Synthesis and properties of 5,6-dihydrodipyrrolo[1,2-*d*;2′,1′-*g*]-[1,4]diazepin-11-one† ‡

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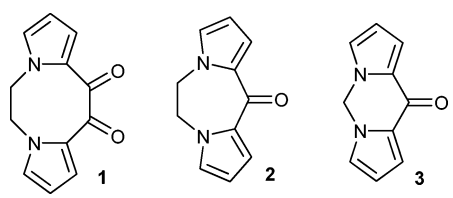
Treatment of 1,2-di(pyrrol-1-yl)ethane **4** with oxalyl chloride gave a low yield of 5,6-dihydrodipyrrolo[1,2-*d*;2′,1′-*g*][1,4]diazepin-11-one **2**, by an unexpected electrophilic substitution–decarbonylation process. The diazepinone **2** is unreactive to electrophiles, but can be deoxygenated to 5,6-dihydro-11*H*-dipyrrolo[1,2-*d*;2′,1′-*g*][1,4]diazepine **9** with lithium aluminium hydride. Reaction of 1,1-di(pyrrol-1-yl)methane **5** with triphosgene gives the related dipyrrolo[1,2-*c*;2′,1′-*f*]pyrimidin-10-one **3**. NMR spectroscopic and X-ray crystal structure comparisons of **2** and **3** show that there is unexpectedly greater conjugation in the compound with the core seven-membered ring, **2**, even though the molecule as a whole is less planar than **3**. The corresponding reactions of **4** or **5** with thiophosgene did not give cyclisation products but the *O*-methyl thioesters **7** and **8** were obtained (89 and 27%, respectively).

Introduction

Oxalyl chloride is sufficiently reactive as an electrophile to acylate pyrrole at the 2-position in the absence of a catalyst.[1] We hoped to extend this process to create the dipyrrolyldiazocine **1** by reaction of 1,2-di(pyrrol-1-yl)ethane with this reagent. In the event, **1** was not obtained but instead the reaction proceeded with decarbonylation to provide the dipyrrolyl-diazepine **2**, which is the parent member of an unknown heterocyclic system.

Here we report the details of this work, comprising the unexpected synthetic route to **2**, and a survey of its chemical properties. The related dipyrrolylpyrimidine **3**[2] was also synthesised by a new method. Comparison of the spectroscopic and structural properties of **2** and **3** allows an analysis of the subtle interplay of the conjugative interactions between the pyrrole and carbonyl moieties in these related skeletons. The studies show, unexpectedly, that there is greater interaction in **2**, containing a core seven-membered ring, even though the six-membered ring species **3** is more planar.



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† This paper is dedicated to Professor Douglas Lloyd, University of St. Andrews, doyen of diazepine chemists, on the occasion of his 88th birthday.

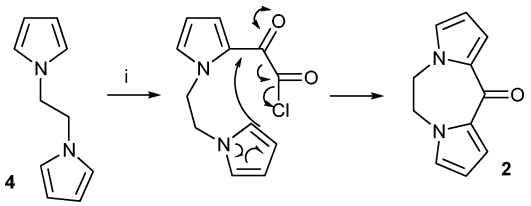
‡ Electronic supplementary information (ESI) available: Experimental, X-ray structure tables, DFT calculations and spectra. CCDC reference numbers CCDC 718605–718607. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b906802n

Results and discussion

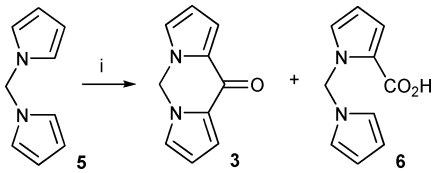
Treatment of 1,2-di(pyrrol-1-yl)ethane[3] **4** with oxalyl chloride in dichloromethane at room temperature under high dilution conditions gave a low recovery of single product after chromatography. Surprisingly, this was identified as 5,6-dihydrodipyrrolo[1,2-*d*;2′,1′-*g*][1,4]diazepin-11-one **2** (19%) by its mass spectrum and by the X-ray crystal structure discussed below. Clearly the cyclisation took place with concomitant decarbonylation of the oxalate moiety (Scheme 1). Decarbonylation of related 3-indoleglyoxalyl chlorides has been known since 1958 to take place in low yields (*ca.* 20%)[4] but the reaction generally requires high temperatures (110–120 °C). The heterocyclic ring system, of which **2** is the parent member, has not been previously reported, though related mono-pyrrolyldiazepines have been made electrochemically.[5]

