Synthesis of mixed heteroatom wurtzitanes

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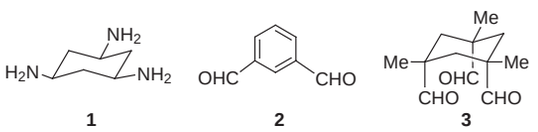
Syntheses of a novel series of mixed heteroatom wurtzitanes (tetracyclo[5.3.1.1^{2,6}.0^{4,9}]dodecanes) are described. *cis*,*cis*-1,3,5-Triformyl-1,3,5-trimethylcyclohexane 3 reacts with equimolar amounts of primary amines to afford the structurally novel 1,7,9-trimethyl-3,5-dioxa-12-azawurtzitanes, containing two different heteroatoms in the wurtzite ring. The mechanism for the reaction of compound 3 with primary amines in $CHCl_3$ is also reported.

Introduction

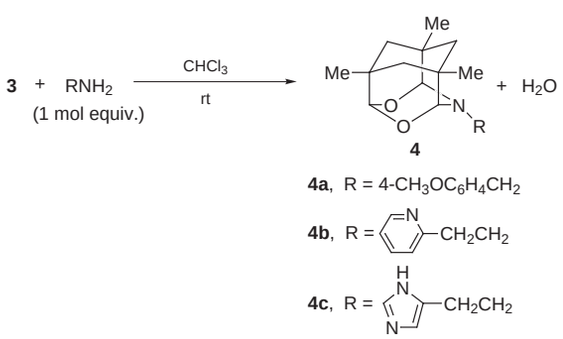
Trisubstituted cyclohexanes have been used as ligands to model metal-containing enzymes[1,2] or phosphate receptors.[3] These ligands were synthesized by using triamines such as compound **1**,[1] not trialdehydes as the starting materials. Casella *et al.* have used dialdehyde **2** as the starting material and studied a family of copper monooxygenase model systems.[4] The advantage of these systems is that histamine or histidine can be easily introduced into the ligands. Recently, we have synthesized trialdehyde **3**[5] and tried to apply this new compound as a new ligand. Here we report the synthesis of structurally novel wurtzitanes (tetracyclo[5.3.1.1^{2,6}.0^{4,9}]dodecanes) containing two different heteroatoms in the ring. We also present a plausible mechanism for the reaction of trialdehyde **3** with primary amines in $CHCl_3$.



