Solution Phase and Single Crystal Diffraction X-Ray Analyses of Diprotonated Porphyrin Isomers—Etioporphyrin, Etioporphycene, and Etiocorrphycene Bishydroperchlorate Salts

Jonathan L. Sessler,* Eric A. Brucker, Vincent Lynch, Michael Choe, Steven Sorey, and Emanuel Vogel*

Dedicated to Professor Kurt Schaffner on the occasion of his 65th birthday

Abstract: The diprotonated, bishydroperchlorate forms of three isomeric β-octaalkyl-substituted tetrapyrrolic macrocycles, namely, etioporphyrin II (**1**), etioporphycene (**2**), and etiocorrphycene (**3**), have been characterized both in chloroform solution, by UV/visible spectroscopy and ^{1}H and proton-correlated 2D ^{15}N NMR methods, and in the solid state, by single-crystal X-ray diffraction analyses. In the solid state, in marked contradistinction to what is observed for the corresponding free-base forms, the macrocyclic portion of these salts were found to be distorted significantly from planarity with the two perchlorate counteranions being held above and below the average N_4 plane by N–H···O hydrogen bonds in all three cases. In solution, ^{1}H and proton-correlated 2D ^{15}N NMR experiments reveal molecular ions of relatively high symmetry (D_{2h}, D_{2h}, and C_{2v} in the case of **1**·$(HClO_4)_2$, **2**·$(HClO_4)_2$, and **3**·$(HClO_4)_2$, respectively) as would be anticipated on the basis of the solid-state results. These same NMR analyses, while revealing slight differences between the three salts in the NH and *meso* ^{1}H NMR spectral regions, also serve to confirm the generalized congeneric nature of **1**·$(HClO_4)_2$, **2**·$(HClO_4)_2$, and **3**·$(HClO_4)_2$ and support the assignment of the latter two species as being porphyrin-like salts. UV/vis analyses further support this conclusion; in all three instances, strong Soret- and Q-like transitions are observed in dichloromethane that are both distinct from each other (λ_{max} = 404, 549, 570, 593; 388, 409, 599, 666; and 419, 559, 604 for **1**·$(HClO_4)_2$, **2**·$(HClO_4)_2$, and **3**·$(HClO_4)_2$, respectively) and from those of the corresponding free-base forms (λ_{max} = 396, 496, 530, 565, 619; 382, 570, 617, 657; and 410, 509, 539, 574, 628 for **1**, **2**, and **3** respectively). Protonation experiments were carried out by exposing dichloromethane solutions of the isomers to aqueous perchlorate/perchloric acid solutions of differing pH. These studies reveal that while porphycene **2** adds two protons readily and concurrently, becoming 50% *diprotonated* when exposed to perchlorate/perchloric solutions with a pH of around 3.6, porphyrin **1** and corrphycene **3** are protonated in a stepwise manner; they become 50% monoprotonated when exposed to perchlorate/perchloric solutions of pH ≈ 3.7 and 3.9, respectively, and diprotonated at pH ≤ 0.8 and 1.3, respectively.

Keywords
corrphycenes · porphycenes · porphyrinoids · protonations · structure elucidation

Introduction

Porphyrin derivatives bearing substituents in the β-pyrrolic, but not *meso*, positions are of extraordinary chemical and biochemical importance. Therefore, not surprisingly, a considerable body of work continues to be devoted to the synthesis and study of pyrrole-substituted porphyrins (e.g, etioporphyrin II, **1**). While these efforts continue to augment our understanding of this all-important class of macrocycles, it is also conceivable that further insights could come from the study of closely related isomers, congeneric systems wherein the key porphyrinic components, namely, four pyrrole subunits and four sp^2-hybridized bridging carbons, are connected to each other in a way that differs from that which is found in natural porphyrins.

To date, several nonnaturally occurring (i.e. synthetic) porphyrin isomers have been reported.[1] Within the "pyrrole-in" series, however, only two synthetic porphyrin isomers are known that have been fully characterized structurally by X-ray diffraction methods in their metal-free forms, namely, porphycene (e.g., **2**) and corrphycene (e.g., **3**).[1b, 1c, 1g, 2] In both cases, these structural analyses were carried out on the free-base forms. Thus, at present, little is known about the structure of the corresponding protonated forms. In this paper we report the

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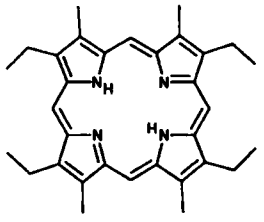
  0947-6539/96/0212-1527 $ 15.00+.25/0

single-crystal X-ray structures of the bishydroperchlorate salts of etioporphycene and etiocorrphycene ($2\cdot(HClO_4)_2$ and $3\cdot(HClO_4)_2$) as well as that of the parent etioporphyrin, $1\cdot(HClO_4)_2$.[3] Also reported are the results of extraction-based protonation and proton-correlated 2D ^{15}N NMR experiments, which provide comparative insight into the nature of these protonated species in the solution state.



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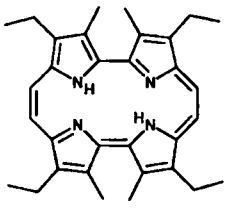

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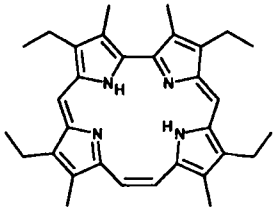

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Experimental Section

X-ray-quality single crystals of the bishydroperchlorate salts of etioporphyrin II [4], $1\cdot(HClO_4)_2$, and etioporphycene [1f], $2\cdot(HClO_4)_2$, were obtained from acetonitrile/isopropyl ether diffusion. Single crystals of the bisperchloric acid salt of etiocorrphycene [1g], $3\cdot(HClO_4)_2$, were obtained from benzene/methanol evaporation. Samples of all three crystals were subject to X-ray diffraction analysis in accord with standard methods [5,6,7]. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Crystallographic Data Centre as supplementary publication no. CCDC-1220-34. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: Int. code +(1223)336-033; e-mail: teched@chemcrys.cam.ac.uk).

pH-dependent extraction experiments were performed by dissolving the porphyrin isomer in dichloromethane at such a concentration as to give an absorption value of roughly 1.0 when the electronic spectrum was recorded in a 1.0 cm cuvette. Aqueous solutions of 100 mM $NaClO_4$ were made up and the pH adjusted with $HClO_4$ so as to provide separate samples with pH values ranging from 5.85 to 0.54. A 25 mL aliquot of each of the aqueous solutions was stirred (by magnetic stir bar) with 4 mL aliquots of the solutions containing the porphyrin isomer until equilibrium was established (ca. 5 min). The organic layer was then decanted off and the visible spectrum recorded.

