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DIASTEREOSELECTIVE REDUCTIVE AMINATION OF PYRAZOLIDINYL ALKYL KETONES*

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Reductive amination of pyrazolidinyl alkyl ketones with sodium triacetoxyborohydride or sodium tripivaloyloxyborohydride takes place diastereoselectively with the formation of aminoalkyl-pyrazolidines of trans structure. The volume of the substituent in the borohydrides does not affect the ratio of stereoisomers.

Keywords: primary and secondary amines, ketones, pyrazolidines, sodium triacetoxyborohydride, diastereoselective reductive amination.

Reductive amination of ketones concerns a widely applied methods of synthesis of amines [1]. In the series of reducing agents used [2-4] sodium triacetoxyborohydride is especially convenient, possessing a high chemoselectivity, which enables the use of a wide circle of amines and carbonyl compounds [5]. However the synthetic possibilities of this compound and its analogs in stereoselective reduction has been little studied [6-9], although the use of spatially hindered reducing agents usually permits stereoselectivity to be increased [8, 9].

In the present work we have studied the reductive amination of ketones **1** and **3**, existing as racemates of *trans* structure [10], using sodium triacetoxyborohydride and sodium tripivaloyloxyborohydride and a series of primary and secondary amines. On reductive amination of racemic ketones **1** and **3** with a nonchiral amine two diastereomers are formed and on using a chiral amine four. The yields and ratios of the resulting diastereomers **2** and **4** are given in Table 1.

The results show that the diastereoselectivity of the process of reductive amination of compounds **1** and **3** does not depend on the volume of the substituents in the sodium triacyloxyborohydride in difference to the data of [8, 9]. Probably the given organic radicals in the reducing agent (methyl in the triacetoxyborohydride and *tert*-butyl in the tripivaloyloxyborohydride) are too far removed from the reaction centers and consequently do not influence the stereochemistry of the process. On using dimethylamine and benzylamine the stereoselectivity of the reaction did not exceed 3.5:1. Diastereomers **2c** were isolated in the pure state by column chromatography and were characterized by spectral methods. On using (*S*)-ethylphenylamine only two

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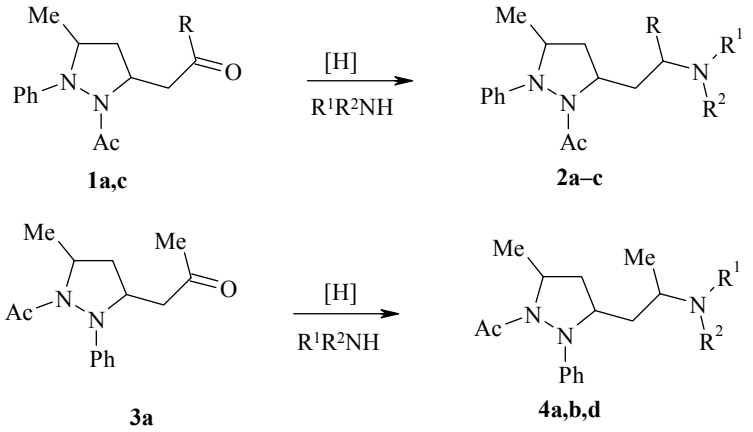
diastereomers of **4d** of the four possible were formed preferentially in a ratio of 3:2, and the two others were not detected by spectral methods, which shows the fairly high stereoselectivity of the process. The diastereomer of **4d** predominating in the mixture was isolated by crystallization as the hydrochloride.



