Porphyrazines with Annulated Diazepine Rings. 3.⊗ Mg^{II} Complex of 4–*tert*–Butylphenyl Substituted Tetra(1,4–diazepino)porphyrazine: Synthesis and Peculiar Effect of Solvent on Its Spectral Properties

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Dedicated to Professor Claudio Ercolani on the occasion of his 75th Birthday.

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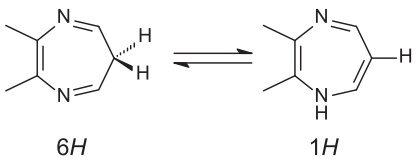
5,7-Di(4-tert-butylphenyl)-6H-1,4-diazepine-2,3-dicarbonitrile, prepared by condensation of di(4-tert-butylbenzoyl) methane with diaminomaleodinitrile, affords upon template cyclotetramerization in the presence of magnesium(II) butoxide in n-butanol the Mg^{II} complex of octa-4-tert-butylphenyl substituted tetra(1,4-diazepino)porphyrazine. The strong solvent effect on its UV-Vis and ^{1}H NMR spectral properties is rationalized in terms of dimerization occurring very likely due to intermolecular hydrogen bonding between diazepine nitrogen atoms and water molecules. The monomer is present exclusively only in diluted solutions of aprotic solvents such as dimethyl sulfoxide and dimethylformamide. Addition of water or methanol leads to dimerization. The dimer exists also in pyridine and tetrahydrofuran solutions, as well in benzene and dichloromethane containing residual water or alcohol. The UV-Vis spectrum of the monomer is typical for Mg^{II} porphyrazines and contains a single Q band at ca. 680 nm. In its ^{1}H NMR spectrum the resonance of the CH_2 protons is not observed at ambient temperatures but appear as a broad signal at 4.4-4.5 ppm above 100 °C, which is characteristic for rapid inversion of the 1,4-diazepine ring in the 6H form. The Q band of the dimer is split into two components (major at 640-645 nm and minor at 680-685 nm). The dimer gives two doublets of the diastereotopic CH_2 protons (5.9-7.1 ppm for the equatorial and 4.8-6.1 ppm for the axial CH_2 protons, depending on the solvent) with characteristic geminal splitting of ca. 11-12 Hz. Formation of the dimer hinders the inversion of diazepine rings and two sharp doublets are observed even above 100 °C.

Keywords: Diazepine annulated porphyrazines, Mg^{II} complex, dimerization, UV-Vis and ^{1}H NMR spectroscopy.

Previously we have reported on the synthesis and properties of porphyrazines with fused 5,7-phenyl substituted 1,4-diazepinerings-symmetricaltetradiazepinoporphyrazines [$Ph_8Dz_4PAH_2$] and its metal complexes [Ph_8Dz_4PAM] (M = 2Li, 2Na, Mg, Zn, Cu, Co, Mn)[1] and low-symmetry monodiazepinotribenzoporphyrazines [Ph_2DzBz_3PAM] (M = 2H, Mg).[2] The annulated 1,4-diazepine rings can exist in principle either in the diimine (6*H*) or in the enamine (1*H*) form (Scheme 1) and some indications have been obtained that spectral properties of diazepinoporphyrazines might be strongly influenced by 6*H*/1*H* tautomerism.

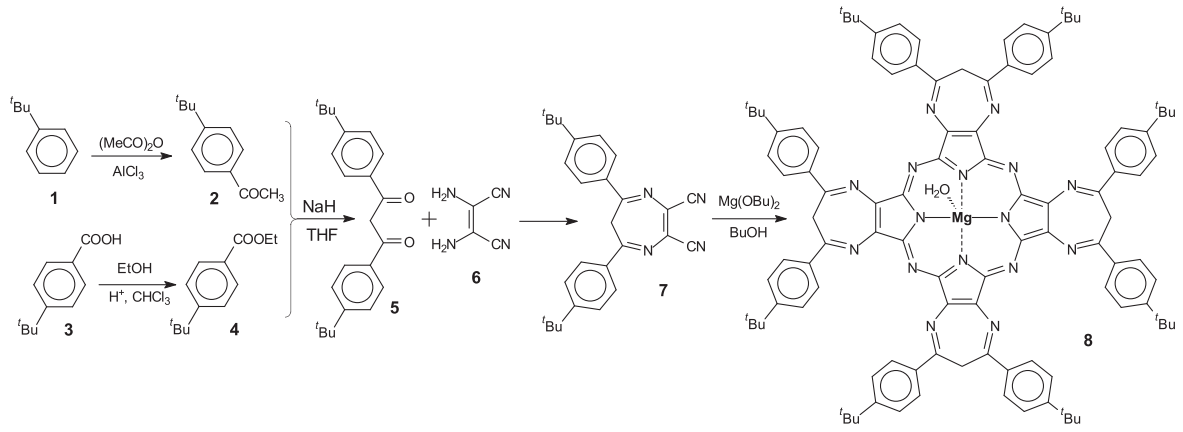


6*H* 1*H*

Scheme 1. 6*H*/1*H* tautomerism of 1,4-diazepines.

