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5,10,15-Triaryl-21,23-dioxacorrole and Its Isomer with a **Protruding Furan Ring**

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An oxa-analogue of 5,10,15-triarylcorrole, i.e., 5,10,15-triaryl-21,23-dioxacorrole (21,23-O₂Cor)H, where two pyrrole rings are replaced by furan moieties, has been produced by condensation of 2,5-bis(arylhydroxymethyl)furan, 2-phenylhydroxymethylfuran, and pyrrole. 2-Phenylhydroxymethylfuran serves as the suitable synthone to introduce a furan ring with the ability create a direct pyrrole-furan $\alpha - \alpha$ bond. The replacement of 2-phenylhydroxymethylfuran by 3-phenylhydroxymethylfuran led to a nonaromatic isomer of (21,23-O₂Cor)H, i.e., (iso-21,23-O₂Cor)H, which accommodates two furan rings. The protruding furan is built into the macrocycle via β and β' carbon atoms with the oxygen atom pointing outward. Crystal structures of the $[(21,23-O_2Cor)H_2]_2[ZnCl_4]$ and $[(iso-21,23-O_2Cor)H_2]Cl$ have been studied by X-ray crystallography. The complex $ZnCl_4^{2-}$ anion is located in a clam-shell-like cavity formed by two 21,23-dioxacorrole cations of the [(21,23-O₂- $Cor)H_2[2]ZnCl_4]$ unit. The 21,23-dioxacorrole cation is only slightly distorted from planarity. In [(iso- $21,23-O_2Cor)H_2$ [Cl, the macrocycle is strongly puckered as the internal ring is contracted by two carbon atoms when compared to regular porphyrin. The chloride anion is located over the center of the macrocycle and is involved in two intra (N)H····Cl and two intermolecular (C)H···Cl interactions to be classified as a tetrafurcate system. The (21,23-O₂Cor)H molecule preserves aromaticity of the parental corrole with characteristic downfield positions of furan and pyrrole resonances in ¹H NMR accompanied the NH resonance at the upfield position (-2.53 ppm). The temperaturedependent features detected in ¹H NMR spectra of (21,23-O₂Cor)H are consistent with the existence of a tautomeric equilibrium which involves two tautomers alternatively protonated on N(22) or N(24) nitrogen atoms. The density functional theory (DFT) has been applied to model the molecular and electronic structure of two tautomers of 21,23-dioxacorrole {22-N, 24-NH}, {22-NH, 24-N}. The total energies calculated using the B3LYP/6-31G**//B3LYP/6-31G* approach demonstrate a very small energy difference (1.4 kcal/mol) between tautomers suggesting their simultaneous presence in equilibrium. Insertion of nickel(II) into (21,23-O₂Cor)H yields five-coordinate (21,23- O_2 Cor)Ni^{II}Cl—the first high-spin nickel(II) in a corrole-like macrocyclic environment.

Introduction

Novel efficient procedures for synthesis of 5,10,15triarylcorroles that are based on condensation of simple building blocks, i.e., (1) pyrrole and aryl aldehydes,¹⁻⁴ (2) dipyromethane and aldehyde,5,6 or oxidant-mediated coupling of tetrapyrromethanes,7 give an incentive to exploit triarylcoroles as suitable ligands.^{8–13} Previously, β -alkylated, meso-unsubstituted corroles have been largely applied to explore properties of corroles and their complexes.14-16

A corrole molecule is an 18 π electron aromatic macrocycle with a direct $\alpha - \alpha$ pyrrole–pyrrole link. Formally, one can consider 5,10,15-triarylcorrole as a molecule derived from 5,10,15,20-tetraarylporphyrins simply by extrusion of a $C-C_6H_5$ moiety. As a matter of fact, the

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first triarylcorrole was prepared in this way.¹⁷ The formation of 5,10,15-triarylcorroles seems to be a natural and predictable consequence of the classical Rothemundlike pyrrole-arylaldehyde condensation considering the mechanism of the process.¹⁸⁻²² Actually, a variety of other macrocylic products accompanying tetraarylporphyrins are formed in the course of condensation.²³⁻²⁶

Potential applications of metallotriarylcorroles in catalytic processes of oxygen atom transfer or cyclopropanation provide the essential stimuli for further synthetic studies.^{8,11} Certainly, the presence of meso aryl rings opens an access to control the electronic structure and overall molecular architecture including an access to the corrole core by means of well-planned peripheral substitutions. First the contracted macrocyclic core has properties significantly different compared with the porphyrins or metalloporphyrins.^{14–16} In particular, metallocorroles revealed a tendency to stabilize the higher oxidation states of coordinated metal ions or metal ion and macrocycle.^{10,13,27-30}

Apart from perimeter substitution, a different strategy, involving core alteration, can be considered as an independent route for controlling the reactivity of metallocorroles. In such an approach, at least one of the inner nitrogen atoms should be replaced by another heteroatom. At present, known core modified heterocorroles are not numerous. In their pioneering investigations of coremodified porphyrins and expanded porphyrins³¹ presented in 1972, Johnson and co-workers introduced β -alkylated 21,24-dioxacorrole, 21-oxacorrole, and 22oxacorrole. Recently, Chandrashekar and co-workers have demonstrated that the $\alpha - \alpha$ coupling of 5,10diphenyl-16-oxatripyrrane and dipyrromethane yields 5,10,15-triaryl-21-oxacorrole.^{32,33} Lindsey and co-workers have remarked that the condensation of 5-(p-tolyl)-

