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Acid–base behavior of triazoleporphyrazines in proton-donating media

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ABSTRACT: The acid–base properties of some peripheral substituted triazoleporphyrazines in proton-donating media with poor-donating character were experimentally studied. The substitution of one pyrrole moiety in the porphyrazine-like compounds by one triazole ring in the triazoleporphyrazines leads to an increase in the basicity. The protonation of the triazoleporphyrazines results in a hypsochromic shift of the Q-bands in the UV–visible spectra. A DFT study of some selected structural models of the unsubstituted triazoleporphyrazine shows that the protonation strongly influences on the molecular electron structure of this compound and that it occurs preferentially through the nitrogen atom located at position 4 of triazole ring. The protonation through the other basic centers (the triazoleporphyrazine is a multicenter conjugated base) leads to different protonated forms which differ notably in their aromatic character. Therefore, this compound could be considered an intramolecular switch of aromaticity.

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KEYWORDS: Triazoleporphyrazines; acid–base behavior; theoretical calculations; aromaticity; HOMA and NICS criteria

INTRODUCTION

The synthesis and investigation of non-centrosymmetric porphyrin analogues are an important direction in current physical organic chemistry.[1] One of the most evident ways to gain access to this kind of compound is the formal substitution of one of the pyrrole rings by an azole system. Following this strategy, triazolephthalocyanines,[2] thiadiazolephthalocyanines[3] and triazoleporphyrins[4] have been synthesized. Recently, a new family of compounds derived from porphyrazine, namely substituted triazoleporphyrazine **1** and its metallocomplexes (for example, Cu complex **3**) were produced[5] (Chart 1).

The analysis of the molecular electron structure of the unsubstituted metal-free triazoleporphyrazine shows that this compound can exist as a mixture of tautomers with different aromaticities.[6] It was concluded that the tautomer with one proton attached to the triazole ring and the other proton located in the macrocycle cavity represents the molecular form with the lowest aromatic character.[6] However, and to our knowledge, other relevant properties of this family of compounds such as the acid–base behavior have not yet been studied. This paper reports an analysis of the acid–base behavior of some selected tetraazaporphyrin triazole derivatives, namely the 1(*H*)-hexakis(4-*tert*-butylphenyl)triazoleporphyrazine (**1**), 1-dodecyl-hexakis(4-*tert*-butylphenyl)triazoleporphyrazine (**2**) and the copper(II) complex **3** (Chart 1).

Our group previously studied the acid–base and coordinating properties of both the porphyrins and porphyrazines.[7,8] Porphyrazines are weak multicenter conjugated bases.[9] Their complexes (MPz) contain up to four *meso*-nitrogen atoms, all of which should be able to participate in acid–base interactions. Thus, sequential equilibria of protonation may be formulated as follows:

$$MPz + H \rightleftharpoons MPzH^{+}$$

$$MPzH^{+}H^{+} \rightleftharpoons MPzH_2^{2+}$$

and so on, where $MPzH^{+}$ and $MPzH_2^{2+}$ are the first and second protonated forms of the MPz initial base, respectively.

According to the modern theory of acid–base interactions, the proton transfer from acid HA to base B is a complex process in which the stages of the acid associate,

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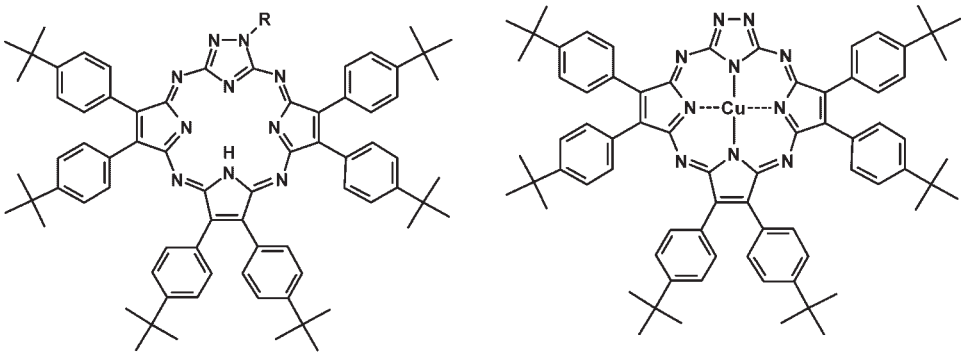