The ^{1}H NMR spectra obtained for [Ph_8Dz_4PAM] and [Ph_2DzBz_3PAM] (M = 2H, Mg, Zn) let us to conclude that the annulated 1,4-diazepine rings in these species are present in the 6*H* form. In the case of monoannulated species, typically for other 1,4-diazepines,[3] two doublets of the diastereotopic axial and equatorial CH_2 protons with characteristic geminal splitting of 11-12 Hz were observed at low temperatures, while at elevated temperatures they merge to a singlet due to rapid inversion of the diazepine ring. In contrast to that, in the case of tetraannulated derivatives [Ph_8Dz_4PAM] (M = 2H, Mg, Zn) two sharp CH_2 doublets were observed even at 100°C indicating the rigidity of the diazepine rings in these species to the inversion process. For these species the axial CH_2 doublet is shifted unusually strong to the low field, and in their UV-Vis spectra the double *Q* band is observed, which is non-typical for the symmetrical porphyrazine complexes. The reasons of these phenomena remained so far unclear. In order to obtain derivatives with enhanced solubility in organic solvents enabling more detailed ^{1}H NMR study, in the present work we have prepared 4-*tert*-butylphenyl substituted derivative, which was isolated as the Mg^{II} aqua complex [(^{t}BuPh)$_8$$Dz_4$PAMg($H_2O$)] (**8**) (Scheme 2).

⊗Parts 1 and 2 – see Ref. [1a,b].



Scheme 2. Synthesis of [(^{t}BuPh)$_8$Dz$_4$PAMg(H$_2$O)] (**8**).

Experimental

General

UV-Vis spectra were registered on a Hitachi-U2000 spectrophotometer. ^{1}H NMR spectra were registered on a Bruker Avance 500 MHz instrument in deuterated solvents purchased from Deutero GmbH and were referenced to the residual peak of the corresponding non-deuterated solvent. All chemicals were obtained from Aldrich and used as received. Solvents were distilled prior use.

Synthetic Procedures

*tert-Butylacetophenone **2***. To a stirred suspension of $AlCl_3$ (32 g, 0.24 mol) in dry *tert*-butylbenzene **1** (68.5 g, 0.51 mol) acetic anhydride (10.2 g, 0.1 mol) was added during 30 min and then heated at 100 °C for further 30 min. Cooled reaction mixture was poured on ice, acidified with conc. aqueous HCl to dissolve aluminium hydroxide; organic products were extracted with diethyl ether and, after vacuum distillation, **2** was obtained as an oil (yield 12 g, 66.5%). MS *m/z* = 177 ([M+H]$^+$). ^{1}H NMR ($CDCl_3$) δ ppm: 7.88 (2H, d, Ar*H*), 7.44 (2H, d, Ar*H*), 2.51 (3H, s, C*H*$_3$) 1.31 (9H, s, ^{t}Bu).

*Ethyl tert-butylbenzoate **4***. Mixture of 4-*tert*-butylbenzoic acid **3** (100 g, 0.56 mol), ethanol (46 g, 1 mol), conc. H_2SO_4 (5 ml) in $CHCl_3$ was refluxed till complete separation of water. After cooling the reaction mixture was washed with water and $NaHCO_3$ solution, the organic layer was dried with Na_2SO_4 and the ethyl ester distilled under vacuum (yield 105 g, 90.7%). ^{1}H NMR ($CDCl_3$) δ ppm: 7.79 (2H, d, Ar*H*), 7.43 (2H, d, Ar*H*), 4.35 (2H, q, C*H*$_2$) 1.36 (3H, t, C*H*$_3$) 1.31 (9H, s, ^{t}Bu).

*Di(4-tert-butylbenzoyl)methane **5***. Solution of **2** (17.6 g, 0.1 mol) and **4** (41.3 g, 0.2 mol) in THF (20 ml) was added drop-wise to a stirred suspension of NaH (6 g, 0.15 mol) in anhydrous THF (130 ml) to regulate the gas evolution (*ca*. 1 h). and then for its completion The reaction mixture was refluxed for further 15 min, cooled, and mixed with acetic acid (10 ml) and ice water (100 ml). Organic layer was separated, combined with ether extracts from the aqueous phase (2×100 ml), and dried over $CaCl_2$. The red oily residue after vacuum distillation of the solvent was crystallized by mixing with light petroleum and recrystallized from methanol (30 ml) to give **5** as yellow solid (yield – 20.2 g, 60%). ^{1} H NMR ($CDCl_3$) δ ppm: 16.99 (1H, s, OH), 7.94 (4H, d, Ar*H*), 7.54 (4H, d, Ar*H*), 6.86 (1H, s, C*H*) 1.39 (18H, s, ^{t}Bu).

