Supporting Information

Synthesis and properties of 5,6-dihydro-dipyrrolo[1,2-d;1',2'-g][1,4]diazepin-11-one.

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Synthesis of 1,2-di(pyrrol-1-yl)ethane 4  
Synthesis of 1,1-di(pyrrol-1-yl)methane 5  
X-Ray crystal structure tables for 2  
Gas-phase structure of 2 calculated at MP2 level using the 6-31G basis set.  
X-Ray crystal structure tables for 3  
Gas-phase structure of 3 calculated at MP2 level using the 6-31G basis set.  
Comparison of X-Ray structures (bond lengths/Å and bond angles/°) of 2 and 3 and corresponding data from \textit{ab initio} calculations.  
Gas-phase structure of 7 calculated at MP2 level using the 6-31G basis set.  
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NMR spectra of 4, 2, 5, 3, 6, 7, 8, 9, 10

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1,2-Di(pyrrol-1-yl)ethane 4
Using the method of ref. 3, pyrrole (0.90 cm³, 13.0 mmol) was added to a stirred suspension of powdered potassium hydroxide (2.90 g, 51.7 mmol, 3.98 equiv.) in DMSO (40 cm³) and the mixture was stirred at room temperature for 3 h. The solution was then heated to 65 ºC and ethane-1,2-ditosylate (7.20 g, 19.5 mmol, 1.50 equiv.) added in 6 aliquots over the course of 60 min. The mixture was kept at 65 ºC for a further 5 h. Workup and purification by Kugelrohr distillation [50-70 ºC (1.5 Torr)] yielded 1,2-di(pyrrol-1-yl)ethane 4 as an off white solid (0.56 g, 54%) mp 107-109 ºC (from ether); (lit., 1 107-108 ºC) (Found: C, 74.95; H, 7.75; N, 17.45. C₁₀H₁₂N₂ requires C, 74.95; H, 7.55; N, 17.5%); δ H 6.46-6.45 (4H, m), 6.14-6.12 (4H, m) and 4.18 (4H, s); δ C 120.41 (4 CH), 108.56 (4 CH) and 50.82 (2 CH₂); m/z 160 (M⁺, 8%), 80 (86), 53 (100) and 39 (93).

1,2-Di(pyrrol-1-yl)methane 5
Pyrrole (9.00 cm³, 130 mmol) was added to a stirred suspension of powdered potassium hydroxide (24.02 g, 0.43 mol, 3.31 equiv.) in DMSO (200 cm³) at room temperature. After 1 h, the mixture was heated to 40 ºC and DCM (6.32 cm³, 98.6 mmol, 0.76 equiv.) was added slowly. The solution was heated at 40 ºC for a further 4 h. Once cool, ether (100 cm³) and water (200 cm³) were added and the layers separated. The aqueous layer was extracted with ether (4 × 50 cm³), the combined organic extracts were washed with water (2 × 40 cm³), brine (2 × 40 cm³), dried (MgSO₄) and the solvent removed under reduced pressure to afford a pale yellow solid. Recrystallisation from chloroform gave 1,2-di(pyrrol-1-yl)methane 5 (6.85 g, 72%) mp 99-101 ºC (from chloroform); (lit., 1 105 ºC) (Found: C, 73.8; H, 6.9; N, 19.15. C₉H₁₀N₂ requires C, 73.95; H, 6.9; N, 19.15%); δ H 6.77 (4H, t, J 2.1), 6.22 (4H, t, J 2.1) and 5.81 (2H, s, CH₂); δ C 119.99 (4 × CH), 109.51 (4 × CH) and 61.56 (CH₂); m/z 146 (M⁺, 35%), 80 (100), 53 (61) and 39 (43).
Table 1. Crystal data and structure refinement for 2 (HM7003).

