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 75\(^{th}\) Birthday.

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-diazepinering-symmetrical tetradiazepinoporphyrinazines [Ph\(_8\)Dz\(_4\)PAH\(_2\)] and its metal complexes [Ph\(_8\)Dz\(_4\)PAM] (M = 2Li, 2Na, Mg, Zn, Cu, Co, Mn)\(^{[1]}\) and low-symmetry monodiazepinotribenzoporphyrazines [Ph\(_2\)DzBz\(_3\)PAM] (M = 2H, Mg).\(^{[2]}\) The annulated 1,4-diazepine rings can exist in principle either in the diimine (6H) or in the enamine (1H) form (Scheme 1) and some indications have been obtained that spectral properties of diazepinoporphyrinazines might be strongly influenced by 6H/1H tautomerism.

\(^*\)Parts 1 and 2 – see Ref. \(^{[1,2]}\).

The \(^1\)H NMR spectra obtained for [Ph\(_8\)Dz\(_4\)PAM] and [Ph\(_2\)DzBz\(_3\)PAM] (M = 2H, Mg, Zn) let us to conclude that the annulated 1,4-diazepine rings in these species are present in the 6H 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\(_8\)Dz\(_4\)PAM] (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 substitut- ed derivative, which was isolated as the Mg\(^{II}\) aqua complex [(\(t\)BuPPh)\(_8\)Dz\(_4\)PAMg(H\(_2\)O)] (8) (Scheme 2).
Experimental

General

UV-Vis spectra were registered on a Hitachi-U2000 spectrophotometer. 1H 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 AlCl3 (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+). 1H NMR (CDCl3) δ ppm: 7.44 (2H, d, ArH), 4.35 (2H, q, C-H), 1.36 (3H, t, CH3) 1.31 (9H, s, t-Bu).

Di(4-tert-butylbenzylo)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 CaCl2. 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%). 1H NMR (CDCl3) δ ppm: 7.43 (2H, d, ArH), 7.46 (4H, d, ArH); 6.04 (4H, d, J=12.8 Hz, eq-C-H); 5.26 (4H, d, J=12.8 Hz, ax-C-H) 1.49 (72H, 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 diamonomaleodinitrile 6 (1.6 g, 15 mmol) in anhydrous ethanol (60 ml) P2O5 (1.5 g) was added and the mixture was stirred for 1 h. After addition of further P2O5 (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%). 1H NMR (CDCl3) δ ppm: 7.92 (4H, d, J=7.6 Hz, ArH), 7.46 (4H, d, J=7.6 Hz, ArH); 5.73 (1H, d, J=11 Hz, CH3); 1.96 (1H, d, J=11 Hz, CH2); 1.31 (18H, s, Bu).

MgII complex [([BuPh)DzPAMg(H2O)]) (8). Magnesium metal (15 mg) was completely dissolved in dry butanol (30 ml) in the presence of a catalytic amount of I2 (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 MgII complex 8 (430 mg, yield 85%). The product was further purified by column chromatography (SiO2, CH2Cl2) which gave two fractions containing the MgII complex as differently hydrated forms 8a and 8b.

MgII complex 8a. Calc. for C108H112N16Mg4H2O8: C, 72.11; H, 6.77; N, 12.34. Found (%): C, 72.37; H, 6.42; N, 11.82. UV-Vis (CH2Cl2) λmax nm (ε): 345 (5.00), 375 (5.01), 589 (4.12), 640 (5.02), 679 (4.81). 1H NMR (THF-d8) δ ppm: 7.79 (16H, s, t-BuPh), 6.04 (4H, d, J=12.8 Hz, eq-C-H), 5.26 (4H, d, J=12.8 Hz, ax-C-H) 1.49 (72H, s, t-Bu).

MgII complex 8b. Calc. for C108H112N16Mg4H2O8: C, 76.55; H, 6.90; N, 13.23. Found (%): C, 76.57; H, 6.84; N, 12.49.

Result 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-butylbenzylo)methane 5, existing in the enol form. Its reaction with diamonomaleodinitrile 6 in anhydrous ethanol provides the dinitrile 7.

Cyclotetramerization of 7 in the presence of magnesium butylate in refluxing n-butanol leads to the MgII complex 8. It was isolated in two forms 8a and 8b obtained in the course of chromatography (SiO2, CH2Cl2) as the major and 2nd minor fractions, respectively. Solid samples obtained from both fractions are differently hydrated species ([([BuPh)DzPAMg(H2O)])×3H2O×CH2Cl2 (8a) and ([([BuPh)DzPAMg(H2O)])×H2O (8b)]. As is usual for the MgII complexes of porphyrazines,1a one water molecule is assumed to be axially coordinated.
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Figure 1. UV-Vis spectra of 8a in DMF (A), DMSO (B), CH₂Cl₂ (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_m = 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 MgII porphyrazines. Thus, the single Q band for the MgII complex of octaphenyl substituted porphyrazine [Ph₈PAMg] is observed at 637 nm (in CHCl₃)[6] and for MgII octaphenyltetrapyrazinoporphyrazine [Ph₈Pyz₄PAMg] 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 [Ph₈Pyz₄PAMg]. In the case of carbocyclic analog of 8a – MgII porphyrazine with fused cycloheptatriene fragments [Ph₈(HTr)PAMg] – the similar spectrum was observed, but the Q band was located at longer wavelength (713 nm in CHCl₃)[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 CH₂Cl₂, 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 (Q̂ band). Similar type II spectra in the same solvents were previously reported for non-tert-butylated derivative [Ph₈Dz₄PAMg(H₂O)].[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 6H 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-porphyrin complexes having a strong exciton coupling between two adjacent macrocyclic units, e.g. for the sandwich and binuclear complexes of porphyrinanes 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 CH₂Cl₂, THF, benzene and pyridine.