Natural abundance ^{15}N NMR chemical shifts were obtained on a Bruker AMX-500 instrument by inverse-mode $^1H-^{15}N$ 2D chemical shift correlation. The ^1H spectral width was 10000 Hz and the ^{15}N width was 5000 Hz. A total of 256 $T1$ values were taken with 24 scans for each interval and a 2 s relaxation delay per scan. The resulting data set was processed with a 45 degree shifted sine bell in both dimensions and zero-filled to yield a 1 K × 1 K data matrix. The experiments were performed without ^{15}N decoupling during the acquisition time at a temperature of 27 °C. Nitrogen-15 shifts are reported relative to NH_4Cl in 1 M HCl ($\delta = 24.9$).

Results and Discussion

Earlier work has served to show that the free-base forms of macrocycles **1**,[8] **2**,[1f] and **3**[1g] are essentially planar. By contrast, the diprotonated forms of these porphyrin isomers show a significant deviation from planarity, as can be seen in the side views in Figures 1, 2, and 3. This deviation, manifest in terms of an alternating up and down tilt of the pyrrole subunits from the mean macrocyclic plane, results in $N-H\cdots O(ClO_3)$ distances

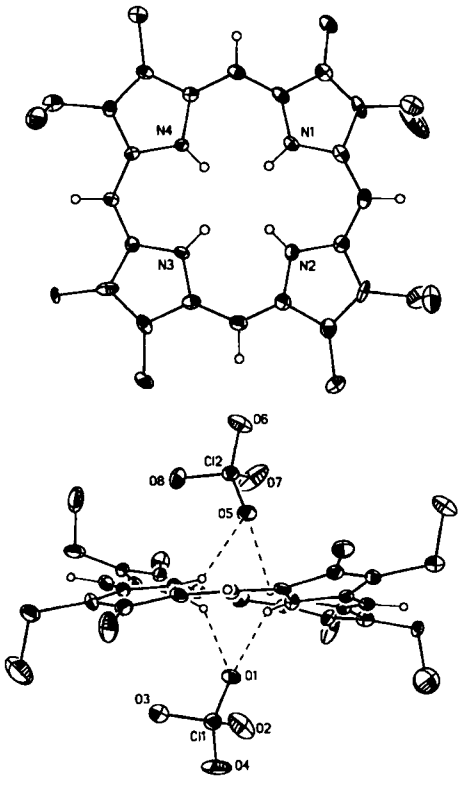

Fig. 1. Top: View of $1\cdot(HClO_4)_2$ perpendicular to the N_4 plane showing the nitrogen labeling scheme. Thermal ellipsoids are scaled to the 10% probability level. H atoms are scaled to an arbitrary size. The perchlorate anions and most hydrogens have been omitted for clarity. Bottom: Side view of $1\cdot(HClO_4)_2$ showing the hydrogen-bonding interactions. Pertinent H-bonding parameters: N1–H1···O5: N···O 2.87 Å, H···O 2.15 Å, N–H···O 136°; N1–H1···O5′: N···O 2.89 Å, H···O 2.12 Å, N–H···O 143°; N2–H2···O1: N···O 2.96 Å, H···O 2.19 Å, N–H···O 144°; N3–H3···O5: N···O 3.12 Å, H···O 2.42 Å, N–H···O 135°; N3–H3···O5′: N···O 2.91 Å, H···O 2.22 Å, N–H···O 133°; N4–H4···O1: N···O 2.92 Å, H···O 2.15 Å, N–H···O 143°.

of 2.87–3.12 Å for $1\cdot(HClO_4)_2$, ca. 2.95 Å for $2\cdot(HClO_4)_2$, and 2.88–3.03 Å for $3\cdot(HClO_4)_2$; these distances are within the range expected for this type of oxy anion-to-NH hydrogen bond (2.8–3.0 Å).[9]

A priori it is not possible to ascertain whether the above distortions from planarity are the result of strong NH–anion interactions that serve to "pull" the pyrrole rings out of the plane or the result of unfavorable proton–proton repulsions that serve to "push" the pyrrole rings out planarity, or some combination thereof. However, the fact that similar pyrrole tilting deviations are observed in two separate structures of monoprotonated octaethylporphyrin ($[OEP\cdot H]^+$) wherein the counter anion is either not coordinated or but weakly so,[10] leads us to conclude that the out-of-plane distortions observed in the present instance result as much (or more) from unfavorable $H\cdots H$ nonbonded contacts within the porphyrin nuclear plane as they do from a stabilizing NH-to-anion hydrogen bonding interactions.[11] This is consistent with what one would predict based on the use of simple space-filling molecular models.

The extent of the above tilt in $1\cdot(HClO_4)_2$, $2\cdot(HClO_4)_2$, and $3\cdot(HClO_4)_2$ is about the same in all three systems (mean deviations of the macrocyclic atoms from the plane are 0.238, 0.269, and 0.260 Å, respectively). When the core nitrogens are considered alone, the porphycene salt $2\cdot(HClO_4)_2$ shows only a slightly greater deviation from planarity than its porphyrin ($1\cdot(HClO_4)_2$) or corrphycene ($3\cdot(HClO_4)_2$) analogues (0.099 vs.

