INDOLES XIII[1]. SYNTHESES AND STEREOCHEMISTRY OF 14*H*-BISINDOLO[2,3-*a*][3,2-*h*]QUINOLIZINE AND OF SOME BENZ[*a*]-INDOLO[3,2-*h*]QUINOLIZINES

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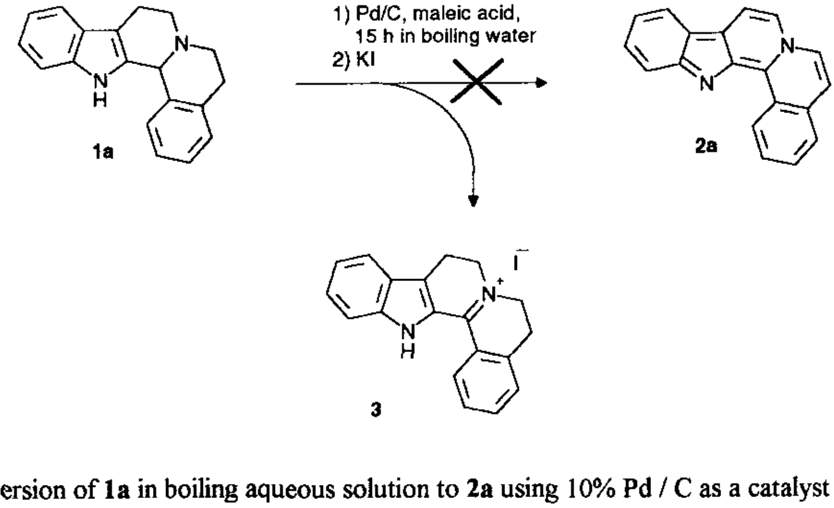
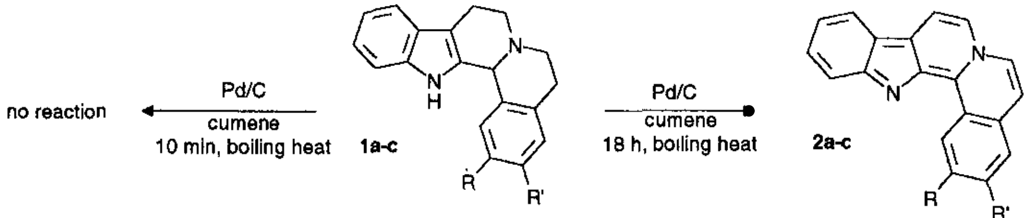
Abstract - Starting from hexahydrobenz[*a*]indolo[3,2-*h*]quinolizines (**1a-c**) and hexahydrobisindolo[2,3-*a*][3,2-*h*]quinolizine (**4**)[2] we succeeded in generating their completely dehydrogenated derivatives. The structures were investigated by ^{1}H- and ^{13}C-nmr spectroscopy as well as by X-ray analysis.

Although the synthesis of the aromatic pentacycle (**2a**) starting from **1a** and applying 10% Pd/C as a catalyst was reported on before,[3] all our efforts to reproduce the author's results failed. Instead the reaction conditions cited in literature[3] led to the formation of cation (**3**) (Scheme 1).



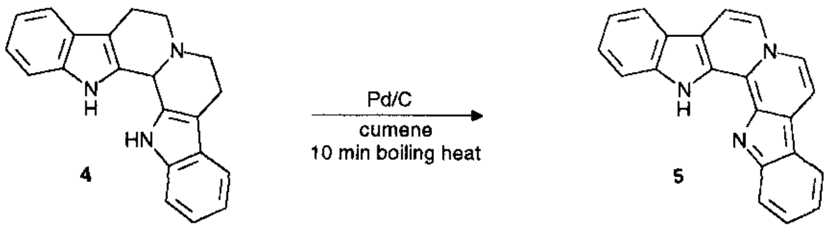
Scheme 1: Conversion of **1a** in boiling aqueous solution to **2a** using 10% Pd / C as a catalyst failed

We found that dehydrogenations were best achieved refluxing the educts with the catalyst (10% Pd/C) in cumene. It took 18 h to convert **1a-c** to their target molecules (**2a-c**), whereas the reaction of **4** was complete within 10 minutes (Schemes 2 and 3). Complete assignement of ^{1}H- and ^{13}C-nmr data (Tables 1 and 2) was possible with the help of HH- and CH-correlation spectra.



