2,3,7,8-Tetra-azatetracyclo[7.3.1.$0^{4,12}0^{6,10}$]tridecanes and 2,4,6,8-Tetra(alkylamino)bicyclo[3.3.1]nonanes

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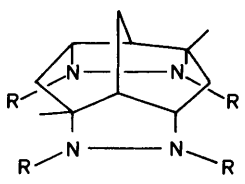
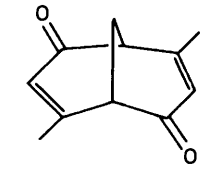
The bishydrazone 4,9-dimethyl-2,3,7,8-tetra-azatetracyclo[7.3.1.$0^{4,12}0^{6,10}$]trideca-1,6-diene on treatment with base gives the bisazo compound 1,6-dimethyl-2,3,7,8-tetra-azatetracyclo-[7.3.1.$0^{4,12}0^{6,10}$]trideca-2,7-diene which on catalytic hydrogenation readily affords the bishydrazine 1,6-dimethyl-2,3,7,8-tetra-azatetracyclo[7.3.1.$0^{4,12}0^{6,10}$]tridecane. On reaction with formaldehyde or benzaldehyde this bishydrazine affords a variety of pentacyclic hydrazines. The reduction of a number of acyl derivatives of the bishydrazine has been studied. Although such reductions lead in some cases to the formation of tetra-alkyl hydrazines, reduction of the tetra-acetyl derivative of the bishydrazine with borane–dimethyl sulphide complex gives a 2,4,6,8-tetra-aminobicyclo[3.3.1]nonane by cleavage of the nitrogen–nitrogen bonds of the hydrazines. Reaction of the tetra-aminobicyclo[3.3.1]nonane with formaldehyde and acetaldehyde to give tetracyclic tetra-amines is reported.

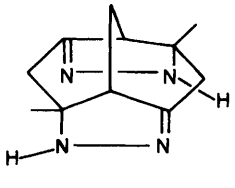
The synthesis of caged polyamines by reaction of electrophiles with suitable primary and secondary amines has been the subject of extensive, recent interest[1] for a variety of reasons. In contrast, there is only an isolated report[2] of the synthesis of caged hydrazines based on the reaction of a bishydrazine. As a result of the establishment of a straightforward route[3] to the bishydrazine (**1**) we have had the opportunity to study the reaction of this bishydrazine with electrophiles. We report in this paper the synthesis from (**1**) of a variety of highly caged polyazapolycyclic skeletons. In addition we report the reduction of derivatives of the bishydrazine (**1**) which leads to the formation of derivatives of a 2,3,7,8-tetra-aminobicyclo-[3.3.1]nonane. Elaboration of these tetra-amines with electrophiles again leads to a novel series of bridged polyamines.



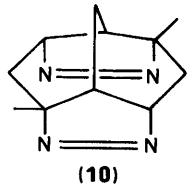
(**1**) R = H
(**2**) R = Et
(**3**) R = CHO
(**4**) R = COMe
(**5**) R = $COCF_3$
(**6**) R = COPh
(**7**) R = Me



(**8**)



(**9**)



(**10**)

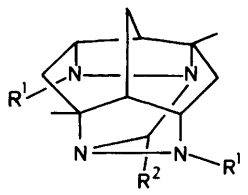
Hydrazine reacts[4] with 4,8-dimethylbicyclo[3.3.1]nona-3,7-diene-2,6-dione (**8**) to give the bishydrazone (**9**). In our earlier study[3] we reported the preparation of the bishydrazine (**1**) from the bishydrazone (**9**) using either lithium aluminium hydride or catalytic hydrogenation. However, both these methods are not ideal. The latter requires elevated hydrogen pressure and the former demands not only isolation of the very air-sensitive bishydrazine (**1**) in a tedious work-up procedure, but the efficiency of this reduction is reduced when scaled up. Hence we sought an improved route to the bishydrazine (**1**).

Based on our earlier conclusion[3] that the fragmentation observed on treatment of the bishydrazone (**9**) with lithium aluminium hydride occurs *via* an initial proton abstraction from nitrogen, and the demonstration[5] that anions derived from hydrazones can be trapped by reaction at carbon, we investigated the behaviour of the bishydrazone (**9**) under basic conditions. In hydrazone–azo equilibria the hydrazone tautomer is normally[6] favoured. However, when the bishydrazone (**9**) is heated under reflux in ethanol containing potassium carbonate, the bisazoalkane (**10**) is isolated in 95% yield. The unusual preference for the azo tautomer can be attributed to the destabilisation of the bishydrazone, which is an anti-Bredt imine. The bisazoalkane can be formed with relief of steric strain. The competitive fragmentation observed with lithium aluminium hydride under aprotic conditions is absent under protic conditions. The bishydrazine (**1**) is readily obtained from the bisazoalkane by catalytic hydrogenation at 1 atm.

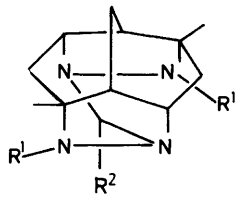
The bishydrazine (**1**) has been treated with a variety of biselectrophiles, and later in this paper the formation of simple amide derivatives of the bishydrazine is described. Attempted reaction with the biselectrophiles, phosgene, thionyl chloride, oxalyl chloride, sulphonyl chloride, and sulphur diphthalimide failed to give well-characterised products. Similarly mesityl oxide,† phorone,‡ hexachloroacetone, acetaldehyde, acetylacetone, or acetonylacetone failed to give any well-characterised products. In contrast, formaldehyde, benzaldehyde, *p*-nitrobenzaldehyde, and acetone give caged polyamines.

By analogy with the formation of polyaza-adamantanes by reaction of formaldehyde with amines, for example 1,3-diazaadamantane from 3,7-diazabicyclo[3.3.1]nonane,[7] reaction of the bishydrazine (**1**) with formaldehyde might be expected to give either diagonally bridged products (**11**) and (**14**) or by reaction, respectively, with one or two equivalents of formaldehyde, the amines (**16**) or (**23**). We find that reaction affords two crystalline products. One is the diagonally bridged amine (**11**) and the other, formed in the presence of an excess of formaldehyde is the amide (**17**). Although chromatography indicates the presence of other minor products in reaction mixtures none have been isolated and characterised.

† 4-Methylpent-3-en-2-one.
‡ 2,6-Dimethylhepta-2,5-dien-4-one.



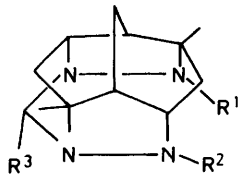
(11) $R^1 = R^2 = H$
(12) $R^1 = Ac, R^2 = H$
(13) $R^1 = Ac, R^2 = Ph$



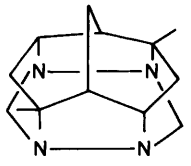
(14) $R^1 = R^2 = H$
(15) $R^1 = Ac, R^2 = Ph$

The structure of the unstable amine (**11**), isolated from reaction of the bishydrazine (**1**) with formaldehyde in methanol and subsequent chromatography, is indicated by features of the ^{13}C n.m.r. spectrum. Observation of only 7 signals in the spectrum of the amine (**11**) indicates a product with an axis of symmetry such as (**11**) or (**14**) and excludes the alternative structure (**16**). Formation of the amine (**11**) is clearly indicated by observation of the methyl resonance at 23.9 p.p.m. in contrast to the equivalent resonance observed at 28.4 p.p.m. in the bishydrazine (**1**). This shift in the position of the methyl resonance would be unexpected in the amine (**14**). Acetylation of the amine (**11**) gives the diamide (**12**).

