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THE EFFECT OF CONFORMATIONAL EQUILIBRIUM ON RATE OF REACTIONS INVOLVING NEIGHBOURING GROUP PARTICIPATION

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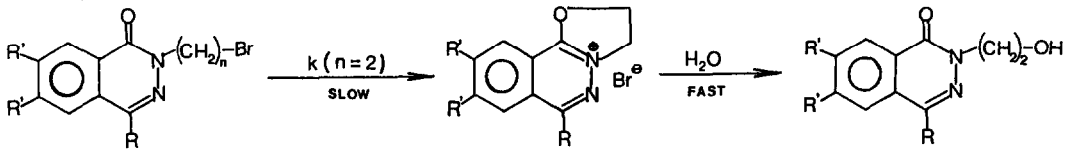
Abstract - The hydrolysis reaction of condensed bromoalkylphthalazinones type 4 is efficiently assisted by the neighbouring hydrazinocarbonyl group. The expected order of anchimeric assistance has been found to be dependent on the chain length. The relatively large values of rate constants are due to an entropy effect firmly supported by computed analysis of the conformational equilibria for the bromoethyl chain appended to phthalazinone (1a) and 2,3-dihydroimidazo[2,1-*a*] phthalazinone (4a), respectively. The results of this analysis are in good agreement with the activation entropy values.

INTRODUCTION

In an earlier paper[1] we have reported on the solvolitic reaction of 2-bromoalkylphthalazinones 1a-i (Scheme 1) effected in boiling 1:4 (v/v) water-ethanol. Our findings were: i) the reactions of the bromoethyl derivatives 1a-h are anchimerically assisted by the neighbouring hydrazinocarbonyl oxygen (1 → 2 → 3; Scheme 1), but the hydrolysis of the bromobutylphthalazinone 1i can not be carried out under the same conditions; ii) for bromoethyl derivatives the cyclization of type 1 → 2 is the rate determining step; iii) in accordance with the general view[2], the relative nucleophilicity of the carbonyl oxygen increases with the decreasing value of the amide-I i.r. frequency.

Recently we have carried out kinetic measurements for the same reactions at different temperatures to obtain exact rate constants and activation parameters characterizing the rate limiting first step. In this report the effect of the chain length and of the presence of the condensed imidazoline ring on neighbouring group participation is discussed quantitatively in solvolitic reactions of tricyclic bromoalkylphthalazinones 4a-c[3,4] and 4d (Scheme 2). A plausible reason is also proposed for the highly increased tendency of tricyclic derivatives 4a-d to form intermediate dications (5a-d; Scheme 2), firmly supported by both the activation parameters and the computed conformational analysis.



1a-i 2a-h 3a-h

1-3	a	b	c	d	e	f	g	h	i
n	2	2	2	2	2	2	2	2	4
R	H	CH_3	C_6H_5	OH	OH	NH_2	Cl	Cl	C_6H_5
R'	H	H	H	H	OCH_3	H	OCH_3	H	H

SCHEME 1

RESULTS AND DISCUSSION

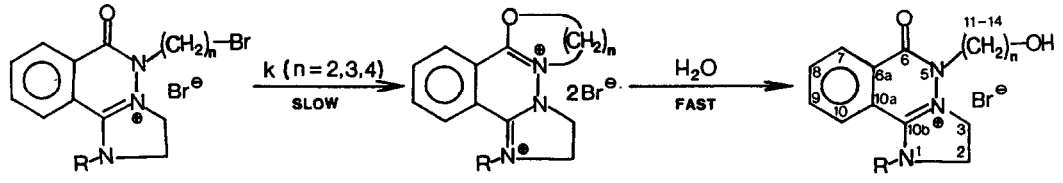
The first order rate constants obtained for the cyclization of the bromoethylphthalazinones 1a-h (Scheme 1, Table 1) carried out in 1:4 (v/v) water-ethanol (0.05 M CH_3COONa--CH_3COOH buffer, pH = 4.83±0.04) are consistent with the relative nucleophilicity of the carbonyl oxygen predicted from the amide-I i.r. frequencies.[2] The electron demand of the cationic type transition state is clearly reflected from the activation enthalpy values unambiguously decreased by the electron releasing substituents (e.g. R = OH, NH_2; R' = = OMe). On the other hand, no significant difference can be observed between the values of activation entropy (Table 1) meaning that on passing to the transition state, the loss of the internal rotational freedom of the bromoethyl chain does not vary with the ring substituents R and R'.