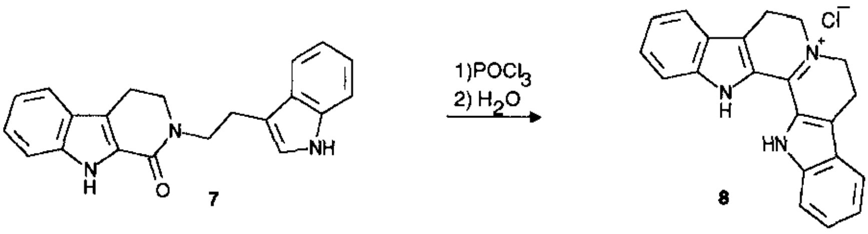
1a,2a: R = R' = H
1b,2b: R = H, R' = OCH_3
1c,2c: R = R' = OCH_3

Scheme 2: Generation of the benz[*a*]indolo[3,2-*h*]quinolizines



Scheme 3: Synthesis of 14*H*-bisindolo[2,3-*a*][3,2-*h*]quinolizine (**5**)

Because it was of some importance in the following discussion of the structure of **5**, the cation (**8**) was prepared starting from the lactam (7) (Scheme 4). The structure of **8** was determined by nmr data.



Scheme 4: Synthesis of the hexahydrobisindolo[2,3-*a*][3,2-*h*]quinolizinium chloride (**8**)

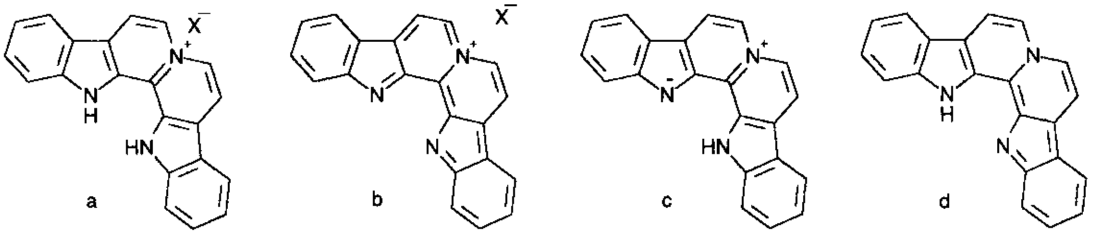
STRUCTURE

The structure is elucidated taking compound (**5**) as an example. There are three different structures of interest which are theoretically conceivable:

a) a cation with its counter-ion (Schemes 5a, b),

b) an internal salt (Scheme 5c),

c) a system carrying no charge at all (Scheme 5d)

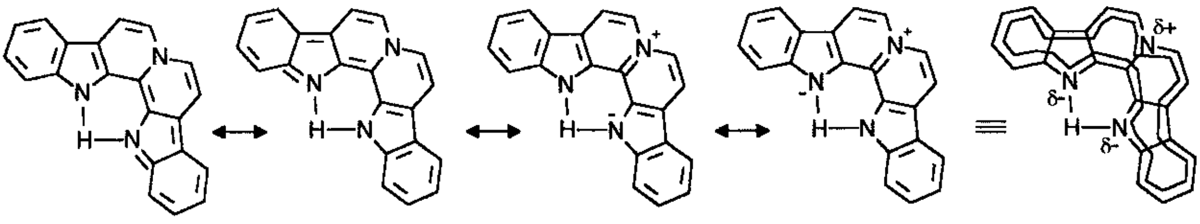


Scheme 5: Possible structures of **5**

Structure in solution: The ^{1}H-nmr spectrum of **5** does neither show any signals between 0 and 6 ppm (except for those emerging from DMSO) nor above 9 ppm. The signals of the water protons and the typical indole NH proton which usually are noticeable at 3.3 and between 10 and 12 ppm respectively are not found in the nmr spectrum of **5**, so the structure in Scheme 5a can be crossed out In contrast to this a broad signal at 6.3 ppm emerges which is not to be seen in the nmr spectrum of the partly dehydrogenated compound (**8**). This low field shift could either be caused by OH^- ions as possible counter-ions (see Schemes 5a,b) or by a NH proton involved in a special mesomeric system including hydrogen bonding.

The mass spectrum (m/z = 307 (100%) and m/z = 308 (25%)) leads us to drop the structure in Scheme 5b , because a peak m/z = 308 in 25% intensity cannot result from a compound with a molecular mass of 306 g/mol ($(M+2)^{2+}/z = 154$). Thus only the structures in Scheme 5c and 5d are left to contemplate on. Comparing the ^{13}C-nmr data of **5** and **8** a positive charge on the nitrogen of the quinolizine moiety may be suggested but considering the investigations of *Park et al* [4,5] a negative charge on the indole nitrogen seems unlikely.

As a result of our observations the best thing to do is to postulate an uncharged aromatic 26π-system comprising mesomeric structures carrying a positive charge on the quinolizine nitrogen and a negative one on one of the indole nitrogens as shown in Scheme 6.

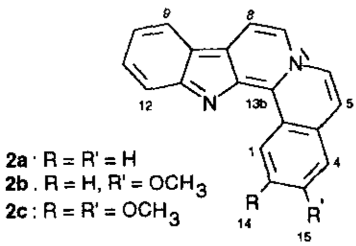


Scheme 6: Supposed structure of **5** in DMSO solution

The same conclusions can as well be drawn for the benzoquinolizines. Their ^{1}H-nmr-spectra don't show any signals of the NH group and no alicyclic signals, due to the 22 π-system of **2**.

