **1** is considerably weaker than for compounds of type **2**, where a shorter distance exists between the phenyl ring and the proton at position 8 of the naphthol ring compared to the corresponding distance between the proton at position 3 in the 1-naphthol derivatives. In compounds of type **2** all four protons in position 2 and 6 in the piperidine ring moiety show different chemical shifts. The shift difference between equ-2, equ-6 and ax-2, ax-6 can be partly attributed to the axial-equatorial chemical shift difference [23]. This splitting indicates that piperidine inversion as well as nitrogen inversion connected with hydrogen bond breakage is rather slow. The shift difference between both axial protons in position 2 and 6 is caused by two effects: In addition to the steric influence of the phenyl ring these two protons are in diastereotopic environments as the piperidine ring is bound to an asymmetric

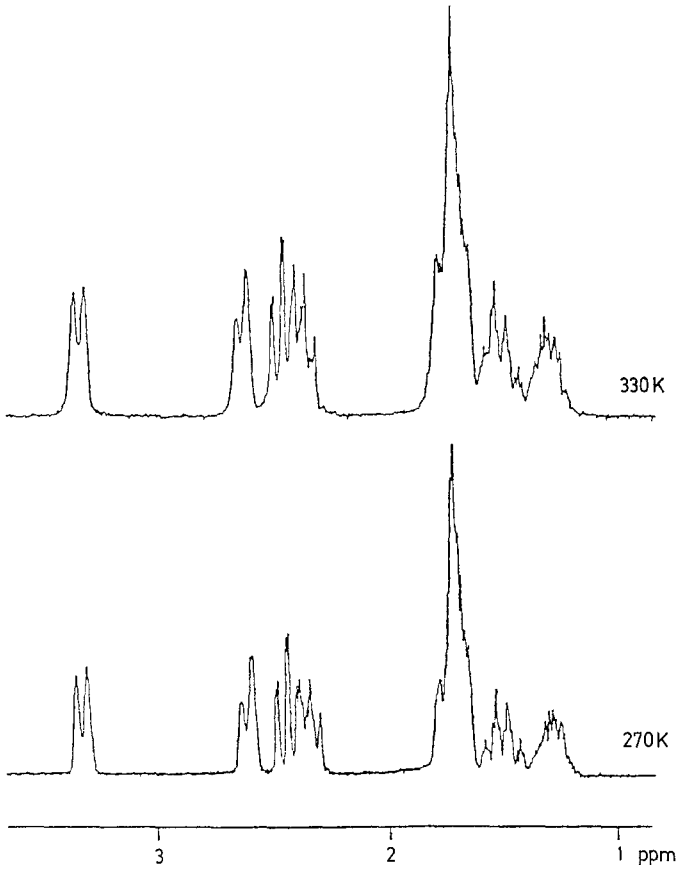


Fig. 3. Piperidine part of the ^{1}H-NMR spectrum of **2i** at 270 K and 330 K

carbon atom. Nevertheless, a comparison to compounds containing identical substructural fragments without hydrogen bonds shows that the shift difference only due to the chiral center is much smaller. Therefore both effects have to be taken into account for an explanation of the shift difference shown in Table 1. In both series of compounds **1** and **2**, no pronounced influence of the substituent in *para*- or *meta*-position at the phenyl ring can be observed.

In contrast to the broad signals of *meta*- or *para*-substituted molecules, *ortho*-substitution causes relatively sharp resonance lines. In Fig. 3, as a typical example the spectrum of the piperidine protons of an *ortho*-substituted compound **2i** is shown. The assignment of these resonance lines was achieved with the help of 2 D-^{1}H-^{13}C shift correlation experiments, as well as by COSY-spectra. Two well separated doublets and two overlapping multiplets were found for the hydrogens at position 2 and 6. The doublets were assigned to the equatorial protons because of their splitting pattern with a large geminal coupling constant and smaller vicinal couplings, which are not resolved in the spectra and are responsible for the line broadening. Both axial hydrogens can be identified by their pattern due to the large geminal, the large vicinal (axial-axial) coupling and the smaller splitting into doublets caused by the equatorial protons at positions 3 and 5, respectively. The small, but significant difference of the equatorial-axial couplings of the axial protons