[H] = $NaBH(O_2CMe)_3$, $NaBH(O_2CCMe_3)_3$; **1 a** R = Me; **c** R = Ph; **2**, **4** **a** R = R^1 = R^2= Me; **b** R = Me, R^1 = H, R^2 = Bn; **c** R = Ph, R^1 = H, R^2 = Bn; **4d** R^1 = H, R^2= CH(Me)Ph

In the ^{1}H NMR spectra of the obtained amines, compared to the initial ketones [10], there was a doublet or doublet of doublets for the proton of the emerging methine group, the signals of the α-protons were displaced from 2.5-4.0 to the 1.5-2.0 ppm region, in compounds **2a,b** and **4a,b** the signals of the methyl group of the functional substituent (singlet at ~2 ppm) were displaced by ~1 ppm towards high field and split into a doublet. The signals of the remaining protons did not undergo significant changes. In the spectra of compound

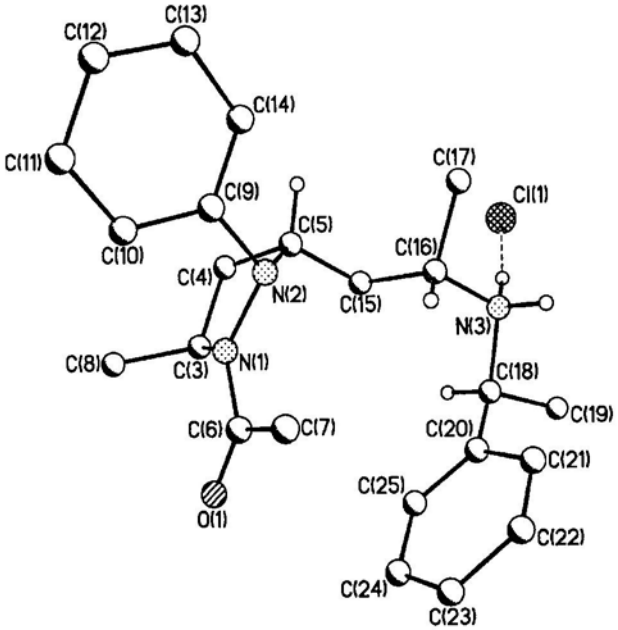


Fig. 1. General shape of the predominant diastereomer of aminoethylpyrazolidine **4d** hydrochloride. Some of the hydrogen atoms are not shown for clarity.

TABLE 1. Yields and Ratios of Diastereomers of Amines **2**, **4**

Ketone	Initial amine	Reaction product	$NaBH(O_2CMe)_3$		$NaBH(O_2CCMe_3)_3$	
			Yield, %	Ratio of diastereomers	Yield, %	Ratio of diastereomers
1a	Me_2NH	**2a**	72	3.5:1	65	3.5:1
	$BnNH_2$	**2b**	65	5:4	58	1:1
1c	$BnNH_2$	**2c**	34	6:5	—*	—*
3	Me_2NH	**4a**	70	2:1	73	2:1
	$BnNH_2$	**4b**	67	2.5:1	37	2.5:1
	RNH_2*[2]	**4d**	40	3:2:0:0	—*	—*

* Reaction not performed.
*[2] R = (*S*)-PhCH(Me).

4d hydrochloride the signal of the methyl group of the acetyl substituent (1.31 ppm) was found at a high field unusual for it, probably due to the anisotropic influence of the aromatic nucleus (see Fig. 1). In the spectrum of **4d** base this signal was found in the usual position. In the IR spectra of the amines the absorption band of the ketone carbonyl group had disappeared and for the benzylamine derivatives **2b,c** and **4b** an absorption band appeared for the NH group at 3300-3400 cm^{-1}.

An X-ray crystallographic analysis was carried out for compound **4d** hydrochloride and its absolute configuration was determined (Fig. 1). The diastereomer was identified as 1-acetyl-3*S*-[2*S*-(1*S*-phenylethylamino)propyl]-5*R*-methyl-2-phenylpyrazolidine. Bond lengths and valence angles for the heterocycle were close to those for previously studied pyrazolidine derivatives [11, 12]: N(1)–N(2) 1.424(3), N(1)–C(3) 1.502(4), N(2)–C(5) 1.493(4), C(3)–C(4) 1.516(4), C(4)–C(5) 1.522(4) Å; C(3)N(1)N(2) 112.2(3), N(1)N(2)C(5) 102.3(2), N(2)C(5)C(4) 102.8(3), C(3)C(4)C(5) 103.9(3)°. The conformation of the heterocycle is a theoretical *envelope* with emergence of atom C(5) by 0.601(2) Å from the plane formed by atoms C(3), C(4), N(1), and N(2). Atoms N(1) and N(2) in their turn are significantly pyramidalized (sums of valence angles were 332.4 and 356.1°) with clearly expressed flattening of the first due to its conjugation with the acetyl fragment. It should be noted that the C(17) methyl group is located directly above the plane of the phenyl ring C(20)–C(25) with the distance of the C(17) atom to the center of the ring being 3.56 Å. Although the minimum H···C distances (3.07 and 3.36 Å) significantly exceed the sum of the van der Waals radii and the H···π interaction is not exerted, such a contact may fully lead to shielding of the methyl group hydrogen atoms in the ^1H NMR spectra.