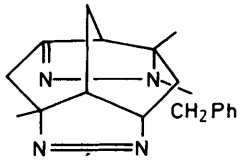
Reaction of the bishydrazine (**1**) with an excess of formaldehyde afforded a stable amide (as indicated by $\nu_{max.}$ 1 653 cm^{-1}). An intramolecular hydride shift from an intermediate diol (**19**) could lead to the amides (**17**) or (**18**). Alternatively from a diagonally bridged diol an intermolecular hydride shift



(16) $R^1 = R^2 = R^3 = H$
(17) $R^1 = Me, R^2 = CHO, R^3 = H$
(18) $R^1 = CHO, R^2 = Me, R^3 = H$
(19) $R^1 = R^2 = CH_2OH, R^3 = H$
(20) $R^1 = R^2 = H, R^3 = Ph$
(21) $R^1 = R^2 = Ac, R^3 = Ph$
(22) $R^1 = R^2 = Ac, R^3 = p\text{-}NO_2C_6H_4$



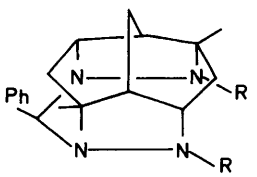
(23)



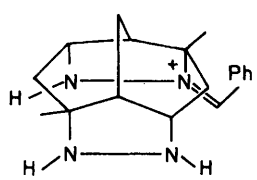
(24)

could afford other amides. An n.O.e. experiment indicated the proximity of the *N*-methyl group (resonance at 2.44 p.p.m.) to the *C*-methyl group (resonance at 1.11 p.p.m.) and also to the methine hydrogen (resonance at 4.03 p.p.m.). Hence we conclude that the amide (**17**) is obtained *via* an intramolecular hydride shift involving the intermediate (**19**) or a related methyleneimmonium cation.

Benzaldehyde reacts with the bishydrazine (**1**) in ethanol in the presence of triethylamine to give the amine (**20**) in 88% yield. Reaction in the absence of triethylamine afforded the amine (**20**) in substantially lower yield, but also gave the azohydrazone (**24**). Neither the use of an excess of benzaldehyde nor reaction for prolonged periods gave further new products. Unlike the formaldehyde series, discrimination between a product from benzaldehyde having diagonal bridging or an alternative structure such as (**20**) cannot be based on the complexity of the ^{13}C n.m.r. spectrum. In no case are these possible products characterised by having an axis of symmetry. Instead, structures are based on an analysis of ^1H n.m.r. data of the amine (**20**) and the related amides. In neat acetic anhydride the amine (**20**) gives the amide (**21**) but in contrast acetylation of the amine (**20**) in pyridine affords the two amides (**13**) and (**15**). The skeleton of the amine (**20**) and of the amide (**21**) may be distinguished from those of the amides (**13**) and (**15**) by observation of both chemical shift data and of the coupling constants associated with the downfield resonances of those methine protons at carbon centres carrying a nitrogen substituent. In the case of the diagonally bridged amides (**13**) and (**15**) the two methine protons observed at δ 5.05 and 5.08 in the amide (**13**) and at δ 3.75 and 3.83 in the amide (**15**) have similar environments and this is reflected both in their chemical shifts and their similar splitting patterns. In contrast, in the amide (**21**) the two very different methine protons are observed at δ 4.03 and 4.97 and their differing environments are further emphasized by observation of very different splitting patterns. Hence it is readily possible to distinguish the diagonally bridged amides (**13**) and (**15**) from the amide (**21**). The relative chemical shift data permits the distinction between the amides (**15**) (δ 3.75 and 3.83) and (**13**) (δ 5.05 and 5.08) to be made. The skeleton of the amine (**20**) can then be assigned by spectral comparison with the amides. Observation of the two methine protons in the spectrum of the amine (**20**) at 3.60 p.p.m. as a quartet (*J* 10 and 7 Hz) and at 3.79 p.p.m. as a six line signal (*J*, 10, 3 and 3 Hz) suggests a common skeleton for the amine (**20**) and the amide (**21**). These coupling constants agree well with predicted values obtained by examination of models of the amine (**20**) and values observed in compounds of related structure [for example the bisazoalkane (**10**)]. However, in both the amine (**20**) and the amide (**21**), obtained by direct reaction with acetic anhydride, the stereochemistry of the phenyl substituent has not yet been defined. The possible structures (**25**) and (**26**) are considered unlikely and the proposed structures (**20**) and (**21**) are favoured on two grounds. Models indicate substantial steric destabilisation of the amine (**25**) and the amide (**26**), and we note an absence of anomalous chemical shifts attributable to the influence of the phenyl substituent. The structure of the amide product (**22**) obtained from reaction of *p*-nitrobenzaldehyde and the bishydrazine (**1**) and subsequent acetylation, is supported by similar evidence.



(25) R = H
(26) R = Ac



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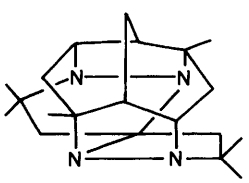
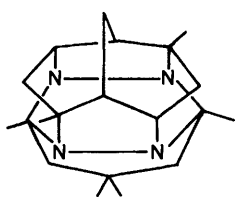
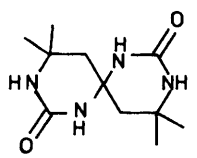


(28)



(29)

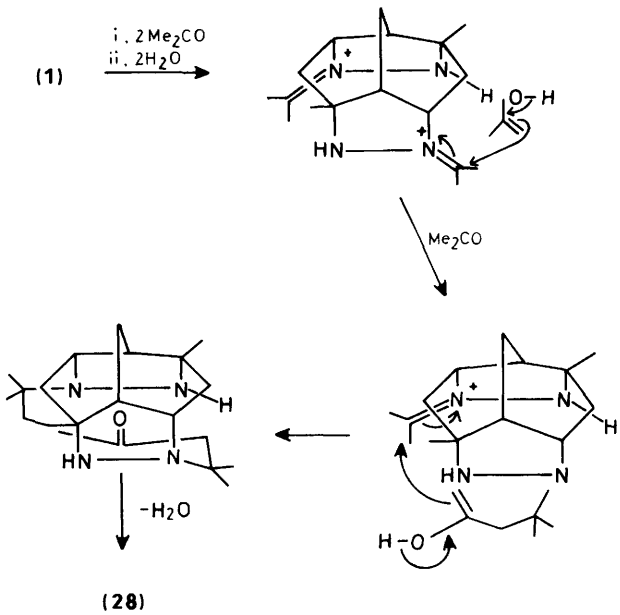


(30)

In the absence of triethylamine, reaction of benzaldehyde with the bishydrazine (**1**) affords a second product, the azohydrazone (**24**). The functionality in (**24**) is indicated by observation of a hydrazone ($\nu_{max.}$ 1 660 cm^{-1} and an imine carbon at δ 154.35) and of an azo group ($\lambda_{max.}$ 330 nm). The presence of a benzyl group is indicated by the coupled resonances at 4.04 and 3.78 p.p.m. (*J* 14 Hz), and the methine resonance at 4.80 p.p.m. has similar features to the equivalent methine resonances in the bisazoalkane (**10**). Although these and other spectroscopic features clearly define the structure of the azohydrazone (**24**) the origin of this product is unclear. Cleavage of the first-formed product (**20**) to give the iminium cation (**27**) might be followed by a subsequent aerial oxidation of the hydrazine moiety to give the azohydrazone (**24**).