Table 1 - Amide-I i.r. frequencies for bromoethylphthalazinones 1a-h, rate constants[a] and activation parameters[a] for ring closures 1a-h → 2a-h in 1:4 (v/v) water-ethanol (0.05 M CH_3COONa - CH_3COOH buffer)

Reaction	R	R'	Amide-I [cm^{-1}]	Rate constants: k [sec^{-1}] 29.0°C	37.5°C	50.0°C	$\Delta H^{\neq}$ [KJ/mol]	$\Delta S^{\neq}$ [J/molK]
1a → 2a	H	H	1642	$1.15\pm0.03\times10^{-4}$	$2.73\pm0.05\times10^{-4}$	$9.22\pm0.22\times10^{-4}$	78.96±1.23	-62.4±2.1
1b → 2b	CH_3	H	1640	$4.37\pm0.10\times10^{-4}$	$1.00\pm0.02\times10^{-3}$	$3.37\pm0.08\times10^{-3}$	73.90±1.15	-64.9±1.8
1c → 2c	C_6H_5	H	1640	$1.28\pm0.02\times10^{-4}$	$3.03\pm0.07\times10^{-4}$	$9.87\pm0.21\times10^{-4}$	76.58±1.19	-66.1±1.9
1d → 2d	OH	H	1634	$2.68\pm0.05\times10^{-3}$	$5.88\pm0.09\times10^{-3}$	$1.74\pm0.03\times10^{-2}$	69.96±1.46	-68.8±2.6
1e → 2e	OH	OCH_3	1630	$4.90\pm0.10\times10^{-3}$	$1.05\pm0.02\times10^{-2}$	$3.04\pm0.07\times10^{-2}$	68.08±1.24	-64.1±2.0
1f → 2f	NH_2	H	1622	$7.49\pm0.18\times10^{-3}$	$1.57\pm0.04\times10^{-2}$	$4.50\pm0.08\times10^{-2}$	66.74±1.33	-64.9±2.2
1g → 2g	Cl	OCH_3	1658	$1.21\pm0.04\times10^{-5}$	$3.07\pm0.08\times10^{-5}$	$1.09\pm0.03\times10^{-4}$	83.03±1.69	-64.5±2.4
1h → 2h	Cl	H	1668	$2.93\pm0.05\times10^{-6}$	$7.70\pm0.17\times10^{-6}$	$2.96\pm0.10\times10^{-5}$	86.96±1.95	-63.2±2.7

[a] Mean values from five to eight separate runs ± the standard deviation.

The hydrolysis of condensed bromoalkyl derivatives 4a-d carried out under the same conditions is also assisted by the neighbouring group participation of the carbonyl oxygen (4 → 5 → 6; Scheme 2). In addition to the results of kinetic studies discussed below the following experiments and findings contribute further evidences for this mechanism: i) preparation of the bis-perchlorates of intermediate dications containing five and six-membered heterorings (5a-b)[3]; ii) these intermediate dications undergo a very fast hydrolysis even under mild conditions to form hydroxyalkyl derivatives 6a-b[3]; iii) conversions 4a-d → 5a-d → 6a-d, including even formation of seven-membered 1,3-oxazepinium ring, can also be carried out on preparative scale (Experimental/iv).



4-6	a	b	c	d
n	2	3	4	4
R	H	H	H	CH_3

SCHEME 2.

For the cyclization type 4 → 5 the expected order of anchimeric assistance[5] dependent on the chain length was observed (Table 2), but the rate constants are significantly larger than predictable from the relatively high amide-I i.r. frequencies (cf. Tables 1 and 2). Even the condensed bromobutyl derivatives 4c,d readily undergo anchimerically assisted cyclization resulting in 1,3-oxazepinium ring, although the bicyclic bromobutyl analogue 1i is completely resistant to any ring closure.[1] It has to be noted here that similar formations of seven-membered rings are either very slow or not observed at all in cases known so far.[1,6]

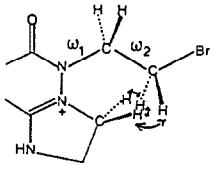
Table 2 - Amide-I i.r. frequencies for the condensed bromoalkyl compounds 4a-d, rate constants[a] and activation parameters[a] for ring closures 4a-d → 5a-d in 1:4 (v/v) water-ethanol (0.05 M CH_3COONa - CH_3COOH buffer)

