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Synthesis and Properties of Tetraphenylporphyrin Molecules Containing Heteroatoms Other than Nitrogen. 5. High Resolution Nuclear Magnetic Resonance Studies of Inner and Outer Aromaticity

Abraham Ulman,*[1] Joost Manassen, Felix Frolow, and Dov Rabinovich

Contribution from the Departments of Plastics Research and Structural Chemistry, The Weizmann Institute of Science, Rehovot, Israel. *Received January 29, 1979*

Abstract: When the two NH groups in tetraphenylporphyrin are replaced by the group 6A heteroatoms S, Se, and Te, bonding interactions within the porphyrin core are found, as is apparent from X-ray analysis results. Because of these interactions, changes in the inner and outer aromatic pathways occur, which are expressed in the chemical shifts of the hydrogen atoms at the periphery of the molecule. The bonding interactions within the core are disrupted by either protonation or complexation, and this finds its expression in the chemical shifts in a consistent way. If two different heteroatoms are introduced, or when the *p*-phenyl hydrogens are substituted in such a way that two phenyl groups carry substituents of different electronic properties, charge transfer occurs between the heteroatoms. This charge transfer changes the inner aromatic pathway, which influences the chemical shift. These shifts relate linearly to the Hammett constant of the substituents. Starting from these results, the concept is developed that the interaction between the heteroatoms acts as an electron drain on the π electrons and especially on the pyrrolenine-N nonbonding electrons. This causes an increased contribution of the 20-membered, extended outer aromaticity Kekulé structures.

Introduction

Recently we published a new synthetic procedure by which the NH groups in the core of tetraphenylporphyrin (TPP) can be exchanged by the heteroatoms S, Se, and Te. By this method we could prepare tetraphenyl-21,23-dithiaporphyrin (S_2TPP),[2] tetraphenyl-21-selena-23-thiaporphyrin (S,SeTPP),[3] tetraphenyl-21,23-diselenaporphyrin (Se_2TPP),[3] and tetraphenyl-21-tellura-23-thiaporphyrin (S,TeTPP).[4] It appeared also to be possible to introduce substituents on the phenyl groups of S_2TPP, either symmetrically so that every phenyl group carries the same substituent, or unsymmetrically with two pairs of phenyl groups carrying different substituents.[5] Figure 1 shows the molecules which form the subject of this study.

Several of these molecules have been analyzed by X-ray structure analysis,[6] and the abnormally short distances between X and Y of Figure 1 (3.05 Å for X = Y = S; 2.89 Å for X = S, Y = Se; 2.85 Å for X = Y = Se and 2.65 Å for X = S, Y = Te) show that a chemical bonding interaction exists between X and Y in these molecules, which increases in the order S, Se, Te. This interaction influences the conjugative pathway in the molecule, which is often called inner and outer aromaticity (ring current). The degree of outer aromaticity can be expected to influence the chemical shifts of H_x and H_y of Figure 1 and to lesser extent that of H_p.

Therefore, we describe here the results of a high resolution (270-MHz) NMR study on these new porphyrins, their conjugate acids, and some of their metal complexes. These results are entirely consistent with the described X···Y interaction and also show charge transfer to occur between X and Y, when they are different or when A and B are different. Moreover, information is obtained on the binding of the proton and the metal ion in the conjugate acid and the metal complexes, respectively.

Results and Discussion

Symmetrical Heterosubstitution. A. Free Bases. In Table I the chemical shifts at room temperature of the symmetrically heterosubstituted (X = Y) porphyrins are given and compared with literature values for TPP, which were measured at −80 °C to get separate values for the pyrrole and pyrrolenine hydrogens.[7]

In order to understand the large downfield shifts of H_x and H_y of Figure 1 and the smaller ones of H_p with substitution, we must discuss the accepted Kekulé structures for porphyrins and construct a model for the core interactions, which apparently occur when the NH groups are substituted by heteroatoms of the sixth row of the Periodic Table having empty d orbitals. In Figure 2, the possible Kekulé structures for the porphyrin molecule are sketched.

