# On Triazoles XLVII [1]. Synthesis of 1,3a,5,6,ωc-Pentaazacycloalka[*e*]acenaphthylenes

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To study the influence of planar or bulky cycloalkane rings attached to the  $1,3a,5,6,\infty$ -pentaazaacenaphthylenes to the reactivity of their 4-alkylthio group toward amines - an unexpected reaction observed recently at 1,3a,5,6,10-pentaazaacephenanthrylenes (**5b**, n = 4) - different size  $1,3a,5,6,\infty$ -pentaazacycloalka[*e*]acenaphthylenes (**5a**, n = 3; **5c**, n = 5; **5d**, n = 6; or **5e**, n = 10) were synthesised and their spectral data compared with that of **5b** (n = 4). Based on the analogy of the chemical shifts of carbon atoms at position 4 with that of **5b**, similar electronic structure and thus a possibility of an analogous nucleophilic attack of amines was proposed and subsequently proved by a preparative method.

J. Heterocyclic Chem., 40, 813 (2003).

In the previous paper of this series [1] we have reported on the synthesis of different 1,3a,5,6,10c-pentaazaacephenanthrylenes (5b, n = 4) observed previously as byproducts of the reaction of derivatives 4b (n = 4) with amines (Scheme 1). Unexpectedly, the 4-alkylthio derivatives **5b** (Q = alkylthio, n = 4) proved to be highly reactive against the nucleophilic attack of amines to yield derivatives **5b** (Q = dialkylamino, n = 4) (Scheme 2). This reaction was contrary to all former results obtained with 3-alkylthio-5-amino-1H-1,2,4-triazoles and their condensed-ring derivatives [1]. The reactivity of the 4-alkylthio groups of the 1,3a,5,6,10c-pentaazaacephenanthrylene derivatives **5b** (Q = alkylthio, n = 4) was explained either with the lack of the "quasi"-aromatic character of the triazole ring in **5b** (Q = alkylthio, n = 4) or a possibility of increasing contribution of the dipolar mesoionic (zwitter ionic) structures to the ground electronic state in solution, decreasing the stability of the C-4 – S bond.

The question arose whether this newly observed reaction worked only in case of 1,3a,5,6,10c-pentaazaacephenanthrylenes (**5b**, n = 4) having a six-membered cyclohexane ring attached to the 1,3a,5,6, $\omega$ c-pentaazaacenaphthylene moiety, or would also proceed with 1,3a,5,6, $\omega$ c-pentaazacycloalka[*e*]acenaphthylenes (**5a**, n = 3; **5c**, n = 5; **5d**, n = 6; or **5e**, n = 10), having different size, a more or less coplanar cyclopentane, or bulky cycloheptane, cyclooctane or cyclododecane rings.

The synthesis of the 1,3a,5,6,9c-pentaazacyclopenta[e]acenaphthylenes (**5a**, n = 3), 1,3a,5,6,11c-pentaazacyclohepta[e]acenaphthylenes (**5c**, n = 5), 1,3a,5,6,12c-pentaazacycloocta[e]acenaphthylenes (**5d**, n = 6), and 1,3a,5,6,16c-pentaazacyclododeca[e]acenaphthylenes (**5e**, n = 10), all representing novel ring systems, was performed analogously to that of 1,3a,5,6,10c-pentaazaacephenanthrylenes (**5b**, n = 4) [1] (Scheme 1).

Thus the cycloalka[d][1,2,4]triazolo[1,5-a]pyrimidin-5( $\omega$ H)-ones (1, n = 3, 5, 6, 10, Q = alkylthio or dialkylamino) [2,3] were converted by heating with phosphorus oxychloride to the corresponding 5-chloro-derivatives **2** (n = 3, 5, 6, 10, Q = alkylthio or dialkylamino) (Method A)



(Table I, for their spectral data see Table II) [4,5] that were reacted with 2-aminoethanol to yield derivatives **3** (n = 3, 5, 6, 10, Q = alkylthio or dialkylamino) (Method B) (Table III, for their spectral data see Table IV) (Scheme 1).

Derivatives **3** (n = 3, 5, 6, 10, Q = alkylthio or dialkylamino) were either converted with thionyl chloride to derivatives **4** (n = 3, 5, 6, 10, Q = alkylthio or dialkylamino) (Method C) (Table III, for their spectral data see Table IV) that could be ring closed by heating neat or boiling in acetonitrile (Method D), or ring closed directly by heating in polyphosphoric acid (Method E) (Table V, for their spectral data see Table VI) (Scheme 1) to the desired derivatives **5a** (n = 3), **5c** (n = 5), **5d** (n = 6) and **5e** (n = 10), respectively.

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Comp ound	n	Q		Reactio	n	Yield (%)	Mp (°C) (Cryst. from)	Molecular Formula		Ca	Analysis ilcd/Fou	s ind		MS EI	Lit. mp (°C)
			Met	Time	Tempe			(MW)	С	Н	Ν	S	Cl		
			hod	(hours)	rature										
					(°C)										
2/1	3	Methylthio	A1	1	90	91	132-133	C₀H₀ClN₄S	44.91	3.77	23.28	13.32	14.73		126-128
		-					(ether)	240.72	45.02	3.92	23.24	13.28	14.85	240	[5]
2/2	3	1-Methylethylthio	A1	1	90	88	91-93	$C_{11}H_{13}CIN_4S$	49.16	4.88	20.85	11.93	13.19		
							( <sup>i</sup> Pr <sub>2</sub> O)	268.77	49.07	4.92	20.88	11.88	13.08		
2/3	3	Dimethylamino	Al	1	85	85	134-138	$C_{10}H_{12}CIN_5$	50.53	5.09	29.46		14.92		
							(ether)	237.69	50.48	5.21	29.55		15.02		
2/4	3	Morpholin-4-yl	Al	1	80	85	216-219	$C_{12}H_{14}CIN_5O$	51.53	5.04	25.04		12.67		213-215
							(ether)	279.72	51.50	5.11	24.98		12.60	279	[5]
2/5	5	Methylthio	A1	2	90	96	120-121	$C_{11}H_{13}CIN_4S$	49.16	4.88	20.85	11.93	13.19		119-120.5
							(EtOAc)	268.77	49.22	4.96	20.78	12.04	13.25		[5]
2/6	6	Methylthio	A2	4	85	85	90.5-92	$C_{12}H_{15}CIN_4S$	50.97	5.35	19.81	11.34	12.54		90.5-92
							(cyclohexane)	282.80	50.88	5.50	19.86	11.28	12.48		[5]
2/7	10	Methylthio	A2	6	85	91	128-129	$C_{16}H_{23}CIN_4S$	56.71	6.84	16.53	9.46	10.46		128-129
							(EtOAc)	338.91	56.64	6.92	16.61	9.51	10.55		[5]

 Table I

 Synthetical and Analytical Data of 5-Chloro-cycloalka[d][1,2,4]triazolo[1,5-a]pyrimidines

 Table II

 Nmr Data of 5-Chloro-cycloalka[d][1,2,4]triazolo[1,5-a]pyrimidines

	CH <sub>2</sub> -6	CH <sub>2</sub> -	Other	Q	C-2	C-5	C-5a	С-	С-	ωa	Other CH <sub>2</sub>	Q
		(ω-1)	$\mathrm{CH}_2$					( <b>ω-1</b> )	( <b>ω-1</b> )a			
2/1	3.09 t	3.17 t	2.27 m	2.72 s (3H)	168.4	132.9	123.1	35.2	173.0	156.8	22.9 (C-7)	13.9
		(CH <sub>2</sub> -8)	(CH <sub>2</sub> -7)					(C-8)	(C-8a)	(C-9a)	28.1 (C-6)	
2/2	3.08 t	3.15 t	2.30 m	4.04 m (1H)	167.6	132.9	123.3	35.1	173.1	156.5	22.9 (C-7)	36.9 (CH)
		(CH <sub>2</sub> -8)	(CH <sub>2</sub> -7)	1.47 d (6H)				(C-8)	(C-8a)	(C-9a)	28.0 (C-6)	23.3 (CH <sub>3</sub> )
2/3	3.01 t	3.08 t	2.24 m	3.16 s (6H)	167.8	131.9	120.6	35.0	170.1	156.4	22.7 (C-7)	37.5
		(CH <sub>2</sub> -8)	(CH <sub>2</sub> -7)					(C-8)	(C-8a)	(C-9a)	28.1 (C-6)	
2/4	3.03 t	3.11 t	2.26 m	3.65 m (NCH <sub>2</sub> )	167.3	132.5	121.4	35.2	171.0	156.3	22.9 (C-7)	45.7 (NCH <sub>2</sub> )
	(8 Hz)	(8 Hz)	(8 Hz)	3.81 m (OCH <sub>2</sub> )				(C-8)	(C-8a)	(C-9a)	28.2 (C-6)	66.4 (OCH <sub>2</sub> )
2/5	3.04 m	3.16 m	1.9 m (2H)	2.72 s (3H)	168.3	134.5	122.8	39.6	169.6	154.0	25.9, 27.1, 28.4,	13.7
		(CH <sub>2</sub> -10)	1.8 m (4H)					(C-10)	(C-10a)	(C-11a)	31.1 (C-8 !)	
2/6	3.03 t	3.10 t	1.84 m (4H)	2.73 s (3H)	168.6	135.1	121.2	36.0	168.5	154.5	25.6, 25.8, 26.8,	13.8
		(CH <sub>2</sub> -11)	1.42 m (4H)					(C-11)	(C-11a)	(C-12a)	28.8, 30.4	
2/7	2.91 m	2.91 m	2.0 m (2H)	2.72 s (3H)	168.9	136.4	121.5	33.1	168.0	154.2	22.3, 23.1, 24.9,	13.8
		(CH <sub>2</sub> -15)	1.8 m (2H)					(C-15)	(C-15a)	(C-16a)	25.8, 26.1, 26.2,	
			1.5 m (12H)								26.7 (2 peaks), 26.8	
			1.0 m (1211)								2017 (2 peano), 2010	

The spectral data of derivatives **1a-5a**, **1c-5c**, **1d-5d** and **1e-5e** were fully analogous to those of the corresponding [1,2,4]triazolo[5,1-b]quinazoline (**1b-4b**) and 1,3a,5,6, 10c-pentaazaacephenanthrylene (**5b**) derivatives, respectively, the structure of which was proved previously [1], giving evidence for their constitution.

pmr (deuteriochloroform)