1 **2** **3**

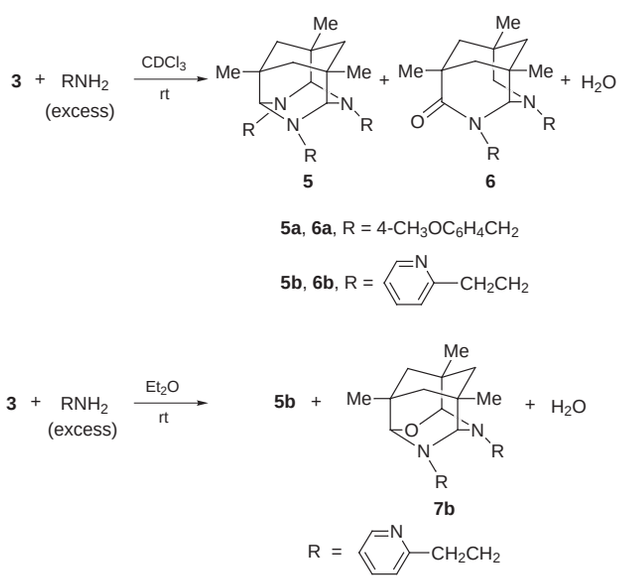
Results and discussion

As shown in Scheme 1, the reaction of trialdehyde **3** with equimolar amounts of primary amines in $CHCl_3$ at room temperature (rt) for 1–3 h yielded dioxa-azawurtzitanes **4** [**4a**, R = 4-methoxybenzyl, 91%; **4b**, R = 2-(pyridin-2-yl)ethyl, 88%; **4c**, R = 2-(imidazol-4-yl)ethyl, 87%]. The ^{1}H and ^{13}C NMR spectra of compounds **4** indicated the characteristic signals of methines in the wurtzite rings (**4a**, δ_H 4.02 and δ_C 87.36 for OCHN; δ_H 4.82 and δ_C 99.67 for OCHO). Heteroatom-containing wurtzitanes have been known since 1974.[6] Nielsen *et al.* first prepared wurtzitanes with more than one heteroatom in the ring.[7] However, they also reported that no formation of the mixed-heteroatom wurtzitanes was confirmed. We have now synthesized the first mixed-heteroatom wurtzitanes. Dioxa-azawurtzitanes **4** contain 1,3-dioxa-5-azacyclohexane rings. In general, it has been difficult to synthesize 1,3-dioxa-5-azacyclohexanes selectively.[8] The high yields of products **4** can be ascribed to the conformational restriction in starting aldehyde **3**.



Scheme 1 Synthesis of dioxa-azawurtzitanes **4**

The reaction of compound **3** with a large excess of primary amines (except histamine) in $CDCl_3$ at rt gave mixtures of triazawurtzitanes **5**[7] and 2-oxo-3,5-diazatricyclo[5.3.1.0^{4,9}]-undecanes **6**[7] [**5a**:**6a** = 3:2, R = 4-methoxybenzyl; **5b**:**6b** = 1:2, R = 2-(pyridin-2-yl)ethyl]. In the case of histamine, formation of compound **6c** was not confirmed. On the other hand, the reaction of trialdehyde **3** with large excess of 2-(2-aminoethyl)pyridine in diethyl ether at rt gave a mixture of triazawurtzitane **5b** and oxadiazawurtzitane **7b** [**5b**:**7b** = 1:1, R = 2-(pyridin-2-yl)ethyl] (Scheme 2). Table 1 shows the chemical shifts of methines for wurtzitanes. Methine signals at lower chemical shift were observed with increasing number of adjacent nitrogen atoms. This order can be accounted for by the inductive effect of the heteroatoms.[9] Triazawurtzitanes **5** and



Scheme 2 Reaction of trialdehyde **3** with a large excess of primary amines

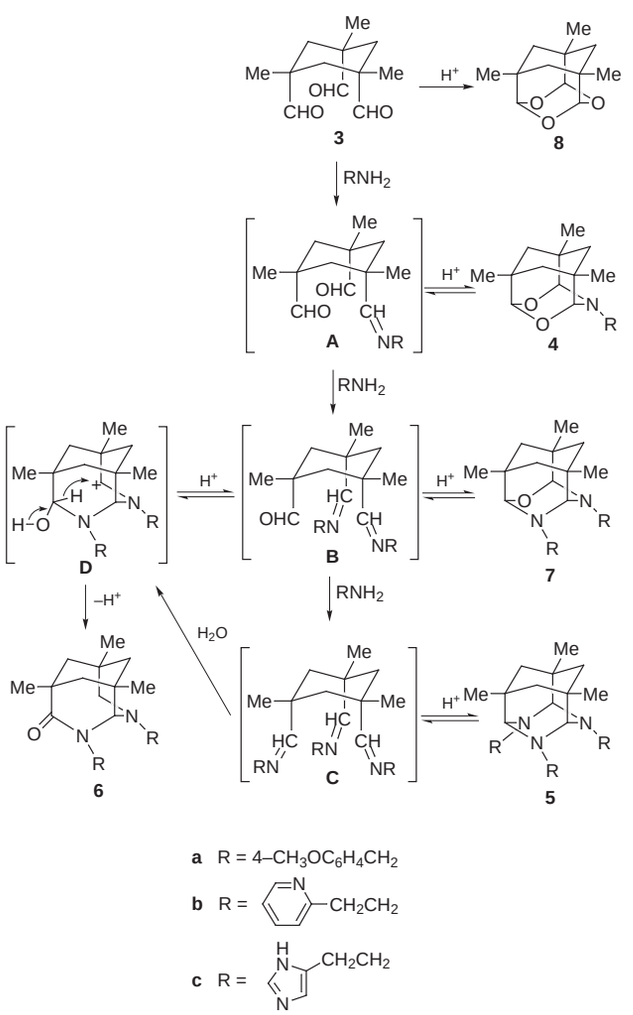
Table 1 Chemical shifts (ppm) of methines for wurtzitanes **4b**, **5b**, **7b** ($CDCl_3$)[a]