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A. CRYSTAL DATA

Empirical formula
C11 H12 N2 O2
C11 H10 N2 O1, (H2 O)

Formula weight 204.23
Wavelength 0.71073 Å
Temperature 150 K
Crystal system Orthorhombic
Space group P 21 21 21

Unit cell dimensions
a = 4.5748(3) Å  alpha = 90 deg.
b = 13.0074(9) Å  beta = 90 deg.
c = 17.0717(12) Å  gamma = 90 deg.
Volume 1015.87(12) Å³

Number of reflections for cell 2777 (3 < theta < 31 deg.)
Z 4
Density (calculated) 1.335 Mg/m³
Absorption coefficient 0.094 mm⁻¹
F(000) 432

B. DATA COLLECTION

Crystal description pale yellow block
Crystal size 0.32 x 0.21 x 0.17 mm
Instrument Area
Theta range for data collection 1.968 to 30.521 deg.
Index ranges -6<=h<=6, -15<=k<=17, -23<=l<=24
Reflections collected 7851
Independent reflections 1750 [R(int) = 0.043]
Scan type \w
Absorption correction Semi-empirical from equivalents
(Tmin= 0.81, Tmax=0.98)

C. SOLUTION AND REFINEMENT.

Solution direct (SIR92 (Altomare et al., 1994))
Refinement type Full-matrix least-squares on F²
Program used for refinement CRYSTALS
Hydrogen atom placement geom
Hydrogen atom treatment constr

Data 1742
Restraints 0
Parameters 136

Goodness-of-fit on F² 1.0260
Conventional R [F>4sigma(F)] R1 = 0.0703 [1426 data]
Rw 0.1841
Final maximum delta/σ 0.000180
Weighting scheme                  Sheldrick Weights
Largest diff. peak and hole       0.77 and -0.34 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 2 (hm7003). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

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Table 3. Bond lengths [Å] and angles [deg] for 2 (hm7003).

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C(5)-C(6)-H(62)  110.4
N(7)-C(6)-H(62)  107.0
H(61)-C(6)-H(62)  110.5
C(6)-N(7)-C(8)  123.7(3)
C(6)-N(7)-C(12)  127.0(3)
C(8)-N(7)-C(12)  109.3(3)
N(7)-C(8)-C(9)  108.7(3)
N(7)-C(8)-H(81)  125.1
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C(8)-C(9)-C(10)  107.1(3)
C(8)-C(9)-H(91)  126.9
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C(10)-C(12)-N(7)  106.5(3)
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C(1)-C(13)-N(4)  106.9(3)
H(151)-O(15)-H(152)  130.4

Symmetry transformations used to generate equivalent atoms:
Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 2 (hm7003).

The anisotropic displacement factor exponent takes the form:

\[-2 \pi^2 [ h^2 a^* a^* U_{11} + \ldots + 2 h k a^* b^* U_{12} ]\]

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Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 2 (hm7003).

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Table 6. Gas-phase structure of 2 calculated at MP2 level using the 6-31G basis set.²

![Image of molecule structure]

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<td>-1.002862</td>
<td>-0.151736</td>
</tr>
<tr>
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<td>1.559281</td>
<td>-0.772899</td>
<td>-0.220618</td>
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<tr>
<td>C</td>
<td>0.570684</td>
<td>-1.825921</td>
<td>-0.514000</td>
</tr>
<tr>
<td>H</td>
<td>-2.683608</td>
<td>2.269530</td>
<td>-0.436673</td>
</tr>
<tr>
<td>H</td>
<td>-3.340043</td>
<td>-1.998118</td>
<td>0.307403</td>
</tr>
<tr>
<td>H</td>
<td>-4.638678</td>
<td>0.358432</td>
<td>-0.250712</td>
</tr>
<tr>
<td>H</td>
<td>-1.108789</td>
<td>-2.782989</td>
<td>0.474688</td>
</tr>
<tr>
<td>H</td>
<td>-0.159705</td>
<td>-1.700705</td>
<td>1.526987</td>
</tr>
<tr>
<td>H</td>
<td>2.683827</td>
<td>2.269646</td>
<td>0.435464</td>
</tr>
<tr>
<td>H</td>
<td>4.638775</td>
<td>0.358390</td>
<td>0.249765</td>
</tr>
<tr>
<td>H</td>
<td>3.339901</td>
<td>-1.998308</td>
<td>-0.307144</td>
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<tr>
<td>H</td>
<td>0.159594</td>
<td>-1.701138</td>
<td>-1.526546</td>
</tr>
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<td>H</td>
<td>1.108699</td>
<td>-2.783118</td>
<td>-0.473954</td>
</tr>
</tbody>
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Table 7. Crystal data and structure refinement for 3 (hm7004).