Interestingly the carbon atom 9 of the 1,3a,5,6,11c-pentaaza-7,8,9,10-tetrahydro-11*H*-cyclohepta[*e*]acenaphthylenes **5/6** (n = 5, Q = methylthio) and **5/7** (n = 5, Q = morpholin-4-yl) and that of the corresponding carbon atom 8 of derivatives **2/5** and **3/5** (Q = methylthio, X = chloro or 2-hydroxyethylamino, respectively) (Scheme 3) was also shifted upfield to 32.4 and 32.5 ppm, and 31.1 and 31.3 ppm, respectively, analogously to that of the corresponding carbon atom 8 of the 6,7,8,9,10,11-hexahydrocyclohepta-[d][1,2,4]triazolo[1,5-*a*]pyrimidin-5-one derivatives **1/5** (Q = methylthio, R<sup>3</sup> = H) and **6/5** (Q = methylthio, R<sup>3</sup> = benzyl), appearing at 32.4 and 31.3 ppm, respectively, attributed previously [3] to the shielding effect of the C=O group.

cmr (deuteriochloroform)

Comp	n	Q	Reaction	Yield	Mp (°C)	Molecular	MS			Analysis		
ound			(hours)	(%)	(Cryst. from)	(MW)	EI	С	Н	N	S	Cl
3/1	3	Methylthio	0.5	97	191-192 (MeOH)	$C_{11}H_{15}N_5OS$		49.79 49.71	5.70 5.81	26.39	12.08	
3/2	3	1-Methylethylthio	1	98	195-196 (CH-CN / EtOH)	$C_{13}H_{19}N_5OS$ 293 39		53.22 53.30	6.53 6.71	23.87 23.78	10.93	
3/3	3	Dimethylamino	8	98	216-217 (EtOH)	$C_{12}H_{18}N_6O$ 262.32		54.95 54.87	6.92 7.01	32.04 32.12	10.97	
3/4	3	Morpholin-4-yl	1	81	225-227 (CH <sub>2</sub> CN / EtOH)	$C_{14}H_{20}N_6O_2$ 304.35		55.25 55.30	6.62 6.73	27.61 27.69		
3/5	5	Methylthio	4	93	216-217 (CH <sub>3</sub> CN / EtOH)	C <sub>13</sub> H <sub>19</sub> N <sub>5</sub> OS 293.39	293	53.22 53.17	6.53 6.64	23.87 23.84	10.93 10.88	
3/6	6	Methylthio	6	95	208-209 (EtOH)	$C_{14}H_{21}N_5OS$ 307.42	307	54.70 54.77	6.89 6.98	22.78 22.71	10.43 10.38	
3/7	10	Methylthio	2	93	202-203.5 (2-PrOH)	C <sub>18</sub> H <sub>29</sub> N <sub>5</sub> OS 363.53		59.47 59.55	8.04 8.11	19.26 19.13	8.82 8.75	
4/1	3	Methylthio	18	92	174-177 (dec) (ether)	C <sub>11</sub> H <sub>14</sub> ClN <sub>5</sub> S 283.78		46.56 46.61	4.97 5.11	24.68 24.66	11.30 11.22	12.49 12.55
4/2	3	1-Methylethylthio	20	86	145-147 (dec) (ether)	C <sub>13</sub> H <sub>18</sub> ClN <sub>5</sub> S 311.84		50.07 50.13	5.82 5.96	22.46 22.39	10.28 10.22	11.37 11.42
4/4	3	Morpholin-4-yl	19	84	175-180 (dec) (ether)	C <sub>14</sub> H <sub>19</sub> ClN <sub>6</sub> O 322.80		52.09 52.01	5.93 6.06	26.03 25.98		10.98 11.02

Table III

Synthetical and Analytical Data of 5-[(2-Hydroxyethyl)amino and 2-Chloroethyl)amino]-cycloalka[d][1,2,4]triazolo[1,5-a]pyrimidines

Scheme 2



 $(Z = O \text{ and } CH_2)$ 





1/5: R<sup>3</sup> = H 6/5: R<sup>3</sup> = benzyl

As expected (Table VI) the ring size of the cycloalka moiety of derivatives **5a** and **5c-5e** (Q = methylthio) strongly influenced the chemical shift of carbon atoms 6a and  $\omega a$ . On the other hand, it did not influence the chemical shift of carbon atoms 4 appearing at 161.5, 161.3, 161.4 and 160.8 ppm, respectively, (Table VI), in full analogy with that of derivative **5b** (Q = methylthio) reported to

appear at 161.8 ppm previously [1]. This fact predicts analogous chemical surrounding, thus similar electronic structure of carbon atom 4, and consequently the possibility of nucleophilic attack of amines.

Based on the above prediction derivatives **5a** (Q = methylthio) and **5c-5e** (Q = methylthio) were reacted at 100 °C with morpholine and piperidine (Method F, Scheme 2) to yield within a short time (1-2 hours) and in good yield (69–78 %) the expected 4-dialkylamino derivatives **5a** and **5c-5e** (Q = morpholin-4-yl and piperidin-1-yl) (Table V).

As a conclusion it can be stated that different size cycloalkanes, either planar or bulky, attached to the 1,3a,5,6, $\omega$ c-pentaazaacenaphthylene do not influence considerably its electronic state. Consequently the 4-alkylthio group of derivatives **5a-5e** (Q = alkylthio) is in all cases activated towards the nucleophilic attack of amines.

#### EXPERIMENTAL

Melting points were determined on a Kofler-Boëtius micro apparatus and are uncorrected. The infrared spectra were obtained as potassium bromide pellets using Perkin-Elmer 882 spectrophotometer. The ultraviolet spectra were obtained using a Varian Cary 1E UV-VIS instrument. The pmr and the cmr measurements were performed on Bruker WM-250 and Varian Unity Inova 400 (400 MHz) instruments. To confirm the assignments in some cases standard Varian HSQC and HMBC 2D-nmr programs were used. The ms spectra were recorded on a Kratos MS25RFA and a VG Trio 1000 instrument using direct inlet probe in EI mode. Dry-column flash chromatography was performed according to [7] on Kieselgel 60 H (Merck 107736) and Aluminium oxide 60 G (Merck 101090).

	Ø	13.1	36.5 (CH) 23.5 (CH <sub>a</sub> )	37.4	45.9 (NCH <sub>2</sub> ) 65.8 (OCH <sub>2</sub> )	13.6	13.2	13.3	13.4	13.4	36.9 (CH) 23.5 (CH <sub>3</sub> )	45.9 (NCH <sub>2</sub> ) 66.4 (OCH <sub>2</sub> )
	Юа	155.7 (C-9a)	155.8 (C-9a)	155.4 (C-9a)	155.4 (C-9a)	153.9 (C-11a)	154.9 (C-12a)	155.0 (C-16a)	155.9 (C-9a)	155.7 (C-9a)	(C-9a)	155.5 (C-9a)
	C-(0-1)a	171.5 (C-8a)	171.9 (C-8a)	169.6 (C-8a)	170.2 (C-8a)	169.0 (C-10a)	165.85 (C-11a)	165.2 (C-15a)	172.0 (C-8a)	173.0 (C-8a)	(C-8a)	171.5 (C-8a)
	C-(@-1)	33.9 (C-8)	34.3 (C-8)	34.1 (C-8)	34.2 (C-8)	38.5 (C-10)	35.2 (C-11)	32.2 (C-15)	34.2 (C-8)	34.1 (C-8)	34.3 (C-8)	34.4 (C-8)
	Other CH <sub>2</sub>	22.3 (C-7)	22.8 (C-7)	(C-1)	22.8 (C-7)	.8, 27.4 C-8 !)	.4, 25.9, 30.1 -10)	.4, 23.1, .7, 25.9, .6, 26.8	22.7 (C-7)	22.9 (C-7)	(C-1)	(C-7)
	C-6	28.0	28.5	28.5	28.5	25.7, 25 31.3 ((	23.5, 25. 28.7, (C- 6	22.0, 22 24.9, 25 26.2, 26 (C- 6	28.3	28.4	28.5	28.6
cmr	C-5a	100.5	100.8	99.5	100.0	106.0	102.9	103.8	100.6	101.1	101.2	100.0
	C-5	143.4	143.9	143.0	143.5	145.7	145.4	146.5	143.2	143.0	142.9	142.4
	C-2	164.3	163.5	166.5	166.1	166.1	165.9	166.0	164.9	166.0	165.3	166.5
	NCH <sub>2</sub> OCH <sub>2</sub> (CICH <sub>2</sub> )	44.8 60.4	44.9 60.8	44.7	44.8 60.8	47.8 61.3	46.7 61.4	46.7 61.4	43.5* 44.0*	43.3* 44.2*	43.5* 44.5*	43.6* 44.3*
	ð	2.65 s (3H)	3.97 m (1H) 1.44 d (6H)	3.04 s (6H)	3.44 m (4H, NCH <sub>2</sub> ) 3.70 m (4H, OCH <sub>2</sub> )	(3H)	2.64 s (3H)	2.60 s (3H)	2.65 s (3H)	2.66 s (3H)	4.0 m (1H) 1.46 d (6H)	3.58 m (4H, NCH <sub>2</sub> ) 3.77 m (4H, OCH <sub>3</sub> )
	CH2-(@-1)	3.13 t (CH <sub>2</sub> -8)	3.18 t (CH <sub>2</sub> -8)	3.10 t (CH <sub>2</sub> -8)	3.08 t (CH <sub>2</sub> -8)	2.98 m (CH <sub>2</sub> -10)	2.91 m (CH <sub>2</sub> -11)	2.7 m (CH <sub>2</sub> -15)	3.12 t (CH <sub>2</sub> -8)	3.14 t (CH <sub>2</sub> -8)	(CH <sub>2</sub> -8)	$(CH_2 - 8)$
	other CH <sub>2</sub>	$\begin{array}{c} 2.09 \text{ qui} \\ (\text{CH}_2 \text{-} 7) \end{array}$	2.17 qui (CH <sub>2</sub> -7)	2.08 qui (CH <sub>2</sub> -7)	2.03 qui (CH <sub>2</sub> -7)	1.85 m (2H) 1.70 m (4H) (CH <sub>2</sub> -7-9)	1.70 qui 1.70 qui 1.49 qui 1.38 qui (CH.7.10)	(CH2 7-10) 1.82 m (2H) 1.63 m (2H) 1.3-1.56 m (12 H) (CH2 7-14)	$(CH_2 - 7)$	2.22 qui (CH <sub>2</sub> -7)	2.21 qui (CH <sub>2</sub> -7)	$\frac{2.16}{(CH_2-7)}$
pmr	$CH_2-6$	2.84 t	2.91 t	2.79 t	2.76 t	2.84 m	2.87 m	2.7 m	2.89 t	2.97 t	2.99 t	2.92 t
	НО	4.98 t	4.86 t	4.98 bs	4.96 t	4.8 bs	4.7 bs	4.7 bs				
	NCH <sub>2</sub> OCH <sub>2</sub> (CICH <sub>2</sub> )	3.64 m (4H)	3.76 m (4H)	3.67 m (4H)	3.60 m (4H)	3.88 q (5.4Hz) 3.76 t	4.08 q (5.3 Hz) 3.78 t	4.07 q (6 Hz) 3.66 t	3.96 q (6.4 Hz) 3.79 t	4.00 m 3.77 t	4.00 m 3.74 t	3.96 q 3.75 t
	HN	7.54 t	6.95 t	6.76 t	7.05 t	6.61 t	6.53 t	6.93 t	7.71t		6.42 t	6.32 t
	Sol vent pmr cmr	q	$^{a+b}_{b}$	$a^+b$	p,	$_{a+c}^{b}$	a+b a+c	a+b a+c	a+b	$^{a+c}$	a a	e,
	Comp ound	3/1	3/2	3/3	3/4	3/5	3/6	3/7	4/1	4/1	4/2	4/4