According to analysis of the crystal packing of compound **4d**, the cations participate in the formation of N–H···Cl (N···Cl 3.150(3)-3.174(3) Å) hydrogen bonds of moderate strength, which unite them in chains directed along the *x* crystallographic axis. The remaining interionic contacts (C–H···Cl, C–H···O, and C–H···H) correspond to weak van der Waals interactions.

On the basis of the structure of the initial heterocycle as a racemate of *trans* structure [10], on condition that (*S*)-phenylethylamine interacts with enantiomers **3a** nonselectively, but the resulting imine is reduced stereoselectively [13], then the structure 1-acetyl-3*R*-[2*R*-(1*S*-phenylethylamino)propyl]-5*R*-methyl-2-phenylpyrazolidine must be assigned to the other (minor) diastereomer of **4d**.

A synthesis has therefore been developed for the previously unavailable *trans* diastereomers of pyrazolidinylalkylamines **2** and **4**. Compounds of this type are a promising class of substances displaying high thrombolytic activity [14].

EXPERIMENTAL

The IR spectra were obtained on a UR-20 instrument in films. The ^{1}H NMR spectra were recorded on Bruker Avance 400 (400 MHz) instruments in $CDCl_3$ at 30°C, the standard was the residual protons of the solvent, δ 7.26 ppm. Coupling constants were measured with a precision of ±0.1 Hz, and the ratio of diastereomers by the ^{1}H NMR method. Elemental analysis was carried out on a Carlo Erba EA1108 CHNS-O CHN microanalyzer. The purity of the obtained compounds was checked by TLC on Silufol plates in the systems petroleum ether–ethyl acetate, 1:1, and chloroform–methanol, 10:1, with visualization with iodine vapor and $FeCl_3$ in alcohol solution. Chromatographic purification of the obtained compounds was carried out by flash chromatography on a dry column of silica gel type L 5/40.

Preparation of Amines (General Method). Glacial acetic acid (125 μl, 2.17 mmol) was added dropwise to a mixture of methylene chloride (1.5 ml) and sodium borohydride (24 mg, 0.62 mmol). After 30 min treatment in an ultrasound bath, ketone (0.31 mmol) and amine (0.37 mmol) were added, and the mixture was stirred for several days (check by TLC). For purification the reaction mixture was washed with saturated potassium carbonate solution (1 ml) and distilled water (2×1 ml). Hexane (1 ml) and a saturated solution of oxalic acid (2 ml) were added to the residue, the mixture shaken, the organic layer was separated, and the aqueous layer extracted with a methylene chloride–hexane, 1:1 mixture. Potassium carbonate (1 g) was added to the aqueous phase and the mixture extracted with a methylene chloride–hexane, 1:1 mixture. The organic extract was evaporated in vacuum, and the residue separated on a dry column in the system chloroform–methanol in a gradient from 100:1 to 1:1 (or petroleum ether–ethyl acetate in a gradient from 10:1 to 0:1).

