Unusual Stabilization of 1,2-Diamino Derivatives of Quincorine and Quincoridine by Carbon Dioxide: Persistent Crystalline *prim*-Ammonium-Carbamate Salts and Their Reactivity towards Isatoic Acid Anhydride

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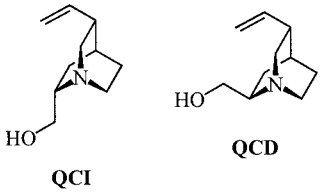
The reaction of *N*-methylisatoic anhydride **1** with a series of quincorine (QCI) and quincoridine (QCD) derivatives furnished the corresponding QCI- and QCD-substituted anthranilic acid amides **4**–**9**. In the synthesis of **4**–**9**, we investigated the influence of the C5 substituent of 2-aminomethyl derivatives of QCI and QCD on their basicity and polarity and, therefore, on their reactivity towards isatoic acid anhydride. By exposing a number of 2-aminomethyl derivatives of QCI and QCD to (carbon dioxide from) air, the formation of carbon dioxide adducts **10**–**15** was observed. In an unusual reaction, we obtained the first set of chiral ammonium carbamates derived from primary amines, which provides a convenient method for purifying and stabilizing aminomethyl derivatives of QCI and QCD. All compounds were fully characterized by spectroscopic methods. In addition, the structure of **11** was proved by X-ray crystal structure determination. The heterocyclic nitrogen atoms display trigonal-pyramidal coordination geometries; the amido group is essentially planar. N-2′ of the ammonium ion is a triple hydrogen bond donor to the carboxylato oxygen atoms of three different carbamate anions. The resulting net effect is a hydrophilic plane parallel to the *ab* plane. The crystal packing involves six classical hydrogen bonds.

Introduction

A number of reports[1] have appeared in recent years since Hoffmann et al. began investigating the physical and chemical properties of quincorine (QCI) and quincoridine (QCD, Scheme 1), two pseudo-enantiomeric 1,2-amino alcohols with four stereogenic centers each, including the 1*S*-configured bridgehead nitrogen atom.[2]



Scheme 1. Quincorine (QCI) and quincoridine (QCD)

The absolute configurations of QCI and QCD were established by Hoffmann[1c][1d][1h] to exhibit the same configuration as their precursor molecules, quinine and quinidine, respectively. QCI and QCD represent chemically interesting building blocks that bear several reactive centers in their structures. Derivatization at C-9 (cf. Figure 1) and/or C-10 and C-11 leads to a multitude of compounds with a quincorine or quincoridine skeleton, that can be used for the synthesis of a large number of new derivatives.

Recently, we reported the synthesis of new members of the family of 1,2-diamines of QCI and QCD that are hydrogenated and didehydrogenated at the C-10 and C-11 centers.[3] Aside from the hydroxyl group in both QCI and QCD, the primary amino group in their 1,2-diamino compounds represents another reactive center that is useful for the preparation of further derivatives of QCI and QCD, such as, e.g., *N*-substituted anthranilamides. In the course of our investigations into the chemical behavior of the 1,2-diamines of QCD and QCI, we found an unusual reactivity towards carbon dioxide that leads to interesting carbamate derivatives. By X-ray crystal structure determination for one selected example, we could prove the molecular structure unambiguously.

Results and Discussion

a) *N*-Methylanthranilamides

Anthranilamides have been used as intermediates in the synthesis of various heterocycles. Their treatments with dimethylformamide[4] and phosgene[5] to form quinazoli-

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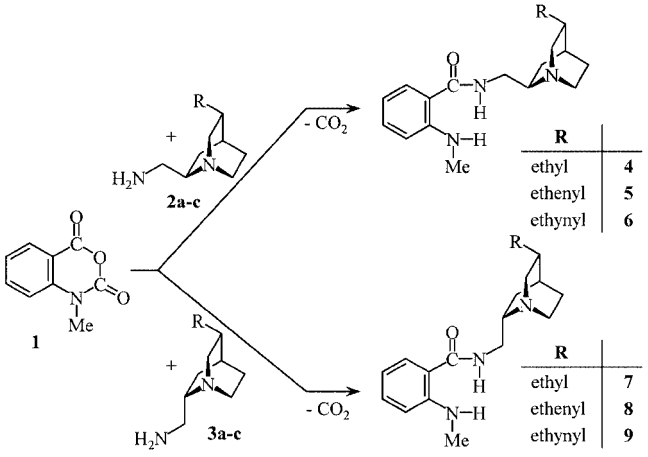
nones, with thionyl chloride to produce benzothiadiazinones,[6] with nitrous acid to yield benzotriazinones,[7] and with dimethyl acetylenedicarboxylate to produce 1,4-benzodiazepine-3,5-diones,[8] have been well documented.

Anthranilamides are precursors to benzodiazaphosphorinones,[9] compounds that are becoming increasingly important as potential cytostatics. In combination with the 2-chloroethylamino grouping, they form novel 2-chloroethylphosphamides chemically related to cyclophosphamide,[10] one of the most common cancerostatics today. Although a number of N-substituted anthranilamides are already known,[11] we intended to synthesize a series of *N*-methylanthranilamides containing either a quincorine or quincoridine unit as a bulky, functionalized substituent.

A simple method for the preparation of anthranilamides is the reaction of *N*-methylisatoic acid anhydride (**1**) with primary amines.[11] By reaction of **1** with the aminomethyl derivatives of QCD and QCI (**2a**−**c** and **3a**−**c**), we synthesized the corresponding anthranilamides **4**−**9** (Scheme 2).



Scheme 2

The course of the reaction was followed easily by monitoring the evolution of carbon dioxide. All the compounds were isolated in pure form and in good yields as yellowish or colorless oils. NMR spectroscopic data, as well as mass spectrometric data, agree with the structures proposed in Scheme 2.