The above reactions have a number of interesting features including (*i*) the failure to obtain hexacyclic products, (*ii*) the formation of pentacyclic products either with or without a diagonal bridge, and (*iii*) the lability permitting rearrangement from one skeleton to another. This lability is certainly evidenced on acetylation of the amine (**20**) in pyridine and probably accounts for the reaction course in formation of the azohydrazone (**24**). With phenyl substitution, a stabilized iminium cation may be expected to be formed more easily than in the formaldehyde series. Hence it is likely that the pentacyclic diagonally bridged product (**11**) obtained with formaldehyde is a kinetic product, whereas formation of the amine (**20**) with benzaldehyde represents a rearrangement to a thermodynamically more stable series. The inability to obtain hexacyclic products with formaldehyde can be attributed to the preference for formation of the amide (**17**) by hydride transfer under more forcing conditions. However we believe that this is only a partial explanation. Significantly, from the pentacyclic amine (**20**), in spite of many attempts, we have been unable to isolate hexacyclic products. For example, the reaction of the amine (**20**) with formaldehyde gave only the amide (**17**) in 45% yield. This difficulty of formation of hexacyclic products is further underlined by the results of attempted reaction of the bishydrazine (**1**) and the pentacyclic compound (**20**) with a variety of acid chlorides. Attempted reaction with phosgene, thionyl chloride, oxalyl chloride and sulphonyl chloride gave only polymeric products. In the case of the bishydrazine (**1**) these results are explained by preferential and irreversible formation of a diagonally bridged skeleton which would be then expected to lead to polymers. The failure of the rigid pentacyclic hydrazine (**20**) to give hexacyclic products is likely to be due to unsatisfactory orbital overlap in the transition state required for cyclisation. Hence again polymerisation is observed.

In contrast, reaction of the bishydrazine (**1**) with acetone under forcing conditions affords a heptacyclic product. Under more mild conditions in ethanol no product was isolated but in toluene in the presence of toluene-*p*-sulphonic acid the hexacyclic product (**28**) was isolated in 35% yield. Mass spectroscopy suggested that this oily, slightly unstable compound was formed by reaction of the hydrazine (**1**) with three equivalents of acetone. The structural assignment was simplified by the observation of only ten resonances in the ^{13}C n.m.r. spectrum, which implied a product having an axis of symmetry. Two possible structures (**28**) and (**29**) can be envisaged. The absence of a resonance of a quaternary carbon in the region 30—40 p.p.m. and the presence of three resonances associated with quaternary centres at 97.7, 59.8, and 58.6 p.p.m. excludes the latter structure. The former structure is further confirmed by a methine resonance at δ 3.56 (triplet *J* 7 Hz). These data are in good agreement with those observed in the related diagonally bridged structures (**11**) and (**13**). The obvious route to (**28**) is *via* prior condensation of acetone to afford phorone. Such a route is known[8] to lead to the formation of the saturated pyrimidine (**30**) from urea and acetone. However we find that direct reaction of phorone with the bishydrazine (**1**) fails to give the heptacyclic compound (**28**). Similarly, the bishydrazine (**1**) does not give the heptacyclic compound (**28**) with mesityl oxide. Tentatively we propose that the heptacycle (**28**) is formed by the route shown in the Scheme. Again, a feature of this reaction is



Scheme.

the avoidance of the formation of a hexacyclic skeleton by bridging the bishydrazine with two equivalents of acetone.

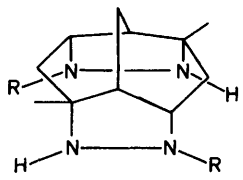
The rigidity of the skeleton of the bishydrazine (**1**) is to be contrasted with the flexibility expected in derivatives of a bicyclo[3.3.1]nonane-2,4,6,8-tetra-amine, available by reductive cleavage of the hydrazine units in the bishydrazine (**1**). Such a tetra-amine must have an *endo* orientation for all four substituents, because of the method of synthesis. However the bicyclo[3.3.1]nonane skeleton is characterised[9] by a conformational equilibrium relating chair–boat and chair–chair conformers. As the difference in energy between these conformers is typically small[10] the likely, most stable conformation of derivatives of bicyclo[3.3.1]nonane-2,4,6,8-tetra-amine and their behaviour with electrophiles are difficult to predict. By establishing a satisfactory entry by reduction of derivatives of the bishydrazine (**1**) to give bicyclo[3.3.1]nonanes, we have been able to resolve these points.

The required reduction of the bishydrazine (**1**) involves the reductive cleavage of a non-aromatic hydrazine. This is substantially more difficult than the reductive cleavage of an aromatic hydrazine. Aliphatic hydrazines have been reduced by catalytic hydrogenation[11] under acidic conditions, but cleavage to give amines[12] often demands elevated hydrogen pressures. No reductive cleavage was observed when the sterically hindered bishydrazine (**1**) was exposed to elevated hydrogen pressures. As tetra-alkylhydrazines are less resistant to hydrogenation we attempted the reduction of the tetraethylbishydrazine (**2**), but even under acidic conditions no reduction was observed. Acyl-substituted hydrazines are more readily reduced by methods[13,14] relying on successive electron and proton transfer steps. In order to apply these methods a number of derivatives of the bishydrazine (**1**) were prepared. Reaction of the bishydrazine (**1**) with formic acid–acetic anhydride gave a tetraformyl derivative (**3**), but reaction with ethyl formate gave

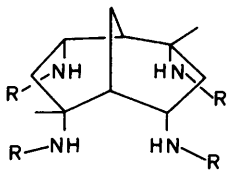
the diformamide (**31**). The preparation of acetamide derivatives including the tetra-acetyl derivative (**4**) has been described earlier. The tetrakis- and bis-trifluoroacetyl derivatives (**5**) and (**32**) were prepared from trifluoroacetic anhydride. The tetrabenzoyl derivative (**6**) was prepared from benzoyl chloride.

Following our earlier methodology[13] the tetrakis(trifluoroacetyl) derivative (**5**) was reduced with aluminium to give the tetra-amine derivative (**33**) in 72% yield. However, isolation of the tetra-amine (**34**), following hydrolysis of the amide (**33**), proved to be impossible. Attempted hydrolysis of the amide (**33**) under both acidic or basic conditions[15] was incomplete, and the tetra-amine (**34**) could not be isolated on attempted work-up. Similarly, separation problems prevented the isolation of the tetra-amine (**34**) following sodium borohydride reduction of the amide (**33**) using the method[16] of Prinzbach *et al.* The most efficient method for reduction of derivatives of the bishydrazine (**1**) and isolation of the products was by use[17] of group III hydrides.