The structure in solid state - X-ray analysis: 5 formed crystals suitable for X-ray analysis when it was crystallised from DMSO. In the solid state DMSO is linked to the remaining proton of an indole moiety by H-bonding. The crystals are of red colour, triclinic and their formula unit is $C_{21}H_{13}N_3$•DMSO. A unit cell is established by 4 formula units Let's have a closer look at the unit cell. It consists of 4 formula units but only two of these can be called identical molecules. Curiously the regular crystalline pattern of **5** is formed by two non-identical molecules differing in the position of the proton on the indole nitrogens (either N^{13} or N^{14}). This entails a different position and direction of the bridging DMSO molecules resulting in the formation of the above mentioned non identical enantiomeric compounds. Apart from the position of the DMSO the compounds are planar. The two molecules forming a unit (compare Scheme 9a) that is to say the non-identical compounds, are stacked in a parallel way although they're not congruent but situated as shown in Scheme 9b. Between units that is to say between identical molecules an interplanar angle of 100° can be detected. The average distance between the atoms of the molecules belonging to the same unit is 335 pm approximately. It is therefore within the range of the vertical cross-section of a double bond in an aromatic compound (e.g. 340 pm in benzene). Thus these molecules are situated in the catchment area of their π-electrons and a mutual interaction is established.

NMR DATA AND X-RAY ANALYSIS



2a : R = R' = H
2b . R = H, R' = OCH_3
2c : R = R' = OCH_3

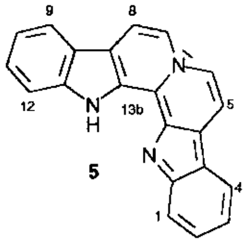


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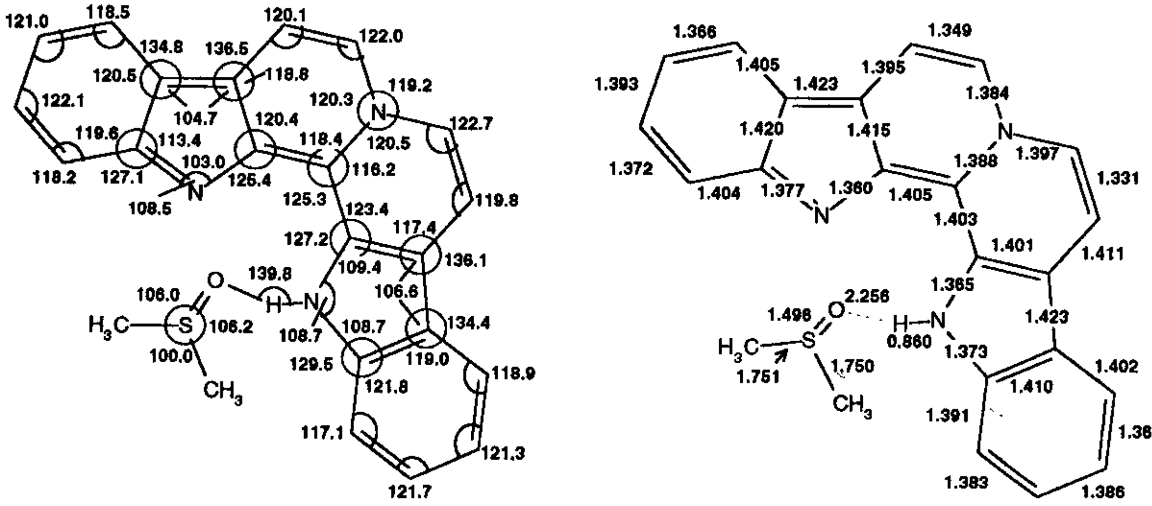
Table 1: ¹H-Nmr shifts of the prepared quinolizines (shifts in ppm, couplings (in brackets) in Hz)

