A Novel Ring Enlargement of 2*H*-Azirine-3-methyl(phenyl)amines *via* Amidinium-Intermediates: A New Synthetic Approach to 2,3-Dihydro-1,3,3-trimethylindol-2-one [1]*

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2*H*-Azirin-3-amines, Ring Enlargement, 2,3-Dihydroindol-2-ones

2,2,*N*-Trimethyl-*N*-phenyl-2*H*-azirin-3-amine (**1a**) was prepared by successive treatment of 2,*N*-dimethyl-*N*-phenylpropanamide (**18**) with phosgene, triethylamine, and sodium azide. Reaction of **1a** in THF solution with boron trifluoride gave 2-amino-1,3,3-trimethyl-3*H*-indolium tetrafluoroborate (**19**) in high yield. The latter reacted with acetic anhydride in pyridine to give a mixture of *N*-(2,3-dihydro-1,3,3-trimethylindol-2-yliden)acetamide (**22**) and 2,3-dihydro-1,3,3-trimethylindol-2-one (**21**). On hydrolysis with aqueous HCl, **22** was converted to **21**. The molecular structures of **19** and **22** were established by X-ray crystal structure determination.

Introduction

Since the first synthesis of a 2*H*-azirin-3-amine by Rens and Ghosez [2], these compounds have proven to be versatile building blocks for the preparation of heterocycles as well as of peptides containing α,α-disubstituted glycines [3]. It has been shown that, depending on the reaction conditions, each of the three ring bonds can be cleaved selectively leading to reactive intermediates such as nitrile ylides and 2-azabuta-1,3-dienes (C-C cleavage) and 1-azaallyl cations (C-N cleavage). In the case of the cleavage of the C=N bond, α-amino acid derivatives are formed *via* an intermediate aziridine (*cf.* [3]). For example reactions of **1** with Brønsted acids proceed *via* protonation of the ring N-atom to give the amidinium intermediate **2** (Scheme 1). Ring opening by cleavage of the original C-N bond leads to acrylamidine derivatives **4**, with the azaallyl cations **3** being likely intermediates [2, 4, 5]. On the other hand, the competing addition of a nucleophile, *e.g.* a carboxylate, onto **2** yields an aziridine **5** which rearranges to a 2-(acylamino)carboxamide **6** (*cf.* [6–9] and refs. cited therein).

Of special interest are reactions of **1** with NH-acidic heterocycles ($pK_a < 8$) leading to new heterocycles with a ring enlarged by three atoms (N-C-C). This rather general ring enlargement reaction proceeds *via* an intermediate aziridine of type **8** followed by two consecutive ring expansions (**8**→**9**→**10**, Scheme 2) [10]. Examples for 7- to 12-membered products **10**–**12**, obtained from 4- to 9-membered starting materials (*e.g.* 4,4-dialkylisoxazolidin-3-one [11] and 3-oxosultams of different ring size [3, 12–16]) are shown in Scheme 2.

The reaction of **1** with trifluoroacetamide gives 4*H*-imidazoles **15a** [17]. A conceivable reaction mechanism *via* aziridine **13** and zwitterion **14** which parallels that of the ring enlargement **7**→**10** is shown in Scheme 3. A serious limitation of this reaction is the acidity of the amides as only substances with $pK_a < 8$ are able to activate **1** by protonation (pK_b of **1**, R^1–R^4 = Me: 7.1 [18]). Therefore, neither benzamide nor acetamide react with **1**. Recently, we were able to overcome this hurdle by activating **1** with boron trifluoride. This complex **16** was shown to react at low temperature

