PROTON MAGNETIC RESONANCE STUDIES OF COMPOUNDS WITH BRIDGEHEAD NITROGEN ATOMS—XV[1]

THE NMR SPECTRA OF *SYN* AND *ANTI* PERHYDRO 7, 11-METHANOPYRIDO [1.2-*c*] (1,3) DIAZOCINE AND THE INFLUENCE OF THE NITROGEN LONE PAIR ON THE GEMINAL COUPLING CONSTANT OF AN ADJACENT METHYLENE GROUP

P. J. Chivers and T. A. Crabb

Chemistry Department, Portsmouth Polytechnic

Abstract—The synthesis, NMR, and IR spectra of *syn* and *anti* perhydro-7, 11-methanopyrido [1.2-*c*] (1,3) diazocine is described and the influence of the nitrogen lone pair of electrons on the geminal coupling constant of an adjacent methylene group is discussed.

MOLECULAR ORBITAL treatment[2] of geminal coupling constants *(J)* has proved to be of considerable use in the correlation[3-6] of such constants with molecular structure. For CH_2 protons α to heteroatoms the theory predicts that both inductive σ-electron withdrawal from and pseudo π-electron transfer from heteroatom lone pairs into the CH_2 system will result in a positive shift in *J*. Whereas the inductive effect is independent of rotation about the carbon-heteroatom bond the hyperconjugative process is predicted to be dependent upon the dihedral angle between the lone pair orbitals and the CH_2 group being maximal when the H—H internuclear axis is perpendicular to the $C(H_2)$—X—R plane (X = heteroatom) and nil when one of the H atoms lies in this plane. The influence of non-bonding orbitals from oxygen and nitrogen on geminal coupling constants has been discussed by Anteunis[7] and from a survey of the literature it has been proposed that an increment of 1·8 Hz be added to *J* each time an α-oxygen or α-nitrogen atom has one of its lone pair orbitals parallel with a CH bond. Most of this discussion related to the effect of an α-O atom on *J* of the methylene group. The similar effect of the non bonding electrons of an α-S atom has also been noted.[8] A comparison of the value of J_{gem} for the N—CH_2—N protons in hexahydropyrimidines(I) having both lone pairs axial (*J* = −8·5 Hz) with that in the imidazolidines(II) (*J* = −3·5 Hz) has led[9] to an estimate of the eclipsing effect of a nitrogen lone pair of ca. 2·5 Hz. To avoid confusion with the Anteunis parallelity effect it must be noted that this eclipsing effect is the increase in *J* arising when a N lone pair changes its dihedral angle with an adjacent CH_2 from 60° (or 180°) Ia to 0° (or 120°) IIa and that in both I and II the N lone pair of electrons is parallel with an adjacent CH bond. It is the purpose of this paper to survey the influence of the nitrogen lone pair* on the *J* of an adjacent methylene indicating correlations of

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* Lone pairs are treated in terms of the simple hybridization model and *J* is assumed to be negative.

importance in the conformational analysis of heterocyclic compounds and to describe the NMR spectra of *syn* and *anti* perhydro-7, 11-methanopyrido [1.2-*c*] (1,3) diazocine (III and IV) in which the lone pair —CH$_2$ geometry is fairly well defined.

I   II

H   Ia   IVa
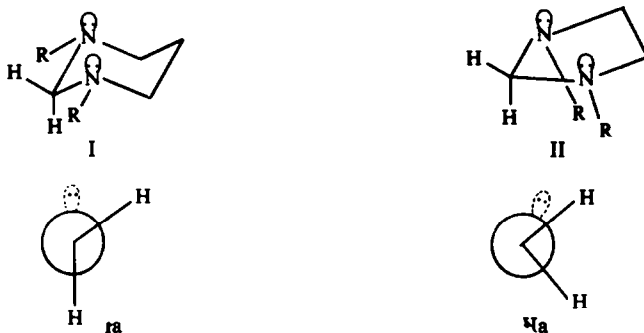
Synthesis and NMR spectra of syn *and* anti *perhydro-7, 11-methanopyrido* [1.2-*c*] (1,3) *diazocine*

The *syn* and *anti* perhydro-7, 11-methanopyrido [1.2-*c*] (1,3) diazocines were synthesized by exactly the same sequence of reactions as those employed[10] in the synthesis of *syn* and *anti* perhydrodipyrido [1.2-*c* 2′,1′-*e*] imidazole but starting from 3-cyanopyridine instead of 2-cyanopyridine. The two isomers were separated by preparative gas liquid chromatography.

