Tetrahedron Vol. 40, No. 7, pp. 1157 to 1165, 1984
Printed in Great Britain.

0040-4020/84 \$3.00 + .00
Pergamon Press Ltd.

DELOCALISATION, CONFORMATION AND BASICITY OF ANILINES

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(*Received in Germany* 24 *October* 1983)

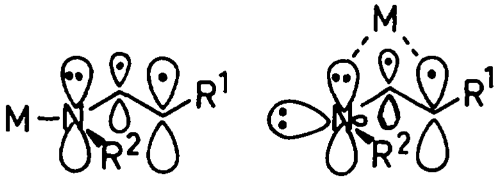
Abstract - ^{13}C spectra of some anilines 1 and annelated anilines 2 are reported. Variations in the chemical shift of the para carbon atom are used to estimate twist angles of the amino group. Results so obtained are compared to base strength. It is found that in twisted anilines a rough correlation between twist angle and base strength exists.

INTRODUCTION

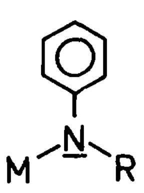
Very recently metallated imines of type I (M mostly = Li) have raised strong interest, since they are quite suitable enolate equivalents, especially in asymmetric synthesis.[3] To understand and predict the selectivity of induction, it is necessary to know the geometry of the metallated intermediates.

In spite of the fact that there is some knowledge about the configuration of the carbon-nitrogen [4] and carbon-carbon [5,6] bonds, the very important question of whether the involved ion pairs are σ-bonded (metallo enamine) or π-bonded (1-azaallylic system) species has, until now, not been answered.[6]

In the course of an attempt [1] to obtain more insight into this problem, we decided to use metallated anilines II (M = Li) as simple model compounds for I, because in this case it is possible to construct by annelation (III) or introduction of steric hindrance fixed structures with respect to the nitrogen plane and the plane of the π-system. It thus seems to be possible to produce σ- as well as π-bonded structures. To understand the experimental results on II and III (M = Li),[1] we needed information on electron delocalisation and conformation of some selected anilines of this type (M = H).



σ-bonded I π-bonded



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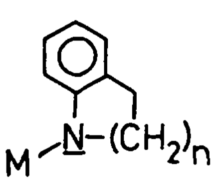


III

These questions have been attacked in the past by chemical methods, especially by base strength measurements [7] and physical methods including electronic spectra,[7] dipole moments,[8] molecular refractions [9] and very recently by photoelectron spectroscopy.[10,11]

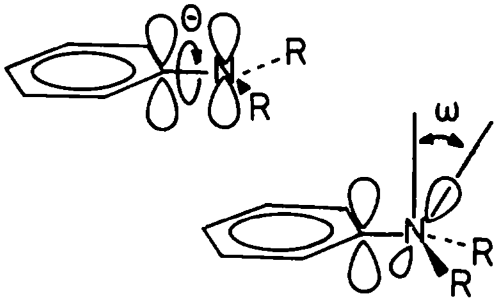
It is well known that ^{13}C magnetic shieldings in aromatic rings correlate quite well with local π-electron densities.[12] Thus the use of ^{13}C spectroscopy seemed to be suitable for our purpose, especially since it had been successfully applied to anilines [13,14] and o-phenylen diamines.[15,16]

The following paper reports on the ^{13}C spectra of a set of anilines $\underline{1}$ and compares the effects found with variations in base strength.$\underline{2}$ To get a consistent set of data, all pK_a-values of $\underline{1}$ and $\underline{2}$ were measured using the same experimental conditions.

RESULTS AND DISCUSSION

<u>^{13}C Spectra of Anilines</u> - Delocalisation of n-orbitals into a π-system as in anilines is controlled by two effects: amount of coplanarity between the n- and π-orbitals and hybridisation of the n-orbital.

The larger the twist angle Θ - that is the angle between the lone pair and the aromatic π-orbitals - and the s-content of the n-orbital as expressed by the bend angle ω, the smaller the delocalisation.