The 16-membered structure corresponds to the inner aromatic pathway, which is used by Gouterman to explain the optical spectra of porphyrins.[8] The 18-membered structure corresponds to the outer aromatic pathway and, according to ring current calculations of Abraham, has a statistical weight of about 30%.[9] The 20-membered extended outer aromatic

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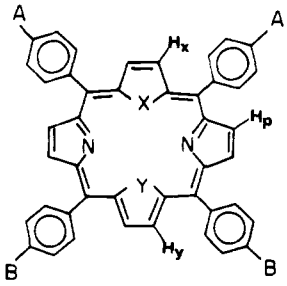

1. X = Y = S; A = B = H
2. A = H; B = OCH_3
3. A = B = OCH_3
4. A = F; B = OCH_2
5. A = Cl; B = OCH_3
6. A = B = Cl
7. A = B = F
9. X ≈ S; Y = Se; A = B = H
10. A = F; B = H
11. X = Y = Se; A = B = H
12. X ≈ S; Y = Te; A = B = H

Figure 1. New heterosubstituted and para-substituted tetraphenylporphyrin molecules.

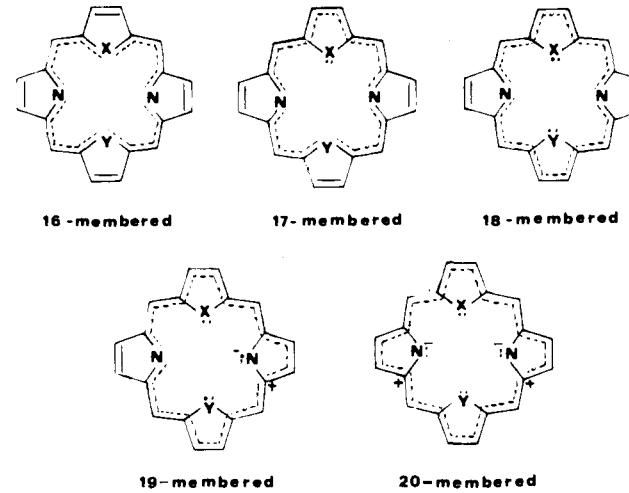

Figure 2. Possible Kekulé structures for the porphyrin molecule.

Table I. Chemical Shifts in the ^1H NMR of Different Symmetrically Heterosubstituted Tetraphenylporphyrins

	pyrrolenine H_p	pyrrole H_x & H_y	thiophene H_x & H_y	selenophene H_x & H_y	X···Y, Å
TPP	8.61	8.90			4.20
S_2TPP	8.675		9.679		3.02
Se_2TPP	8.862			9.893	2.85

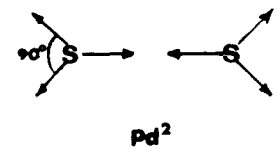

Figure 3. pd^2 hybridization of the sulfur atoms.

pathway is important for the structure of the conjugate acid,[10] but according to recent calculations of Abraham all the peripheral double bonds have to be considered when the NMR properties of porphyrins in general are discussed.[11] The 17- and 19-membered structures are intermediate cases, which are included for completeness sake.

The S···S (general X···Y) interaction, which is found in the X-ray structure determination, can be described by using a simple valence bond model. If we assume a pd^2 hybridization of the full p_z orbital with the empty d_{xz} and d_{yz} orbitals, we get three pd^2 orbitals as shown in Figure 3.

Two of these orbitals are orthogonal, which agrees with the experimentally found CSC angle of 91.8°, and the third is in the right direction to explain the S···S interaction.[12,13] The average electron density in each of the pd^2 orbitals is $^2/_3$ of an electron and, as they are originated from d orbitals situated in the *xz* and *yz* planes, they can interact with the molecular π system. The shorter the X···Y distance, the stronger is the attractive interaction and more effective the overlap between the two pd^2 orbitals involved. In the extreme hypothetical case where a complete chemical bond is formed, each of the heteroatoms donates one electron. Thus, the greater the X···Y interaction, the less electron density is available on the heteroatoms for the inner aromatic pathway. This results in greater statistical weight of the outer aromatic pathway (18-membered structure). Because H_x and H_y are closer to the outer aromatic pathway this will result in downfield shifts in the NMR spectrum as is found experimentally.[14] Table I shows appreciable downfield shifts of these hydrogens when going from pyrrole to selenophene and correlation with the increasing X···Y interaction in these molecules.