	OCHO		OCHN		NCHN	
Compd	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
4b	4.75	99.59	4.07	88.15		
5b					3.15	77.82
7b			4.14	88.93	3.08	77.40

[a] Where R = 2-(pyridin-2-yl)ethyl.

oxadiazawurtzitanes **7** are not so stable. Allowing a CD_3OD solution of compound **5b** to stand at rt yielded tricycle **6b**. The reduction of compound **5b** with selenophenol[10] in $CHCl_3$ also mainly gave tricycle **6b**. The reaction between trialdehyde **3** and the primary amines in $CDCl_3$ was monitored by ^1H NMR spectroscopy to allow us to understand the mechanism for the formation of tricycles **6**. The spectral changes upon the reaction of trialdehyde **3** with a large excess of histamine in $CDCl_3$ showed the formation of compound **4c** in the first stage, followed by the gradual build-up of compound **5c**. But in the case of the reaction between compound **3** and 2-(2-aminoethyl)-pyridine (1.4 mol equiv.) in $CDCl_3$, compounds **7b** and **4b** were concurrently formed in the first stage. After 13 h, all compound **7b** was consumed to give tricycle **6b**, and the signals of compound **4b** did not change. This finding suggests the isomerization of oxadiazawurtzitane **7b** to 2-oxo-3,5-diazatricyclo[5.3.1.$0^{4,9}$]undecane **6b**.

Scheme 3 shows a plausible mechanism for the reaction



Scheme 3 A possible mechanism for reaction of trialdehyde **3** with primary amines

between trialdehyde **3** and the primary amines in $CHCl_3$. Nielsen *et al.* reported that the reaction of *cis*,*cis*-1,3,5-triformylcyclohexane with primary amines in refluxing ethanolic acetic acid leads to 2-oxo-3,5-diazatricyclo[5.3.1.$0^{4,9}$]undecanes and mentioned the hydride-transfer mechanism with an iminium ion intermediate.[7] We have reported before that micro amounts of acids in $CHCl_3$ catalyse the cyclization of trialdehyde **3** to trioxawurtzitane **8**.[5] The findings and literature data suggest that oxadiazawurtzitane **7b** is in equilibrium with the corresponding diimine **B**, and that tricycle **6b** is easily formed from **B** through a hydride transfer in intermediate **D**. The formation of tricycle **6b** from triazawurtzitane **5b** suggests that water reacts with the corresponding triimine **C**, and that this reaction is inhibited in the presence of large amounts of primary amines. Furthermore, compound **4c** did not react at all with a large excess of 4-methoxybenzylamine in diethyl ether, and trioxawurtzitane **8** did not react with a large excess of 4-methoxybenzylamine even in $CHCl_3$. These findings suggest that acids in $CHCl_3$ catalyse the isomerization between dioxaazawurtzitanes **4** and the corresponding imines **A**, and that trioxawurtzitane **8** is not in equilibrium with trialdehyde **3**. Nielsen *et al.* reported that triazawurtzitanes without methyl groups are in equilibrium with the corresponding triimines.[7] We could not find evidence for the corresponding imines. Thermal stability of the wurtzitanes can be ascribed to the *ipso* methyl groups.

Conclusions

We have demonstrated the synthesis of a novel series of mixed heteroatom wurtzitanes. The synthetic method for dioxaazawurtzitanes **4** is useful for a selective preparation of 1,3-dioxa-5-azacyclohexane derivatives. Triazawurtzitanes **5** and oxadiazawurtzitanes **7** are not stable and change to 2-oxo-3,5-diazatricyclo[5.3.1.$0^{4,9}$]undecanes **6** easily.