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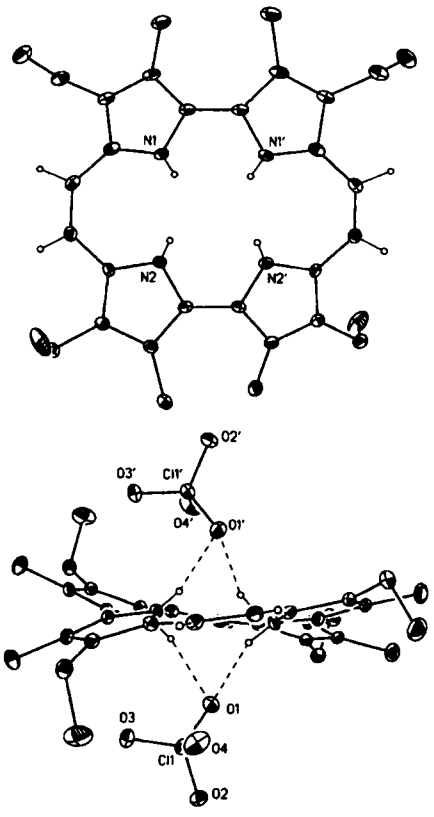

Fig. 2. Top: View of $2\cdot(HClO_4)_2$ perpendicular to the N_4 plane showing the nitrogen labeling scheme. The complex lies around a crystallographic twofold rotation axis at 0, y, 1/4 bisecting the bipyrrole bond. Atoms marked by a prime are related by $-x$, y, $0.5-z$. Thermal ellipsoids are scaled to the 30% probability level. H atoms are scaled to an arbitrary size. The perchlorate anions and most hydrogens have been omitted for clarity. Bottom: Side view of $2\cdot(HClO_4)_2$ showing the hydrogen-bonding interactions. Pertinent H-bonding parameters: N1–H1···O1: N···O 2.94 Å, H···O 2.12 Å, N–H···O 159°; N2'–H2'···O1: N···O 2.96 Å, H···O 2.18 Å, N–H···O 162°; H1–O–H2' 81°.

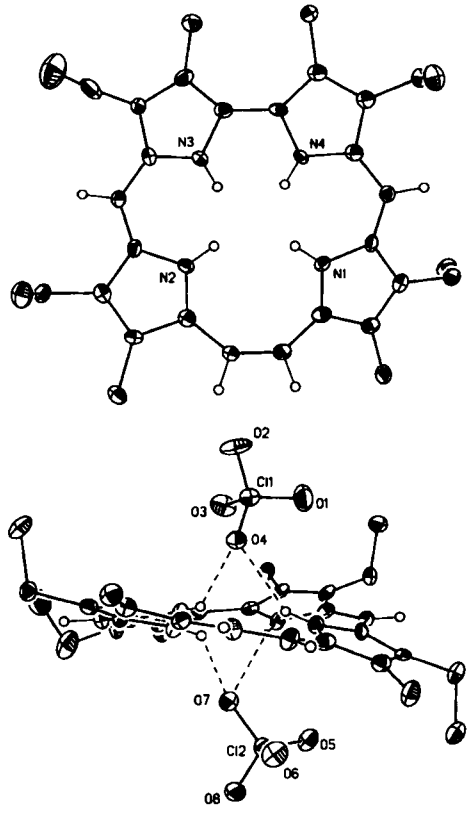

Fig. 3. Top: View of $3\cdot(HClO_4)_2$ perpendicular to the N_4 plane showing the nitrogen labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. H atoms are scaled to an arbitrary size. The perchlorate anions and most hydrogens have been omitted for clarity. Bottom: Side view of $3\cdot(HClO_4)_2$ showing the hydrogen-bonding interactions. Pertinent H-bonding parameters: N1–H1···O4: N···O 3.03 Å, H···O 2.18 Å, N–H···O 157°; N3–H3···O4: N···O 2.90 Å, H···O 2.01 Å, N–H···O 174°; N2–H2···O7: N···O 2.92 Å, H···O 2.17 Å, N–H···O 140°; N4–H4···O7: N···O 2.88 Å, H···O 2.12 Å, N–H···O 142°.

0.087 or 0.087 Å, respectively). This minor difference could simply reflect the fact that the core size of the porphycene salt (2.745 from N1 to N1'; 2.917 Å from N1 to N2; 4.015 Å from N1 to N2') is smaller than that of the porphyrin (2.985 Å from N1 to N2; 4.215 Å from N1 to N3) or corrphycene salts (3.522 Å from N1 to N2; 2.879 from N2 to N3; 2.617 from N3 to N4; 4.203 Å from N1 to N3), and thus allows for a less facile in-plane accommodation of the four internal hydrogens.

The single formal ethene bridge in $3\cdot(HClO_4)_2$ is slightly strained compared to the two ethene bridges present in $2\cdot(HClO_4)_2$. This is evidenced by the fact that the average pyrrole-C-C angle is expanded from 132.8° in the porphycene salt to 139.4° in the corrphycene dication. However, this bridge and the pyrroles to which it is attached do lie closer to planarity in the case of this latter salt, $3\cdot(HClO_4)_2$, than in the porphycene system, $2\cdot(HClO_4)_2$: torsion angles of 5.9 and 9.9° are observed for these two systems, respectively. Finally, within this same ethene bridge, greater single bond/double bond/single bond equalization is observed in the case of $2\cdot(HClO_4)_2$ (C-C=C-C bond lengths = 1.395, 1.385, and 1.392 Å) than $3\cdot(HClO_4)_2$ (C-C=C-C bond lengths = 1.398, 1.362, and 1.425 Å). While in neither case does the degree of bond equivalence approach completeness (as it does for the free-base "parents" **2** and **3**), it still remains within delocalized limits. Thus these two diprotonated systems, like their porphyrin "control" $1\cdot(HClO_4)_2$, are safely considered as being true Hückel-type $4n+2$ dications, at least as judged by this purely structural analysis.