Contact  Fraser J. White, f.j.white@sms.ed.ac.uk

A. CRYSTAL DATA

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C10 H8 N2 O</td>
</tr>
<tr>
<td>C10 H8 N2 O</td>
<td></td>
</tr>
<tr>
<td>Formula weight</td>
<td>172.18</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Temperature</td>
<td>150(2) K</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P -1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>a = 7.6509(2) Å</td>
<td>alpha = 102.228(2) deg.</td>
</tr>
<tr>
<td>b = 9.1569(3) Å</td>
<td>beta = 93.332(2) deg.</td>
</tr>
<tr>
<td>c = 12.0975(4) Å</td>
<td>gamma = 99.815(2) deg.</td>
</tr>
<tr>
<td>Volume</td>
<td>812.26(4) Å³</td>
</tr>
<tr>
<td>Number of reflections for cell</td>
<td>? (&lt; theta &lt; ? deg.)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.408 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.094 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>360</td>
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</table>

B. DATA COLLECTION

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal description</td>
<td>orange block</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.28 x 0.25 x 0.13 mm</td>
</tr>
<tr>
<td>Instrument</td>
<td>Bruker Smart Apex CCD</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.73 to 30.53 deg.</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-10&lt;=h&lt;=10, -12&lt;=k&lt;=12, -16&lt;=l&lt;=17</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>11866</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>4583 [R(int) = 0.0416]</td>
</tr>
<tr>
<td>Scan type</td>
<td>Omega Scans</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>(Tmin= 0.8167, Tmax=0.9849)</td>
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C. SOLUTION AND REFINEMENT.

<table>
<thead>
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<tr>
<td>Solution</td>
<td>direct (Shelxs Sheldrick)</td>
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<tr>
<td>Refinement type</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Program used for refinement</td>
<td>SHELXL-97</td>
</tr>
<tr>
<td>Hydrogen atom placement</td>
<td>geom</td>
</tr>
<tr>
<td>Hydrogen atom treatment</td>
<td>constr</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>4583/ 0/ 235</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.026</td>
</tr>
<tr>
<td>Conventional R [F&gt;4sigma(F)]</td>
<td>R1 = 0.0597 [3122 data]</td>
</tr>
<tr>
<td>Rw</td>
<td>0.1396</td>
</tr>
<tr>
<td>Final maximum delta/sigma</td>
<td>0.000</td>
</tr>
<tr>
<td>Weighting scheme</td>
<td></td>
</tr>
</tbody>
</table>
calc \( w = 1/\left( s^2 \cdot (F_o^2)^2 + (0.0520P)^2 + 0.2206P \right) \) where \( P = (F_o^2 + 2F_c^2)/3 \)

Largest diff. peak and hole       0.281 and -0.220 e\,A\(^{-3}\)

