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INVESTIGATION OF UNSUBSTITUTED PORPHYRAZINE BY PROTON NMR AND THE STRUCTURE OF PORPHYRAZINE LIGANDS

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The proton NMR spectra of unsubstituted porphyrazine (tetraazaporphine) and of its Zn complex in pyridine-D_5 and in CF_3COOD have been obtained for the first time. The observed strong deshielding of the pyrrole hydrogen atoms of these compounds compared with porphyrins indicates the existence of strong intramolecular hydrogen bonds with neighboring pyrrolenic nitrogen atoms. An unsymmetrical bridge structure is proposed for the reaction center of unsubstituted porphyrazine with significantly ionized N−H bonds. It is suggested that a symmetrical bridge structure, almost completely ionized, may exist only in the presence of such strong electron-accepting substituents as halogen in the pyrrole rings of the porphyrazine macrocycle.

Unsubstituted porphyrazine or H_2Pz (Ia), also known as tetraazaporphine H_2TAP, was obtained for the first time by Linstead and Whalley in 1952 [1]. However, it has been studied little up to the present compared with porphine H_2P and phthalocyanine H_2Pc (tetrabenzoporphyrazine), which are related to it structurally. Numerous studies on H_2Pz have been devoted to an investigation of its coordinating activity [2-5], its state and stability in acidic media [6-8], determination of its acid dissociation constants [9], and analysis of the electronic luminescence and IR spectra [10]. The molecule of compound (Ia) has been the subject of several quantum chemical investigations in which the parameters of the electronic absorption [11-14] and PMR [15] spectra were calculated. However, the PMR spectra of unsubstituted H_2Pz or of its complexes have not been obtained experimentally up to the present. The data on substituted derivatives $H_2PzR_4R_4^1$ (Ib-d) [16-19] show the presence of a significant low field shift for the signal of the intracyclic protons of the NH grouping (H_{NH}) compared with porphyrins themselves and with the estimated value for H_2Pz [15]. The difference in position of the H_{NH} proton signal for octaethylporphyrazine (Ib) ($\delta_{NH} = -2.21$ ppm) [16] and for tetra(t-butyl)porphyrazine (Ic) ($\delta_{NH} = -2.45$ ppm) [17, 18], and also for the tetrabromo derivative (Id) ($\delta_{NH} = +1.43$ ppm) [19] proved to be unusually large. The PMR spectra of unsubstituted porphyrazine (Ia) and of its Zn complex ZnPz (II) have been investigated for the first time in the present study to clarify the nature of such strong influences of substituents on the chemical shift of the H_{NH} protons in porphyrazines.

The PMR spectrum of compound (Ia) in Py-D_5 (Fig. 1a) contains two singlets. The resonance of the protons of the β-carbon atoms of the four pyrrole rings was observed at low field (8H, $\delta_{CH} = 9.24$ ppm) and the signal of the intracyclic H_{NH} protons, heavily screened by the π-electron ring current of the macrocycle, was found at high field (2H, $\delta_{NH} = -0.97$ ppm). There was only one singlet for the β-protons ($\delta_{CH} = 9.40$ ppm) in the PMR spectrum of the Zn complex (II) in Py-D_5 (Fig. 1c). Unlike the spectra in Py-D_5, only one broad signal belonging to the β-protons was observed in CF_3COOD for both compounds [$\delta_{CH} = 9.45$ for ZnPz (II) and $\delta_{CH} = 9.29$ ppm for H_2Pz (Ia)] (Fig. 1b).

The data of the PMR spectra enable certain special features of the structure of the macrocyclic ligand to be clarified. They may be particularly useful for solving the problem of the character of the N−H bond in the reaction center and of the localization of the intracyclic hydrogen atoms. However, structure A has been established for porphine H_2P with localized NH bonds (bonded structure) [20], and structure B with completely ionized N−H bonds has been proposed for H_2Pz [9]. The first contains two pairs of nonequivalent pyrrole rings, and in the second all the pyrrole rings are equivalent, but there are β-protons of two types. Consequently, two signals must be observed for the β-protons in both cases. However, only one signal was observed for these protons for H_2P ($\delta_{CH} = 9.53$ ppm) [21] as a result of tautomerism with the intracyclic NH grouping. It was split only at low temperatures (about −20°C). Separation of the β-proton singlet was not observed for H_2Pz on reducing the temperature to −35°C (freezing of the pyridine limits the possibility of measuring at −69°C in the case of $H_2Pz(t\text{-}Bu)_4$ (Ic)