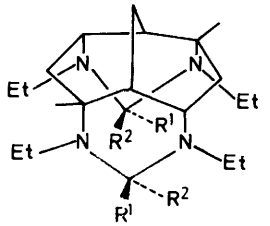
Reduction of the tetraformyl derivative (**3**) with borane–dimethyl sulphide complex[18] gives the tetramethyl derivative (**7**) without cleavage of the hydrazine nitrogen–nitrogen bonds. Similarly, the tetra-acetyl derivative with lithium aluminium hydride[18] affords the tetraethyl derivative (**2**). In contrast, reduction of the tetra-acetyl derivative (**4**) with borane–dimethyl sulphide complex gives the tetra-amine (**35**) in 64% yield with cleavage of the nitrogen–nitrogen bonds. Although such a reductive cleavage with borane complexes has precedent,[17] the contrasting course of the reduction of the tetraformyl derivative (**3**) and the tetra-acetyl derivative (**4**) is striking. In the earlier study the hydrazines cleaved by borane complexes were again sterically hindered. It appears that this steric congestion is an important factor in determining the course of borane reductions of hydrazines.



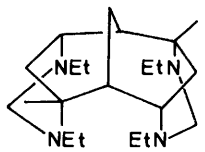
(**31**) R = CHO
(**32**) R = $COCF_3$



(**33**) R = $COCF_3$
(**34**) R = H
(**35**) R = Et



(**36**) R^1 = R^2 = H
(**37**) R^1 = Me, R^2 = H
(**38**) R^1 = H, R^2 = Me



(**38**)

The tetra-amine (**35**) can be purified by bulb-to-bulb distillation but suffers discolouration when allowed to stand. Reaction with formaldehyde gives a single product (**36**) in 96% yield. Again the observation of only 11 resonances in the ^{13}C n.m.r. spectrum of the product (**36**) indicates an axis of symmetry and hence suggests either the formation of the tetracyclic tetra-amine (**36**) or the alternative structure (**38**). The former structure is indicated from i.r. data. Molecular models show that in the alternative structure (**38**), all four six-membered rings must adopt boat conformations. In contrast in the tetra-amine (**36**) all four six-membered rings can adopt a chair conformation. In such polycyclic frameworks, notably the bicyclo[3.3.1]nonane skeleton,[19] a C–H deformation mode is observed at 1 490 cm^{-1}. This abnormally high value is associated with a methylene–methylene interaction. In the tetra-amine (**36**) a band is observed at 1 490 cm^{-1}; such a band would not be expected from the alternative structure (**38**) having the boat conformation.

In a similar manner acetaldehyde reacts with the tetra-amine (**35**) to give a single product (**37**) isolated in 83% yield. The formation of the same tetracyclic skeleton is shown by the similarity of the n.m.r. spectra of the two tetracyclic products and by the deformation mode at 1 490 cm^{-1} in the i.r. spectrum of the tetra-amine (**37**). The ambiguity concerning the position of the methyl substituents has not been completely resolved. However models predict that the isomer (**39**) will be characterised by extra adverse steric interactions relative to the isomer (**37**) and is therefore less likely to be formed under equilibrating conditions.

The formation of the tetracycle (**38**) with formaldehyde and analogous amines by reaction with acetaldehyde, is only possible if the tetra-amine (**35**) adopts a boat conformation. The formation instead of the tetracyclic (**36**) and (**37**) may be attributed in part, to the preference for the formation of the all-chair structure of (**35**). The double condensation on converting the bicyclic (**35**) to the tetracyclic (**36**) and (**37**) contrasts with the failure of the more rigid tetracyclic (**1**) to undergo double condensation to give hexacyclic products with formaldehyde.

Experimental

General methods have been described[13] previously.

1,6-*Dimethyl*-2,3,7,8-*tetra-azatetracyclo*[7.3.1.$0^{4,12}$.$0^{6,10}$]*trideca*-2,7-*diene* (**10**).—4,9-Dimethyl-2,3,7,8-tetra-azatetracyclo[7.3.1.$0^{4,12}0^{6,10}$]trideca-1,6-diene[3] (**9**) (2.7 g, 13.2 mmol) and potassium carbonate (3.6 g, 2.4 mmol) in absolute ethanol (50 ml) were heated under reflux under nitrogen for 4 h. The resulting suspension was cooled to room temperature and the solvent was removed under reduced pressure. The residue was extracted with methylene dichloride (100 ml) and the organic extract was filtered and the filtrate was concentrated under reduced pressure to afford as a white solid 1,6-dimethyl-2,3,7,8-tetra-azatetracyclo[7.3.1.$0^{4,12}0^{6,10}$]trideca-2,7-diene (**10**) (2.57 g, 95%), identical with material obtained by the lithium aluminium hydride–aluminium chloride route.[3]

2,9-*Dimethyl*-1,7,8,12-*tetra-azapentacyclo*[6.4.1.1^{2,6}.$0^{3,11}$.$0^{5,9}$]*tetradecane* (**11**).—1,6-Dimethyl-2,3,7,8-tetra-azatetracyclo[7.3.1.$0^{4,12}0^{6,10}$]tridecane (**1**) (200 mg) and aqueous formaldehyde (40%; 0.16 ml) were stirred at room temperature in methanol (25 ml) for 19 h. The solvent was removed to afford a brown oil. Preparative thin layer chromatography [eluant: methanol–chloroform (1:9)] afforded some bisazoalkane (**10**) and, as the more polar fraction, 2,9-dimethyl-1,7,8,12-tetra-azapentacyclo[6.4.1.1^{2,6}.$0^{3,11}$.$0^{5,9}$]tetradecane (**11**) in 20% yield. Recrystallisation of the eluate from ethyl acetate gave the title compound, m.p. 185—187 °C (Found: M^+, 220.1687. $C_{12}H_{20}N_4$ requires M, 220.1724); δ_H 1.24 (6 H, s, Me), 1.1—2.2 (8 H complex) 3.5—3.8 (4 H, complex), and 4.50 (2 H, s, NCH_2N); δ_C 20.73 (C-4), 23.88 (Me), 35.41 (C-10 and C-14), 46.27 (C-3 and C-5), 63.55 (C-6 and C-11), 64.85 (C-2 and C-9), and 81.87 (C-13).