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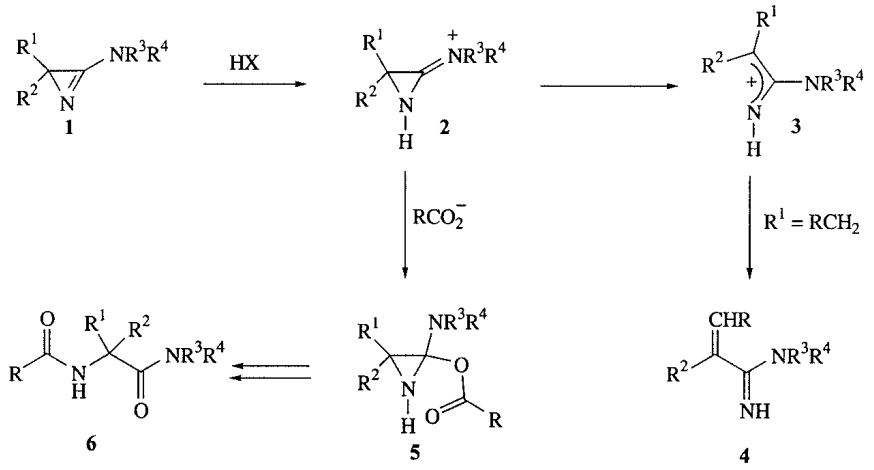
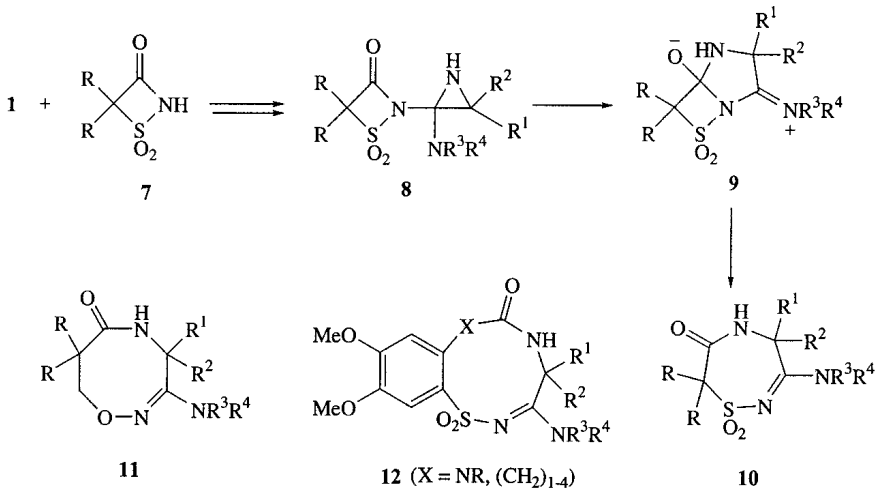


Scheme 1.

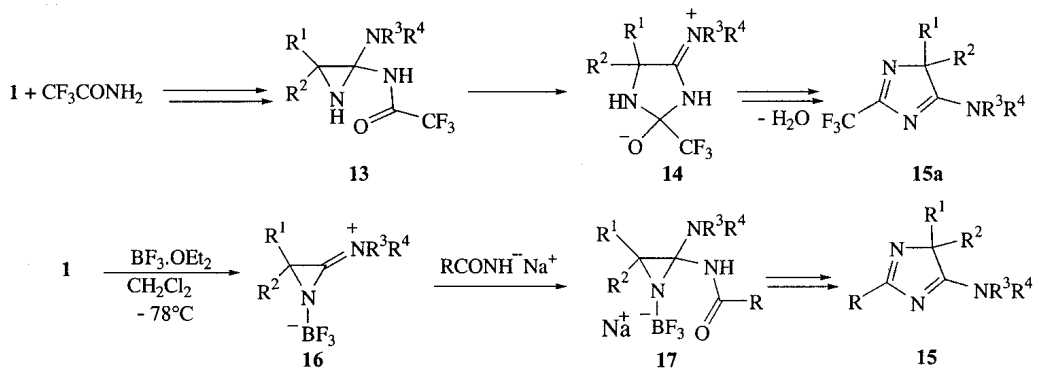


Scheme 2.

with the sodium salt of carboxamides to give the corresponding 4*H*-imidazoles **15** (Scheme 3). We propose that aziridine **17** is an intermediate that undergoes a ring enlargement analogous to **13**→**14**→**15a**.

The activation of **1** by treatment with boron trifluoride has also been used in the reactions with enolates of esters, thioesters, and carboxamides to give 1,5-dihydro-2*H*-pyrrol-2-ones, and even the enolate of acetophenone reacts with the BF_3-complex of **1** leading to a 2*H*-pyrrol-3-amine derivative [19]. Furthermore, these complexes undergo reactions with α-amino acid esters in which 3,6-dihydropyrazin-2(1*H*)-ones are formed as the main product; the same products are obtained when 2*H*-azirin-3-amines **1** are reacted with α-amino acid ester hydrochlorides [20].

In the present paper, we present the first results of a novel ring enlargement reaction of 2,2,*N*-trimethyl-*N*-phenyl-2*H*-azirin-3-amine (**1a**, R^1–R^3 = Me, R^4 = Ph) with BF_3 in the absence of external nucleophiles leading to a 2,3-dihydroindol-2-one (indoline-2-one).