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dipyrromethane and furylpyrromethanediol yielded 5,10,15-triaryloxacorrole in addition to the expected 5,10,15,20-tetraaryl-21-oxaporphyrin.³⁴ Lee and co-workers have reported on an original way to produce 5,10,15triaryl-21-oxacorrole and, for the first time, the isomeric 5,10,15-triaryl-22-oxacorrole.³⁵ Finally, the Vogel group succeeded^{36,37} in preparation of tetraoxacorrole cation and octaethyltetroxacorrole cation, although these results are practically available in the review articles.^{15,16} A complementary area of corrole modifications, which can be described as a replacement of carbon atom(s) in the corrole skeleton by heteroatom(s), yielded 10-oxacorrole, 10-thiacorrole,^{38,39} and 5,10,15-triazacorrole (corrolazine).40

Complexes of 5,10,15-triaryl-21-oxacorrole with nickel-(II), copper(II), cobalt(II), and rhodium(I) have been investigated.³³ The monooxacorrole acts as a dianionic ligand that stabilizes nickel(II) (low-spin) and copper(II) complexes. These observations remain in contrast with corroles that act as a trianionic ligand favoring higher oxidation states of complexes.²⁷ Previously, we have elucidated a relationship between the number of oxygen atoms and the coordination properties of nickel(II) and nickel(I) in the conceptually related series of 5,10,15,20tetraphenylporphyrin, 5,10,15,20-tetraaryl-21-oxaporphyrin, and 5,10,15,20-tetraaryl-21,23-dioxaporphyrin.41-43 Thus, considering the fundamental changes introduced by replacement of one nitrogen atom by oxygen to yield 21-oxacorrole, we have found it important to explore the properties of other compounds in the series.

Here, we describe the synthesis and spectroscopic properties of the first 21,23-dioxacorrole, i.e., 5,10,15triaryl-21,23-dioxacorrole and its isomer with a protruding furan ring. In particular, the applicability of 2-phenylhydroxymethylfuran and 3-phenylhydroxymethylfuran as synthones in the oxacorrole ring construction have been explored.

Result and Discussion

Synthesis and Characterization of 5-Phenyl-10,15bis(p-tolyl)-21,23-dioxacorrole. The synthesis involves the condensation of 2,5-bis(p-tolylhydroxymethyl)furan 1 and 2-phenylhydroxymethylfuran 2, with pyrrole (1: 1:2 molar ratio), carried out in dichloromethane and catalyzed by BF₃·Et₂O. After oxidation with *p*-chloranil, 5-phenyl-10,15-bis(p-tolyl)-21,23-dioxacorrole 3 is obtained in 8% yield. The reaction is presented in Scheme 1.

The reaction applies 2-phenylhydroxymethylfuran as the suitable synthone to introduce the furan ring, which

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is able to create the direct pyrrole–furan $\alpha-\alpha$ bond. The synthesis resembles that which led to formation of 21,23dioxaporphyrin but requires an $\alpha-\alpha$ condensation between the pyrrole and furan rings of **2**.⁴¹ A similar step has been previously suggested in the process of formation of monoxacorrole.³⁵ The identity of **3** has been confirmed by high-resolution mass spectrometry, ¹H NMR spectroscopy, and X-ray crystallography.

Spectroscopic Characterization of 21,23-Dioxacorrole. 5-Phenyl-10,15-bis(p-tolyl)-21,23-dioxacorrole **3** demonstrates spectroscopic properties typical of corroles and core-modified corroles. The UV-vis spectrum of **3** is triarylcorrole-like. The spectrum presents a markedly split Soret band (397 and 422 nm) (Figure 1) and a series of Q-bands in the 480–640 nm range. Presumably, the split Soret band reflects the symmetry lowering due to the trans localization of two oxygen atoms, and this feature is preserved after protonation. The isosbestic points corresponding to a single protonation steps have been detected in the course of titration of a dichloromethane solution of **3** with TFA followed by electronic spectroscopy. The acid titration is accompanied by a distinct color change from violet to blue-green.

The complete assignment of all ¹H NMR resonances for **3**, shown in Figure 2, has been obtained by means of 2D ¹H NMR COSY and NOESY experiments using the unique NOE correlation between H(3)–*o*-H(5-phenyl) as a starting point. All perimeter furan [9.53 (H(2)), 9.14 (H(3)) (AB, ³J_{AB} = 4.2 Hz), 9.30 (H(13)), 8.94 (H(12)) (AB, ³J = 4.6 Hz)] and pyrrole [8.96 (H(7)), 8.70 (H(8)) (AB, ³J = 4.6 Hz), 9.24 (H(18)), 8.83 (H(17)) (AB, ³J = 4.2 Hz)] are downfield shifted due to the ring current effect. Essentially, molecule **3** preserves the aromaticity of the parent corrole. Consistent with the aromacity of **3**, the broad NH resonance has been located at –2.53 ppm (298 K).

21,23-Dioxacorrole 3 tautomerizes via a rapid exchange of the NH proton between two structurally unequivalent nitrogen atoms of 3' and 3'' as seen in Scheme 2. Significant spectral changes have been detected in variable-temperature ¹H NMR studies carried out for 3 in dichloromethane- d_2 solutions (Figure 2, traces A and B). As the temperature gradually decreases, the resonances H(2), H(13), H(7), and H(8) broaden selectively. Even at the lowest temperature studied (188 K in dichloromethane d_2) the dynamic process is still close to the fast exchange limit and a single, eventually very broad line is seen for each dynamically related couple. We have concluded that a low exchange rate has not been achieved at the accessible low-temperature limits of chlorinated solvents. Hypothetically, two well-resolved AB sets corresponding to 3' and 3", respectively, are expected for each five-



FIGURE 1. Electronic spectra of $(21,23-O_2Cor)H$ **3** (solid line), $(21,23-O_2Cor)H_2^+$ **3**-H (dashed line), and $(21,23-O_2Cor)Ni^{II}Cl$ **7** (dotted line) in dichloromethane.