The NMR and IR spectra of the first isomer off the chromatography column is in accord with it being the *syn* isomer existing in conformation III. The appearance of strong bands in the 2800–2600 cm^{-1} region of the IR spectrum is evidence for the presence of the *trans*-fused quinolizidine moiety (3 αCH bonds anticoplanar with the N lone pair). In the NMR spectrum the C6 axial and equatorial protons absorb at 6·72 and 6·33 τ respectively, the corresponding protons in V absorbing[1] at 7·56 and

III   IV

V   VI
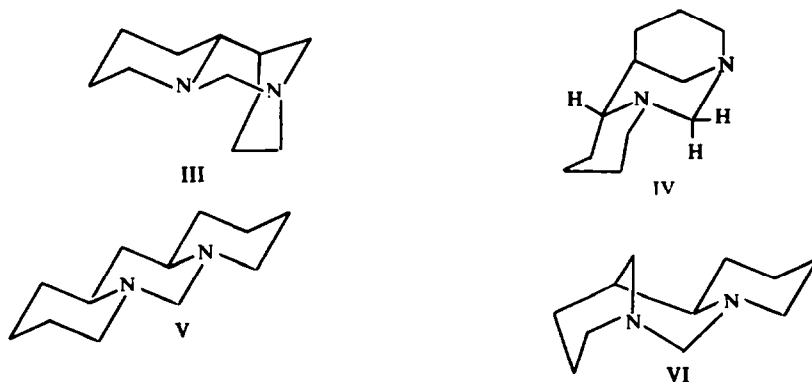
6·56 τ. This deshielding of the C6 axial proton in going from V to III is consistent with the loss of the preferential shielding[11] of this proton by the anticoplanar N7 lone pair and the equatorial C8 methylene which is operative in V. The magnitude of this deshielding (0·84 ppm) is unusually large. The *J* between the C6 methylene protons is —11·2 Hz, 2·7 Hz more negative than the corresponding *J* in V. This is in agreement

with structure III since it is to be expected[5] that this stereochemistry with one lone pair axial and the other equatorial will produce a more negative J than structures such as V in which both lone pairs are axial. Both C6 methylene protons are long range coupled ($J = 1$ Hz) and since the planar zig-zag stereochemistry is the most favourable one for the production of sizeable values of ^4J this provides additional support for III in which H6eq and H11eq as well as H6ax and H8ax are linked by a planar zig-zag arrangement of bonds. There is no long range coupling of the C6 methylene protons in V approaching 1 Hz in magnitude. A boat conformation for the C ring would elimi-nate the ^4J involving H6ax and a comparison of III with the 3-azabicyclo[3.3.1]-nonane system[12] also suggests the absence of boat rings. The five proton multiplet between 6·8 to 7·5 τ corresponds to those protons skew to the N lone pair (i.e. C11, C8, C4eq) and the H4ax proton absorbs at ca. 7·9 τ.

The second isomer off the column must possess the *anti* configuration and the spectral evidence favours the all chair conformation IV with a suggestion that the chairs may be partially flattened as in the 3-azabicyclo[3.3.1]nonanes.[12] There is only one α-CH bond anticoplanar with a N lone pair in IV and this is compatible with the very weak absorbtion in the 2800–2600 cm^{-1} region of the IR and rules out the presence of significant amounts of the boat conformation VI which has three α-CH bonds correctly orientated for the production of strong Bohlmann bonds.