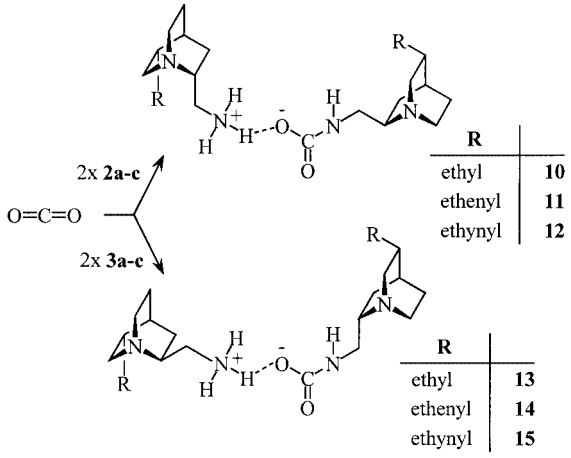
It is remarkable that the reactions of the alkyne derivatives **2c** and **3c** with isatoic acid anhydride reached completion much faster, as determined by monitoring the reaction course by TLC, than those of the alkyl and vinyl derivatives **2a**,**b** and **3a**,**b**. This behavior is probably due to the influence of the alkyne substituent on the basicity of the molecule, which is a phenomenon that was first observed and discussed by Hoffmann.[1b] It was assumed that the distortion of the azabicyclic cage affects the basicity of the bridgehead nitrogen atom, leading to higher polarity and, hence, reactivity. Recent investigations[12] on 1,2-amino alcohol analogues of **2a**−**c** and **3a**−**c** have shown that the electronic properties of the 1,2-amino alcohol functionality in these compounds are modified by the electronic properties of the C-5 substituent and by its steric demand. Accordingly, the polarity and basicity of this important class of substances can be tuned by varying this substituent.

b) Ammonium Carbamates of QCD and QCI

The principle that secondary amines can absorb carbon dioxide from air to form *sec*-ammonium *N*-carboxylates (carbamates) was first noted by Knorr[13] for morpholine. The corresponding structure of morpholinium morpholine-4-carboxylate has been determined.[14−16] Other related adducts of heterocyclic secondary amines are known, but seem to be much less stable; their exact nature has not been established. Recently, the piperidine derivative was reported in detail.[17]

Among the wide range of aliphatic carbamic acid derivatives, dialkylammonium dialkylcarbamates have received an exceptional amount of interest concerning their structures, molecular aggregation, and thermal behaviors. Among them, the first member of this series, dimethylammonium dimethylcarbamate, is a distillable liquid that garners additional interest with respect to its preparative uses.[18]

To the best of our knowledge, the corresponding adducts of aliphatic primary amines have not been reported yet and, thus, we now present the first examples of chiral ammonium carbamates derived from chiral primary amines (Scheme 3).

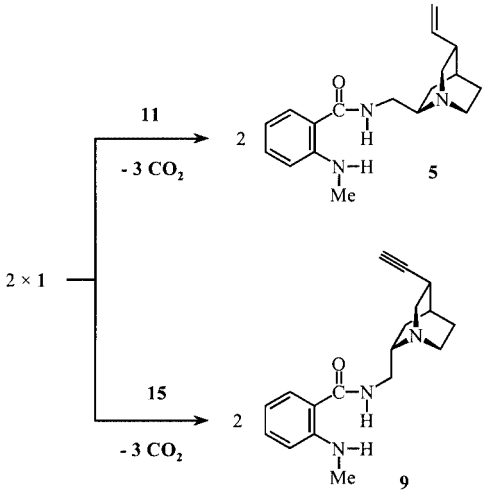


Scheme 3

When exposed to (carbon dioxide-containing) air or treated with carbon dioxide in diethyl ether, the liquid 1,2-diamines of QCD and QCI (**2a**−**c** and **3a**−**c**) react spontaneously within a few minutes to form the corresponding *prim*-ammonium carbamate salts. All these compounds were obtained as colorless solids with melting points between 70 and 120 °C. Amazingly, carbon dioxide is split off upon heating the neat compounds **10**−**15** to temperatures above 120 °C in vacuo, and then the pure diamines **2a**−**c** and **3a**−**c** can be recovered by distillation. According to this method, for the first time it now becomes possible to remove even the smallest traces of 1,2-amino alcohols of QCI and QCD (always detectable by gas chromatography and by TLC in varying amounts) from the corresponding

1,2-diamines by washing the ammonium carbamate salts with diethyl ether before reconversion of the salt-like compounds into the covalent 1,2-diamines by simple distillation in vacuo. Furthermore, the use of the ammonium carbamate salts in preparative chemistry has a number of advantages: a) a simple and convenient purification of the primary 1,2-diamines of QCI and QCD by crystallization of the ammonium carbamate salts; b) complexes of this type can be used directly as reagents in the chemistry of the aminomethyl group of QCI and QCD; c) stabilization of the reactive and sensitive *prim*-amino groups in **10**−**15** becomes possible; d) the reactivity and sensitivity of RNH_2 towards oxidation is diminished and, thus, handling and manipulation of these derivatives is simplified.

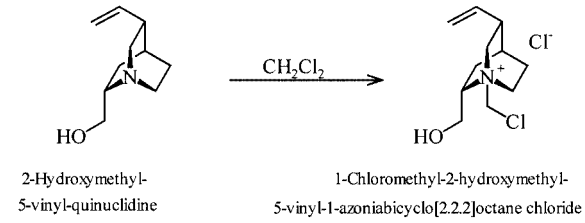
To prove the assumptions above concerning stability, reactivity and sensitivity of the new ammonium carbamates of QCI and QCD, we employed **11** and **15** as selected examples (Scheme 4), instead of **2b** and **3c**, in the reaction with isatoic acid anhydride.



Scheme 4

We obtained reaction products identical with those described in the reaction according to Scheme 2. The reaction time, conditions, and yield were comparable in both cases using both methods.

In the course of our investigations of compounds **10**−**15** by ^{13}C NMR and IR spectroscopy, we found an additional absorption for the *C*(:O)-carbon atom as well as significant shifts for the ^{13}C NMR resonances of the C-9 carbon atoms relative to those of the monomeric, covalent 1,2-diamines.[3] Also, intensive IR vibrations in the characteristic ranges 3400−3500, 2300−3000, and 1650−1800 cm^{-1} indicate the presence of RC(:O)NHR′- and RNH_3^+-fragments in **10**−**15**. These features provide strong evidence for the existence of the proposed molecular structures of the ammonium carbamate salts indicated in Scheme 3. It is remarkable that, contrary to the behavior of 2-hydroxymethyl-5-vinylquinuclidine (QCI) towards dichloromethane (Scheme 5),[1c] the formation of corresponding 1-chloromethyl-substituted azonia chlorides was not observed when the free 1,2-diamines **3a**−**c** or compounds **13**−**15** were stored for several days in dichloromethane solution. As observed,[1c] hydrogen bonds between OH and chloride are formed, stabilizing the final chloromethyl azonium chlorides of QCI. After substitution of the OH group by an NH_2 unit, this kind of interaction does not take place.



Scheme 5. Spontaneous reaction of CH_2Cl_2

To prove the existence of the ammonium carbamate salts unambiguously, an X-ray crystal structure was determined for one selected example (**11**, Figure 1).