FIGURE 2. ¹H NMR spectra: (A) $(21,23-O_2Cor)H$ (dichloromethane- d_2 , 233 K), (B) $(21,23-O_2Cor)H$ (dichloromethane- d_2 , 298 K, (C) $(21,23-O_2Cor)H_2^+$ (TFA/dichloromethane- d_2), 1/5 v/v, 298 K). Insets (not to scale) in traces B and C present the NH resonances. Peak labels follow systematic position numbering from Scheme 3 or denote proton groups: *o*, *m*, *p*-ortho, meta, and para positions of *meso*-phenyl (Ph) or *meso-p*-tolyl (Tol) rings, respectively.

membered ring once the process is determined to be slow on the ¹H NMR time scale. Interestingly, the markedly different dynamic behavior can be observed even for

SCHEME 2



doublets that belong to the same AB multiplet, e.g., H(2) and H(3); H(13) and H(12). Presumably the chemical shift difference determined for exchangeable pairs H(2)-3', H(2)-3"; H(13)-3', H(13)-3"; H(7)-3', H(7)-3"; and H(8)-**3**′, H(8)-**3**″ are in the range where the slow exchange limit is approached but above the collapsing point. The shift differences for the accompanying dynamic pairs H(3)-3', H(3)-3"; H(12)-3', H(12)-3"; H(17)-3', H(17)-3", and H(18)-3', H(18)-3" are markedly smaller. Eventually, the slightly dynamically broadened lines assigned to these hydrogen atoms could be seen at low-temperature limits. It is important to notice that even at 298 K the exchange of NH protons play an essential role. It is clearly demonstrated by the pronounced differences in the line width of the AB multiplets as reflected by peculiar differences in heights of scalar coupled doublets (Figure 2, traces A and B). All chemical shifts varied as temperature decreased, which is due to changes in populations of the two tautomers.

The ¹H NMR spectroscopic titration with TFA carried out in dichloromethane- d_2 at 228 K demonstrated that the addition of the proton results in a smooth change of the chemical shifts, which suggests fast exchange between 3 and 3-H and facilitates resonance assignment via the straightforward correlation of shifts between the neutral and cationic forms. Protonation takes place at nitrogen atoms, as documented by a rise of two NH resonances at -1.46 and -1.98 ppm (Figure 2, trace C). The protonation is accompanied by the downfield shift of β -H furan resonances and the upfield relocation of β -H pyrrole resonances. Importantly, the shift of NH protons is strongly dependent on the choice of acid (TFA, -1.46, -1.98 ppm; HCl, -0.83, -0.9 ppm), which implies an interaction between the 21,23-dioxacorrole monocation and the respective anion. The essential differences of the chemical shifts and spectral patterns reflect immediately the different properties of counteranions.44,45

The monocationic form(**3**-H)TFA becomes the major species at the 1:1 macrocycle to TFA molar ratio (Figure 2, trace C). In further steps of the titration (not shown), all β -H resonances moved gradually downfield. Presumably, the independent interaction of the (**3**-H)TFA ionic aggregate with the bulk of TFA through a network of hydrogen bonds accounts for these changes. Such a behavior was previously detected in titrations of 5,10,15,20-tetraphenylsaphyrin or 2-*N*-methyl-5,10,15,20-tetraphenyl-21-carbaporphyrin with TFA.^{44,45}

The HMQC and HMBC studies resulted in the full assignment of all ¹³C resonances of **3**-H (the studies on



FIGURE 3. Crystal structure of the 5,10,15-triaryl-21,23-dioxacorrole cation of $[(21,23-O_2Cor)H_2]_2[ZnCl_4]$ (top, perspective view; bottom, side-view phenyl groups omitted for clarity). The N(1)…N(2) distance = 3.685 Å. The vibrational ellipsoids represent 50% probability.

the monocation allowed the avoidance of the broadening due to tautomeric equilibria seen for neutral **3**). In general, all shifts are in the range expected for a corrole or an aromatic heterocorrole.

Crystal Structure of [(21,23-O₂Cor)H₂]₂[ZnCl₄]. The structure has been studied by X-ray crystallography. The perspective views of the molecule are shown in Figure 3.

The cation is only slightly distorted from planarity as seen in Figure 3 despite two NH protons in the center. The hydrogen atoms of the NH groups were clearly located in a difference map, and their positions were subsequently refined. The geometry of tetrachlorozinc-(II) anion is typical. The Zn^{II}–Cl distances of 2.277(1), 2.307(1), 2.277(1), and 2.307(1) Å are comparable with the 2.245–2.289 Å range reported for $ZnCl_4^{2-}$.^{46,47} The anion is located in a clam-shell like cavity formed by two 21,23-dioxacorrole cations of the [(21,23-O₂Cor)H)₂]₂-[ZnCl₄] unit (Figure 4). The dihedral angle between the 21,23-dioxacorole planes equals 61.5°. There are three (Zn)Cl····HC hydrogen bonding interactions of the trifurcate geometry between the Cl(1) anion of $ZnCl_4^{2-}$ and two β -H and ortho-H ((β -C)H)···Cl, 2.8 Å (2.8 Å), ((β -C)-H)·· ·Cl, 118.1° (128.3°); ((o-C)H···Cl), 2.8 Å, ((o-C)-H···Cl, 149°). Both hydrogen atoms involved in the interaction are located on the adjacent $[(21,23-O_2Cor)H)_2]_2[ZnCl_4]$ fragment which points into the open side of the clamlike cavity toward the chloride. In addition, the Cl(2) interacts with two hydrogen atoms (see the figure in the Supporting Information).

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FIGURE 4. Views of a clam-shell-like arrangement of the $[(21,23\text{-}O_2Cor)H)_2]_2[ZnCl_4]$ unit.