Table IV

Nmr Data of 5-[(2-Hydroxyethyl)amino and 2-Chloroethyl)amino]-cycloalka[d][1,2,4]triazolo[1,5-a]pyrimidines

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Synthetical and Analytical DatMethodStartingReactionMethodStartingTimeE1 $3/1$ $14$ E1 $3/1$ $14$ E1 $3/3$ $27$ E1 $3/3$ $22$ E1 $3/4$ $9$ E1 $3/5$ $8.5$ E1 $3/5$ $8.5$ E1 $3/6$ $3$ E2 $3/7$ $4.5$ E2 $3/7$ $4.5$	Synthetical and Analytical Data of 1,3a         Method       Starting       Reaction       Yield         Material       Time       Temperature       (%)         Hours)       27       140       91         [a]       3/1       14       140       80         [a]       3/2       56       reflux       67         [b]       4/2       66       reflux       67         [b]       3/3       22       130       90         [b]       4/4       110       reflux       67         [b]       4/4       100       71       72         [b]       4/4       100       71       72         [b]       4/4       100       71       72         [b]       1       100       71       72         [b]       3/5       8.5       140       75         [a]       3/6       1.5       100       71         [b]       1.5       100       70       75         [b]       3/6       3       140       75         [b]       3/6       3       140       76         [b]       5/8 <td< th=""><th>Synthetical and Analytical Data of 1,3a,5,6,00c-Pentaazz         Method       Starting       Reaction       Yield       Mp (°C)         Material       Time       Temperature       (%)       (Cryst. from)         Imaterial       Time       Temperature       (%)       (Cryst. from)         Imaterial       114       140       80       197-202 (dec)         Iaj       27       140       91       (CH<sub>3</sub>CN)         E2       3/2       21       140       91       (CH<sub>3</sub>CN)         E1       3/3       22       130       90       196-199         E1       3/4       0.25       130       90       196-199         E2       3/4       0.25       180       54       234-239 (dec)         E2       3/4       0.25       180       77       (ether)         E1       3/5       8.5       140       75       216-219 (dec)         E1       3/6</th><th>Synthetical and Analytical Data of 1,3a,5,6,00c-Pentaazacycloalka[e];           Method         Starting         Reaction         Yield         Mp (°C)         Molecular           Method         Starting         Reaction         Yield         Mp (°C)         Molecular           Material         Time         Temperature         (%)         (Cryst. from)         formula           Method         Starting         Reaction         Yield         Mp (°C)         Molecular           Method         Starting         Reaction         (°C)         Molecular         (MW)           F         3/1         14         0         0         177         (CH3CN)         241/30           F         5/1         1         1         100         71         175-177         Ci<sub>1</sub>H<sub>13</sub>N<sub>6</sub>           F         5/1         1         1         100         71         2175-218         244.30</th><th>Synthetical and Analytical Data of 1,3a,5,6,0c-Pentaazacycloalka[e]acenaphth           Method         Sarting         Reaction         Yield         Mp (°C)         Molecular           Material         Time         Temperature         (%)         (Cryst. from)         Formula         C           Imaterial         Time         Temperature         (%)         (Cryst. from)         Molecular           Material         Time         Temperature         (%)         (Cryst. from)         Formula           Imaterial         Time         Temperature         (%)         (Cryst. from)         Formula           P         27         1440         91         197-202 (dec)         247.32         53.42           E1         3/3         22         130         90         196-199         274.40%         53.670           E1         3/3         22         130         90         196-199         244.30%         56.60           D1         4/4         110         refluer         77         clether)         284.37         63.36           D2         4/4         0.25         180         54         58.50         56.60           E1         3/5         8.5         173-177</th><th>Synthetical and Analytical Data of 1,3a,5,6,00-Pentaazacycolalka[e]acempthlylenes           Method Starting         Reaction         Yield         Mp (°C)         Molecular         Analytical Lata of 1,3a,5,6,00-Pentaazacycloalka[e]acempthlylenes           Material         Time         Temperature         (%)         (Cryst. from)         Molecular         Analytical Calcular           Material         Time         Temperature         (%)         (Cryst. from)         Formula         C         H           Bit         27         140         80         197-202 (dec)         C<sub>1</sub>H<sub>3</sub>N/s         53.33         5.44           Bit         3/3         2         130         77         (H3,N)         27.33         53.42         53.06         6.62         6.66         6.63         6.63         6.63         6.63         6.63         6.63         6.63         6.63         6.70         6.22         7.09         6.34         7.09         6.34         6.34         6.34         6.36         6.36         6.36         6.36         6.36         6.34         7.09         6.33         7.09         6.34         7.09         7.09         7.01         7.09         7.01         7.01         7.01         7.01         7.01         7.01</th><th>Synthetical and Analytical Data of 1,34,5,6,00-Pentaazacycloalka[e]acemphthylenes           Method         Starting         Reaction         Yield         Molecular         Analysis           Material         Time         Temperature         (%)         (Cryst. from)         Formula         CaldFound           Haterial         Time         Temperature         (%)         (Cryst. from)         Formula         CaldFound           Haterial         Time         Temperature         (%)         (Cryst. from)         Formula         CaldFound           13         27         140         91         107-202 (dec)         <math>247.32</math>         5.34         2.83         3.440           13         27         140         91         153-157         <math>214.30</math>         5.90         6.05         3.423           12         21         10         77         16bc10         275.38         5.640         6.22         25.43           12         21         10         77         153-157         <math>214.30^{\circ}</math>         58.70         6.22         25.43           12         21         21         21         21         22         23         22         24.43         28.57         22         24.43</th><th></th><th>Synthetical and Analytical Data of 1,3a,5,6,00- Pentazzeycloalke[e]accamphthylenes           Method         Samthetical and Analytical Data of 1,3a,5,6,00- Pentazzeycloalke[e]accamphthylenes         Material         Relation         Wight         Material         Relation         Wight         Material         Calcd Found         MS         MS           Imace         Temperature         (%)         (%)         (Cryst. from)         Pomula         Calcd Found         S         Material         Material         Material         Material         (%)         (Cryst. from)         Fomula         Calcd Found         S         Material         Material         Material         Material         Material         Material         Material         Material         (%)         (Cryst. from)         Pomula         Calcd Found         S         Material         Material</th></td<>	Synthetical and Analytical Data of 1,3a,5,6,00c-Pentaazz         Method       Starting       Reaction       Yield       Mp (°C)         Material       Time       Temperature       (%)       (Cryst. from)         Imaterial       Time       Temperature       (%)       (Cryst. from)         Imaterial       114       140       80       197-202 (dec)         Iaj       27       140       91       (CH <sub>3</sub> CN)         E2       3/2       21       140       91       (CH <sub>3</sub> CN)         E1       3/3       22       130       90       196-199         E1       3/4       0.25       130       90       196-199         E2       3/4       0.25       180       54       234-239 (dec)         E2       3/4       0.25       180       77       (ether)         E1       3/5       8.5       140       75       216-219 (dec)         E1       3/6	Synthetical and Analytical Data of 1,3a,5,6,00c-Pentaazacycloalka[e];           Method         Starting         Reaction         Yield         Mp (°C)         Molecular           Method         Starting         Reaction         Yield         Mp (°C)         Molecular           Material         Time         Temperature         (%)         (Cryst. from)         formula           Method         Starting         Reaction         Yield         Mp (°C)         Molecular           Method         Starting         Reaction         (°C)         Molecular         (MW)           F         3/1         14         0         0         177         (CH3CN)         241/30           F         5/1         1         1         100         71         175-177         Ci <sub>1</sub> H <sub>13</sub> N <sub>6</sub> F         5/1         1         1         100         71         2175-218         244.30	Synthetical and Analytical Data of 1,3a,5,6,0c-Pentaazacycloalka[e]acenaphth           Method         Sarting         Reaction         Yield         Mp (°C)         Molecular           Material         Time         Temperature         (%)         (Cryst. from)         Formula         C           Imaterial         Time         Temperature         (%)         (Cryst. from)         Molecular           Material         Time         Temperature         (%)         (Cryst. from)         Formula           Imaterial         Time         Temperature         (%)         (Cryst. from)         Formula           P         27         1440         91         197-202 (dec)         247.32         53.42           E1         3/3         22         130         90         196-199         274.40%         53.670           E1         3/3         22         130         90         196-199         244.30%         56.60           D1         4/4         110         refluer         77         clether)         284.37         63.36           D2         4/4         0.25         180         54         58.50         56.60           E1         3/5         8.5         173-177	Synthetical and Analytical Data of 1,3a,5,6,00-Pentaazacycolalka[e]acempthlylenes           Method Starting         Reaction         Yield         Mp (°C)         Molecular         Analytical Lata of 1,3a,5,6,00-Pentaazacycloalka[e]acempthlylenes           Material         Time         Temperature         (%)         (Cryst. from)         Molecular         Analytical Calcular           Material         Time         Temperature         (%)         (Cryst. from)         Formula         C         H           Bit         27         140         80         197-202 (dec)         C <sub>1</sub> H <sub>3</sub> N/s         53.33         5.44           Bit         3/3         2         130         77         (H3,N)         27.33         53.42         53.06         6.62         6.66         6.63         6.63         6.63         6.63         6.63         6.63         6.63         6.63         6.70         6.22         7.09         6.34         7.09         6.34         6.34         6.34         6.36         6.36         6.36         6.36         6.36         6.34         7.09         6.33         7.09         6.34         7.09         7.09         7.01         7.09         7.01         7.01         7.01         7.01         7.01         7.01	Synthetical and Analytical Data of 