

Figure 2. 3D NOESY-COSY spectroscopy: The top spectrum shows the  $NH-C_aH$  cross-peak region of a 300-MHz soft-NOESY experiment on buserilin. Same acquisition and processing parameters as for the 3D COSY-COSY.) The spectrum was recorded in 96 h. The three inserted blocks give cross sections parallel to  $\omega_2(C_aH)$  and  $\omega_3(NH)$  axes of a 3D NOESY-COSY experiment. Peaks are labeled with the one-letter codes of the amino acids forming origin and destination of coherence transfer. Contours are drawn for positive and negative intensities.

A soft-NOESY spectrum, again of buserilin, showing the NH-C<sub>a</sub>H cross-peak region is given in Figure 2. Severe overlap of intra- and interresidue NOE cross peaks makes the interpretation difficult. In particular the overlap of the peaks  $NH^{(R)}-C_{\alpha}H^{(R)}$  and  $NH^{(W)}-C_{\alpha}H^{(H)}$  as well as of  $NH^{(R)}-C_{\alpha}H^{(L)}$ ,  $NH^{(L)}-C_{\alpha}H^{(L)}$ , and  $NH^{(L)}-C_{\alpha}H^{(S)}$ , should be noted. The NOE-SY-COSY experiment involving the coherence transfer processes

$$\mathbf{NH} \xrightarrow{\mathrm{intra}} \mathbf{C}_{\alpha} \mathbf{H} \xrightarrow{\mathrm{intra}} \mathbf{NH}$$

provides a spread in the third dimension by the intraresidue J correlation of  $C_{\alpha}H$  and NH protons. The pulse sequence reads  $(\pi/2)^{(\rm NH)} - (\pi) - \Delta - t_1 - (\pi/2) - \tau_{\rm m} - (\pi/2)^{(\rm C_{\alpha}H)} - t_2 - (\beta) - t_3.$ The  $-(\pi)-\Delta$ -refocusing element removes peak shape distortions. Three cross sections parallel to  $\omega_2$  and  $\omega_3$  through the 3D spectrum are included in Figure 2. Because the NH resonances of R and H, and of L and S, do not overlap, it is possible to separate all mentioned coincidences except for the peaks  $NH^{(R)}-C_{\alpha}\dot{H}^{(L)}(R/L)$ and  $NH^{(L)}\!\!-\!\!C_{\alpha}H^{(L)}(L/L)$  that overlap even in the 3D spectrum, because NH<sup>(R)</sup> and NH<sup>(L)</sup> are almost isochronous. However, the small L/L + R/L cross peaks in the 2D section (a) compared to (b) indicate that the L/L correlation is much weaker than the R/L correlation. A more complete separation of the R/L and L/L cross peak can be achieved in a different part of the full 3D spectrum, involving the transfer

$$C_{\alpha}H \xrightarrow{\text{NOE}} \text{NH} \xrightarrow{J} C_{\alpha}H$$

that is not displayed here.

Selective 11.9-ms Hermite-shaped pulses<sup>8</sup> were used. 3D absorption peakshapes are obtained by independent time proportional phase incrementation (TPPI) of all pulses preceding the first and second mixing sequences, respectively.

The results obtained with 3D NMR spectroscopy applied to a small peptide are encouraging in view of application to medium-size proteins where more severe overlap among cross peaks

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calls for additional resolution.

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## First Example of Organic Reaction Implying the Axial Ligand in Metalloporphyrin Series. Synthesis, Characterization of 4-Substituted (Tetrazolato)indium(III) Porphyrin Complexes, and Molecular Structure of (4-Phenyltetrazolato)-(2,3,7,8,12,13,17,18-octaethylporphinato)indium(III)

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Organic azides are powerful reagents in heterocyclic chemistry and have been the focus of a considerable number of papers.<sup>2,3</sup> On the contrary, chemistry of metal coordinated azides is scarce, and few reported works demonstrate that the reactivity of such ligands is comparable to organic azides.<sup>4-8</sup> The biological interest

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of the metal-nitrogen bond is well known,<sup>9</sup> but in metalloporphyrin series only the thermal and photochemical decomposition of the axial azide ligand has been reported.<sup>10-14</sup> We report here the first investigation related to an (azide)indium(III) porphyrin unit ((OEP)InN<sub>3</sub> or (TPP)InN<sub>3</sub>) toward organic nitriles (C<sub>6</sub>H<sub>5</sub>CN or CH<sub>3</sub>CN). Such a reaction leads to a five-membered heterocycle bonded to the metal atom. To date the axial ligand of a metalloporphyrin system has never been implicated in a classical organic reaction.