*5,7-Di(4-tert-butylphenyl)-6H-1,4-diazepine-2,3-dicarbonitrile **7***. To solution of **5** (5 g, 15 mmol) and diaminomaleodinitrile **6** (1.6 g, 15 mmol) in anhydrous ethanol (60 ml) P_2O_5 (1.5 g) was added and the mixture was stirred for 1 h. After addition of further P_2O_5 (1.5 g) the mixture was refluxed for 6 h, then its volume was reduced to 30% by evaporation of the solvent and the precipitate was filtered and washed with ethanol to give **7** as orange crystals (yield 5.77 g, 95%). ^{1}H NMR ($CDCl_3$) δ ppm: 7.92 (4H, d, *J* = 7.6 Hz, Ar*H*), 7.46 (4H, d, *J* = 7.6 Hz, Ar*H*) 5.73 (1H, d, *J* = 11 Hz, C*H*$_2$), 1.96 (1H, d, *J* = 11 Hz, C*H*$_2$), 1.31 (18H, s, ^{t}Bu).

*Mg^{II} complex, [(^{t}BuPh)$_8$Dz$_4$PAMg(H$_2$O)], **8***. Magnesium metal (15 mg) was completely dissolved in dry butanol (30 ml) in the presence of a catalytic amount of I_2 (2-3 hours). The suspension of magnesium butoxide was cooled, the dinitrile **7** (500 mg, 1.22 mmol) was added and the mixture was refluxed for 5-6 h. The dark green solid obtained after evaporation of the solvent was recrystallized from acetone to give the crude Mg^{II} complex **8** (430 mg, yield 85%). The product was further purified by column chromatography (SiO_2, CH_2Cl_2) which gave two fractions containing the Mg^{II} complex as differently hydrated forms **8a** and **8b**.

Mg^{II} complex **8a**. Calc. for $C_{108}H_{112}N_{16}Mg\times4H_2O\times CH_2Cl_2$ (%): C, 72.11; H, 6.77; N, 12.34. Found (%): C, 72.37; H, 6.42; N, 11.82. UV-Vis (CH_2Cl_2) λ_{max} nm (lgε): 345 (5.00), 375 (5.01), 589 (4.12), 640 (5.02), 679 (4.81). ^{1}H NMR (THF-d_8) δ ppm: 8.22 (16H, d, ^3J=7.9 Hz, Ar*H*), 7.41 (16H, d, ^3J=7.9 Hz, Ar*H*), 6.04 (4H, d, ^2J=12.8 Hz, eq-C*H*$_2$) 5.26 (4H, d, ^2J=12.8 Hz, ax-C*H*$_2$) 1.49 (72H, s, ^{t}Bu). Mg^{II} complex **8b**. Calc. for $C_{108}H_{112}N_{16}Mg\times2H_2O$ (%): C, 76.55; H, 6.90; N, 13.23. Found (%): C, 76.57; H, 6.84; N, 12.49.

Results and Discussion

Synthesis

The dinitrile precursor **7** has been obtained according to Scheme 2 starting from *tert*-butylbenzene **1** and *tert*-butyl benzoic acid **3**, which were first converted to *tert*-butylacetophenone **2** and ethyl *tert*-butylbenzoate **4**. Their condensation in the presence of NaH affords di(4-*tert*-butylbenzoyl)methane **5**, existing in the enol form. Its reaction with diaminomaleodinitrile **6** in anhydrous ethanol provides the dinitrile **7**.

Cyclotetramerization of **7** in the presence of magnesium butylate in refluxing *n*-butanol leads to the Mg^{II} complex **8**. It was isolated in two forms **8a** and **8b** obtained in the course of chromatography (SiO_2, CH_2Cl_2) as the 1st major and 2nd minor fractions, respectively. Solid samples obtained from both fractions are differently hydrated species [(^{t}BuPh)$_8$Dz$_4$PAMg(H$_2$O)]×3H$_2$O×CH_2Cl_2 (**8a**) and [(^{t}BuPh)$_8$Dz$_4$PAMg(H$_2$O)]×H$_2$O (**8b**). As is usual for the Mg^{II} complexes of porphyrazines,[1a] one water molecule is assumed to be axially coordinated.