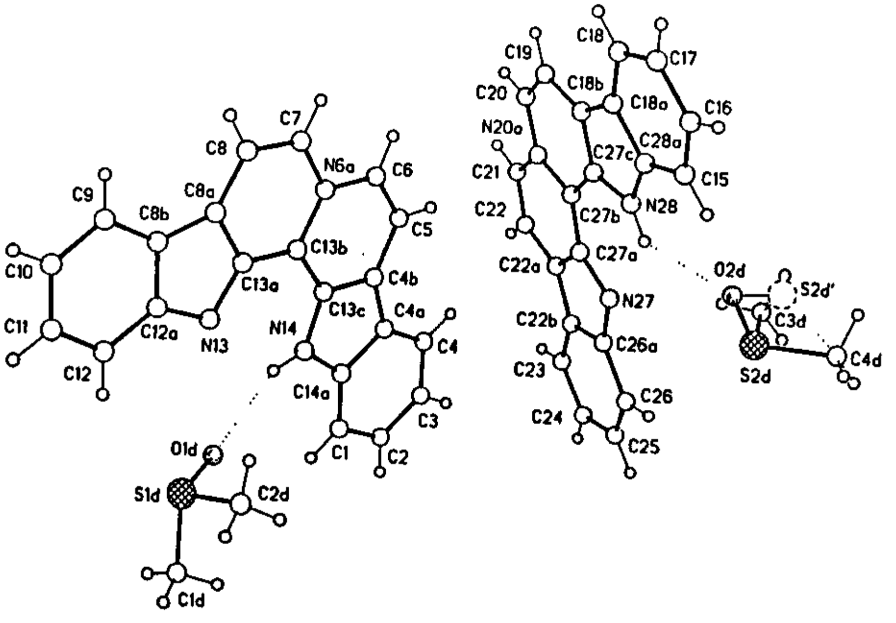
	2a	**2b**	**2c**	**5**
1-H	11.52 d (7.5)	8.68 d (8)	11.27 s	8.10 dt (8, 1)
2-H	8.00 ddd (7.5, 6.5, 1.2)	7 38 dd (8, 2)	-	7.54 ddd (8, 7, 1)
3-H	7.855 td (8.0, 1.5)	-	-	7.28 ddd (8, 7, 1)
4-H	8.02 dd (8.0, 1.2)	7.33 d (2)	7 455 s	8.33 dt (8, 1)
5-H	7.83 d (7.5)	7.74 d (8)	7.68 d (7.5)	8.47 d (7)
6-H	8.83 d (7.5)	8.55 d (8)	8.52 d (7.5)	8.85 d (7)
7-H	8.66 d (7.5)	8.66 d (8)	8.69 d (7.5)	as 6-H: 8.85 d (7)
8-H	8.61 d (7.5)	8.38 d (8)	8.48 d (7.5)	as 5-H· 8.47 d (7)
9-H	8.33 dd (7.5, 1.2)	8.10 d (8)	8.28 dt (7.5, 1)	as 4-H: 8.33 dt (8, 1)
10-H	7.15 ddd (8.5, 6.5, 1.2)	7.28 ddd (7.5, 8, 1)	7.125 ddd (7.5,6.5, 1)	as 3-H: 7.28 ddd (8, 7, 1)
11-H	7.505 ddd (7.5, 6.5, 1.2)	7.55 ddd (7.5, 8, 1)	7.45 ddd (8.5, 6.5, 1)	as 2-H· 7.54 ddd (8, 7, 1)
12-H	7.915 dd (8.4, 1.2)	7.65 d (8)	7.85 dt (8.5, 1)	as 1-H: 8.10 dt (8, 1)
13-H	-	-	-	with water: 6 3
14-H	-	4.13	-	-
15-H	-	3.95	3.85	-

Table 2: ¹³C-Nmr shifts of the prepared quinolizines (shifts in ppm)

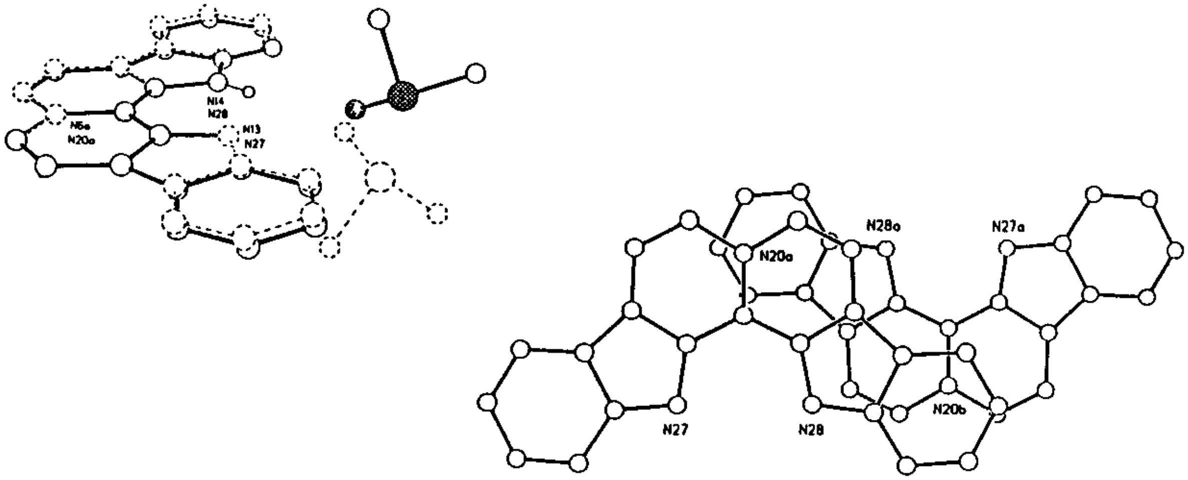
	2a	**2b**	**2c**	**5**
C-1	131.10	131.19	106 98	122 93
C-2	128.99	109.42	151.88	126.26
C-3	130.32	162.41	150.39	116.23
C-4	126.27	121.02	112.05	121.00
C-4a	131 15	129.78	126.57	121.84
C-4b	-	-	-	120.70
C-5	117.99	122 86	117.22	113.51
C-6	131 05	132.26	129.57	119.00
C-7	117.18	121.08	119.14	as C-6: 119.00
C-8	114.59	113.755	114.41	as C-5: 113.51
C-8a	121.51	120.145	121.00	as C-4b: 120.70
C-8b	128.41	128.62	126.69	as C-4a: 121.84
C-9	121.31	121.00	121 26	as C-4:121.00
C-10	117.18	115.26	117.56	as C-3: 116.23
C-11	126.69	129.06	126.04	as C-2: 126.26
C-12	118.76	122.43	121.41	as C-1: 122.93
C-12a	142.85	143.41	142.53	148.10
C-13a	130.00	133.755	131.56	136 00
C-13b	126.71	117.57	121.99	124.62
C-13c	156.17	134.59	155.35	as C-13a: 136.00
C-14	-	-	55.94	-
C-14a	-	-	-	as C-12a. 148.10
C-15	-	56.79	55.75	-