The starting material, (P)InN<sub>3</sub><sup>15,16</sup> (10.30 mmol) was refluxed under inert atmosphere in freshly distilled benzonitrile (30 cm<sup>3</sup>) or a mixture of acetonitrile methylene chloride (3/1). The reaction was monitored by IR spectroscopy in the range 1800–2200 cm<sup>-1</sup> to observe the dissapearance of the  $\nu_{as}(N_3)$  vibration mode; the reaction was complete in 10 h. Then the solution was evaporated to dryness under vacuum, and the crude product was recrystallized from toluene. The yield was close to 60%. The compounds 1–4 were characterized by elemental analyses, mass spectrometry, UV–vis, IR and <sup>1</sup>H NMR spectroscopy.<sup>17</sup>

Elemental analysis and mass spectral data of 1-4 suggest the molecular formula (P)In[(N<sub>4</sub>C)R], where  $R = CH_3$  or  $C_6H_5$ .

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(16) The starting materials, (P)InN<sub>3</sub>, were obtained from (P)InCl complexes. A typical experiment is described as follows: to a solution of (P)InCl (0.55 mmol) in methylene chloride was added NaN<sub>3</sub> (18.5 mmol). The reaction mixture was stirred for 12 h at room temperature, then the solution was filtered off, and the solvent was removed in vacuo. The crude product was recrystallized from toluene. The yield was close to 60%.

was recrystallized from toluene. The yield was close to 60%. (17) Elemental analysis and spectroscopic data of (**OEP**)In[(N<sub>4</sub>C)C<sub>6</sub>H<sub>5</sub>], 1: UV-vis λ<sub>max</sub> nm (ε × 10<sup>-3</sup> M<sup>-1</sup>·cm<sup>-1</sup>) 385 (69.7), 407 (460.3), 539 (18.4), 576 (20.6) (in THF); IR ν (cm<sup>-1</sup>) 305, 678, 737, 785, 1363, 3066 (CSI pellet); <sup>1</sup>H NMR δ (ppm) 6.68 (2 H, d, o-H), 6.44 (2 H, m, m-H), 6.41 (1 H, m, p-H), 10.42 (4 H, s, meso-H), 3.95 (16 H, m, α-CH<sub>2</sub>), 1.80 (24 H, t, β-CH<sub>3</sub>) (in C<sub>6</sub>D<sub>6</sub> from SiMe<sub>4</sub> at 294 K). Anal. Calcd for C<sub>43</sub>H<sub>49</sub>N<sub>8</sub>In: C, 65.2; H, 6.2; N, 14.1. Found: C, 65.2; H, 6.1; N, 13.6. (**TPP)In**(N<sub>4</sub>C)C<sub>6</sub>H<sub>3</sub>, **2**: UV-vis λ<sub>max</sub> nm (ε × 10<sup>-3</sup> M<sup>-1</sup>·cm<sup>-1</sup>) 402 (30.9), 425 (394.7), 560 (11.9), 600 (5.6) (in THF); IR ν (cm<sup>-1</sup>) 668, 735, 1365, 3070 (CsI pellet); <sup>1</sup>H NMR δ (ppm) 6.87 (2 H, m, o-H), 6.56 (3 H, m, m, p-H), 9.04 (8 H, s, pyrr-H), 8.02 (8 H, m, o-H<sub>2</sub>), 7.45 (12 H, m, m, p-H<sub>2</sub>) (in C<sub>6</sub>D<sub>6</sub> from SiMe<sub>4</sub> at 294 K). Anal. Calcd for C<sub>51</sub>H<sub>33</sub>N<sub>8</sub>In: C, 70.2; H, 3.8; N, 12.8. Found: C, 69.6; H, 3.9; N, 12.5. (**OEP)In**((N<sub>4</sub>C)CH<sub>3</sub>], 3: UV-vis λ<sub>max</sub> nm (ε × 10<sup>-3</sup> M<sup>-1</sup>·cm<sup>-1</sup>) 386 (70.4), 407 (483.6), 539 (20.0), 577 (22.9) (in THF); IR ν (cm<sup>-1</sup>) 805, 1315 (CsI pellet); <sup>1</sup>H NMR δ (ppm) 0.38 (3 H, s, CH<sub>3</sub>), 10.39 (4 H, s, meso-H), 3.95 (16 H, m, α-CH<sub>2</sub>), 1.81 (24 H, t, β-CH<sub>3</sub>) (in C<sub>6</sub>D<sub>6</sub> from SiMe<sub>4</sub> at 294 K). Anal. Calcd for C<sub>38</sub>H<sub>47</sub>N<sub>8</sub>In: C, 62.5; H, 6.4; N, 15.3. Found: C, 62.4; H, 6.6; N, 14.8. (**TPP)In**((N<sub>4</sub>C)CH<sub>3</sub>], 4: UV-vis λ<sub>max</sub> nm (ε × 10<sup>-3</sup> M<sup>-1</sup>·cm<sup>-1</sup>) 402 (49.0), 424 (591.5), 560 (18.0), 600 (7.1) (in THF); IR ν (cm<sup>-1</sup>) 808, 1255, 1380 (CsI pellet); <sup>1</sup>H NMR δ (ppm) -0.33 (3 H, s, CH<sub>3</sub>), 9.09 (8 H, s, pyrr-H), 8.03 (8 H, m, o-H<sub>2</sub>), 7.44 (12 H, m, m, p-H<sub>2</sub>) (in C<sub>6</sub>D<sub>6</sub> from SiMe<sub>4</sub> at 294 K). Anal. Calcd for C<sub>46</sub>H<sub>31</sub>N<sub>8</sub>In: C, 68.0; H, 3.8; N, 13.8. Found: C, 67.3; H, 3.7, N, 13.0. Electronic absorption spectral data in tetrahydrofuran of the investigated compounds in this study<sup>17</sup> are comparable to those of the (P)InX complexes where X is an anionic ligand like  $Cl^{-,18,19}$  So, the (tetrazolato)indium porphyrin complexes have electronic absorption spectra belonging to the "normal" class.<sup>20</sup>