TABLE 2. Crystallographic Data, Main Parameters of the X-Ray Diffraction Experiment, and Refinement of the Crystal Structure of **4d** Salt

Compound	**4d**
Empirical formula	$C_{27}H_{40}ClN_3O_3$
Mass of formula unit	490.07
Color, crystal shape	Colorless needles
Crystal size, mm	0.15×0.15×0.25
Temperature, K	120(2)
Crystal system	Rhombic
Space group	$P\,2_12_12_1$
a, Å	7.7712(10)
b, Å	12.442(2)
c, Å	28.128(5)
V, Å^3	2719.8(8)
Z (*Z*′)	4 (1)
F(000)	1056
D_{calc},·g·cm^{-3}	1.197
Absorption coeff., μ, cm^{-1}	2.26
Scanning type	ω
Range of θ, deg	3.19-28.00
Number of reflections	
measured	10382
independent (R_{int})	6390 (R_{int} = 0.037)
with $I>2\sigma(I)$	3295
Number of parameters used	258
$R(F_{hkl})$: R_1	0.0544
wR_2	0.1084
GOF	0.993
Residual electron density, e·Å^{-3} (d_{min}/d_{max})	0.269-0.234

1-Acetyl-5-(2-dimethylaminopropyl)-3-methyl-2-phenylpyrazolidine (2a). Yield 72%, oil. Two diastereomers, ratio 3.5:1. IR spectrum, ν, cm^{-1}: 1670 (CO).

Predominant isomer. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.99 (3H, d, *J* = 6.6, γ-CH_3); 1.21 (3H, d, *J* = 7.0, 3-CH_3); 1.49 (1H, m, H-4); 1.81 (1H, m, H-α); 1.96, 1.99 (2H, m, H'-α, H'-4); 2.02 (3H, s, CH_3CO); 2.17 (6H, s, $(CH_3)_2N$); 2.59 (1H, m, H-β); 4.09 (1H, m, H-3); 4.40 (1H, m, H-5); 6.88-6.97 (3H, m, H-*o*,*p*); 7.23 (2H, m, H-*m*).

Minor isomer. ^{1}H NMR spectrum, δ, ppm (J, Hz): 0.94 (3H, d, *J* = 6.4, γ-CH_3); 1.18 (1H, m, H-α); 1.21 (3H, d, *J* = 7.0, 3-CH_3); 1.80 (1H, m, H'-α); 1.99 (1H, m, H-4); 2.02 (3H, s, CH_3CO); 2.20 (6H, s, $(CH_3)_2N$)]; 2.24 (1H, m, H'-4); 2.59 (1H, m, H-β); 4.09 (1H, m, H-3); 4.40 (1H, m, H-5); 6.88-6.97 (3H, m, H-*o*,*p*); 7.23 (2H, m, H-*m*). Found, %: C 69.79; H 9.54; N 13.71. $C_{17}H_{27}N_3O$. Calculated, %: C 70.55; H 9.40; N 14.52.

1-Acetyl-5-(2-benzylaminopropyl)-3-methyl-2-phenylpyrazolidine (2b). Yield 65%, oil, two diastereomers, 5 : 4. IR spectrum, ν, cm^{-1}: 1670 (CO), 3330 (NH).

Predominant isomer. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.16 (3H, d, *J* = 6.2, γ-CH_3); 1.22 (3H, d, *J* = 6.7, 3-CH_3); 1.31 (1H, m, H-α); 1.75, 1.83 (2H, m, H-4, H'-α); 2.04 (3H, s, CH_3CO); 2.04 (1H, m, H'-4); 2.77 (1H, m, H-β); 3.66 (1H, d, *J* = 12.0, C$\underline{H}_2$Ph); 3.84 (1H, d, *J* = 12.0, C$\underline{H}'_2$Ph); 4.07 (1H, m, H-3); 4.58 (1H, m, H-5); 6.92-6.98 (3H, m, H-*o*,*p*, C_6H_5); 7.22-7.42 (7H, m, $CH_2C_6\underline{H}_5$, H-*m*, N-$C_6\underline{H}_5$).

