dynamical equilibrium[10] were eliminated by using alternating 45° and 135° detection pulses and accumulating eight consecutive FIDs.

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[7] COD
[8] Due to the antiphase structure of the signals, the quartet appears with the intensities -1, -1, -1, 1, whereas the triplet appears with the intensities -1, 1, 0. The antiphase triplet, therefore, resembles a doublet with a doubled coupling constant.
[12] Magnetization in the thermal equilibrium refers to “conventional” magnetization that is determined by the Boltzmann distribution. It differs fundamentally from the magnetization resulting from a PHIP experiment: The latter is represented by the time-averaged density matrix \( \hat{\rho}_{\text{TR}} = \int_0^\infty \hat{\rho}(t) dt \) (for the experiments described in this paper).


Boaz Turner, Mark Botoshansky, and Yoav Eichen∗

Calix[n]pyrroles derived from pyrrole and simple ketones have recently become the subject of intensive research aimed at the development of novel ligands,[1] molecular hosts for anionic species[2–4] and for uncharged species such as simple alcohols, amines, and amides.[5] Octaalkylcalix[4]pyrroles, which are readily accessible, are hosts for fluoride and chloride ions both in solution and in the solid state. Some of these hosts exhibit a remarkable selectivity for binding fluorides rather than other halides even though the guest anion is bound outside the cavity.[5]


Acid-catalyzed condensation of pyrrole with aromatic ketones such as benzophenone, di-(2-pyridyl) ketone and 9-fluorenone results in formation of the corresponding diaryl-(2-pyryrol)methanes 1–3 in moderate to good yields (reaction a in Scheme 1). The diaryl-di-(2-pyryrol)methane products failed to react further with the corresponding aromatic ketones to form linear polymers or cyclic products even after prolonged reaction times or at elevated temper-

COMMUNICATIONS


Scheme 1. Synthesis of the meso-substituted calix[4] and calix[6]pyrroles. a) Ketone/pyrrole = 1:2, BF3·OEt2, ethanol, room temperature, 7 days; b) pyrrole derivatives from reaction a) in ethanol/acacetone (1/1), trifluoroacetic acid, room temperature, 7 days; c) pyrrole derivatives from reaction a) in ethanol/acacetone (1/1), BF3·OEt2, room temperature, 7 days.
atures, in contrast to the reaction of pyrrole and pyrrole derivatives with most aliphatic ketones.[6] Curiously, pyrrole failed to react with aromatic ketones bearing electron-donating or electron-withdrawing groups in the para position (e.g. 4,4′-dichloro-, 4,4′-dimethoxy-, or 2,7-dinitro-9-fluorenone). Table 1 summarizes some experimental results for the acid-catalyzed reaction of diaryl ketones with pyrroles.

Although diaryldi-(2-pyrrolyl)methanes fail to react further with aromatic ketones, they react readily with simple aliphatic ketones, such as acetone, in the presence of catalytic amounts of trifluoroacetic acid (reaction b in Scheme 1) to yield the corresponding meso-1,1,3,3,5,5-hexamethyl-meso-2,2,4,4,6,6-hexamethylicalix[6]pyrroles 4 and 5. The corresponding meso-1,1,3,3-tetraaryl-meso-2,2,4,4-tetramethylicalix[4]pyrroles 6–8 were isolated as the main products when BF₃·OEt or methane-sulfonic acid were used as the acid catalyst (reaction c in Scheme 1). The experimental results are summarized in Table 1.

Table 1. Condensation reactions between ketones and pyrroles.

<table>
<thead>
<tr>
<th>Ketone</th>
<th>Pyrrole</th>
<th>Prod. Yield [%]</th>
<th>M.p. [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzophenone pyrrole</td>
<td>1</td>
<td>22[a], 39[b]</td>
<td>263–264</td>
</tr>
<tr>
<td>4,4′-dimethoxybenzophenone pyrrole</td>
<td>–</td>
<td>–</td>
<td>––[a, b, c, d]</td>
</tr>
<tr>
<td>4,4′-dichlorobenzophenone pyrrole</td>
<td>–</td>
<td>–</td>
<td>––[a, b, c, d]</td>
</tr>
<tr>
<td>9-fluorenone pyrrole</td>
<td>3</td>
<td>58[c]</td>
<td>238–239</td>
</tr>
<tr>
<td></td>
<td>–</td>
<td>–</td>
<td>–[b, c, d]</td>
</tr>
<tr>
<td>2,7-dinitro-9-fluorenone pyrrole</td>
<td>–</td>
<td>–</td>
<td>–[a, b, c, d]</td>
</tr>
<tr>
<td>dt-(2-pyridyl) ketone</td>
<td>2</td>
<td>25[c]</td>
<td>165–166</td>
</tr>
<tr>
<td></td>
<td>–</td>
<td>–</td>
<td>–[b, c, d]</td>
</tr>
<tr>
<td>dibenzosuberone pyrrole</td>
<td>–</td>
<td>–</td>
<td>–[a, b, c, d]</td>
</tr>
<tr>
<td>acetone</td>
<td>1</td>
<td>60[c]</td>
<td>243–244</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>9[c]</td>
<td>247–248</td>
</tr>
<tr>
<td>acetone</td>
<td>2</td>
<td>20[c]</td>
<td>302–303</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>26[d]</td>
<td>307–308</td>
</tr>
<tr>
<td>acetone</td>
<td>3</td>
<td>38[c]</td>
<td>302–303</td>
</tr>
</tbody>
</table>