It could be argued that these shifts are due to changing electronegativity of the heteroatoms as was found for the free heterocycles.[15] There are no linear or other kinds of correlation between the chemical shifts of these hydrogens and the electronegativities of the *individual* heteroatoms. However, it can be shown[16] that a linear relationship exists between these chemical shifts and the first reduction potential of these molecules ("electronegativity of the molecule"). Thus, though changing of electronegativity can be expected to cause shifts in the NMR spectrum, the shifts described above should be attributed to the attractive interaction between the heteroatoms, which also cause changes in the energy levels of the HOMO and the LUMO of these molecules.[16] Moreover, as will become clear in the course of this report, changes induced by protonation, complexation, and phenyl substitution are in full agreement with the model sketched above.

The downfield shift of the pyrrolenine hydrogens (H_p in Figure 1) with heterosubstitution, especially for Se_2TPP, cannot be explained by considering the 16- and 18-membered structures of Figure 2 only. An increase in the contribution of the extended outer aromatic pathway (20-membered structure) does explain the observed shifts, because the pyrrolenine hydrogens are closer to the ring current in this Kekulé structure. Thus, electron donation from the pyrrolenine nitrogens to the X···Y interaction, which is the reason for the extended outer aromaticity, increases with the increasing X···Y interaction. This phenomenon will become clearer when considering the conjugate acids.

B. Conjugate Acids. In Table II the chemical shifts of the different conjugate acids are given with the values for the free bases in parentheses. Introduction of positive charges in the system can be expected to cause downfield shift, which is only partly observed.

The downfield shift of the thiophene hydrogens is very slight on protonation, while the selenophene hydrogens shift upfield appreciably. In order to understand these results, which are entirely consistent, we have to consider three different effects: (a) Protonation or complexation can be expected to break the inner core interaction. This can be rationalized by the fact that protonations of the pyrrolenine N-nonbonding electron avoid the electron donation to the X···Y interaction which decreases the stability of the molecule (in the case of S, TeTPP protonation is accompanied by immediate decomposition). Moreover, the introduction of two protons causes electrostatic repulsion as well as steric crowding in the porphyrin core. These are released by the tilting of the different heterocycles out of the NLS plane causing considerable nonplanarity.[17] In the metal complexes, the metal ion interupts the overlap in the core

Table II. Chemical Shifts in the ^1H NMR of the Different Symmetrical Heterosubstituted Tetraphenylporphyrin Conjugate Acids and Zn(II) Complexes[a]

	pyrrolenine H_p	pyrrole H_x & H_y	thiophene H_x & H_y	selenophene H_x & H_y
$TPPD_2^{2+}$	8.852 (8.61)	8.852 (8.90)		
$S_2TPPD_2^{2+}$	8.951 (8.675)		9.695 (9.676)	
S_2TPPZn-(II)	8.900 (8.675)		9.902 (9.676)	
$Se_2TPPD_2^{2+}$	8.884 (8.832)			9.198 (9.893)
Se_2TPPZn-(II)	8.911 (8.832)			9.193 (9.893)

[a] Values of Table I in parentheses.

causing the same effect. When the attractive interaction is broken, the heteroatoms are free to contribute their full electron density to the inner aromaticity by which the statistical weight of the outer aromaticity decreases and this results in upfield shift of H_x and H_y. (b) The introduction of positive charges into the porphyrin molecule causes downfield shift of these hydrogens. (c) The nonplanarity of the conjugate acids as described above leads to the release of the repulsive interaction between the ortho hydrogen of the phenyl and the β hydrogen of the porphyrin allowing the phenyl ring to rotate toward the porphyrin plane. These two structural changes cause shielding effects on the β hydrogens, which results in upfield shift.[18,19]

From Tables I and II we see that the net effect in the case of TPP is an upfield shift of 0.04 ppm. In S_2TPP, where the inner interaction is not strong, the net effect is a small downfield shift of 0.019 ppm for the thiophene hydrogens. For the Se_2TPP molecule where the interaction is strong, the dominant effect is that of the contribution of the full electron density of the selenium atoms to the inner aromatic pathway and the net effect is an upfield shift of 0.695 ppm.