Although the tricycle **3** could not be made by the oxalyl chloride method, it could be obtained in 29% yield by reaction of 1,1-di(pyrrol-1-yl)methane[3] **5** with triphosgene in toluene (Scheme 2); high dilution conditions were not required. The carboxylic acid **6** was a minor product (8%) after chromatography. This is a shorter route to **2** than has been previously documented.[2a]

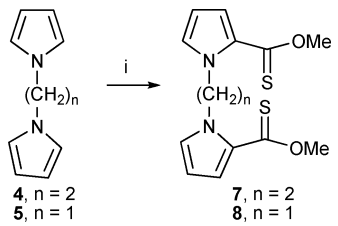
In contrast, neither **4** nor **5** gave cyclised products with thiophosgene. Instead, the analogous *O*-methyl thioesters **7** and **8** were obtained in 89 and 27% yields, respectively, after chromatography (Scheme 3). *O*-Methyl 1*H*-pyrrole-2-carbothioate esters are rare,[6] though the *S*-methyl isomers



Scheme 1 *Reagents and conditions*: (i) oxalyl chloride, 20 °C.



Scheme 2 *Reagents and conditions*: (i) triphosgene, toluene, 110 °C.



Scheme 3 *Reagents and conditions*: (i) thiophosgene, chloroform, 20 °C.

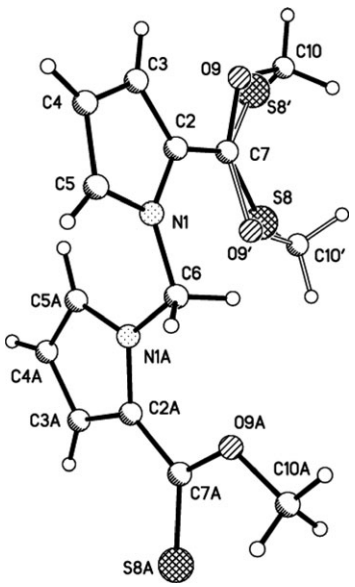


Fig. 1 X-Ray crystal structure of **8**, showing the crystallographic numbering scheme.

have been better characterised.[6,7] The constitution of **8** was established unambiguously by X-ray crystallography (Fig. 1) and provides the first data for this general structure. The structure shows some disorder around one of the carbothioate groups. The conjugation path from the nitrogen lone pair to the carbothioate esters is demonstrated by the differences in the lengths of the C–N bonds in both rings [*e.g.* N1A–C2A 1.391(2) Å; N1A–C5A 1.354(2) Å].

The nature of the saturated bridge causes small but significant effects on the NMR spectra of **2** and **3**. The compound with the central seven-membered ring **2** is apparently more polarised than its six-membered ring analogue **3** since it shows both the most shielded and the most deshielded signal for the pyrrole rings in ^{1}H and ^{13}C NMR spectra. In their electron impact mass spectra, both **2** and **3** apparently lose the elements of a pyrrole moiety as the initial

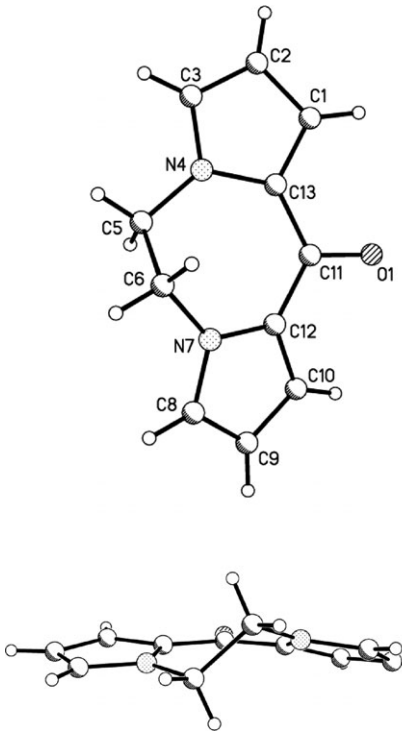


Fig. 2 X-Ray crystal structure of **2**, showing the crystallographic numbering scheme.