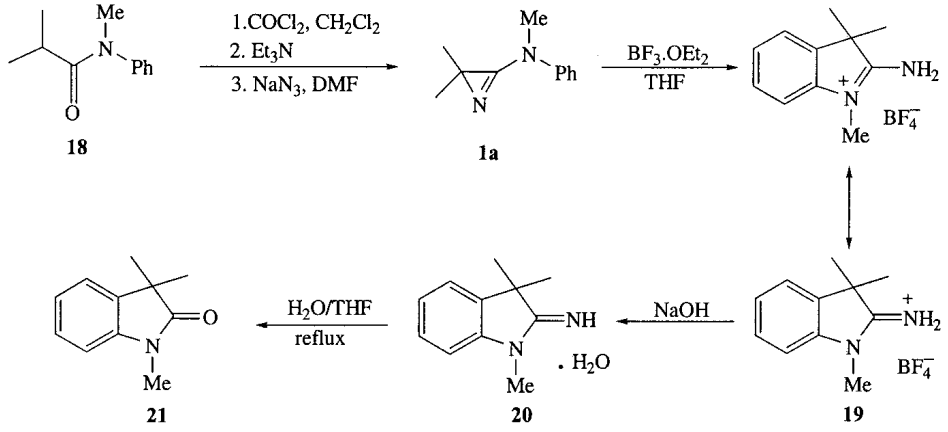


Scheme 3.

Results and Discussion

The starting material **1a** [21] was prepared from 2,*N*-dimethyl-*N*-phenylpropanamide (**18**) according to the protocol of Rens and Ghosez [2] (see also [3, 22]). Addition of an equimolar amount of $BF_3.OEt_2$ to a stirred solution of **1a** in THF or Et_2O at −78 °C gave 2-amino-1,3,3-trimethyl-3*H*-indolium tetrafluoroborate (**19**) in up to 81.5% yield as colorless crystals (m.p. 246.5–247.7 °C) (Scheme 4). The structure of the product has been established on the basis of its spectroscopic data, elemental analysis, and an X-ray crystal structure analysis (Fig. 1). The most characteristic data are three strong absorptions at 1695, 1680, and 1610 cm^{-1} in the IR spectrum (KBr), two NH signals (δ = 10.07 and 9.77 ppm), a singlet for MeN at δ = 3.49 ppm (^{1}H NMR, D_6-DMSO), and a singlet at δ = 175.6 ppm (^{13}C NMR, D_6-DMSO) for C(2) of the indolium ring. In the crystal structure, the extraannular N(2)–C(2) bond is slightly shorter (1.305(4) Å) than the intraannular N(1)–C(2) bond (1.333(4) Å, Table 1), which suggests delocalization of the formal double bond and the cationic charge across the N(1)–C(2)–N(2) region of the cation. The ring system of the indolium cation is planar including the Me group at N(1). Each H atom of the terminal amino group forms an interionic hydrogen bond with an F atom; the two interactions being with different anions. These interactions link two cations and two anions into a centrosymmetric $C^+\cdots A^-\cdots C^+\cdots A^-$ loop with a secondary graph set motif [24] of R_4^4 (12). The unitary graph set motif for each individual interaction is D.

Treatment of an aqueous solution of **19** at 0 °C with aqueous NaOH (30%) and extraction with dichloromethane gave a yellow oily substance **20**



Scheme 4.

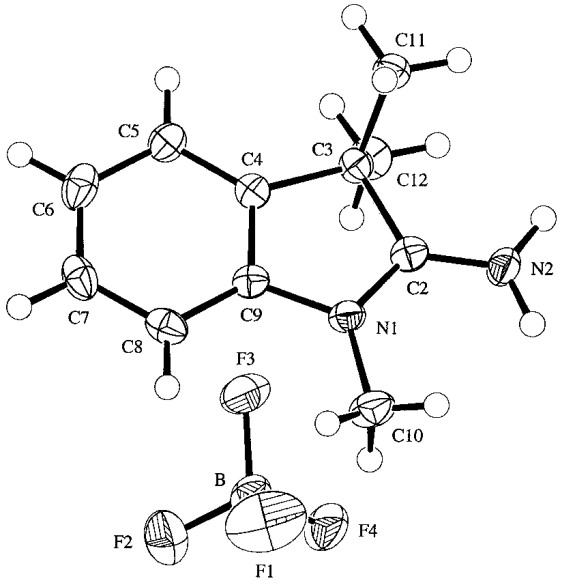


Fig. 1. ORTEP plot [23] of the molecular structure of **19** (arbitrary numbering of the atoms; 50% probability ellipsoids).