UV/visible absorption spectral analyses carried out in dichloromethane solution are also consistent with the conclusion that the doubly protonated forms of isomers **2** and **3**, like that of etioporphyrin **1**, are porphyrin-like in character. All three salts, $1\cdot(HClO_4)_2$, $2\cdot(HClO_4)_2$, and $3\cdot(HClO_4)_2$, display intense absorption bands in the Soret region that are shifted compared to those of the corresponding free-base forms. They also display fewer Q-type transitions than do the unprotonated "starting materials" (Table 1). Specifically, for etioporphyrin **1** in CH_2Cl_2 the Soret band sharpens considerably upon protonation and shifts from 396 to 404 nm, while the number of Q-type transitions decreases from four to three. In the process, the color of the solution changes from dark red to purple. In the case of etioporphycene **2** in CH_2Cl_2, protonation serves to turn the original blue solution green. It also causes the Soret band at 382 nm to split into two peaks (at 409 and 388 nm) and the number of Q-type transitions to decrease from three to two. Finally, protonation of etiocorrphycene **3** in CH_2Cl_2 causes the Soret band to increase in intensity (but not split) and the number of Q-bands to be reduced to two. In this instance, the Soret band shifts slightly to the red (from 410 to 419 nm) upon protonation, and the color changes from yellow-red to purple.

The substantial changes observed in the UV/vis region of the electronic spectrum provide a spectroscopic handle for monitoring quantitatively the effects of protonation. Here, the critical issue would involve a determination of the relative basicity of the inner pyrrolenine nitrogens. Unfortunately, none of these

Table 1. UV/Vis spectra (λ_{max} in nm, ε in $cm^{-1}M^{-1}$).

	Solvent	Soret		Q Bands					Ref.
1	CH_2Cl_2	396 (152000)		496 (13600)	530 (9240)	565 (6110)		619 (4630)	this work
1	$CHCl_3$	400 (160000)							[24]
1	dioxane			496 (13600)	528 (9500)	566 (5950)	595 (1360)	621 (5180)	[24]
1·$[HClO_4]_2$	CH_2Cl_2 [a]	404 (398000)		548 (15000)	571 (5300)	593 (6700)			this work
1·$[HClO_4]_2$	CH_2Cl_2 [b]	404 (477000)		549 (15100)	570 (5600)	593 (6300)			this work
2	CH_2Cl_2	382 (144200)		570 (34200)	617 (18400)	657 (30000)			[1f]
2·$[HClO_4]_2$	CH_2Cl_2 [a]	388 (116000)	407 (77600)	597 (21500)	664 (25200)				this work
2·$[HClO_4]_2$	CH_2Cl_2 [b]	388 (138000)	409 (95700)	599 (26800)	666 (28100)				this work
3	CH_2Cl_2	410 (142400)		509 (13350)	539 (3480)	574 (5730)	584 (sh)	628 (1860)	this work
3	benzene	415 (139400)		511 (13700)	540 (3800)	577 (5600)	584 (4300)	632 (1900)	[1g]
3·$[HClO_4]_2$	CH_2Cl_2 [c]	418 (262000)		560 (14200)	595 (6210)				this work
3·$[HClO_4]_2$	CH_2Cl_2 [b]	419 (320000)		559 (16100)	604 (6830)				this work

[a] Recrystallized salt (CH_2Cl_2–hexanes). [b] With excess $HClO_4$ added. [c] Crude salt obtained by extraction (CH_2Cl_2) from aqueous perchloric acid.

etio-type isomeric porphyrins is soluble in water. As a result, no true, single-phase pK_a titrations could be run. Thus, an extraction-based approach to assessing basicity was employed. This involved taking aliquots of a solution of the free-base macrocycle in dichloromethane and equilibrating them with aqueous solutions of increasing acidity.[14] Plotting the change in absorption of the macrocycle-containing dichloromethane solution at a given wavelength versus the pH of the acidic solution with which it is in contact produces a titration-like curve.

This method, which we have used before,[15] does not give a true measure of the absolute basicities for systems **1**–**3**. Nonetheless, it was expected to produce *relative* pK_a values of reasonable accuracy. This is because the dichloromethane/water solubilities (and hence partition coefficients) for the various forms of these purely isomeric compounds should all be roughly the same. In the event, analyses carried out in this way reveal that porphycene **2** adds two protons readily and concurrently under these conditions; it becomes 50% *diprotonated* when exposed to perchlorate/perchloric solutions of pH ≈ 3.6 (Fig. 5). On the other hand, porphyrin **1** and corrphycene **3** are protonated in a stepwise manner. They become 50% *monoprotonated* when exposed to perchlorate/perchloric solutions of pH ≈ 3.7 and 3.9, respectively, and diprotonated at pH ≤ 0.8 and 1.3, respectively (Figs. 4 and 6).[18]

While the reasons for the above differences in protonation behavior (i.e., porphycene vs. porphyrin and corrphycene) are not currently understood, they could reflect important differences in in-cavity structure. Specifically, in the case of porphycene it is tempting to speculate that a first protonation

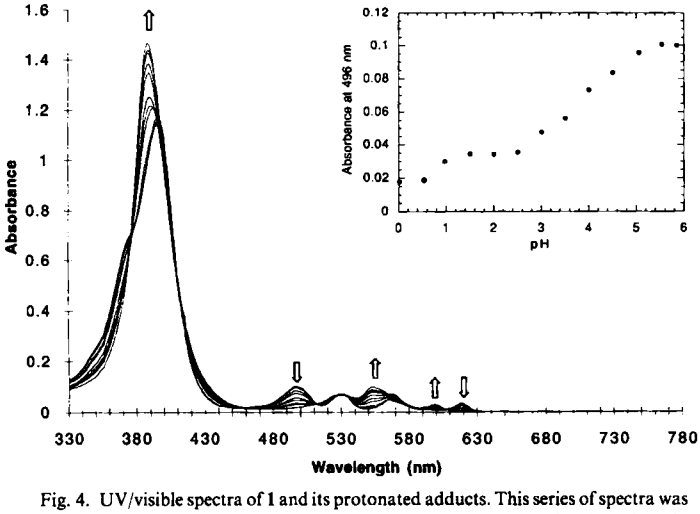

Fig. 4. UV/visible spectra of **1** and its protonated adducts. This series of spectra was obtained by recording the spectrum of **1** initially dissolved as its free-base form in dichloromethane and then after being stirred in the presence of aqueous perchloric acid solutions of known, decreasing pH. Inlay shows the change in absorbance at 496 nm as a function of pH. A derivative plot of this latter curve yields two inflection points at pH values of 3.7 and ≤0.8, respectively.