The C6 methylene protons in the *anti* isomer absorb at 5·71 and 6·63 τ. In IV the C6 axial proton is deshielded[13] by the C1 and C3 methylene groups and so should absorb from 0·36 ppm to 0·9 ppm to lower field than the C6 axial proton in III. This leads to the assignment of the signal at 5·71 τ to the C6 axial proton representing a deshielding by the C1 and C3 groups of 0·62 ppm. Support for this assignment comes from a study of the long range couplings involving the C6 methylene protons. An examination of IV shows that the C6 axial proton is linked to only one other proton (C8ax) through 4 bonds and by a planar zig-zag path, whereas the C6 equatorial proton is linked to two protons (C11eq and C10beq) by this type of pathway. The high-field part of the C6 methylene AB quartet appears as well resolved triplets ($J_{gem} = -10\cdot5$ Hz, J6eq11eq = J6eq10beq = 1·5 Hz) and the low-field part as doublets (J6ax8ax = 1 Hz) confirming the assignment of the lowfield signals to the C6ax proton.

The J between the C6 methylene protons ($-10\cdot5$ Hz) is 0·6 Hz more positive in the *anti* isomer than in the *syn* isomer and this is probably due to slight flattening of the chair in IV to minimize some of the gauche-butane and gauche-propylamine inter-actions. The multiplet between 6·8 and 7·4 τ now corresponds to the seven protons present in IV skew to the N lone pairs (C1, C8, C11, C10beq).

The influence of the N atom on the J of an adjacent methylene

Four years have now elapsed since the first discussion[4] of J in heterocyclic systems when the conviction was expressed that J must vary with the projected angle (θ) between the CH_2 group and an adjacent lone pair orbital in an analogous manner to that demonstrated for an adjacent π-bond.

It seems timely, therefore, particularly now that the values for J for the stereo-chemically defined systems described above are known, to test such a J-θ relationship because of its potential in conformational analysis. The heterocyclic compounds on which the following discussion is based are shown in Tables 1 and 2 and the observed

variation in J with the number of adjacent N atoms and the orientation of the N lone pair in 6-membered ring systems is summarized in Table 3. Since variation in X—CH_2—Y angle affects J[4-6] compounds in which serious distortions of the chair conformations are expected to be present have not been tabulated.

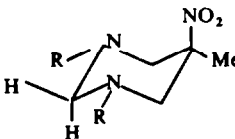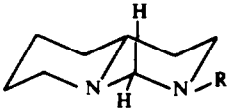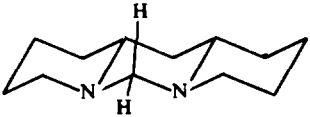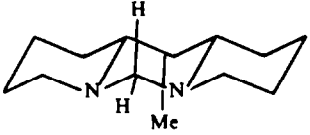TABLE 1. J FOR METHYLENE PROTONS ADJACENT TO N IN 6-MEMBERED RINGS
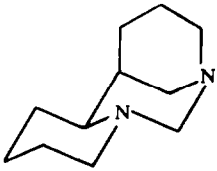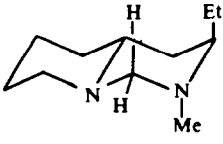
Compound	J	Reference
Methylene group between two axial N lone pairs		
R = cyclohexyl	−8·6	14
R = i-propyl	−8·4	
R = t-butyl	−8·6	15
R = i-propyl	−8·5	
	−8·5	19
	−8·7	19
Methylene group between one axial and one equatorial N lone pair		
	−11·3	this paper
	−11·4	15

TABLE 1 (*continued*)
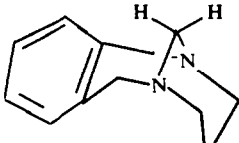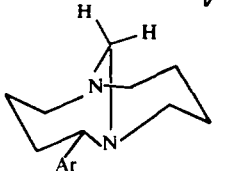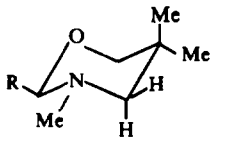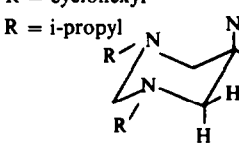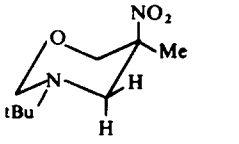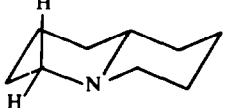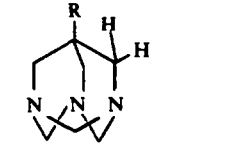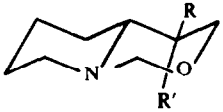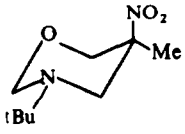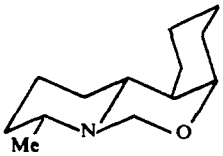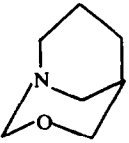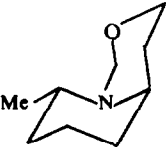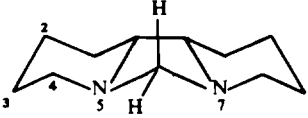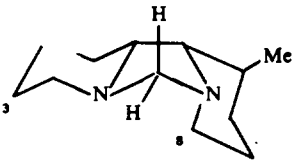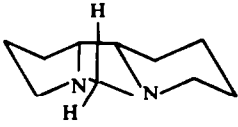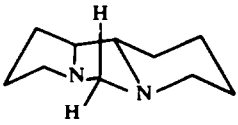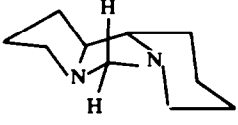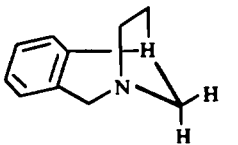
Compound	*J*	Reference