breakdown, possibly initiated by ionisation at the carbonyl group and α-cleavage, followed by hydrogen transfer(s) and cleavage of the N–CH_2 bond.

The X-ray crystal structures of **2** and **3** are shown in Fig. 2 and 3, respectively. The diazepinone **2** as a whole has a non-planar structure where the central 7-membered ring is a half-chair, reminiscent of the structures of 2,3-dihydro-1,4-diazepines and their salts.[8] In solution, the ring inversion of **2** is rapid on the NMR timescale, even at −60 °C, in contrast to the situation with 2,3-dihydro-1,4-diazepinium salts.[9] The mean deviation from the best plane of the two 5-membered rings and the carbonyl group is 0.15 Å. The internal N–C bonds of both pyrrole rings are longer than the corresponding external N–C bonds indicating the presence of a conjugation path from the nitrogen atoms around the outer periphery of the aromatic rings to the shared carbonyl group [N7–C12 1.379(4) Å, N7–C8 1.351(5) Å, N4–C13 1.390(4) Å, N4–C3 1.354(4) Å].

Gas-phase structures of **2** and **3** were calculated at MP2 level using the 6-31G basis set[10] (ESI‡) and the data show similar trends to those obtained from the solid-state structures.

The dipyrrole **3** crystallises with two independent molecules in the asymmetric unit (data for molecule A are quoted). It is also non-planar and the normals to the best planes of the 5-membered rings subtend a butterfly angle of 8.6°. At 0.063 Å, the mean deviation from the best plane of the two 5-membered rings and the carbonyl group is less than the corresponding value for the diazepinone **2**. Compound **3** also exhibits a clear external conjugation path from the nitrogen atoms to the carbonyl groups, indicated by the difference in N–C bond lengths of the pyrrole rings [N4A–C12A 1.384(2) Å,

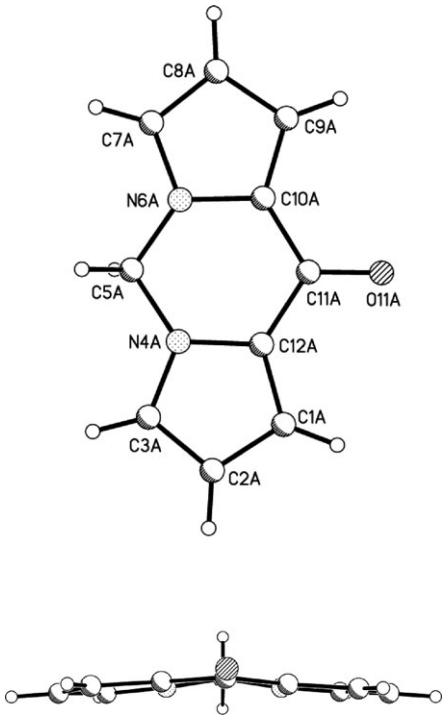


Fig. 3 X-Ray crystal structure of one of the independent molecules of **3**, showing the crystallographic numbering scheme.

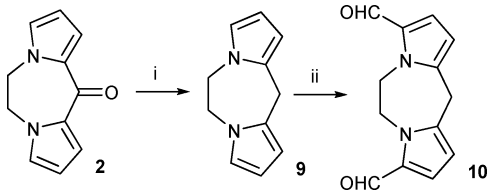
N4A–C3A 1.351(2) Å, N6A–C10A 1.385(2) Å, N6A–C7A 1.358(2) Å].