1 R = H
2 R = $C_{12}H_{25}$

3

Chart 1. Triazoleporphyrazines studied experimentally in this present work

$$B{:}+HA \rightleftharpoons B{:}\cdots HA \rightleftharpoons B{:}\cdots H^{\delta+}\cdots A^{\delta-} \rightleftharpoons B{:}H^{+}\cdots A^{-} \rightleftharpoons B{:}H^{+} + A^{-}$$

acid associate — H-associate — ion–ion associate — protonated form

Scheme 1. Stages of the proton transfer from an acid HA to a Lewis basis B

H-associate, ion–ion associate and fully ionized protonated form, can be distinguished (Scheme 1).

The forms considered in Scheme 1 differ in the degree to which the proton is transferred from the acid molecule to the electron donor center. In a proton-donating medium with poor ionizing ability, donor centers of the π-conjugation multicenter base can participate in a weak acid–base interaction with acid molecules forming associates. The full transfer of the proton from the acid to the base can only proceed in media with good ionizing ability.

In comparison with porphyrazine, the triazoleporphyrazine molecule has two extra nitrogen atoms (those of the azole ring), which could be considered as additional centers of the protonation. This fact must influence the acid–base behavior of this class of compounds. In this work, experimental and theoretical procedures were combined to study the acid–base properties of the triazoleporphyrazines and, consequently, to establish their particularities with respect to related compounds.

RESULTS AND DISCUSSION

Experimental data

The acidification of benzene solutions of compounds **1–3** with a small addition of acetic acid ($c = 0.4\,\mathrm{mol\,l^{-1}}$, $H_0 = 7.5$) results in a hypsochromic shift of the Q-bands in the UV–visible spectra. An example of this behavior for **3** is shown in Fig. 1.

The formation of the first acid form of the studied compounds is completed in media having acidities that

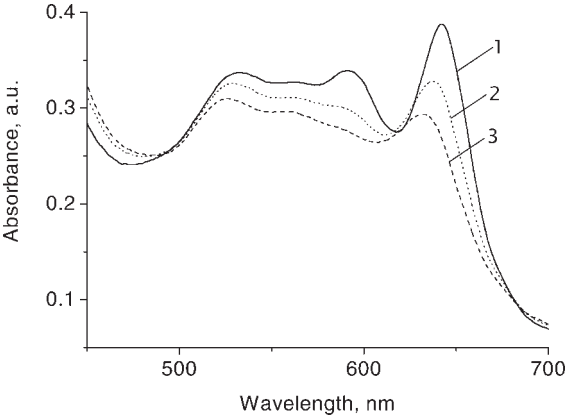


Figure 1. UV–visible spectra of solutions of **3** in (1) benzene, (2) benzene–HOAc ($H_0 = 6.44$) and (3) benzene–HOAc ($H_0 = 6.17$)

are stronger than those corresponding to pure acetic acid, i.e. in H_2SO_4–antipyrine–HOAc mixtures ($H_0 = 3.95$ for **1** and **2** and 4.60 for **3**). On replacing the benzene solvent with H_2SO_4–antipyrine–HOAc, the maximum Q-bands are shifted hypsochromically by 473, 376 and 755 $\mathrm{cm^{-1}}$ for **1**, **2** and **3**, respectively. Taking into account that the displacements of the Q maxima described here are obtained in media with poor ionizing ability, it can be concluded that they are related to the formation of ion–ion associates.

The stability constant of the acid form i (K_{si}) was determined following Hammett's equation:[10] $pK_{si} = nH_0 + \log I_i$, where H_0 is the Hammett's function of acidity, $I_i = C_i/C_{i-1}$ is the relation of the concentrations of the i (current) and $i-1$ (previous) protonated forms and n is the number of donor centers involved in the acid–base interactions at the stage under consideration.