in position 2 and 6 indicates that the chair conformation of the piperidine ring is slightly distorted. The signal of the equatorial proton at position 4 appears at highest field, well separated from the overlapping signals of the protons at positions 3 and 5 and the axial proton in position 4. Only one large geminal coupling together with various smaller couplings can be observed in that signal. Also the axial proton at position 5 shows an absorption shifted to higher field between the absorption of the overlapping protons and the signal of the equatorial proton at position 4. Three large coupling (two axial-axial and one geminal) together with two smaller couplings can be observed for this proton. These chemical shift values can be compared e.g. with those of phenyladamantylpiperidine (**4**) [24, 25], a compound where one carbon of an adamantane ring system is bound to a phenyl ring and to a piperidine nitrogen atom, leading to a similar but symmetric moiety as in **1** and **2**. This compound has no hydrogen bond but exists in one preferred conformation having the nitrogen lone pair in axial position due to the steric influence of the large aliphatic tricycle. The chemical shift values of the piperidine ring protons of **4** and its hydrochloride derivative **5** are also given in Table 1. The absorption of the 2-equatorial proton of **2i** lies between the values of **4** and **5** where a positive charge at the nitrogen increases the chemical shift values. The hydrogen bond in **2i** increases therefore the shift values too, but as no proton transfer occurs, no pronounced change appears at the piperidine ring. The proton in position 6-equ is mainly influenced by the shielding zone of the aryl ring and is shifted upfield. The resonances of the protons in position 2-ax and 6-ax are again between the corresponding values of **4** and **5**. In contrast to **4** and **5**, in **2i** the chemical shift values of the protons 4-equ and 4-ax are reversed.

Temperature Dependence of ^{1}H-*NMR Spectra*

The ^{1}H-NMR spectra of the *ortho*-substituted compounds of type **2** are more or less identical at room temperature and at low temperature (see Fig. 3), whereas the spectra of the other compounds, especially their piperidine part, are highly temperature dependent. In all cases low temperature leads to relatively sharp absorption lines with the same pattern and assignment as in *ortho*-substituted compounds at room temperature. As a typical example the variable temperature spectra of **2i** are shown in Fig. 3. As below 245 K no change in the spectra can be observed anymore, the chemical shifts of all the compounds can be compared at such a temperature. The chemical shifts of the piperidine protons of compounds of type **1**, **2**, and **3** at 240 K are summarized in Table 2. The signals of the protons in position 2-equ are identical for all compounds and slightly shifted to lower field compared to that of **3**, whereas the resonances of H(6-equ) are shifted to higher field, which can be attributed to the shielding by the phenyl ring. There exists also a small difference of the absorption of the proton 2-equ between compounds of type **1** and **2** which is caused by the different steric interactions of the naphthyl ring with the phenyl ring. A similar difference can also be observed for the proton 6-equ and the proton in position 5-ax. The protons in position 3,5-equ and 6 show more or less no dependence on the aryl substituent as well as on the position of the naphthyl ring. The differences of the resonance positions of the protons in position 2-equ between **1** and **2** are small, but an influence of the aryl substitution

Table 2. Chemical shifts of the piperidine protons together with the methine and hydroxyl protons of compounds of types **1**, **2**, and **3** at 240 K; all values are given in ppm with reference to internal *TMS*

Compound	ppm								
	2-equ	6-equ	2-ax	6-ax	3,5-equ 4-ax	5-ax	4-equ	H_A	H_B
1a	3.31	2.76	2.11	1.89	1.72	1.72	1.23	4.56	13.72
1b	3.30	2.75	2.09	1.87	1.72	1.72	1.24	4.50	13.58
1c	3.29	2.76	2.08	1.89	1.72	1.72	1.24	4.52	13.57
								4.45	13.48
1d	3.38	2.72	2.27	2.20	1.74	1.55	1.27	5.38	13.80
2a	3.32	2.63	2.09	1.92	1.69	1.52	1.24	5.07	14.27
2b	3.31	2.65	2.09	1.92	1.68	1.53	1.24	5.04	14.10
2c	3.31	2.66	2.10	1.94	1.70	1.54	1.25	5.10	14.12
								5.03	14.08
2d	3.31	2.64	2.09	1.94	1.69	1.55	1.24	5.06	14.11
								5.02	14.02
2e	3.30	2.64	2.02	1.94	1.69	1.56	1.26	5.04	14.14
								5.01	14.02
2g	3.32	2.70	2.17	2.13	1.70	1.52	1.25	5.61	14.28
2h	3.31	2.61	2.27	2.32	1.69	1.48	1.24	5.81	14.57
2i	3.32	2.61	2.33	2.43	1.70	1.49	1.26	5.80	14.71
3	3.10		2.12		1.70	1.70	1.27	4.12	13.22