The C–O bond in **2** [C11–O1, 1.251(4) Å] is longer than that of **3** [C11A–O11A, 1.236(2) Å] suggesting that there is a greater level of conjugation in the former molecule. This result is consistent with the NMR data described above, but is unexpected because of the greater overall planarity of **3** (*cf*. Fig. 2 and 3).

Compound **2** is relatively unreactive. It is stable for a number of weeks in DTFA at room temperature, but no deuterium exchange took place under these conditions. It was recovered unchanged when subjected to Vilsmeier formylation, even though related benzoylpyrroles are known to react.[11] Only starting material was recovered after flash vacuum pyrolysis at 900 °C; no clean decarbonylation[12] or homolysis of the C5–C6 bond occurred. For comparison, FVP of **4** at 900 °C gave some pyridine, presumably formed by homolysis of the CH_2–CH_2 bond and ring expansion of the resulting (pyrrol-1-yl)methyl radicals.[13]

As found for benzoylpyrroles,[1] treatment of the diazepinone **2** with hydride reagents resulted in complete deoxgenation to afford 5,6-dihydro-11*H*-dipyrrolo[1,2-*d*;2′,1′-*g*][1,4]diazepine **9** as a yellow solid in 67% yield (Scheme 4). Corresponding signals in the ^{1}H and ^{13}C NMR spectra due to the pyrrole ring are more shielded in **9** than in its ketone analogue **2**.

As expected, **9** is more reactive towards electrophiles than **2**, and Vilsmeier formylation provided the dialdehyde **10** in 30% yield (Scheme 4). That the formylation takes place in the free α-position of the pyrrole rings was supported by the presence of two doublets (^3J 4.0), consistent with $J_{3,4}$ in pyrrole systems.[14] However, initial attempts at hydride abstraction from **9** were not successful.



Scheme 4 *Reagents and conditions:* (i) $LiAlH_4$, ether, 20 °C; (ii) DMF–$POCl_3$, 1,2-dichloroethane, 20 °C.

Conclusions

The work described in this paper provides the first route to the parent member, **2**, of the 5,6-dihydrodipyrrolo[1,2-*d*;2′,1′-*g*]-[1,4]diazepin-11-one series. Analysis of NMR spectra and X-ray crystal structures shows that **2** is more polarised than its analogue with a central 6-membered ring, **3**, but **2** proved to be unexpectedly unreactive to mild electrophiles. Reaction of 1,2-di(pyrrol-1-yl)ethane **4** or the analogous methane derivative **5** with thiophosgene provided *O*-methyl thioesters which were fully characterised, with the structure supported in one case by X-ray crystallography.

Experimental

^{1}H and ^{13}C NMR spectra were recorded at 250 and 63 MHz, respectively, for solutions in [^{2}H]chloroform unless otherwise stated. Coupling constants are quoted in Hz. ^{13}C NMR signals refer to one CH resonance unless otherwise stated. Mass spectra were recorded under electron impact conditions.

5,6-Dihydrodipyrrolo[1,2-*d*;2′,1′-*g*][1,4]diazepin-11-one 2

Solutions of 1,2-di(pyrrol-1-yl)ethane **4** (0.26 g, 1.6 mmol) in dichloromethane (10 mL) and oxalyl chloride (0.23 g, 1.8 mmol, 1.1 equiv.) in dichloromethane (10 mL) were added at the same rate to a volume of dichloromethane (100 mL) at room temperature, over approximately 15 min. The resulting brown-black solution was stirred at room temperature for a further 18 h. Water (20 mL) was added, the layers were separated and the combined organics were washed with water (2 × 20 mL) and brine (2 × 20 mL), dried (K_2CO_3) and the solvent was removed under reduced pressure. The resulting black solid (0.16 g) was purified by dry flash chromatography on silica [ethyl acetate–petroleum ether 40–60 °C (1 : 2) changing to ethyl acetate–petroleum ether 40–60 °C (2 : 1)] to give 5,6-dihydrodipyrrolo[1,2-*d*;2′,1′-*g*][1,4]diazepin-11-one **2** as a yellow solid (56 mg, 19%), mp 105–106 °C (found: 186.07884. $C_{11}H_{10}N_2O$ requires *M* 186.07876) (found: C, 68.4; H, 5.55; N, 14.45%. $C_{11}H_{10}N_2O{\cdot}0.33H_2O$ requires C, 68.75; H, 5.55; N, 14.6%); δ_H (360 MHz) 7.31 (2H, dd, ^3J 4.0 and ^4J 1.9), 6.79 (2H, apparent t), 6.23 (2H, dd, *J* 4.0 and 2.5) and 4.47 (4H, s); δ_C (63 MHz) 170.01 (quat), 132.64 (2 quat), 127.70 (2 CH), 120.51 (2 CH), 109.61 (2 CH) and 49.96 (2 CH_2); *m*/*z* 186 (M^+, 100%), 158 (5), 120 (38) and 93 (25).