In anilines delocalisation of the lone pair on nitrogen causes an upfield shift of the ortho and para carbon atoms.[13,14] Since steric effects are absent, the latter is a convenient probe for delocalisation. This was shown for the first time by Lauterbur looking for steric inhibition of delocalisation in anilines.[13]

Since delocalisation is influenced by both twisting and bending on nitrogen, the induced variation of the shift of the para carbon atom cannot distinguish between the two.[17]

Nevertheless, in closely related systems like anisoles and diphenylethers [18] as well as thioethers,[17] variations in para carbon chemical shifts have been used to make a more quantitative estimate for the twist angle Θ, assuming that changes in hybridisation are not important within the series.

According to the well known cos Θ dependence of overlap, the equation:

$$\cos\Theta = (\delta_{CP}^{min} - \delta_{CP}) / (\delta_{CP}^{min} - \delta_{CP}^{max})$$

can be derived, δ_{CP}^{min} and δ_{CP}^{max} being the limiting values for zero ($\Theta = 90^{o}$) and complete ($\Theta = 0^{o}$) overlap, respectively.

This equation is said to overestimate the twist angle, and the sometimes used [18] $\cos^{2}\Theta$-dependence to underestimate it.[19]

To obtain more insight into conformation of anilines, we adopted this method neglecting possible changes in hybridisation of the nitrogen atom.

We therefore measured the ^{13}C spectra of anilines $\underline{1a}$ - $\underline{k}$ and annelated anilines $\underline{2a}$-$\underline{h}$.

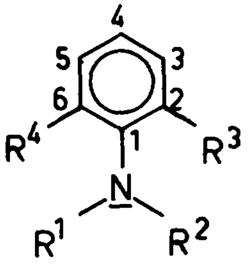
As a weakly polar solvent with no hydrogen bonding we used benzene-d_6.

The results are given in Tables 1 and 2. The assignment is straightforward in the case of unsubstituted and 2,6-disubstituted anilines from intensity and "off resonance" multiplicity arguments.

Much more difficult is the assignment in the case of 2-mono substituted anilines $\underline{1b}$, $\underline{e}$, $\underline{h}$ and all the annelated anilines $\underline{2}$.

To distinguish between C-3 and C-5, the para shielding of an alkyl group of about 2-3 ppm [21] has been used. Of the two signals in question the one at higher field has thus been assigned to C-5. More important is to distinguish between C-4 and C-6.

For aniline $\underline{1e}$ we used single-frequency low power decoupling for assignment. In this case a high field doublet in the ^{1}H NMR spectrum is well separated from other aromatic signals. From the splitting pattern this signal is undoubtedly to be ascribed to H-6.



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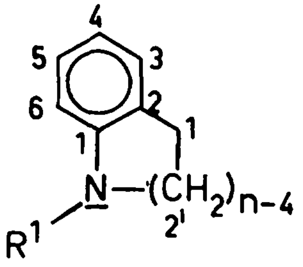


2

	R^1	R^2	R^3	R^4
a	H	H	H	H
b	H	H	CH_3	H
c	H	H	CH_3	CH_3
d	CH_3	H	H	H
e	CH_3	H	CH_3	H
f	CH_3	H	CH_3	CH_3
g	CH_3	CH_3	H	H
h	CH_3	CH_3	CH_3	H
i	CH_3	CH_3	CH_3	CH_3
j	CH_3	C_2H_5	H	H
k	C_2H_5	C_2H_5	H	H

	R^1	n
a	H	5
b	H	6
c	H	7
d	H	8
e	CH_3	5
f	CH_3	6
g	CH_3	7
h	CH_3	8

Irradiation causes the high field signal at 109.4 ppm to give a singlet. The same technique has been applied to compounds 1b, 2a and 2e.