There is an appreciable effect from the aromatic character of the macrocycle on the furan portions. The $C_{\alpha}-C_{\beta}$ and $C_{\beta}-C_{\beta}$ bond lengths are practically identical. Thus, in these macrocycles, the $C_{\alpha}-C_{\beta}$ distances are longer and the $C_{\beta}-C_{\beta}$ distances are shorter than in free furan.⁴⁸ These bond changes indicate that the π delocalization of the furan ring is altered in 21,23-dioxacorrole. A similar influence of the aromatic macrocycle on the delocalization pattern in the furan ring was observed in the case of tetraoxa[18]porphyrin (1.1.1.1) dication,⁴⁹ ozaphyrin,⁵⁰ 21-oxaporphyrin, and 21,23-dioxaporphyrin.⁴¹

Synthesis and Characterization of the 21,23-Dioxacorrole Isomer with a Protruding Furan Ring. In the course of our investigations on 21,23dioxacorrole, we have realized that the replacement of 2-phenylhydroxymethylfuran 2 with 3-phenylhydroxymethylfuran 4 should provide the similar spatial arrangement in the course of condensation as that seen at Scheme 1, also providing an access to the reactive α position. Potentially the condensation involving 1 and 4 and pyrrole could result in 5, i.e., an isomer of 3 with a resembling structural skeleton. The structure 5 results form the formal reshuffling of the oxygen atom and the 2-CH group of 21,23-dioxacorrole to give 21-carba-2,23dioxacorrole 5.

Contrary to our expectation based upon steric reasons and the known reactivity differences between the α and β positions of furan, the condensation has taken place at the only available and sterically hindered β position. As the result, we have obtained **6**, i.e., an isomer of **3**, with a protruding furan ring. The only other macrocyclic





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FIGURE 5. Electronic spectra of **6** (solid line) and $6-H^+$ (dashed line) in dichloromethane.

product identified in the reaction was 5,10,15,20-tetra-(*p*-tolyl)-21,23-dioxaporphyrin.

Formally, structures **3**, **5**, and **6** preserve the common fragment of 21,23-dioxacorrole that is related to the acyclic 5,10-bis(*p*-tolyl)-14-(phenylhydroxymethyl)-16-oxatripyrrin. In **3** and **6**, both ends of the acyclic chain are linked by the furan ring at the α and α' positions for **3** and the β and β' positions for **6**. The $\beta-\alpha'$ connectivity of furan in the hypothetical **5** could not be realized in the described reaction conditions.

Spectroscopic Characterization of the 21,23-Di-oxacorrole Isomer. The electronic spectrum of **6** and its monocation is presented in Figure 5. The UV–vis spectrum of **3** is different from that detected for the isomeric 21,23-oxacorrole and its monocation. A split Soret band has been observed at 375 and 409 nm accompanied by a broad band at 753 nm.

The isosbestic points corresponding to a single protonation step have been detected in the course of titration of a dichloromethane solution of **6** with TFA, followed by electronic spectroscopy. The broad band of **6**-H shows a remarkably bathochromic shift to 962 nm. The acid titration is accompanied by a distinct color change from green to brown. The electronic spectra resemble those of other porphyrin related molecules which preserve conjugation in the tripirryne fragment but delocalization through the macrocycle is blocked by the completing linkage, e.g., 6,11,16,21-tetraphenyl-*m*-benziporphyrin (neutral, 723, dication 920 nm)⁵¹ or 5,10,15,20-tetraphenyl-2-thia-21-carbathiaporphyrin (neutral 697, 756, dication 908 nm).^{52,53}

The complete assignment of **6** all ¹H NMR resonances shown in Figure 6 has been obtained by means of ¹H NMR COSY and NOESY experiments using the H(4)– o-H(6-phenyl) ring and H(2)–H(19) dipolar correlations as a starting point for the analysis of connectivity. For topological reasons, the molecule **6** cannot retain macrocyclic aromacity typical of porphyrins or corroles. The ¹H NMR spectrum of **6** presents the β -H resonances at positions consistent with a nonaromatic structure (6.87 (H(2)), 6.29 (H(4)), ⁴J = 2.1 Hz; 6.39 (H(8)), 5.88 (H(9)),

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FIGURE 6. ¹H NMR spectra of **6**: (A) **6** (chloroform-*d*, 298 K), (B) **6**-H (chloroform-*d*, 298 K). Peak labels follow systematic position numbering of the macrocycle ring or denote proton groups: *o*, *m*, *p*—ortho, meta, and para positions of *meso*-phenyl (Ph) or *meso-p*-tolyl rings, respectively. Inset presents the AA'BB' multiplet of 11-*p*-tolyl as measured in dichloromethane- d_2 .

SCHEME 3



 ${}^{3}J$ = 4.8 Hz; 6.24 (H(14)), 6.11 (H(11)), ${}^{3}J$ = 4.8 Hz; 5.87 (H(19)), 5.75 (H(18)), ${}^{3}J$ = 4.1 Hz). The marked downfield shift of the NH resonance at 17.71 ppm is convincing in this matter. Scalar coupling NH to H(18) and H(19), detected in COSY, is consistent with the prevalence of the tautomer **6** presented in Scheme 3.

The resonances of 6-phenyl and 16-*p*-tolyl present, respectively, as the AA' BB' and AA'BB'C spectroscopic patterns expected for *meso*-aryls. The ortho and meta protons of 11-*p*-tolyl are accidentally isochronous and so behave as a group of chemically equivalent nuclei, showing no internal coupling. They present an A₄ singlet in chloroform-*d*. Changing the solvent to dichloromethane- d_2 (Figure 6, trace A, inset) or protonation led to changes in the chemical shifts, and the normal AA'BB' spectrum of *p*-tolyl was then observed. The ¹H NMR spectroscopic titration with TFA carried out in chloroform-*d* at 298 K takes place at nitrogen atoms, as documented by the appearance of two NH resonance at 16.63 and 16.53 ppm (Figure 6, trace B).