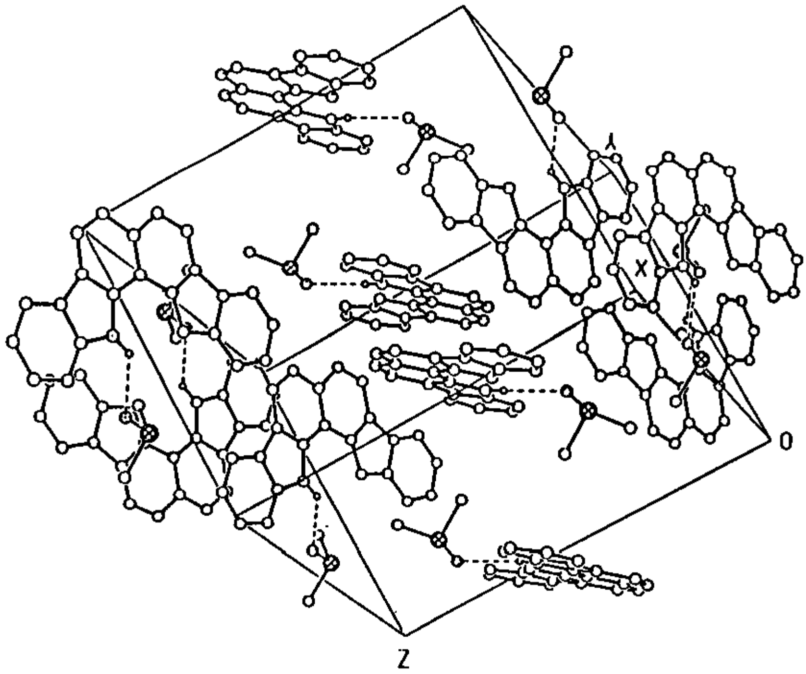
Scheme 7: Data of X-ray analysis: a) binding angles [°] b) bond lengths [Å] of 14-*H*-bisindolo[2,3-*a*][3,2-*h*]-quinolizine (**5**)



Scheme 8: Two molecules of **5** forming one unit



Scheme 9: a) Two molecules of **5** at maximum congruence, b) View of the unit cell illustrating the incongruent stacking of two molecules **5** forming a unit



Scheme 10: View on a unit cell

Let's summarise and point out again: The crystalline structure of **5** is formed by two non-identical molecules which don't carry any charges. This is a strong evidence of the fact that in DMSO solution as well the charged mesomeric structures don't contribute and may be crossed out. Nevertheless it's worthwhile mentioning the fact that one cannot always compare structures and conformations in solution with those in the solid state as crystallisation patterns are often influenced by additional conditions such as the solution properties of the different mesomeric structures involved. Thus conclusions drawn from X-ray experiments may therefore not be valid for solutions of the same compounds.

EXPERIMENTAL

For general materials, methods and the preparation of educts see.[2]

14*H*-Bisindolo[2,3-*a*][3,2-*h*]quinolizine (5)

A solution of 0.62 g (2 mmol) of **4** in 20 ml of distilled cumene is heated to 180°C. A saturated nitrogen atmosphere is generated and 0.4 g of 10% Pd / C are added to the reaction mixture. The resulting dispersion is refluxed for 10 min, cooled rapidly and thereafter diluted by 100 ml of ethanol. The catalyst is collected by vacuum suction and washed well with 750 ml of ethanol. The filtrate and the washing solutions are combined and evaporated until the remaining volume is about 100 ml. A bright orange solid precipitates. The crude product is crystallized from ethanol to yield long needles of orange colour. Yield: 0.23 g (37 %), mp: 286°C, ir (KBr): 3370 (NH), 1635, 1615, 1590, 730 cm^{-1}, nmr: see Tables 1 and 2, ms: 307 (100 %), 308 (25 %), 306 (19 %), 305 (12 %); exact mass. 307.1114 (calcd for $C_{21}H_{13}N_3$: 307.1109)