The typical vibrational frequencies of the compounds 1-4 are in good agreement with the proposed molecular formula (P)In- $[(N_4C)R]$ .<sup>17</sup> The vibrations in the ranges 785-808 cm<sup>-1</sup> and 1315-1380 cm<sup>-1</sup> are due to the asymmetric and symmetric tetrazole ring deformations, respectively.<sup>21-25</sup> For the complexes 1 and 2 three other absorption bands close to 673, 736, and 3068 cm<sup>-1</sup> are observed which are unambiguously attributable to the phenyl substituent. At lower wavenumbers, a broad band due to the indium-nitrogen vibrator<sup>23</sup> is observed at 305 cm<sup>-1</sup> when the macrocycle is the octaethylporphyrin ring. On the basis of these above results,<sup>17</sup> it appears that only one isomer is formed. However, the 1-3 dipolar cycloaddition of azido complexes with nitriles can lead to two isomers, i.e., an axial coordinated 4-R or 5-R ligand may be formed (Scheme I).<sup>6,24-26</sup>

The low field chemical shifts of axial ligand protons agree well with a large distance between these protons and the metal center favoring the 4-substituted isomer. The spectra are also in good agreement with a coplanar arrangement of the phenyl substituent and the tetrazole ring since two or three different signals are observed for the ortho, meta, and para protons.<sup>17</sup> However, a definitive structure cannot be established by <sup>1</sup>H NMR results because the two coordination schemes are virtually energetically equivalent<sup>27</sup> and already reported in organometallic chemistry.<sup>7,26,27</sup>

To establish definitively the linkage mode, the molecular crystal structure of  $(OEP)In[(N_4C)C_6H_5]$  has been solved by an X-ray diffraction experiment.<sup>28</sup> Figure 1 shows the ORTEP view of complex 1. The tetrazole ligand coordinated to the indium atom is substituted by the aryl group in the 4-position. The five-membered ring is planar and nearly perpendicular to the porphyrin four nitrogen plane. The In-N<sub>ax</sub> distance (2.183 (5) Å) is slightly larger than the In-C<sub>ax</sub> distance previously reported for the group 13  $\sigma$ -bonded porphyrin complexes.<sup>29-31</sup> The more significant difference concerns the metal out-of-plane distance ( $\Delta 4N = 0.463$  (0) Å;  $\Delta Por = 0.494$  (0) Å) which is lower than those already reported for pentacoordinated indium(III) porphyrins.<sup>31</sup> The doming character is weak, and the ORTEP view of 1 could explain why the isomer I formation is sterically promoted. The dihedral angle between the phenyl and tetrazole rings is only 11.6° favoring an orbital conjugation between the two cycles which was already