Experimental

General

The IR spectrum of compound **6b** was measured on a Hitachi 270-30 infrared spectrophotometer. Mass spectra were run on a Finnigan MAT TSQ70 or JEOL DX-303 spectrometer. ^1H (500 MHz) and ^{13}C (125.7 MHz) NMR spectra were recorded in $CDCl_3$ on a JEOL JNM-LA500 spectrometer. *J*-Values are given in Hz.† All reactions were performed in oven-dried glassware equipped with a magnetic stirring bar under argon, using standard syringe techniques. All solvents were of anhydrous grade. *cis*,*cis*-1,3,5-Triformyl-1,3,5-trimethylcyclohexane **3** was prepared by our previously reported procedure.[5] All other reagents were of commercial grade.

12-(4-Methoxybenzyl)-1,7,9-trimethyl-3,5-dioxa-12-aza-wurtzitane {12-(4-methoxybenzyl)-1,7,9-trimethyl-3,5-dioxa-12-azatetracyclo[5.3.1.$1^{2,6}$.$0^{4,9}$]dodecane} 4a

Trialdehyde **3** (14.2 mg, 0.068 mmol) was added to a solution of 4-methoxybenzylamine (10.9 mg, 0.079 mmol) in $CHCl_3$ (8 ml). After the mixture had been stirred for 3 h, volatiles were removed under reduced pressure. The residue was extracted with hexane (10 ml). After the solution had been filtered, the solvent was removed under reduced pressure to give *title compound* **4a** (20.3 mg, 91%) as a viscous oil (Found: M^+, 329.1997. $C_{20}H_{27}NO_3$ requires *M*, 329.1991); δ_H 0.75 (1 H, d, $^2J_{HH}$ 11.8, CH_aH_e), 0.84 (2 H, d, $^2J_{HH}$ 11.8, CH_aH_e), 0.94 (6 H, s, CH_3),

† ^1H and ^{13}C NMR spectra for the wurtzitanes are available as supplementary material (SUPPL. NO. 57381, 12 pp.). For details of the Supplementary Publications Scheme see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 1*, available *via* the RSC Web page (http://www.rsc.org/authors).

1.01 (3 H, s, CH_3), 1.40 (2 H, d, $^2J_{HH}$ 11.8, CH_aH_e), 1.53 (1 H, d, $^2J_{HH}$ 11.8, CH_aH_e), 3.78 (3 H, s, OCH_3), 4.02 (2 H, s, OCHN), 4.18 (2 H, s, NCH_2Ar), 4.82 (1 H, s, OCHO), 6.83 (2 H, d, $^3J_{HH}$ 8.3, ArH) and 7.24 (2 H, d, $^3J_{HH}$ 8.3, ArH); δ_C 28.19 (CH_3), 28.70 (CH_3), 35.33 [$(CH_2)_2CCH_3$], 35.44 [$(CH_2)_2CCH_3$], 42.30 (CCH_2C), 44.18 (CCH_2C), 53.25 (NCH_2Ar), 55.22 (OCH_3), 87.36 (OCHN), 99.67 (OCHO) and 113.65, 129.62, 131.12 and 158.60 (aromatic carbons); *m/z* (EI) 329 (M^+, 100%).

1,7,9-Trimethyl-12-[2-(pyridin-2-yl)ethyl]-3,5-dioxa-12-azawurtzitane {1,7,9-trimethyl-12-[2-(pyridin-2-yl)ethyl]-3,5-dioxa-12-azatetracyclo[5.3.1.1^{2,6}.0^{4,9}]dodecane} 4b