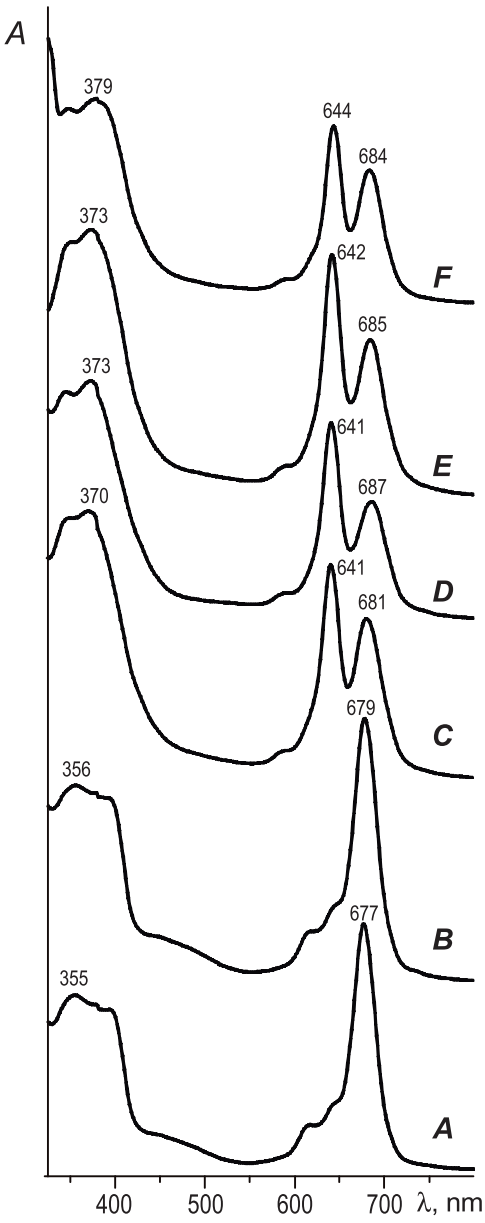


Figure 1. UV-Vis spectra of **8a** in DMF (*A*), DMSO (*B*), CH_2Cl_2 (*C*), THF (*D*), benzene (*E*) and pyridine (*F*). Concentration ~5 μM.

*Spectral Properties of **8a***

UV-Vis spectra of **8a** exhibit a strong solvent dependence (Figure 1) indicating that this complex can exist in two spectroscopically different forms (I and II).

The spectra in DMSO and DMF (type I, see Figure 1 spectra *A*,*B*) contain a single intense absorption band in the visible region (λ_{max} = 679 nm in DMSO and 677 nm in DMF) arising due to the lowest π-π* transition of the symmetrical porphyrazine π-chromophore (*Q* band). The broad Soret band in the UV-region has the main maximum at *ca*. 355 nm and a shoulder at *ca*. 400 nm; in addition a broad less intense absorption is observed in the 420-520 nm region. Such spectral pattern is typical for Mg^{II} porphyrazines. Thus, the single *Q* band for the Mg^{II} complex of octaphenyl substituted porphyrazine [Ph_8PAMg] is observed at 637 nm (in $CHCl_3$)[4] and for Mg^{II} octaphenyltetrapyrazinoporphyrazine [Ph_8Pyz_4PAMg] at 655 nm (in pyridine),[5] while the maxima of the broad Soret bands are located at *ca*. 370 nm for both species. This indicates that annulated diazepine rings in **8a** are stronger involved in the conjugation with the porphyrazine π-chromophore than pyrazine rings in [Ph_8Pyz_4PAMg]. In the case of carbocyclic analog of **8a** – Mg^{II} porphyrazine with fused cycloheptatriene fragments [$Ph_8(HTr)_4$PAMg] – the similar spectrum was observed, but the *Q* band was located at longer wavelength (713 nm in $CHCl_3$)[6] than in **8a** having two electronegative nitrogen atoms in each of the seven-member ring.

Unlike the type I spectra observed in DMSO and DMF, the spectra of **8a** in CH_2Cl_2, THF, benzene, and pyridine (type II, see Figure 1 spectra *C*-*F*) contain two bands in the visible region - the more intense band at *ca*. 640-645 nm (*Q* band) and the less intense band at 680-690 nm (Q_n band). Similar type II spectra in the same solvents were previously reported for non-*tert*-butylated derivative [$Ph_8Dz_4PAMg(H_2O)$].[1a] The more intense visible band was assigned to the porphyrazine π-π*-transition (*Q* band), while the appearance of the long-wave component was connected with the presence of the diazepine ring in the 6*H* form and out-of-plane direction of the lone pairs of nitrogen atoms enabling the change transfer *n*-π* transition from the diazepine ring to the porphyrazine macrocycle.[1a]

However, it should be noted that spectra with similar double *Q* band are typical for bis-porphyrazine complexes having a strong exciton coupling between two adjacent macrocyclic units, *e.g*. for the sandwich and binuclear complexes of porphyrazines and phthalocyanines.[7,8] Therefore alternatively the type II spectra with a double *Q* band can be assigned to dimeric form of **8a** existing in such solvents as CH_2Cl_2, THF, benzene and pyridine.

It is known that aqua-complexes of Mg^{II} porphyrazines and Mg^{II} phthalocyanines can form dimeric species due to intermolecular H-bonding between and nitrogen atoms of one macrocycle (in the *meso*-positions and in the fused heterocycles) and water molecule coordinated to the Mg atom in the neighbouring macrocyclic unit. This kind of dimerization was observed both in the solid state[9] and in $CHCl_3$ solution.[10] However dissolution in pyridine or addition of methanol, which form H-bonds with the coordinated water molecule or substitute it, leads to monomers with a single sharp *Q* band. This is in contrast to the present species for which the type II spectra with a double *Q* band exist both

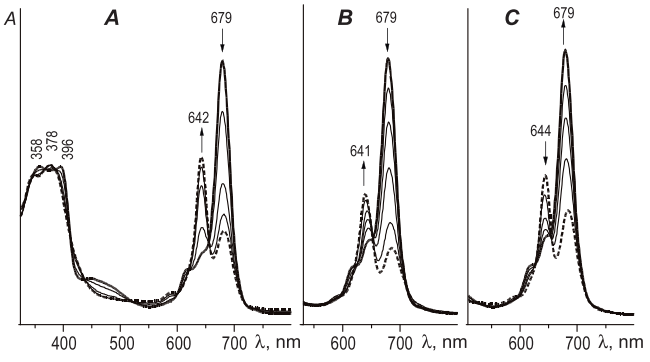


Figure 2. UV-Vis spectra of **8a** in DMSO (bold solid lines) and mixtures of DMSO with MeOH (*A*), H_2O (*B*) and pyridine (*C*). Dashed lines correspond to 50% MeOH (*A*), 20% H_2O (*B*), 100% pyridine (*C*). Thin lines show the intermediate spectra.