Table 8. Atomic coordinates (x 10\(^4\)) and equivalent isotropic displacement parameters (A\(^2\) x 10\(^3\)) for 3 (hm7004).  \( U(\text{eq}) \) is defined as one third of the trace of the orthogonalized \( U_{ij} \) tensor.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>( U(\text{eq}) )</th>
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</thead>
<tbody>
<tr>
<td>C(1A)</td>
<td>5609(3)</td>
<td>2026(2)</td>
<td>11543(2)</td>
<td>33(1)</td>
</tr>
<tr>
<td>C(2A)</td>
<td>6300(3)</td>
<td>2710(2)</td>
<td>12669(2)</td>
<td>39(1)</td>
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<td>C(3A)</td>
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<td>4124(2)</td>
<td>12675(2)</td>
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<tr>
<td>N(4A)</td>
<td>7201(2)</td>
<td>4316(2)</td>
<td>11596(1)</td>
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<tr>
<td>C(5A)</td>
<td>7899(3)</td>
<td>5717(2)</td>
<td>11266(2)</td>
<td>31(1)</td>
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<tr>
<td>N(6A)</td>
<td>7883(2)</td>
<td>5430(2)</td>
<td>10043(1)</td>
<td>27(1)</td>
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<tr>
<td>C(7A)</td>
<td>8722(3)</td>
<td>6414(2)</td>
<td>9461(2)</td>
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<tr>
<td>C(8A)</td>
<td>8223(3)</td>
<td>5838(2)</td>
<td>8323(2)</td>
<td>38(1)</td>
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<tr>
<td>C(9A)</td>
<td>7039(3)</td>
<td>4460(2)</td>
<td>8204(2)</td>
<td>33(1)</td>
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<tr>
<td>C(10A)</td>
<td>6818(2)</td>
<td>4218(2)</td>
<td>9281(1)</td>
<td>25(1)</td>
</tr>
<tr>
<td>O(11A)</td>
<td>4843(2)</td>
<td>1875(1)</td>
<td>9032(1)</td>
<td>33(1)</td>
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<td>C(11A)</td>
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<td>C(12A)</td>
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<td>3040(2)</td>
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<tr>
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<td>O(11B)</td>
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<td>8088(2)</td>
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Table 9. Bond lengths [Å] and angles [deg] for 3 (hm7004).

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<th>Bond</th>
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<td>C(1A)-C(12A)</td>
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<td>C(1A)-H(1A)</td>
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<tr>
<td>C(2A)-C(3A)</td>
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</tr>
<tr>
<td>C(3A)-N(4A)</td>
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</tr>
<tr>
<td>C(3A)-H(3A)</td>
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<tr>
<td>N(4A)-C(12A)</td>
<td>1.384(2)</td>
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<tr>
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</tr>
<tr>
<td>C(5A)-N(6A)</td>
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</tr>
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<tr>
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<tr>
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<tr>
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<tr>
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</tr>
<tr>
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<tr>
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</tr>
<tr>
<td>C(5B)-H(5B1)</td>
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</tr>
<tr>
<td>C(5B)-H(5B2)</td>
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</tr>
<tr>
<td>N(6B)-C(7B)</td>
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</tr>
<tr>
<td>N(6B)-C(10B)</td>
<td>1.388(2)</td>
</tr>
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<td>C(7B)-C(8B)</td>
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<tr>
<td>C(7B)-H(7B)</td>
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<tr>
<td>C(8B)-C(9B)</td>
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<tr>
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<tr>
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<tr>
<td>C(10B)-C(11B)</td>
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</tr>
</tbody>
</table>
O(11B)-C(11B)  1.238(2)
C(11B)-C(12B)  1.444(3)