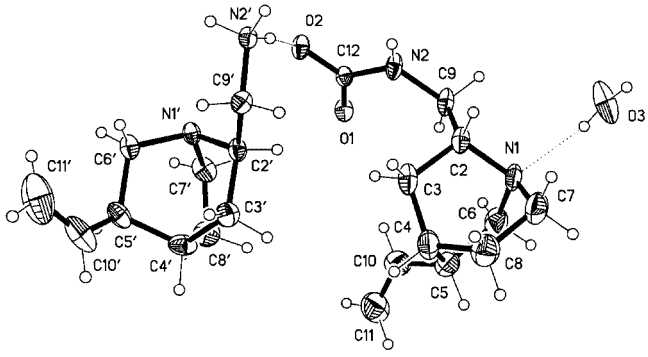


Figure 1. Structure of **11** in the crystal; selected interatomic distances [pm] and bond angles [°]: O1−C12 125.4(4), O2−C12 128.0(4), N1−C6 147.0(5), N2−C12 136.6(4), N2−C9 145.0(4), N2′−C9′ 147.0(4), C2′−C9′ 151.9(5); C12−N2−C9 124.2(3), N2−C9−C2 112.3(3), N1′−C2′−C9′ 112.2(3), N2′−C9′−C2′ 113.4(3)

The single-crystal X-ray structure of **11** reveals the first example of a *prim*-ammonium *N*-carboxylate (carbamate). The heterocyclic nitrogen atoms display trigonal-pyramidal coordination geometry. The N-1 and N-1′ atoms both lie 50.9 pm out of a plane defined by the adjacent carbon atoms. The amido group is essentially planar; the mean deviation of a plane defined by C-9, 2-H, N-2, C-12, O-1, and O-2 is only 4.0 pm. The crystal packing involves six classical hydrogen bonds (Table 1).

Table 1. Hydrogen bond geometries for **11** [pm and °]

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	∠(DHA)
N(2)−H(2)···O(3)#1[a]	90(2)	199(2)	286.3(4)	164(3)
N(2′)−H(2C′)···O(2)	89(2)	194(2)	281.8(4)	168(3)
N(2′)−H(2B′)···O(1)#2	90(2)	205(2)	286.6(4)	151(3)
N(2′)−H(2A′)···O(2)#3	90(2)	185(2)	269.2(3)	157(3)
O(3)−H(2 W)···O(1)#1	85(3)	191(3)	273.8(4)	165(5)
O(3)−H(1 W)···N(1)	86(3)	201(3)	284.1(4)	160(5)

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x + 1, y - 1/2, -z$; #2: $x, y - 1, z$; #3: $-x, y - 1/2, -z$.

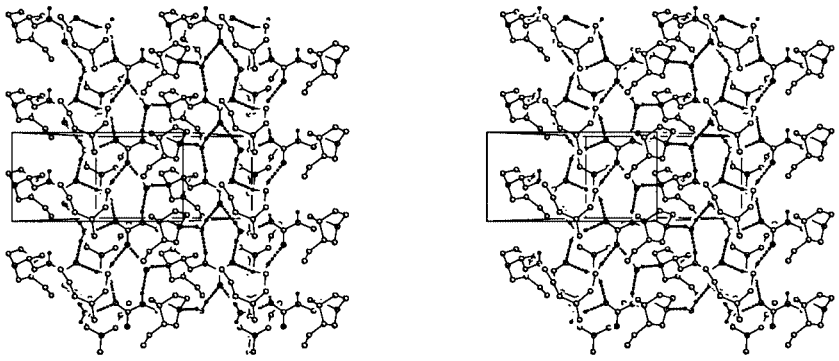


Figure 2. Packing diagram of compound **11**; hydrogen atoms not involved in hydrogen bonding have been omitted for clarity

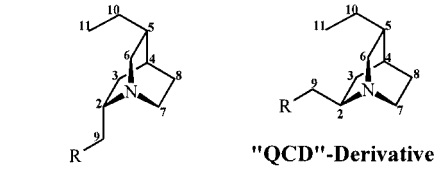
The H atoms of the cocrystallized water molecule act as hydrogen bond donors to the tertiary nitrogen atom and a carboxyl oxygen atom of two neighboring carboxylate anions. The amido N-2 atom is a donor to a water oxygen atom. The N-2′ ammonium ion is a triple hydrogen bond donor to carboxylato oxygen atoms of three different carbamate anions. The resulting net effect is a hydrophilic plane parallel to the *ab* plane (Figure 2).

Experimental Section

General: Experimental conditions and instruments used for the NMR spectroscopic and mass spectrometric investigations are identical to those mentioned in ref.[1e]

Starting compounds **2a**−**c** and **3a**−**c** were synthesized according to methods described in the literature[1,3] or are available from Buchler GmbH, Braunschweig, Germany.

^{1}H and ^{13}C NMR spectroscopic resonances were assigned using the following numbering scheme:



General Procedure for the Synthesis of 4−9: A solution of the aminomethylquinuclidine (**2a**−**c** or **3a**−**c**) was added dropwise to a solution of *N*-methylisatoic acid anhydride (**1**) in dichloromethane. After stirring for 3 h at room temp., the solution was filtered to remove insoluble components. Subsequent evaporation of the solvent in vacuo afforded the product compounds as highly viscous oils. For purification, the oily products were converted into their hydrochloride salts using aqueous 2N HCl. After being washed three times with dichloromethane, the aqueous phase was brought to pH > 11 (KOH), and the anthranilamides were extracted with dichloromethane. After drying (Na_2SO_4), the solvent was evaporated, leaving the oily products. All compounds contain one molecule of water per formula unit (elementary analyses carried out twice).