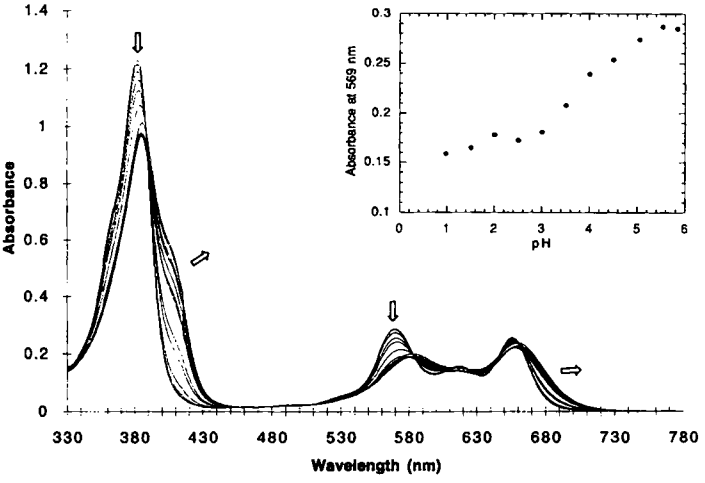

Fig. 5. UV/visible spectra of **2** and its protonated adducts. This series of spectra was obtained by recording the spectrum of **2** initially dissolved as its free-base form in dichloromethane and then after being stirred in the presence of aqueous perchloric acid solutions of known, decreasing pH. Inlay shows the change in absorbance at 569 nm as a function of pH. A derivative plot of this latter curve yields one inflection point at a pH value of 3.6.

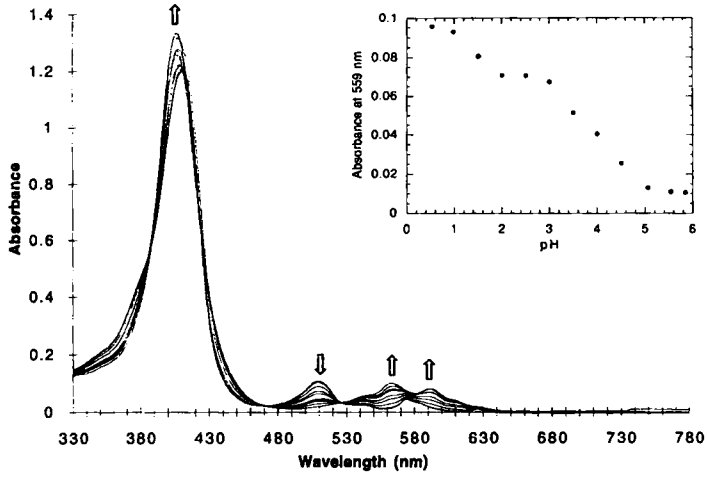

Fig. 6. UV/visible spectra of **3** and its protonated adducts. This series of spectra was obtained by recording the spectrum of **3** initially dissolved as its free-base form in dichloromethane and then after being stirred in the presence of aqueous perchloric acid solutions of known, decreasing pH. Inlay shows the change in absorbance at 559 nm as a function of pH. A derivative plot of this latter curve yields two inflection points at pH values of 3.9 and 1.4, respectively.

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would serve to distort the tetrapyrrolic structure sufficiently that the strong internal N–H ··· H hydrogen bonding network would be destroyed. The electrostatic "price" of binding a second proton on the last remaining pyrrolenine-type nitrogen of the now monoprotonated skeleton would then be correspondingly reduced. Such considerations, which are a restatement of earlier arguments voiced in steric terms,[13] would be considered to be less important in the case of porphyrin and corrphycene as here there is less evidence for a strong internal N–H ··· H hydrogen bonding network.

The ^{1}H NMR spectra of the three free-base isomers **1**, **2**, and **3**, recorded in $CDCl_3$, all show, as expected for aromatic molecules, internal hydrogen signals that are shifted to higher field and *meso* hydrogen resonances that are shifted to lower field than would be expected for similar systems lacking a strong diamagnetic ring current.[19] Protonation, to give **1**·$(HClO_4)_2$, **2**·$(HClO_4)_2$, and **3**·$(HClO_4)_2$, serves to accentuate these effects, with the diagnostic NH and *meso*-CH signals being shifted to yet higher and lower fields, respectively. This is as expected given the fact that protonation converts macrocycles containing well-defined Hückel-type $(4n+2)$ π-electron pathways into systems wherein more complete delocalization is possible. In other words, protonation serves to increase the number of available resonance structures in compounds **1**–**3**. It also introduces positive charges that should enhance any deshielding effects.

In the case of **2**, protonation also serves to break the strong internal N–H ··· H hydrogen-bonding network. This allows the N–H protons in the protonated product (**2**·$(HClO_4)_2$) to resonate at chemical shifts typical of analogous porphyrin species (i.e. in the $\delta = -3$ to -5 region), while those of the free base, locked up in N–H ··· H hydrogen bonds, cannot. The net result is a $\Delta\delta$ value for the conversion of **2** to **2**·$(HClO_4)_2$ (4.26 ppm) that is considerably larger than that observed upon diprotonation of either **1** or **3** ($\Delta\delta = 0.92$ and 1.68 ppm, respectively). These NMR findings thus support the conclusion made earlier in the context of the direct pK_a "titrations" that the protonation chemistry of porphycene is slightly different from that of either **1** or **3**. Still, like these two congeners, porphycene **2** is in fact readily protonated in the presence of strong acid to give a species that acts very much like a true diprotonated porphyrin analogue.

Compounds **1**–**3** were further characterized in solution by means of ^{1}H–^{15}N-coupled 2D NMR spectroscopy. This method has been applied to the analysis of porphyrins[20] and chlorins[21] and provides a complement to the ^{15}N-CPMAS-NMR techniques that have been used to analyze successfully the problem of NH tautomerism of porphyrin and porphycene in the solid state.[1d] When this ^{15}N NMR method was applied to the free-base forms of **1**, **2**, or **3** dissolved in $CDCl_3$, either at room temperature or $-50\,^\circ$C, no good ^{15}N signal was obtained. However, in the case of the diprotonated species, well-resolved spectra were obtained even at room temperature (c.f. Figs. 7–9). In the case of **1**·$(HClO_4)_2$ and **2**·$(HClO_4)_2$, one ^{15}N NMR shift was observed in the 2D chemical shift correlation analyses. By contrast, for **3**·$(HClO_4)_2$, two shifts were observed. In all cases, the chemical shifts were in the $\delta = 125$–135 range and were doublets with coupling constants of ≤ 95 Hz.