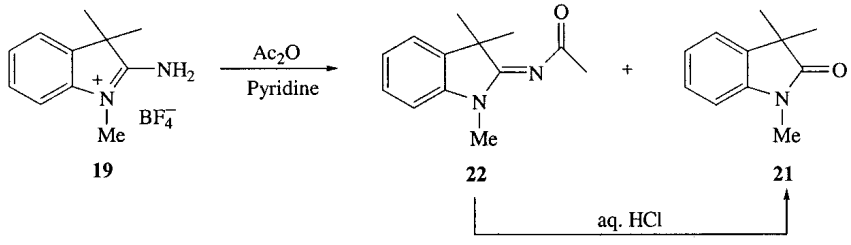
which, according to the spectroscopic data and elemental analysis, is either a hydrate of 2,3-dihydro-1,3,3-trimethylindol-2-imine or the corresponding indolium hydroxide. This product was transformed to the known [25] 2,3-dihydro-1,3,3-trimethylindol-2-one (**21**, Scheme 4) in modest yield upon refluxing in H_2O/THF.

Reaction of the tetrafluoroborate **19** with acetic anhydride in pyridine at ca. 23 °C for 16 h, followed by aqueous workup and chromatographic separation led to *N*-(2,3-dihydro-1,3,3-trimethylindol-2-yliden)acetamide (**22**) and **21** as colorless crystals (m.p. 61.8–62.1 and 49.7 °C, respectively) in a ratio of ca. 2:1 (Scheme 5). Most likely, the *N*-acetyl derivative **22** has partly been hydrolysed under the workup conditions. Compound **22** could also be obtained from **20** when the latter was treated with acetic anhydride in pyridine. Hydrolysis of **22** with aqueous HCl gave the indolin-2-one **21**.

The structure of **22** was determined on the basis of the spectroscopic data and elemental analysis. The IR spectrum (KBr) shows strong absorptions at 1711, 1651, and 1606 cm^{-1}. Three signals for Me groups appear in the ^1H and ^{13}C NMR spectra ($CDCl_3$): at δ = 3.20/27.3 ppm for MeN, at 2.29/28.3 for MeCO, and at 1.51/25.9 for $Me_2C(3)$. It is worth mentioning that the two Me groups at C(3) show only one signal, *i.e.* the N-acetyl group freely rotates under the NMR conditions. In the EI-MS, the most characteristic peaks are at *m*/*z* 216 ($M^{+\cdot}$), 201, 186, 175, and 160. Finally, the structure was proved by an X-ray crystal structure determination (Fig. 2). The fused rings form an almost planar system. Atom N(2) of the exocyclic C=N bond deviates significantly by 0.21Å from this plane and the C=O bond is not coplanar with the C=N bond [torsion angle O(11)–C(11)–N(2)–C(2) 62.5(3)°], which indicates reduced conjugation in this region of the molecule. For a comparison, the C,N-bond lengths of **19** and **22** are listed in Table 1.

Reaction mechanisms

Although we have previously studied BF_3-catalyzed reactions of 2*H*-azirin-3-amines **1** in the presence of nucleophilic reagents, the ring enlargement to indole derivatives described in the present paper has never been observed before. Obviously, the external nucleophiles react efficiently by addition onto the amidinium C atom to give an aziridine (*cf.* **17**, Scheme 3). The ring opening to a 1-azaallyl cation has only been observed for protonation in the absence of a nucleophile (Scheme 1). In the presently described ring enlargement of **1a** to the indole derivative **3**, the N-



Scheme 5.