The same manner as that employed in the preparation of analogue **4a** was used with 2-(2-aminoethyl)pyridine (11.7 mg, 0.096 mmol). Dioxa-azawurtzitane **4b** (26.5 mg, 88%) was obtained as a yellow viscous oil from trialdehyde **3** (20.2 mg, 0.096 mmol); δ_H 0.62 (1 H, d, $^2J_{HH}$ 11.7, CH_aH_e), 0.79 (2 H, d, $^2J_{HH}$ 11.7, CH_aH_e), 0.91 (6 H, s, CH_3), 0.97 (3 H, s, CH_3), 1.23 (1 H, d, $^2J_{HH}$ 11.7, CH_aH_e), 1.37 (2 H, d, $^2J_{HH}$ 11.7, CH_aH_e), 2.92 (2 H, t, $^3J_{HH}$ 7.3, CH_2pyr), 3.46 (2 H, t, $^3J_{HH}$ 7.3, CH_2N), 4.07 (2 H, s, OCHN), 4.75 (1 H, s, OCHO), 7.07 (1 H, m, pyrH), 7.11 (1 H, m, pyrH), 7.54 (1 H, m, pyrH) and 8.49 (1 H, m, pyrH); δ_C 28.12 (CH_3), 28.72 (CH_3), 35.21 [$(CH_2)_2CCH_3$], 35.29 [$(CH_2)_2CCH_3$], 37.39 (CH_2pyr), 42.29 (CCH_2C), 43.93 (CCH_2C), 49.79 (CH_2N), 88.15 (OCHN), 99.59 (OCHO) and 121.03, 123.29, 135.97, 149.17 and 160.38 (pyridine carbons); *m/z* (EI) 314 (M^+, 100%) and 222 ($M^+ - CH_2$pyr, 34).

12-[2-(Imidazol-4-yl)ethyl]-1,7,9-trimethyl-3,5-dioxa-12-azawurtzitane {12-[2-(imidazol-4-yl)ethyl]-1,7,9-trimethyl-3,5-dioxa-12-azatetracyclo[5.3.1.1^{2,6}.0^{4,9}]dodecane} 4c

Trialdehyde **3** (20.7 mg, 0.098 mmol) was added to a suspension of histamine (11.7 mg, 0.11 mmol) in $CHCl_3$ (10 ml). After the mixture had been stirred for 3 h, volatiles were removed under reduced pressure. The residue was extracted with two 5-ml portions of $CHCl_3$. After the extract had been filtered, the solvent was removed under reduced pressure. *Title compound* **4c** was purified as a viscous oil by washing with hexane (26.0 mg, 87%); δ_H 0.74 (1 H, d, $^2J_{HH}$ 11.6, CH_aH_e), 0.82 (2 H, d, $^2J_{HH}$ 11.6, CH_aH_e), 0.96 (6 H, s, CH_3), 0.98 (3 H, s, CH_3), 1.36 (1 H, d, $^2J_{HH}$ 11.6, CH_aH_e), 1.38 (2 H, d, $^2J_{HH}$ 11.6, CH_aH_e), 2.73 (2 H, t, $^3J_{HH}$ 7.2, CH_2im), 3.33 (2 H, t, $^3J_{HH}$ 7.2, CH_2N), 4.07 (2 H, s, OCHN), 4.75 (1 H, s, OCHO), 6.75 (1 H, s, imH) and 7.49 (1 H, s, imH); δ_C 25.31 (CH_2im), 28.06 (CH_3), 28.77 (CH_3), 35.19 [$(CH_2)_2CCH_3$], 35.27 [$(CH_2)_2CCH_3$], 42.24 (CCH_2C), 44.16 (CCH_2C), 49.44 (CH_2N), 87.96 (OCHN), 99.51 (OCHO), 118.65 (br, imidazole carbon) and 134.24 (imidazole carbon).