It is known that aqua-complexes of MgII porphyrazines and MgII phthalocyanines can form dimeric species due to intermolecular H-bonding between 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 CHCl₃ 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 in DMSO and DMF, and mixtures of DMSO with MeOH (A), H₂O (B) and pyridine (C). Dashed lines correspond to 50% MeOH (A), 20% H₂O (B), 100% pyridine (C). Thin lines show the intermediate spectra.
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in weakly solvating solvents (benzene, CH\textsubscript{2}Cl\textsubscript{2}, CHCl\textsubscript{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\textsubscript{6}D\textsubscript{6} or CD\textsubscript{2}Cl\textsubscript{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\textsubscript{4} (ca. 5%) to a solution of 8a in C\textsubscript{6}D\textsubscript{6} or CD\textsubscript{2}Cl\textsubscript{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, $^J = 7.9$ Hz) belonging to the ortho- and meta-phenyl protons and a singlet of the tert-butyl protons at 1.2-1.5 ppm. 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\textsubscript{2} protons in the equatorial and axial positions (eq-CH\textsubscript{2} and ax-CH\textsubscript{2}). Similar well-resolved spectra are observed in pure Py-d\textsubscript{5} and in THF-d\textsubscript{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 (6H tautomer) with equivalent tert-butylphenyl groups.

The solubility of 8a in DMSO and DMF is lower than in CH\textsubscript{2}Cl\textsubscript{2}, THF or pyridine. The $^1$H NMR spectrum of a saturated solution (~0.1 mM) in DMSO-d\textsubscript{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\textsubscript{2}Cl\textsubscript{2} (20 mM) (A) and 8a in CD\textsubscript{2}Cl\textsubscript{2} (B), CD\textsubscript{2}Cl\textsubscript{2} + 5% CD\textsubscript{3}OD (C), pyridine-d\textsubscript{5} (D), and THF-d\textsubscript{8} (E). Concentration of 8a ~1-2 mM. Residual protons of the solvent are indicated by asterisk.](image)

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<th>Table 1. Solvent dependence of chemical shifts for 7, 8a and related compounds.</th>
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<td><strong>Compound</strong></td>
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<td><strong>Chemical shift (δ, ppm)</strong></td>
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* With addition of 5% CD\textsubscript{3}OD. 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 (8.5 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 monodiazipine derivative [Ph,DzBz,PAMg] (8.5 and 7.6 ppm in DMSO-d$_6$). 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. Indeed, in the case of monodiazipineporphyrazine [Ph,DzBz,PA- Mg(H$_2$O)] 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$_4$) and or as a singlet at 4.42 ppm at elevated temperature (363 K in DMSO-d$_6$).

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](image1.png)

**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](image2.png)

**Figure 5.** $^1$H NMR spectra of 8a in DMF-d$_7$ at 393 K (saturated solution).

![Figure 6](image3.png)

**Figure 6.** Temperature dependence of the $\alpha$-CH$_2$ resonances in the $^1$H NMR spectra of 7 (20 mM) (*A-C*) and 8a (5 mM) (*D-F*) in pyridine-d$_5$. 
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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-\(d_6\) solutions (Figure 6).

In the case of the dinitrile 7 two doublets of diastereotropic CH\(_2\) protons (2.25 and 6.33 ppm) with characteristic geminal splitting \(J = 11\) 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 \((T_c \sim 363\) K in Py-\(d_6\)) 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-\(d_6\), the \(T_c \sim 273\) 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-\(d_6\) 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-\(d_6\), 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 monodiazepinophosphoryazine \([\text{Ph},\text{DzBz},\text{PAMg(H}_2\text{O})]\)). 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 \([\text{Ph},\text{DzBz},\text{PAMg(H}_2\text{O})]\).

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 occurring 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 \(\pi\)-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 monodiazepinophosphoryazine \([\text{Ph},\text{DzBz},\text{PA-Mg(H}_2\text{O})]\). 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.

The dimer is stable in solvents, which can not compete with the diazepine nitrogens in H-bonding with water molecule (CH\(_2\)Cl\(_2\), 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 2\(^{nd}\) 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\(_2\)Cl\(_2\) contains in the visible region two bands of almost equal intensity at 643 and 683 nm. In the \(^1\)H NMR spectra in Py-\(d_6\), two doublets of diastereomers at \(8.4-8.5\) ppm and \(7.4-7.5\) ppm are shifted to the stronger field as compared to the dinitrile 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 tetradiazepinophosphoryazine bearing two tert-butylphenyl groups in each annulated diazepine ring has been 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 been obtained that hydrated complex exists in the dimeric form which is stable in nonsolvating solvents (CH\(_2\)Cl\(_2\), 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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Figure 7. One of possible structures for the dimeric form of 8a, obtained by molecular modeling.
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