The same conclusion can be drawn from the chemical shifts of the pyrrolenine hydrogens. They are shifted downfield appreciably in TPP and S_2TPP on protonation. With Se_2TPP, on the other hand, the large shift occurs when the S is replaced by Se in the free base and not on its protonation. This confirms that the 20-membered, extended outer aromatic structures contribute significantly to the Se_2TPP free base structure and that this contribution does not increase much on protonation as in the previous cases.[10] This shows that the strong interaction between the selenium atoms acts as an electron drain on the pyrrolenine electrons as does the introduction of proton or a metal ion. This is also expressed in other physical properties of Se_2TPP, such as its redox potential.[16]

C. Metal Complexes. In Table II the chemical shifts of the Zn(II) complexes are shown along with those of the free bases in parentheses. It is apparent that the same concept exists as with the conjugate acids. Thus the pyrrolenine hydrogens shift downfield on complexation, but much more in S_2TPP than in Se_2TPP. The selenophene hydrogens shift upfield as in the conjugate acid and for the same reason. The difference is in the shift of the thiophene hydrogens, which are displaced considerably more downfield on complexation with Zn(II) than occurs with protonation. The most obvious explanation is that the protons are bound to the nitrogens only, while apparently the Zn(II) ion is bound to the sulfur atoms as well.

Unsymmetrical Heterosubstitution. Charge Transfer. In Table III the chemical shifts are shown for those porphyrins where X is different from Y (unsymmetrical heterosubstitution). The values of the corresponding shifts for the symmetrically substituted porphyrins of Table I are given in parentheses.

Table III. Chemical Shifts in the ^1H NMR of Different Unsymmetrically Heterosubstituted Tetraphenylporphyrins[a]

	thiophene H_x	selenophene H_y	tellurophene H_y
S, SeTPP	9.604 (9.676)	9.979 (9.893)	
S, TeTPP	9.053 (9.676)		10.141
F_2S, SeTPP	9.578	9.985	

[a] Values of Table I in parentheses.

Table IV. Chemical Shifts in the ^1H NMR of Different Symmetrically Para-Substituted S_2TPP Free Bases and Conjugate Acids

	free base thiophene H_x & H_y	conjugate acid thiophene H_x & H_y
S_2TPP	9.676	9.695
$(CH_3O)_4S_2TPP$	9.692	9.442
Cl_4S_2TPP	9.669	9.669
F_4S_2TPP	9.657	9.863

We see here the interesting phenomenon that, when one of the S atoms in S_2TPP is exchanged for Se, the thiophene hydrogens are shifted upfield and this effect is much enhanced with Te. On the other hand, when one of the Se atoms in Se_2TPP is replaced by S, the selenophene hydrogens shift downfield.

This can be explained by taking into consideration the different electron donor properties of these atoms. Because of the X···Y interaction, charge transfer occurs from Se to S. Therefore, there is more inner aromaticity through the S than in the symmetrical case, which causes upfield shift. Similarly there is less inner aromaticity through the Se, which causes downfield shift.

The effect of substitution on the phenyl groups will be discussed in the next section, but here we can illustrate this charge transfer effect dramatically by para substitution of the H by the electron attracting F group on the phenyl rings adjacent to the thiophene side of the molecule. If the charge transfer hypothesis is the right one, we would expect that the F groups will enhance the charge transfer from Se to S, by which we should get more inner aromaticity and more upfield shift of the hydrogens at the thiophene side, although from the electron-withdrawing properties of the F substituent one would expect the opposite to occur. From Table III it is apparent that the charge transfer directs the shifts of the thiophene (and selenophene) hydrogens on F substitution. The effect of para substitution will now be dealt with in detail.

Symmetrical Para Substitution. A. Free Bases. In Table IV the influence of electron-donating and electron-withdrawing substituents on the chemical shifts of the thiophene hydrogens in S_2TPP is shown.