1,34,5,6,00-Pentaazacycloalka[e]acemphthylenes           Method         Starting         Reaction         Yield         Molecular         Analysis           Material         Time         Temperature         (%)         (Cryst. from)         Formula         CaldFound           Haterial         Time         Temperature         (%)         (Cryst. from)         Formula         CaldFound           Haterial         Time         Temperature         (%)         (Cryst. from)         Formula         CaldFound           13         27         140         91         107-202 (dec) $247.32$ 5.34         2.83         3.440           13         27         140         91         153-157 $214.30$ 5.90         6.05         3.423           12         21         10         77         16bc10         275.38         5.640         6.22         25.43           12         21         10         77         153-157 $214.30^{\circ}$ 58.70         6.22         25.43           12         21         21         21         21         22         23         22         24.43         28.57         22         24.43		Synthetical and Analytical Data of 1,3a,5,6,00- Pentazzeycloalke[e]accamphthylenes           Method         Samthetical and Analytical Data of 1,3a,5,6,00- Pentazzeycloalke[e]accamphthylenes         Material         Relation         Wight         Material         Relation         Wight         Material         Calcd Found         MS         MS           Imace         Temperature         (%)         (%)         (Cryst. from)         Pomula         Calcd Found         S         Material         Material         Material         Material         (%)         (Cryst. from)         Fomula         Calcd Found         S         Material         Material         Material         Material         Material         Material         Material         Material         (%)         (Cryst. from)         Pomula         Calcd Found         S         Material         Material
Synthetical and Analytical Dat         Starting       Reaction         Material       Time         Time       Temperature $3/1$ $14$ $140$ $3/2$ $27$ $140$ $3/2$ $27$ $140$ $3/3$ $22$ $130$ $3/3$ $22$ $130$ $3/4$ $0.25$ $130$ $3/4$ $9$ $130$ $3/4$ $0.25$ $180$ $3/4$ $0.25$ $180$ $3/4$ $0.25$ $180$ $3/4$ $9$ $130$ $3/4$ $9$ $130$ $3/4$ $9$ $130$ $3/5$ $8.5$ $140$ $3/6$ $3$ $100$ $3/6$ $3$ $100$ $3/6$ $3$ $100$ $3/7$ $4.5$ $120$	Synthetical and Analytical Data of 1,3a         Starting       Reaction       Yield         Material       Time       Temperature       (%)         3/1       14       140       80         3/2       26       reflux       67         3/3       22       130       90         3/3       22       130       77         3/3       22       130       77         3/3       22       130       77         3/3       22       130       77         3/4       0.25       180       77         3/4       9       130       89         3/1       1       100       71         3/4       9       130       89         3/4       9       130       77         3/5       8.5       140       75         3/6       1.5       100       70         3/6       3       140       72         3/6       3       140       72         3/7       45       100       69         3/7       45       100       69	Synthetical and Analytical Data of 1,3a,5,6,00c-Pentaazz         Starting       Reaction       Yield       Mp (°C)         Material       Time       Time       Mp (°C)         Material       Time       Time       Mp (°C)         Material       Time       Time       Time       Mp (°C)         Material       Time       Time       Time       Mp (°C)         Material       Time       Time       Time       Mp (°C)         At       14       140       80       197-202 (dec)         3/3       22       130       90       107-107         3/3       22       130       90       107-199         3/3       22       130       90       106-199         3/4       0       77       (CH <sub>3</sub> CN)       (CH <sub>3</sub> CN)         3/4       0       71       175-177       (ether)         3/4       0       73       230-236 (dec)       (ether)         3/4       9       1300       89       216-219 (dec)         3/4       9       130       77       216-219 (dec)         3/5       8.5       140       75       216-219 (dec)	Synthetical and Analytical Data of 1,3a,5,6,00c-Pentaazacycloalka[e]         Starting       Reaction       Yield       Mp (°C)       Molecular         Material       Time       Temperature       (%)       (Cryst. from)       Formula         Mouse       (°C)       No       MW       MW         Material       T       140       80       197-202 (dec)       C <sub>11</sub> H <sub>13</sub> N <sub>5</sub> S         372       22       130       77       (CH <sub>3</sub> CN)       247.32         373       22       130       90       196-199       C <sub>13</sub> H <sub>17</sub> N <sub>5</sub> S         373       22       130       77       (CH <sub>3</sub> CN)       244.30         41       1       100       71       175-177       C <sub>13</sub> H <sub>16</sub> N <sub>6</sub> O         314       92       100       71       175-177       C <sub>13</sub> H <sub>16</sub> N <sub>6</sub> O         314       9       54       234-239 (dec)       C <sub>14</sub> H <sub>16</sub> N <sub>6</sub> O	Synthetical and Analytical Data of 1,3a,5,6,00c-Pentaazacycloalka[e]acenaphth           Sharting         Reaction         Yield         Mp (°C)         Molecular           Material         Time         Temperature         (%6)         (Cryst. from)         Formula         C           Material         Time         Temperature         (%6)         (Cryst. from)         Molecular         C           Material         Time         Temperature         (%6)         (Cryst. from)         Molecular         C           3/1         14         140         80         197-202 (dec)         C <sub>11</sub> H <sub>13</sub> N <sub>5</sub> S         53.42           3/2         66         reflux         67         153-157         C <sub>13</sub> H <sub>17</sub> N <sub>5</sub> S         53.42           3/2         2         130         90         196-199         C <sub>13</sub> H <sub>15</sub> N <sub>5</sub> S         56.70           3/2         2         130         90         155-115         C <sub>13</sub> H <sub>15</sub> N <sub>5</sub> S         56.70           3/1         1         100         71         ether)         275.38         56.60           3/1         9         155-115         C <sub>13</sub> H <sub>15</sub> N <sub>6</sub> S         58.73         58.73           4/4         0.25         180         275.236 (dec)         C <sub>1</sub>	Synthetical and Analytical Data of 1,3a,5,6.0c-Pentaazacycloalka[e]acenaphthylenes           Starting         Reaction         Yield         Mp (°C)         Molecular         Analytical Late           Material         Time         Temperature         (%)         (Cryst. from)         Formula         Caled           Material         Time         Temperature         (%)         (Cryst. from)         Formula         Caled           Material         Time         Temperature         (%)         (Cryst. from)         Formula         Caled           3/1         14         140         80         197-202 (dec)         C <sub>11</sub> H <sub>13</sub> N/s         53.42         5.30           3/2         2         130         77         (CH <sub>3</sub> CN)         24A.30         58.91         6.36           3/1         1         100         71         (CH <sub>3</sub> CN)         24A.30         58.32         7.21           3/2         2         130         71         (CH <sub>3</sub> CN)         24A.30         6.33         7.31           4/4         110         reflux         67         155.157         C <sub>13</sub> H <sub>13</sub> N/s         58.79         6.44           4/4         1         1         105.193         274.23 (dec)         284.37 <td>Synthetical and Analytical Data of 1,3a,5,6,00c-Pentaazacycloalka[e]acenaphthylenes           Slatting         Raction         Yield         Mp (°C)         Molecular           Material         Time         Time         Time         Time         CaseAfenud         Analysis           Material         Time         Time         (°G)         (Cryst. from)         P(MU)         C         H         N           Material         Time         Time         (°G)         (Cryst. from)         P(MU)         C         H         N           Molecular         (°G)         (Cryst. from)         P(MU)         C         H         N           Material         Time         Time         Time         S3.2         S3.3         S3.44         S3.23           Molecular         C         153-157         C<sub>13</sub>H<sub>10</sub>N<sub>58</sub>         S6.70         6.22         S5.44         S3.23           Molecular         C         153-157         C<sub>13</sub>H<sub>10</sub>N<sub>58</sub>         S6.70         6.33         23.23         S3.23           Molecular         C         134-170         Z<sub>14</sub>H<sub>10</sub>N<sub>58</sub>         S6.70         6.33         23.42         S3.44         S3.53           Molecular</td> <td>Synthetical and Analytical Data of L3A,56,00c-Pentaazacycloalka[e]acenaphthylenes           Starting         Reaction         Yield         Mp (°C)         Molecular         Analysis           Material         Time         Temperature         (%)         (Cryst. from)         Formula         CalcdFound         S           Material         Time         Temperature         (%)         (Cryst. from)         Formula         CalcdFound         S           Material         Time         Temperature         (%)         (Cryst. from)         Formula         CalcdFound         S           Material         Time         Temperature         (%)         (Cryst. from)         Formula         CalcdFound         S           Material         Time         Temperature         (%)         Cryst. from)         Formula         CalcdFound         S           Material         Time         Temperature         (%)         Cryst. from)         241,3,5         S</td> <td>Synthetical and Analytical Data of 1,3a,5,60c-Pentazazoyoloalka[e]acemphlhylenes           Starting Material Time         Reaction Time         Yield (%)         Mp (°C) (°G)         Molecular (MM)         Analysis Caled/Found         Ms           1         14         140         80         (°G)         Cayst. from)         Pormula         Analysis         Ms           31         14         140         80         (°G)         Cayst. from)         Pormula         2.7         12.92         247           32         6         reflux         67         153-157         C<sub>1</sub>H<sub>13</sub>Ns         53.42         5.33         11.64         275           32         2         130         70         90         6.60         34.40         27           33         2         11         100         71         175-177         C<sub>14</sub>H<sub>3</sub>Ns         56.80         6.60         34.40         274           34         9         11         100         71         175-177         C<sub>14</sub>H<sub>3</sub>Ns         56.30         6.34         29.43         244           34         0.25         18         6.33         6.34         29.35         284         37.09         276         284           34</td>	Synthetical and Analytical Data of 1,3a,5,6,00c-Pentaazacycloalka[e]acenaphthylenes           Slatting         Raction         Yield         Mp (°C)         Molecular           Material         Time         Time         Time         Time         CaseAfenud         Analysis           Material         Time         Time         (°G)         (Cryst. from)         P(MU)         C         H         N           Material         Time         Time         (°G)         (Cryst. from)         P(MU)         C         H         N           Molecular         (°G)         (Cryst. from)         P(MU)         C         H         N           Material         Time         Time         Time         S3.2         S3.3         S3.44         S3.23           Molecular         C         153-157         C <sub>13</sub> H <sub>10</sub> N <sub>58</sub> S6.70         6.22         S5.44         S3.23           Molecular         C         153-157         C <sub>13</sub> H <sub>10</sub> N <sub>58</sub> S6.70         6.33         23.23         S3.23           Molecular         C         134-170         Z <sub>14</sub> H <sub>10</sub> N <sub>58</sub> S6.70         6.33         23.42         S3.44         S3.53           Molecular	Synthetical and Analytical Data of L3A,56,00c-Pentaazacycloalka[e]acenaphthylenes           Starting         Reaction         Yield         Mp (°C)         Molecular         Analysis           Material         Time         Temperature         (%)         (Cryst. from)         Formula         CalcdFound         S           Material         Time         Temperature         (%)         (Cryst. from)         Formula         CalcdFound         S           Material         Time         Temperature         (%)         (Cryst. from)         Formula         CalcdFound         S           Material         Time         Temperature         (%)         (Cryst. from)         Formula         CalcdFound         S           Material         Time         Temperature         (%)         Cryst. from)         Formula         CalcdFound         S           Material         Time         Temperature         (%)         Cryst. from)         241,3,5         S	Synthetical and Analytical Data of 1,3a,5,60c-Pentazazoyoloalka[e]acemphlhylenes           Starting Material Time         Reaction Time         Yield (%)         Mp (°C) (°G)         Molecular (MM)         Analysis Caled/Found         Ms           1         14         140         80         (°G)         Cayst. from)         Pormula         Analysis         Ms           31         14         140         80         (°G)         Cayst. from)         Pormula         2.7         12.92         247           32         6         reflux         67         153-157         C <sub>1</sub> H <sub>13</sub> Ns         53.42         5.33         11.64         275           32         2         130         70         90         6.60         34.40         27           33         2         11         100         71         175-177         C <sub>14</sub> H <sub>3</sub> Ns         56.80         6.60         34.40         274           34         9         11         100         71         175-177         C <sub>14</sub> H <sub>3</sub> Ns         56.30         6.34         29.43         244           34         0.25         18         6.33         6.34         29.35         284         37.09         276         284           34
iical and Analytical Dat Reaction Time Temperature (hours) (°C) 27 140 27 140 26 reflux 22 130 22 130 22 130 1 100 1 100 8.5 140 8.5 140 8.5 140 1.5 100 1.5 100 22 130 22 130 22 130 22 130 22 2 2 30 23 2 2 30 24 2 30 25 2 30 26 2 30 27 2 30 20 20 2 30 20 20 20 2	iceal and Analytical Data of 1,3a Reaction Yield (hours) (°C) 27 140 80 27 140 91 (%) 26 reflux 67 2 130 90 27 130 90 21 100 71 110 reflux 72 0.25 180 54 9 130 89 1 100 71 1.5 100 70 1.5 100 70 1.5 100 69 2 130 54 9 130 87 1.1 100 71 1.1 100 71 1.1 100 71 1.2 100 70 1.5 100 69 2 130 73 3 140 72 3 140 72 1.5 100 70 1.5	ical and Analytical Data of 1,3a,5,6,0c-Pentaazz Reaction Yield Mp ( $^{\circ}$ C) (hours) ( $^{\circ}$ C) (Cryst. from) Time Temperature (hours) ( $^{\circ}$ C) ( $^{\circ}$ G) (Cryst. from) 27 140 80 197-202 (dec) 28 130 90 196-199 (CH <sub>3</sub> CN) 10 reflux 67 153-157 2130 90 196-199 (CH <sub>3</sub> CN) 11 100 71 175-177 (ether) 9 130 54 234-239 (dec) 9 130 89 216-228 (dec) 1.5 100 71 231-238 (dec) 1.5 100 70 215-228 (dec) 1.5 100 70 215-228 (dec) 1.5 100 70 215-228 (dec) 3 140 75 216-219 (dec) 3 140 75 216-219 (dec) 1.5 100 69 215-223 (dec) 4.5 130 73 235.73 (dec) (ether)	ical and Analytical Data of 1,3a,5,6,00c-Pentaazacycloalka[e] Reaction Yield Mp (°C) Molecular (%6) (Cryst. from) Formula (MW) (hours) (°C) (°C) 91 197-202 (dec) $C_{11}H_{13}N_5S$ 27 140 80 197-202 (dec) $C_{13}H_{16}N_6S$ 28 130 90 196-199 $C_{13}H_{16}N_6S$ 2130 90 196-199 $C_{13}H_{16}N_6S$ 214.30 11 10 reflux 72 230-236 (dec) $236.34$ 11 100 71 175-177 $C_{13}H_{26}N_6S$ 9 130 89 216-228 (dec) $286.34$ 0.25 180 54 234-239 (dec) 9 130 89 216-228 (dec) $286.34$ 1.5 100 70 215-228 (dec) $286.34$ 1.5 100 70 215-228 (dec) $C_{14}H_{18}N_6S$ 1.5 2140 75 216-219 (dec) $C_{13}H_{17}N_5S$ 1.5 100 70 215-222 (dec) $C_{14}H_{19}N_5S$ 1.5 100 70 215-222 (dec) $C_{14}H_{19}N_5S$ 1.5 100 69 225-237 (dec) $C_{14}H_{19}N_5S$ 45 130 73 73 273 5-776 $C_{14}H_{19}N_5S$	ical and Analytical Data of 1,3a,5,6,00c-Pentaazzoycloalka[e]acenaphth Reaction Yield Mp (°C) Molecular (°b) (Cryst. from) Formula (MW) C (hours) (°C) (°C) $(2^{+})$ ( $2^{+}$ )	ical and Analytical Data of 1,3a,5,6,00c-Pentaazacycloalka[e]acemaphthylenes Reaction Yield Mp (°C) Molecular Analytical Temperature (°) (Cryst. from) Formula (MW) C H (hours) (°C) (°C) (Cryst. from) Formula (MW) C H (hours) (°C) 275,385 53.42 5.30 277 140 91 (CH <sub>3</sub> CN) 247,32 53.38 5.44 66 reflux 67 153-157 $C_{13}H_{10}N_6$ 58.00 6.60 22 130 90 196-199 $C_{24}H_{6}N_6$ 58.00 6.60 22 130 90 196-199 $C_{24}H_{6}N_6$ 59.00 6.60 110 reflux 72 (CH <sub>3</sub> CN) 284.37 63.32 7.21 110 reflux 72 (EHeer) 284.37 63.32 7.09 9 130 89 216-228 (dec) 286.34 58.59 6.44 0.25 180 85 4 234-239 (dec) 9 130 89 216-228 (dec) 286.34 58.59 6.44 1.5 100 70 216-228 (dec) 286.34 58.59 6.44 1.5 (CH <sub>3</sub> CN) 284.37 63.32 7.05 8.5 140 77 216-228 (dec) 2.44 $B_{6}N_6$ 63.36 7.09 1.6 (CH <sub>3</sub> CN) 286.34 58.59 6.47 1.5 100 70 215-228 (dec) 2.44 $B_{6}N_6$ 61.13 7.05 (CH <sub>3</sub> CN) 289.41 58.16 6.57 8.5 140 77 216-228 (dec) 2.44 $B_{6}N_6$ 61.13 7.05 8.5 140 77 216-228 (dec) 2.44 $B_{6}N_6$ 61.13 7.05 8.5 140 77 216-228 (dec) 2.44 $B_{6}N_6$ 61.13 7.05 8.5 140 70 215-222 (dec) 2.44 $B_{6}N_6$ 61.13 7.05 8.16 (CH <sub>3</sub> CN) 289.41 58.16 6.58 1.5 100 69 225-237 (dec) 2.04 $B_{6}N_6$ 61.13 7.05 8.14 10 6.12 (CH <sub>3</sub> CN) 289.41 58.16 6.58 8.14 10 6.02 (CH <sub>3</sub> CN) 289.41 58.16 6.58 8.14 10 6.02 (CH <sub>3</sub> CN) 289.41 58.16 6.58 8.14 10 70 215-222 (dec) 2.04 $B_{6}N_6$ 6.17 7.37 8.14 10 6.10 70 215-223 (dec) 2.05 $B_{6}N_6$ 6.17 7.37 8.14 10 6.10 69 225-237 (dec) 2.14 $A_{6}N_6$ 6.217 7.37 8.15 (cH <sub>3</sub> CN) 2.280.41 58.16 6.58 8.16 (cH <sub>3</sub> CN) 2.280.41 58.17 7.48 6.57 7.48 6.57 7.58 6.57 7.58 6.57 7.58 6.57 7.58 6.57 7.58 6.57 7.58 7.57 7.58 7.57 7.58 7.57 7.58 7.57 7.58 7.57 7.58 7.57 7.58 7.57 7.58 7.57 7.58 7.57 7.58 7.57 7.58 7.57 7.58 7.57 7.58 7.57 7.58 7.57 7.58 7.57 7.58 7.57 7.58 7.57 7.58 7.57 7.58 7.55 7.57 7.58 7.55 7.55	tical and Analytical Data of 1,3a,5,6,00-Pentaazacycloalka[e]acenaphthylenes           Reaction         Yield         Mp (°C)         Analysis           Time         Temperature         (°C)         Mp (°C)         Molecular         Analysis           7         Temperature         (°C)         (°C)         Mp (°C)         Molecular         Analysis           14         140         80         197-202 (dec) $C_{13}H_{13}N_5$ 55.70         6.22         25.43           2         130         77         (CH3CN) $C_{13}H_{13}N_5$ 56.70         6.23         23.40           2         130         77         (CH3CN) $C_{13}H_{23}N_6$ 63.36         7.09         29.55           2         130         77         (CH3CN) $C_{14}H_{3N}N_6$ 58.70         6.22         25.43           110         refturk         67         157-177 $C_{14}H_{3N}N_6$ 58.70         6.23         29.25           110         refturk         72         230-236 (dec) $C_{14}H_{3N}N_6$ 58.670         6.22         25.43           110         refturk         72         234-239 (dec)         236.34		ical and Analytical Data of L,3a,5,6,00c-Pentaazasycloalka[e]acemphitylenes Reaction Yield Mp (°C) Molecular Analysis MS (nours) (°C) (°C) (°C) Molecular (MW) C H N S 300 (°C) (°C) (°C) (°C) (°C) (°C) (°C) (°C)
Analytical Dat aaction Temperature (°C) (°C) 140 140 130 130 130 130 100 100 100 100 100 10	Analytical Data of 1,3a eaction Yield (%) Temperature (%) (°C) (%) 140 80 140 91 reflux 67 130 90 100 71 180 54 130 89 100 71 140 75 140 75 140 75 140 75 140 75 130 70 1100 69	Analytical Data of 1,3a,5,6,00c-Pentaazz         aaction       Yield       Mp ( $^{\circ}$ C)         Temperature       (%6)       (Cryst. from)         (°C)       91       (P1, 32, 157)         130       90       197-202 (dec)         130       77       (ether)         130       71       (T5-177)         130       71       (F1, 5, 177)         100       71       (T5-177)         1100       71       (T5-177)         180       54       234-239 (dec)         130       75       216-219 (dec)         140       75       216-219 (dec)         100       70       215-222 (dec)         100       70       215-222 (dec)         100       69       225-237 (dec)         130       73       2233.5-726		Analytical Data of 1,3a,5,6,0c-Pentaazacycloalka[e]acenaphth           aaction         Yield         Mp (°C)         Molecular           Temperature         (%6)         (Cryst. from)         Formula         C           Temperature         (%6)         (Cryst. from)         Formula         C           Temperature         (%6)         (Cryst. from)         Formula         C $(^{\circ}C)$ 80         197-202 (dec) $C_{11}H_{13}N_{5}S$ 55.70           130         90         196-199 $C_{12}H_{16}N_{6}S$ 58.91           130         77         (ether)         275.38         56.80           130         90         196-199 $C_{12}H_{16}N_{6}S$ 58.91           100         71         175-177 $C_{13}H_{15}N_{6}S$ 58.73           reflux         72         230-236 (dec) $C_{14}H_{18}N_{6}O$ 58.73           100         71         175-177 $C_{15}H_{16}N_{6}S$ 58.50           130         54         231.238 (dec) $C_{14}H_{18}N_{6}O$ 58.73           190         73         236.236 (dec) $C_{14}H_{19}N_{5}S$ 56.66           180         516-228 (dec) <td>Analytical Data of 1,3a,5,6,00c-Pentaazacycloalka[e]acenaphthylenes           action         Yield         Mp (°C)         Molecular         Analytical           Temperature         (%6)         (Cryst. from)         Formula         Calcd           Temperature         (%6)         (Cryst. from)         Formula         Calcd           Temperature         (%6)         (Cryst. from)         Formula         Calcd           Temperature         00         197-202 (dsc)         C<sub>13</sub>H<sub>15</sub>N<sub>5</sub>S         53.342         5.30           130         77         (CH<sub>3</sub>CN)         244.30         58.91         6.73           130         71         (CH<sub>3</sub>CN)         244.30         58.91         6.73           130         71         175-177         C<sub>13</sub>H<sub>16</sub>N<sub>6</sub>S         59.00         6.63           130         71         175-177         C<sub>13</sub>H<sub>16</sub>N<sub>6</sub>S         58.91         6.73           130         71         275.38         56.60         6.34         44           130         71         244.30         58.73         6.34         44           130         71         231-238 (dsc)         6.34         44         709           130         89         244&lt;</td> <td>Analytical Data of 1.3a,5,6,00-Pentaazacycloalkaf e Jacenaphthylenes           action         Yield         Mp (°C)         Molecular         Analysis           Temperature         (%)         (Cryst. from)         Pormula         Caled/Found           (°C)         80         197-202 (dec)         <math>C_{11}H_{13}N_{5}S</math>         53.42         53.30         28.32           