Minor isomer. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.09 (3H, d, *J* = 6.4, γ-CH_3); 1.22 (3H, d, *J* = 6.6, 3-CH_3); 1.54 (1H, m, H-α); 1.75, 1.83 (2H, m, H-4, H'-α); 1.96 (1H, ddd, *J* = 12.4, *J* = 7.7, *J* = 2.3, H'-4); 2.07 (3H, s, CH_3CO); 2.84 (1H, q, *J* = 6.3, H-β); 3.71 (1H, d, *J* = 12.6, CH_2Ph); 3.82 (1H, d, *J* = 12.4, C$\underline{H}'_2$Ph); 4.12 (1H, m, H-3); 4.58 (1H, m, H-5); 6.92-6.98 (3H, m, H-*o*,*p*, N-$C_6\underline{H}_5$); 7.22-7.42 (7H, m, $CH_2C_6\underline{H}_5$, H-*m*, N–$C_6\underline{H}_5$). Elemental analysis was carried out on the phenylthiocarbamoyl derivative. Found, %: C 72.09; H 7.14; N 11.21. $C_{29}H_{34}N_4OS$. Calculated, %: C 71.57; H 7.04; N 11.51.

1-Acetyl-5-(2-benzylamino-2-phenylethyl)-3-methyl-2-phenylpyrazolidine (2c). Ratio of diastereomers, 6:5.

Predominant isomer. Yield 19%, oil. IR spectrum, ν, cm^{-1}: 1665 (CO), 3325 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.19 (3H, d, *J* = 6.8, 3-CH_3); 1.81 (2H, m, H-α, H'-α); 1.90, 1.98 (2H, m, H-4, H'-4); 2.09 (3H, s, CH_3CO); 2.30 (1H, br. s, NH); 3.54 (1H, d, *J* = 12.4, C$\underline{H}_2$Ph); 3.58 (1H, d, *J* = 12.4 C$\underline{H}'_2$Ph); 3.79 (1H, dd, *J* = 8.7, *J* = 5.0, H-β); 4.09 (1H, m, H-3); 4.52 (1H, m, H-5); 6.90-7.40 (15H, Ar).

Minor isomer. Yield 15%, oil. IR spectrum, ν, cm^{-1}: 1665 (CO), 3325 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.18 (3H, d, *J* = 6.7, 3-CH_3); 1.58 (2H, m, H-α, H-4); 1.60 (1H, m, H'-4); 1.78 (1H, s, NH); 2.04 (3H, s, CH_3CO); 2.44 (1H, m, H'-α); 3.47 (2H, m, C$\underline{H}_2$Ph); 3.62 (1H, m, H-β); 3.98 (1H, m, H-3); 4.55 (1H, m, H-5); 6.9-7.4 (15H, Ar). Elemental analysis was carried out on the phenylthiocarbamoyl derivative. Found, %: C 72.09; H 7.14; N 11.21. $C_{34}H_{35}N_4OS$. Calculated, %: C 74.56; H 6.44; N 10.23.

1-Acetyl-3-(2-dimethylaminopropyl)-5-methyl-2-phenylpyrazolidine (4a). Yield 70%, oil, two diastereomers, ratio 2:1. IR spectrum, ν, cm^{-1}: 1670 (C=O).

Predominant isomer. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.07 (3H, d, *J* = 6.2, γ-CH_3); 1.22 (1H, m, H-α); 1.40 (3H, d, *J* = 6.4, 5-CH_3); 1.78 (2H, m, H-4, H'-α); 2.00 (1H, ddd, *J* = 12.3, *J* = 7.8, *J* = 0.9, H'-4); 2.02 (3H, s, CH_3CO); 2.23 (6H, s, $(CH_3)_2N$); 2.74 (1H, m, H-β); 4.02 (1H, m, H-3); 4.38 (1H, m, H-5); 6.86-7.27 (5H, m, C_6H_5).