The $\log I_i$ –H_0 dependences have a linear character for **1–3** in benzene–acetic acid media (Fig. 2). The slopes of the $\log I_i/H_0$ lines for Eqn (1) are 0.97, 0.79 and 1.14 for **1**, **2** and **3**, respectively. This result indicates that the number of donor centers participating in acid–base

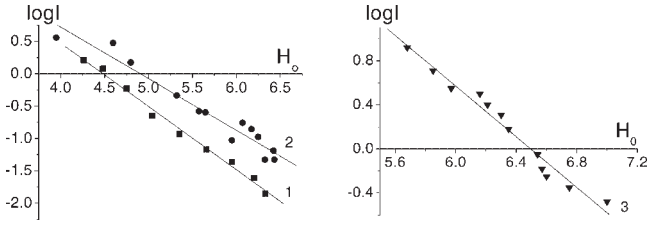


Figure 2. Log$I$–H_0 relationships for the equilibrium of the ion–ion associate formation in the benzene–acetic acid system. Series 1–3 correspond to compounds **1**–**3**

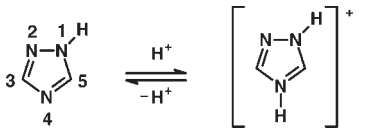
interaction, determined according to Eqn (1) as the slope of the $\log I_i/H_0$ dependences, is one in all the systems studied. Hence the spectrophotometric titration data show that only one molecule of acid takes part in the interaction with ligands and Cu complex in the first stage. Porphyrazines become rapidly destroyed with further increase in acidity.

The stability constants of the first acid forms for **1**, **2** and **3** that were also determined from Hammett's equation are 4.48 ± 0.18, 4.90 ± 0.32 and 6.50 ± 0.41, respectively.

The pK_{s1} values of **1** and **2** are of the same order of magnitude, suggesting that the protonation center is the same in both cases. Nevertheless, the basicity of **2** is significantly higher than that of **1**. This can be understood by considering (i) the electron-donating ($+I$) effect of the alkyl substituent and (ii) that the proton acceptor center belongs to its own triazole ring.

The introduction of a Cu ion in the macrocycle leads to an increase in basicity by two orders of magnitude with respect to **1** and **2**. This may indicate that the protonation center in the metal complex differs from that in **1** and **2** besides the fact that the protonation through the N atom in position 4 of the triazole ring (for nomenclature see Scheme 2) is impossible owing to the presence of the metal cation at the center of the macrocycle cavity.

The comparison of the pK_{s1} values obtained in this work for the triazoleporphyrazines (which ranged from 4.48 to 6.50) and those reported for the tetraazaporphyrins[9] (1.00 and -1.33 for the octaphenyltetraazaporphyrin and its Cu complex, respectively) shows an increase in the basicity on substitution of one pyrrole ring by the triazole ring in the macrocycle. It was shown previously[9] that the first stage of the acid–base interaction in tetraazaporphyrins proceeds through one of the four *meso*-nitrogen atoms and leads to a bathochromic shift of the Q-band in the spectra.



Scheme 2. Formation of the first protonated form of 1,2,4-triazole

The protonation of the internal nitrogen (i.e. the pyrroline nitrogen) in the first stage of an acid–base interaction in the unsymmetrical monoazaporphine was observed and resulted in a hypsochromic shift of the long-wave Q-band.[9] Also, it is well known[11,12] that protonation of the isolated 1,2,4-triazole ring occurs through the nitrogen atom located at position 4 of the ring (Scheme 2).

On the basis of this body of results, one can expect that the high basicity of the metal-free triazoleporphyrazines compared with the related porphyrazines and the hypsochromic shift of the absorption Q-bands in their UV–visible spectra, observed in acid–base processes, are conditioned by the protonation of the N atom at position 4 of the triazole ring.