The above observations are consistent with slow intramolecular exchange of the N–H protons. First, sharp peaks are observed. This indicates that the spectra were not recorded under conditions of intermediate exchange. Second, two separate shifts are observed for **3**·$(HClO_4)_2$. This adduct, lacking a paired set of in-plane C_2 symmetry axes, would be expected to give rise to a single shift were the internal N–H protons undergoing fast exchange. Salts **1**·$(HClO_4)_2$ and **2**·$(HClO_4)_2$, on the other hand, are of such a symmetry that a single shift would be expected under conditions of both fast and slow exchange. Thus, the observation of a single shift does not necessarily indicate slow exchange in these cases. However, the similarity of the chemical shift values for all three salts and the fact that, in accord with previous work with protonated porphyrins,[22] these are in the range expected for pyrrole-like nitrogens ($\delta \approx 110$–115[1d, 20a, 21b]), rather than pyrrolenine-type ones ($\delta \approx 215$–225[1d, 20a, 21b]), makes such an extrapolation reasonable.

The doubled nature of the peaks and the coupling constants of ≤ 95 Hz, observed in all three cases, provides yet a further

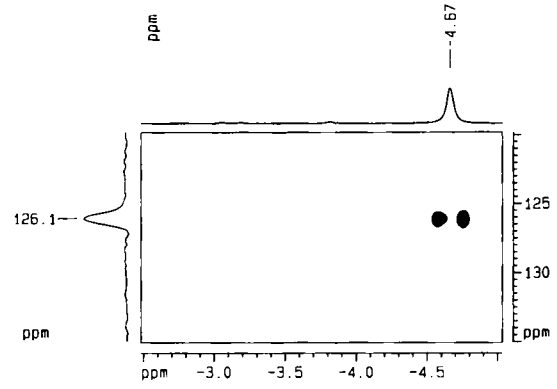

Fig. 7. 2D ^{1}H–^{15}N-coupled NMR spectra of **1**·$(HClO_4)_2$ in deuterated chloroform. The vertical axis shows the chemical shift of the ^{15}N signals, while the horizontal axis shows those of the proton resonances.

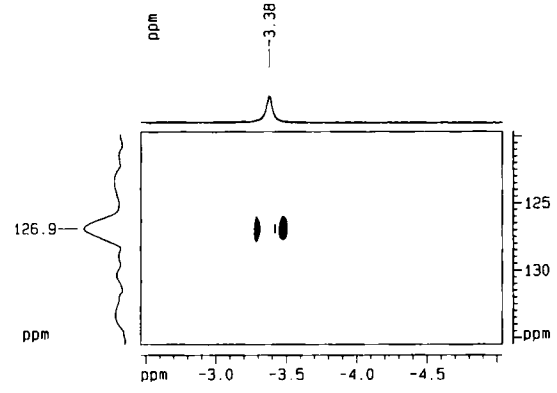

Fig. 8. 2D ^{1}H–^{15}N-coupled NMR spectra of **2**·$(HClO_4)_2$ in deuterated chloroform. The vertical axis shows the chemical shift of the ^{15}N signals, while the horizontal axis shows those of the proton resonances.

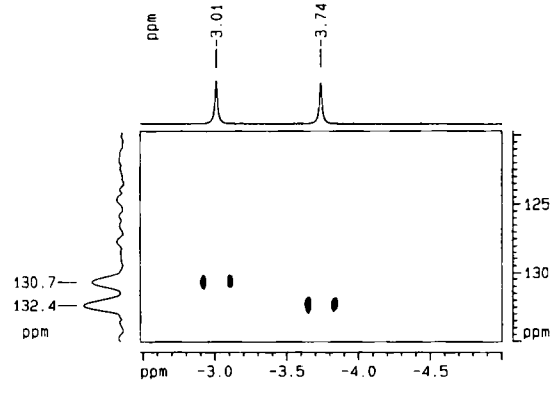

Fig. 9. 2D ^{1}H–^{15}N-coupled NMR spectra of **3**·$(HClO_4)_2$ in deuterated chloroform. The vertical axis shows the chemical shift of the ^{15}N signals while the horizontal axis shows those of the proton resonances.

indication of slow exchange. Previous work with porphyrins[20] and chlorins[21] has served to show that doubled peaks and coupling constants on the order of 95–100 Hz are to be expected in cases where the N–H protons are undergoing slow exchange. By contrast, triplet signals with coupling constants on the order of 50–70 Hz are anticipated under conditions of fast exchange.[20–22] Thus, taken together, these ^{15}N–^{1}H NMR data provide a consistent picture of a situation wherein the internal N–H protons are locked in place, at least on the NMR timescale. This is very different from what is generally observed[1d, 1g, 20, 22, 23] in the case of the corresponding free-base forms.

Conclusion

Compounds **1**–**3** provide a "matched set" of isomers that can be used to explore various issues related to the structure and properties of porphyrin-type macrocycles. In this paper we have shown that all three species can be readily diprotonated to yield materials that are quite different, both in solution and in the solid state, from their better characterized free-base "parents". We have also shown that porphycene **2**, with its strong internal N–H···H hydrogen bonding network, differs slightly from its congeners **1** and **3** when it comes to its protonation characteristics. Current work is focused on exploring fully the metalation chemistry of these systems and determining whether this feature or some other associated with structures **1**–**3** serves to mediate their ability to act as tetracoordinating ligands. Results of these investigations will be reported in due course.

Acknowledgements: This work was supported by the National Science Foundation (J. L. S., Grant CHE-9122161), the Alexander von Humboldt-Stiftung (J. L. S., Senior Scientist Award), and a Deutsche Forschungsgemeinschaft Grant (E. V.). We wish to thank Dr. Marilyn Olmstead for her help in solving the X-ray structure of **3**·$(HClO_4)_2$.