According to the model of the core interaction we may again expect the competition of two effects: (a) according to general theory, electron-donating substituents are expected to cause upfield shift and electron-withdrawing substituents to cause downfield shift; (b) electron-donating substituents are expected to strengthen the X···Y interaction. This can be rationalized by the fact that this interaction acts as an electron drain on the electron density of the porphyrin which finds its expression in the positive shifts of both the reduction and the oxidation potentials of these molecules.[16] Thus, donation of electron density to the π system of these porphyrins counteracts the effect of the core interaction, which is accompanied by strengthening of this interaction and, according to the suggested model, by less inner aromaticity and downfield shifts. For the same reasons, electron-attracting substituents will cause upfield shifts.

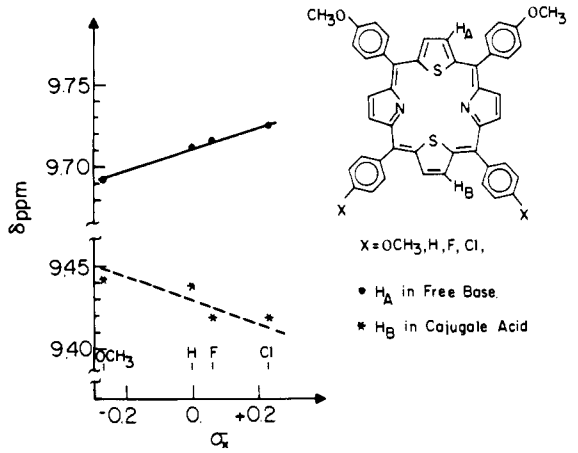

Figure 4. A plot of the chemical shifts of H_A and H_B in the ^1H NMR of unsymmetrically para-substituted S_2TPP as a function of the X Hammett substituent constant.

From Table IV we see that the shifts are small, but that effect b seems to be slightly stronger, which means that the methoxy group causes a slight downfield shift while Cl and F cause slight upfield shifts. If this is the correct explanation, then in the conjugate acids, where the inner interaction is disrupted, effect a must direct the chemical shifts.

B. Conjugate Acids. From Table IV it appears that electron-donating methoxy substituents now cause an appreciable upfield shift and electron-attracting F an appreciable downfield shift. The Cl substituent does not seem to influence the shift appreciably. In spite of this exception, the general picture is as expected: in the free bases there is a competition between two effects causing small shifts, while in the conjugate acids where only one effect is active we find large shifts in the expected direction.

Unsymmetrical Para Substitution. A. Free Bases. In Table V the shifts of H_A and H_B in Figure 4 are given, when two methoxy groups in tetra(*p*-methoxyphenyl)-21,23-dithiaporphyrin are exchanged for other substituents.

The shifts are small but significant. From Figure 4 it can be seen that these shifts can be accommodated on a Hammett plot for H_A, which cannot be done for H_B.

This is again in agreement with the core interaction model and the charge transfer effects on unsymmetrical substitution. Substituents more electron attracting than methoxy cause charge transfer from the sulfur of the thiophene carrying H_A to the sulfur of the thiophene carrying H_B. The result according to the model described above will be less inner aromaticity through the donor S and consequently more outer aromaticity at that side of the molecule. This results in downfield shift of H_A which, however small, can be fitted on a Hammett plot.

B. Conjugate Acids. From Table V it is apparent that, because of the core interaction, there is no direct influence of X on H_A. On the other hand, from Figure 4 it can be seen that some kind of Hammett plot can now be constructed for the shifts of H_B as a function of X. The spread is larger and the slope is contrary to what could be expected. We have no ready explanation for why in this case H_B shifts upfield with the more electron-attracting substituents.

Conclusions

From the results given in this paper, it has become clear that the chemical shifts in the ^1H NMR of symmetrically and unsymmetrically hetero- and para-substituted tetraphenylporphyrins can be explained by changes in the pathway of inner and outer aromaticity.

Table V. Chemical Shifts in the ^1H NMR of Different Unsymmetrical Para-Substituted S_2TPP Free Bases and Conjugate Acids

	free base thiophene		conjugate acid thiophene	
	H_A[a]	H_B[a]	H_A[a]	H_B[a]
$(CH_3O)_4S_2TPP$	9.692	9.692	9.442	9.442
$(CH_3O)_2S_2TPP$	9.712	9.653	9.850	8.439
$(CH_3O)_2F_2S_2TPP$	9.716	9.632	9.514	9.418
$(CH_3O)_2Cl_2S_2TPP$	9.725	9.628	9.546	9.419

[a] Of Figure 4.