can be observed. An increase of the size of the substituent in *ortho*-position at the phenyl ring causes a downfield shift. The same effect can be observed for the absorption of proton 2-ax. As an explanation for such a dependence, a steric interaction of the *ortho*-substituent has to be assumed, which prevents the aryl ring from rotation and changes the average position of the aryl ring slightly in comparison to *meta*- and *para*-substituted derivatives.

The chemical shift of the methin proton is mainly affected by the naphthyl ring position, where a difference of ca. 0.5 ppm can be detected for the 1- and 2-position at the naphthyl ring. Evidently, the type and position of the substituent on the aryl ring influences the absorption of the methine proton too. The chemical shift of the hydrogen bond proton is strongly dependent on the substitution and it is also, as a special property of such a bond, influenced by the temperature.

An interesting phenomenon is observed for the *meta*-substituted derivatives of both types **1** and **2**. In the low temperature NMR spectra of these compounds a splitting of the methin proton (H_A) and of the hydroxyl proton (H_B) occurs, which can be explained by freezing of the rotation of the phenyl ring. Such a hindrance leads to two energetically nearly equivalent conformations with different orientations of the aryl substituent. Such differences of the substituent influence mainly those signals, which are very sensitive to the substitution, the absorption of H_A and H_B, respectively. For some aromatic protons a considerable splitting can also be observed, but in general the pattern of the naphthyl- and the overlapping phenyl

Table 3. Dynamic data of the piperidine ring inversion of compounds of types **1** and **2**

Compound	Coalescence temperature (K)	ΔG^* (kJ/mol)
1a	285	56.8
1b	282	56.2
1c	280	56.0
1d	320	64.0
2a	325	64.6
2b	325	65.0
2e	325	65.0
2i	ca. 375[a]	ca.75[a]
3	280	54.5

[a] Extrapolated value

protons is complicated and difficult to analyze completely. Compounds with *ortho*-substitution do not show such splittings because only one favorable position of the bulky substituent is possible for steric reasons. In *para*-substituted compounds the two frozen conformations with respect to phenyl ring rotation are identical.

The aforementioned temperature dependence of compounds of type **1** and **2** are caused by dynamic effects. Estimation of the coalescence temperature allows the calculation of the activation barriers. The activation energy together with the coalescence temperature of some selected compounds are given in Table 3. The coalescence temperatures of the *ortho*-substituted compounds of type **2** are higher than 330 K, the highest temperature accessible because of the boiling point of the solvent. Hence, their coalescence temperature and activation energies were estimated by extrapolation of the spectra in comparison to their analogues of type **1**. The coalescence temperature and the calculated ΔG^*-values reflect the steric hindrance of the piperidine ring inversion caused by the aryl ring substitution. The energy of the ring inversion of unsubstituted piperidine has been derived as 43.5 kJ/mol, more or less the same value as for cyclohexane [24]. N-substitution causes an increase of the energy, depending on the electronic properties and the size of the substituent; e.g. an N-methyl substitution enhances ring inversion (and nitrogen inversion) activation energy to 50.2 kJ/mol, chlorine instead of methyl causes an increase to 56.4 kJ/mol [26]. The relatively large alkyl-(hydroxynaphthyl)-substituent in **3** together with hydrogen bonding causes an enhancement of the activation energy to 54.5 kJ/mol. The phenyl substitution at the methylene bridge increases the activation energy drastically in compounds of type **2**, but only slightly in compounds of type **1**. The large values of the activation energies for type **2** compounds are therefore mainly caused by the steric repulsion of the phenyl ring and the naphthyl proton at position 8, which influences the conformation of the piperidine ring and the ring with the hydrogen bond. *Ortho*-substitution at the phenyl ring leads to a much stronger geometric distortion and a considerable increase of the activation energy is therefore observed. The large steric interaction is also reflected in the chemical shift differences discussed before.

