**Supplementary Information**

for

**Self-assembly of 3,5-Bis(ethoxycarbonyl)pyrazolate Anions and Ammonium Cations of β-Phenylethylamine and Homoveratrylamine into Hetero-Double-stranded Helical Structures**

by

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1. Experimental Section

The starting materials were purchased from commercial sources and used without further purifications. Pyrazole-3,5-dicarboxylic acid (Aldrich), and sodium hydroxide (Merck). Phenethylamine and homoveratrylamine hydrochlorides were purchased from Sigma-Aldrich.

The solvents were dried using standard techniques. Melting points were determined in a Reichert–Jung hot-stage microscope and are uncorrected. \(^1H\) and \(^{13}C\) NMR spectra were recorded on a Varian Unity Inova-300 spectrometer. The chemical shifts are reported in parts per million (ppm) from tetramethylsilane but were measured against the solvent signals. FAB mass spectra were obtained on a VG AutoSpec spectrometer using a \(m\)-nitrobenzyl alcohol (NBA) matrix. IR spectra were recorded with a Perkin-Elmer 681 S2 spectrometer. Elemental analyses were provided by the Departamento de Análisis, Centro de Química Orgánica “Manuel Lora Tamayo”, CSIC, Madrid, Spain.

**Diethyl 1H-pyrazole-3,5-dicarboxylate [L].** The titled compound was obtained from pyrazole-3,5-dicarboxylic acid as previously described.\(^1\) Yield 80%. Mp 54-55 °C (n-hexane) (lit.,\(^1\) m.p. 53-54 °C). Found: C, 50.80; H, 5.51; N, 13.34 %. Calcd for C\(_9\)H\(_{12}\)N\(_2\)O\(_4\) : C, 50.94; H, 5.70; N, 13.20 %. \(\nu_{max}(\text{KBr})/\text{cm}^{-1} \) 3260 (NH) and 1730 (CO). \(\delta_{300 \text{MHz; DMSO-}d_6; \text{Me}_4\text{Si}}\) 14.62 (1 H, s, NH), 7.18 (1 H, s, 4-H), 4.31 (4H, c, 7-H), 1.31 (6H, t, 8-H). \(\delta_{75 \text{MHz; DMSO-}d_6; \text{Me}_4\text{Si}}\) 160.89 (C-6, br s), 158.98 (C-6’, br s), 143.56 (C-3, vbr s), 134.74 (C-5, vbr s), 110.83 (C-4), 60.87 (C-7), 14.10 (C-8). \(m/z\) (FAB-MS) 213 (MH\(^+\), 100 %), 425 (2MH\(^+\), 19).

**Sodium 3,5-bis(ethoxycarbonyl)pyrazolate [H,L]Na.** To a solution of diethyl 1H-pyrazole-3,5-dicarboxylate (50 mg, 0.23 mmol) in anhydrous ethanol (30 mL) vigorously stirred at 25 °C, sodium hydroxide (9 mg, 0.23 mmol) dissolved in anhydrous ethanol (10 mL) was slowly added. When the addition was complete the reaction was allowed to proceed for 1h, and then the organic solvent was partially evaporated. A solid was formed which, after it was filtered off and dried in vacuo gave compound 1 as a crystalline solid.
Preparation of Solid Binuclear Ammonium Pyrazolate complexes 2 and 3.

A solution of sodium salt 1 (200 mg, 0.85 mmol) in chloroform (10 mL) was heated at 30 °C until a clear solution was obtained. Then, it was slowly cooled to room temperature and a solution of the corresponding ammonium chloride (0.85 mmol) in chloroform (5 mL) was added dropwise under stirring. The reaction mixture was allowed to proceed for 24 h. The small amount of the resulting insoluble salt was filtered off and the clear solution evaporated in vacuum to afford the corresponding ammonium pyrazolate complex as a pure solid in almost quantitative yield.