Minor isomer. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.88 (3H, d, *J* = 6.6, γ-CH_3); 1.28 (1H, m, H-α); 1.40 (3H, d, *J* = 6.4, 5-CH_3); 1.78 (1H, m, H-4); 1.81 (1H, ddd, *J* = 12.6, *J* = 8.7, *J* = 0.7, H'-α); 1.93 (1H, ddd, *J* = 12.6, *J* = 8.0, *J* = 0.7, H'-4); 1.99 (3H, s, MeCO); 2.26 (6H, s, $(CH_3)_2N$); 2.88 (1H, m, H-β); 4.25 (1H, m, H-5); 4.38 (1H, m, H-3); 6.91 (1H, m, H-*p*); 7.07 (2H, m, H-*o*); 7.25 (2H, m, H-*m*). Found, %: C 70.06; H 9.44; N 14.35. $C_{17}H_{27}N_3O$. Calculated, %: C 70.55; H 9.40; N 14.52.

1-Acetyl-3-(2-benzylaminopropyl)-5-methyl-2-phenylpyrazolidine (4b). Yield 67%, oil, two distereomers, 2.5:1. IR spectrum, ν, cm^{-1}: 1670 (amide), 3330 (NH).

Predominant isomer. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.25 (3H, d, *J* = 6.1, γ-CH_3); 1.30 (1H, m, H-α); 1.39 (3H, d, *J* = 6.4, 5-CH_3); 1.68 (1H, m, H'-α); 1.76 (1H, m, H-4); 1.96 (1H, m, H'-4); 1.92 (3H, s, CH_3CO); 2.89 (1H, m, H-β); 3.72 (1H, d, *J* = 13.1, C$\underline{H}_2$Ph); 3.85 (1H, d, *J* = 13.1, C$\underline{H}'_2$Ph); 4.07 (1H, m, H-3); 4.37 (1H, m, H-5); 6.87 (1H, t, *J* = 7.2, H-*p,* N–C_6H_5); 6.98 (2H, d, *J* = 8.1, H-*o*, N–C_6H_5); 7.12-7.41 (7H, m, $CH_2C_6\underline{H}_5$, H-*m*, N-$C_6\underline{H}_5$).

Minor isomer. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.19 (3H, d, *J* = 6.3, γ-CH_3); 1.37 (1H, m, α-H); 1.39 (3H, d, *J* = 6.2, 5-CH_3); 1.51 (1H, m, H'-α); 1.81 (1H, ddd, *J* = 12.6, *J* = 8.7, *J* = 7.2, H'-α); 1.92 (1H, dd, *J* = 12.4, *J* = 7.8, H'-4); 2.00 (3H, s, CH_3CO); 2.96 (1H, m, H-β); 3.75 (1H, d, *J* = 12.6, C$\underline{H}_2$Ph); 4.03 (1H, d, *J* = 12.7, C$\underline{H}'_2C_6H_5$); 4.36 (2H, m, H-3,5); 6.87 (1H, t, *J* = 7.15, H-*p*, N–C_6H_5); 6.98 (2H, d, *J* = 8.1, H-*o,* N–C_6H_5); 7.12-7.41 (7H, m, $CH_2C_6\underline{H}_5$, H-*m*, N–C_6H_5). Elemental analysis was carried out on the phenylthiocarbamoyl derivative. Found, %: C 71.64; H 7.09; N 11.41. $C_{29}H_{34}N_4OS$. Calculated, %: C 71.57; H 7.04; N 11.51.

1-Acetyl-5-methyl-3-[2-(1-phenylethylamino)propyl]-2-phenylpyrazolidine (4d). Yield was 40%, oil, two diastereomers, ratio 3:2. IR spectrum, ν, cm^{-1}: 1660 (C=O), 3320 (NH).