Acetylation of the amine (**11**) with acetic anhydride (18 h at room temperature) afforded a crude amide, which was purified, following removal of acetic anhydride under reduced pressure,

by filtration through basic alumina eluting with ethyl acetate. Recrystallisation from ethyl acetate gave 7,12-*diacetyl*-2,9-*dimethyl*-1,7,8,12-*tetra-azapentacyclo*[6.4.1.$1^{2,6}$.$0^{3,11}$.$0^{5,9}$]-*tetradecane* (**12**), m.p. 273—274 °C (Found C, 62.9; H, 8.0; N, 18.5. $C_{16}H_{24}N_4O_2$ requires C, 63.1; H, 7.9; N, 18.4%); $\nu_{max.}$($CHCl_3$) 1 630 cm^{-1}; *m/z* 304 (M^+, 6%), 261 (56), and 43 (100); δ_H 1.11 (6 H, s, Me), 1.70 (2 H, t, *J* 3 Hz, 4-H), 2.10 (6 H, s, COMe), 1.8—2.3 (6 H, complex), 4.39 (2 H, s, NCH_2N), and 5.00 (2 H, t, *J* 7 Hz, 6-H and 11-H); δ_C 20.14 (C-4), 20.19 (Me), 31.76 (CO*Me*), 34.60 (C-10 and C-14), 42.84 (C-3 and C-5), 53.98 (C-6 and C-11), 65.60 (C-2 and C-9), 82.45 (C-13), and 169.02 (CO).

6,11,12-*Trimethyl*-1,7,8,12-*tetra-azapentacyclo*[5.5.1.$1^{2,6}$.-$0^{3,11}$.$0^{5,9}$]*tetradecane*-8-*carbaldehyde* (**17**).—The bishydrazine (**1**) (200 mg) was dissolved in aqueous formaldehyde (40%; 10 ml) in light petroleum (b.p. 60—80 °C) (10 ml) and the mixture was well stirred at room temperature for 5 h. The organic layer was discarded and the aqueous layer was extracted with dichloromethane (3 × 25 ml). Work-up of the organic phase and flash chromatography [eluant: ethyl acetate–ethanol (4:1)] of the residue afforded as white crystals the title compound (80 mg, 45%), m.p. 133—136 °C (from ethyl acetate) (Found: C, 64.1; H, 8.6; N, 21.3. $C_{14}H_{22}N_4O$ requires C, 64.1; H, 8.4; N, 21.4%); $\nu_{max.}$($CHCl_3$) 1 653 cm^{-1}; δ_H 1.09 (3 H, s, Me), 1.17 (3 H, s, Me), 1.0—2.5 (8 H, complex), 2.44 (3 H, s, NMe), 4.02 (1 H, d, *J* 14 Hz, 13-H), 4.04 (1 H, dt, *J* 10.3 and 3 Hz, 2-H), 4.59 (1 H, d, *J* 14 Hz, 13-H), 4.63 (1 H, dd, *J* 10, 7 Hz, 9-H), and 8.22 (1 H, s, CHO); δ_C 21.18 (C-4), 27.16 and 30.02 (2 × Me), 28.84 (C-14), 40.67 (C-10), 42.05 (Me), 43.20 and 44.69 (C-3 and C-5), 52.45 and 53.29 (C-2 and C-9), 60.59 and 62.96 (C-6 and C-11), 73.51 (C-13), and 162.65 (CHO).

6,11-*Dimethyl*-13-*phenyl*-1,7,8,12-*tetra-azapentacyclo*-[5.5.1.$1^{2,6}$.$0^{3,11}$.$0^{5,9}$]*tetradecane* (**20**).—To a solution of the bishydrazine (**1**) (0.5 g) and triethylamine (0.4 ml) in ethanol (25 ml) was added dropwise benzaldehyde (0.26 g) in ethanol (2.5 ml) and the resulting solution was stirred for 16 h at room temperature. Removal of the solvent under reduced pressure afforded a white residue which was recrystallised from ethyl acetate to give the title compound (626 mg, 88%), m.p. 165—168 °C, $\nu_{max.}$($CHCl_3$) 3 400—3 200 cm^{-1}; δ_H 1.06 (3 H, s, Me), 1.17 (3 H, s, Me), 1.2—2.25 (8 H, complex), 3.61 (1 H, q, *J* 10, 7 Hz, 9-H), 3.79 (1 H, dt, *J* 10.3 and 3 Hz, 2-H), 4.3 (2 H, br, NH), 5.24 (1 H, s, 13-H), and 7.1—7.9 (5 H, ArH); δ_C 21.92 (C-4), 28.71 (C-14), 29.82 and 30.92 (Me), 40.66 (C-10), 45.68 and 46.87 (C-3 and C-5), 58.61 (C-2 and C-9), 60.44 and 61.28 (C-6 and C-11), 86.77 (C-13), and 125.91, 127.04, 127.64 and 146.64 (ArC).

The amine (**20**) was acetylated under differing reaction conditions. When the amine (**20**) (652 mg) was stirred in acetic anhydride (5 ml) at room temperature for 24 h removal of the solvent afforded a brown oil (809 mg). This residue was purified by filtration through basic alumina (eluant: ethyl acetate) and then by recrystallisation from ethyl acetate to give, as white crystals, 8,12-*diacetyl*-6,11-*dimethyl*-13-*phenyl*-1,7,8,12-*tetra-azapentacyclo*[5.5.1.1.^{2,6}.$0^{3,11}$.$0^{5,9}$]*tetradecane* (**21**) (112 mg, 13%), m.p. 283—284.5 °C (Found: C, 69.2; H, 7.5; N, 14.9. $C_{22}H_{28}N_4O_2$ requires C, 69.5; H, 7.4; N, 14.7%); $\nu_{max.}$($CHCl_3$) 1 625 cm^{-1}; δ_H 1.05 (3 H, s, Me), 1.65 (3 H, s, Me), 2.17 (3 H, s, COMe), 2.31 (3 H, s, COMe), 1.3—2.5 (7 H, complex), 2.63 (1 H, dd, *J* 17, 7 Hz, 14-H), 4.03 (1 H, m, 2-H), 4.89 (1 H, s, 13-H), 4.97 (1 H, dd, *J* 10, 6 Hz, 9-H), and 7.2—8.1 (5 H, ArH); δ_C 20.40 (C-4), 22.59 (COMe), 24.14 (COMe), 27.87 (C-14), 29.74 (Me), 30.60 (Me), 35.47 (C-10), 43.84 and 45.70 (C-3 and C-5), 53.31 (C-2 and C-9), 61.54 (C-6 and C-11), 86.84 (C-13), 126.54, 127.82, 128.89, and 142.09 (ArC), and 167.13 and 171.23 (CO).