Benz[*a*]indolo[3,2-*h*]quinolizine (2a)

0.4 g of 10% Pd / C are added to a solution of 0.55 g (2 mmol) of **2** in 12 ml of distilled cumene and refluxed for 18 h at 180°C while a saturated nitrogen atmosphere is maintained. 60 ml of ethanol are added to the cooled dispersion, the catalyst is filtered off and washed with 600 ml of hot ethanol. The organic liquids are evaporated to dryness and 10ml of diisopropyl ether are added to the residue. The resulting mixture is refluxed and diluted with as much ethanol as necessary to solve the precipitated oily crude product. After one night in refrigerator an orange crystalline solid can be filtered off. Yield: 0.15 g (28 %), mp: 212°C, ir (KBr): 1680, 1640, 1605, 1585 cm^{-1}, nmr· see Tables 1 and 2, ms. 269 (20 %), 168 (100 %), 267 (35 %), 44 (15 %); exact mass: 268.1001 (calcd for $C_{19}H_{12}N_2$: 268.1000)

3-Methoxybenz[*a*]indolo[3,2-*h*]quinolizine (2b)

0.6 g (2 mmol) of **1b**, 12 ml of distilled cumene and 0.4 g of 10% Pd / C are reacted as described for compound (**2a**). The combined organic layers are evaporated to a volume that allowes effective collection of the precipitated solid. The crude product is cristallized from ethanol to yield crystals of light yellow colour. Yield: 0.1 g (16 %), mp: 261°-263°C(decomp.), ir (KBr): 1640, 1615, 1595 cm^{-1}, nmr see Tables 1 and 2, ms: 299 (35 %), 298 (100 %), 283 (35 %), 257 (50 %), exact mass: 298.1110 (calcd for $C_{20}H_{14}N_2O$. 298.1106)

2,3-Dimethoxybenz[*a*]indolo[3,2-*h*]quinolizine (2c)

0.67 g (2 mmol) of **1c**, 12 ml of distilled cumene and 0.4 g of 10% Pd / C are reacted as described for compound (**2a**). The crude product is crystallized from ethanol to yield long tiny orange needles which break when filtered. Yield: 0.32 g (49 %), mp. 222.5°-223°C, ir (KBr) 1640, 1610, 1590 cm^{-1}, nmr: see Tables 1 and 2, ms: 329 (40 %), 328 (100 %), 327 (80 %), 297 (60 %); exact mass: 320.1208 (calcd for $C_{21}H_{16}N_2O_3$: 320.1204)

5,6,7,8,13,14-Hexahydrobisindolo[2,3-*a*][3,2-*h*]quinolizinium chloride (8)

Phosphorus oxychloride (60 ml, 0,64 mol) are added to 6.6 g of the lactam (7) (20 mmol) in a 50 ml two necked flask fitted with a reflux condenser and the resulting dispersion is refluxed for 1 h. The flask is cooled by an ice water bath and 280 ml of 10 % sodium hydroxide solution are very slowly added through a dropping funnel. After stirring for 12 h the resulting dispersion is filtered. The dried crude product is crystallized from CH_2Cl_2 / methanol (5:1) and filtered while still hot. The filtrate is allowed to cool slowly, during the process a fluorescent and voluminous light orange solid precipitates. More product can be collected when evaporating some of the filtrate. Yield: 4.5 g (65 %), mp > 350°C, colouring at 280°C, ir (KBr): 3440 (NH), 1620, 1550, 735 cm^{-1}, ^{1}H-nmr (trifluoroacetic acid): 7.7 (broad; 2H), 7.3 (broad; 2H), 7.1 (broad; 4H), 3.95 ppm (broad; 4H), 3.1 ppm (broad; 4H), ^{13}C-nmr (trifluoroacetic acid, couplings are not given here): 149.40, 144.00, 131.26, 128.37, 126.29, 124.66, 124.33, 122.70, 114.70, 52.48, 21.48 ppm, ms: 311 (100 %), 310 (95 %), 309 (98 %), 308 (85 %), 294 (25 %), 36 (28 %, HCl), exact mass. 311.1415 (calcd for $C_{21}H_{17}N_3$ $(m-1)^+$. 311.1423), Anal. Calcd for $C_{21}H_{18}N_3Cl \bullet 1\frac{1}{4}\ H_2O$: C: 68.09, H: 5.49, N: 11.35. Found: C: 68.08, H: 4.92, N: 11.23.