Theoretical study

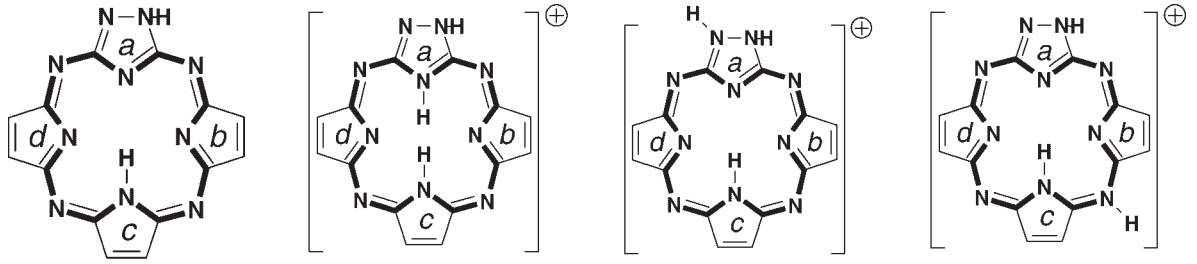
In order to find both the nature of the protonation center and an explanation for the observed hypsochromic shift of the absorbtion Q-bands in the UV–visible spectra, a theoretical study of the protonated forms of the unsubstituted metal-free triazoleporphyrazine was carried out.

The spectral data reveal that **1** and **2** exist in solutions of low-polarity solvents mostly as low aromatic forms[5] which correspond to the tautomer with one proton attached to the triazole ring and the other located in the macrocycle cavity[6] (model structure **4** in the present work).

For studying the effects of protonation on the molecular electronic structure of the triazoleporphyrazine at an adequate theoretical level with reasonably small computational effort, we selected three model protonated structures derived from the low-aromatic free-base triazoleporphyrazine **4**. Two of these structures are protonated in the triazole ring, **5a** (position 4) and **5b** (position 2), and one is protonated in a *meso* N-atom, **5c** (Chart 2).

Preliminary geometry optimizations of the peripheral substituted molecules **1**, **2** and **3** demonstrated that the phenyl rings are out of the plane of the central core. They are located quasi-perpendicularly with respect to the triazoleporphyrazine macrocycle. This result agrees with x-ray investigations of porphyrazines having the same substituents.[13] This non-planarity makes the conjugation effect of the substituents on the central core negligible. Hence both conjugation and inductive effects of the substituents, which are not large here, give a weak electronic influence of the peripheral substituents on the macrocyclic core. Correspondingly, this simplification leads to the model structures depicted in Chart 2.

The full optimization geometry performed at the DFT [B3LYP/6–31(d,p)] level yields plane configurations for the protonated forms **5a**–**c**. The bond lengths and bond angles of **4** and **5a**–**c** are given in the Supplementary Material. The protonation provokes a strong perturbation of the geometric parameters although, as was found for the neutral tautomeric forms,[6] the planarity of the molecules is preserved.



4 **5a** **5b** **5c**

Chart 2. Neutral (**4**) and protonated (**5a–c**) structures of the unsubstituted free-base triazoleporphyrazine considered in this work. The internal cross of the structures is emphasized in bold

Table 1. Total and relative energies of the protonated forms **5a–c**

Structure	E_{tot} (a.u.)	ΔE_{rel} (kJ mol^{-1})
4	−1085.7577133	—
5a	−1086.1604513	0
5b	−1086.1296643	80.75
5c	−1086.1359859	64.16

A considerable increase in the C—N (N—N) bond lengths is observed when the N atom captures a proton. For example, if a proton addition occurs on the nitrogen atom located at position 4 of triazole ring, the C—NH^+—C bonds elongate by more than 0.020 Å (see the Supplementary Material). The proton addition at the position 2 of the triazole ring (structure **5b**) strongly modifies the molecular geometry, especially that of the triazole moiety, and leads to a structure of higher symmetry (C_{2v}) than the others. For instance, the N—N bond length in structure **5b** (1.356 Å) is the largest in the series **4**, **5a–c**.