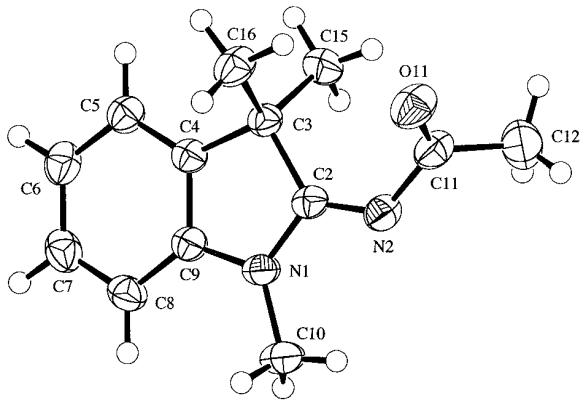


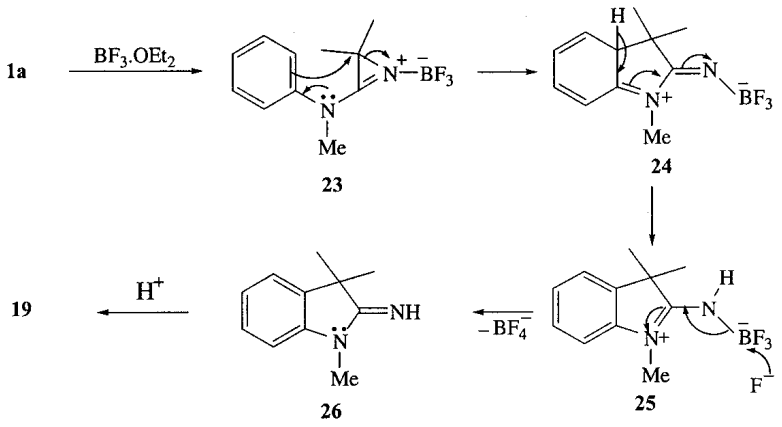
Fig. 2. ORTEP plot [23] of the molecular structure of **22** (arbitrary numbering of the atoms; 50% probability ellipsoids).

Table 1. CN bond lengths (Å) in the crystal structures of **19** and **22**.

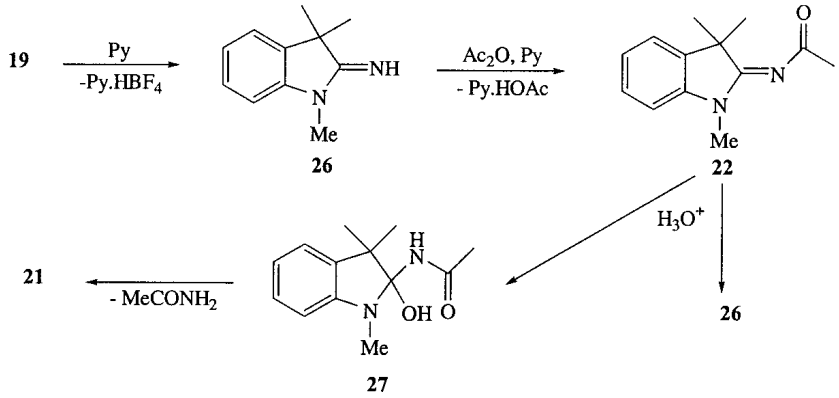
Atom	**19**	**22**
N(1)–C(2)	1.333(4)	1.370(2)
N(1)–C(9)	1.422(4)	1.405(2)
N(1)–C(10)	1.462(4)	1.455(2)
N(2)–C(2)	1.305(4)	1.282(2)
N(2)–C(11)		1.386(2)

phenyl residue acts as an internal nucleophile. The BF_3-complex **23** can undergo the ring enlargement to **25** by an intramolecular electrophilic aromatic substitution (Scheme 6). Alternatively, the ring-opening of **23** to the corresponding 1-azaallyl cation is conceivable, the latter being attacked by the phenyl ring to give **24**. The decomplexation of **25** can occur by a reaction with fluoride ion, which has possibly been generated from BF_3 and traces of water. This could explain the formation of the tetrafluoroborate **19**.

Although the hydrolysis of the tetrafluoroborate **19** to indolin-2-one **21** can be achieved by treatment with NaOH followed by refluxing in H_2O/THF, the procedure *via* the acetylated **22** gave more satisfying results. The latter was partly hydrolyzed during the washing of the chloroform solution with water, complete hydrolysis was achieved on treatment with aqueous HCl. It is likely that the intermediate **27** is formed which



Scheme 6.



Scheme 7.

leads to the product by elimination of acetamide (Scheme 7). On the other hand, the de-acetylation to **26** and subsequent hydrolysis of the amidine group cannot be excluded.

Conclusions

With the presented results, a novel ring enlargement reaction of *N*-phenyl-2*H*-azirin-3-amines has been established. This reaction, leading to 2-amino-2,3-dihydro-1,3,3-trimethylindolium tetrafluoroborate (**19**) opens a new access to 1,3,3-trisubstituted indolin-2-ones. Among a multitude of biologically active indole derivatives, compounds containing the indolinone ring system are very common, *e.g.* some cardiotonics [26, 27]. Furthermore, N-alkylated indolin-2-ones show adrenergic potentiating activity, and some antidepressant compounds were prepared from *N*-phenylindolin-2-ones as well as from *N*-phenylindolines [28]. Indolin-2-ones are also useful intermediates in alkaloid synthesis, *e.g.* the Calabar bean alkaloid [29] physostigmin [30] (latest published syntheses [31] (racemic), [32] (enantioselective)) which is considered to be one of the first compounds to be recognized as an acetyl choline-blocking agent and is used clinically in the treatment of glaucoma [33].