in weakly solvating solvents (benzene, CH_2Cl_2, $CHCl_3$) and in strongly coordinating pyridine. Moreover upon addition of pyridine, methanol or even water to the solution of **8a** in DMSO, the type I spectra with a single *Q* band is transformed to the type II spectra containing a double *Q* band (Figure 2). The final spectrum obtained in each case depends on the composition of the binary mixture. Complete conversion to the type II spectrum requires addition of 20% water or 50% MeOH, and occur in 100% pyridine.

[1]H NMR spectra of **8a** (Figure 3, Table 1) also evidence that depending on the solvent this species can exist in different forms I and II and provide further arguments for their assignment as monomer and dimer, respectively. Spectra in non-coordinating and weakly solvating solvents such as C_6D_6 or CD_2Cl_2 (Figure 3 *B*) contain very broad absorption in the aromatic region and evidence about strong association of **8a** in solutions with concentration 1-2 mM. Addition of methanol-d_4 (*ca*. 5%) to a solution of **8a** in C_6D_6 or CD_2Cl_2 leads to a very well resolved spectrum (Figure 3 *C*). Along with two doublets in the aromatic region (8.0-8.3 and 7.3-7.4 ppm, ^3J = 7.9 Hz) belonging to the *ortho*- and *meta*-phenyl protons and a singlet of the *tert*-butyl protons at 1.2-1.5 ppm, two doublets are observed at 6.0-6.5 and 4.8-5.4 ppm. They can be unequivocally assigned on the basis of their integral intensity and characteristic geminal splitting ^2J = 12.2 Hz to the resonances of the diastereotopic CH_2 protons in the equatorial and axial positions (*eq*-CH_2 and *ax*-CH_2). Similar well-resolved spectra are observed in pure Py-d_5 and in THF-d_8 (Figure 3 *D* and *E*). Such spectral pattern is similar with that observed for the dinitrile precursor **7** (Figure 3 *A*) and indicates that in these solvents **8a** exists as a single form II which have all fused 1,4-diazepine rings in the diimine form (6*H* tautomer) with equivalent *tert*-butylphenyl groups.

The solubility of **8a** in DMSO and DMF is lower than in CH_2Cl_2, THF or pyridine. The ^{1}H NMR spectrum of a saturated solution (~0.1 mM) in DMSO-d_6 indicates the presence of two species (Figure 4 *A*). The first one contains the similar set of resonances as the type II form existing in pure pyridine and THF: two doublets of *ortho*- and *meta*-protons in the aromatic region (8.02 and 7.43 ppm), the

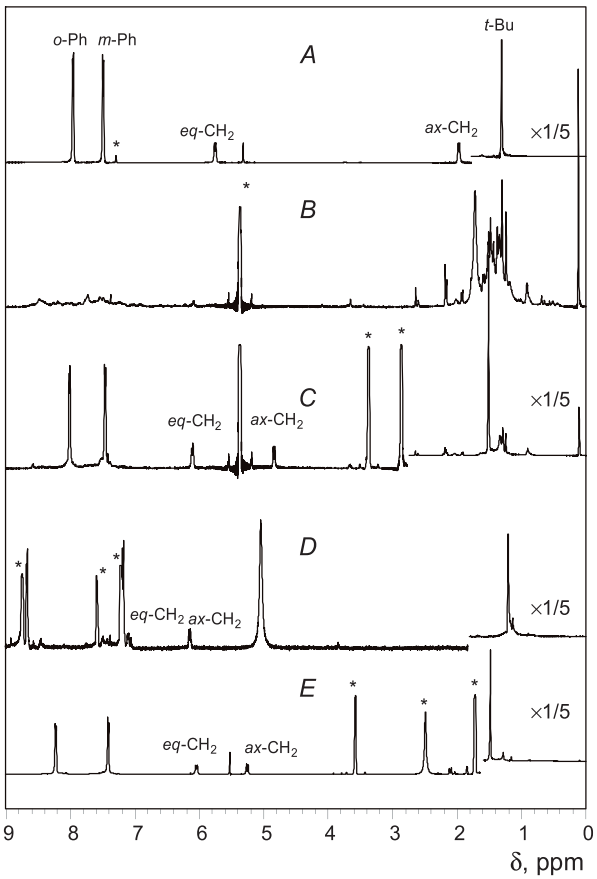


Figure 3. ^{1}H NMR spectra of **7** in CD_2Cl_2 (20 mM) (*A*) and **8a** in CD_2Cl_2 (*B*), CD_2Cl_2 + 5% CD_3OD (*C*), pyridine-d_5 (*D*), and THF-d_8 (*E*). Concentration of **8a** ~1-2 mM. Residual protons of the solvent are indicated by asterisk.