140         80         197-202 (dec)         <math>C_{13}H_{17}N_{5}S</math>         55.44         28.27           130         90         197-202 (dec)         <math>C_{13}H_{10}N_{6}S</math>         55.43         54.44         28.27           130         90         196-199         <math>C_{13}H_{10}N_{6}S</math>         56.80         6.36         25.38           130         90         196-199         <math>C_{13}H_{10}N_{6}S</math>         58.91         6.73         24.20           130         90         196-199         <math>C_{13}H_{10}N_{6}S</math>         58.91         6.73         24.40           130         71         175-177         <math>C_{14}H_{10}N_{6}S</math>         58.71         29.49         29.35           100         71         175-177         <math>C_{14}H_{10}N_{6}S</math>         58.59         6.44         29.35           100         71         175-216         <math>C_{14}H_{18}</math></td> <td></td> <td></td>	Analytical Data of 1,3a,5,6,00c-Pentaazacycloalka[e]acenaphthylenes           action         Yield         Mp (°C)         Molecular         Analytical           Temperature         (%6)         (Cryst. from)         Formula         Calcd           Temperature         (%6)         (Cryst. from)         Formula         Calcd           Temperature         (%6)         (Cryst. from)         Formula         Calcd           Temperature         00         197-202 (dsc)         C <sub>13</sub> H <sub>15</sub> N <sub>5</sub> S         53.342         5.30           130         77         (CH <sub>3</sub> CN)         244.30         58.91         6.73           130         71         (CH <sub>3</sub> CN)         244.30         58.91         6.73           130         71         175-177         C <sub>13</sub> H <sub>16</sub> N <sub>6</sub> S         59.00         6.63           130         71         175-177         C <sub>13</sub> H <sub>16</sub> N <sub>6</sub> S         58.91         6.73           130         71         275.38         56.60         6.34         44           130         71         244.30         58.73         6.34         44           130         71         231-238 (dsc)         6.34         44         709           130         89         244<	Analytical Data of 1.3a,5,6,00-Pentaazacycloalkaf e Jacenaphthylenes           action         Yield         Mp (°C)         Molecular         Analysis           Temperature         (%)         (Cryst. from)         Pormula         Caled/Found           (°C)         80         197-202 (dec) $C_{11}H_{13}N_{5}S$ 53.42         53.30         28.32           140         80         197-202 (dec) $C_{13}H_{17}N_{5}S$ 55.44         28.27           130         90         197-202 (dec) $C_{13}H_{10}N_{6}S$ 55.43         54.44         28.27           130         90         196-199 $C_{13}H_{10}N_{6}S$ 56.80         6.36         25.38           130         90         196-199 $C_{13}H_{10}N_{6}S$ 58.91         6.73         24.20           130         90         196-199 $C_{13}H_{10}N_{6}S$ 58.91         6.73         24.40           130         71         175-177 $C_{14}H_{10}N_{6}S$ 58.71         29.49         29.35           100         71         175-177 $C_{14}H_{10}N_{6}S$ 58.59         6.44         29.35           100         71         175-216 $C_{14}H_{18}$		
	a of 1,3a Yield (%) 91 91 97 77 71 71 71 71 72 72 72 72 73 73 73 73	a of 1,3a,5,6,00c-Pentaazz Yield Mp (°C) (%6) (Cryst. from) 80 197-202 (dec) 91 (CH <sub>3</sub> CN) 67 153-157 77 (ether) 90 196-199 (CH <sub>3</sub> CN) 71 175-177 (ether) 72 230-236 (dec) 73 234-239 (dec) 71 231-238 (dec) 71 231-238 (dec) 71 231-238 (dec) 71 231-238 (dec) 72 216-219 (dec) 73 215-222 (dec) 69 225-237 (dec) 69 225-237 (dec) 61 ether) 73 223:5-226	a of 1,3a,5,6,00c-Pentaazacycloalka[e] Yield Mp ( $^{\circ}$ C) Molecular ( $^{\circ}$ 6, (Cryst. from) Formula (MW) 80 197-202 (dec) C <sub>11</sub> H <sub>13</sub> N <sub>5</sub> S 91 (CH <sub>3</sub> CN) 247.32 67 153-157 C <sub>13</sub> H <sub>17</sub> N <sub>5</sub> S 77 (ether) 244.30 71 175-177 C <sub>13</sub> H <sub>16</sub> N <sub>6</sub> O 67 155-177 C <sub>13</sub> H <sub>16</sub> N <sub>6</sub> O 71 175-177 C <sub>13</sub> H <sub>16</sub> N <sub>6</sub> O 72 230-236 (dec) 286.34 54 234-239 (dec) 286.34 75 216-228 (dec) 286.34 76 213-238 (dec) 286.34 77 231-238 (dec) 286.34 78 234-239 (dec) 286.34 79 216-228 (dec) 286.34 70 215-222 (dec) C <sub>13</sub> H <sub>17</sub> N <sub>5</sub> S 70 215-222 (dec) C <sub>13</sub> H <sub>16</sub> N <sub>5</sub> O 71 231-238 (dec) 314.39 72 214-217 (dec) C <sub>14</sub> H <sub>16</sub> N <sub>5</sub> S 73 273 (dec) C <sub>14</sub> H <sub>16</sub> N <sub>5</sub> S 72 214-217 (dec) C <sub>14</sub> H <sub>16</sub> N <sub>5</sub> S 73 273 (dec) C <sub>14</sub> H <sub>16</sub> N <sub>5</sub> S 73 273 (dec) C <sub>14</sub> H <sub>16</sub> N <sub>5</sub> S 73 273 (dec) C <sub>14</sub> H <sub>16</sub> N <sub>5</sub> S 73 273 (dec) C <sub>14</sub> H <sub>16</sub> N <sub>5</sub> S 73 273 (dec) C <sub>14</sub> H <sub>16</sub> N <sub>5</sub> S 73 273 (dec) C <sub>14</sub> H <sub>16</sub> N <sub>5</sub> S 73 273 (dec) C <sub>14</sub> H <sub>16</sub> N <sub>5</sub> S 73 273 (dec) C <sub>14</sub> H <sub>16</sub> N <sub>5</sub> S 73 273 (dec) C <sub>17</sub> H <sub>419</sub> N <sub>5</sub> S 73 273 5.776 C <sub>17</sub> H <sub>419</sub> N <sub>5</sub> S 73 273 5.776 C <sub>17</sub> H <sub>419</sub> N <sub>5</sub> S	a of 1.3a,5,6,00c-Pentaazacycloalka[e]acemaphth Yield Mp (°C) Molecular (MW) C (°b) (Cryst. from) Formula (MW) C 80 197-202 (dec) $C_{11}H_{13}N_5S$ 53.42 91 (CH <sub>3</sub> CN) 247.32 53.38 67 153-157 $C_{13}H_{17}N_5S$ 56.70 77 (ether) 275.38 56.80 90 196-199 $C_{12}H_{16}N_6$ 59.00 (CH <sub>3</sub> CN) 244.30 58.91 71 175-177 $C_{13}H_{20}N_6$ 63.36 73 (ether) 286.34 58.59 54 224-236 (dec) $C_{14}H_{18}N_6O$ 58.71 71 231-238 (dec) $C_{13}H_{18}N_6O$ 58.73 71 231-238 (dec) $C_{13}H_{18}N_6O$ 58.73 66 71 231-238 (dec) $C_{13}H_{18}N_6O$ 58.73 75 216-219 (dec) $C_{13}H_{18}N_6O$ 58.73 70 215-222 (dec) $C_{13}H_{18}N_6O$ 58.71 71 231-238 (dec) $C_{13}H_{18}N_6O$ 58.73 70 215-222 (dec) $C_{13}H_{18}N_6O$ 58.71 71 231-238 (dec) $C_{13}H_{18}N_6O$ 58.73 66(6) 733-75.38 56.66 72 236-237 (dec) $C_{13}H_{18}N_6O$ 61.13 72 214-217 (dec) $C_{14}H_{18}N_5S$ 58.10 6108 73 223.5-226 $C_{14}H_{18}N_5S$ 58.10 6108 73 233.5-226 $C_{14}H_{28}N_6O$ 62.17 6109 328.42 62.71	a of 1,3a,5,6,00c-Pentaazacycloalka[e]acemaphthylenes Yield Mp ( $^{\circ}$ C) Molecular Ana ( $^{\circ}$ 6) (Cryst. from) Formula Calcd (MW) C H <sub>3</sub> CN) S 53.42 5.30 91 197-202 (dec) C <sub>11</sub> H <sub>13</sub> N <sub>5</sub> S 55.70 6.22 77 (ether) 247.32 53.38 5.44 67 153-157 C <sub>13</sub> H <sub>17</sub> N <sub>5</sub> S 56.70 6.22 196-199 C <sub>13</sub> H <sub>16</sub> N <sub>6</sub> 59.00 6.60 196-199 C <sub>13</sub> H <sub>16</sub> N <sub>6</sub> 53.00 6.60 171 (T55-177 C <sub>13</sub> H <sub>16</sub> N <sub>6</sub> 53.00 6.60 175 214.30 58.73 6.34 71 175-177 C <sub>13</sub> H <sub>16</sub> N <sub>6</sub> 53.36 7.09 66.7 (CH <sub>3</sub> CN) 286.34 58.59 6.44 54 234-236 (dec) 286.34 58.59 6.44 54 234-236 (dec) 286.34 58.59 6.44 71 231-238 (dec) 286.34 58.59 6.44 72 216-219 (dec) C <sub>13</sub> H <sub>16</sub> N <sub>6</sub> 0 58.73 6.36 70 215-222 (dec) C <sub>13</sub> H <sub>17</sub> N <sub>5</sub> S 56.70 6.22 61.17 (CH <sub>3</sub> CN) 275.38 56.66 6.17 70 215-222 (dec) C <sub>13</sub> H <sub>13</sub> N <sub>6</sub> 0 61.13 7.05 61.14 (cHer) 289.41 58.16 6.58 61.14 (cHer) 288.41 58.16 6.58 61.14 (cHer) 288.41 58.16 6.58 71 231-238 (dec) C <sub>13</sub> H <sub>17</sub> N <sub>5</sub> S 56.70 6.22 71 (CH <sub>3</sub> CN) 275.38 56.66 6.17 70 215-222 (dec) C <sub>13</sub> H <sub>13</sub> N <sub>5</sub> S 58.10 6.62 61.14 (cHer) 238.41 58.16 6.58 61.16 (cH <sub>5</sub> CN) 238.41 58.16 6.58 61.16 (cH <sub>5</sub> CN) 288.41 58.16 6.58 61.16 (cH <sub>5</sub> CN) 288.41 58.16 6.58 61.16 (cH <sub>5</sub> CN) 288.41 58.16 6.58 61.17 7.37 61.16 (cHer) 33.84.2 6.22 7.45 73 (cHer) 32.84.2 6.22 7.45 745 (cHer) 32.84.2 6.22 7.45 745 (cHer) 73 (cHer) 73 7.65 745 (cHer) 73 7.65 746 (cHer) 73 7.65 746 (cHer) 73 7.65 747 7.75 748 (cHer) 73 7.65 748 (cHer) 748 (cHer) 73 7.65 748 (cHer) 748 (cHer) 73 7.65 748 (cHer) 748 (cHer) 748 (cHer) 748 (cHer) 73 7.75 748	a of 1,3a,5,6,oo-Pentaazacycloalka[e]acenaphthylenes Yield Mp $^{\circ}$ C Molecular Calcd/Found (MW) C H Analysis (%) (Cryst. from) Formula C. Analysis (MW) C H A N (MW) C H A N (CH <sub>3</sub> CN) 247.32 53.32 5.44 28.27 (CH <sub>3</sub> CN) 247.30 58.91 6.73 34.40 (CH <sub>3</sub> CN) 244.30 58.91 6.73 34.40 (CH <sub>3</sub> CN) 244.30 58.91 6.71 29.49 (ether) 286.34 58.59 6.44 29.28 54 234-239 (dec) 286.34 58.59 6.44 29.28 54 234-239 (dec) 286.34 58.59 6.44 29.28 54 234-239 (dec) 236.38 56.66 6.17 25.38 71 175-117 C <sub>13</sub> H <sub>3</sub> N <sub>6</sub> O 58.73 6.56 6.17 25.38 72 216-219 (dec) C <sub>13</sub> H <sub>17</sub> N <sub>5</sub> S 56.70 6.22 25.43 73 216-219 (dec) C <sub>14</sub> H <sub>9</sub> N <sub>5</sub> S 56.70 6.22 25.43 70 215-228 (dec) C <sub>13</sub> H <sub>17</sub> N <sub>5</sub> S 56.70 6.22 25.43 70 215-228 (dec) C <sub>14</sub> H <sub>9</sub> N <sub>5</sub> S 56.70 6.22 25.43 70 215-228 (dec) C <sub>14</sub> H <sub>9</sub> N <sub>5</sub> S 56.70 6.22 25.53 70 216-219 (dec) C <sub>14</sub> H <sub>9</sub> N <sub>5</sub> S 56.70 6.22 25.53 70 216-219 (dec) C <sub>14</sub> H <sub>9</sub> N <sub>5</sub> S 56.70 6.22 25.53 70 216-219 (dec) C <sub>14</sub> H <sub>9</sub> N <sub>5</sub> S 56.70 6.22 25.53 70 216-219 (dec) C <sub>14</sub> H <sub>9</sub> N <sub>5</sub> S 56.70 6.22 25.53 712 214-217 (dec) C <sub>14</sub> H <sub>9</sub> N <sub>5</sub> S 56.10 6.22 25.53 713 7.05 26.73 714 2017 7.37 25.59 715 205.74 2017 7.37 25.59 715 205.74 70 7.15 205.74 70 7.15 25.54 715 205.74 70 7.15 25.54 716 205.75 76.74 7.15 25.54 717 7.37 25.54	a of 1,3a,5,6,oc-Pentaazacycloalka[e]acenaphthylenes           Yield         Mp (°C)         Molecular         Analysis           (%)         (Cryst. from)         Formula         CalcdFound         N           (%)         (Cryst. from)         Formula         CalcdFound         N           (%)         (Cryst. from)         Formula         CalcdFound         N         S           80         197-202 (dec) $C_{11}H_{13}N_{5}S$ 55.33         5.44         28.27         12.92           67         153-157 $C_{13}H_{15}N_{5}S$ 56.70         6.22         25.43         11.64           71         (ether)         275.38         56.80         6.36         29.46         29.55           71         (f)         (f)         53.22         7.21         29.49         29.55           71         (f)         284.37         63.32         7.09         29.55         11.64           71         215-177         Cl <sub>3</sub> H <sub>16</sub> N <sub>6</sub> O         58.59         6.44         29.35         11.64           71         2175-177         Cl <sub>3</sub> H <sub>16</sub> N <sub>6</sub> O         58.50         6.54         29.35         11.64           71         2175-177         Cl <sub>3</sub> H <sub>16</sub> N <sub>6</sub> O	a of 1,3a,5,6,00-Pentaazacycloalka[e]acenaphthylenes           Yield         Mp (°C)         Molecular         Analysis         MS $(96)$ (Cryst. from)         Formula         Calcd/Found         EI $(96)$ (Cryst. from)         Formula         Analysis         EI $(96)$ (Cryst. from)         Formula         Calcd/Found         S $(7)$ $(197-202 (dec)$ $247.32$ $53.38$ $5.44$ $28.32$ $12.902$ $67$ $157-167$ $247.32$ $53.38$ $5.44$ $28.27$ $247$ $77$ (ether) $247.30$ $88.91$ $6.36$ $25.538$ $11.64$ $275$ $77$ (ether) $244.30$ $88.91$ $6.70$ $6.22$ $25.43$ $11.64$ $71$ $175-177$ $244.30$ $88.91$ $6.30$ $244$ $29.35$ $71$ $175-177$ $244.30$ $85.36$ $6.34$ $29.35$ $244$ $711$ $175-177$ $244.30$ $85.34$ $29.35$ $29.44$