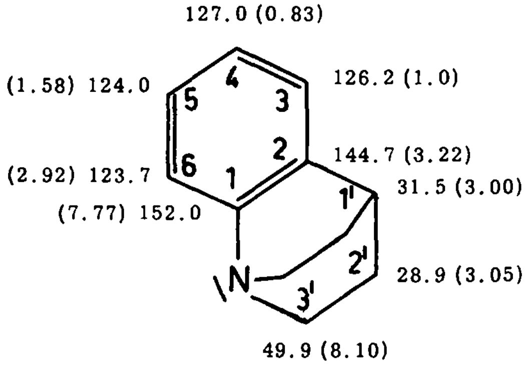
In all other cases the separation in the ^1H NMR spectrum was too small so that this method failed.

For anilines 2b-d the assignment was possible by determination of LIS-values (see Table 2) using Yb $(dpm)_3$.

With N-alkylated anilines 2f-h no complexation occurred. Hence assignments given for these compounds are only based on the fact that C-6 in all other cases resonates at higher field.

To estimate the angle Θ by means of the above equation, it is necessary to determine the limiting values for C-4.

As a model for minimum overlap we used benzoquinuclidine 3, introduced by Wepster et al[22] as "orthogonal aniline". From assignment by means of LIS we derived a value of 127.0 ppm for C-4 (see Fig. 1).



3

Fig. 1. ^{13}C-Chemical shifts (benzene-d_6, $TMS_{int.}$) and relative LIS-values for benzoquinuclidine 3.

Table 1. ^{13}C-Chemical shifts [a] of anilines 1.

Nr.	C-1	C-2	C-3	C-4	C-5	C-6	N-CH$_3$	C-2-CH$_3$ or/and C-6-CH$_3$
a [b]	147.2	115.1	129.4	118.1	129.4	115.1	-	-
b [b]	145.3	122.1	130.5	118.4	127.1	115.0	-	17.1
c [b]	143.2	121.4	128.4 [c]	117.9	128.4 [c]	121.4	-	17.3
d	149.8	112.5	129.3	117.0	129.3	112.5	30.3	-
e	147.6	121.8	130.1	117.1	127.5	109.4	30.4	17.3
f	148.0	129.2	129.1	121.9	129.1	129.2	35.1	18.2
g [b]	150.8	112.8	129.1	116.7	129.1	112.8	40.1	-
h [b]	153.0	132.2	131.3	122.9	126.7	118.6	44.1	18.3
i	149.7	136.9	129.1	125.2	129.1	136.9	42.4	19.1
j	149.6	112.9	129.4	116.5	129.4	112.9	37.2 [d]	-
k	148.1	112.4	129.4	116.0	129.4	112.4	- [e]	-

[a] Benzene-d$_6$, TMS$_{\text{int.}}$

[b] Measured by P.C. Lauterbur[13] as neat liquids relative to external CS$_2$. His values are in good agreement with ours.

[c] Lit.[13]: 124.6, calculated with δ_{CS_2} = 192.8.[20] [d] $\delta_{CH_2CH_3}$ = 11.2, 46.8 ppm.

[e] $\delta_{CH_2CH_3}$ = 12.7, 44.4 ppm.

Table 2. ^{13}C-Chemical shifts [a] of annelated anilines 2

Nr.	C-1	C-2	C-3	C-4	C-5	C-6	N-CH$_3$	C-1'	C-2'	C-3'	C-4'	C-5'
a	152.2	129.2	127.3	118.3	124.6	109.3	-	29.8	47.3	-	-	-
b	145.2 (5.66)	121.0 (2.51)	129.5 (1.00)	116.6 (0.80)	126.8 (0.74)	114.2 (2.86)		27.3 (1.71)	22.3 (2.35)	42.0 (5.49)	-	-
c	151.0 (5.65)	133.6 (2.67)	130.9 (1.00)	120.8 (0.78)	126.7 (0.77)	119.5 (2.71)		36.3 [b] (1.95)	32.2 [b] (2.85)	27.7 [b] (1.88)	48.7 (6.17)	-
d	147.8 (5.61)	134.5 (2.30)	130.4 (1.00)	122.4 (0.84)	127.1 (0.91)	122.6 (2.91)		31.9 [b] (1.54)	31.3 [b] (1.18)	28.9 [b] (1.93)	25.1 [b] (1.45)	51.0 (6.48)
e	153.6	130.1	127.4	117.8	124.2	107.2	35.8	28.2	56.0	-	-	-
f	146.8	122.6	128.8	116.4	127.2	111.1	38.7	28.0	22.8	51.1	-	-
g	152.8	135.5	130.0	121.2	126.8	116.3	42.9	35.3 [b]	30.2 [b]	25.9 [b]	56.9	-
h	150.7	142.5	129.6	125.1	127.1	121.5	44.2	33.0 [b]	32.8 [b]	28.7 [b]	27.2 [b]	62.4