Discussion

The molecules whose ^{1}H-NMR spectra were recorded, consist of two aromatic ring systems joined by a sp^3-hybridized carbon atom to which a heterocyclic aliphatic ring is joint with an orientation perpendicular to the naphthyl ring. The nitrogen atom of piperidine forms an intramolecular hydrogen bond to the hydroxyl group at the naphthyl ring, thereby leading to the formation of a six-membered ring. For steric reasons this ring system is not planar, which was shown in the solid phase by X-ray diffraction studies [1], as well as, by empirical [27] and semiempirical [1] calculations of the molecular geometry in gas phase. The existence of an intramolecular hydrogen bond in solution was proved by electron absorption, fluorescence [28] and by NMR-spectroscopic studies [11]. For the compounds and solvents used, there is no indication of proton transfer. The intramolecular processes which can take place in the compounds of type **1** and **2** are summarized in Fig. 4.

Proton transfer of the naphthol proton to the nitrogen is of no importance for conformational changes, because, as mentioned before, the equilibrium is strongly shifted towards the hydrogen bonded system as shown in Fig. 4. The opening of the hydrogen bond would allow a free rotation of the naphthyl ring, of the hydroxyl group, and the piperidine ring around the C−N axis. In addition, hydrogen bond breaking would allow nitrogen inversion. Such a process can be observed in aqueous solution [6] but not in the solvents used in this investigation. Therefore it can be concluded that the barrier to nitrogen inversion will be increased from its normal value by the strength of the hydrogen bond. The movement of the relatively flexible ring including the hydrogen bond is coupled widely with processes of higher activation barriers and cannot be separated from the movements of the other parts of the molecule. Due to the bulky substituents in close vicinity, the equilibrium between various conformations is shifted in such a way that only one favored geometry can be detected. This is in contrast to similar systems, e.g. *o*-hydroxythiobenzamides [29, 30], in which different conformations can be found at frozen equilibrium. The major source for the dynamic phenomena in compounds of type **1** and type **2** is the inversion of the piperidine ring. Again caused by steric repulsion one conformation dominates, but the dynamics of the ring inversion can be clearly observed in the ^{1}H-NMR spectra and its activation barrier can be determined. From the ΔG^*-values it is evident, that hydrogen bonding increases the piperidine ring inversion slightly. The substitution at the methylene bridge by an aryl ring creates a chiral center but there is only a weak influence in the case of *meta*- or

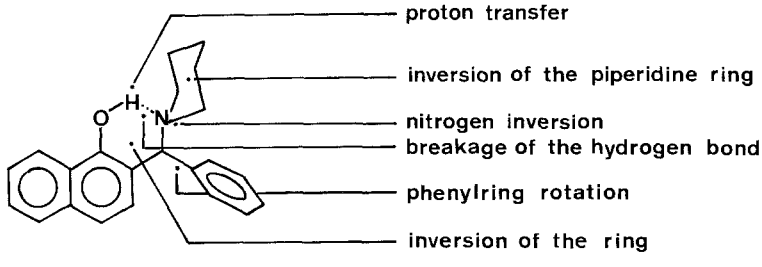


Fig. 4. Possible intramolecular processes of compounds of types **1** and **2**

para-substituted compounds of type **1**, that means that the steric interaction between the aryl ring and the naphthyl ring does not interfere with the dynamics of the piperidine ring. In the case of compounds **2** the free energies of activation increase substantially due to a stronger interaction of the naphthyl ring with the phenyl ring which also influences the piperidine ring geometry. The interaction of the two aromatic ring systems is mainly affected by the steric repulsion of the phenyl ring and the hydrogen at position 8 of the naphthyl ring, which is rather close to the phenyl ring. For this steric reason the rotation axis of the aryl ring is nearly perpendicular to the plane of the naphthyl ring, which can be also observed in the solid state by X-ray diffraction studies. At room temperature the phenyl ring is able to rotate in *para*- and *meta*-substituted compounds. At lower temperatures, the rotation is frozen, which leads to two different conformations for *meta*-substituted compounds. *Ortho*-substituted aryl rings cannot rotate because steric repulsion of the naphthyl ring and the piperidine ring is large in nearby positions. A preferred conformation with the *ortho*-substituent forced into opposite direction with respect to the center of the molecule is established even at room temperature. Additionally the steric interaction of the bulky *ortho*-substituent leads to a drastic increase of ΔG^* in dependence on its size.

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