Received: June 3, 1996 [F383]

[1] Porphyrin Isomers: a) J. L. Sessler, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1348–1350. Porphycenes: b) E. Vogel, M. Köcher, H. Schmickler, J. Lex, *ibid.* **1986**, *25*, 257–259. c) E. Vogel, M. Balci, K. Pramod, P. Koch, J. Lex, O. Ermer, *ibid.* **1987**, *26*, 928–931. d) B. Wehrle, H.-H. Limbach, M. Köcher, O. Ermer, E. Vogel, *ibid.* **1987**, *26*, 934–936. e) E. Vogel, *Pure Appl. Chem.* **1990**, *62*, 557–564. f) E. Vogel, P. Koch, X.-L. Hou, J. Lex, M. Lausmann, M. Kisters, M. A. Aukauloo, P. Richard, R. Guilard, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1600–1604. Corrphycenes: g) J. L. Sessler, E. A. Brucker, S. J. Weghorn, M. Kisters, M. Schäfer, J. Lex, E. Vogel, *ibid.* **1994**, *33*, 2308–2312. h) M. A. Aukauloo, R. Guilard, *New J. Chem.* **1994**, *18*, 1205–1207. i) H. Falk, Q.-Q. Chen, R. Micura, *Monatssh. Chem.* **1996**, *127*, 77–83. Metallocorrphycenes: j) E. Vogel, J. L. Sessler, unpublished results. Hemiporphycenes: k) H. Callot, *New J. Chem.* **1995**, *19*, 155–159. l) E. Vogel, J. L. Sessler, unpublished results. N-confused (inverted) porphyrins: m) H. Furuta, T. Asano, T. Ogawa, *J. Am. Chem. Soc.* **1994**, *116*, 767–768. n) P. J. Chielewski, L. Latos-Grazynski, K. Rachlewicz, T. Glowiak, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 779–781.

[2] In recent, as yet unpublished work, the structure of a third pyrrole-in free-base porphyrin isomer, hemiporphycene, has been solved [11]. This same isomer has been characterized structurally as its nickel(II) complex [1k].

[3] The systematic names for compounds **1**–**3** are 2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-21,22,23,24-tetraazapentacyclo[16.2.1.1^{6,9}.1^{11,14}.1^{16,19}]tetracosa-1,3,5,7,9(22),10,12,14,16(24),17,19-undecene (etioporphyrin II), 2,7,12,17-tetraethyl-3,6,13,16-tetramethyl-21,22,23,24-tetraazapentacyclo[16.2.1.1^{5,8}.1^{11,14}.1^{15,18}]tetracosa-1,3,5(22),6,8,10,12,14,16,18(24),19-undecene (etioporphycene), and 2,7,11,18-tetraethyl-3,6,12,17-tetramethyl-21,22,23,24-tetraazapentacyclo[16.2.1.1^{2,5}.1^{7,10}.1^{13,16}]tetracosa-1(20),2(21),3,5,7,9,11,13(23),14,16,18-undecene (etiocorrphycene), respectively.

[4] This porphyrin was synthesized according to the procedure of H. L. Anderson, J. K. M. Sanders, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1400–1403, but with formaldehyde replacing the benzaldehyde derivative originally used.

[5] **1**·$(HClO_4)_2$: $[C_{32}H_{40}N_4]$ Cl_2O_8, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 9.198(4)$, $b = 10.878(5)$, $c = 16.694(7)$ Å, $\alpha = 95.10(4)$, $\beta = 90.49(4)$, $\gamma = 97.18(4)°$, $V = 1650(1)$ Å^3, $\rho_{calcd} = 1.37$ mg m^{-3} (173 K), $F(000) = 716$. Data collected at 173 K on a Nicolet P3 diffractometer, graphite monochromator, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $2\theta_{max} = 45°$, 4312 independent reflections, 1804 with $F_0 > 4.0\sigma(F_0)$; the final $R(F) = 0.0898$, $R_w(F) = 0.0866$, and goodness of fit = 2.047 for 441 parameters.

[6] **2**·$(HClO_4)_2$: $[C_{32}H_{40}N_4]$ Cl_2O_8, monoclinic, space group C2/c, $Z = 4$, $a = 15.042(2)$, $b = 14.088(3)$, $c = 15.276(3)$ Å, $\beta = 97.433(3)°$, $V = 3210(1)$ Å^3, $\rho_{calcd} = 1.406$ mg m^{-3} (173 K), $F(000) = 1432$. Data collected at 173 K on a Nicolet P3 diffractometer, graphite monochromator, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $2\theta_{max} = 50°$, 2826 independent reflections, 1789 with $F_0 > 4.0\sigma(F_0)$; the final $R(F) = 0.0513$, $R_w(F) = 0.0500$, and goodness of fit = 1.22 for 277 parameters.

[7] **3**·$(HClO_4)_2$: $[C_{32}H_{40}N_4]$ Cl_2O_8, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 8.903(2)$, $b = 11.304(2)$, $c = 16.130(3)$ Å, $\alpha = 90.640(0)$, $\beta = 92.600(0)$, $\gamma = 95.530(0)°$, $V = 1613.9(5)$ Å^3, $\rho_{calcd} = 1.398$ mg m^{-3} (120 K), $F(000) = 716$. Data collected at 120 K on a Siemens P4 diffractometer, nickel filter monochromator, $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å), $2\theta_{max} = 112°$, 4201 independent reflections, 2519 with $F_0 > 6.0\sigma(F_0)$; the final $R(F) = 0.0985$, $R_w(F) = 0.0988$, and goodness of fit = 0.86 for 415 parameters.

[8] Etioporphyrin II is structurally equivalent to octaethylporphyrin, whose X-ray structure has been solved: J. W. Lauher, J. A. Ibers, *J. Am. Chem. Soc.* **1973**, *95*, 5148–5152.

[9] S. C. Wallwork, *Acta Crystallogr.* **1962**, *15*, 758–759.

[10] a) C. P. Hrung, M. Tsutsui, D. L. Cullen, E. F. Meyer, *J. Am. Chem. Soc.* **1976**, *98*, 7878–7880. b) N. Hirayama, A. Takenaka, Y. Sasada, E.-I. Watanabe, H. Ogoshi, Z.-I. Yoshida, *J. Chem. Soc. Chem. Commun.* **1974**, 330–331.