Phenethylamine complex 2 \([H_{1.1}L]_2(R^1-NH_3)_2\). Reaction of sodium salt 1 (200 mg, 0.85 mmol) with phenethylamine hydrochloride (0.85 mmol) gave 2 (95%). Mp 108-110 °C (EtOH) as a white solid. Found: C, 61.12; H, 6.88; N, 12.45 %. Calc. for C_34H_46N_6O_8 : C, 61.25; H, 6.95; N, 12.60 %. \(\nu_{\text{max}}\text{(KBr)/cm}^{-1} \text{ 2758, 2656, 2555, 2489, 2131 (NH}_3^+\text{) and 1720 (CO), 1704 (CO).}\) \(\delta_{\text{H}}\text{(300 MHz; DMSO-}d_6\text{; Me}_4\text{Si)} \text{ 7.30-7.15 (10H, m, H}_\text{Arom}, \text{ 7.12 (2H, s, 4-H), 4.25 (8H, c, J}_6.7, 7\text{-H), 2.83 (4H, t, J}_6.6, \alpha\text{-H), 2.70 (4H, t, J}_6.6, \beta\text{-H), 1.27 (12H, t, J}_6.7, 8\text{-H).}\) \(\delta_{\text{C}}\text{(75 MHz; DMSO-}d_6\text{; Me}_4\text{Si)} \text{ 161.13 (C}-6,6', \text{ 140.40 (C}-3,5\text{, 139.25 (C}-1', \text{ 128.66 (C}-3', \text{ 128.39 (C}-2', \text{ 126.17 (C}-4', \text{ 110.92 (C}-4\text{, 60.10 (C}-7\text{, 42.15 (C}-\alpha\text{, 37.01 (C}-\beta\text{, 14.23 (C}-8.\text{ m/z (FAB-MS) 546 [(M+1)^+ - C}_8\text{H}_1\text{N}^+, 2 \%], 425 [(2L+1)^+, 22], 334 [(M/2 +1)^+, 13], 289 [(M/2)^+ - 2\text{C}_3\text{H}_6^+, 6], 275 [(M/2)^+ - 2\text{C}_3\text{H}_6\text{O}^+, 4], 213 [(L+1)^+, 100], 122 [(C}_8\text{H}_1\text{N})^+, 40].\) After this compound was redissolved in ethanol and the solution slowly allowed evaporating we obtained crystals valid for X-ray diffraction.

Homoveratrylamine complex 3 \([H_{1.1}L]_2(R^2-NH_3)_2\). Reaction of sodium salt 1 (200 mg, 0.85 mmol) with homoveratrylamine hydrochloride (0.85 mmol) gave 3 (95%). Mp 115-117 °C (EtOH) as a white solid. Found: C, 57.74; H, 6.76; N, 10.46 %. Calc. for C_{38}H_{54}N_6O_12 : C, 58.00; H, 6.92; N, 10.68 %. \(\nu_{\text{max}}\text{(KBr)/cm}^{-1} \text{ 2835, 2758, 2674, 2591, 2495, 2149 (NH}_3^+\text{) and 275 [(M+1)^+, 22], 334 [(M/2 +1)^+, 13], 289 [(M/2)^+ - 2\text{C}_3\text{H}_6^+, 6], 275 [(M/2)^+ - 2\text{C}_3\text{H}_6\text{O}^+, 4], 213 [(L+1)^+, 100], 122 [(C}_8\text{H}_1\text{N})^+, 40].\) After this compound was redissolved in ethanol and the solution slowly allowed evaporating we obtained crystals valid for X-ray diffraction.
1719, 1705 (CO). δH(300 MHz; DMSO-d6; Me4Si) 7.11 (2H, s, 4-H), 6.90-6.60 (6H, m, HArom), 4.25 (8H, c, J 7.1, 7-H), 4.12 (6H, brs, NH3+), 3.71 (6H, s, MeO), 3.69 (6H, s, MeO), 2.79 (4H, t, J 7.0, α-H), 2.60 (4H, t, J 7.0, β-H), 1.27 (12H, t, J 7.0, 8-H) ppm. δC(75 MHz; DMSO-d6; Me4Si) 160.77 (C-6,6´), 148.62 (C-3´), 147.14 (C-4´), 140.07 (C-3,5), 132.12 (C-1´), 120.43 (C-6´), 112.51 (C-5´), 110.86 (C-2´), 100.95 (C-4), 60.27 (C-7), 55.50 (MeO), 55.36 (MeO), 42.94 (C-E), 37.80 (C-β), 14.21 (C-8). m/z (FAB-MS) 606 [(M+1) + - C10H15NO2, 1.5 %], 425 [(2L+1)+, 21], 394 [(M/2 + 1)+, 6], 366 [(M/2) + - C2H5]+, 1], 335 [(M/2) + - 2C2H5]+, 1], 213 [(L+1)+, 79], 182 [(C10H15NO2)+, 100].