Experimental Section

General

Thin-layer chromatography (TLC): Merck TLC aluminium sheets, silica gel 60 F_{254}. Preparative TLC: Merck PLC plates (glass), silica gel 60 F_{254}, 2 mm. Column chromatography (CC): Uetikon-Chemie Chromatographiegel C-560. High performance liquid chromatography (HPLC): Varian-590, Nucleosil 100–7; detection at λ = 254 nm. M.p. Mettler-FP-5 apparatus or Büchi 510 apparatus; uncorrected. IR Spectra: Perkin-Elmer-781 spectrophotometer or Perkin-Elmer-1600-FT-IR spectrophotometer; in KBr unless otherwise stated. ^{1}H (300 MHz) and ^{13}C NMR (75.5 MHz) Spectra: Bruker ARX-300 instrument; at 300 K; ^{13}C signal multiplicity from DEPT spectra. MS: Finnigan SSQ-700 or MAT-90 instrument for CI.

*2,2,*N-*Trimethyl*-N-*phenyl*-2H-*azirin-3-amine* (**1a**) [21]

A solution of 2,*N*-dimethyl-*N*-phenylpropanamide (**18**) in CH_2Cl_2 was treated with $COCl_2$ followed by HCl elimination using Et_3N. The resulting 2-chloroenamine was purified by distillation, dissolved in diethyl ether (Et_2O) and reacted with NaN_3 to give **1a** in 60–70% yield.

2-Amino-2,3-dihydro-1,3,3-trimethylindolium tetrafluoroborate (**19**)

To a stirred solution of **1a** (484 mg, 2.4 mmol) in THF (60 ml) at –78 °C, $BF_3 \cdot OEt_2$ (0.63 ml of approx. 48% BF_3 in Et_2O, ca. 2.4 mmol) was added. Then, the solution was allowed to warm up slowly to ca. 23 °C, and stirred for 12 h. After addition of Et_2O, a colorless precipitate was formed, which was filtered and recrystallized from ethanol (EtOH): 463 mg (68.6%) of **19**; colorless crystals, m.p. 246.5–247.7 °C.

In an analogous experiment with 174 mg (1.0 mmol) of **1a** in 25 ml of Et_2O, a colorless precipitate was formed during the addition of ca. 1 mmol of $BF_3 \cdot OEt_2$ at –78 °C. After warming up to 23 °C, the mixture was stirred for 12 h, filtered, and the residue was recrystallized from EtOH to

give 214 mg (81.5%) of **19**. IR (KBr): ν = 3390*m*, 3315*m*, 3240*m*, 3200*m*, 3160*s*, 3100*s*, 3040*s*, 2960*s*, 1695*s*, 1680*s*, 1615*s*, 1505*s*, 1470*s*, 1430*s*, 1370*m*, 1355*s*, 1305*s*, 1260*s*, 1205*s*, 1120*s*, 1080*s*, 1030*s*, 940*w*, 865*w*, 765*s*, 740*m*, 695*m*, 660*s* cm^{-1}. ^1H NMR (D_6-DMSO): δ = 10.07 (*s*, NH), 9.77 (*s*, NH), 7.51 (*d-like*, 1 arom. H), 7.41 (*t-like*, 1 arom. H), 7.30 (*d-like*, 1 arom. H), 7.24(*t-like*, 1 arom. H), 3.49 (*s*, CH_3N), 1.52 (*s*, 2 CH_3). ^{13}C NMR (D_6-DMSO): δ = 175.6 (*s*, N=C-NH_2), 141.2, 136.5 (2*s*, 2 arom. C), 128.4, 124.8, 122.4, 110.7 (4*d*, 4 arom. CH), 46.8 (*s*, C-3), 29.3 (*q*, CH_3N), 24.0 (*q*, 2 CH_3). CI-MS: *m*/*z* (%) = 175 (2, $[M\text{-}BF_4]^+$), 159 (4). Analysis for $C_{11}H_{15}BF_4N_2$ (262.05): calcd. C 50.42, H 5.77, N 10.69; found: C 50.35, H 5.76, N 10.76.

2-Amino-2,3-dihydro-1,3,3-trimethylindole hydrate (**20**)