[a] Benzene-d$_6$, TMS$_{\text{int.}}$. Relative LIS values in brackets.

[b] Assignment uncertain.

As a value for maximum overlap we used 116.1 ppm from N-phenylpyrrolidine[14] and 116.6 ppm from 2b for N, N-dialkylated and N-monoalkylated anilines respectively. For N-unsubstituted anilines a value of 117.9 ppm (1c) seems to be appropriate.

The deviations of the shifts of C-4 from the benzoquinuclidine value ($\Delta\delta$ C-4) for anilines 1 and 2 are compiled in Table 3 together with the conformation derived and a more quantitative estimate of twist angle Θ using the equation given above.

Included are some values derived from PE-spectroscopic work of Turner.[10] The agreement is encouraging.

Inspection of Table 1 shows clearly that nearly all anilines of type 1 are more or less coplanar. The only exceptions are observed with compounds where at least two methyl groups, one on nitrogen and one on C-2, have to interfere. In these cases (1f, 1h) large twist angles are observed, reaching a value of nearly 90° in tetramethylaniline 1i. Similar conclusions have been derived by Wepster from UV spectroscopy.[9]

On the other hand, the annelated anilines 2 are obviously strongly twisted in the case of the seven and eight membered ring, the N-methyl derivatives 2g and 2h a bit more than the unsubstituted ones 2c and 2d. The six membered ring compounds 2b and 2f are coplanar.

More difficult to understand are the values for the five membered ring compounds 2a and 2e, also expected to be coplanar with a more or less sp^2-hybridized nitrogen atom.

Perhaps "peri-interaction" between hydrogen on C-6 and the substituent on nitrogen causes some rehybridization to sp^3. This would diminish the steric effects and at the same time the delocalisation. That strong steric compression exists can be seen from the anomalous highfield shift of C-6 in 2a and 2e. It is interesting to note that PE spectroscopy shows no difference between 2a and 2b.[10]

pK_a-Measurements - Nash and Maciel,[14] in a paper concerned with a ^{13}C NMR study of anilines, postulated moderate correlation of para carbon shifts with basicity. The only exception reported had been N, N-diethylaniline (1k).

We found that in the case of anilines of type 1 no such correlation exists. This is seen very clearly by comparison of 1c with 1k and 1i with 1j, both pairs differing strongly in one property and having nearly the same value of the other (Table 3).

Indeed compounds 1 of the coplanar type varied over the range of 2.4 pK_a-units (3.67 for 1c to 6.04 for 1k) and exhibit almost no change in para carbon shift. Hence this large variation in basicity cannot be caused by resonance effects in the anilines and has been explained by different solvation of the free base by hydrogen bonding[14] or by different steric strain in the protonated base.[9,22]

On the other hand, the anilines 2 do show some regular behaviour between shift and pK_a-values (Table 3). Using the $\Delta\delta$ C-4-values moderate linear correlations can be drawn - one for the NH-compounds 2a-d and one for the NCH$_3$-compounds 2e-h (Fig. 2) - the stronger twisted anilines being the stronger bases as expected. Obviously steric hindrance of resonance now influences basicity but is not the only important factor. This can be seen from the result that twisted anilines of type 1 do not fit the appropriate lines, 1h being the only exception (Fig. 2).

For 1f and 1i lower base strengths were found as might be expected. Following Wepster's argument,[9,22] the weaker basicities in these cases were probably due to severe steric inhibition of cation solvation caused by the effect of two ortho methyl groups, which is not found with one ortho methyl group only (1h).