***N*-Methyl-*N*′-[(1*S*,2*R*,4*S*,5*R*)-5-ethyl-1-azabicyclo[2.2.2]oct-2-ylmethyl]anthranilamide (4):** QCD amine **2a** (1.0 g, 5.9 mmol) was treated according to the general procedure to afford **4** (1.37 g, 77%) as a highly viscous, yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.84 (t, *J* = 7.3 Hz, 3 H, 11-H), 1.02−1.07 (m, 1 H, 3-H_a), 1.45 (ddt, *J* = 2.1, 8.3, 7.9 Hz, 1 H, 8-H_a), 1.29 (m, 2 H, 10-H), 1.50−1.55 (m, 1 H, 8-H_b), 1.58−1.65 (m, 2 H, 3-H_b, 4-H), 2.31 (dd, *J* = 13.4, 7.1 Hz, 1 H, 9-H_a), 2.33−2.45 (m, 1 H, 5-H), 2.53 (dd, *J* = 11.9, 4.3 Hz, 1 H, 7-H_a), 2.62−2.69 (m, 1 H, 2-H), 2.72−2.75 (m, 1 H, 7-H_b), 2.74−2.89 (m, 3 H, 6-H, 9-H_b), 2.81 (s, 3 H, CH_3N), 5.89 [br. s, 1 H, N(*H*)CH_3], 7.41 [br. s, 1 H, C(:O)N*H*], 7.28−7.86 (m, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 11.95 (CH_3, C-11), 25.59 (CH_2, C-3, C-8), 25.77 (CH_2, C-10), 27.72 (CH, C-4), 29.31 (NCH_3), 37.66 (CH, C-5), 41.13 (CH_2, C-7), 49.12 (CH_2, C-6), 54.88 (CH, C-2), 68.30 (CH_2, C-9), 110.81 (CH, Ar-C), 114.34 (CH, Ar-C), 127.58 (CH, Ar-C), 132.51 (C_q, Ar-C), 150.44 (C_q, Ar-C), 169.71 [C_q, C(:O)] ppm. EI-MS: *m*/*z* (%) = 301 (95) [M^+], 283 (15), 244 (5), 169 (35), 152 (25), 138 (35), 134 (100), 110 (50), 77 (15). $C_{18}H_{27}N_3O{\cdot}H_2O$ (319.45): calcd. C 67.68, H 9.15, N 13.15%; found C 66.52, H 8.65, N 12.94%.

***N*-Methyl-*N*′-[(1*S*,2*R*,4*S*,5*R*)-5-vinyl-1-azabicyclo[2.2.2]oct-2-ylmethyl]anthranilamide (5):** QCD amine **2b** (1.0 g, 6.0 mmol) was treated according to the general procedure to afford **5** (1.46 g, 81%) as a highly viscous, yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.12−1.70 (m, 4 H, 3-H, 8-H), 1.89 (dq, *J* = 2.1, 1.8 Hz, 1 H, 4-H), 2.43−2.48 (m, 1 H, 5-H), 2.61 (dd, *J* = 12.8, 4.9 Hz, 1 H, 7-H_a), 2.68−2.77 (m, 1 H, 2-H), 2.83−2.94 (m, 4 H, 6-H, 7-H_b, 9-H_a), 2.92 (s, 3 H, CH_3N), 3.00 (dd, *J* = 13.6, 10.6 Hz, 1 H, 9-H_b), 5.02 (ddd, 1 H, *J* = 11.1, 1.2, 0.9 Hz, 11-H), 5.06 (ddd, 1 H, *J* = 16.9, 1.4, 0.9 Hz, 11-H), 5.62 [br. s, 1 H, N(*H*)CH_3], 5.82 (ddd, 1 H, J_{trans} = 17.1, J_{cis} = 10.9, *J* = 4 Hz, 10-H), 7.69 [br. s, 1 H, C(:O)N*H*], 7.28−7.86 (m, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 25.71 (CH_2, C-3), 26.88 (CH_2, C-8), 27.53 (CH, C-4), 29.62 (NCH_3), 39.88 (CH, C-5), 41.04 (CH_2, C-7), 49.00 (CH_2, C-6), 54.88 (CH, C-2), 66.48 (CH_2, C-9), 110.83 (CH, Ar-C), 114.34 (CH, Ar-C), 114.62 (CH_2, C-11), 127.55 (CH, Ar-C), 132.54 (C_q, Ar-C), 140.30 (CH, C-10), 150.46 (C_q, Ar-C), 169.70 [C_q, C(:O)] ppm. EI-MS: *m*/*z* (%) = 299 (40) [M^+], 167 (10), 149 (30), 134 (100), 106 (15), 77 (20). $C_{18}H_{25}N_3O{\cdot}H_2O$ (317.44): calcd. C 68.11, H 8.57, N 13.24%; found C 67.82, H 8.33, N 13.03%.

***N*-Methyl-*N*′-[(1*S*,2*R*,4*S*,5*R*)-5-ethynyl-1-azabicyclo[2.2.2]oct-2-ylmethyl]anthranilamide (6):** QCD amine **2c** (1.0 g, 6.1 mmol) was treated according to the general procedure to afford **6** (1.49 g, 82%) as a highly viscous, yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.05−1.67 (m, 4 H, 3-H, 8-H), 1.82 (dq, *J* = 2.3, 1.6 Hz,

1 H, 4-H), 2.12 (d, J = 2.8 Hz, 1 H, 11-H), 2.47−2.51 (m, 1 H, 5-H), 2.64 (dd, J = 12.2, 5.1 Hz, 1 H, 7-H_a), 2.63−2.79 (m, 1 H, 2-H), 2.80−2.91 (m, 4 H, 6-H, 7-H_b, 9-H_a), 2.87 (s, 3 H, CH_3N), 3.05 (dd, J = 13.3, 10.8 Hz, 1 H, 9-H_b), 5.74 [br. s, 1 H, N(H)CH$_3$], 7.12 [br. s, 1 H, C(:O)NH], 7.21−7.79 (m, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 25.44 (CH_2, C-3), 25.91 (CH_2, C-8), 27.26 (CH, C-4), 29.62 (NCH_3), 41.00 (CH, C-5), 48.56 (CH_2, C-7), 51.21 (CH, C-6), 54.78 (CH, C-2), 67.79 (CH_2, C-9), 69.34 (CH, C-11), 87.08 (C, C-10), 110.86 (CH, Ar-C), 114.33 (CH, Ar-C), 127.49 (CH, Ar-C), 132.57 (C_q, Ar-C), 150.46 (C_q, Ar-C), 169.67 [C_q, C(:O)] ppm. EI-MS: m/z (%) = 297 (5) [M$^+$], 129 (10), 84 (80), 49 (100). $C_{18}H_{23}N_3O{\cdot}H_2O$ (315.42): calcd. C 68.54, H 7.99, N 13.32%; found C 68.12, H 7.84, N 13.44%.