Reaction	n	R	Amide-I [cm^{-1}]	Rate constants: k [sec^{-1}]			$\Delta H^{\neq}$	$\Delta S^{\neq}$
				29.0°C	37.5°C	50.0°C	[KJ/mol]	[J/molK]
4a → 5a	2	H	1671	$1.45\pm0.03\times10^{-3}$	$3.88\pm0.09\times10^{-3}$	$1.52\pm0.02\times10^{-2}$	88.43±1.74	-6.7±0.2
4b → 5b	3	H	1668	$1.19\pm0.02\times10^{-4}$	$3.09\pm0.07\times10^{-4}$	$1.16\pm0.01\times10^{-3}$	85.58±1.45	-36.8±1.0
4c → 5c	4	H	1662	$3.07\pm0.07\times10^{-6}$	$8.09\pm0.20\times10^{-6}$	$3.11\pm0.08\times10^{-5}$	87.09±1.80	-62.4±2.6
4d → 5d	4	CH_3	1662	$3.10\pm0.09\times10^{-6}$	$8.14\pm0.19\times10^{-6}$	$3.12\pm0.09\times10^{-5}$	86.71±1.57	-63.6±2.6

[a] Mean values from five to eight separate runs ± the standard deviation.

The contradiction between the enhanced tendency of 4a-d to undergo cyclization and the high amide-I frequencies cannot be resolved even by assuming that the ring closure occurs more easily on the deprotonated molecules with somewhat larger electron density on the carbonyl oxygen atom, since practically the same rate constants and activation parameters were obtained for both the reactions of the 4d N-methyl derivative and the N-protonated analogue 4c (Table 2). Moreover, a comparison of the activation enthalpy values for the two series of ring closures (1 → 2 and 4 → 5) suggests that the positively charged amidinium moiety has a similar effect on the energy of the transition state as does chlorine (cf. Tables 1 and 2). It follows that it is a significant entropy effect and not enthalpy that accounts for the accelerated ring closure of the condensed bromoalkylphthalazinones 4a-d. This view is unambiguously proved by the comparison of the activation entropy values listed in Tables 1 and 2. On the other hand, the order of the chain length dependent anchimeric assistance observed for the hydrolysis of 4a-d - according to expectations[6] - can also be explained with the activation entropy values (Table 2). It is interesting to note that practically the same entropy effect was obtained for ring closures 4c,d → 5c,d (Scheme 2; n = 4) and 1a-h → 2a-h (Scheme 1; n = 2).

The phenomenom discussed above is closely related to the geminal dialkyl effect dealt with thoroughly in literature.[7] In general, this effect is considered to involve the following two main contributing factors: i) the resultant decrease in the rotamer distribution unprofitable for cyclization[8]; ii) the relief of the steric strain on passing to the transition state.[9] The results of the computed conformational analysis carried out for 1a and 4a clearly indicate that the rotation of the bromoethyl chain is greatly restricted by the imidazolinium ring (cf. Figure 1), thus the rotamer distribution must be much more favourable for cyclization in the condensed derivative 4a than that in phthalazinone 1a, as will be discussed below. On the other hand, comparing the relative energies of the local minima of the conformational energy surfaces (Table 3), the relief of the steric strain on passing to the transition state seems to be less important contributing factor in this case.



Steric crowd at $\omega_1 = 0^\circ$ (or 360°) and $\omega_2 = 180^\circ$ for the condensed bromoethyl compound 4a.
Definition of dihedral angles ω_1 and ω_2:
ω_1: defined by N-N-C-C sequence
ω_2: defined by N-C-C-Br sequence.

FIGURE 1

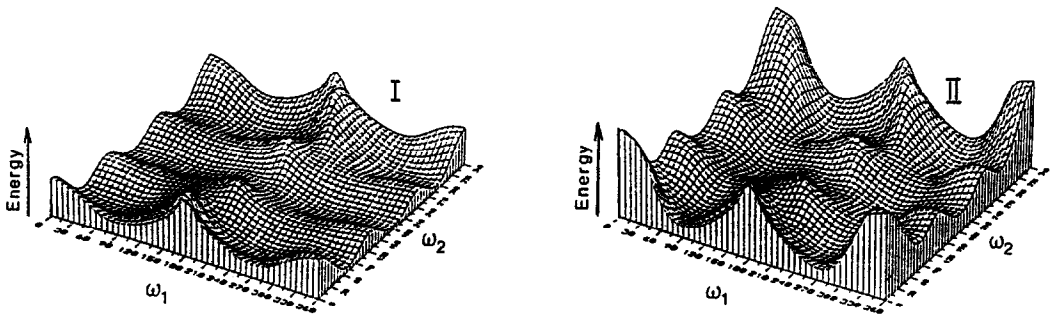
The data of the relaxed conformational energy surfaces were calculated in function of the two dihedral angles ω_1 and ω_2 in the bromoethyl chain (Figure 2) for 1a and its condensed derivative 4a, respectively. (Definition of ω_1 and ω_2 can be found on Figure 1.) The stepwise increment of the torsional angles was 15° while zero was taken as the energy of the absolute minimum in both calculations.