Reaction of triphosgene with 1,1-di(pyrrol-1-yl)methane 5

Triphosgene (0.14 g, 0.49 mmol, 0.34 equiv.) was added to a stirred solution of 1,1-di(pyrrol-1-yl)methane[5] **5** (0.21 g, 1.44 mmol) in toluene (5 mL) and the mixture was heated

under reflux for 3 h. Once cool, nitrogen was bubbled through the solution to remove any residual phosgene present. The toluene was removed under reduced pressure and the crude material was purified by dry flash column chromatography on silica [ethyl acetate–petroleum ether 40–60 °C (1 : 1) changing to ethyl acetate] to afford dipyrrolo[1,2-*c*;2′,1′-*f*]pyrimidin-10-one **3** (71 mg, 29%), mp 160–161 °C (lit.,[2a] mp 162–164 °C) (found: C, 68.5; H, 4.35; N, 16.0%. $C_{10}H_8N_2O{\cdot}0.1H_2O$ requires C, 69.05; H, 4.7; N, 16.1%); δ_H 7.10 (2H, m), 6.96 (2H, s), 6.36 (2H, br s) and 6.06 (2H, s); δ_C 167.32 (quat), 129.15 (2 quat), 123.47 (2 CH), 113.72 (2 CH), 111.66 (2 CH) and 59.13 (CH_2); *m*/*z* 172 (M^+, 96%), 171 (100) and 144 (27); data are compatible with literature values.[2a] A small amount of 1-(pyrrol-1-yl)-1-(2-carboxypyrrol-1-yl)methane **6** (22 mg, 8%) was identified from its spectra: δ_H 7.14 (1H, dd, *J* 4.0, *J* 1.8), 6.91 (1H, dd, *J* 2.6, *J* 1.9), 6.87 (2H, t, *J* 2.2), 6.34 (2H, s, CH_2), 6.21 (1H, dd, *J* 4.0, *J* 2.7) and 6.17 (2H, t, *J* 2.1); δ_C 165.59 (quat), 128.99 (quat), 121.37 (quat), 120.61 (2 CH), 120.55 (quat), 109.78 (CH), 109.49 (2 CH) and 59.85 (CH_2); *m*/*z* 190 (M^+, 100%).