TABLE 1. Selected Bond Lengths of 6

	6			furan of
	regular	protruding	furan	21-oxaporphyrin
$O-C_{\alpha}$	1.397(3)	1.373(3)	1.370	1.380(4)
$C_{\alpha}-C_{\beta}$	1.429(3)	1.356(3)	1.322	1.403(4)
$C_{\beta}-C_{\beta}$	1.363(3)	1.461(3)	1.425	1.363(4)



FIGURE 7. Crystal structure of (**6**-H)Cl (top, perspective view; bottom, side-view phenyl groups omitted for clarity). The vibrational ellipsoids represent 50% probability.

Crystal Structure of the Corrole Isomer with a Protruding Furan Ring. The structure of (**6**-H)Cl was determined by X-ray crystallography. A selection of important bond distances is reported in Table 1.

The macrocycle is strongly puckered as its internal ring is contracted by two carbon atoms when compared to a regular porphyrin or by one when to corrole. The arrangements of the furan and pyrrole rings is demonstrated by the respective projections in Figure 7. In the crystal, the monocation of **6** acts as an anion receptor. Two NH groups are involved in the N–H···Cl hydrogen bond. The hydrogen bond distances N(1)···Cl(1) of 3.136-(2) Å and N(2)···Cl(1) of 3.111(2) Å are in the limits found for other coordination of chloride anions by porphyrins or expanded porphyrins cations.⁵⁴

In the crystal, pairs of molecules are positioned about the center of symmetry however without any face-toface $\pi-\pi$ contact. Two molecules of any dimeric units do not overlay. Their arrangement is best seen in Figure 8. The view is oriented so that one looks upon two nearly parallel planes of the protruding furan rings and presents three molecules engaged in interaction with the same chloride anion. The separation between the mean plane of protruding rings equals 2.59 Å and the regular ones 3.22 Å. The chloride–chloride separation is 7.235-(2) Å. Figure 8 reveals the interesting aspect of the structure. There are two intermolecular hydrogen bonding interactions: C(52)H····Cl(1), (H···Cl(1), 2.58 Å; C(52)–

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FIGURE 8. Views of (6-H₂)Cl showing the chloride-HC interactions between adjacent molecules in the solid.



FIGURE 9. DFT-optimized structures of tautomers of 3 and 6. Projections emphasize the conformations of the macrocycle.

H····Cl(1), 155.9°; C(2')H····Cl(1), (H···Cl(1)), 2.75 Å, C(2)-H····Cl, 156.4°.

The intra and intermolecular C-H···Cl interactions are still quite uncommon.55 The relevant Cl····HC distances in organic compounds are in the 2.57-2.94 Å range and the majority of these systems contain the chloride anion.⁵⁶ Intermolecular and intramolecular interactions between MCl and H-C groups have also been documented for halide complexes of the early transition metal ions, nobium, iridium, rhodium and platinium where the H····Cl distance varies over a range of 2.38-2.94 Å.⁵⁷⁻⁵⁹ In the literature, the (C)H····Cl distance has been considered as the criterion of interaction and-at presentseems to be accepted as a sign of the (C)H····Cl hydrogen bond. The determined (C)H····Cl distances for (6-H)Cl and for discussed above [(21,23-O₂Cor)H)₂]₂-[ZnCl₄] are in the limit attributed to such interactions. The chloride anion Cl(1) of (6-H)Cl is involved in two intra- and two intermolecular Cl···H interactions that are classified as a tetrafurcate system.⁵⁸ A net of hydrogen bonds (C)H····Cl and (N)H····Cl is extended on the whole crystal structure.

Examination of the crystallographic data demonstrated that the π bonds in the oxatripirryn unit are largely localized in the manner indicated at the valence structure 6. The comparison of bond lengths of two furan moieties is particularly important in the analysis. The "protruding" furan ring preserves all features of the isolated furan and the bond lengths are practically unperturbed, i.e., $C_{\beta}-C_{\beta} > C_{\alpha}-C_{\beta}$. There is an appreciable effect of conjugation on the second furan moiety. Here, the $C_{\alpha}-C_{\beta}$ distances are longer and the C_{β} - C_{β} distances are shorter than in the free furan.⁴⁸ These bond changes indicate that the π delocalization through the furan ring is altered. A similar influence on the π delocalization pattern in the furan ring has been observed in the case of aromatic 21,23-dioxacorrole as discussed above.

DFT Calculations. 5-Phenyl-10,15-bis(p-tolyl)-21,23dioxacorrole and its isomer with the protruding furan ring contain only one exchangeable proton, and a feasible tautomeric process may involve two accessible nitrogen positions (Schemes 1 and 2). Consequently, the experimentally observed tautomeric equilibrium for neutral forms of **3** and the presence of a single form for **6** have raised the question of the relative stability of the involved tautomers. To approach this problem we have applied the density functional theory (DFT) in the similar way as previously described for inverted porphyrins, sapphyrin, diheterosapphyrins or selenaporphyrin.60-63 The density functional theory methods and the high level of ab initio calculations have been recently applied to porphyrins, porphyrin isomers, metalloporphyrins, and related systems.^{60–66}

In order of simplification of all calculations the corresponding phenyl and *p*-tolyl groups of **3** or **6** have been

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TABLE 2. Calculated Energies

compd	B3LYP/6-31G**//B3LYP/6-31G*a	relative energy b		
3′	-991.1672	0		
3″	-991.1649	1.44		
6′	-991.1368	0		
6 ″	-991.1346	1.38		
^a Hartree. ^b Energies in kilocalories per mole.				

replaced by hydrogen atoms. The density functional theory calculations have been carried out using geometry determined by X-ray crystallography as a starting point of the DFT optimization procedure. The optimized structural parameters are contained in the Supporting Information. The optimized bond lengths (Figure 9) resemble those found by X-ray crystallography. The differences between the bond lengths between the DFT optimized and crystal values are in the range of a few hundredths of an angstrom.