The amine (**20**) (283 mg) was also acetylated in pyridine (5 ml) and acetic anhydride (1 ml) at room temperature for 48 h. The products were isolated by removal of the solvent under reduced pressure, filtration through a short alumina column (eluant: ethyl acetate) and then flash chromatography of the filtrate. Elution with ethyl acetate–ethanol (3:1) afforded as the less polar fraction 7,12-*diacetyl*-6,11-*dimethyl*-13-*phenyl*-1,7,8,12-*tetra-azapentacyclo*[6.4.1.$1^{2,6}$.$0^{3,11}$.$0^{5,9}$]*tetradecane* (**15**) (215 mg, 59%), m.p. 197—198 °C (ethyl acetate–ether) (Found: C, 69.4; H, 7.5; N, 14.9. $C_{22}H_{28}N_4O_2$ requires C, 69.5; H, 7.4; N, 14.7%); $\nu_{max.}$($CHCl_3$) 1 635 cm^{-1}; δ_H 1.61 (3 H, s, Me), 1.67 (3 H, s, Me), 1.76 (3 H, s, COMe), 1.79 (3 H, s, COMe), 1.6—1.9 (4 H, complex), 2.19 and 2.26 (2 H, complex, 3-H and 5-H), 2.50 (2 H, m, 10-H and 14-H), 3.75 and 3.83 (2 H, m, 2-H and 9-H), 5.42 (1 H, s, 13-H), and 7.2—7.5 (5 H, ArH); δ_C 18.63, 22.74, 23.42, 24.79, 25.12, 33.61, 33.79, 46.64, 46.80, 58.01, 64.72, 65.41, 93.87, 127.63, 128.03, 128.84, 138.83, 168.99, and 171.61. The more polar fraction was identified as 7,12-*diacetyl*-2,9-*dimethyl*-13-*phenyl*-1,7,8,12-*tetra-azapentacyclo*[6.4.1.$1^{2,6}$.$0^{3,11}$.$0^{5,9}$]-*tetradecane* (**13**) (67 mg, 18%), m.p. 217—219 °C (ethyl acetate–ether) (Found: C, 69.8; H, 7.4; N, 14.9. $C_{22}H_{28}N_4O_2$ requires C, 69.5; H, 7.4; N, 14.7%); $\nu_{max.}$($CHCl_3$) 1 640 cm^{-1}; δ_H 1.20 (3 H, s, Me), 1.31 (3 H, s, Me), 1.83 (3 H, s, COMe), 1.88 (3 H, s, COMe), 1.7—2.1 (4 H, complex), 2.16 and 2.24 (2 H, m, 3-H and 5-H), 2.30 (2 H, q, *J* 16 Hz, 10-H and 14-H), 5.05 and 5.08 (2 H, m, 6-H and 11-H), 5.60 (1 H, s, 13-H), and 7.2—7.5 (5 H, ArH); δ_C 19.92, 20.47, 20.62, 31.68, 32.04, 33.39, 34.93, 42.71, 43.27, 54.11, 54.66, 66.76, 92.71, 127.47, 127.92, 128.69, and 139.30.

3-*Benzyl*-4,9-*dimethyl*-2,3,7,8-*tetra-azatetracyclo*[7.3.1.-$0^{4,12}$.$0^{6,10}$]*trideca*-1,7-*diene* (**24**).—The bishydrazine (**1**) (410 mg) and benzaldehyde (460 mg) were heated under reflux in ethanol (50 ml) under nitrogen for 21 h. The solvent was removed under reduced pressure and on addition of a little ethyl acetate the amine (135 mg, 23%) precipitated. After filtration the mother liquor was concentrated and subjected to preparative thin layer chromatography. The bisazoalkane (**10**) (81 mg) was isolated as the more polar fraction (eluant: ethyl acetate) and the less polar fraction, a yellow oil was identified as the title compound, *m/z* 294 (M^+); $\lambda_{max.}$ 260 (2 600) and 330 (380); δ_H 1.34 (3 H, s, Me), 1.68 (3 H, s, Me), 1.2—2.9 (8 H, complex), 3.78 (1 H, d, *J* 14 Hz C*H*$_2$Ph), 4.04 (1 H, d, *J* 14 Hz, C*H*$_2$Ph), 4.80 (1 H, q, *J* 11, 8 Hz, 6-H), and 7.1—7.5 (5 H, ArH); δ_C 17.91 (C-11), 24.08 (Me), 25.37 (Me), 26.22 and 33.67 (C-5 and C-13), 34.42 and 48.33 (C-10 and C-12), 52.56 (*C*H$_2$Ph), 71.25 (C-4), 88.84 (C-6), 96.99 (C-9), 126.76, 128.26, 128.50 and 139.89 (ArC), and 154.35 (C-1).

8,12-*Diacetyl*-6,11-*dimethyl*-13-(p-*nitrophenyl*)-1,7,8,12-*tetra-azapentacyclo*-[5.5.1.$1^{2,6}$.$0^{3,11}$.$0^{5,9}$]*tetradecane* (**22**).—1,6-Dimethyl-2,3,7,8-tetra-azatetracyclo[7.3.1.$0^{4,12}$.$0^{6,10}$]-tridecane (**1**) (0.3 g, 1.4 mmol) and triethylamine (0.25 ml, 2 mmol) were dissolved in ethanol (40 ml). *p*-Nitrobenzaldehyde (0.22 g, 1.4 mmol) was added and the resulting solution was stirred for 16 h at room temperature. Removal of the solvent under reduced pressure afforded a red solid (500 mg) which was dissolved in acetic anhydride (2 ml) and stirred for 16 h. Removal of the solvent and subsequent crystallisation of the residue with ether afforded as an off white solid 8,12-*diacetyl*-6,11-*dimethyl*-13-(p-*nitrophenyl*)-1,7,8,12-*tetra-azapentacyclo*-[5.5.1.$1^{2,6}$.$0^{3,11}$.$0^{5,9}$]tetradecane (**22**) (208 mg, 42%), m.p. 285—288 °C (ethyl acetate) (Found: C, 61.8; H, 6.3; N, 16.2. $C_{22}H_{27}N_5O_4$ requires C, 62.1; H, 6.4; N, 16.5%); $\nu_{max.}$($CHCl_3$) 1 650 and 1 695 cm^{-1}; δ_H 1.16 (3 H, s, Me), 1.67 (3 H, s, Me), 2.18 (3 H, s, COMe), 2.32 (3 H, s, COMe), 1.4—2.7 (8 H, complex), 4.08 (1 H, d, *J* 8 Hz, 2-H), 4.96 (1 H, s, 13-H), 5.01 (1 H, m, 9-H), and 8.1—8.3 (4 H, ArH); δ_C 20.18 (C-4), 22.53 (CO*Me*), 24.03 (CO*Me*), 28.09 (C-14), 29.66 (Me), 30.51 (Me), 35.47 (C-10), 43.68 and 45.54 (C-3 and C-5), 53.07 (C-2), 53.33 (C-9), 61.59 (C-6), 61.67 (C-11), 86.10 (C-13), 127.65, 128.47, 147.62 and 149.10 (ArC), and 166.84 and 171.09 (CO).

Reaction of 1,6-*Dimethyl*-2,3,7,8-*tetra-azatetracyclo*[7.3.1.-$0^{4,12}.0^{6,10}$]*tridecane* (**1**) *with Acetone*.—1,6-Dimethyl-2,3,7,8-tetra-azatetracyclo[7.3.1.$0^{4,12}.0^{6,10}$]tridecane (**1**) (250 mg), acetone (1 ml), and toluene-*p*-sulphonic acid (50 mg) in toluene (40 ml) were heated under reflux in the presence of 3 Å molecular sieves for 5 h. The resulting solution was concentrated under reduced pressure to give a brown oil (344 mg) which was purified by filtration through alumina (eluant: ethyl acetate) to give the heptacycle (**28**) as a colourless oil (140 mg, 35%) (Found: M^+, 328.2913. $C_{20}H_{32}N_4$ requires M, 328.2620); δ_H 1.23 (6 H, s, 2 × Me), 1.27 (6 H, s, 2 × Me), 1.35 (6 H, s, Me), 1.62 (2 H, t, J 3 Hz, CH_2), 1.65 (2 H, dd, J 10, 6 Hz, CH_2), 2.2—2.4 (8 H complex), and 3.56 (2 H, t, J 7 Hz, CH); δ_C 21.39 (CH_2), 22.98 (Me), 33.69 (Me), 33.74 (Me), 34.40 (CH), 44.60 (CH_2), 58.62, 58.68 and 59.81, 61.02 (CH), and 97.70.