Reaction of thiophosgene with 1,2-di(pyrrol-1-yl)ethane 4

Solutions of 1,2-di(pyrrol-1-yl)ethane **4** (0.13 g, 0.84 mmol) in chloroform (10 mL) and thiophosgene (0.07 mL, 0.91 mmol, 1.08 equiv.) in chloroform (10 mL) were added at the same rate to a volume of chloroform (100 mL) at room temperature over 15 min. After stirring at room temperature for 60 min, water was added and the layers were separated. The organic layer was then washed with water (2 × 30 mL) and brine (2 × 20 mL), dried (K_2CO_3) and the solvent was removed under reduced pressure to afford an intermediate (0.21 g) with the following spectroscopic data: δ_H 7.50 (2H, dd, *J* 4.5, 1.8), 6.73 (2H, dd, *J* 2.4, 2.0), 6.13 (2H, dd, *J* 4.5, 2.5) and 4.88 (4H, s); δ_C 181.69 (2 quat), 138.83 (2 quat), 138.49 (2 CH), 125.39 (2 CH), 110.05 (2 CH) and 49.73 (2 CH_2). Purification of the crude material by dry flash column chromatography on silica [ethyl acetate–petroleum ether 40–60 °C (1 : 3) changing to ethyl acetate–methanol] afforded 1,2-di[2-(carbothiomethoxy)-pyrrol-1-yl]ethane **7** as a brown solid (0.13 g, 89%), mp 122–123 °C (found: M^+ 308.0645. $C_{14}H_{16}N_2O_2S_2$ requires *M* 308.0648); δ_H (360 MHz) 7.18 (2H, dd, *J* 4.1, *J* 1.9), 6.40 (2H, dd, *J* 2.5, *J* 1.9), 5.99 (2H, dd, *J* 4.1, *J* 2.5), 4.85 (4H, s) and 4.17 (6H, s); δ_C (63 MHz) 199.45 (2 quat), 132.30 (2 quat), 132.03 (2 CH), 112.00 (2 CH), 108.51 (2 CH), 57.01 (2 CH_3) and 50.34 (2 CH_2); *m*/*z* 308 (M^+, 100%), 275 (27) and 154 (32).

Reaction of thiophosgene with 1,1-di(pyrrol-1-yl)methane 5

Solutions of 1,1-di(pyrrol-1-yl)methane **5** (0.14 g, 0.96 mmol) in chloroform (10 mL) and thiophosgene (0.08 mL, 1.04 mmol, 1.08 equiv.) in chloroform (10 mL) were added at the same rate to a volume of chloroform (100 mL) at room temperature over 15 min. After stirring at room temperature for 60 min, water was added and the layers were separated. The organic layer was then washed with H_2O (2 × 30 mL) and brine (2 × 30 mL), dried (K_2CO_3) and the solvent was removed under reduced pressure. The residue (0.58 g) had the following characteristics: δ_H 7.54–7.50 (2H, m), 7.05 (2H, s, CH_2), 7.01 (2H, t, *J* 1.9) and 6.29 (2H, dd, *J* 4.3, *J* 2.7); δ_C 181.65 (2 quat), 138.82 (2 quat), 134.96 (2 CH), 124.95 (2 CH), 110.97 (2 CH) and 62.15 (CH_2). Purification of this material by flash column chromatography [ethyl acetate–petroleum ether 40–60 °C (1 : 1) changing to ethyl acetate–methanol] afforded 1,1-di[2-(carbothiomethoxy)pyrrol-1-yl]-methane **8** (42 mg, 27%), mp 98–99 °C (found: 294.0483. $C_{13}H_{14}N_2O_2S_2$ requires *M* 294.0490); δ_H (360 MHz) 7.22 (2H, dd, *J* 4.1, *J* 1.9), 7.07 (2H, s), 6.77 (2H, apparent t, *J* 2.3), 6.15 (2H, dd, *J* 4.1, *J* 2.8) and 4.13 (6H, s); δ_C (63 MHz) 199.44 (2 quat), 132.89 (2 quat), 129.28 (2 CH), 120.56 (2 CH), 109.63 (2 CH), 60.91 (CH_2) and 57.24 (2 CH_3); *m*/*z* 294 (M^+, 29%), 154 (53), 153 (100), 138 (29) and 94 (35).