C(12A)-C(1A)-C(2A)  107.48(17)
C(12A)-C(1A)-H(1A)  126.3
C(2A)-C(1A)-H(1A)  126.3
C(3A)-C(2A)-C(1A)  107.54(17)
C(3A)-C(2A)-H(2A)  126.2
C(1A)-C(2A)-H(2A)  126.2
N(4A)-C(3A)-C(2A)  108.37(17)
N(4A)-C(3A)-H(3A)  125.8
C(2A)-C(3A)-H(3A)  125.8
C(3A)-N(4A)-C(12A)  109.24(16)
C(3A)-N(4A)-C(5A)  125.05(15)
C(12A)-N(4A)-C(5A)  125.17(14)
N(6A)-C(5A)-N(4A)  109.52(14)
N(6A)-C(5A)-H(5A1)  109.8
N(4A)-C(5A)-H(5A1)  109.8
N(6A)-C(5A)-H(5A2)  109.8
N(4A)-C(5A)-H(5A2)  109.8
H(5A1)-C(5A)-H(5A2)  108.2
C(7A)-N(6A)-C(10A)  109.07(15)
C(7A)-N(6A)-C(5A)  125.01(15)
C(10A)-N(6A)-C(5A)  125.34(15)
N(6A)-C(7A)-C(8A)  108.34(17)
N(6A)-C(7A)-H(7A)  125.8
C(8A)-C(7A)-H(7A)  125.8
C(7A)-C(8A)-C(9A)  107.80(17)
C(7A)-C(8A)-H(8A)  126.1
C(9A)-C(8A)-H(8A)  126.1
C(10A)-C(9A)-C(8A)  107.60(17)
C(10A)-C(9A)-H(9A)  126.2
C(8A)-C(9A)-H(9A)  126.2
C(9A)-C(10A)-N(6A)  107.17(16)
C(9A)-C(10A)-C(11A)  132.38(16)
N(6A)-C(10A)-C(11A)  120.25(15)
O(11A)-C(11A)-C(12A)  122.37(16)
O(11A)-C(11A)-C(10A)  122.27(16)
C(12A)-C(11A)-C(10A)  115.36(15)
C(1A)-C(12A)-N(4A)  107.35(16)
C(1A)-C(12A)-C(11A)  131.91(17)
N(4A)-C(12A)-C(11A)  120.73(15)
C(12B)-C(1B)-C(2B)  107.72(17)
C(12B)-C(1B)-H(1B)  126.1
C(2B)-C(1B)-H(1B)  126.1
C(3B)-C(2B)-C(1B)  107.55(18)
C(3B)-C(2B)-H(2B)  126.2
C(1B)-C(2B)-H(2B)  126.2
N(4B)-C(3B)-C(2B)  108.24(17)
<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
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<td>C(2B)-C(3B)-H(3B)</td>
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<td>C(3B)-N(4B)-C(12B)</td>
<td>109.22(16)</td>
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<td>C(3B)-N(4B)-C(5B)</td>
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<td>C(12B)-N(4B)-C(5B)</td>
<td>124.48(15)</td>
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<td>N(6B)-C(5B)-H(5B1)</td>
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<td>N(6B)-C(5B)-H(5B2)</td>
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<td>N(4B)-C(5B)-H(5B2)</td>
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<td>H(5B1)-C(5B)-H(5B2)</td>
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Table 10. Anisotropic displacement parameters (A^2 x 10^3) for 3 (hm7004). The anisotropic displacement factor exponent takes the form: 

\[-2 \pi^2 [ h^2 a^* a^* U_{11} + ... + 2 h k a^* b^* U_{12} ]\]
Table 11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for 3 (hm7004).

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Table 12. Gas-phase structure of 3 calculated at MP2 level using the 6-31G basis set.\textsuperscript{2}

![Diagram of a molecule]

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Table 13. Comparison of X-Ray structures (bond lengths/Å and bond angles/°) of 2 and 3 and corresponding data from \textit{ab initio} calculations.

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| C(2)-C(3)-N(4)  | 109.4(3) | 108.20 | N(4A)-C(3A)-C(2A)  | 108.37(17) | 107.53  |
| C(3)-N(4)-C(5)  | 122.9(3) | 123.58 | C(3A)-N(4A)-C(12A)| 109.24(16) | 109.54  |
| C(3)-N(4)-C(13) | 108.8(3) | 109.13 | C(3A)-N(4A)-C(5A)  | 125.05(15) | 126.28  |
| C(5)-N(4)-C(13) | 128.2(3) | 127.29 | C(12A)-N(4A)-C(5A)| 125.17(14) | 123.15  |
| N(4)-C(5)-C(6)  | 111.5(3) | 111.41 | N(6A)-C(5A)-N(4A)  | 109.52(14) | 108.26  |
| C(5)-C(6)-N(7)  | 110.6(3) | 111.41 | C(7A)-N(6A)-C(10A)| 109.07(15) | 109.54  |
| C(6)-N(7)-C(8)  | 123.7(3) | 123.58 | C(7A)-N(6A)-C(5A)  | 125.01(15) | 126.28  |
| C(6)-N(7)-C(12) | 127.0(3) | 127.28 | C(10A)-N(6A)-C(5A)| 125.34(15) | 123.15  |
| C(8)-N(7)-C(12) | 109.3(3) | 109.13 | N(6A)-C(7A)-C(8A)  | 108.34(17) | 107.53  |
| N(7)-C(8)-C(9)  | 108.7(3) | 108.20 | C(7A)-C(8A)-C(9A)  | 107.80(17) | 108.02  |
| C(8)-C(9)-C(10) | 107.1(3) | 107.52 | C(10A)-C(9A)-C(8A)| 107.60(17) | 107.66  |
| C(9)-C(10)-C(12) | 108.4(3) | 108.15 | C(9A)-C(10A)-N(6A)| 107.17(16) | 107.21  |
| C(12)-C(11)-C(13) | 124.1(3) | 124.30 | C(9A)-C(10A)-C(11A)| 132.38(16) | 131.86  |
| C(12)-C(11)-O(1) | 118.9(3) | 117.85 | N(6A)-C(10A)-C(11A)| 120.25(15) | 120.16  |
| C(13)-C(11)-O(1) | 116.9(3) | 117.85 | O(11A)-C(11A)-C(12A)| 122.37(16) | 122.37  |
| C(11)-C(12)-C(10) | 126.2(3) | 125.39 | O(11A)-C(11A)-C(10A)| 122.27(16) | 122.37  |
| C(11)-C(12)-N(7) | 127.3(3) | 127.60 | C(12A)-C(11A)-C(10A)| 115.36(15) | 115.23  |
| C(10)-C(12)-N(7) | 106.5(3) | 107.00 | C(1A)-C(12A)-N(4A)| 107.35(16) | 107.20  |
| C(11)-C(13)-C(1) | 125.0(3) | 125.39 | C(1A)-C(12A)-C(11A)| 131.91(17) | 131.85  |
| C(11)-C(13)-N(4) | 128.0(3) | 127.60 | N(4A)-C(12A)-C(11A)| 120.73(15) | 120.16  |
| C(1)-C(13)-N(4) | 106.9(3) | 107.00 | |