Especially striking is the fact that the described core interactions can be disrupted by protonation and complexation and in this case the chemical shifts with very few exceptions follow the expected course.

The core interactions between X and Y act as an electron drain on the π electrons, much like that which occurs on protonation or complexation of tetraphenylporphyrin, by which the contribution of the 20-membered Kekulé structure is enhanced.

The kind of charge transfer effects which can be shown to be induced by unsymmetrical substitution can, therefore, also be expected to occur in metal complexes of tetraphenylporphyrin. It may be of interest, therefore, to synthesize unsymmetrically para-substituted TPP and to measure the chemical shifts of their complexes with diamagnetic metal ions.

Experimental Section

NMR spectra were determined with a Bruker 270-MHz spectrometer. All measurements were taken at room temperature (25 °C) in $CDCl_3$ (Merck) which was passed through a short column of basic alumina shortly before the experiment. Tetramethylsilane (Merck) was used as internal reference (δ ppm). The concentration of the porphyrin solutions was 5×10^{-4} M (no aggregation effects were found; the same values were also observed in solution of 2×10^{-4} M). For measurements of the NMR spectra of the conjugate acids, vapors of deuterated trifluoroacetic acid (DTFA, Fluka) were introduced into the NMR tube (thus practically no concentration change occurs). There was an immediate change of the color from red-brown to green. Me_4Si was used as internal reference and is shifted 0.36 Hz downfield in the presence of DTFA.

For the preparation of the metal complexes, see reference 2; all the complexes were prepared by this method.

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(1) Address correspondence to this author at the Department of Chemistry, Northwestern University, Evanston, Ill. 60201.
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Reduced Nicotinamide Adenine Dinucleotide (NADH) Models. 14.[1] Metal Ion Catalysis of the Reduction of α,β-Unsaturated Ketones by 1,4-Dihydropyridines. A Model of Δ^4-3-Ketosteroid Reductases

Ronald A. Gase[2] and Upendra K. Pandit*

Contribution from the Organic Chemistry Laboratory, University of Amsterdam, Nieuwe Achtergracht 129, Amsterdam, The Netherlands. *Received April 17, 1978*

Abstract: The reduction of (*E*)-2-, (*E*)-3- and (*E*)-4-cinnamoylpyridines by 1,4-dihydropyridine derivatives, to the corresponding dihydro ketones, is catalyzed by Zn^{2+} and Mg^{2+} ions. Kinetic measurements show that the rate of reduction is fastest in the case of the 2 isomer, in which the metal ion is simultaneously complexed with the nitrogen and the oxygen sites. The latter example is regarded as a model of electrophilic catalysis of the NADH-dependent enzymatic reduction of Δ^4-3-ketosteroids. Reduction of the above-mentioned substrates, as well as that of the (corresponding) isomeric β-benzoylvinylpyridines, with 1,4-dihydropyridine-*4,4-d*$_2$ reveals that in all reduction products the deuterium atom is located at the β position with respect to the carbonyl group. Furthermore, in the reaction of (*E*)-2-cinnamoylpyridine with *N*-benzyl-1,4-dihydronicotinamide-*4,4-d*$_2$ the primary kinetic isotope effect shows that C(4)–H bond cleavage is involved in the rate-determining step. These results are interpreted in terms of a mechanism involving either a hydride transfer or a sequential transfer of an electron (e) and a hydrogen atom (H·).