Methylene group between two equatorial N lone pairs

| | −13·0 | 16 |
| | −15·0 | 17 |

Methylene group adjacent to one axial N lone pair

| | −11·5 | 18 |

R = cyclohexyl
R = i-propyl

	−12·0	9
	−12·0	14
	−10·6	19

Methylene group adjacent to one equatorial N lone pair

| | −13·6 | 20 |

TABLE 1 (continued)

Compound	J	Reference
Methylene group between oxygen atom and one axial N lone pair		

R = Me, R′ = H
R = H, R′ = Me | −7·8 | 21

−7·7 | 14

−7·5 | 21

Methylene group between oxygen atom and one equatorial N lone pair

−10·5 | 18

−10·0 | 22

Lythramine | −11·0 | 23

(a) N *lone pair skew to both methylene* CH *bonds.* The introduction of a N atom with an equatorial lone pair into a cyclohexane ring (Table 3, Compound 1 → 2) produces a negative shift in J. A large number of values of J for CH_2 groups possessing electronegative α-substituents confirm the result of molecular orbital theory[2] predicting positive changes in J by inductive removal of electrons from the symmetric molecular orbital. There is every reason to assume, therefore, that the inductive effect of the N atom in Compound 2 produces a positive shift in J and so the skew lone pair must be giving rise to a marked negative shift in J of at least 1–2 Hz. The difference between J in Compounds 4 and 5 (Table 3) is only apparently at variance with this conclusion

TABLE 2. J FOR METHYLENE PROTONS ADJACENT TO N IN 5-MEMBERED RINGS

Compound	No.	J	Reference
	1	−3·5	24, 10
	2	−8·0	10
	3	−6·8 to −7·3	25
	4	−4·0	25
	5	−6·0 to −7·0	25
	6	−11·5	16

since it has been observed that the I effect of α-substituents on J is not additive, the combined I effect of two identical substituents being much greater than twice the effect of one. This is well illustrated by the values of J for the series CH_4, CH_3Cl, CH_2Cl_2 of −12·4, −10·8, and −7·5 Hz and for the series cyclohexane, tetrahydropyran, 1,3-dioxan of −12·6, −11·5 −6 Hz. The inductive effect of the N atom in the dihetero systems 5 and 7 (Table 3) is thus apparently greater than in Compound 2 so that the J values in Compounds 5 and 7 also show the negative shift produced by a skew N lone pair of electrons.