Table 1. Solvent dependence of chemical shifts for **7**, **8a** and related compounds.

Compound	Solvent	Temp.	Chemical shift (δ, ppm)				
			eq-CH_2	*ax*-CH_2	*o*-Ph	*m*-Ph	^{t}Bu/ *p*-Ph
7	$CDCl_3$	r.t.	5.73	1.96	7.92	7.46	1.31
	Py-d_5	r.t.	6.33	2.23	8.30	7.49	1.12
$Ph_2Dz(CN)_2$	$CDCl_3$	r.t.	5.74	1.98	7.93	7.41	7.50
	DMSO-d_6	r.t.	6.19	2.32	n.r.	n.r.	n.r.
$BzDzPh_2$	Py-d_5	223 K	5.66	2.18	n.r.	n.r.	n.r.
		353 K	3.80		n.r.	n.r.	n.r.
8a	C_6D_6 [a]	r.t.	6.46	5.36	8.31	7.27	1.18
	CD_2Cl_2 [a]	r.t.	6.06	4.79	7.96	7.41	1.47
	THF-d_8	r.t.	6.04	5.26	8.22	7.41	1.49
	Py-d_5	r.t.	7.03	6.10	8.63	7.16	1.20
	DMSO-d_6	r.t.	5.93	5.01	8.50	7.66	1.36
					8.02	8.43	1.44
	DMF-d_7	393 K	4.50		8.62	7.67	1.35
			6.12	5.26	8.27	7.50	1.44
[Ph_2DzBz_3-PAMg(H_2O)]	THF-d_8	210 K	6.45	2.55	8.78	7.6-7.7	
	DMSO-d_6	363 K	4.42		8.54	7.6-7.7	

[a] With addition of 5% CD_3OD. r.t. – room temperature; n.r. – not reported.

singlet of the *tert*-butyl group at 1.44 ppm and two broad signals of diastereotopic CH_2 protons at 5.93 and 5.01 ppm. For the other species the signals of *ortho*- and *meta*-protons are observed in a lower field (8.50 and 7.66 ppm); the *tert*-butyl singlet is at 1.36 ppm and the signal of the CH_2 protons is absent. In the spectrum of diluted solution (0.027 mM, Figure 4 *B*) the intensity of signals at 8.02, 7.43 and 1.44 ppm characteristic for the type II form is decreased and two resonances of the CH_2 protons practically disappear. It was possible to record the UV-Vis spectrum of this 0.027 mM solution in a thin cuvette (Figure 5 insert *C*, solid line). It corresponds to a type I form (*Q* band at 679 nm) with some admixture of the type II form (a small maximum at 640 nm) which disappears completely only in a more diluted solution (0.004 mM, Figure 5 insert *C*, dotted line). These data show that type I form of **8a** is predominant in the diluted DMSO solutions while in saturated ones it coexists with the type II form.

The positions of the *ortho*- and *meta*-proton resonances for the type I form (8.50 and 7.66 ppm) are similar with the corresponding *ortho*- and *meta*-phenyl resonances in the spectrum of the monodiazepine derivative [Ph_2DzBz_3PAMg] (8.5 and 7.6 ppm in DMSO-d_6[2]). The absence of the CH_2 signals corresponding to this set of *tert*-butylphenyl resonances is explained by rapid inversion of the diazepine rings leading to strong broadening of resonances in the spectra measured near the coalescence temperature T_c. Very often 1,4-diazepine derivatives have the T_c value close to ambient temperatures, and resonances of the diastereotopic CH_2 protons can be observed only at low temperatures as two doublets or as a singlet at elevated temperatures.[3] Indeed, in the case of monodiazepinoporphyrazine [Ph_2DzBz_3PA-$Mg(H_2O)$] the CH_2 resonances also could not be seen at room temperature (the coalescence temperature T_c ~ 265 K), but can be observed as two doublets below 210 K (6.45 and 2.55 ppm in THF-d_8) and or as a singlet at 4.42 ppm at elevated temperature (363 K in DMSO-d_6).[2]

For our Mg^{II} complex **8a** we have also recorded the ^{1}H NMR spectra in DMSO-d_6, in DMF-d_7 and in Py-d_5 at various temperatures. The high temperature spectra recorded in DMSO-d_6 were only of very poor quality in the 3-5 ppm region, probably due to large water content. However, in the spectrum recorded at 393 K there was an indication for the appearance of a new broad signal at *ca*. 4.4 ppm. The signal of the CH_2 protons under conditions of the rapid inversion of diazepine rings can be better seen in DMF-d_7 at 393 K (Figure 5). This spectrum contains two set of signals - 8.62 and 8.27 ppm for *ortho*-, 7.67 and 7.50 ppm for *meta*-phenyl protons, 1.35 and 1.44 ppm for *tert*-butyl protons indicating that two forms of **8a** (I and II) coexist in a saturated DMF-d_7 solution. In addition to the equatorial and axial CH_2 signals of the type II set (6.12 and 5.26 ppm), the broadened signal corresponding to the type I set appears at 4.50 ppm above 370 K. Unfortunately, at low temperatures the solubility in DMF is decreased and strong association occurs. This does not allow us to observe the splitting of this signal in the conditions of a slow ring inversion process.