Table 3 - Characteristic points[a] of the potential energy surfaces calculated in function of dihedral angles ω_1 and ω_2[b] for compounds 1a and 4a, respectively

For compound 1a						For compound 4a					
ω_1	ω_2	ω_1	ω_2	Energy[c]		ω_1	ω_2	ω_1	ω_2	Energy[c]	
[degree]				[KJ/mol]		[degree]				[KJ/mol]	
0	180	360	180	3.98	tr	0	180	360	180	27.66	tr
45	285	315	75	11.67	tr	30	270	330	90	42.27	tr
60	60	300	300	0.64	m	75	60	285	300	5.42	m
75	120	285	240	18.79	tr	75	120	285	240	18.77	tr
90	0	270	360	18.12	tr	90	0	270	360	16.81	tr
90	180	270	180	0.00	m	90	180	270	180	0.00	m
90	240	270	120	17.24	tr	90	240	270	120	15.39	tr
105	300	255	60	0.15	m	105	300	255	60	0.31	m
150	105	210	255	28.73	tr	150	105	210	255	30.33	tr
180	180	180	180	12.76	m[d]	180	180	180	180	12.99	m[d]

[a] tr = transition state; m = local minimum. [b] Extended for the whole region including point pairs of the same energy (cf. Figures 1,2 and 3). [c] Relative values. [d] Conformation profitable for ring closure.

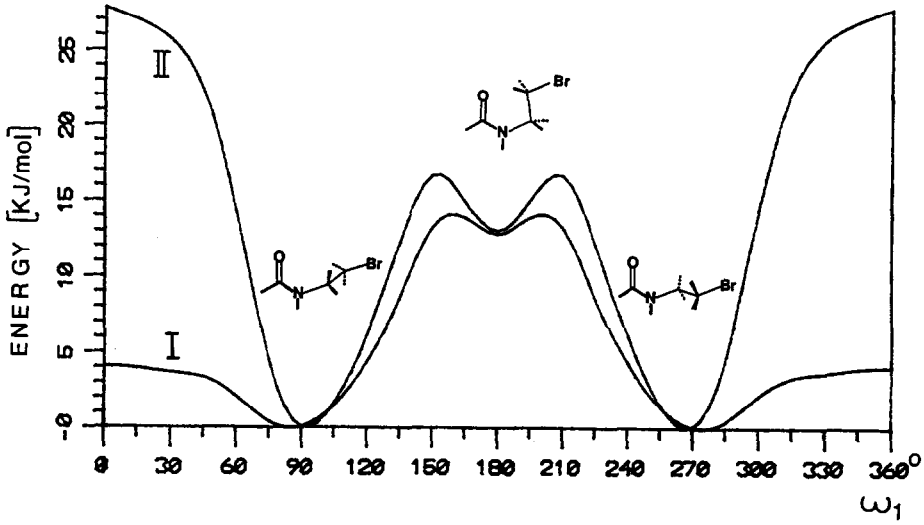
The conformational energy surfaces and their cuts at $\omega_2 = 180^\circ$ (Figure 3) show a significant similarity in the middle region ($\omega_1 \approx 180^\circ$, $\omega_2 \approx 180^\circ$) for both compounds and a conspicuous difference in the terminal regions ($\omega_1 \approx 0^\circ$ and 360°) suggesting the following main conclusions: i) for the condensed derivative 4a, the rotation between the two equivalent minima ($\omega_1 \approx 90^\circ$, $\omega_2 \approx 180^\circ$ and $\omega_1 \approx 270^\circ$, $\omega_2 \approx 180^\circ$; cf. Table 3) can take place exclusively through the conformation profitable for cyclization; ii) for bromoethylphthalazinone



Conformational energy surfaces in function of dihedral angles ω_1 and ω_2 for bromoethyl-phthalazinone 1a (surface I) and for the condensed analogue 4a (surface II), respectively.

FIGURE 2

1a the rotation between the same two minima has a higher barrier toward the "reactive" conformation (middle region) than toward the terminal regions.