TABLE 3. J FOR METHYLENE PROTONS IN 6-MEMBERED RING SYSTEMS

No.	System	J	No.	System	J	No.	System	J
1		$-12\cdot6$	4		$-11\cdot5$	7		-13
2		$-13\cdot6$	5		$-10\cdot5$	8		$-11\cdot3$
3		$-11\cdot5$	6		$-7\cdot5$	9		$-8\cdot5$
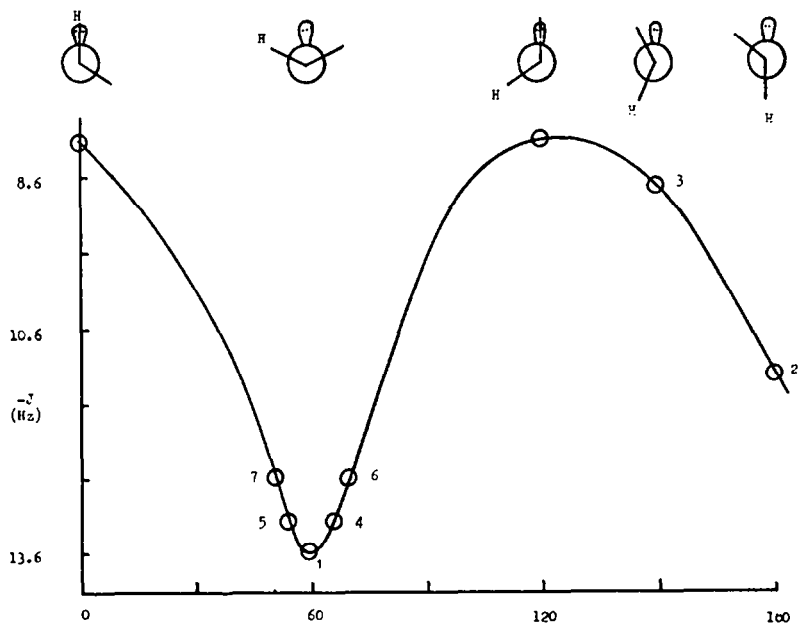
FIG 1. Variation of J of methylene group protons with dihedral angle θ with one adjacent N lone pair orbital.

(b) N *lone pair and one* CH *bond anticoplanar.* The effect of changing the orientation of the N lone pair from bisecting the HCH angle ($\theta = 60°$) to an anticoplanar position ($\theta = 180°$) can be estimated from the difference in J (Table 3) between compounds 2 and 3 (2·1 Hz), compounds 5 and 6 (3·0 Hz), compounds 7 and 8 (1·7 Hz) and compounds 8 and 9 (2·8 Hz). Thus a change in θ from 60° to 180° can produce a change in J varying from 1·7 to 3·0 Hz. For the purpose of constructing Fig 1 the average value of $J = 2·4$ Hz is taken and points 1 and 2 plotted. It is worth noting the J of $-10·5$ Hz for 2,4-diethyl-hexahydro-1,5-methanobenzo [e] (1,3) diazocine.[16] This is intermediate between the values for systems 8 and 9 (Table 3) and indicate that this compound exists at room temperature as an equilibrium mixture of VII with both lone pairs anticoplanar with the CH and of VIII with one lone pair axial and the other equatorial.

VII   VIII
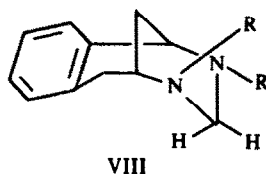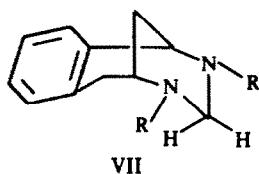
(c) *5-Membered rings containing* N. Correlations between J and θ based on data obtained on five-membered ring systems are open to two major objections: (a) the conformation of the ring is not easy to define so that there will be a large possible error in measuring θ and (b) although the stereochemistry of fused systems are better defined than monocyclic systems, strain at the ring fusions might well alter the hybridization of the N atom.[26] Compound 6 (Table 2) with both N lone pairs bisecting the CH_2 has been previously discussed.[9] The discrepancy between its J ($-11·5$ Hz) and that (-13 Hz) of its 6-membered ring analogue, Compound 7 (Table 3) is explicable[4] in terms of alteration in the N—C—N angle due to the two-carbon bridge (Table 2, No. 6). Bridged carbocyclic systems of this type also show[4] a more positive J than does the unstrained system. The preferred conformations of, and the dihedral angles between the CH_2 and adjacent N lone pairs of electrons in the remaining five-membered ring containing systems shown in Table 2 have been discussed in detail in earlier publications.[24,25]