5,6-Dihydro-11*H*-dipyrrolo[1,2-*d*;2′,1′-*g*][1,4]diazepine 9

A solution of 5,6-dihydrodipyrrolo[1,2-*d*;2′,1′-*g*][1,4]diazepin-11-one **2** (0.18 g, 0.94 mmol) in chloroform (5 mL) was added to a stirred suspension of lithium aluminium hydride (83 mg, 2.2 mmol, 2.3 equiv.) in dry ether (5 mL). Stirring was continued for 1 h at room temperature, after which more of the hydride reagent was added until the starting material was consumed (TLC). The excess of hydride was destroyed by sequential addition of wet ether, water and dilute hydrochloric acid (2 M). The separated organic layer was washed with water, dried ($MgSO_4$) and the solvent was removed under reduced pressure to afford the crude material as a black film. It was dissolved in chloroform and treated with decolourising charcoal; filtration followed by removal of the solvent under reduced pressure afforded 5,6-dihydro-11*H*-dipyrrolo[1,2-*d*;2′,1′-*g*][1,4]diazepine **9** as a yellow solid (0.11 g, 0.63 mmol, 67%) (found: 172.09930. $C_{11}H_{12}N_2$ requires *M* 172.09950); δ_H (360 MHz) 6.56 (2H, dd, *J* 2.7, *J* 1.8), 6.04 (2H, t, *J* 3.1), 5.95 (2H, m), 4.29 (4H, s, 2 CH_2) and 4.06 (2H, s, CH_2); δ_C (63 MHz) 129.59 (2 quat), 120.83 (2 CH), 107.32 (2 CH), 106.48 (2 CH), 47.66 (2 CH_2) and 25.80 (CH_2); *m*/*z* 172 (M^+, 18), 171 (100), 156 (35), 143 (29), 117 (27), 104 (38), 85 (59) and 65 (40).

Reaction of a solution of pyrrolo[1,2-*d*;2′,1′-*g*][1,4]diazepin-11-one **2** (0.275 mmol) in MeOH (2 mL) with a solution of sodium borohydride (8.3 mg, 0.22 mmol, 0.79 equiv.) at room temperature in MeOH (1 mL) gave, after work-up and purification by dry flash chromatography on silica [DCM–hexane (1: 1)], impure 5,6-dihydro-11*H*-dipyrrolo[1,2-*d*;2′,1′-*g*][1,4]diazepine **9** (14.7 mg, <37%). The product is unstable on silica.

5,6-Dihydro-11*H*-dipyrrolo[1,2-*d*;2′,1′-*g*][1,4]diazepine-3,8-dicarbaldehyde 10

DMF (0.06 mL, 0.78 mmol, 2.10 equiv.) was added to 1,2-dichloroethane (3 mL) and the solution was cooled to 0 °C. After 5 min, phosphoryl chloride (0.07 mL, 0.75 mmol, 2.0 equiv.) was added, followed 5 min later by a solution of 5,6-dihydro-11*H*-dipyrrolo[1,2-*d*;2′,1′-*g*][1,4]diazepine **9** (63.5 mg, 0.37 mmol) in 1,2-dichloroethane (2 mL) The mixture was stirred at room temperature for 19 h, then washed with water (20 mL), dilute sodium hydroxide solution (2 M, 10 mL) and brine (10 mL), and the organic fraction was dried ($MgSO_4$). The solvent was removed under reduced pressure to yield a dark brown film (0.1641 g) which was purified by dry flash

column chromatography on silica [Et_2O–petroleum ether 40–60 °C changing to Et_2O–petroleum ether 40–60 °C (2 : 1)] to afford 5,6-dihydro-11*H*-dipyrrolo[1,2-*d*;2′,1′-*g*]-[1,4]diazepine-3,8-dicarbaldehyde **10** as a yellow solid (25.3 mg, 0.11 mmol, 30%), mp 103–104 °C (found: 228.08939. $C_{13}H_{12}N_2O_2$ requires *M* 228.08933); δ_H (360 MHz) 9.46 (2H, s, 2 CHO), 6.85 (2H, d, *J* 4.0), 6.12 (2H, d, *J* 4.0), 4.94 (4H, s, 2 CH_2) and 4.17 (2H, s, CH_2); δ_C (63 MHz) 179.14 (2 CHO), 138.07 (2 quat), 132.06 (2 quat), 124.51 (2 CH), 105.49 (2 CH), 45.66 (2 CH_2) and 26.36 (CH_2); *m*/*z* 228 (M^+, 100%), 199 (69), 185 (23), 142 (93), 105 (22) and 100 (41).