It is apparent that the DFT-optimized skeleton of **3** is practically planar for each tautomer. The DFT optimized structure of **6**'(N(21)H,N(23)), **6**''(N(21),N(23)H), **6**-H⁺ are nearly planar as well. Thus, the strong folding of (**6**-H)-Cl observed in the crystal has not been reproduced.

Therefore, the real preference of geometry in the crystal may be finally determined by other factors, not directly included into the DFT optimization. For instance, this structural difference can be related to the marked overlap within the pair of molecules detected in the crystal structure. The presence of the bulky aromatic meso substituents can be of importance. In this case, the established influence of the methyl substitution on geometry of sapphyrin is particularly informative.⁶¹ Analogously, it was recently demonstrated that softness of the ruffling deformation of regular porphyrins limits possibility to accurate reproduce a solid-state structure by molecular calculation.⁶⁶

The calculated total energies, using the B3LYP/6-31G**//B3LYP/6-31G* approach (Table 2) demonstrate that relative stability of postulated tautomers increases in the order $\mathbf{3}' > \mathbf{3}''$ and $\mathbf{6}' > \mathbf{6}''$. The $\mathbf{3}'$ form of (O₂Cor)H is only slightly more stable as shown by the DFT studies as the energy difference between 3' and 3" equals 1.4 kcal/mol. At present the appropriate experimentally determined thermodynamic values to compare quantitatively the calculated relative stability of tautomers are not accessible. However the small energy difference between 3' and 3'' accounts for their simultaneous presence in equilibrium as evidenced by VT dependence of the spectroscopic pattern discussed above. The related correlation between the DFT determined relative stability and NMR dynamic behavior have been discussed for tautomerism of hemiporphycene and dihetrosapphyrins.58,67-70

Formation of a Nickel Complex. In preliminary studies, we have probed the coordination properties of **3**



FIGURE 10. ¹H NMR spectra: (A) $(2,23-O_2Cor)Ni^{II}Cl$, (B) $(21,23-O_2Cor-d_4)Ni^{II}Cl$ in dichloromethane- d_2 at 298 K. Labels: pyrr, pyrrole; f, furan.

and **6**. Previously, we documented that this ion is easily bound by 21-heteroporphyrins including 21-oxaporphyrin.^{21,41} The size of the coordination core of porphyrins (heteroporphyrins) was suggested to be instrumental as the controlling factor of nickel porphyrin and nickel heteroporphyrin properties.

Insertion of nickel(II) into 5,10,15-triaryl-21,23-dioxaporphyrin has been readily achieved using the Adler method, i.e., boiling a mixture of **3** and nickel(II) chloride in DMF. The reaction results in the formation of a fivecoordinate (21,23-O₂Cor)Ni^{II}Cl complex. The severe crowding in the core of **6** seems to be responsible for the fact that this molecule was completely resistant toward coordination of nickel(II) in conditions probed for **3**.

The electronic absorption spectra of **7** is included in Figure 1. The corrole-like spectrum is present for **7** with a Soret band and the Q-bands. The complex **7** is paramagnetic as clearly demonstrated by ¹H NMR spectrum with well resolved set of downfield shifted eight β -H resonances consistent with its C_1 symmetry in positions typical for high-spin, five-coordinate nickel(II) heteroporphyrins^{21,41,43} or nickel(II) carbaporphyrinoids.^{71,72}

The detected differentiation of *o*- and *m*-phenyl resonances suggests that the phenyl rotation with respect to the $C_{meso}-C_{phenyl}$ bond is slow. Apparently, two sides of the corrole macrocycle are not equivalent, as expected for the five-coordinate (21,23-O₂Cor)Ni^{II}Cl complex. The resonance assignments, which are given above each peak in Figure 10, have been made on the basis of relative intensities, line widths, site-specific deuteration, and 2D COSY experiments.

This particular spectroscopic observation demonstrates that modification of the corrole macrocyle by virtue of replacement of NH group(s) by one or two oxygen donors controls the ground electronic state of the resulting nickel corrolates. Thus, in addition to low-spin nickel(II) corrole π -cation radical²⁷ and diamagnetic nickel(II) oxacorole,³⁰ the formation for first time of the high-spin nickel(II) 21,23-dioxacorole has been achieved.

Conclusion

The modification of the corrole core by introduction of an oxygen instead of the NH group deeply modified

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macrocyclic coordinating properties. It is important to notice that this replacement is expected to preserve the size of the macrocyclic core considering similarity of oxygen and nitrogen atom radii analogously as demonstrated for porphyrins and oxaporphyrins. The introduction of oxygen changes the charge of the resulting ligands (-3, corrole; -2; 21-oxacorrole; -1, 21,23-dioxacorrole). Their potential in control of coordinating properties of the metal ion has been demonstrated using the selected case of nickel(II) where for the very first time the highspin nickel(II) has been detected in the corrole like shrunk macrocyclic environment.