5,6,7,8,13-Pentahydrobenz[*a*]indolo[3,2-*h*]quinolizinium iodide (3)

A mixture of 0.35 g (1.2 mmol) of **1a**, 0.7 g (6.0 mmol) of maleic acid, 0.2 g of 10 % Pd/C and 20 ml of water is refluxed for 15 h. The catalyst is filtered off, washed with a little water and the filtrate is neutralized by sodium bicarbonate. The addition of a saturated solution of potassium iodide leads to the precipitation of a light orange solid. The solid is collected by vacuum suction, dried and crystallized from ethanol. Yield: 0.1 g (30 %), mp 285°C, nmr: 8.8 (s; <1H, NH), 8.1 (d; J = 7 Hz, 1H, H-1), 7.2-8.0 (m; 7H), 4 3 (t; J = 8 Hz, 2H), 4.1 (t; J = 7 Hz, 2H), 3 35 (t; J = 8 Hz, 2H), 3.3 ppm (t; J = 7 Hz, 2H) ms: 273.2 (100%, M^+), 154 (50%), 136 (40%), 107 (15%), Anal. Calcd for $C_{19}H_{16}N_2I \bullet {}^2/_3\ H_2O$: C: 55.31, H: 4.20, N: 6.79. Found: C: 55.07, H· 4.28, N: 6.94.

X-ray analysis of 5

Diffraction data were collected on a Nicolet R3m - diffractometer at 293 K with graphite monochromated MoKα radiation (λ = 0.71073 Å). The crystals (red blocks, 0.90 × 0.45 × 0.40 mm^3) are triclinic, space group $P\bar{1}$ (No. 2) with 4 formula units $C_{21}H_{13}N_3$-DMSO in the unit cell: a = 11.533 (1) Å, b= 11.914 (1) Å, c= 15.948 (2) Å, α = 88.08 (1)°, β = 84.18 (1)°, γ = 62.32 (1)°, V= 1930.3 (4) $Å^3$, ρ (calcd) = 1.326 g / cm^3, μ (CuKα) 0.17 mm^{-1}, F(000) = 806. There were 7059 reflections (ω-scan, scan range 1.93°- 25.05°) collected with 6794 independent (R_{int} = 0.031) and 7059 observed reflections The structure was solved with SHELXTL PLUS by direct methods and refined with full matrix-least squares refinement on F (509 parameters 7 restraints with F^2 (SHELXL-93) to $wR^2 = 0.1273$ ($w^{-1} = \sigma^2 (F_o)^2 + (0.0758\ p)^2$ with $P = (F_o^2 + 2\ F_c^2)/3$; R_1 = 0.050 for $I > 2\sigma$ (I)). The non-hydrogen atoms were refined anisotopically, H-atoms by using a riding model. The absolute structure was modified by Flack parameters (X = -0.09 (8)), the H (N) were refined free.

Table 3: Atomic coordinates (× 10^4) and equivalent isotropic displacement coefficients (Å2 × 10^3) of **5** U(eq) is defined as one third of the trace of orthoganlized Uij tensor

	x	y	z	U(eq)		x	y	z	U(eq)
C(1)	6607(3)	7211(3)	5716(2)	57(1)	C(16)	2183(3)	8915(3)	-472(2)	78(1)
C(2)	7880(3)	6499(3)	5353(2)	65(1)	C(17)	1516(3)	8199(3)	-326(2)	79(1)
C(3)	8157(3)	5725(3)	4653(2)	69(1)	C(18)	2028(3)	7102(3)	125(2)	68(1)
C(4)	7184(3)	5617(3)	4297(2)	64(1)	C(18A	3233(2)	6726(3)	452(2)	53(1)
C(4A)	5878(2)	6326(2)	4641(2)	50(1)	C(18B	4045(2)	5680(2)	945(2)	50(1)
C(4B)	4647(2)	6450(2)	4446(2)	48(1)	C(19)	3982(3)	4603(3)	1289(2)	57(1)
C(5)	4218(3)	5921(2)	3844(2)	60(1)	C(20)	4962(3)	3775(3)	1722(2)	57(1)
C(6)	2945(3)	6246(3)	3857(2)	60(1)	N(20A	6032(2)	3954(2)	1860(1)	47(1)
N(6A)	1989(2)	7115(2)	4442(1)	50(1)	C(21)	7004(3)	3045(2)	2317(2)	53(1)
C(7)	685(3)	7401(3)	4414(2)	60(1)	C(22)	8060(3)	3155(2)	2492(2)	53(1)
C(8)	-279(3)	8217(3)	4970(2)	57(1)	C(22A	8215(2)	4204(2)	2201(1)	45(1)
C(8A)	23(2)	8797(2)	5598(2)	47(1)	C(22B	9134(2)	4655(2)	2282(1)	44(1)
C(8B)	-683(2)	9660(2)	6282(2)	50(1)	C(23)	10301(3)	4202(3)	2669(2)	54(1)
C(9)	-2009(3)	10298(3)	6607(2)	63(1)	C(24)	10980(3)	4892(3)	2611(2)	60(1)
C(10)	-2336(3)	11066(3)	7301(2)	73(1)	C(25)	10512(3)	6032(3)	2172(2)	59(1)
C(11)	-1379(3)	11210(3)	7683(2)	70(1)	C(26)	9374(3)	6507(2)	1791(2)	53(1)
C(12)	-78(3)	10624(3)	7373(2)	60(1)	C(26A	8650(2)	5821(2)	1838(2)	45(1)
C(12A	288(2)	9839(2)	6655(2)	48(1)	N(27)	7498(2)	6120(2)	1496(1)	45(1)
N(13)	1534(2)	9167(2)	6253(1)	44(1)	C(27A	7244(2)	5138(2)	1724(1)	42(1)
C(13A	1347(2)	8538(2)	5626(2)	42(1)	C(27B	6148(2)	5004(2)	1542(1)	42(1)
C(13B	2343(2)	7674(2)	5050(2)	43(1)	C(27C	5132(2)	5849(2)	1080(2)	44(1)
C(13C	3689(2)	7313(2)	5036(2)	43(1)	N(28)	5028(2)	6933(2)	689(1)	48(1)
N(14)	4279(2)	7705(2)	5576(1)	46(1)	C(28A	3884(2)	7474(2)	301(2)	51(1)
C(14A	5611(2)	7116(2)	5349(2)	47(1)	S(2D)	7684(1)	8073(1)	-240(1)	64(1) a)
S(1D)	3478(1)	10235(1)	7470(1)	64(1)	S(2D')	7333(7)	7666(6)	-806(4)	64(1) b)
O(1D)	4340(2)	8904(2)	7159(1)	68(1)	O(2D)	6346(2)	8240(2)	-195(2)	104(1)
C(1D)	4493(4)	10688(4)	7956(3)	102(1)	C(3D)	8761(3)	6464(3)	-435(2)	79(1)
C(2D)	3191(5)	11190(4)	6578(3)	123(2)	C(4D)	7969(4)	8659(3)	-1248(2)	90(1)
C(15)	3368(3)	8573(3)	-170(2)	64(1)					