After this compound was re-dissolved in ethanol and the solution slowly allowed evaporating we obtained crystals valid for X-ray diffraction.

References


2. NMR Spectra

a) 1H NMR [300 MHz, DMSO-d6] of 2
b) $^{13}$C NMR (75 MHz, DMSO-$d_6$) of 2
c) $^1$H NMR [300 MHz, DMSO-d$_6$] of 3

Homoveratrylamine complex

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d) $^{13}$C NMR (75 MHz, DMSO-d$_6$) of 3

Homoveratrylamine complex
3. - **Crystallographic Data**

Data collection of compounds 2 and 3 was performed at 293 K on a Nonius Kappa-CCD single crystal diffractometer, using Mo Kα radiation (λ=0.7173 Å). Data collection strategy was calculated with the program Collect.\(^1\) Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack.\(^2\)

The crystal structure was solved by direct methods, using the program SIR-97.\(^3\) Anisotropic least-squares refinement was carried out with SHELXL-97.\(^4\) All non hydrogen atoms were anisotropically refined except C8 and C9. These atoms and their respective hydrogens were refined as a two half-occupancy systems due to the occurrence of disorder in this part of the chain. The hydrogen atoms were located in calculated positions using HFIX cards.

Geometrical calculations were made with PARST.\(^5\) The crystallographic plots were made with ORTEP.\(^6\)

1. **COLLECT**, Nonius BV, 1997-2000

4.- **Table of Selected Hydrogen bonds for compounds 2 and 3.**

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<thead>
<tr>
<th>Compound (2)</th>
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<tbody>
<tr>
<td>Donor-H</td>
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<tr>
<td>N3 -H3A</td>
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<tr>
<td>0.89</td>
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<tr>
<td>1.03</td>
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<td></td>
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</tr>
<tr>
<td>0.89</td>
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<tr>
<td>1.03</td>
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</table>

<table>
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<tr>
<th></th>
<th>N3 -H3C</th>
<th>N3 -N2' (3)</th>
<th>H3C -N2' (3)</th>
<th>N3 -H3C</th>
<th>N3 -N2' (3)</th>
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<td>0.89</td>
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<td>1.03</td>
<td>2.06</td>
<td>175 (**)*</td>
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</table>


Equivalent positions:

(0) x,y,z
(1) x-1/2,-y+1/2,+z-1/2
(2) -x,-y,-z
(3) x-1/2,-y-1/2,+z-1/2
(4) -x+1,-y+1,-z
(5) -x,-y-1,-z
**Compound (3)**

<table>
<thead>
<tr>
<th>Donor-H</th>
<th>Donor...Acceptor</th>
<th>H...Acceptor</th>
<th>Donor-H......Acceptor</th>
</tr>
</thead>
<tbody>
<tr>
<td>N3</td>
<td>-H3A</td>
<td>N3</td>
<td>...N2' (1)</td>
</tr>
<tr>
<td>0.89</td>
<td>2.865 (.003)</td>
<td>1.98</td>
<td>171</td>
</tr>
<tr>
<td>1.03</td>
<td>1.84</td>
<td>171 (**))</td>
<td></td>
</tr>
</tbody>
</table>

| N3      | -H3B             | N3           | ...N2 (2)             | H3B ...N2 (2) | N3 -H3B ...N2 (2) |
| 0.89    | 2.965(.003)      | 2.11         | 160                   |
| 1.03    | 1.98             | 158 (**))    |

| N3      | -H3C             | N3           | ...N1 (3)             | H3C ...N1 (3) | N3 -H3C ...N1 (3) |
| 0.89    | 2.873(.003)      | 2.03         | 158                   |
| 1.03    | 1.90             | 156 (**))    |


Equivalent positions:

(0) x,y,z
(1) x+1,+y,+z
(2) -x+1/2,+y-1/2,-z+1/2
(3) -x+1/2,+y+1/2,-z+1/2
(4) -x,-y+1,-z
(5) x+1,+y-1,+z
(6) x,-y-1,+z
(7) x,+y+1,+z
Figure S1. View along the b-axes showing the hydrogen bond pattern (dotted lines) of crystal structures 1 (A), (ref. 11) 2 (B) and 3(C).