2,3,7,8-*Tetraformyl*-1,6-*dimethyl*-2,3,7,8-*tetra-azatetracyclo*-[7.3.1.$0^{4,12}.0^{6,10}$]*tridecane* (**3**).—Formic acid (6 ml) was added to acetic anhydride (12.5 ml) at 0 °C, over 15 min, with constant stirring. The solution was warmed to 60 °C and this temperature was maintained for 2 h. To the cold solution was added tetrahydrofuran (10 ml) and the resulting solution was added dropwise to a suspension of the bishydrazine (**1**) (500 mg) in tetrahydrofuran (20 ml). The mixture was stirred at room temperature for 3 h and then the solvents were removed under reduced pressure to give directly, as an amorphous solid, the title compound (0.66 g, 87%), m.p. 295—297 °C (decomp.); m/z 292, 264, 236, and 208; $\nu_{max.}$ 1 680, 1 665, and 1 640 cm^{-1}. The relative insolubility of the amide (**3**) prevented satisfactory recording of ^1H or ^{13}C spectra.

1,6-*Dimethyl*-3,8-*bis*(*trifluoroacetyl*)-2,3,7,8-*tetra-azatetra-cyclo*[7.3.1.$0^{4,12}.0^{6,10}$]*tridecane* (**32**).—To a stirred suspension of 1,6-dimethyl-2,3,7,8-tetra-azatetracyclo[7.3.1.$0^{4,12}.0^{6,10}$]tridecane (**1**) (200 mg) and potassium carbonate (0.75 g) in dichloromethane (50 ml) was added trifluoroacetic anhydride (0.67 ml) over 15 min. The resulting suspension was stirred at room temperature for 14 h and then filtered. The filtrate was concentrated under reduced pressure and the residual oil was purified by flash chromatography (eluant: ethyl acetate) to afford the *title compound* (69 mg, 18%), m.p. 219—220 °C (ethyl acetate) (Found: M^+, 400.2175 $C_{15}H_{18}F_6N_4O_2$ requires M, 400.1173); $\nu_{max.}$ 3 270, 3 190, and 1 680 cm^{-1}; δ_H[$(CD_3)_2CO$] 2.14 and 2.32 (6 H, 2 × Me), 1.7—2.7 (8 H, complex), 4.79 (2 H, m, 4-H and 9-H), 6.09 (1 H, br, NH), and 6.36 (1 H, br, NH).

2,3,7,8-*Tetra*(*trifluoroacetyl*)-1,6-*dimethyl*-2,3,7,8-*tetra-aza-tetracyclo*[7.3.1.$0^{4,12}.0^{6,10}$]*tridecane* (**5**).—The bishydrazine (**1**) (0.4 g) and trifluoroacetic anhydride (2.5 ml) were dissolved in pyridine (20 ml) and the solution was stirred at room temperature for 14 h. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane. This solution was washed with hydrochloric acid (2M; 3 × 50 ml) and with water (50 ml). The combined aqueous phases were washed with dichloromethane (50 ml) and the combined organic layers were dried, filtered, and concentrated to give a white residue (520 mg). Purification by flash chromatography afforded, as a white solid, the title compound (480 mg, 42%), m.p. 244—246 °C (ethyl acetate–ether) (Found: C, 38.5; H, 2.7; N, 9.5; $C_{19}H_{16}F_{12}N_4O_4$ requires C, 38.5; H, 2.7; N, 9.4%); $\nu_{max.}$(Nujol) 1 740 and 1 695 cm^{-1}; δ_H[$(CD_3)_2CO$] 1.0—3.2 (14 H, complex) and 4.98 (2 H, t, J 9 Hz, 4-H and 9-H); δ_C 18.20, 28.02, 32.13, 41.95, 58.53, 67.36, 116.55, and 161.94.

3,8-*Diformyl*-1,6-*dimethyl*-2,3,7,8-*tetra-azatetracyclo*[7.3.1.-$0^{4,12}.0^{6,10}$]*tridecane* (**31**).—The bishydrazine (**1**) (500 mg) was dissolved in ethyl formate (50 ml) and the solution was heated under reflux for 36 h. The solvent was removed under reduced pressure and the yellow, oily residue (1.16 g) was purified by flash chromatography [eluant: ethyl acetate–methanol (1:1)] to give the title compound as a white solid (130 mg, 20%), m.p. 250—255 °C (Found: M^+, 264.1730. $C_{13}H_{20}N_4O_2$ requires M, 264.1584); $\nu_{max.}$($CHCl_3$) 1 670 and 1 625 cm^{-1}; δ_H 1.09 (3 H, s, Me), 1.23 (3 H, s, Me), 1.6—2.6 (8 H, complex), 4.42 and 4.75 (2 H, m, 4-H and 9-H), 5.69 (1 H, br, NH), 6.10 (1 H, br NH), and 8.19 (2 H, 2 × CHO); δ_C 19.34, 30.73, 36.22, 36.64, 39.94, 40.77, 53.03, 53.42, 53.54, 53.78, 59.15, 59.57, 75.99, 77.27, 78.55, 154.05, and 162.5.

2,3,7,8-*Tetrabenzoyl*-1,6-*dimethyl*-2,3,7,8-*tetra-azatetracyclo*-[7.3.1.$0^{4,12}.0^{6,10}$]*tridecane* (**6**).—The bishydrazine (1 g), benzoyl chloride (2.8 ml), and pyridine (20 ml) were stirred at 60 °C for 14 h. The resulting suspension was cooled to room temperature and partitioned between dichloromethane and water. The organic phase was washed with hydrochloric acid (4M; 3 × 25 ml) and water (25 ml). The combined aqueous phases were washed with dichloromethane (2 × 25 ml) and the combined organic layers were dried and evaporated under reduced pressure to give a yellow oil (2.84 g). Crystallisation from ethyl acetate gave, as a white solid, the title compound (2.6 g, 87%), m.p. 320—330 °C (decomp.) (dichloromethane–ethyl acetate) (Found: C, 74.7; H, 5.9; N, 8.9. $C_{39}H_{36}N_4O_4$ requires C, 75.0; H, 5.8; N, 9.0%); $\nu_{max.}$($CHCl_3$) 1 680 and 1 640 cm^{-1}; δ_H 1.65—2.05 (10 H complex), 2.41 (2 H, m, 10-H and 12-H), 4.0—5.4 (4 H, complex), 6.85—8.8 (20 H, ArH); δ_C 19.33, 28.72, 32.47, 42.13, 58.39, 64.24, 126.92, 127.76, 128.48, 128.73, 130.17, 132.07, 133.57, 135.77, 168.86, and 173.21.