[a] Methanesulfonic acid as catalyst. [b] BF₃·Et₂O as catalyst. [c] Trifluoroacetic acid as catalyst. [d] No reaction under the given conditions.

Crystals of meso-1,1,3,3,5,5-hexamethyl-meso-2,2,4,4,6,6-hexamethylicalix[6]pyrrole (4) suitable for an X-ray structure determination were obtained in the form 4·3acetone·H₂O·CHCl₃ by slow evaporation of a chloroform/acetone solution (1:1 v/v). The macrocycle 4 forms an asymmetric, conelike structure in which all three diphenylmethylene units are situated on one side of the macrocycle, while the dimethylmethylene groups are situated on the other side (Figure 1a). One phenyl ring of each diphenylmethylene unit points perpendicular to the macrocycle plane, while the other points towards the cavity of the macrocycle. The pyrrole rings in 4 adopt a 1,3,5-alternate conformation, in contrast to the more abundant cone conformation found in calix[6]arenes[7] or the less abundant 1,2,3-alternate conformation.[8] The N–H groups of the 1,3,5 pyrrole rings point towards the side of the meso-dimethylene groups and are almost perpendicular to the macrocycle plane. The N–H groups of the other three pyrrole rings point towards the center of the cavity. The distance d(H···H) between the protons of the latter three pyrrole rings is 4.93 Å and the cross section of the cavity measures about 60 Å². The macrocycle is composed of three different regions: a) An aromatic part formed by three phenyl rings of the meso-diphenylmethyline moieties. b) A central part containing three acidic protons of three pyrrole rings pointing towards the center of the cavity. c) An aliphatic part composed of three methyl groups from the meso-dimethylmethyline moieties with three N–H groups of three pyrrole rings pointing out of the cavity. All the solvent molecules in the crystal are situated outside the cavity, probably due to a
The ketone (2.5 mmol) and freshly distilled pyrrole (5 mmol) were dissolved in dry ethanol (45 mL). BF$_3$ ·OEt$_2$ (0.3 mL) was added to the solution, and the reaction mixture was stirred for one week at room temperature. Then solvents were removed under reduced pressure to give a viscous residue, which was dissolved in dichloromethane and washed with aqueous ammonia solution. The aqueous phase was extracted with dichloromethane (50 mL). The organic phase was dried with anhydrous sodium sulfate, and purified by chromatography over silica (alumina for the pyridine derivatives).

General procedure for the preparation of meso-$1,1,3,3,5,5$-hexamethylmeso-$2,2,4,4,6,6$-hexa-(2-aryl)calix[6]pyroles and meso-$1,1,3,3,5,5$-tetramethylmeso-$2,2,4,4$-tetraarylcalic[4]pyroles: The di-(2-aryl)di-(2-pyrrolyl)methane (1.1 mmol) was added to a mixture of dry acetonitrile (30 mL) and dry ethanol (30 mL). Trifluoroacetic acid (0.3 mL) in the case of calix[6]pyroles or BF$_3$ ·OEt$_2$ (0.15 mL) in the case of calix[4]pyroles were added to the solution and the reaction mixture was stirred at room temperature for one week. Solvents were removed under reduced pressure and the viscous residue was dissolved in dichloromethane and washed with aqueous ammonia solution. The aqueous phase was extracted with dichloromethane (50 mL). The organic phase was dried with anhydrous sodium sulfate and purified by chromatography over silica (alumina for the pyridine derivatives).