Predominant (3*S*,2*S*,1*S*,5*R*)-diastereomer was isolated as the hydrochloride, recrystallized from ethyl acetate; mp 195-200°C (decomp.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz), free base: 1.13 (3H, d, *J* = 6.4, γ-CH_3); 1.22 (1H, m, H-α); 1.27 (3H, d, *J* = 6.3, C$\underline{H}_3$CHPh); 1.39 (3H, d, *J* = 6.4, 5-CH_3); 1.73, 1.79 (2H, m, H'-α, H-4); 1.85 (3H, s, CH_3CO); 2.00 (1H, dd, *J* = 12.4, *J* = 7.6, H'-4); 2.81 (1H, m, H-β); 3.85 (1H, q, *J* = 6.6, MeC$\underline{H}$Ph); 4.06 (1H, m, H-3), 4.37 (1H, m, H-5); 6.90-6.97 (3H, m, H-*o*,*p*, N–$C_6\underline{H}_5$), 7.20-7.40 (7H, m, $CHC_6\underline{H}_5$, H-*m*, N–$C_6\underline{H}_5$); hydrochloride ($CDCl_3$): 1.32 (3H, s, CH_3CO); 1.41 (3H, d, *J* = 6.4, 5-CH_3); 1.80 (1H, m, H-4); 1.85 (3H, d, *J* = 6.6, γ-CH_3); 1.90 (3H, d, *J* = 6.6, C$\underline{H}_3$CHPh); 1.96 (2H, m, H-α, H'-α); 2.05 (1H, dd, *J* = 12.7, *J* = 7.72, H'-4); 3.16 (1H, m, H-β); 4.00 (1H, m, MeC$\underline{H}$Ph); 4.33 (2H, m, H-3,5); 6.86-7.64 (10H, m, $CHC_6\underline{H}_5$, N–$C_6\underline{H}_5$); 9.93 (1H, m, N–H); 10.23 (1H, m, N–H').

Minor diastereomer. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.08 (3H, d, *J* = 6.4, γ-CH_3); 1.22 (1H, m, H-α); 1.36 (3H, d, *J* = 6.4, C$\underline{H}_3$CHPh); 1.43 (3H, d, *J* = 6.6, 5-CH_3); 1.73, 1.79 (2H, m, H'-α, H-4); 2.00 (1H, m, H'-4); 2.03 (3H, s, CH_3CO); 2.93 (1H, m, H-β); 4.15 (1H, q, *J* = 6.5, MeC$\underline{H}$Ph); 4.22 (2H, m, H-3,5); 6.90-6.97 (3H, m, H-*o*,*p*, N–C_6H_5); 7.20-7.40 (7H, m, $CHC_6\underline{H}_5$, H-*m*, N–C_6H_5). Found, %: C 68.67; H 8.24; N 10.31. $C_{23}H_{31}N_3O\cdot HCl$. Calculated, %: C 68.72; H 8.02; N 10.45.

X-Ray Structural Investigation of a Crystal of Salt 4d grown in absolute ethyl acetate was carried out on a SMART 1000 CCD 3-circle diffractometer (MoKα radiation, graphite monochromator, ω-scanning) at 120 K. The structure was solved by the direct method and refined on F^2_{hkl} by least squares in an anisotropic full matrix approximation. The hydrogen atoms of the NH_2 group were located from Fourier electron density difference syntheses and refined in an isotropic approximation. The positions of H on C atoms were calculated geometrically and were refined in an isotropic approximation according to the rider model with parameters $U_{iso}(H_i) = 1.2U_{eq}(C_i)$, for methyl groups $U_{iso}(H_{ii}) = 1.5\ U_{eq}(C_{ii})$, where $U(C_i)$ and $U(C_{ii})$ are the equivalent thermal parameters for the carbon atoms to which the appropriate H atoms are linked. Analysis of the Fourier difference syntheses showed the presence of residual peaks of electron density with height reaching 3.86 e/Å^3 and corresponding to randomized solvent (probably ethyl acetate used in the synthesis). Since refining the randomization did not lead to realistic geometric parameters, the contribution of the solvent to structural amplitudes was calculated with the aid of the SQUEEZE procedure [15]. On calculating the mass of the formula unit, *F*(000), and the density, the presence of one molecule of ethyl acetate for one cation was taken into consideration in the composition. The main crystallographic data and the refinement parameters are given in Table 2. All the calculations were carried out with the SHELXTL PLUS set of programs [15]. The complete crystallographic information has been deposited in the Cambridge Structural Data Bank (deposit No. CCDC 678483)

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