A number of pyridine nucleotide linked dehydrogenases catalyze the redox equilibrium >C=C< ⇌ >CH—CH<, involving the double bond function of α,β-unsaturated ketones.[3] Although several examples of the reduction of electrophilic olefins by NAD(P)H models have been reported in the literature,[4] the systems studied thus far correspond to "internally activated" substrates rather than models in which the activation of the substrate is derived from catalytic features corresponding to those present in the enzyme. For a variety of pyridine nucleotide dependent dehydrogenases, an electrophilic catalysis of the reduction step (mediated by coordinated or covalently bound electrophiles) has been postulated.[5,6] Model reactions illustrating electrophilic catalysis of the reduction of α,β-unsaturated ketones may be visualized in terms of the reduction of the double bond in systems corresponding to A or B (Figure 1) by suitable 1,4-dihydropyridines. In A, an electrophilic catalyst is subtended toward the carbonyl oxygen by virtue of its coordination to a suitable site on the protein matrix. In B, on the other hand, the same electrophile is attached to the apoenzyme via a covalent bond. In the current phase of our work on the reduction of conjugated enones, attention has been directed to model system A. At a molecular level a system such as A is subject to extensive variation.

We have chosen the pyridyl ketones **3a–c** as model substrates, since they allow the investigation of electrophilic catalysis of the reduction step, according to the mechanism implied in A. Metal ions that are known to coordinate to the pyridine nitrogen could potentially act as electrophilic centers. In the case of 2-cinnamoylpyridine (**3a**), it is anticipated that a metal cation would directly coordinate with both the nitrogen of the pyridine ring and the oxygen of the carbonyl group. Since exclusive nitrogen coordination in **3a** also activates the α,β-unsaturated carbonyl function via electron withdrawal, catalysis due to direct interaction between the electrophile and the C=O group should be revealed by comparison of reduction rates of the 2- and 4-cinnamoylpyridines (**3a** and **3c**). In this article we present evidence for bidentate coordination of **3a** with magnesium and zinc ions and show that such coordination leads to catalysis of reduction of **3a** by 1,4-dihydropyridine derivatives (NADH models).

Experimental Section

Methods. UV spectra were determined using a Cary Model 14 recording spectrophotometer with acetonitrile as solvent. Infrared spectra as well as far-infrared spectra of enones **3a–c**, **4a–d**, **3a**·$HClO_4$, **4a**·$HClO_4$ and the complexes **9a** and **9b** were taken on a Beckman IR-4250 spectrophotometer using KBr pellets (IR) or Nujol mulls (far-IR). IR spectra of other compounds were taken on a Perkin-Elmer 125 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian HA-100 or XL-100-12 instrument. Chemical shifts are reported in units of δ, downfield from internal tetramethylsilane, except for the spectra in CD_3CN, where δ_{CD_3CN} = 1.94 ppm was employed as an internal standard. ^{13}C NMR spectra were recorded on a Varian XL-100 spectrometer. Chemical shifts are reported in parts per million from internal Me_4Si. Coupling constants are given in hertz. Elemental analyses have been performed by H. Pieters of this laboratory.

Materials. Acetonitrile was dried by successive distillation over P_4O_{10} and K_2CO_3 and distilled again, before storage.[7] Prior to use the stored solvent was freshly distilled. $Mg(ClO_4)_2$ and $Zn(ClO_4)_2$ were employed as their hexaethanolates,[8] $M^{2+}(C_2H_5OH)_6(ClO_4^-)_2$ (M^{2+} = Mg^{2+} or Zn^{2+}).

1-Benzyl-1,4-dihydronicotinamide (BNAH, **2**)[9] and **3,5-diethoxycarbonyl 2,6-dimethyl-1,4-dihydropyridine** (HE, **1**)[10] were prepared according to literature procedures. **1-(2-Pyridyl)-3-phenylprop-2-en-1-one** (2-CP, **3a**) was synthesized according to the method of Annigeri and Siddappa[11] and recrystallized from ethanol. For the synthesis of **3-(2-pyridyl)-1-phenylprop-2-en-1-one** (2-iCP, **4a**), the procedure of Marvel et al.[12] was modified according to the method described by Hünig et al.[13] The product was recrystallized from ether/*n*-hexane, 1:5 (v/v), and obtained in 55% yield.

1-(3-Pyridyl)-3-phenylprop-2-en-1-one (3b), **1-(4-pyridyl)-3-phenylprop-2-en-1-one (3c)**, **3-(3-pyridyl)-1-phenylprop-2-en-1-one (4b)**, and **3-(4-pyridyl)-1-phenylprop-2-en-1-one (4c)** (3-CP, 4-CP, 3-iCP,

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