**Experimental Section**

General: NMR spectra were recorded on a Bruker AC-200F spectrometer. Mass spectra were recorded by using a triple quadrupole TSQ-70 Spectrometer (Finnigan MAT). Melting points were recorded on a PL-DSC (Polymer Laboratories) machine. Elemental analysis were performed on a CHN Analyzer (Perkin Elmer). All reagents and solvents were used as received unless stated. Anhydrous solvents were dried before use by using standard methods. Acid catalysts and pyrrole were distilled before use.

General procedure for the preparation of diarylidi-(2-pyrrolylmethanes: The ketone (2.5 mmol) and freshly distilled pyrrole (5 mmol) were dissolved in dry ethanol (45 mL). BF$_3$ ·OEt$_2$ (0.3 mL) was added to the solution, and the reaction mixture was stirred for one week at room temperature. Then solvents were removed under reduced pressure to give a

ether/dichloromethane solution (1:1 v/v). Apparently, the small number of water molecules present in the crystallization solution were trapped by the macrocycle host, forming a solid-state complex. The calix[4]pyrrole receptor 6 adopts a 1,2-alternate conformation, the less abundant conformation of calix[4]arene$^{[4]}$ and calix[4]pyrrole systems.$^{[4]}$ The two water molecules are attached to the macrocycle plane. The water molecules are attached to the macrocycle through two, almost equivalent, hydrogen bonds between the oxygen atom of the water molecule and two acidic N–H protons of adjacent pyrrole rings, ($d$($\text{NH} \cdots \text{O}$) = 2.170(5) and 2.144(4) Å, $\alpha$(N–H $\cdots$ O) = 161.1° and 160.1°, respectively). One of the hydrogen donors of each water molecule is bound to an oxygen atom of a diethyl ether molecule, ($d$($\text{OH} \cdots \text{OEt}_2$) = 1.753(5) Å, $\alpha$(O–H $\cdots$ OEt$_2$) = 177.9°), while the other is “sandwiched” between two adjacent electron-rich pyrrole rings, probably due to $\pi$–$\pi$ interactions ($d$(X–H $\cdots$ HO) = 2.84 Å, $\alpha$(X–H $\cdots$ N) = 127.8°, $\alpha$(X–H $\cdots$ HO) = 177.9°, $\alpha$(X–H $\cdots$ OEt$_2$) = 128.5° and 116.2°). The cross section of the cavity measures about 30 Å$^2$, and is more crowded than that of its calix[6]pyrrole analogue. The two crystalline complexes 4 and 6 are monomeric and do not form hydrogen bond networks in the crystal lattice. Preliminary studies suggest that meso-aryl-substituted calix[x]pyrroles can act as efficient hosts for neutral and charged molecules in solution and in the solid state. The investigation of the host–guest chemistry of the new systems, such as the ditopic meso-tetra- and meso-hexapyrindinacalixpyrroles is currently in progress.

**Figure 1a** depicts the packing of the macrocycle molecules in the crystal. The X-ray structure of crystals of the dihydrate diether complex of meso-$1,1,3,3,5,5$-hexamethylmeso-$2,2,4,4,6,6$-hexa-(2-aryl)calix[6]pyroles and meso-$1,1,3,3,5,5$-tetramethylmeso-$2,2,4,4$-tetraarylcalic[4]pyroles: The di-(2-aryl)di-(2-pyrrolyl)methane (1.1 mmol) was added to a mixture of dry acetonitrile (30 mL) and dry ethanol (30 mL). Trifluoroacetic acid (0.3 mL) in the case of calix[6]pyroles or BF$_3$ ·OEt$_2$ (0.15 mL) in the case of calix[4]pyroles were added to the solution and the reaction mixture was stirred at room temperature for one week. Solvents were removed under reduced pressure and the viscous residue was dissolved in dichloromethane and washed with aqueous ammonia solution. The aqueous phase was extracted with dichloromethane (50 mL). The organic phase was dried with anhydrous sodium sulfate and purified by chromatography over silica (alumina for the pyridine derivatives).