***N*-Methyl-*N*′-[(1*S*,2*S*,4*S*,5*R*)-5-ethyl-1-azabicyclo[2.2.2]oct-2-ylmethyl]anthranilamide (7):** QCI amine **3a** (1.0 g, 5.9 mmol) was treated according to the general procedure to afford **7** (1.51 g, 85%) as a highly viscous, yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.71−0.83 (m, 1 H, 3-H_a), 0.85 (t, J = 7.1 Hz, 3 H, 11-H), 1.35−1.54 (m, 4 H, 8-H, 10-H), 1.58−1.71 (m, 1 H, 4-H), 2.04−2.11 (m, 1 H, 3-H_b), 2.42−2.45 (m, 1 H, 6-H_a), 2.54−2.69 (m, 2 H, 7-H_a, 9-H_a), 2.70−2.79 (m, 2 H, 2-H, 9-H_b), 2.84−2.97 (m, 1 H, 7-H_b), 2.91 (s, 3 H, CH_3N), 3.19 (dd, J = 13.1, 9.2 Hz, 1 H, 6-H_b), 5.51 [br. s, 1 H, N(H)CH$_3$], 7.36 [br. s, 1 H, C(:O)NH], 7.22−7.81 (m, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 12.07 (CH_3, C-11), 25.11 (CH, C-4), 26.27 (CH_2, C-10), 27.51 (CH_2, C-3), 28.62 (CH_2, C-8), 29.63 (NCH_3), 37.49 (CH, C-5), 40.24 (CH_2, C-7), 54.69 (CH_2, C-6), 57.46 (CH, C-2), 62.05 (CH_2, C-9), 110.83 (CH, Ar-C), 114.35 (CH, Ar-C), 127.58 (CH, Ar-C), 132.53 (C_q, Ar-C), 150.44 (C_q, Ar-C), 169.74 [C_q, C(:O)] ppm. EI-MS: m/z (%) = 301 (M$^+$, < 1), 179 (10), 166 (10), 105 (10), 88 (100), 84 (30), 58 (70), 49 (40). $C_{18}H_{27}N_3O{\cdot}H_2O$ (319.45): calcd. C 67.68, H 9.15, N 13.15%; found C 67.69, H 8.84, N 12.79%.

***N*-Methyl-*N*′-[(1*S*,2*S*,4*S*,5*R*)-5-vinyl-1-azabicyclo[2.2.2]oct-2-ylmethyl]anthranilamide (8):** QCI amine **3b** (1.0 g, 6.0 mmol) was treated according to the general procedure to afford **8** (1.49 g, 83%) as a highly viscous, yellowish oil. $[\alpha]_D^{20}$ = +52.8 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.75−0.81 (m, 1 H, 3-H_a), 1.33−1.51 (m, 2 H, 8-H), 1.89 (sext, J = 2.9 Hz, 1 H, 4-H), 2.04 (d, J = 2.2 Hz, 1 H, 11-H), 2.07−2.14 (m, 1 H, 3-H_b), 2.42−2.48 (m, 1 H, 5-H), 2.51 (dd, J = 12.9, 5.4 Hz, 1 H, 7-H_a), 2.54−2.59 (m, 1 H, 9-H_a), 2.68 (dd, J = 13.4, 10.1 Hz, 1 H, 9-H_b), 2.78−2.82 (m, 3 H, 2-H, 6-H_a, 7-H_b), 2.91 (s, 3 H, CH_3N), 3.24 (dd, J = 12.9, 9.9 Hz, 1 H, 6-H_b), 5.60 [br. s, 1 H, N(H)CH$_3$], 7.55 [br. s, 1 H, C(:O)NH], 7.27−7.85 (m, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 26.45 (CH_2, C-3), 27.40 (CH, C-4), 27.88 (CH_2, C-8), 29.62 (NCH_3), 39.86 (CH, C-5), 42.01 (CH_2, C-7), 54.87 (CH_2, C-6), 55.74 (CH, C-2), 62.16 (CH_2, C-9), 110.84 (CH, Ar-C), 114.35 (CH_2, C-11), 127.56 (CH, Ar-C), 132.56 (C_q, Ar-C), 141.75 (CH, C-10), 150.45 (C_q, Ar-C), 169.72 [C_q, C(:O)] ppm. EI-MS: m/z (%) = 299 (10) [M$^+$], 151 (5), 136 (100), 134 (20), 105 (10), 88 (15), 77 (10), 57 (10), 41 (15). $C_{18}H_{25}N_3O{\cdot}H_2O$ (317.44): calcd. C 68.11, H 8.57, N 13.24%; found C 67.91, H 8.29, N 13.19%.

***N*-Methyl-*N*′-[(1*S*,2*S*,4*S*,5*R*)-5-ethynyl-1-azabicyclo[2.2.2]oct-2-ylmethyl]anthranilamide (9):** QCI amine **3c** (1.0 g, 6.1 mmol) was treated according to the general procedure to afford **9** (1.47 g, 81%) as a highly viscous, yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.81−0.87 (m, 1 H, 3-H_a), 1.35−1.56 (m, 2 H, 8-H), 1.85 (sext, J = 3.1 Hz, 1 H, 4-H), 2.04 (d, J = 2.7 Hz, 1 H, 11-H), 2.06−2.14 (m, 1 H, 3-H_b), 2.46−2.53 (m, 1 H, 5-H), 2.58 (dd, J = 13.5, 5.2 Hz, 1 H, 7-H_a), 2.55−2.59 (m, 1 H, 9-H_a), 2.67 (dd, J = 12.8, 10.1 Hz, 1 H, 9-H_b), 2.81−2.91 (m, 3 H, 2-H, 6-H_a, 7-H_b), 2.84 (s, 3 H, CH_3N), 3.26 (dd, J = 13.3, 9.9 Hz, 1 H, 6-H_b), 5.66 [br. s, 1 H, N(H)CH$_3$], 7.51 [br. s, 1 H, C(:O)NH], 7.31−7.89 (m, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 26.12 (CH_2, C-3), 27.49 (CH, C-4), 28.02 (CH_2, C-8), 29.81 (NCH_3), 39.70 (CH, C-5), 41.98 (CH_2, C-7), 54.81 (CH_2, C-6), 55.72 (CH, C-2), 61.12 (CH_2, C-9), 70.12 (CH, C-11), 87.71 (C, C-10), 110.79 (CH, Ar-C), 127.53 (CH, Ar-C), 132.61 (C_q, Ar-C), 150.51 (C_q, Ar-C), 169.69 [C_q, C(:O)] ppm. EI-MS: m/z (%) = 297 (M$^+$, < 1), 202 (5), 129 (60), 86 (100), 49 (95). $C_{18}H_{23}N_3O{\cdot}H_2O$ (315.42): calcd. C 68.54, H 7.99, N 13.32%; found C 68.46, H 7.85, N 13.19%.

General Procedures for the Synthesis of 10−15

Method A: QCD and QCI amines **2a**−**c** and **3a**−**c**, respectively, were exposed to air for 24 h. During this time, the oily starting compounds converted into colorless solids by reaction with carbon dioxide from air. The products were characterized without any further purification.

Method B: QCI and QCD amines **2a**−**c** and **3a**−**c** (contaminated with small traces of the corresponding 1,2-amino alcohols) were dissolved in dry diethyl ether (20 mL). A stream of dry carbon dioxide was bubbled through this solution for ca. 10 min. During this time, a colorless solid precipitated, which was filtered off, washed with diethyl ether (10 mL), and then dried in vacuo. After conversion into the covalent 1,2-diamines by distillation in vacuo, 1,2-amino alcohols were no longer detectable by TLC or gas chromatography.