The magnitudes of total and relative electronic energies of the protonated forms **5a–c** are shown in Table 1. The cationic configuration **5a** that bears a proton at position 4 of the triazole ring is found to be the most stable among the forms examined. This suggests that it is the first protonated form of the triazoleporphyrazine, which, in turn, agrees well with the behavior of 1,2,4-triazole[12] in an acidic medium. It seems that structure **5a** is additionally stabilized by the formation of an inner porphyrazine-like macrocycle. This fact is proved by the equalization of the bond lengths of the internal cross (see Supplementary Material).

One-proton addition gives rise to a strong perturbation in the electronic charges of all the molecules, but especially at the N atom that bonds the proton and at the neighboring C atoms. Thus, when the N atom accepts a proton, the negative charge of the N atom and the positive charge of the C atoms bound to the N atom are increased.

The analysis of the charge distribution over all the molecule shows that in the cases of **5a** and **5b**, the positive charge is locally accumulated on the triazole ring, reaching values of +1.025 and +0.969, respectively. In contrast, the positive charge is more uniformly distributed over the whole molecule when the proton addition takes place along the exocyclic (*meso*) atom.

Aromaticity is one of the most important characteristics of the tetrapyrrole macrocycles because it is responsible, in many respects, for several features which characterize these compounds, e.g. high stability, light absorption, acid–base interactions. Recently, we reported on the aromaticity of the unsubstituted metal-free triazoleporphyrazine.[6] It could be expected that the presence of two additional nitrogen atoms instead of a —C═C— bridge located directly in the macrocyclic core would open a way to give access to the conjugated systems by means, for example, of protonation. In fact, the protonated forms of **1** and **3** were measured in the gas phase by mass spectrometry (see Ref. 5 for **1** and **3**; for **2**, see the selected data quoted above). In order to estimate the influence of the protonation on the aromatic properties, both geometry-(EN, GEO and HOMA) and magnetic (NICS)-based criteria of aromaticity[14,15] were evaluated for the protonated forms of triazoleporphyrazine. Table 2 gives the calculated values of geometry-based criteria of aromaticity for the studied systems.

Proton addition to either position 4 of the triazole ring (structure **5a**) or to the exocyclic-*meso* N atom (structure **5c**) leads to the equalization of the bond lengths in the cations. The GEO values decrease from 0.464 for non-protonated structure **4** to 0.450 and 0.407 in **5a** and **5c**, respectively. The average bond lengths of these cations tend towards the optimal magnitude (EN criterion).[14,15] As a result, HOMA values of the cationic systems **5a** and **5c** are higher than those of the neutral molecule **4**.

In **5a**, the formation of a porphyrazine-like internal cross explains the global increase in the HOMA, but simultaneously the local HOMA aromaticity index of triazole ring is increased to 0.956. The description of the aromaticity based on geometry criteria is in good agreement with that obtained by means of magnetic-based criteria (NICS).

The value of the NICS index calculated at the center of the macrocycle **5a** (Fig. 3) changes from −6.90 (**4**) to

Table 2. EN, GEO and HOMA indices for structures **4** and **5a–c** optimized by B3LYP/6–31G(d,p)

Structure	EN	GEO	HOMA
4^6 (whole system)	**0.122**	**0.464**	**0.414**
Triazole ring (a)	0.044	0.034	0.922
Pyrrole ring (b)	0.332	0.812	−0.144
Pyrrole ring (c)	0.332	0.484	0.184
Pyrrole ring (d)	0.316	0.801	−0.117
Internal cross	*0.015*	*0.094*	*0.891*
5a (whole system)	**0.117**	**0.450**	**0.433**
Triazole ring (a)	0.028	0.016	0.956
Pyrrole ring (b)	0.346	0.767	−0.113
Pyrrole ring (c)	0.322	0.506	0.172
Pyrrole ring (d)	0.344	0.732	−0.076
Internal cross	*0.019*	*0.077*	*0.904*
5b (whole system)	**0.133**	**0.541**	**0.326**
Triazole ring (a)	0.057	0.037	0.906
Pyrrole ring (b)	0.371	0.959	−0.330
Pyrrole ring (c)	0.357	0.566	0.077
Pyrrole ring (d)	0.371	0.959	−0.330
Internal cross	*0.011*	*0.078*	*0.911*
5c (whole system)	**0.111**	**0.407**	**0.482**
Triazole ring (a)	0.040	0.053	0.907
Pyrrole ring (b)	0.264	0.715	0.021
Pyrrole ring (c)	0.256	0.391	0.353
Pyrrole ring (d)	0.402	0.666	−0.068
Internal cross	*0.018*	*0.124*	*0.858*