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Figure 1. ORTEP view of the complex 1. Selected bond distances (Å) and angles (°) are as follows: In-N(1), 2.126 (4); In-N(2), 2.129 (4); In-N(3), 2.132 (4); In-N(4), 2.125 (4); In-N(5), 2.183 (5); N(1)-In-N(2), 87.0 (2); N(1)-In-N(3), 155.0 (2); N(1)-In-N(4), 87.6 (2); N(1)-In-N(5), 99.0 (2); N(2)-In-N(3), 87.2 (2); N(2)-In-N(4), 154.8 (2); N(2)-In-N(5), 102.7 (2); N(3)-In-N(4), 87.3 (2); N(3)-In-N(5), 106.0 (2); N(4)-In-N(5), 102.4 (2).

predicted by <sup>1</sup>H NMR data. Finally, it is therefore likely that the compounds 2-4 bear a 4-substituted tetrazole. However, no definitive mechanism can be established.

The (azide)indium(III) porphyrins exhibit a similar reactivity toward other dipolarophiles like benzyne leading to (benzotriazolato)indium(III) porphyrins. Such reactions of azido metalloporphyrins are also observed when the central atom is a transition metal. Also the synthesis and the characterization of the corresponding iron(III) complexes are underway.

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Supplementary Material Available: Tables of positional parameters, thermal parameters, interatomic distances, interatomic angles, and dihedral angles for non-hydrogen atoms (23 pages). Ordering information is given on any current masthead page.

## $D_{2h}$ -Bishomohexaprismane ("Garudane"). Design of the Face-to-Face 2 + 2 Dimer of Norbornadiene

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Dimerization of norbornadiene with metal complexes has been actively investigated in recent years from mechanistic and synthetic perspectives.<sup>1</sup> As many as five novel dimers have been characterized, but the true, face-to-face, 2 + 2 dimer 1 ("garudane"),<sup>2</sup>

formally a 1,4-bishomohexaprismane of  $D_{2h}$  symmetry, has remained elusive. In fact, for over a quarter of a century now, <sup>la,b,k</sup> the structure 1 has been repeatedly considered for one of the ubiquitous heptacyclic dimers of norbornadiene, but on incisive structural scrutiny has always yielded to the alternative formulation 2 ("isogarudane").<sup>If,h,j,k</sup> Understandably, the union of two norbornadiene moieties to furnish 1 is disfavored both on entropic as well as strain energy considerations.<sup>3</sup> Nevertheless, 1 is architecturally a fascinating, heptacyclic,  $C_{14}H_{16}$  hydrocarbon, and its synthetic design constitutes an attractive and challenging proposition. Looking further ahead, 1 and its derivatives are particularly promising precursors for hexaprismane through ring contraction protocols.<sup>4</sup> In this communication, we disclose our synthetic strategy leading to the *first* synthesis of 1,4-bishomohexaprismane (1).



Among the various strategic options for attaining 1, that conceptualized in 3 and involving a formal 2C5 (1,3-cyclopentadiene)  $+ C_4$  (cyclobutadiene) union through thermal 4 + 2 and photochemical 2 + 2 cycloaddition processes appealed to us the most. Imparting practical shape to this theme required deployment of a cyclobutadiene equivalent that could twice function as a 2 component in the 4 + 2 cycloadditions, control the stereochemistry to facilitate the intramolecular 2 + 2 photocycloaddition, and, finally make the functional group adjustment to the hydrocarbon level. Synthetic logic and literature precedences<sup>5</sup> led to the identification of approach 4, the "2,5-dibromobenzoquinone between the two cyclopentadienes" as the stratagem for achieving 1,4-bishomohexaprismane (1).



Our synthetic pursuit commenced from the readily available but previously overlooked tricyclic quinone 5.6a,b Diels-Alder reaction of 5 with cyclopentadiene furnished the desired endo, syn adduct 6 and the undesired endo, anti adduct, 65:35, in quantitative yield.<sup>6b,7</sup> The ene-dione moiety in 6 was regio- and stereose-

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<sup>(2)</sup> The protruding bridges ("wings") in 1 are reminiscent of "Garuda" (Sanskrit), the mythological Hindu demi-god, part-bird, part-man, see: Encyclopaedia Britannica, Micropaedia 1981; Vol. IV, p 425. According to the von Baeyer system of nomenclature: heptacyclovon Baeyer system of not (9.3.0.0<sup>2,5</sup>.0<sup>3,13</sup>.0<sup>4,8</sup>.0<sup>6,10</sup>.0<sup>9,12</sup>)tetradecane. nomenclature:

<sup>(3)</sup> The strain energy of 1 and 2 has been estimated to be 93.00 and 49.24 kcal/mol according to the MM-2 calculations performed by Professor E. Osawa, Hokkaido University, Japan.

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