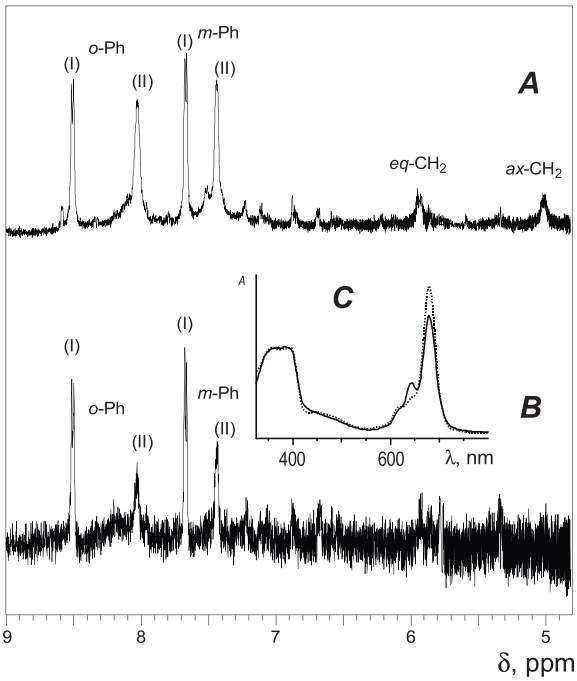


Figure 4. ^{1}H NMR spectra of **8a** in DMSO-d_6 at 298 K. *A* - saturated solution (*ca*. 0.1 mM); *B* - diluted solution (0.027 mM). The UV-Vis spectrum of this solution is shown in the insert *C* (solid line) in comparison with the spectrum of 0.004 mM solution (dotted line).

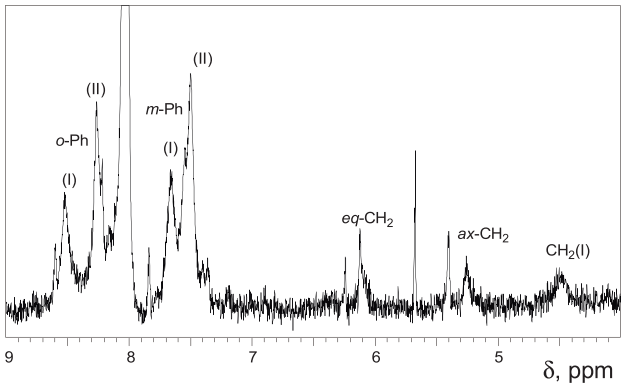


Figure 5. ^{1}H NMR spectra of **8a** in DMF-d_7 at 393 K (saturated solution).

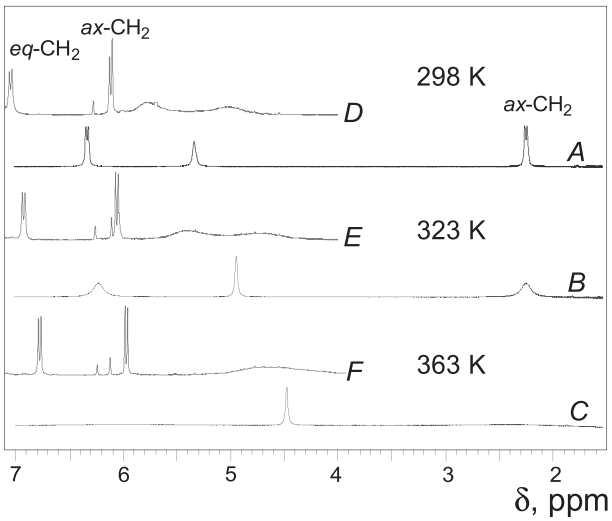


Figure 6. Temperature dependence of the α-CH_2 resonances in the ^{1}H NMR spectra of **7** (20 mM) (*A*-*C*) and **8a** (5 mM) (*D*-*F*) in pyridine-d_5.

We have also studied the influence of temperature on the ^{1}H NMR spectra of the dinitrile precursor **7** and the Mg^{II} complex **8a** in Py-d_5 solutions (Figure 6).