(1*S*,2*R*,4*S*,5*R*)-5-Ethyl-1-azabicyclo[2.2.2]oct-2-ylmethylammonium *N*-{(1*S*,2*R*,4*S*,5*R*)-5-Ethyl-1-azabicyclo[2.2.2]oct-2-ylmethyl}-carbamate (10): QCD amine **2a** (1.0 g, 5.9 mmol) was treated according to the general procedures A/B to afford the corresponding ammonium carbamate **10** (1.1 g, 99%), m.p. 87 °C. $[\alpha]_D^{20}$ = +124.5 (c = 1.0, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3482, 2947, 2888, 2684, 2599, 1681, 1529, 1449, 1379, 1364, 1324, 1298, 1283, 1026, 674, 644, 612 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.89 (t, J = 7.1 Hz, 3 H, 11-H), 1.34 (m, 2 H, 10-H), 1.35−1.52 (m, 2 H, 3-H_a, 8-H_b), 1.55 (ddt, 1 H, J = 1.9, 8.2, 7.4 Hz, 8-H_a), 1.57−1.69 (m, 2 H, 3-H_b, 4-H), 2.11−2.16 (m, 1 H, 5-H), 2.41 (dd, J = 13.4, 7.5 Hz, 1 H, 9-H_a), 2.49 (dd, J = 12.2, 5.1 Hz, 1 H, 7-H_a), 2.69−2.74 (m, 1 H, 2-H), 2.77−2.79 (m, 1 H, 7-H_b), 2.81−3.09 (m, 3 H, 6-H, 9-H_b), 6.99 [br. s, 1 H, C(:O)NH], 9.44 (br. s, 3 H, $^+$NH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 12.04 (CH_3, C-11), 25.33 (CH_2, C-10), 25.21 (CH_2, C-8), 25.91 (CH, C-4), 26.86 (CH_2, C-3), 38.64 (CH, C-5), 44.59 (CH_2, C-7), 49.59 (CH_2, C-6), 57.77 (CH_2, C-9$_b$), 57.94 (CH, C-2), 66.33 (CH_2, C-9$_a$), 166.47 [C(:O)] ppm. $C_{21}H_{40}N_4O_2$ (380.57): calcd. C 66.28, H 10.59, N 14.72%; found C 66.09, H 10.72, N 14.52%.

(1*S*,2*R*,4*S*,5*R*)-5-Vinyl-1-azabicyclo[2.2.2]oct-2-ylmethylammonium *N*-{(1*S*,2*R*,4*S*,5*R*)-5-vinyl-1-azabicyclo[2.2.2]oct-2-ylmethyl}-carbamate (11): QCD amine **2b** (1.0 g, 6.0 mmol) was treated according to the general procedures A/B to afford the corresponding ammonium carbamate **11** (1.1 g, 98%), m.p. 76 °C. $[\alpha]_D^{20}$ = +143.3 (c = 1.0, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3499, 3116, 3068, 2940, 1615, 1523, 1489, 1465, 1220, 1129, 1087, 825, 666 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.02−1.14 (m, 1 H, 3-H_a), 1.54−1.59 (m, 2 H, 8-H), 1.71−1.77 (m, 1 H, 4-H), 2.01 (dddd, J = 13.1, 9.9, 4.2, 2 Hz, 1 H, 3-H_b), 2.19−2.34 (m, 1 H, 5-H), 2.67 (ddd, J = 13.9, 7.4, 1.1 Hz, 1 H, 6-H_a), 2.75−3.01 (m, 5 H, 6-H_b, 9-H_a, 7-$H_{a,b}$, 2-H), 3.36−3.42 (m, 1 H, 9-H_b), 5.09 (ddd, J = 17.8, 1.4, 0.8 Hz, 1 H, 11-H), 5.02 (ddd, J = 13.3, 1.3, 1.0 Hz, 1 H, 11-H), 5.87 (ddd, J = 17.7, 11.1, 4.0 Hz, 1 H, 10-H), 7.12 [br. s, 1 H, C(:O)NH], 9.29 (br. s, 3 H, $^+$NH_3) ppm. ^{13}C NMR (100 MHz,

$CDCl_3$, 25 °C): δ = 25.54 (CH_2, C-8), 25.81 (CH, C-4), 27.12 (CH_2, C-3), 38.75 (CH, C-5), 41.10 (CH_2, C-7), 48.31 (CH_2, C-6), 55.71 (CH, C-2), 56.99 (CH_2, C-9_b), 67.39 (CH_2, C-9_a), 114.33 (CH_2, C-11), 140.16 (CH, C-10), 164.58 [C(:O)] ppm. $C_{21}H_{36}N_4O_2$ (376.54): calcd. C 66.99, H 9.64, N 14.88%; found C 66.74, H 9.66, N 14.71%.

Crystal Data of 11: The measurement was performed at −100 °C using a Siemens SMART CCD system with Mo-K_α X-radiation (λ = 0.71073 Å) and a graphite monochromator. A selected crystal of **11** was coated with mineral oil, mounted on a glass fiber and transferred to the cold nitrogen stream (Siemens LT-2 attachment). A full hemisphere of the reciprocal space was scanned by ω in three sets of frames of 0.3°. The SADABS routine was applied as an absorption correction. Compound **11**, $C_{21}H_{36}N_4O_2{\cdot}H_2O$, M = 394.55, monoclinic, space group $P2_1$, a = 12.8974(1), b = 6.7516(2), c = 14.0743(4) Å, β = 116.906(2)°, U = 1092.90(5) Å^3, Z = 2, D = 1.199 Mg·m^{-3}, $F(000)$ = 432, μ(Mo-K_α) = 0.08 mm^{-1}, max./min. transmission 1.00/0.62, colorless prism 0.42 × 0.18 × 0.02 mm. A total of 6173 reflections were collected, over a range of 1.6 < θ < 25.7°, of which 3676 were independent (R_{int} = 0.051, completeness 89.9%). The structure was solved by direct methods.[19] Refinement was by full-matrix least-squares on F^2 and converged to $R1$ = 0.058 (conventional) and $wR2$ = 0.134 (all data), with goodness of fit = 0.97, 272 refined parameters, weighting scheme [σ^2 (F_o^2) +0.0561P)^2], where P = [(F_o^2 +2F_c^2)/3]. The N−H and O−H hydrogen atoms were refined freely. The absolute structure could not be determined reliably.[20]