Crystal data for 5,6-dihydrodipyrrolo[1,2-*d*;2′,1′-*g*]-[1,4]diazepin-11-one 2‡

$C_{11}H_{10}N_2O$ (H_2O), *M* = 204.23, orthorhombic, *a* = 4.5748(3), *b* = 13.0074(9), *c* = 17.0717(12) Å, *V* = 1015.87(12) Å^3, *T* = 150 K, space group $P2_12_12_1$, *Z* = 4, D_c = 1.335 g cm^{-3}, absorption coefficient μ(Mo-Kα) = 0.094 mm^{-1}, 7851 data measured, 1750 unique (R_{int} = 0.0430). The structure was solved by direct methods (SIR92) and refined against F^2 (CRYSTALS) to yield a final *R* factor of 0.0703 [based on *F* and 1426 data with $F > 4\sigma(F)$] and wR_2 = 0.1841 (based on F^2 and all data).

Crystal data for dipyrrolo[1,2-*c*;2′,1′-*f*]pyrimidin-10-one 3‡

$C_{10}H_8N_2O$, *M* = 172.18, triclinic, *a* = 7.6509(2), *b* = 9.1569(3), *c* = 12.0975(4) Å, α = 102.228(2)°, β = 93.332(2)°, γ = 99.815(2)°, *V* = 812.26(4) Å^3, *T* = 150(2) K, space group $P\bar{1}$, *Z* = 4, D_c = 1.408 g cm^{-3}, absorption coefficient μ(Mo-Kα) = 0.094 mm^{-1}, 4583 independent reflections (R_{int} = 0.0416). 11 866 data measured, 4583 unique (R_{int} = 0.0416). The structure was solved by direct methods (SHELXS) and refined against F^2 (SHELXL) to yield a final *R* factor of 0.0597 [based on *F* and 3122 data with $F > 4\sigma(F)$] and wR_2 = 0.1396 (based on F^2 and all data).

Crystal data for 1,1-di[2-(carbothiomethoxy)pyrrol-1-yl]-methane 8‡

$C_{13}H_{14}N_2O_2S_2$, *M* = 294.38, triclinic, *a* = 8.0365(2), *b* = 8.9123(2), *c* = 11.2816(3) Å, α = 98.8420(10)°, β = 107.7310(10)°, γ = 111.5210(10)°, *V* = 683.11(3) Å^3, *T* = 150(2) K, space group $P\bar{1}$, *Z* = 2, D_c = 1.431 g cm^{-3}, absorption coefficient μ(Mo-Kα) = 0.388 mm^{-1}, 11 638 data measured, 3705 unique (R_{int} = 0.0269). The structure was solved by Patterson methods (DIRDIF) and refined against F^2 (SHELXL) to yield a final *R* factor of 0.0481 [based on *F* and 3502 data with $F > 4\sigma(F)$] and wR_2 = 0.1180 (based on F^2 and all data). One C(S)OMe group (based on C7) is disordered by a 2-fold rotation about C2–C7. The occupancy ratio refined to 0.795(3) : 0.205(3). The two part weight moieties were restrained to be geometrically similar.

Calculations

Gas-phase structures of **2** and **3** were calculated at MP2 level using the 6-31G basis set (ESI‡).[10]

FVP reactions

FVP experiments were carried out by distillation of the substrate *in vacuo* through an electrically heated silica furnace tube (35 × 2.5 cm). Products were trapped in a U-tube situated at the exit point of the furnace and cooled with liquid nitrogen. Pyrolysis conditions are quoted as follows: substrate, quantity, furnace temperature (T_f), inlet temperature (T_i), pressure range (*P*), pyrolysis time (*t*) and products.

FVP of 5,6-dihydrodipyrrolo[1,2-*d*;2′,1′-*g*][1,4]diazepin-11-one 2

FVP of 5,6-dihydrodipyrrolo[1,2-*d*;2′,1′-*g*][1,4]diazepin-11-one **2** (15.0 mg, T_f 900 °C, T_i 120–200 °C, *P* 0.032 Torr, *t* 15 min) gave starting material only, though in poor recovery.

FVP of 1,2-di(pyrrol-1-yl)ethane 4

FVP of 1,2-di(pyrrol-1-yl)ethane **4** (11.2 mg, T_f 900 °C, T_i 140 °C, *P* 0.032 Torr, *t* 10 min) gave starting material and pyridine as the only products.

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