Table 1: *Geometry optimisation performed with 6-31G basis set.

Though the absolute values differ, the trends in the experimental solid-state parameters noted in the Tables above for structures 2 and 3 are almost identical to the MP2 values calculated.

The calculated values for the lengths of the internal C-N bonds of the pyrrole are slightly longer than the external bonds, but the difference is not as pronounced as in the solid state.

The carbonyl bond lengths are: 2, 1.280 Å; 3, 1.273 Å; therefore 2 shows a greater level of conjugation than 3, although once again the difference is not as pronounced as in the crystal structures.

The calculated internal angles at the carbonyls are exactly the same as in the crystal structures.
Table 14. Gas-phase structure of 7 calculated at MP2 level using the 6-31G basis set.2

![Structure Diagram]

<table>
<thead>
<tr>
<th>Atom</th>
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<th>Y</th>
<th>Z</th>
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<td>-1.971850</td>
<td>-1.014747</td>
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<tr>
<td>C</td>
<td>2.326704</td>
<td>-0.609064</td>
<td>-0.673281</td>
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<tr>
<td>N</td>
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<td>-0.267937</td>
<td>-1.069611</td>
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<tr>
<td>C</td>
<td>0.404163</td>
<td>-1.397687</td>
<td>-1.616016</td>
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<tr>
<td>C</td>
<td>1.322399</td>
<td>-2.458153</td>
<td>-1.595679</td>
</tr>
<tr>
<td>C</td>
<td>0.250190</td>
<td>0.978093</td>
<td>-0.824311</td>
</tr>
<tr>
<td>C</td>
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<td>0.289111</td>
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<td>-0.101450</td>
<td>1.066471</td>
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<tr>
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<td>-1.162615</td>
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<td>C</td>
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<td>-2.205651</td>
<td>1.860602</td>
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<tr>
<td>C</td>
<td>-2.493078</td>
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<tr>
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<td>-0.379651</td>
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<td>-0.384496</td>
<td>-0.160070</td>
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<tr>
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<td>-0.772833</td>
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<tr>
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<tr>
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<td>2.634261</td>
<td>0.589150</td>
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<tr>
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<td>0.652295</td>
</tr>
<tr>
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<td>-0.857315</td>
</tr>
<tr>
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<td>-1.948575</td>
</tr>
<tr>
<td>H</td>
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<tr>
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<td>2.057826</td>
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<td>-2.326000</td>
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<td>-1.771146</td>
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<td>-0.059162</td>
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<td>2.366527</td>
<td>1.601236</td>
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<td>H</td>
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<td>3.531433</td>
<td>0.584501</td>
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<tr>
<td>H</td>
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<td>1.992481</td>
<td>0.812649</td>
</tr>
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<td>H</td>
<td>0.710958</td>
<td>1.108606</td>
<td>1.290476</td>
</tr>
</tbody>
</table>
Table 15. Crystal data and structure refinement for 8 (hm8001).