CCDC-211270 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

(1*S*,2*R*,4*S*,5*R*)-5-Ethynyl-1-azabicyclo[2.2.2]oct-2-ylmethylammonium *N*-{(1*S*,2*R*,4*S*,5*R*)-5-Ethynyl-1-azabicyclo[2.2.2]oct-2-ylmethyl}-carbamate (12): QCD amine **2c** (1.0 g, 6.1 mmol) was treated according to the general procedures A/B to afford the corresponding ammonium carbamate **12** (1.1 g, 99%), m.p. 104 °C. $[\alpha]_D^{20}$ = +159.1 (c = 1.0, $CHCl_3$). IR (KBr): ṽ = 3491, 3109, 3080, 2994, 2862, 1696, 1569, 1457, 1382, 1365, 1303, 1160, 1052, 1029, 999, 905, 813, 635 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.39−1.65 (m, 4 H, 3-H, 8-H), 1.81 (dq, J = 2.2, 2.0 Hz, 1 H, 4-H), 2.06 (d, J = 2.4 Hz, 1 H, 11-H), 2.47−2.42 (m, 1 H, 5-H), 2.66 (dd, J = 12.3, 5.1 Hz, 1 H, 7-H_a), 2.71−2.78 (m, 1 H, 2-H), 2.86−2.99 (m, 4 H, 6-H, 7-H_b, 9-H_a), 3.12 (dd, J = 13.2, 10.1 Hz, 1 H, 9-H_b), 7.23 [br. s, 1 H, C(:O)N*H*], 9.51 (br. s, 3 H, $^+$NH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 25.44 (CH_2, C-3), 26.01 (CH_2, C-8), 27.19 (CH, C-4), 38.28 (CH, C-5), 44.13 (CH_2, C-7), 48.21 (CH_2, C-6), 57.92 (CH_2, C-9_b), 58.16 (CH, C-2), 67.84 (CH_2, C-9_a), 69.38 (CH, C-11), 87.11 (C, C-10), 165.28 [C(:O)] ppm. $C_{21}H_{32}N_4O_2$ (372.51): calcd. C 67.71, H 8.66, N 15.04%; found C 67.86, H 8.79, N 14.91%.

(1*S*,2*S*,4*S*,5*R*)-5-Ethyl-1-azabicyclo[2.2.2]oct-2-ylmethylammonium *N*-{(1*S*,2*S*,4*S*,5*R*)-5-Ethyl-1-azabicyclo[2.2.2]oct-2-ylmethyl}-carbamate (13): QCI amine **3a** (1.0 g, 5.9 mmol) was treated according to the general procedures A/B to afford the corresponding ammonium carbamate **13** (1.0 g, 97%), m.p. 105 °C. $[\alpha]_D^{20}$ = +35.3 (c = 1.0, $CHCl_3$). IR (KBr): ṽ = 3455, 3271, 2927, 2883, 2684, 2612, 1695, 1559, 1489, 1451, 1372, 1344, 1298, 1216, 1097, 1008, 814, 674, 644, 612, 596 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.72−0.83 (m, 1 H, 3-H_a), 0.89 (t, J = 6.9 Hz, 3 H, 11-H), 0.98−1.43 (m, 2 H, 8-H), 1.49−1.77 (m, 1 H, 4-H), 1.81−1.84 (m, 1 H, 3-H_b), 2.33−2.42 (m, 1 H, 5-H), 2.49−2.75 (m, 2 H, 6-H_a, 7-H_a), 2.79−2.98 (m, 2 H, 2-H, 9-H_a), 3.11−3.15 (m, 2 H, 7-H_b, 9-H_b), 3.21 (dd, J = 13.7, 9.1 Hz, 1 H, 6-H_b), 7.09 [br. s, 1 H, C(:O)N*H*], 9.13 (br. s, 3 H, $^+$NH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 12.04 (CH_3, C-11), 25.66 (CH, C-4), 26.51 (CH_2, C-10), 27.38 (CH_2, C-3), 28.14 (CH_2, C-8), 38.29 (CH, C-5), 39.53 (CH_2, C-7), 54.50 (CH_2, C-9_b), 57.95 (CH_2, C-6), 57.43 (CH, C-2), 64.13 (CH_2, C-9_a), 163.98 [C(:O)] ppm. $C_{21}H_{40}N_4O_2$ (380.57): calcd. C 66.28, H 10.59, N 14.72%; found C 66.06, H 10.77, N 14.50%.

(1*S*,2*S*,4*S*,5*R*)-5-Vinyl-1-azabicyclo[2.2.2]oct-2-ylmethylammonium *N*-{(1*S*,2*R*,4*S*,5*R*)-5-Vinyl-1-azabicyclo[2.2.2]oct-2-ylmethyl}-carbamate (14): QCI amine **3b** (1.0 g, 6.0 mmol) was treated according to the general procedures A/B to afford the corresponding ammonium carbamate **14** (1.1 g, 99%), m.p. 101 °C. $[\alpha]_D^{20}$ = +36.8 (c = 1.0, $CHCl_3$). IR (KBr): ṽ = 3479, 3248, 2911, 2859, 2681, 2607, 1695, 1551, 1462, 1387, 1366, 1337, 1301, 1282, 1219, 1121, 1056, 1004, 816, 663, 614, 594 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.93 (dddd, J = 13.7, 8.8, 4.9, 2.6 Hz, 1 H, 3-H_a), 1.56−1.64 (m, 2 H, 8-H), 1.71−1.78 (m, 1 H, 4-H), 1.89−1.98 (m, 1 H, 3-H_b), 2.31−2.38 (m, 1 H, 5-H), 2.61−2.69 (m, 2 H, 6-H_a, 7-H_a), 2.99−3.11 (m, 3 H, 7-H_b, 9-H_a, 2-H), 3.14 (dd, J = 15.1, 9.6 Hz, 1 H, 6-H_b), 3.29−3.34 (m, 1 H, 9-H_b), 5.10 (ddd, J = 10.1, 1.0, 1.0 Hz, 1 H, 11-H), 5.12 (ddd, J = 16.3, 1.3, 1.1 Hz, 1 H, 11-H), 5.91 (ddd, J = 16.6, 10.3, 4.0 Hz, 1 H, 10-H), 7.17 [br. s, 1 H, C(:O)N*H*], 9.29 (br. s, 3 H, $^+$NH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 25.02 (CH, C-4), 27.11 (CH_2, C-3), 28.72 (CH_2, C-8), 38.89 (CH, C-5), 39.52 (CH_2, C-7), 55.16 (CH_2, C-6), 55.71 (CH, C-2), 55.90 (CH_2, C-9_b), 65.48 (CH_2, C-9_a), 114.13 (CH_2, C-11), 140.89 (CH, C-10), 164.61 [C(:O)] ppm. $C_{21}H_{36}N_4O_2$ (376.54): calcd. C 66.99, H 9.64, N 14.88%; found C 66.74, H 9.69, N 14.70%.