The novel building block 2-furancarbinol has been introduced to produce diheterocorroles. This methodology provides the route to family of heterocorroles, which can act as monoanionic ligands. The formation of the 21,23-dioxaporphyrin isomer with a protruding furan ring confirms an ability of the furan molecule to act in acid or Lewis acid catalyzed condensation as provider of different structurally building blocks: regular ($\alpha - \alpha'$), short ($\beta - \beta'$ or $\alpha - \beta$), and eventually inverted ($\alpha - \beta'$). Interestingly, the $\alpha - \beta$ connectivity was detected in furochlorphin, which contains an exocyclic furan ring, albeit this molecule is obtained in the course of aerobic oxidation of 1,2,3,7,13,17,18,19-octamethyl-8,12-diethyl-octadehydrocorrinatonickel(II) chloride.⁷³

Experimental Section

Preparation of Precursors. 2,5-Bis(*p*-tolylhydroxymethyl)furan was synthesized according to known procedures.⁷⁴

3-(Phenylhydroxymethyl)furan. This compound was synthesized in a one-pot synthesis by addition of 9 mL of 3 M solution of phenylmagnesium bromide in diethyl ether to an THF solution (100 mL) containing 2 mL (23 mmol) of 3-fural-dehyde. After 30 min 40 mL of 1% sulfuric acid was added. Subsequently solid Na₂CO₃ was added until the liberation of CO_2 ceased. The solution was extracted with diethyl ether (three times). All organic layers were collected and dried with MgSO₄. After filtration and evaporation, a crude 3-(phenyl-hydroxymethyl)furan was obtained quantitatively, as a pale yellow solid, and used without further purification. ¹H NMR (500 MHz, CDCl₃): 7.4 (m, 2H), 7.35 (m, 3H), 7.29 (m, 2H), 6.32 (s, 1H), 5.75 (s, 1H), 2.62 (s, 1H).

2-(Phenylhydroxymethyl)furan. This compound was synthesized as 3-phenylhydroxymethylfuran using 2-furaldehyd instead of the 3-furaldehyde. Expected product was obtained quantitatively as an orange oil. The compound is sufficiently pure (>95% by ¹H NMR) for use in subsequent reactions. ¹H NMR (500 MHz, CDCl₃): 7.41 (m, 2H), 7.36 (m, 3H), 7.29 (m, 1H), 6.30 (m, 1H), 6.10 (s, 1H), 5.79 (d, 1H, ³*J* = 3.4 Hz), 2.63 (d, 1H, ³*J* = 3.4 Hz).

5-Phenyl-10,15-bis(*p*-tolyl)-21,23-dioxacorrole. 2,5-Bis-(phenylhydroxymethyl)furan (308 mg, 1 mmol), 2-(phenylhydroxymethyl)furan (174 mg, 1 mmol), and pyrrole (0.14 mL, 2 mmol) were added to deoxygenated dichloromethane (100 mL). After addition of boron trifluoride etherate (50.4 μ L), the reaction mixture was stirred in the dark. *p*-Chloranil (0.6147 g, 2.5 mmol) was added, and the solution was heated under reflux (1 h) and then evaporated to dryness under reduced pressure by rotatory evaporation. The dark residue was dissolved in dichloromethane and chromatographed on a basic alumina column to remove tarry products. A chloroform fraction was immediately chromatographed again on basic alumina (grade III), and the slow-moving blue fraction was eluted with dichloromethane and evaporated to dryness. Recrystallization of **3** as a cation(HCl) from dichloromethane/ hexane (1:1 v/v) produced 48 mg of [3-H]⁺ (yield 8%).

(21,23-O₂Cor)H. UV-vis (λ_{max} (nm) (log ϵ)): 397 (4.89), 422 (4.88), 495 (3.91), 538 (4.12), 595 (3.93), 637 (4.07).

(21,23-O₂Cor)H₂⁺. UV-vis (λ_{max} (nm) (log ϵ)): 395 (5.09), 421 (4.93), 533 (3.99), 564 (4.06), 601 (4.45).

(21,23-O₂Cor)H. ¹H NMR (500.13 MHz, CDCl₃): 9.53 (d, 1H, ${}^{3}J$ = 4.21 Hz), 9.30 (d, 1H, ${}^{3}J$ = 4.59 Hz), 9.24 (d, 1H, ${}^{3}J$ = 4.21 Hz), 9.14 (d, 1H, ${}^{3}J$ = 4.21 Hz), 8.96 (d, 1H, ${}^{3}J$ = 4.59 Hz), 8.94 (d, 1H, ${}^{3}J$ = 4.59 Hz), 8.83 (d, 1H, ${}^{3}J$ = 4.21 Hz), 8.70 (d, 1H, ${}^{3}J$ = 4.59 Hz), 8.32 (d, 2H, ${}^{3}J$ = 6.89 Hz), 8.22 (d, 2H, ${}^{3}J$ = 7.65 Hz), 8.07 (d, 2H, ${}^{3}J$ = 8.03 Hz), 7.83 (t, 2H, ${}^{3}J$ = 7.65 Hz), 7.78 (d, 1H, ${}^{3}J$ = 7.60 Hz), 7.64 (d, 2H, ${}^{3}J$ = 7.65 Hz), 7.58 (d, 2H, ${}^{3}J$ = 8.03 Hz), 2.72 (s, 3H), 2.71 (s, 3H).

 $\begin{array}{l} \textbf{(21,23-O_2Cor)H_2^+}. \ ^{13}C\ NMR\ (125.7\ MHz,\ CDCl_3);\ 154.89, \\ 152.62,\ 148.46,\ 144.27,\ 141.32,\ 139.06,\ 138.57,\ 137.77,\ 137.66, \\ 137.54,\ 135.61,\ 135.54,\ 135.27,\ 135.09,\ 135.07,\ 129.30,\ 128.97, \\ 128.57,\ 128.46,\ 128.34,\ 127.94,\ 127.14,\ 127.03,\ 126.07,\ 125.24, \\ 123.28,\ 118.89,\ 117.48,\ 116.99,\ 115.87,\ 110.89,\ 21.53,\ 21.51. \\ HRMS\ (ESI,\ m/z):\ 557.2224\ (557.2229\ calcd\ for\ C_{39}H_{28}N_2O_2 + H^+). \end{array}$

Isomer of 21,23-Dioxacorrole, 6. 2,5-Bis(phenylhydroxymethyl)furan (392 mg, 1.27 mmol), 3-(phenylhydroxymethyl)furan (221 mg, 1.27 mmol), and pyrrole (0.176 mL, 2.54 mmol) were added to deoxygenated dichloromethane (150 mL). After addition of boron trifluoride etherate (50.4 μ L), the reaction mixture was stirred in the dark. DDQ (0.721 g, 3.175 mmol) was added, and the solution was stirred for 20 min. The resulting mixture was evaporated to dryness under reduced pressure by rotatory evaporation. The dark residue was dissolved in dichloromethane and chromatographed on a basic alumina column. The green fraction was eluted with dichloromethane and evaporated to dryness. Recrystallization from dichloromethane/hexane (1:1 v/v) of a cationic form (HCl) of **6** gave 31 mg (yield 4%).