A solution of **19** (100 mg, 0.38 mmol) in the least amount of water was cooled to 0 °C, and 10 ml of aqueous NaOH (30%) were added. The mixture was stirred for 20 min and extracted with CH_2Cl_2. The organic phase was washed with brine and dried over Na_2SO_4 to give 67 mg (92%) of **20** as a yellow oil. IR (film): ν = 3300*m*, 3060*w*, 2970*m*, 2930*m*, 2870*w*, 1645*s*, 1610*s*, 1500*s*, 1470*s*, 1460 *m*, 1390*m*, 1365*m*, 1310*m*, 1250*w*, 1220*w*, 1185*w*, 1160*w*, 1120*s*, 1075*m*, 1020*m*, 1005*m*, 940*m*, 860*w*, 780*w*, 750*s*, 700*m*, 630*m* cm^{-1}. ^1H NMR (D_6-DMSO): δ = 7.22–7.12, 6.89–6.79 (2*m*, 4 arom. H), 3.12 (*s*, CH_3N), 1.28 (*s*, 2 CH_3). ^{13}C NMR (D_6-DMSO): δ = 174.7 (*s*, N=C-NH_2), 144.6, 135.8 (2*s*, 2 arom. C), 127.5, 121.8, 119.9, 106.5 (4*d*, 4 arom. CH), 43.6 (*s*, C-3), 26.5 (*q*, CH_3N), 26.2 (*q*, 2 CH_3). ^1H NMR ($CDCl_3$): δ = 7.17 (*t-like*, 1 arom. H), 7.08 (*d-like*, 1 arom. H), 6.88 (*t-like*, 1 arom. H), 6.66 (*d-like*, 1 arom. H), 3.19 (*s*, CH_3N), 1.29 (*s*, 2 CH_3). ^{13}C NMR ($CDCl_3$): δ = 177.0 (*s*, N=C-NH_2), 144.4, 135.8 (2*s*, 2 arom. C), 127.7, 121.9, 120.7, 106.8 (4*d*, 4 arom.CH), 44.6 (*s*, C-3), 27.1 (*q*, CH_3N), 26.6 (*q*, 2 CH_3). CI-MS: *m*/*z* (%) = 176 (12), 175 (100, $[M\text{-}NH_3]^+$ or $[M\text{-}OH]^+$). Analysis for $C_{11}H_{16}N_2O$ (192.26): calcd. C 68.72, H 8.39, N 14.57; found C 68.40, H 8.29, N 14.18.

N-*(2,3-Dihydro-1,3,3-trimethylindol-2-yliden)-acetamide* (**22**)

To a solution of **19** (300 mg, 1.14 mmol) in pyridine (3 ml), acetic anhydride (Ac_2O, 3 ml) was added and the mixture was stirred at ca. 23 °C for 16 h. Then, the solvent was evaporated and the residue dissolved in $CHCl_3$, washed with H_2O and brine, and dried over Na_2SO_4. After filtration, evaporation and column chromatography (hexane/Et_2O 5:2), the two products were purified by means of HPLC (Nucleosil 100–7, hexane/ethyl acetate 10:3, 0.5 ml/min, 13 atm): 80 mg (37.0%) of **22** as colorless crystals, m.p. 61.8–62.1 °C. IR (KBr): ν = 3055*w*, 2969*m*, 2929*m*, 2869*w*, 1711*s*, 1651*s*, 1606*s*, 1494*s*, 1472*s*, 1460*s*, 1428*m*, 1385*s*, 1353*s*, 1306*m*, 1287*m*, 1248*m*, 1212*s*, 1158*m*, 1128*s*, 1079*m*, 1045*w*, 1019*m*, 1000*w*, 947*s*, 856*w*, 802*w*, 754*s*, 709*w*, 699*w* cm^{-1}. ^1H NMR ($CDCl_3$): 7.25 (*t-like*, 1 arom. H), 7.15 (*d-like*, 1 arom. H), 7.03 (*t-like*, 1 arom. H), 6.81 (*d-like*, 1 arom. H), 3.20 (*s*, CH_3N), 2.29 (*s*, $COCH_3$), 1.51 (*s*, 2 CH_3). ^{13}C NMR ($CDCl_3$): 181.8 (*s*, N-C=O), 165.8 (*s*, N-C=N), 143.0, 136.9 (2*s*, 2 arom. C), 127.7, 122.1, 121.5, 107.8 (4*d*, 4 arom. CH), 46.8 (*s*, C-3), 28.3, 27.3 (2*q*, $COCH_3$, CH_3N), 25.9 (*q*, 2 CH_3). EI-MS: *m*/*z* (%) = 216 (34, $M^{+\cdot}$), 215 (31), 201 (57), 186 (25), 175 (57), 160 (100).