Table V

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[a] Type 1 by-product isolated, see Note [6].

			pmr (deut	eriochlorof	orm)						cmr (deuteriochlo	roform)			
Comp ound	CH <sub>2</sub> -2 CH <sub>2</sub> -3	CH2-7	other CH <sub>2</sub>	$CH_2-\omega$	ð	C-2 C-3	C-4	C-5a	C-6a	C-7	other C	C-®	C-0a	C-øb	ð
5/1	3.96 s (4H)	2.85 m	2.11 m (CH <sub>2</sub> -8)	2.79 m (CH <sub>2</sub> -9)	2.81 s (3H)	42.9 41.3	161.5	154.3	164.5	35.0	21.9 (C-8)	27.0 (C-9)	111.8 (C-9a)	142.6 (C-9h)	13.8
5/2	3.93 s	2.85 t	2.10 m	2.77 t	4.20 m (1H)	43.0	160.7	154.4	164.7	35.1	22.0 (C-8)	27.0	111.6	142.6	39.2 (CH)
5/3	(4H) 3.91 t	2.76 t	(CH <sub>2</sub> -8) 2.06 m	(CH <sub>2</sub> -9) 2.72 t	1.54 d (6H) 3.20 s	41.2 44.8	162.8	155.3	163.0	34.8	21.7 (C-8)	(C-9) 27.0	(C-9a) 111.4	(C-9b) 143.2	23.0 (CH <sub>3</sub> ) 39.5
5/4	3.83 t 3.91 t	2.78 t	$(CH_2-8)$ 2.06 m	(CH <sub>2</sub> -9) 2.73 t	(6H) 3.55 m (4H)	43.7 45.0	163.5	155.6	163.4	35.0	22.0 (C-8)	(C-9) 27.2	(C-9a) 112.0	(C-9b) 143.5	48.8
5	3.71 t		$(CH_2-8)$	(CH <sub>2</sub> -9)	1.70 m (6H)	44.5						(C-9)	(C-9a)	(C-9b)	25.3 23.8
5/5	3.91 t 3.76 t	2.78 t	2.07 qui (CH <u></u> 8)	2.73 t (CH <sub>2</sub> -9)	3.62 m (4H) 3.82 m (4H)	44.7 44.1	162.8	155.1	163.2	34.9	21.8 (C-8)	27.1 (C-9)	112.3 (C-9a)	143.2 (C-9h)	47.7 (NCH <sub>2</sub> ) 65.9 (OCH <sub>2</sub> )
5/6	3.92 m	2.80	1.83 qui (CH <sub>2</sub> -9)	2.73 m	2.80 s	43.1	161.3	151.5	162.2	38.8	32.4 (C-9)	23.6	113.6	144.3	13.8
	(4H)	Ш	1.65 qui (CH <sub>2</sub> -8) 1.57 aui (CH <sub>2</sub> -10)	(CH <sub>2</sub> - 11)	(3H)	40.8					26.8 (C-10) 25.8 (C-8)	(C-11)	(C-11a)	(C-11b)	
5/7	3.91 t	2.73	1.82 qui (CH <sub>2</sub> -9)	2.69 m	3.63 m (4H)	44.7	162.8	152.5	161.0	38.5	32.5 (C-9)	23.6	114.2	144.9	47.7 (NCH <sub>2</sub> )
[a]	3.71 t	Е	1.63 qui (CH <sub>2</sub> -8) 1.55 qui (CH <sub>2</sub> -10)	(CH <sub>2</sub> - 11)	3.81 m (4H)	43.5					26.9 (C-10) 25.7 (C-8)	(C-11)	(C-11a)	(C-11b)	65.8 (OCH <sub>2</sub> )
5/8	3.92 m	2.72	1.78 qui (2H)	2.72 m	2.80 s	43.1	161.4	152.0	158.8	34.5	29.7, 29.2,	23.7	111.6	143.6	13.8
	(4H)	E	1.66 qui (2H) 1.45 m (4H) (CH2- 8-11)	(CH <sub>2</sub> - 12)	(3H)	40.9					26.6, 26.0 (C- 8-11)	(C-12)	(C-12a)	(C-12b)	
5/9	3.91 t	2.66	1.76 qui (2H)	2.66 m	3.62 m (4H)	44.8	162.9	153.1	157.6	34.2	29.6, 29.3,	23.8	112.1	144.3	47.7 (NCH <sub>2</sub> )
[a]	3.70 t	Е	1.64 qui (2H) 1.45 m (4H) (CH 8-11)	(CH <sub>2</sub> - 12)	(NCH <sub>2</sub> ) 3.82 m (4H) (OCH <sub>2</sub> )	43.7					26.6, 26.1 (C- 8-11)	(C-12)	(C-12a)	(C-12b)	65.9 (OCH2)
5/10	3.98 s (4H)	2.68 t	1.88 m (2H) 1.73 m (2H) 1.3-1.6 m (12 H) (CH-2 8-15)	2.64 t (CH <sub>2</sub> - 16)	2.82 s (3H)	42.3 41.2	160.8	151.7	162.3	31.8	26.2 (two peaks), 26.0 (two peaks), 25.5, 24.1, 23.3, 23.1 (C- 8-15)	22.1 (C-16)	111.8 (C-16a)	144.4 (C-16b)	13.9
5/11	3.92 t 3.67 t	2.57 t	$1.322 \times 1.012$ $1.70 \times (2H)$ $1.70 \times (2H)$ $1.3-1.6 \times (12 H)$ $(CH_2 - 8-15)$	2.54 t (CH <sub>2</sub> - 16)	$\begin{array}{c} 3.61 \text{ m } (4\text{H}) \\ (\text{NCH}_2) \\ 3.81 \text{ m } (4\text{H})) \\ (\text{OCH}_2) \end{array}$	44.9 43.8	163.4	153.1	157.8	31.3	26.3, 26.05, 26.0, 25.9, 25.4, 24.1, 23.3, 23.1 (C- 8-15)	22.1 (C-16)	112.7 (C-16a)	145.1 (C-16b)	47.8 (NCH <sub>2</sub> ) 65.9 (OCH <sub>2</sub> )