a) s.o.f.= 0.89(<1); b) s o.f.= 0.11(<1)

Table 4: Hydrogen coordinates (×10^4) and isotropic displacement parameters (Å×10^3) of **5**

	x	y	z	U(eq)
H(1)	6425(3)	7731(3)	6184(2)	68
H(2)	8567(3)	6540(3)	5584(2)	77
H(3)	9024(3)	5269(3)	4421(2)	83
H(4)	7385(3)	5083(3)	3833(2)	76
H(5)	4822(3)	5346(2)	3440(2)	72
H(6)	2680(3)	5880(3)	3460(2)	72
H(7)	467(3)	7020(3)	4001(2)	72
H(8)	-1146(3)	8392(3)	4934(2)	69
H(9)	-2651(3)	10200(3	6356(2)	76
H(10)	-3212(3)	11500(3	7521(2)	88
H(11)	-1630(3)	11721(3	8164(2)	84
H(12)	544(3)	10742(3	7632(2)	72
H(14)	3882(2)	8234(2)	5989(1)	55
H(1D1)	4737(4)	10229(4	8469(3)	153
H(1D2)	4029(4)	11581(4	8081(3)	153
H(1D3)	5270(4)	10504(4	7584(3)	153
H(2D1)	2631(5)	11040(4	6241(3)	184
H(2D2)	4012(5)	10988(4	6253(3)	184
H(2D3)	2771(5)	12066(4	6751(3)	184
H(15)	3811(3)	9055(3)	-275(2)	76
H(16)	1812(3)	9649(3)	-786(2)	93
H(17)	708(3)	8469(3)	-538(2)	95
H(18)	1584(3)	6620(3)	211(2)	82
H(19)	3267(3)	4466(3)	1217(2)	68
H(20)	4921(3)	3058(3)	1937(2)	68
H(21)	6917(3)	2339(2)	2507(2)	64
H(22)	8686(3)	2539(2)	2804(2)	63
H(23)	10610(3)	3445(3)	2962(2)	64
H(24)	11758(3)	4601(3)	2865(2)	72
H(25)	10993(3)	6482(3)	2139(2)	71
H(26)	9082(3)	7269(2)	1505(2)	63
H(28)	5585(2)	7223(2)	687(1)	57
H(3D1)	8732(3)	5987(3)	58(2)	118 a)
H(3D2)	8500(3)	6171(3)	-900(2)	118 a)
H(3D3)	9639(3)	6350(3)	-569(2)	118 a)
H(3D4)	8564(3)	5828(3)	-170(2)	118 b)
H(3D5)	9426(3)	6088(3)	-897(2)	118 b)
H(3D6)	9073(3)	6814(3)	-32(2)	118 b)
H(4D1)	7438(4)	9562(3)	-1253(2)	136 a)
H(4D2)	8881(4)	8454(3)	-1349(2)	136 a)
H(4D3)	7742(4)	8276(3)	-1680(2)	136 a)
H(4D4)	7280(4)	9384(3)	-1484(2)	136 b)
H(4D5)	8309(4)	8933(3)	-817(2)(	-817(2)
H(4D6)	8662(4)	8207(3)	-1682(2)	136 b)

a) s.o.f. = 0.89 (<1); b) s.o.f. = 0.11 (<1)

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