Contact Simon Parsons, s.parsons@ed.ac.uk

A. CRYSTAL DATA

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C13 H14 N2 O2 S2</td>
</tr>
<tr>
<td>Formula weight</td>
<td>294.38</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 A</td>
</tr>
<tr>
<td>Temperature</td>
<td>150(2) K</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 8.0365(2) Å, alpha = 98.8420(10) deg.</td>
</tr>
<tr>
<td></td>
<td>b = 8.9123(2) Å, beta = 107.7310(10) deg.</td>
</tr>
<tr>
<td></td>
<td>c = 11.2816(3) Å, gamma = 111.5210(10) deg.</td>
</tr>
<tr>
<td>Volume</td>
<td>683.11(3) Å³</td>
</tr>
<tr>
<td>Number of reflections for cell</td>
<td>8646 (2.5 &lt; theta &lt; 30 deg.)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.431 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.388 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>308</td>
</tr>
</tbody>
</table>

B. DATA COLLECTION

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal description</td>
<td>orange block</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.45 x 0.37 x 0.26 mm</td>
</tr>
<tr>
<td>Instrument</td>
<td>Bruker Smart APEX CCD</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.99 to 29.97 deg.</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-11&lt;=h&lt;=9, -12&lt;=k&lt;=12, -15&lt;=l&lt;=15</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>11638</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3705 [R(int) = 0.0269]</td>
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<tr>
<td>Scan type</td>
<td>omega and phi</td>
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<tr>
<td>Absorption correction</td>
<td>Multiscan</td>
</tr>
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<td>(Tmin= 0.753, Tmax=0.903)</td>
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C. SOLUTION AND REFINEMENT.

<table>
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<th>Value</th>
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<tr>
<td>Solution</td>
<td>Patterson (DIRDIF)</td>
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<td>Refinement type</td>
<td>Full-matrix least-squares on F^2</td>
</tr>
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<td>Program used for refinement</td>
<td>SHELXL-97</td>
</tr>
<tr>
<td>Hydrogen atom placement</td>
<td>geom</td>
</tr>
<tr>
<td>Hydrogen atom treatment</td>
<td>riding</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>3705/5/201</td>
</tr>
<tr>
<td>Goodness-of-fit on F^2</td>
<td>1.145</td>
</tr>
<tr>
<td>Conventional R [F&gt;4sigma(F)]</td>
<td>R1 = 0.0481 [3502 data]</td>
</tr>
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<td>Weighted R (F^2 and all data)</td>
<td>wR2 = 0.1180</td>
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<tr>
<td>Extinction coefficient</td>
<td>0.018(3)</td>
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<tr>
<td>Final maximum delta/sigma</td>
<td>0.000</td>
</tr>
<tr>
<td>Weighting scheme</td>
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<tr>
<td>calc w=1/[(s^2+(F0^2+2F2^2))^2+(0.0469P)^2+(0.3545P)] where P=(F0^2+2F2^2)/3</td>
<td></td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.425 and -0.300 e.A⁻³</td>
</tr>
</tbody>
</table>
Table 16. Atomic coordinates (x 10^4), equivalent isotropic displacement parameters (Å^2 x 10^3) and site occupancies for 8 (hm8001). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
<th>Occ</th>
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<td>N(1)</td>
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<td>-1673(2)</td>
<td>3166(1)</td>
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<tr>
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<td>-2386(2)</td>
<td>4185(1)</td>
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<tr>
<td>C(3)</td>
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<td>30(1)</td>
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<tr>
<td>C(4)</td>
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<td>3145(2)</td>
<td>35(1)</td>
<td>1</td>
</tr>
<tr>
<td>C(5)</td>
<td>9996(2)</td>
<td>-1814(2)</td>
<td>2549(2)</td>
<td>31(1)</td>
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<tr>
<td>C(6)</td>
<td>7576(2)</td>
<td>-857(2)</td>
<td>2770(2)</td>
<td>28(1)</td>
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</tr>
<tr>
<td>C(7)</td>
<td>8095(2)</td>
<td>-2537(2)</td>
<td>5061(2)</td>
<td>27(1)</td>
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</tr>
<tr>
<td>S(8)</td>
<td>6272(1)</td>
<td>-2160(1)</td>
<td>5017(1)</td>
<td>34(1)</td>
<td>0.80(1)</td>
</tr>
<tr>
<td>O(9)</td>
<td>8994(3)</td>
<td>-3131(3)</td>
<td>5998(2)</td>
<td>32(1)</td>
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<tr>
<td>C(10)</td>
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<td>36(1)</td>
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<tr>
<td>S(8')</td>
<td>8252(6)</td>
<td>-3313(4)</td>
<td>6187(3)</td>
<td>42(1)</td>
<td>0.20(1)</td>
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<td>O(9')</td>
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<td>-1732(11)</td>
<td>4679(7)</td>
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<td>2302(2)</td>
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Table 17. Bond lengths [Å] and angles [deg] for 8 (hm8001).