1,7,9-Trimethyl-3,5,12-tris-[2-(pyridin-2-yl)ethyl]-3,5,12-triazawurtzitane {1,7,9-trimethyl-3,5,12-tris-[2-(pyridin-2-yl)-ethyl]-3,5,12-triazatetracyclo[5.3.1.1^{2,6}.0^{4,9}]dodecane} 5b

Trialdehyde **3** (20.1 mg, 0.096 mmol) was added to a solution of 2-(2-aminoethyl)pyridine (210 mg, 1.72 mmol) in diethyl ether (15 ml). After the mixture had been stirred for 4 days, volatiles were removed under reduced pressure. The residue was extracted with three 5-ml portions of hexane, and the extract was evaporated under reduced pressure. After the contents had been checked by ^{1}H NMR ($CDCl_3$), $CDCl_3$ was removed under reduced pressure rapidly, and diethyl ether (5 ml) was added to the residue. After being stirred for 1 week, followed by filtration, the filtrate was concentrated to remove volatiles. This repeating procedure afforded *title compound* **5b** as an oil without the formation of tricycle **6b** (34.8 mg, 70%); δ_H 0.42 (3 H, d, $^2J_{HH}$ 11.1, CH_aH_e), 0.78 (9 H, s, CH_3), 1.16 (3 H, d, $^2J_{HH}$ 11.1, CH_aH_e), 2.73 (6 H, t, $^3J_{HH}$ 6.8, CH_2pyr), 3.06 (6 H, t, $^3J_{HH}$ 6.8, CH_2N), 3.15 (3 H, s, NCHN), 7.01 (3 H, m, pyrH), 7.08 (3 H, m, pyrH), 7.48 (3 H, m, pyrH) and 8.46 (3 H, m, pyrH); δ_C 30.55 (CH_3), 35.77 [$(CH_2)_2CCH_3$], 38.70 (CH_2pyr), 45.43 (CCH_2C), 52.78 (CH_2N), 77.82 (NCHN) and 120.78, 123.67, 135.74, 148.97 and 161.08 (pyridine carbons).

1,7,9-Trimethyl-2-oxo-3,5-bis-[2-(pyridin-2-yl)ethyl]-3,5-diazatricyclo[5.3.1.0^{4,9}]undecane 6b

Triazawurtzitane **5b** (31.4 mg, 0.060 mmol) was added to a solution of selenophenol[10] (93.2 mg, 0.59 mmol) in $CHCl_3$ (3 ml). After the mixture had been stirred for 1 day, volatiles were removed under reduced pressure. The residue was treated with diethyl ether (20 ml)–dil. aq. NaOH (20 ml). The organic layer was extracted with two 20-ml portions of dil. HCl. The acidic solution was neutralized with dil. aq. NaOH and extracted with three 10-ml portions of diethyl ether. After the combined extract had been washed with saturated aq. NaCl and dried with $MgSO_4$, the solvent was removed under reduced pressure to afford *title compound* **6b** (15.5 mg, 62%) (Found: M^+, 418.2705. $C_{26}H_{34}N_4O$ requires *M*, 418.2733); ν_{max}(KBr)/cm^{-1} 1648 (CO); δ_H 0.51 (1 H, d, $^2J_{HH}$ 11.6, CH_aH_e), 0.55 (3 H, s, CH_3), 0.81 (1 H, d, $^2J_{HH}$ 12.2, CH_aH_e), 0.87 (3 H, s, CH_3), 0.99 (1 H, d, CH_aH_e), 1.00 (1 H, d, CH_aH_e), 1.04 (3 H, s, CH_3), 1.28 (1 H, d, $^2J_{HH}$ 11.6, CH_aH_e), 1.57 (1 H, d, $^2J_{HH}$ 13.8, CH_aH_e), 2.09 (1 H, d, $^2J_{HH}$ 11.9, CH_2N), 2.45 (1 H, d, $^2J_{HH}$ 11.9, CH_2N), 2.90 (1 H, m, CH_2CH_2N), 2.90 (1 H, m, CH_2CH_2pyr), 2.90 (1 H, m, CH_2CH_2pyr), 2.90 (1 H, m, CH_2CH_2pyr), 3.10 (1 H, m, CH_2CH_2pyr), 3.19 (1 H, m, CH_2CH_2N), 3.25 (1 H, m, CH_2CH_2N), 3.77 (1 H, s, NCHN), 4.14 (1 H, m, CH_2CH_2N), 7.09 (4 H, m, pyrH), 7.54 (2 H, m, pyrH) and 8.51 (2 H, m, pyrH); δ_C 26.69 (CH_3), 29.19 (CH_3), 31.80 (CH_3), 31.85 [$(CH_2)_2CCH_3$], 34.75 [$(CH_2)_2CCH_3$], 36.29 (CH_2CH_2pyr), 37.30 (CH_2CH_2pyr), 39.72 [$(CH_2)_2CCH_3$], 44.58 (CCH_2C), 46.34 (CCH_2C), 47.41 (CH_2CH_2N), 49.51 (CCH_2C), 54.13 (CCH_2N), 54.88 (CH_2CH_2N), 83.33 (NCHN), 121.12, 121.33, 123.44, 124.17, 136.08, 136.26, 149.15, 149.24, 159.73 and 160.16 (pyridine carbons) and 178.87 (CO); *m/z* (EI) 418 (M^+, 100%) and 326 ($M^+ - CH_2$pyr, 67).