[11] In this context, it is of interest to note that in the one previous X-ray structure of $[OEP{\cdot}H_2]^{2+}{\cdot}2[RhCl_2(CO)_2]^-$, the only other diprotonated octaalkylporphyrin of whose structure we are aware [12], the porphyrin dication was found to be essentially planar. This establishes that the oft-discussed [10b,13] destabilizing H···H nonbonded interactions, presumed to occur within the core of diprotonated porphyrins, need not necessarily give rise to deviations from planarity, even though this often [10,13] appears to be the case.

[12] E. Cetinkaya, A. W. Johnson, M. F. Lappert, G. M. McLaughlin, K. W. Muir, *J. Chem. Soc. Dalton Trans.* **1974**, 1236–1243.

[13] a) E. B. Fleischer, *Acc. Chem. Res.* **1970**, *3*, 105–112. b) A. Stone, E. B. Fleischer, *J. Am. Chem. Soc.* **1968**, *90*, 2735–2748. c) E. B. Fleischer, A. L. Stone, *J. Chem. Soc. Chem. Commun.* **1967**, 332–333.

[14] The acid chosen here was $HClO_4$ so as to maintain a congruence between these extraction experiments and the X-ray diffraction ones carried out in the solid state.

[15] This two-phase extraction–UV/visible spectroscopy method was used previously to determine the approximate pK_a's of a similar alkyl-substituted aromatic macrocycle, 3,8,12,13,17,22-hexaethyl-2,7,18,23-tetramethylsapphyrin [16]. The values obtained in this way, 3.5 and 9.5 [16], were later compared to those of a water-soluble derivative, 4.8 and 8.8, as determined by a more direct aqueous titration method involving a detergent [17]. Based on this prior work, we conclude that this extraction–UV/visible method, although precise, may be inaccurate by 1 to 2 pK_a units. Nonetheless, in the present instance, such an extraction-based approach should permit meaningful comparisons between isomers.

[16] H. Furuta, M. J. Cyr, J. L. Sessler, *J. Am. Chem. Soc.* **1991**, *113*, 6677–6678.

[17] V. Král, H. Furuta, K. Shreder, V. Lynch, J. L. Sessler, *J. Am. Chem. Soc.* **1996**, *118*, 1595–1607.

[18] In the case of porphycene and corrphycene, two tautomeric forms can be considered for the proposed monoprotonated intermediates. However, in the present study no direct information about these states was obtained. Certainly, in the case of porphyrin per se, observation of the porphyrin monocation is generally considered to be difficult (see: *Porphyrins and Metalloporphyrins* (Ed.: K. M. Smith), Elsevier, Amsterdam; 1975, pp. 11–13). Such species, however, have been isolated and characterized in the solid state; see ref. [10].

[19] ^1H NMR (250 MHz, $CDCl_3$): **1**: $\delta = -3.74$ (brs, 2H, NH), 1.89 (t, 6H, ethyl), 1.90 (t, 6H, ethyl), 3.64 (s, 6H, methyl), 3.66 (s, 6H, methyl), 4.10 (q, 4H, ethyl), 4.11 (q, 4H, ethyl), 10.10 (s, 4H, *meso*); **1**·$(HClO_4)_2$: $\delta = -4.66$ (brs, 4H, NH), 1.84 (t, 12H, ethyl), 3.70 (s, 12H, methyl), 4.15 (q, 8H, ethyl), 10.65 (s, 4H, *meso*); **2**: $\delta = 0.87$ (brs, 2H, NH), 1.72 (t, 12H, ethyl), 3.58 (s, 12H, methyl), 3.87 (q, 8H, ethyl), 9.54 (s, 4H, *meso*); **2**·$(HClO_4)_2$: $\delta = -3.39$ (brs, 4H, NH), 1.70 (t, 12H, ethyl), 3.56 (s, 12H, methyl), 3.81 (q, 8H, ethyl), 10.07 (s, 4H, *meso*); **3**: $\delta = -2.06$ (brs, 2H, NH), 1.81 (t, 6H, ethyl), 1.82 (t, 6H, ethyl), 3.55 (s, 6H, methyl), 3.66 (s, 6H, methyl), 3.97 (q, 4H, ethyl), 4.00 (q, 4H, ethyl), 9.89 (s, 2H, *meso*), 9.91 (s, 2H, *meso*); **3**·$(HClO_4)_2$: $\delta = -3.74$ (s, 2H, NH), −3.01 (s, 2H, NH), 1.75 (t, 6H, ethyl), 1.78 (t, 6H, ethyl), 3.48 (s, 6H, methyl), 3.64 (s, 6H, methyl), 3.95 (q, 4H, ethyl), 4.05 (q, 4H, ethyl), 10.30 (s, 2H, *meso*), 10.54 (s, 2H, *meso*).

[20] a) C. S. Irving, A. Lapidot, *J. Chem. Soc. Chem. Commun.* **1977**, 184–186. b) M. Schlabach, B. Wehrle, H. Rumpel, J. Braun, G. Scherer, H. H. Limbach, *Ber. Bunsenges. Phys. Chem.* **1992**, *96*, 821–833. c) M. Schlabach, H. H. Limbach, E. Bunnenberg, A. Y. L. Shu, B. R. Tolt, C. Djerassi, *J. Am. Chem. Soc.* **1993**, *115*, 4554–4570.

[21] a) M. Schlabach, G. Scherer, H. H. Limbach, *J. Am. Chem. Soc.* **1991**, *113*, 3550–3558. b) R. Bonnett, B. D. Djelal, G. E. Hawkes, P. Haycock, F. Pont, *J. Chem. Soc. Perkin Trans 2* **1994**, 1839–1843.

[22] D. Gust, J. D. Roberts, *J. Am. Chem. Soc.* **1977**, *99*, 3637–3640.

[23] a) C. B. Storm, Y. Teklu, *J. Am. Chem. Soc.* **1972**, *94*, 1745–1747. b) R. J. Abraham, G. E. Hawkes, K. M. Smith *Tetrahedron Lett.* **1974**, 1483–1486.

[24] Ref. [18], p. 873.