Table 3. Conformations, twist angles Θ and pK_a-values of anilines 1 and 2.

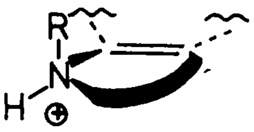
Nr.	$\Delta\delta$C-4	conformation	cos Θ [a]	Θ [a]	pK_a-value [b]
1a	8.9	coplanar	0.98	12°	4.22
1b	8.6	coplanar	0.95	19°	4.11
1c	9.1	coplanar	1	0°	3.67
1d	10.0	coplanar	0.96	16°	4.39
1e	9.9	coplanar	0.95	18°	4.29
1f	5.1	twisted	0.49	61°	5.19
1g	10.3	coplanar	0.94	$19^{\circ}(23^{\circ})$[c]	4.60
1h	4.1	twisted	0.38	$68^{\circ}(64^{\circ})$[c]	5.26
1i	1.8	twisted	0.17	$80^{\circ}(81^{\circ})$[c]	5.01
1j	10.5	coplanar	0.96	16°	5.38
1k	11.0	coplanar	1	0°	6.04
2a	8.7	"twisted"	0.84	33°	4.97
2b	10.4	coplanar	1	0°	4.01
2c	6.2	twisted	0.60	53°	5.14
2d	4.6	twisted	0.44	64°	6.11
2e	9.2	"twisted"	0.84	32°	4.45
2f	10.6	coplanar	0.97	13°	4.14
2g	5.8	twisted	0.53	58°	4.73
2h	1.9	twisted	0.17	80°	5.80
3	0	twisted	0	90°	6.75[d]

[a] by means of the equation given. [b] measured in water/ethanol (70/30) using potentiometric titration. [c] from PE spectroscopy[10] using benzoquinuclidine ($\Delta E = 0.7$ eV) and julolidine ($\Delta E = 2.55$ eV) as limiting cases according to the equation $\cos\Theta = (\Delta E - 0.7)/1.85$.
[d] measured in water/ethanol (50:50).

Tertiary anilines are usually stronger bases than secondary ones. In the case of annelated anilines 2 the reverse has been found.

The explanation of this unexpected result could be based again on consideration of effects within the protonated bases. For these two conformers IV and V are possible. If one assumes V being favoured because of more effective solvation of the less hindered pseudoequatorial hydrogen, the cations derived from tertiary anilines are disfavoured by the pseudoaxial methyl group compared to hydrogen in secondary anilines.

IV



V

Additional annelation as in the case of benzoquinuclidine 3 should diminish this effect by relief of steric strain. In this case 3 is to be expected to fit the relationship of secondary anilines. Extrapolation of the corresponding relationship up to the $\Delta\delta$ C-4-value of 3 gave a pK_a-value of 7.1, in fair agreement with the values of 7.79 (H_2O) and 6.75 (50% ethanol) measured by Wepster.[22]