NMR monitoring experiments

2-(Imidazol-4-yl)ethyl derivatives. Histamine (18.9 mg, 0.17 mmol) was added to a solution of trialdehyde **3** (4.6 mg, 0.02 mmol) in $CDCl_3$ (0.6 ml). After the solution had been kept at rt for 1 h, dioxa-azawurtzitane **4c** was the main product. After 3 days, compound **4c** was consumed to give mainly triazawurtzitane **5c**.

3,5,12-*Tris*-[2-(*imidazol*-4-*yl*)*ethyl*]-1,7,9-*trimethyl*-3,5,12-*triazawurtzitane* {3,5,12-*tris*-[2-(*imidazol*-4-*yl*)*ethyl*]-1,7,9-*trimethyl*-3,5,12-*triazatetracyclo*[5.3.1.1^{2,6}.0^{4,9}]*dodecane*} **5c**.—δ_H 0.61 (3 H, d, $^2J_{HH}$ 11.0, CH_aH_e), 0.93 (9 H, s, CH_3), 1.38 (3 H, d, $^2J_{HH}$ 11.0, CH_aH_e), 2.55 (6 H, t, $^3J_{HH}$ 6.6, CH_2im), 2.71 (6 H, t, $^3J_{HH}$ 6.6, CH_2N), 3.16 (3 H, s, NCHN), 6.75 (3 H, s, imH) and 7.50 (3 H, s, imH); δ_C 26.54 (br, CH_2im), 30.67 (CH_3), 35.73 [$(CH_2)_2CCH_3$], 45.60 (CCH_2C), 53.23 (CH_2N), 78.01 (NCHN) and 134.20 (imidazole carbons).

2-(Pyridin-2-yl)ethyl derivatives. 2-(2-Aminoethyl)pyridine (18.6 mg, 0.15 mmol) was added to a solution of trialdehyde **3** (4.8 mg, 0.02 mmol) in $CDCl_3$ (0.6 ml). Oxadiazawurtzitane **7b**, as well as dioxa-azawurtzitane **4b**, was formed just after the addition. Storage of solution at rt for 5 days gave triazawurtzitane **5b** and the 2-oxo-3,5-diazatricyclo[5.3.1.0^{4,9}]undecane **6b** (**5b** : **6b** = 1 : 2).

2-(2-Aminoethyl)pyridine (16.1 mg, 0.13 mmol) was added to a solution of trialdehyde **3** (20 mg, 0.1 mmol) in $CDCl_3$ (0.6 ml). After the solution had been kept at rt for 1 h, oxadiazawurtzitane **7b**, as well as compound **4b**, was formed. After 13 h, all of the initial product **7b** was consumed to give tricycle **6b**. The signals of compound **4b** did not change.