2,6-*Dimethyl*-2(endo), 4(endo), 6(endo), 8(endo)*tetrakis*-(*trifluoroacetamido*)*bicyclo*[3.3.1]*nonane* (**33**).—The bishydrazine derivative (**32**) (500 mg) was suspended in ethyl acetate–water (9:1; 45 ml). Strips of aluminium amalgam (2 g) were added and the reaction mixture was stirred for 15 min at room temperature and then heated under reflux for a further 1 h. The cold suspension was filtered, and the residue washed with ethyl acetate (50 ml) and then dichloromethane (50 ml). The combined filtrate and washings were concentrated under reduced pressure and the residue was taken up in dichloromethane (100 ml). The resulting solution was dried, filtered, and concentrated to give a white residue. Recrystallisation from ethyl acetate–ether afforded the *title compound* (72%), m.p. 230—235 °C (Found: C, 37.9; H, 3.4; N, 9.2. $C_{19}H_{20}F_{12}N_4O_4$ requires C, 38.3; H, 3.4; N, 9.4%); $\nu_{max.}$(Nujol) 3 360, 3 300, 1 735, 1 705, and 1 680 cm^{-1}; δ_H 1.90 (6 H, s, Me) 1.95—2.45 (4 H, complex), 2.71 (2 H, m, 10-H and 12-H), 2.90 (2 H, AB system, J 12 Hz, 5-H and 13-H), 4.49 (2 H, m, 4-H and 8-H), and 7.9 (4 H, br, NH); δ_C 26.98, 28.60, 38.27, 38.99, 50.81, 59.23, 116.76, and 157.94.

2(endo), 4(endo), 6(endo), 8(endo)-*Tetrakis*(*ethylamino*)-2,6-*dimethylbicyclo*[3.3.1]*nonane* (**35**).—The tetra-amide (**4**) (0.75 g) in tetrahydrofuran (100 ml) was cooled to 0 °C. Borane–dimethyl sulphide complex (2M; 10 ml) was added over 10 min and the resulting suspension was stirred at 0 °C for 1 h and then heated under reflux for 20 h. Most of the solvent (90 ml) was removed by distillation at atmospheric pressure. The residue was cooled to room temperature and hydrochloric acid (4M; 50 ml) was added. The resulting solution was heated under reflux for 1.5 h, cooled to room temperature, and basified by addition of solid sodium hydroxide. The suspension was extracted with dichloromethane (4 × 50 ml) and the combined organic phases were washed with water, dried, filtered, and evaporated under reduced pressure to give a green oil (579 mg). Bulb-to-bulb distillation afforded, as a low melting solid, the *title compound* (**35**) (417 mg, 64%), b.p. 120—130 °C at 0.5 mmHg; m/z (c.i., NH_3) 325 (M^+ + 1); $\nu_{max.}$($CHCl_3$) 3 260, 2 980, 2 940, 2 880,

and 1 470 cm^{-1}; δ_H 1.07 (6 H, t, *J* 7 Hz, Me), 1.09 (6 H, t, *J* 7 Hz, Me), 1.21 (6 H, s, Me), 1.65 (2 H, t, *J* 3 Hz, 9-H), 1.75—1.9 (6 H, complex), 2.4—2.7 (12 H, complex), and 2.86 (2 H, m, 4-H and 8-H); δ_C 15.52 (Me), 15.90 (Me), 27.05 (CH_3), 29.76 (CH_2), 35.09 (CH_2), 41.97 (CH), 42.19 (CH_2), 42.26 (CH_2), 57.67 and 60.55 (CH).

2,4,8,10-*Tetraethyl*-1,7-*dimethyl*-2,4,8,10-*tetra-azatetracyclo*[9.3.1.$0^{5,14}$.$0^{7,12}$]*pentadecane* (**36**).—The tetra-amine (**35**) (175 mg) and formaldehyde (0.2 ml; 40%) were stirred in methanol (10 ml) for 16 h at room temperature. The solvent was removed under reduced pressure to give a brown oil (200 mg). Bulb-to-bulb distillation afforded, as a colourless oil, the *title compound* (**36**) (181 mg, 96%) b.p. 110—130 °C at 1 mmHg (Found: M^+, 348.3209. $C_{21}H_{40}N_4$ requires *M*, 348.3253); $\nu_{max.}$($CHCl_3$) 2 980, 2 950, 2 840, and 1 485 cm^{-1}; δ_H 1.04 (6 H, t, *J* 7 Hz, Me), 1.08 (6 H, t, *J* 7 Hz, Me), 1.22 (6 H, s, Me), 1.66 (2 H, t, *J* 3 Hz, 13-H), 1.74 (2 H, m, 12-H and 14-H), 1.99 (2 H, m, 6-H and 15-H), 2.24 (2 H, t, *J* 13 Hz, 6-H and 15-H), 2.5—2.9 (8 H, complex), 2.95 (2 H, m, 5-H and 11-H), and 3.37 and 3.58 (4 H, AB system, *J* 11 Hz, 3-H and 9-H); δ_C 13.32 (Me), 15.08 (Me), 24.75 (C-13), 26.16 (C-6 and C-15), 26.21 (Me), 36.90 (C-12 and C-14), 39.75 (CH_2), 46.10 (CH_2), 54.69 (C-5 and C-11), 56.20 (C-1 and C-7), and 61.08 (C-3 and C-9).

2,4,8,10-*Tetraethyl*-1,3,7,9-*tetramethyl*-2,4,8,10-*tetra-aza-tetracyclo*[9.3.1.$0^{5,14}$.$0^{7,12}$]*pentadecane* (**37**).—The tetra-amine (**35**) (125 mg) and acetaldehyde (1 ml) in ethanol (5 ml) were stirred for 18 h at room temperature. The solvent was removed under reduced pressure to give a yellow oil (163 mg). Bulb-to-bulb distillation afforded, as a colourless oil, the *title compound* (**37**) (121 mg, 83%), b.p. 100—125 °C at 1 mmHg; *m/z* (c.i., CH_4) 377 ($M^+ + 1$); $\nu_{max.}$($CHCl_3$) 2 980, 2 940, 2 880, and 1 490 cm^{-1}; δ_H 1.01 (12 H, t, *J* 7 Hz, Me), 1.19 (6 H, s, Me), 1.25 (6 H, d, *J* 6 Hz, Me), 1.54 (2 H, q, *J* 7 Hz, 6-H and 15-H), 1.68 (2 H, t, *J* 3 Hz, 13-H), 1.75 (2 H, m, 12-H and 14-H), 2.27 (2 H, t, *J* 13 Hz, 6-H and 15-H), 2.2—2.8 (8 H, complex), 2.92 (2 H, m, 5-H and 11-H), and 4.12 (4 H, q, *J* 6 Hz, 3-H and 9-H); δ_C 15.11 (Me), 19.59 (C-13), 20.45 (Me), 26.60 (Me), 27.22 (Me), 28.88 (C-6 and C-15), 34.91 (C-12 and C-14), 39.15 (CH_2), 40.92 (CH_2), 54.36 (C-5 and C-11), 57.92 (C-1 and C-7), and 65.19 (C-3 and C-9).

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