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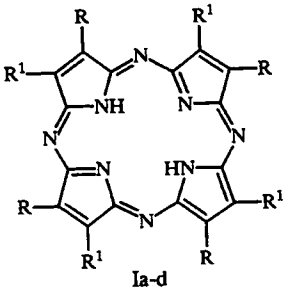
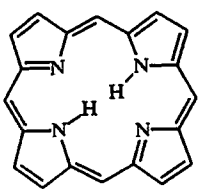
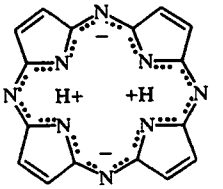


Ia-d

a $R = R^1 = H$; b $R = R^1 = Et$;
c $R = H$, $R^1 = t$-Bu; d $R = H$, $R^1 = Br$



A



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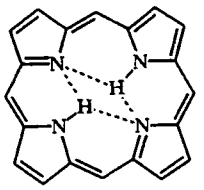
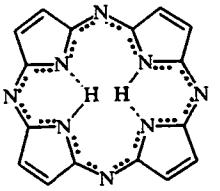
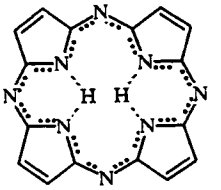


C



D



E

in CS_2 [17]. The lower coalescence temperature for porphyrazines points more in favor of a delocalized structure such as the ionized form B, in which the proton exchange process must occur at a rate greater than in form A with localized N−H bonds. For the delocalized structure B, the role of the inner 16-membered loop of π-conjugation grows, and as a result the $C\beta = C\beta$ bond becomes more isolated than in the localized structure A. The observed high field shift for the β-protons in H_2Pz (Ia) compared with H_2P confirms the greater isolation of the β-carbon atoms from the main conjugation loop.

More reliable evidence for the ionic character of the NH bonds in porphyrazines is given by an analysis of the chemical shifts of the H_{NH} protons (see Table 1). The signal of the latter in H_2Pz (Ia) is shifted strongly towards high field (by almost 3 ppm) compared with H_2P ($\delta_{NH} = -3.94$ ppm [21]). Since tetraaza substitution in porphyrins increases the aromaticity of the macrocycle [15, 23] and at the same time reduces the size of the central coordination area [24, 25], a shift towards high field might be expected for the resonance of the H_{NH} protons. Estimates based on calculation of the π-electron ring current predict a high field shift of 0.8 ppm as a result of meso substitution of the four methine bridges (=CH-) in H_2P by four aza bridges (=N-) in H_2Pz [15]. Consequently, the observed opposite low field shift of 3 ppm may be linked only with changes in the state of the N−H bonds themselves. Their strong polarization and consequent increase in the positive charge on the intracyclic hydrogen atoms in H_2Pz, the lower shielding of the H_{NH} protons by the π-electron ring current must be displayed as a low field shift of the resonance of the latter. Calculation of the chemical shift of the N_{HN} protons carried out in [15] was based on the localized structure A. For H_2P, where in fact a similar structure is present, a very good agreement with experiment was achieved (calculated value $\delta_{NH} = -3.82$ ppm, experimental −3.94 ppm [21]). The calculated value for H_2Pz obtained for a structure of type A ($\delta_{NH} = -4.62$ ppm) differed markedly from the experimental determined in the present study ($\delta_{NH} = -0.97$ ppm). Consequently to achieve more correct results it is necessary to use a model taking into account the strong ionic character of the N−H bonds in porphyrazines.

Structure C, allowing for the presence of weak hydrogen bonds, has already been proposed for porphyrins themselves [26, 27]. Although in structure C the intracyclic hydrogen atoms also do not deviate from the lines connecting opposite pyrrole nitrogen atoms, each of them forms two equivalent hydrogen bonds with two neighboring nitrogen atoms. There are no x-ray structural data up to the present for porphyrazine ligands, but analysis of the structurally related phthalocyanine (tetrabenzoporphyrazine) carried out by Fleischer [28] showed that the hydrogen atoms are located near the line connecting the opposite meso nitrogen atoms. The quantum chemical calculations of Berkovitch−Yellin and Ellis [14] also point in favor of a bridge structure for both H_2Pc and H_2Pz.