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<th>Length [Å]</th>
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<td>1.443(2)</td>
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<td>1.475(2)</td>
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<tr>
<td>C(2)-N(1)-C(6)</td>
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<td>C(3)-C(2)-N(1)</td>
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Symmetry transformations used to generate equivalent atoms:

Table 18. Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for 8 (hm8001).
The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 \left[ h^2 a^*^2 U_{11} + ... + 2 h k a^* b^* U_{12} \right]$$

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Table 19. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for 8 (hm8001).

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Table 20. Gas-phase structure of 8 calculated at MP2 level using the 6-31G basis set.

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$\text{C}_{11}\text{H}_{10}\text{N}_{2}\text{O}$
dept135

\[ \text{C}_{11}\text{H}_{10}\text{N}_{2}\text{O} \]

dept90

\[ \text{C}_{11}\text{H}_{10}\text{N}_{2}\text{O} \]
1,1-Di(pyrrol-1-yl)methane 5

$^1H$

$^{13}C$

C$_9$H$_{10}$N$_2$
Dipyrrrolo[1,2-\(c;1',2'-f\)]pyrimidin-10-one 3

\[ \text{C}_{10}\text{H}_{8}\text{N}_{2}\text{O} \]

\( ^1\text{H} \)

\( ^{13}\text{C} \)
Supplementary Material (ESI) for New Journal of Chemistry
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depth135

C$_{10}$H$_8$N$_2$O


depth90
1-(Pyrrol-1-yl)-1-(2-carboxypyrrol-1-yl)methane 6

$^1$H
Supplementary Material (ESI) for New Journal of Chemistry
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$^{13}$C

C$_{10}$H$_{10}$N$_2$O$_2$

dept135
dept90

C_{10}H_{10}N_{2}O_{2}
Initial product from the reaction of thiophosgene with 1,2-di(pyrrol-1-yl)ethane
1,2-Di[2-(carbothiomethoxy)pyrrol-1-yl]ethane 7

\[ \text{C}_{14}\text{H}_{16}\text{N}_{2}\text{O}_{2}\text{S}_{2} \]

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Initial product from reaction of thiophosgene with 1,1-di(pyrrol-1-yl)methane
1,1-Di[2-(carbothiomethoxy)pyrrol-1-yl]methane 8

$\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_2\text{S}_2$

$^1\text{H}$

$^{13}\text{C}$
5,6-Dihydro-11H-dipyrrolo[1,2-d;2',1'-g][1,4]diazepine 9

\[ C_{11}H_{12}N_2 \]
C$_{11}$H$_{12}$N$_2$
5,6-Dihydro-11H-dipyrolo[1,2-d;2',1'-g][1,4]diazepine-3,8-dicarbaldehyde 10

$^1H$

$^{13}C$

$C_{13}H_{12}N_2O_2$