**Figure 2**. Molecular structure of 6 (stereoview). Nonacidic hydrogen atoms and one set of ether/dichloromethane solution (1:1 v/v). Apparently, the small number of water molecules present in the crystallization solution were trapped by the macrocycle host, forming a solid-state complex. The calix[4]pyrrole receptor 6 adopts a 1,2-alternate conformation, the less abundant conformation of calix[4]arene$^{[4]}$ and calix[4]pyrrole systems.$^{[4]}$ The two water molecules are attached to the macrocycle plane. The water molecules are attached to the macrocycle through two, almost equivalent, hydrogen bonds between the oxygen atom of the water molecule and two acidic N–H protons of adjacent pyrrole rings, ($d$($\text{NH} \cdots \text{O}$) = 2.170(5) and 2.144(4) Å, $\alpha$(N–H $\cdots$ O) = 161.1° and 160.1°, respectively). One of the hydrogen donors of each water molecule is bound to an oxygen atom of a diethyl ether molecule, ($d$($\text{OH} \cdots \text{OEt}_2$) = 1.753(5) Å, $\alpha$(O–H $\cdots$ OEt$_2$) = 177.9°), while the other is “sandwiched” between two adjacent electron-rich pyrrole rings, probably due to $\pi$–$\pi$ interactions ($d$(X–H $\cdots$ HO) = 2.84 Å, $\alpha$(X–H $\cdots$ N) = 127.8°, $\alpha$(X–H $\cdots$ HO) = 177.9°, $\alpha$(X–H $\cdots$ OEt$_2$) = 128.5° and 116.2°). The cross section of the cavity measures about 30 Å$^2$, and is more crowded than that of its calix[6]pyrrole analogue. The two crystalline complexes 4 and 6 are monomeric and do not form hydrogen bond networks in the crystal lattice. Preliminary studies suggest that meso-aryl-substituted calix[x]pyrroles can act as efficient hosts for neutral and charged molecules in solution and in the solid state. The investigation of the host–guest chemistry of the new systems, such as the ditopic meso-tetra- and meso-hexapyrindinacalixpyrroles is currently in progress.

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8: 38 %; m.p. 306 – 307 °C; 1H NMR (200 MHz, CDCl3): δ = 7.90 (br. s, 4H, NH), 7.73 (d, 4H, fluorene-H), 7.38 (m, 12H, fluorene-H), 5.89 (t, 4H, pyrrole-H), 3.53 (s, 4H, pyrrole-H), 1.23 (s, 12H, CH3); 13C NMR (50.03 MHz, CDCl3): δ = 148.4, 140.1, 139.7, 123.6, 127.8, 127.4, 127.0, 124.0, 106.3, 103.7, 55.6, 39.9, 28.6; MS (CI): m/z: 673.0 [M+H]+; CHN analysis: calcd for C48H40N4 · H2O: C 83.45, H 6.13, N 8.11; found: C 83.56, H 6.15, N 8.0.

Crystal structure determination: Crystallographic data were collected by using a Philips PW 1100 four-circle, computer-controlled, diffractometer by using graphite crystal monochromated MoKα radiation (λ = 0.7107 Å) with θ/2θ scan (scan width: 1.2°, scan rate: 3′ min⁻¹). Unit cell parameters were determined by a least-squares fitting of the setting angles of 25 centered reflections. The intensities of three standard reflections were measured every 120 min during the data collection. No absorption correction was performed. All non-hydrogen atoms were found by direct methods (SHELXS-86) and refined anisotropically (SHELXL-93). Hydrogen atoms were found by using a difference Fourier map and refined isotropically. The structures were solved by direct methods and refined on |

Mevalonate-Independent Biosynthesis of Terpenoid Volatiles in Plants: Induced and Constitutive Emission of Volatiles**

Jörn Piel, Jens Donath, Katja Bandemer, and Wilhelm Boland*

Dedicated to Professor Lothar Jaenicke on the occasion of his 75th birthday

Plants utilize volatiles to overcome constraints that resulted from their stationary way of life. Volatiles may serve as attractants for pollinators[1, 2] or may attract prey to carnivorous plants[3] over long distances. Herbivore-induced plant volatiles can even serve as cues to direct predators into the vicinity of their prey.[4, 5] This signaling of the plant to the third trophic level is frequently interpreted as “a plant’s cry for help”.[6] Emission of volatiles such as ethylene, methyl jasmonate, or methyl salicylate by plants under attack may even induce defense and resistance genes in undamaged neighboring plants.[7, 8] For example, in the dicotyledonous lima bean (Phaseolus lunatus) volatile emission can be induced by treatment with jasmonic acid or spider mite infestation.[9, 10] As shown in Figure 1, a large proportion of the emitted volatiles are terpenoids. Particularly noteworthy are the two homoterpenes 4,8-dimethylnona-1,3,7-triene (DMNT) and 4,8,12-trimethyltrideca-1,3,7,11-triene (TMTT) emitted by many higher plants in response to herbivore attack[12, 13] and which are known to attract insectivorous.[14, 15] Both homoterpenes are synthesized de novo: mass spectro-

Keywords: calyxpyrroles · porphyrinogens · porphyrinoids · supramolecular chemistry