6. UV-vis $(\lambda_{\max} \text{ (nm) } (\log \epsilon))$: 375 (4.45), 409 (4.39), 753 (3.61).

6-H⁺. UV–vis (λ_{max} (nm) (log ϵ)): 390 (4.51), 468 (4.34), 962 (3.99).

6. ¹H NMR (500.13 MHz, CDCl₃): 17.71 (s, 1H), 7.29 (m, 5H), 7.20 (d, 2H, ${}^{3}J = 8.04$ Hz), 7.13 (d, 2H, ${}^{3}J = 8.04$ Hz), 7.09 (s, 4H), 6.87 (d, 1H, ${}^{4}J = 2.1$ Hz), 6.39 (d, 1H, ${}^{3}J = 4.8$ Hz), 6.29 (d, 1H, ${}^{4}J = 2.1$ Hz), 6.24 (d, 1H, ${}^{3}J = 4.8$ Hz), 6.11 (d, 1H, ${}^{3}J = 4.8$ Hz), 5.88 (d, 1H, ${}^{3}J = 4.8$ Hz), 5.87 (d, 1H, ${}^{3}J = 4.1$ Hz), 5.75 (d, 1H, ${}^{3}J = 4.1$ Hz), 2.35 (s, 3H), 2.32 (s, 3H).

6-H⁺. ¹³C NMR (125.7 MHz, CDCl₃): 168.93, 162.01, 153.44, 151.5, 145.79, 143.52, 142.52, 141.24, 139.09, 138.59, 137.03, 135.12, 133.96, 132.58, 131.95, 130.66, 130.27, 130.06, 130.04, 129.41, 129.4, 127.84, 127.69, 126.67, 123.98, 123.93, 122.29, 119.95, 116.02, 107.39, 21.48, 21.24. HRMS (ESI, *m/z*): 557.2224 (557.2229 calcd for $C_{39}H_{28}N_2O_2 + H^+$).

 $(21,23-O_2Cor)H)_2]_2[ZnCl_4].$ (21,23- $O_2Cor)H$ (2 mg) in dichloromethane and ZnCl₂ (20 mg) in methanol (10 mL) were mixed together, stirred for 1 h, and evaporated to dryness. (21,23- $O_2Cor)H)_2]_2[ZnCl_4]$ was washed out from the solid residue and recrystallized from dichloromethane/hexane (yield, 4 mg).

(21,23-O₂Cor)Ni^{II}Cl. A 56 mg (0.1 mmol) portion of **3** and 600 mg (3 mmol) of NiCl₂·4H₂O were dissolved in 50 mL of DMF. After 2 h of refluxing, the solvent was removed in a stream of nitrogen. The remaining solid was dissolved in freshly distilled dichloromethane and filtered to remove inorganic salt. The solution was chromatographed on silica gel (mesh 35–70), and the expected product was eluted with chloroform as a deep green band. Recrystalization from chloroform/hexane (50/50 v/v) yielded 18 mg (27%) of (21,23-O₂Cor)Ni^{II}Cl.

(21,23-O₂Cor)Ni^{II}Cl. UV-vis (λ_{max} (nm)): 400, 439, 529, 567, 620. MS (ESI, *m/z*): 613.14 (613.1426 calcd for [C₃₉H₂₇N₂O₂-Ni]⁺).

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5,10,15-Triaryl-21,23-dioxacorrole

Preparation of samples. Dichloromethane- d_2 and chloroform-d used for NMR samples were passed through basic alumina before use. The solution of the trifluroacetic acid in dichloromethane- d_2 was added by syringe to the ¹H NMR tube containing 3 or 6 as a neutral form. The progress of the reaction was followed by ¹H NMR spectroscopy.

Instrumentation. NMR spectra were recorded on a Bruker Avance 500 spectrometer. Absorption spectra were recorded on a diode-array Hewlett-Packard 8453 spectrometer.

Mass spectra were recorded on an AD-604 spectrometer using the electrospray and liquid matrix secondary ion mass spectrometry techniques.

Calculation Method. The calculations were carried out with the GAUSSIAN98 program.⁷⁵ All structures were optimized within X-ray geometry of the system using the density functional theory (DFT) with Becke's three-parameter exchange functionals and the gradient-corrected functionals of Lee, Yang, and Parr (DFT (B3LYP)).^{58,76–78} The final estimations of the total energies were performed at the B3LYP level with the 6-31G** basis set using the B3LYP/6-31G* fully optimized structures.

X-ray Data Collection and Refinement. Crystals of 3 and 6 were prepared by diffusion of hexane into the dichloromethene solution contained in a thin tube. Data were collected at 100 K on a Kuma KM-4 CCD diffractometer. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Crystal data are compiled in Table S1 (Supporting Information).

The structures were solved by direct methods with SHELXS-97 and refined by full-matrix least-squares method using SHELXL-97 with anisotropic thermal parameters for the non-H atoms. Scattering factors were those incorporated in SHELXS-97. $^{\rm 58,79,80}$

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Supporting Information Available: Tables of crystal data, bond lengths and angles, anisotropic thermal parameters, computational results (Cartesian and computational results (Cartesian coordinates, four tables); additional coordinates, four tables), and additional NMR are included. This material is available free of charge via the Internet at http://pubs.acs.org.

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