The strong ionic character of the N−H bonds in porphyrazines is confirmed by data on their acid dissociation. The acid dissociation constant for H_2Pz proved to be ten orders of magnitude greater than for H_2P (pK_a values in DMSO were 12.36 [9] and 22.35 [29] respectively). However, the completely ionized structure B, suggested for H_2Pz on the basis of these data [9], seems too idealized. It cannot explain the strong effect of substituents on the chemical shift of the H_{NH} protons. For several porphyrazines it is better to use one of the models with a strong intramolecular hydrogen bond, in which there is either

TABLE 1. Chemical Shifts of NH Protons (δ_{NH}, ppm) for Porphyrins and Porphyrazines

Compound	δ_{NH}, ppm	Literature
Porphine H_2P	-3,94	[21]
Octaethylporphine H_2PEt_8	-3,4	[22]
Porphyrazine H_2Pz	-0,97	This study
Octaethylporphyrazine H_2PzEt_8	-2,21	[18]
Tetra(t-butyl)porphyrazine, $H_2Pz(t\text{-}Bu)_4$	-2,45	[16, 17]
Tetrabromoporphyrazine, H_2PzBr_4	+1,43	[19]

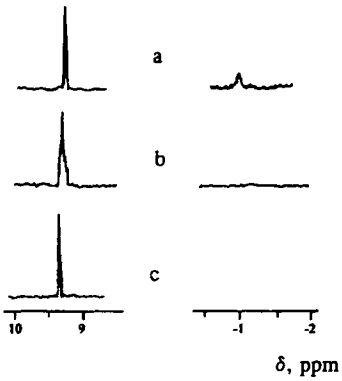


Fig. 1. PMR spectra of compounds (Ia) (a, b) and (II) (c) in Py-D_5 (a, c) and in CF_3COOD (b).

an unsymmetrical hydrogen bond $N^{\delta'-} - H^{\delta+} \ldots N^{\delta-}$ (structure D) or a symmetrical three-center bond $N^{\delta-} \ldots H^{2\delta+} \ldots N^{\delta-}$ (structure E). Within the framework of these models it is easy to explain the existence of a correlation between the dissociation constants and the chemical shift of the H_{NH} protons for porphyrins and porphyrazines (Fig. 2). Azo substitution in the meso positions reduces the size of the central coordination cavity of the porphyrin macrocycle [25] while improving the condition of the intramolecular hydrogen bond. This, together with the strengthening of the polarization of the N–H bond as a result of the large electronegativity of the meso nitrogen atoms compared with meso methine atoms, leads to a transformation of structure C with covalent N–H bonds and a weak hydrogen bond into structure D with significantly polarized N–H bonds and a strong hydrogen bond. This change in the structure of the reaction center is reflected in the PMR spectra as a low field displacement of the signal for the H_{NH} protons.

For porphyrins themselves, only a small effect was observed on the position of the resonance signal of the H_{NH} protons by substituents in the pyrrole rings (see Table 1). The N–H bonds of porphyrazines with delocalized structures D and E are polarized, unlike in the porphyrins with a localized structure C. As a result, the position of the H_{NH} proton signal may be changed within wider limits, depending on the substituent in the β position of the pyrrole rings of the porphyrazine macrocycle. In the presence of electron-donating substituents such as alkyl groups the N–H bond has a less ionic character. For the ethyl and tert-butyl substituted porphyrazines (Ib, c), the δ_{NH} signal is displaced towards high field by 1.24-1.48 ppm compared with H_2Pz (Ia). On the other hand, the acidity of the N–H bond is markedly increased (pK_a 7.26 in DMSO [30]) for H_2PzBr_4 (Id) as a result of the electron-accepting effect of the bromine atoms. This leads to a displacement of δ_{NH} by 2.4 ppm towards low field. The large deshielding effect in this case may be explained by the strongly delocalized structure E which is close to the completely ionized structure B. It is interesting to note that in this connection the rate of complex formation of H_2PzBr_4 (Id) with metal salts is comparable with the rates of ionic reactions [30]. A far slower rate for this process was observed for alkyl derivatives [31], since in this case fission of the more covalent N–H bonds in structure D occurs in the activation process of the reaction. Since ionization of the N–H bonds in porphyrin ligands is an important factor determining their reactivity in complex formation [2], a good correlation exists between the chemical shifts of the H_{NH} protons (δ_{NH}) and the rate constants k_v^{298} for the reaction of these ligands with $Zn(OAc)_2$ in pyridine [2, 30-32] (see Fig. 3).