The change in J from $-8·5$ Hz for *syn* perhydrodipyrido [1.2-*c*, 2′.1′-*f*] pyrimidine (Table 1) to $-3·5$ Hz for *syn* perhydrodipyrido [1.2-*c*, 2′.1′-*e*] imidazole (Table 2) in which the values of θ are 180° and ca 150° respectively is due to two lone pairs changing their orientation with respect to the adjacent methylene. Thus ΔJ for the 180° → 150° change in orientation of one lone pair is 2·5 Hz and this allows the plotting of point 3 in Fig 1 with $\theta = 150°$ and its ordinate 2·5 Hz greater than that of point 2. The change from $\theta = 150°$ in Compound 1 (Table 2) to $\theta =$ ca. 60° in Compound 2 (Table 2) (only the N7 lone pair changes its orientation in this pair of compounds) is accompanied by $\Delta J = -4·5$ Hz giving points 4 and 5 in Fig 1. In compound 3 (Table 2) the N7 lone pair makes a smaller angle than 60° with the pseudoaxial C6H bond and the dihedral angle between the N5 lone pair and the CH bond is smaller than in Compound 2 explaining the smaller ΔJ values (3·3 to 3·8 Hz) in going from Compound 1 to 3 than from 1 to 2 (Table 2). Compound 3 then allows us to

very tentatively plot points 6 and 7 in Fig 1. No compounds with $\theta = 0°$ ($\theta = 120°$) are available for study, but such compounds with their full eclipsing of an adjacent CH should give rise to the most positive J for such a system. It is unlikely, however, that such compounds would exhibit J values differing by more than 1 Hz from those in which $\theta = 150°$ and accordingly two points have been plotted at 0° and 120° with ordinates ca. 0·5 Hz more positive than that of point 3. The most positive value of J for a CH_2 group adjacent to N in a five-membered ring so far recorded is $-8·6$ Hz.[5]

The resultant Fig 1 does seem to indicate a smooth relationship between J and θ but the range of ΔJ for a particular $\Delta\theta$ as well as possible hybridization change effects makes this rather speculative curve applicable to conformational problems only when used with extreme care.

EXPERIMENTAL

The NMR spectra were determined on a Jeol 100 MHz spectrometer as 10% solutions in $CDCl_3$ with TMS as internal reference. IR spectra were recorded on a Perkin–Elmer 457 spectrophotometer, using 0·1M solns in $CDCl_3$. Elemental analysis were carried out by Dr. F. Pascher and E. Pascher, Microanalytical Laboratory, Bonn, Germany.

5-*Ethoxy*-1-(3-*pyridyl*)1-*pentanone*. A soln of the Grignard reagent, prepared from 1-bromo-4-ethoxy-butane (70 g) and Mg (13 g), in dry ether (250 ml) was allowed to drop slowly into a vigorously stirred soln of 3-cyano-cyanopyridine (50 g) in dry ether (350 ml). The reaction mixture was stirred overnight, and then acidified with dil HCl. The acidic soln after separation of the ether layer was basified with NH_4OH and extracted twice with ether (200 ml). The combined ether extracts were dried, the ether evaporated, and the residual oil distilled, to give 5-ethoxy-1-(3-pyridyl) 1-pentanone (26 g), b.p. 92–94°/0·1 mm, n_D^{20} 1·5013. (Found: C, 69·29; H, 8·17; N, 6·88: $C_{12}H_{17}NO_2$ requires: C, 69·54; H, 8·27; N, 6·76%).

1-*Amino*-5-*ethoxy*-1-(3-*pyridyl*) *pentane*. A soln of hydroxylamine hydrochloride (20 g) and 5-ethoxy-1-(3-pyridyl) 1-pentanone (24 g) in 90% EtOH (500 ml) was refluxed overnight. The alcohol was removed under vacuum to leave a thick syrup to which water (50 ml) was added together with enough K_2CO_3 to neutralize the soln. The oxime was extracted with ether (150 ml), the ether soln dried and the ether evaporated. The oxime could not be distilled or induced to crystallize and was, therefore, used without purification.

The crude oxime (26 g) was dissolved in 95% EtOH (250 ml), and Zn dust (125 g) and glacial AcOH (200 ml) added alternately in small amounts over a period of 2 hr. During the addition the temp was kept below 50°. After standing for 3 hr the excess Zn and zinc acetate was filtered off and washed with cold EtOH. waThe EtOH was evaporated and the soln made alkaline with 30% NaOH aq.