Conformational energy in function of the torsional angle ω_1 (at $\omega_2 = 180^o$) for 1a (curve I) and for 4a (curve II), respectively.

FIGURE 3

To sum up, considering the results of the computed conformational analysis, it can be concluded that in the condensed derivatives 4a-d the imidazolinium ring forces the bromoalkyl chain into the proximity of the carbonyl oxygen thus significantly increasing the chance of ring closure. This view is obviously in good accordance with the entropy effect obtained from the kinetic studies.

EXPERIMENTAL

i) *Kinetic studies* - Experiments were carried out in 1:4 (v/v) water-ethanol at constant pH 4.83±0.03 (0.05 M CH_3COONa - CH_3COOH) and three different temperatures (29.0±0.1°C, 37.5±0.1°C, 50.0±0.1°C). The initial concentration of the bromoalkyl compounds varied between 5 x 10^{-3} - 2 x 10^{-4} M. Cyclizations were followed up potentiometrically by a bromide ion selective electrode (Radelkis OP-Br-0711P). Using standard NaBr solutions in the concentration range 2 x 10^{-2} - 2 x 10^{-5} M, the electrode potential was calibrated at the three applied temperatures. Rate constants were directly calculated from the slope of the rectilinear curves obtained by continuous detection of the electrode potential. Duplicate determinations agreed to within 3% or better. A silver-silver chloride electrode (Radelkis OP 0820P) equipped with double salt bridge (1M KCl¦1M KNO_3) was applied as reference.

The release of bromide ions due to the S_N2 displacement reaction involving the direct attack of the nucleophilic acetate anion on the bromoalkyl chain was taken into correction with pseudo first order rate constants obtained from the reactions of 2-(4-bromobutyl)-4--phenylphthalazinone (1i) which is completely resistant to intramolecular ring closure.[1]

Regarding the accuracy of the measurements, the substraction of the pseudo first order rate constants (29.0°C : 2.7±0.1 x 10^{-7} sec^{-1}; 37.5°C : 5.7±0.1 x 10^{-7} sec^{-1}; 50.0°C : : 17.5±0.2 x 10^{-7} sec^{-1}) from the measured rate constant was only necessary in cases when the difference between the orders of magnitude was not larger than two. The pseudo first order rate constants proved to be directly proportional to the concentration of the buffer solution which varied between 0.05 - 0.2 M.

ii) *Molecular mechanical calculations* - For the calculation of the potential energy surfaces Allinger's MMP2 (QCPE 395) program (description: see in Ref. 10) was used.

iii) *Preparation of 5-(4-bromobutyl)-2,3-dihydro-1-methyl-imidazo[2,1-a]phthalazin-6(5H)--one-4-ium-bromide (4d)*

Dissolved in abs. ethanol (100 ml) were 0.23 g of sodium, then 2.9 g (0.01M) of 4-[N--methyl-(2-hydroxyethylamino)]phthalazin-1(2H)-one[11] and 6.48 g (0.03 M) of 1,4-dibromobutane. The solution was refluxed for 3 hrs then evaporated. The residue was triturated with chloroform (30 ml), and the insoluble parts were filtered off. After evaporation of the chloroformic filtrate the yellowish oily residue was dissolved in 48% HBr (10 ml). The solution was refluxed for 90 min, then evaporated under reduced pressure in the presence of NaBr (3.1 g). The crystalline product contaminated with NaBr was extracted with hot, freshly absolutized ethanol. The ethanolic solution was concentrated to about one quarter of its volume then cooled. The precipitated crystals were collected, washed with Et_2O (10 ml) and dried over P_2O_5. Yield: 2.04 g (49.0%). M.p.: 301-3°C. Anal. (calc./found %) C 43.2/43.4, H 4.6/4.6, N 10.1/10.2, Br 38.1/38.1. Ir (KBr, cm^{-1}) amide-I 1667, $\nu_{C=N}$, $\nu_{C=C}$(Ar) 1609. ^{1}H-nmr (δ, ppm) (2,11)-H 4.23 and 4.28 (overlapping t's; 4H), 3-H 4.83 (t, 10.4 Hz, 2H), 14-H 3.75 (t, 6.3 Hz, 2H), N-CH_3 3.32 (s, 3H), ArH (7-10) 8.2 - 8.6 (m, 4H). ^{13}C-nmr (δ, ppm) C(6,10b) 159.1 163.7, C(6a,10a) 129.2 124.3, C(8,9) 137.0 135.2, C(7,10) 129.3 123.1, C(2,3) 53.0, 50.9, C(11,14) 46.0 31.2, C(12,13) 28.5 34.1, N-CH_3 30.2.