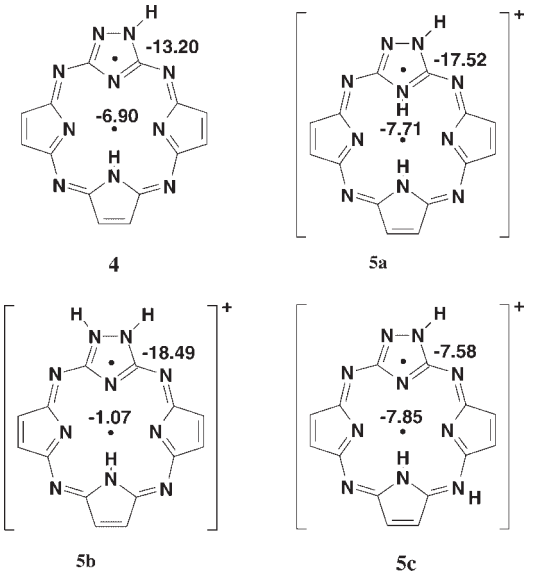


Figure 3. Calculated NICS values (ppm) for the studied compounds **4^6** and **5a–c**

−7.71 ppm, which, in turns, means that the aromaticity increases. Similar behavior was observed for the triazole ring of **5a**: the proton addition at position 4 of the triazole ring (**5a**) produces an increase in the local aromaticity in this group. The NICS value at the center of the triazole ring changes from −13.20 (**4**) to −17.52 (**5a**) ppm. This increase in the aromaticity in structure **5a** may also explain the hypsochromic displacement of the low-energy Q-band observed at the UV–visible spectrum of **1** and **2** in an acidic medium of growing strength.

In structure **5b**, the strong alternation of double and single bonds of pyrrole rings b and d (Fig. 3) induces a considerable increase in the GEO values (Table 2). Therefore, the global aromaticity of **5b** decreases as the value obtained for the global HOMA (0.326) indicates. The NICS value calculated at the center of the macrocycle cavity in **5b** (−1.07 ppm) confirms the very low aromatic character of this cation. The most aromatic part of this cation is the internal cross (depicted in Chart 2 in bold) as the HOMA index 0.911 obtained for this part of the molecule (Table 2) indicates. Accordingly, the single protonation of the triazoleporphyrazine throughout the position 2 of the triazole ring represents an intramolecular switch for aromaticity.

When protonation occurs in the exocyclic N atom (**5c**), the HOMA increases to 0.482. This increase is caused mostly by the HOMA contributions of pyrrole rings to the HOMA of the whole system. Since the N_{meso}—C_{α} bond lengths become elongated, the HOMA value of the internal cross decreases from 0.891 (**4**) to 0.858 (**5c**). However, the N atom which is the acceptor of a proton is maintained as a good conductor of electron effects over molecule **5c**, as the NICS value of −7.85 ppm indicates.

CONCLUSION

The behavior of hexakis(4-*tert*-butylphenyl)triazoleporphyrazine, its Cu complex and its 1-dodecyl derivative was studied in proton-donating media. It was established that triazoleporphyrazines are able to be protonated in a proton-donating medium with poor ionizing ability (HOAc–benzene) and, consequently, ion–ion associates should be formed. The stability constants of the acid forms show that a replacement of a pyrrole moiety by a triazole ring in the porphyrazine leads to an increase in basicity. The protonation of the triazoleporphyrazines results in a hypsochromic shift of the Q-bands in the UV–visible spectra.