In the case of the dinitrile **7** two doublets of diastereotopic CH_2 protons (2.25 and 6.33 ppm) with characteristic geminal splitting ^2J = 11 Hz are observed already at room temperature and disappear upon heating (Figure 6 *A*-*C*). Their position is typical for other 1,4-diazepine derivatives having the 6*H* form, but the coalescence temperature (T_c ~ 363 K in Py-d_5) is higher, which might be connected with electron-withdrawing influence of the CN-groups increasing the rigidity of the diazepine ring to the inversion process. For 5,7-diphenyl-2,3-benzo-1,4-diazepine[3] in Py-d_5 the T_c ~ 273 K and two CH_2 doublets observed only upon cooling (2.18 and 5.66 ppm at 223 K) merge to a singlet at elevated temperature (3.80 ppm at 353 K). It is remarkable that for the Mg^{II} complex **8a** the doublets of the CH_2 protons are retained sharp in a Py-d_5 solution even at elevated temperatures (Figure 6 *D*-*F*). Moreover, for **8a** the resonances of the equatorial and especially of the axial CH_2 protons (7.03 and 6.10 ppm in Py-d_5, respectively) are shifted to the low field as compared to the dinitrile **7** (by 0.7 and 3.9 ppm) or other compounds containing 1,4-diazepine ring in the 6*H* form (*e.g.* 5,7-diphenyl-2,3-benzo-1,4-diazepine or Mg^{II} complex of monodiazepinoporphyrazine [$Ph_2DzBz_3PAMg(H_2O)$]). At the same time the resonances of aromatic protons in the *ortho*- and *meta*-positions of the phenyl rings for the form II of **8a** are shifted to the stronger field as compared to the form I and monodiazepine species [$Ph_2DzBz_3PAMg(H_2O)$].

All these peculiarities that are observed in the ^{1}H NMR spectra of the form II being in agreement with double *Q* band in its UV-Vis spectra are indicative about a dimeric nature of this form. One can suppose that the dimer can be formed due to hydrogen bonding between diazepine nitrogens of two neighbouring macrocycles occuring with participation of water and/or other solvent molecules. As can be seen from Table 1 the solvent has a considerable influence on the chemical shifts of the protons in the form II, especially on the position of CH_2 doublets. Molecular model of one of various possible dimeric structures (Figure 7) illustrates that due to steric hindrance between two adjacent parallel macrocyclic units only a single boat shape conformation is possible for all diazepine rings and they should be resistant to the inversion process. Influence of the π-ring currents in the adjacent macrocycle and phenyl rings causes the observed shifts of the proton resonances in the dimeric form II as compared to the monomer I and monodiazepinoporphyrazine [Ph_2DzBz_3PA-$Mg(H_2O)$]. Very strong down-field shift observed for the resonance of the axial proton of the CH_2 group might indicate that this proton due to its considerable acidic properties is also involved in hydrogen bonding.

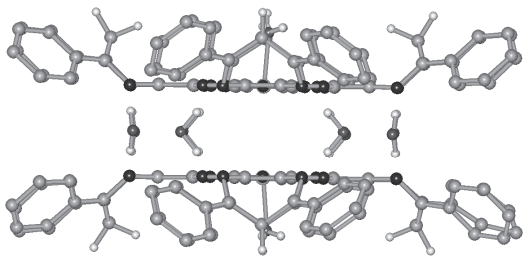


Figure 7. One of possible structures for the dimeric form of **8a**, obtained by molecular modeling.

The dimer is stable in solvents, which can not compete with the diazepine nitrogens in H-bonding with water molecule (CH_2Cl_2, benzene, THF, pyridine and other similar solvents). However upon dissolution in aprotic solvents such as DMF and DMSO the dimers are destroyed since these solvents, strongly solvating water, "extract" water molecules from the dimeric units. The dimerization occurs again when excess of water is added.

*Spectral Properties of Form **8b***

The form **8b** obtained as the 2nd minor fraction during chromatography of the crude Mg^{II} complex **8**, has lesser content of hydrated water. The preliminary spectral study indicates that less hydrated form **8b** is most likely a monomer, which is dimerized in the appropriate conditions. Indeed, both UV-Vis and ^{1}H NMR spectra of **8b** recorded promptly after dissolution in solvents, in which form **8a** exists exclusively as a dimer, correspond to the mixture of two species. Thus, the spectrum in CH_2Cl_2 contains in the visible region two bands of almost equal intensity at 643 and 683 nm. In the ^{1}H NMR spectra in Py-d_5 two set of signals are observed. The minor set (aromatic doublets at 8.65 and 7.16 ppm, CH_2 doublets at 7.04 and 6.11 and *tert*-butyl singlet at 1.21 ppm) is similar to the signals observed for **8a** (form II). The other set contains aromatic multiplets at 8.4-8.5 ppm and 7.4-7.5 ppm and *tert*-butyl singlets at 1.14-1.17 ppm.

Conclusions

Mg^{II} complex of tetradiazepinoporphyrazine bearing two *tert*-butylphenyl groups in each annulated diazepine ring has being prepared. Its UV-Vis and ^{1}H NMR spectra exhibit a strong solvent dependence, which is interpreted as being due to the presence of dimeric and/or monomeric forms. Evidence has being obtained that hydrated complex exists in the dimeric form which is stable in nonsolvating solvents (CH_2Cl_2, benzene), in THF and pyridine. The monomeric form exist only in diluted aprotic solvents like DMF and DMSO, while concentrated solutions contain mixture of the monomeric and dimeric forms. Addition of water or methanol to diluted DMSO solution also leads to dimerization. It is supposed that dimerization occurs due to hydrogen bonding between the diazepine nitrogen atoms in the neighbouring macrocyclic units through intermediate water and solvent molecules. Study of the free base macrocycle and complexes with transition metals as well as the preparation of single crystals suitable for X-Ray diffraction study are in progress.

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