1,7,9-*Trimethyl*-5,12-*bis*-[2-(*pyridin*-2-*yl*)*ethyl*]-3-*oxa*-5,12-*diazawurtzitane* {1,7,9-*trimethyl*-5,12-*bis*-[2-(*pyridin*-2-*yl*)-*ethyl*]-3-*oxa*-5,12-*diazatetracyclo*[5.3.1.1^{2,6}.0^{4,9}]*dodecane*} **7b**.—δ_H 0.46 (2 H, d, $^2J_{HH}$ 11.8, CH_aH_e), 0.65 (3 H, s, CH_3), 0.73 (1 H, d, $^2J_{HH}$ 11.9, CH_aH_e), 0.87 (6 H, s, CH_3), 1.11 (2 H, d, $^2J_{HH}$ 11.8, CH_aH_e), 1.38 (1 H, d, $^2J_{HH}$ 11.9, CH_aH_e), 2.80 (4 H, m, CH_2pyr), 3.08 (1 H, t, $^4J_{HH}$ 1.8, NCHN), 3.26 (2 H, td, CH_2N), 3.66 (2 H, ddd, CH_2N), 4.14 (2 H, d, $^4J_{HH}$ 1.8, OCHN), 7.08

(4 H, m, pyrH), 7.52 (2 H, m, pyrH) and 8.47 (2 H, m, pyrH); δ_C 28.88 (CH_3), 29.44 (CH_3), 35.45 [$(CH_2)_2CCH_3$], 36.47 [$(CH_2)_2CCH_3$], 38.33 (CH_2pyr), 42.12 (CCH_2C), 45.19 (CCH_2C), 52.09 (CH_2N), 77.40 (NCHN), 88.93 (OCHN) and 120.95, 123.54, 135.92, 149.04 and 160.51 (pyridine carbons).

4-Methoxybenzyl derivatives. 4-Methoxybenzylamine (24 mg, 0.18 mmol) was added to a solution of trialdehyde **3** (10.7 mg, 0.05 mmol) in $CDCl_3$ (0.6 ml). Storage of the solution at rt for 2 weeks gave triazawurtzitane **5a** and the 2-oxo-3,5-diazatricyclo[5.3.1.$0^{4,9}$]undecane **6a** (**5a**:**6a** = 3:2).

3,5,12-*Tris*-(4-*methoxybenzyl*)-1,7,9-*trimethyl*-3,5,12-*triazawurtzitane* {3,5,12-*tris*-(4-*methoxybenzyl*)-1,7,9-*trimethyl*-3,5,12-*triazatetracyclo*[5.3.1.$1^{2,6}$.$0^{4,9}$]*dodecane*} **5a**.—δ_H 0.67 (3 H, d, $^2J_{HH}$ 11.2, CH_aH_e), 0.89 (9 H, s, CH_3), 1.58 (3 H, d, $^2J_{HH}$ 11.2, CH_aH_e), 3.20 (3 H, s, NCHN), 3.79 (9 H, s, OCH_3), 3.91 (6 H, s, NCH_2Ar), 6.79 (6 H, d, $^3J_{HH}$ 8.8, ArH) and 7.07 (6 H, d, $^3J_{HH}$ 8.8, ArH); δ_C 30.43 (CH_3), 36.37 [$(CH_2)_2CCH_3$], 45.87 (CCH_2C), 55.24 (OCH_3), 57.06 (NCH_2Ar), 76.42 (NCHN) and 113.35, 129.50, 133.61 and 158.33 (aromatic carbons).

3,5-*Bis*-(4-*methoxybenzyl*)-1,7,9-*trimethyl*-2-*oxo*-3,5-*diazatricyclo*[5.3.1.$0^{4,9}$]*undecane* **6a**.—δ_C 26.99 (CH_3), 29.58 (CH_3), 31.68 (CH_3), 32.09 [$(CH_2)_2CCH_3$], 35.15 [$(CH_2)_2CCH_3$], 39.97 [$(CH_2)_2CCH_3$], 45.04 (CH_2), 46.99 (CH_2), 48.92 (CH_2), 49.81 (CH_2), 54.95 (CH_2), 55.22 (OCH_3), 55.28 (OCH_3), 58.86 (CH_2), 79.07 (NCHN), 113.75, 113.88, 128.97, 129.06, 130.38, 131.40, 158.66 and 158.72 (aromatic carbons) and 179.16 (CO).

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