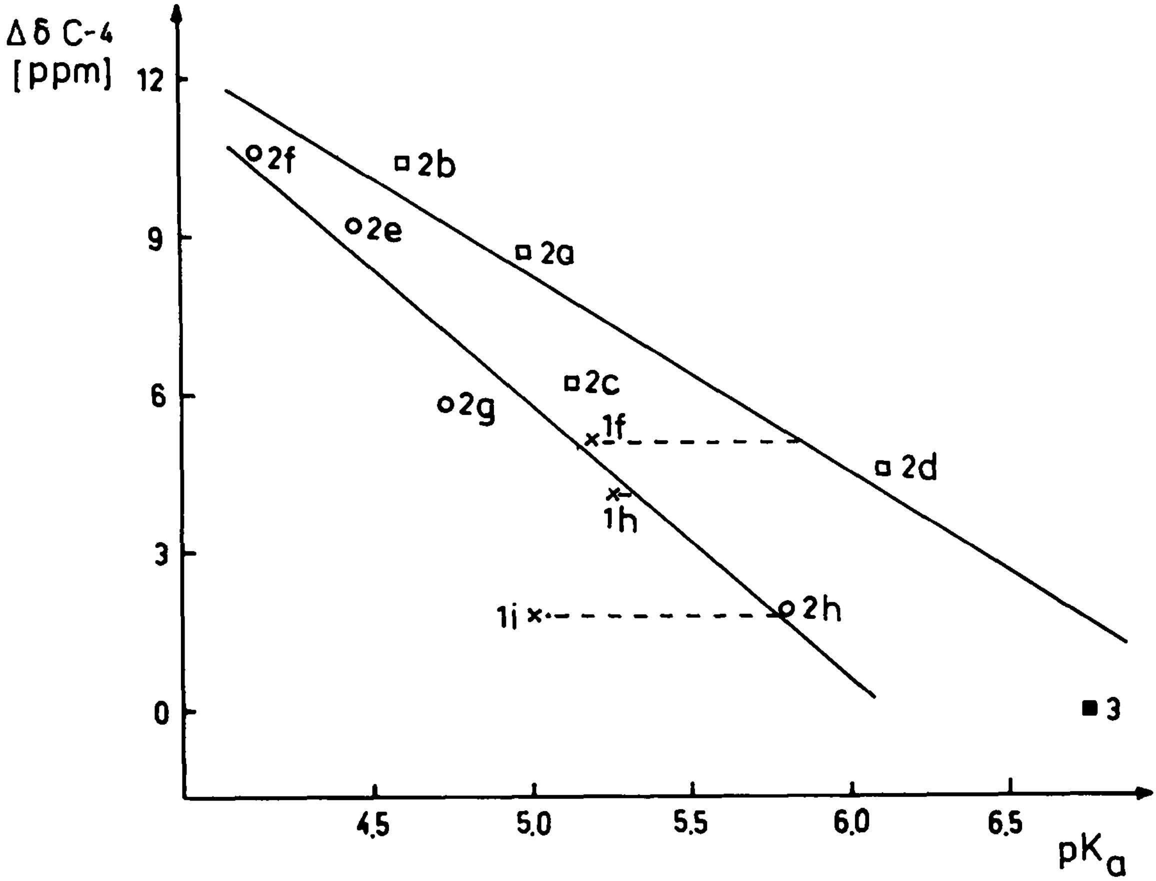


Fig. 2. Correlation of para carbon chemical shift with base strength.

CONCLUSION

Variation of para carbon shifts seem to be a valuable tool for estimating twist angles of anilines.

Whereas no relationship between twist angles so obtained and base strengths has been found in the case of anilines 1, with annelated anilines 2 such a relationship exists. The latter is modified by steric and solvation effects within the anilinium cations.

EXPERIMENTAL

^1H NMR spectra: Jeol JNM-MH-100 spectrometer, TMS internal standard.

^{13}C NMR spectra: Varian XL-100 spectrometer, proton noise decoupled, TMS internal standard. Lanthanide induced shifts were determined by means of Yb $(dpm)_3$ using the relative method.[23] Potentiometric titration in EtOH/H_2O (30/70) was done at 20° (ionic strength I = 0.005-0.002) using an Elpo N-512 pH-meter. The error is estimated to be on the order of ± 0.03 pK_a units.

Compounds 1a, b, c, d, g, j, k, 2a, b are commercially available. They were distilled before use. 1e, f, h, i were prepared by standard methods.[24]

2,3,4,5-Tetrahydro-1H-1-benzazepine (2c)

2c was prepared by a modified procedure of Horning[25]: a solution of 2,3,4,5-tetrahydro-1H-1-benzazepin-2-one[26] (30.0 g, 0.181 mol) in benzene (800 ml) was added to a suspension of $LiAlH_4$ (12.0 g) in benzene (250 ml). The mixture was refluxed with stirring for 2h, cooled and water (5 ml) was added dropwise over a period of 5 min. The precipitate was dissolved by adding a solution of KOH (120 g) in water (200 ml). The aqueous layer was separated and extracted with benzene (5 x 200 ml). The combined benzene solutions were concentrated under reduced pressure and the residue was chromatographed over alumina with petrol ether (b.p.: 60-80°). The solution obtained was concentrated and the residue distilled under reduced pressure, collecting 2c at 125-128°/15 Torr (17.5 g, 64%).