Quantum chemical investigations show that the protonation of the triazoleporphyrazines strongly influences both their molecular electron structure and aromaticity. The cation formed by proton addition to the exocyclic nitrogen atom seems to be the most aromatic cation. The investigations of the protonated forms confirm that the high basicity of triazoleporphyrazines is conditioned by protonation of the nitrogen atom located at position 4 of triazole ring, the corresponding protonated form having more aromatic character than the neutral structure. However, the addition of one proton to the nitrogen atom at position 2 of the triazole ring is responsible for the dramatic decrease in the aromaticity of the macrocycle. Hence the triazoleporphyrazines could be used as an intramolecular switch for aromaticity.

EXPERIMENTAL

Synthesis

Compound **2** was obtained following the general procedure described by Islyaikin *et al.*[5] A mixture of 3, 4-di[4-(*tert*-butyl)phenyl]pyrroline-2,5-diimine (0.324 g, 0.9 mmol), 2,5-diamino-1-dodecyl-1,2,4-triazole (0.080 g, 0.3 mmol) and freshly distilled *n*-BuOH (30 ml) was stirred under reflux for 28 h. After rotoevaporation of the solvent, the precipitate was triturated with MeOH and purified by column chromatography: (i) silica gel, hexane–ethyl acetate (10:1), (ii) silica gel, toluene. TLC [hexane–toluene–BuOH (10:1:1)], $R_f = 0.6$. Yield: 0.030 g (7.8%). Elemental analysis: $C_{86}H_{104}N_{10}$ (1277.83) calculated C 80.84, H 8.20, N 10.96; found C 80.45, H 8.46, N 10.63%.

Selected data are as follows: MS (FAB), matrix *m*-NBA, $[M]^+$ 1276.5 (26.4%), $[M+H]^+$ 1277.5 (51.1%), $[M+2H]^+$ 1278.5 (87.9%), $[M+3H]^+$ 1279.6 (100.0%); UV–visible, $CHCl_3$, 244.0 (4.78), 328 (4.65), 421.0 (4.60), 535 (4.55), 624 (3.73); IR (KBr), $\bar{\nu}$ (cm^{-1}), 3298 (NH), 2960, 2926, 2856 (*t*-Bu), 1585 (C═C, C═N), 1460, 1363, 1268, 1109, 1088, 1022, 972, 837, 802, 728, 670, 616, 565.

Measurements

The experimental study of the acid–base interaction of **1–3** was carried out by the UV–visible spectrophotometric method.[9] UV–visible measurements were carried out with a Hitachi U-2000 spectrophotometer with temperature-controlled cells at wavelengths that correspond to the absorption maximum of the non-protonated forms (531.0 nm for **1**, 538.0 nm for **2** and 634.5 nm for **3**). Solutions with constant concentrations of **1–3** and different acidities were used. The acidities in the interval $H_0 = 4.83$–7.00 were fixed by means of mixtures of benzene–acetic acid (HOAc)[9] containing HOAc from 0 to 15.62 mol l^{-1}. Solutions with higher acidities ($H_0 =$ 3.95–4.27) than those obtained with benzene–HOAc mixtures were produced using H_2SO_4–antipyrine–HOAc[11] solutions at low concentration of sulfuric acid.

Calculations

The geometry optimization of structures **5a–c** was carried out at the density functional theory (DFT) level. The functional employed was the Becke three-parameter (B3LYP) hybrid functional,[16] which has been widely used in theoretical studies of pyrrole macrocycles.[17] Also, the 6–31G(d,p)[18] basis set was selected. In order to verify that the optimized structures correspond to a minimum, they were fully characterized by vibrational analysis using second derivatives. Positive frequencies and eigenvalues of the Hessian were obtained in every case. The present work was computationally supported by the Gaussian 98 package.[19] The data calculated for the triazoleporphyrazine **4** at the same theoretical level have been presented elsewhere.[6]

The aromaticity of the described structures was evaluated by two quantitative criteria: (a) the geometry-based index, namely the harmonic oscillator model of aromaticity (HOMA) and (b) nucleus independent chemical shifts (NICS).[14,15] The GIAO method[20] was used to evaluate NICS indices. They were evaluated in the present work both at the geometric center of the macrocyclic cavity and at the center of the triazole ring as indicated in Chart 2.

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