(1*S*,2*S*,4*S*,5*R*)-5-Ethynyl-1-azabicyclo[2.2.2]oct-2-ylmethylammonium *N*-{(1*S*,2*R*,4*S*,5*R*)-5-Ethynyl-1-azabicyclo[2.2.2]oct-2-ylmethyl}-carbamate (15): QCI amine **3c** (1.0 g, 6.1 mmol) was treated according to the general procedures A/B to afford the corresponding ammonium carbamate **15** (1.1 g, 98%), m.p. 118 °C. $[\alpha]_D^{20}$ = +34.1 (c = 1.0, $CHCl_3$). IR (KBr): ṽ = 3468, 2903, 2678, 2603, 1682, 1555, 1464, 1384, 1368, 1346, 1213, 1008, 990, 664 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.75−0.81 (m, 1 H, 3-H_a), 1.33−1.47 (m, 2 H, 8-H), 1.87 (sext, J = 3.1 Hz, 1 H, 4-H), 1.94−1.97 (m, 1 H, 3-H_b), 2.07 (d, J = 2.4 Hz, 1 H, 11-H), 2.46−2.51 (m, 1 H, 5-H), 2.59 (dd, J = 12.9, 5.0 Hz, 1 H, 7-H_a), 2.61−2.69 (m, 1 H, 9-H_a), 2.76 (dd, J = 13.4, 10.6 Hz, 1 H, 9-H_b), 2.81−2.91 (m, 3 H, 2-H, 6-H_a, 7-H_b), 3.19 (dd, J = 12.9, 9.9 Hz, 1 H, 6-H_b), 7.25 [br. s, 1 H, C(:O)N*H*], 9.21 (br. s, 3 H, $^+$NH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 26.41 (CH_2, C-3), 26.94 (CH, C-4), 26.83 (CH_2, C-8), 37.30 (CH, C-5), 39.81 (CH_2, C-7), 55.31 (CH_2, C-9_b), 57.77 (CH_2, C-6), 57.85 (CH, C-2), 65.98 (CH_2, C-9_a), 67.98 (C, C-11), 88.24 (CH, C-10), 163.87 [C(:O)] ppm. $C_{21}H_{32}N_4O_2$ (372.51): calcd. C 67.71, H 8.66, N 15.04%; found C 67.51, H 8.65, N 14.93%.

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[1] [1a] H. M. R. Hoffmann, O. Schrake, *Tetrahedron: Asymmetry* **1998**, *9*, 1051−1057. [1b] O. Schrake, W. M. Braje, R. Wartchow, H. M. R. Hoffmann, *Tetrahedron: Asymmetry* **1998**, *9*, 3717−3722. [1c] C. von Riesen, R. Wartchow, H. M. R. Hoffmann, *Z. Kristallogr. NCS* **1998**, *213*, 483−484. [1d] R. Wartchow, O. Schrake, W. M. Braje, H. M. R. Hoffmann, *Z. Kristallogr. NCS* **1999**, *214*, 285−286. [1e] O. Schrake, V. S. Rahn, J. Frackenpohl, W. M. Braje, H. M. R. Hoffmann, *Org. Lett.* **1999**, *1*, 1607−1610. [1f] O. Schrake, M. H. Franz, R. Wartchow, H. M. R. Hoffmann, *Tetrahedron* **2000**, *56*, 4453−4465. [1g] W. M. Braje, J. Frackenpohl, O. Schrake, R. Wartchow, W. Beil, H. M. R. Hoffmann, *Helv. Chim. Acta* **2000**, *83*, 777−792. [1h] J. Frackenpohl, S. Röper, H. M. R. Hoffmann, R. Wartchow, *Z. Kristallogr. New Cryst. Struct.* **2000**, *215*, 437−438. [1i] S. Röper, J. Frackenpohl, O. Schrake, R. Wartchow, H. M. R. Hoffmann, *Org. Lett.* **2000**, *2*, 1661−1664.

[2] H. M. R. Hoffmann, T. Plessner, C. von Riesen, *Synlett* **1996**, 690−692.

[3] I. Neda, T. Kaukorat, C. Hrib, *Tetrahedron: Asymmetry* **2002**, *13*, 1327−1330.

[4] M. Manhas, S. Amin, *J. Heterocycl. Chem.* **1977**, *14*, 161−164.

[5] S. Hayao, H. Harere, W. Strycker, T. Leipzig, R. Kulp, H. Hartzler, *J. Med. Chem.* **1965**, *8*, 807−812.

[6] A. Santilli, J. Osdene, *J. Org. Chem.* **1964**, *29*, 2717−2720.

[7] M. Gibson, M. Green, *Tetrahedron* **1965**, *21*, 2191−2195.

[8] N. Heindel, T. Lemke, *J. Heterocycl. Chem.* **1966**, *3*, 389−402.

[9] I. Neda, T. Kaukorat, R. Schmutzler, U. Niemeyer, B. Kutscher, J. Pohl, J. Engel, *Phosphorus, Sulfur and Silicon* **2000**, *162*, 81−218.

[10] N. Brock, *Cancer Res.* **1989**, *49*, 1−28.

[11] G. Hardtmann, G. Koletar, O. Pfister, *J. Heterocycl. Chem.* **1975**, *12*, 565−576 and references cited therein.

[12] P. Rademacher, K. Kowski, H. M. R. Hoffmann, L. O. Haustedt, J. Holzgrefe, *ChemPhysChem* **2002**, *3*, 957−962.

[13] L. Knorr, *Ann. Chem.* **1898**, *301*, 1−18.

[14] C. J. Brown, L. R. Gray, *Acta Crystallogr., Sect. B* **1982**, *38*, 2307−2308.

[15] M. Czugler, P. Bombicz, I. Csoregh, O. Gallardo, *Z. Kristallogr.* **1995**, *210*, 368−369.

[16] R. B. von Dreele, R. L. Bradshaw, W. J. Burke, *Acta Crystallogr., Sect. C* **1983**, *39*, 253−255.

[17] M. Freytag, P. G. Jones, *Acta Crystallogr., Sect. C* **1999**, *55*, 1874−1877.

[18] W. Schroth, H.-D. Schädler, J. Andersch, *Z. Chem.* **1989**, *29*, 129−135.

[19] G. M. Sheldrick, *SHELXTL*, Structure Determination Software Programs, Version 5.03 (PC), Siemens Analytical X-Ray Instruments, Madison, WI, USA, **1995**.

[20] G. M. Sheldrick, *SHELXL-97. A program for crystal structure refinement*, Universität Göttingen, **1997**.

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