m.p.: 37-39° (m.p.$_{\text{lit.}}$: 32°;[27] b.p.$_{\text{lit.}}$: 131-132°, 16 Torr).[27]

Calc. for $C_{10}H_{13}N$: C, 81.6; H, 8.9; N, 9.5

Found: C, 81.9; H, 9.0; N, 9.1%.

^{1}H NMR (CCl_4): δ 1.3-1.8 (m, 4H); 2.5-3.0 (m, 4H); 3.4 (s, 1H); 6.3-7.0 (m, 4H).

1,2,3,4,5,6-Hexahydro-1-benzazocine (2d)

2d was prepared as described for 2c: a solution of 1,2,3,4,5,6-hexahydro-1-benzoazocin-2-one[26] (5.25 g, 0.03 mol) in benzene (30 ml) was added to a suspension of $LiAlH_4$ (2.2 g) in benzene (100 ml) and refluxed for 35h. 2d was distilled at 131-133°/18 Torr to yield 2.59 g (61%).

Calc. for $C_{11}H_{15}N$: C, 81.9; H, 9.4; N, 8.6

Found: C, 81.7; H, 9.6; N, 8.3%.

^{1}H NMR (CCl_4): δ 1.3-1.7 (m, 6H); 2.6-2.8 (m, 2H); 2.85-3.15 (m, 3H); 6.6-7.0 (m, 4H).

1-Methyl-1,2,3,4,5,6-hexahydro-1-benzazocine (2h)

To 1,2,3,4,5,6-hexahydro-1-benzazocine 2d (1.6 g, 0.010 mol) dissolved in THF (20 ml) was dropped n-butyllithium (0.012 mol) in hexane (7.5 ml) at 0°. After 0.5 h methyl iodide (2.1 g, 0.015 mol) was added. After stirring for 12 h at room temperature petrol ether (15 ml, b.p.: 30-50°) and water (15 ml) were added. The organic layer was separated, washed with water (15 ml) and dried over sodium carbonate. After removal of the solvent the residue was distilled with a Kugelrohr oven at 160°/12 Torr to yield 1.35 g (77%).

Calc. for $C_{12}H_{17}N$: C, 82.3; H, 9.7; N, 8.2

Found: δ C, 82.5; H, 9.5; N, 8.2%.

^{1}H NMR (CCl_4): 1.2-1.7 (m, 6H); 2.5-2.8 (m, 7H); 6.8-7.2 (m, 4H).

1-Methylindoline (2e)

2e was prepared as described for 2h to give a colourless liquid (0.97 g, 73%), b.p. 120°/12 Torr.

^{1}H NMR (C_6D_6): δ 2.59 (s, 3H); 2.72 (t, J = 7.2 Hz, 2H); 3.05 (t, J = 7.4 Hz, 2H); 6.28 (d, J = 7.2 Hz, 1H); 6.53 (t, J = 7.2 Hz, 1H); 6.89 (d, 1H); 6.93 (t, 1H).

1-Methyl-1,2,3,4-tetrahydroquinoline (2f)[29]

2f was prepared as described for 2h to give a colourless liquid (1.04 g, 71%), b.p. 160°/12 Torr.

1-Methyl-2,3,4,5-tetrahydro-1H-1-benzazepine (2g)

2g was prepared as described for 2h to give a colourless liquid, b.p. 160°/12 Torr (0.97 g, 60%).

Calc. for $C_{11}H_{15}N$: C, 81.9; H, 9.4; N, 8.6

Found: C, 81.8; H, 9.2; N, 8.8%

^{1}H NMR (CCl_4): δ 1.4-1.7 (m, 4H); 2.5-2.9 (m, 7H); 6.5-7.0 (m, 4H).

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