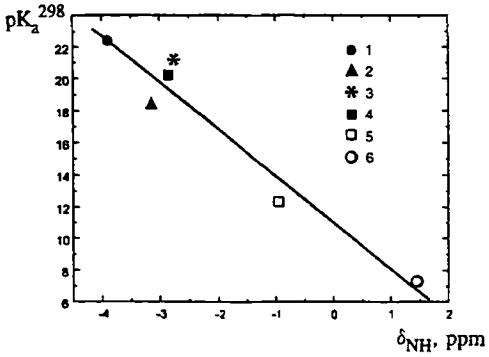


Fig. 2. Correlation between the chemical shift of the H_{NH} protons (δ_{NH}) and the acid dissociation constants (pK_a^{298}) in DMSO for the porphyrins: 1) H_2P, 2) tetrabenzoporphine, 3) tetraphenylporphine, and 4) tetra(p-chlorophenyl)porphine, and also the porphyrazines: 5) H_2Pz (Ia), and 6) H_2PzBr_4 (Id). The values of δ_{NH} for porphyrins are taken from [21] and the values of pK_a^{298} from [23, p. 51], [29], and [30] for H_2PzBr_4.

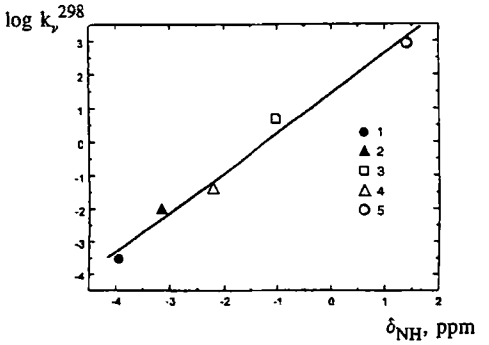


Fig. 3. Correlation between the chemical shifts of the H_{NH} protons (δ_{NH}) and the rate of complex formation with $Zn(OAc)_2$ in pyridine (log k_y^{298}) for porphyrins: 1) H_2P and 2) tetrabenzoporphyrin, and also for porphyrazines: 3) H_2Pz (Ia), 4) H_2PzEt_8 (Ib), and 5) H_2PzBr_4 (Id). The values of δ_{NH} for porphins were taken from [21] and the values of log k_y^{298} for porphines from [23, p. 67] and [32], and for porphyrazines from [2, 30, 31].

Additional confirmation of the existence of structure D for H_2Pz (Ia) and H_2PzEt_8 (Ib) was obtained recently by x-ray photoelectron spectroscopy [33, 34]. Three peaks, corresponding to the bond energy of the nitrogen 1s electrons of the meso nitrogen atoms and of two types of intracyclic nitrogen atoms, which were observed in the case of H_2Pz (399.05, 400.27, and 398.30 eV [34]) and H_2PzEt_8 (398.75, 399.95, and 398.10 eV [33]), are compatible with the unsymmetrical structure D, but not with the symmetrical structures E and B for which only two peaks of equal intensity might have been expected. The difference in bond energies of the nitrogen 1s electrons of the two types of intracyclic nitrogen atoms in structure D in porphyrazines (1.85 eV for H_2PzEt_8) is significantly less than for structure C in porphyrins (2.10 eV for H_2PzEt_8).

Disappearance of the H_{NH} proton signal in the PMR spectrum of H_2Pz (Ia) in CF_3COOD (Fig. 1b) may be explained by deuterium exchange. This process has also been observed for porphyrins [21], and in the case of H_2Pz it is facilitated by the increased acidity of the N−H bond. The interaction of H_2P with acids leads to double protonation at the center of the porphyrin ring with the formation of the more symmetrical dication H_4P^{2+}, and the signal of the β protons becomes narrower. Unlike the porphyrins, H_2Pz (Ia) forms a less symmetrical monocation H_2PzH^+ (D_2PzD^+) in acids in which one of the outer meso nitrogen atoms is protonated [8]. The rapid exchange reaction with the medium involving all four meso nitrogen atoms does not permit resolution of the expected multiplet of β protons and leads only to broadening of the signal.

The signal of the eight equivalent β protons observed for ZnPz (II) in Py-D_5 as a narrow singlet is also broadened in CF_3COOD as a result of the formation of the $ZnPzD^+$ monocation [35]. The resonance signal of the β protons in ZnPz is displaced towards low field compared with H_2Pz, which contains no metal atom. This assumes strengthening of the π-electron ring current and conjugation of the ethylenic double bonds with the main chromophore as the result of complex formation.

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EXPERIMENTAL

The PMR spectra of compounds (Ia) and (II) were measured on a Tesla BM 467A (60 MHz) spectrometer, internal standard being TMS. Since H_2Pz (Ia) and its complexes are very poorly soluble in nonsolvating solvents, the PMR spectra were obtained in pyridine-D_5 (PyD_5) and CF_3COOD, in which the solubility proved to be adequate ($\sim 10^{-3}$ M) because of their marked solvating properties. Compounds (Ia) and (II) were synthesized by the method of Linstead and Whalley [1].

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