iv) *Hydrolysis reaction of 4a-d; Preparation of HBr salt of 2,3-dihydroimidazo[2,1-a]-phthalazin-6(5H)-ones: -5-(2-hydroxyethyl) (6a); -5-(3-hydroxypropyl) (6b); -5-(4-hydroxybutyl) (6c) and 2,3-dihydro-5-(4-hydroxybutyl)-1-methylimidazo[2,1-a]phthalazin-6(5H)-one--4-ium-bromide (6d).*

0.01 M of the corresponding bromoalkyl compound was dissolved in hot water-ethanol (4 ml - 16 ml). The solution was refluxed for ca. 20 min, then cooled and neutralized with 1N NaOH (10 ml). After evaporation of the neutral solution the residue was extracted with hot abs. ethanol (80 ml). The ethanolic solution was evaporated to obtain the crystalline hydroxyalkyl derivative. Yield: 88-97%. Analytical and spectral data for the products recrystallized from ethanol are listed in Tables 4 and 5.

Table 4 - M.p.'s, analyses and characteristic i.r. bands for hydroxylalkyl compounds 6a-d[a] obtained from the hydrolysis of 4a-d

Compound	M.p.[°C]	Elemental anal. [%][b] C	H	N	Br	I.R. [KBr, cm^{-1}] νO-H	νN^+-H	amide-I	νC=N
6a	226-9	46.2 46.2	4.5 4.4	13.5 13.7	25.6 25.7	3364	3150-2600	1662	1607
6b	167-9	47.9 48.0	4.9 5.0	12.9 12.8	24.5 24.5	3330	3150-2600	1668	1605
6c	194-5	49.4 49.7	5.3 5.1	12.3 12.4	23.5 23.4	3360	3150-2600	1660	1608
6d	225-6	50.9 50.8	5.7 5.5	11.9 12.1	22.5 22.5	3420	—	1665	1605

[a] Recryst. from ethanol. [b] Upper row: calculated; lower row: found.

Table 5 - ^{1}H- and ^{13}C-nmr data (δ, ppm) for compounds 6a - d in DMSO-d_6 solution[a]

Compound	2-H[b] / 3-H[b]	11-H[c] / 14-H[d]	C(6) / C(10b)	C(6a)[e] / C(10a)[e]	C(8)[f] / C(9)[f]	C(7) / C(10)	C(2) / C(3)	C(11) / C(14)	C(12) / C(13)
6a	4.26 4.84	4.54 3.72	160.2 156.7	129.9 126.2	136.7 136.3	129.2 125.3	45.4 52.7	51.3 60.1	- -
6b	4.25 4.84	4.42 3.64	159.0 156.6	128.3 125.4	136.4 136.2	129.7 124.7	45.6 52.9	50.5 60.2	32.1 -
6c	4.25[g] 4.86	4.29[g] 3.55	159.3 155.4	130.1 126.6	137.2 135.7	129.3 125.6	45.6 53.0	50.0 61.4	27.3 34.2
6d	4.24[g] 4.81	4.27[g] 3.56	159.2 163.7	129.0 124.2	137.0 135.2	129.5 123.2	52.9 50.9	50.1 62.0	27.0 34.0

[a] The numbering of atoms is given in Scheme 2. on Formula 6. Further signals: ArH(7-10) 8.2-8.6 (m, 4H); N-H 10.0-10.5 (s, 1H) for 6a-c; N-CH_3 (^{1}H/^{13}C) 3.32 (s, 3H)/30.2; O-H 5.4-5.1 (t, 5.3±0.2 Hz, 1H); 12-H 2.03 (~qi, 2H) for 6b; 12,13-H 1.8-2.0 (m, 4H) for 6c,d. [b] t(2H), J=10.2±0.3 Hz. [c] t(2H), J=6.3±0.2 Hz. [d] ~qa(2H). [e] Assignments of the C(6a, 10a) carbon lines were proved by DEPT measurements. [f] Assigments may also be reversed for the signed line pairs. [g] Overlapping signals assigned by DR measurements.

For potentiometric measurements a Radelkis OP 208/1 precision pH meter was used. M.p.'s (uncorrected) were determined on a Boetius micro hot stage. Ir spectra were obtained on a Zeiss IR-75 instrument in KBr pellets. Nmr spectra were recorded on a Bruker AM-8P PFT spectrometer at 80 (^{1}H) and 20 MHz (^{13}C), using DSS as internal reference.

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