As a minor compound, 40 mg (20.0%) of *2,3-dihydro-1,3,3-trimethylindol-2-one* (**21**) were obtained as colorless crystals, m.p. 49.7 °C ([25]: 50 °C). IR (KBr): ν = 3060*w*, 2960*m*, 2920*w*, 2860*w*, 1720*s*, 1615*s*, 1495*s*, 1470*m*, 1460*m*, 1380*s*, 1375*m*, 1350*s*, 1310*m*, 1250*m*, 1125*s*, 1070*m*, 1045*w*, 1020*w*, 940*w*, 760 *m*, 745*m*, 700*m* cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.16 (*t-like*, 1 arom. H), 7.12 (*d-like*, 1 arom. H), 6.96 (*t-like*, 1 arom. H), 6.75 (*d-like*, 1 arom. H), 3.12 (*s*, CH_3N), 1.30 (*s*, 2 CH_3). ^{13}C NMR ($CDCl_3$): (see [34]). Analysis for $C_{11}H_{13}NO$ (175.23): calcd. C 75.40, H 7.48, N 7.99; found: C 75.21, H 7.41, N 7.79.

Hydrolysis of **20** *and* **22**. A solution of **20** (100 mg, 0.52 mmol) in H_2O/THF (1:1 *v*/*v*, 15 ml each) was refluxed for 3 days and extracted with Et_2O. The organic phase was washed with brine and dried over Na_2SO_4 to give 86 mg (94%) of **21**.

A solution of **22** (50 mg, 0.23 mmol) in 10% HCl (5 ml) was refluxed for 1 h and extracted with Et_2O. The organic phase was washed with aqueous $NaHCO_3$ solution, brine, and dried over Na_2SO_4 to give 37 mg (91%) of **21**.

X-Ray crystal-structure determination of **19** *and* **22** (see Figs 1 and 2, Table 2) [35].

All measurements were made on a *Rigaku AFC5R* diffractometer using graphite-monochromated Mo–K_α radiation (λ 0.71069Å) and a 12 kW rotating anode generator. The data collection and refinement parameters are given in Table 2, and views of the molecules are shown in Figs 1 and 2. The intensities were corrected for Lorentz and polarization effects and, in the case of **19**, an empirical absorption correction based on azimuthal scans of several reflections [36] was applied. Each structure was solved by direct methods using SIR 92 [37] for **19** and SHELXS 97 [38] for

Table 2. Crystallographic data for compounds **19** and **22**.

	19	**22**
Crystallized from	EtOH	hexane
Empirical formula	$C_{11}H_{15}BF_4N_2$	$C_{13}H_{16}N_2O$
Formula weight [g mol^{-1}]	262.06	216.28
Crystal color, habit	colorless, prism	colorless, prism
Crystal dimensions [mm]	0.20 × 0.25 × 0.40	0.25 × 0.28 × 0.40
Temperature [K]	173(1)	173(1)
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
Z	4	2
Reflections for cell determination	25	25
2θ Range for cell determination [°]	35–40	37–39
Unit cell parameters a [Å]	21.485(2)	8.526(1)
b [Å]	6.371(2)	9.947(2)
c [Å]	9.295(1)	8.492(2)
α [°]	90	103.68(2)
β [°]	102.564(8)	118.68(1)
γ [°]	90	93.64(2)
V [Å^3]	1241.9(3)	600.5(2)
D_x [g cm^{-3}]	1.401	1.196
μ(Mo–K$_\alpha$) [mm^{-1}]	0.125	0.0769
Scan type	ω / 2θ	ω / 2θ
$2\theta_{(max)}$ [°]	55	55
Total reflections measured	3190	2935
Symmetry independent reflections	2853	2750
Reflections used [$I > 2\sigma(I)$]	1780	2144
Parameters refined	164	146
Final R	0.0590	0.0469
wR ($w = [\sigma^2(F_o) + (0.005F_o)^2]^{-1}$)	0.0504	0.0491
Goodness of fit	2.376	2.401
Secondary extinction coefficient	$1(2) \times 10^{-7}$	$5.7(5) \times 10^{-6}$
Final Δ_{max}/σ	0.0003	0.0002
$\Delta\varrho$ (max; min) [e Å^{-3}]	0.35; −0.31	0.31; −0.18

22, respectively, which revealed the positions of all non-hydrogen atoms. The non-hydrogen atoms were refined anisotropically. All of the H-atoms were fixed in geometrically calculated positions (d(C-H) = 0.95 Å) and each was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent atom. Refinement of the structures was carried out on F using full-matrix least-squares procedures, which minimized the function $\Sigma w(|F_o| - |F_c|)^2$. Corrections for secondary extinction were applied.

Neutral atom scattering factors for non-hydrogen atoms were taken from [39a], and the scattering factors for H-atoms were taken from [40]. Anomalous dispersion effects were included in F_c [41]; the values for f' and f'' were those of [39b]. The values of the mass attenuation coefficients are those of [39c]. All calculations were performed using the teXsan crystallographic software package [42].

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