The soln was extracted with ether (3 × 150 ml), the extracts were dried and evaporated and the residual oil distilled, to give 1-amino-5-ethoxy-(3-pyridyl pentane (16·5 g) b.p. 85–86°/0·2 mm, n_D^{20} 1·4997. (Found: C, 68·97; H, 9·68; N, 13·24. $C_{12}H_{20}N_2O$ requires: C, 69·19; H, 9·68; N, 13·45%).

3-(2-*Piperidyl*) *pyridine*. A mixture of 1-amino-5-ethoxy-(3-pyridyl) pentane (15 g) and 48% aqueous HBr (150 ml) was placed in a flask fitted with a 50 cm vertical air condenser, the upper end of which being fitted to a downward pointing coil condenser. The mixture was heated so that the EtBr formed during the cyclization slowly distilled over and the heating was continued until the theoretical amount of EtBr had been collected. The reaction mixture was evaporated to ½ bulk and then basified with 30% NaOH aq. The oily amine containing layer was extracted with ether, and the ether soln dried and evaporated. The residual oil was distilled to give 3-(2-piperidyl) pyridine (9·6 g) b.p. 58–60°/0·07 mm, n_D^{20} 1·5321. (Found: C, 73·79; H, 8·70; N, 16·94. $C_{10}H_{14}N_2$ requires: C, 74·03; H, 8·70; N, 17·27%).

2-3′-*Dipiperidyl*. A soln of 3-(3-piperidyl) pyridine (9 g) in glacial AcOH (150 ml) was hydrogenated at 60 psi over Adams PtO_2 catalyst. The soln was filtered, evaporated to ½ bulk and made basic with 30% NaOH aq. The soln was extracted with ether (3 × 150 ml), the extracts were combined, dried and the ether evaporated. The residual oil was distilled to give 2-3′-dipiperidyl (7·4 g) b.p. 63–64°/0·05 mm. On standing, the 2-3′-dipiperidyl solidified and was obtained as white crystalline needles, m.p. 33–34° on recrystallization from light petroleum (b.p. 40–60°). (Found: C, 71·11; H, 12·01; N, 16·57. $C_{10}H_{20}N_2$ requires: C, 71·37; H, 11·98; N, 16·65%).

Perhydro-7,11-*methanopyrido* [1.2-*c*] (1,3) *diazocine*. 36% Aqueous formaldehyde (6 ml) was added to 2-3′-dipiperidyl (6 g) and the mixture shaken for 5 min at room temp. The soln was basified with excess

30% NaOH aq, and extracted with ether (3×100 ml). The ether extracts were combined dried and the ether evaporated. The residual oil was distilled and the fraction b.p. $64-68°/0.15$ mm was collected. The mixture was shown to be a 50:50 mixture of the two isomers by analytical GLC on a Perkin–Elmer F11 chromatograph, using a 2 metre $\times \frac{1}{8}$ in. aluminium column packed with $12\frac{1}{2}\%$ w/w Carbowax on 60–80 mesh chromsorb W. The mixture was separated automatically on a Pye 105 preparative chromatograph, using a 15 ft $\times \frac{3}{8}$ in. glass column packed with $12\frac{1}{2}\%$ w/w Carbowax 20M on 60–80 mesh chromosorb W.

The first isomer off the column was the *syn* isomer and possessed the following characteristics: b.p. $54°/0.07$ mm, n_D^{20} 1.5064. (Found: C, 73.16; H, 11.44; N, 15.31. $C_{11}H_{20}N_2$ requires: C, 73.28; H, 11.18; N, 15.54%); NMR: C6eq (6.33 τ), C6ax (6.72 τ); IR (cm^{-1}): 2805 (M) 2764 (S) 2714 (W) 2681 (W) 2660 (W).

The second isomer off the column was the *anti* isomer and possessed the following characteristics: b.p. $63-64°/0.1$ mm, n_D^{20} 1.5105. (Found: C, 73.21; H, 11.40; N, 15.31; $C_{11}H_{20}N_2$ requires: C, 73.28; H, 11.18; N, 15.54%); NMR: C6eq (6.63 τ) C6ax (5.71 τ); IR (cm^{-1}): 2813 (W) 2771 (W) 2720 (W).

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