Nmr data of 1,3a,5,6, $\infty$ c-Pentaazacycloalka[e]acenaphthylenes Table VI

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# G. Berecz and J. Reiter

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[a] Assignment corroborated by 2D-nmr.

General Method for the Synthesis of 5-Chloro-2-Q-cycloalka[*d*][1,2,4]triazolo[1,5-*a*]pyrimidine Derivatives **2**.

#### Method A.

To a suspension of 0.03 mole of the corresponding cycloalka[d][1,2,4]triazolo[1,5-a]pyrimidin-5( $\omega$ H)-one (1) and 23.0 g (0.15 mole, 14.0 ml) of phosphorus oxychloride 0.79 g (0.01 mole, 0.8 ml) of pyridine was added. The mixture was stirred at the temperature and for time given in Table I. The brown solution obtained was decomposed by pouring it into 200 g of crushed ice and stirred for 1 hour.

# Method A1.

The crystals that precipitated were collected by filtration and washed free of acids with cold water and 5 % aqueous sodium hydrogen carbonate solution. The air-dried product was dry-column flash chromatographed on Kieselgel 60 H (eluents: different mixtures of *n*-hexane and chloroform of continuously increasing polarity) to yield after evaporation of the appropriate fractions *in vacuo* the corresponding 5-chloro-2-Q-cycloalka[*d*][1,2,4]triazolo[1,5-*a*]pyrimidine derivative **2**, that was recrystallised from an appropriate solvent (Table I, for the spectral data see Table II).

# Method A2.

The oily product separated was taken in chloroform, the chloroform solution was washed with cold water and 5 % aqueous sodium hydrogen carbonate solution until the washings were neutral. After drying over anhydrous sodium sulphate and evaporating the solvent the residue was purified as in A1.

# General Method for the Synthesis of 5-(2-Hydroxyethyl)amino-2-Q-cycloalka[d][1,2,4]triazolo[1,5-a]pyrimidine Derivatives **3**.

#### Method B.

To a suspension of 0.024 mole of the appropriate 5-chloro derivative (2) in a mixture of 25 ml of 2-propanol and 25 ml of chloroform 3.24 g (0.053 mole, 3.2 ml) of 2-aminoethanol was added and refluxed for time given in Table III. The reaction mixture was evaporated *in vacuo* to dryness, the crystalline residue was suspended in 50 ml of water, collected by filtration and washed with water and a small amount of acetonitrile to yield the corresponding 5-(2-hydroxyethyl)amino-2-Q-cycloalka[d]-[1,2,4]triazolo[1,5-a]pyrimidine derivative**3**, pure enough for further reactions. An analytical sample was recrystallised from an appropriate solvent (Table III, for the spectral data see Table IV).

General Method for the Synthesis of 5-(2-Chloroethyl)amino-2-Q-cycloalka[*d*][1,2,4]triazolo[1,5-*a*]pyrimidines (**4**).

#### Method C.

To a suspension of 0.02 mole of the corresponding 5-(2-hydroxyethyl)amino-2-Q-cycloalka[d][1,2,4]triazolo[1,5-a]-pyrimidine derivative **3** in 60 ml of dichloromethane 4.76 g (0.04 mole, 2.9 ml) of thionyl chloride was added with stirring. A slightly exothermic reaction took place and the yellow solution obtained began to crystallise in 30 minutes. The thick suspension was stirred overnight at room temperature (the time is given in Table III). The crystals (probably **4**.HCl) were collected by filtration and washed with dichloromethane. The product was suspended in 50 ml of chloroform and to the mixture 4.05 g (0.04 mole, 5.6 ml) of triethylamine was added. The solution obtained was washed with water (2 x 20 ml), dried over anhydrous sodium sulphate and evaporated *in vacuo* to dryness. The residue was

purified by dry-column flash chromatography on Kieselgel 60 H (eluents: dichloromethane and a 50:1 mixture of dichloromethane and methanol). The appropriate fractions were collected, evaporated *in vacuo* to dryness, the residue was triturated with ether and collected by filtration to yield 5-(2-chloroethyl)amino-2-Q-cycloalka[d][1,2,4]triazolo[1,5-a]pyrimidines (4) (Table III, for their spectral data see Table IV).

General Method for the Synthesis of  $1,3a,5,6,\omega$ -Pentaazacycloalka[*e*]acenaphthylenes (5) by Ring Closure of the Corresponding 5-(2-Chloroethyl)amino-2-Q-cycloalka[*d*]-[1,2,4]triazolo[1,5-*a*]pyrimidines (4).

### Method D1.

A suspension of 0.015 mole of the appropriate 5-(2chloroethyl)amino-2-Q-cycloalka[d][1,2,4]triazolo[1,5-a]pyrimidine (**4**) in 30 ml of acetonitrile was refluxed for the time given in Table V. The solution obtained was evaporated *in vacuo* to dryness, the residue was suspended in 50 ml of chloroform, 1.67 g (0.0165 mole, 2.3 ml) of triethylamine was added to it and the solution obtained was washed with 3 x 15 ml of water. The chloroform layer was dried over anhydrous sodium sulphate, evaporated to dryness and the residue was purified by dry-column flash chromatography on Aluminium oxide 60 G (eluents: different mixtures of *n*-hexane and chloroform of continuously increasing polarity). The appropriate fractions were collected, evaporated *in vacuo* to dryness and the residue collected by filtration from a suitable solvent (Table V, for the spectral data see Table VI).

#### Method D2.

5-(2-Chloroethyl)amino-6,7-dihydro-8*H*-2-(morpholin-4-yl)cyclopenta[d][1,2,4]triazolo[1,5-a]pyrimidine (**4**/**4**) (0.81 g, 0.0025 mole) was heated with stirring under argon atmosphere at 180 °C for 15 minutes. After cooling the product was dissolved in methanol, to the solution 0.135 g (0.0025 mole) of sodium methoxide was added, the mixture was evaporated *in vacuo* to dryness and the residue was subjected to dry-column flash chromatography (see Method D1).

General Method for the Synthesis of  $1,3a,5,6,\omega$ c-Pentaazacycloalka[*e*]acenaphthylenes (**5**) by Ring Closure of the Corresponding 5-(2-Hydroxyethyl)amino-2-Q-cycloalka[*d*]-[1,2,4]triazolo[1,5-*a*]pyrimidine Derivatives **3** in Polyphosphoric Acid.

#### Method E.

To 0.015 mole of the corresponding 5-(2-hydroxyethyl)amino-2-Q-cycloalka[d][1,2,4]triazolo[1,5-a]pyrimidine (**3**) a six-fold amount (g/g) of polyphosphoric acid (Fluka) was added and the mixture "stirred" at an oil bath temperature and for time given in Table V. During the reaction the starting material was slowly dissolved and a honey-like mixture was obtained. This was cautiously dissolved in 3 x 50 ml of water keeping the inner temperature below 50 °C. The brown solution obtained [6] was neutralised with powdered sodium hydrogen carbonate added in small portions under vigorous stirring (heavy foaming). The pH of the solution was then adjusted with concentrated aqueous ammonia solution to 9-10.

### Method E1.

The product that crystallised was immediately collected by filtration and washed with ice-cold water. After drying it was purified by dry-column flash chromatography on Aluminium oxide 60 G (eluent: dichloromethane). The appropriate fractions were collected, evaporated *in vacuo* to dryness, the residue was triturated with a suitable solvent and collected by filtration (Table V).

#### Method E2.

In case the product did not crystallise the solution was immediately extracted with chloroform, the combined chloroform layers were dried, evaporated *in vacuo* to dryness and purified as in E1.

Nucleophilic Displacement of the 4-Methylthio Group of  $1,3a,5,6,\omega$ c-Pentaazacycloalka[*e*]acenaphthylenes (**5**, Q = methylthio) with Dialkylamines.

#### Method F.

A mixture of 0.005 mole of the corresponding 4-methylthio-1,3a,5,6, $\omega$ c-pentaazacycloalka[*e*]acenaphthylenes (**5**, **Q** = methylthio) and 0.05 mole of the corresponding dialkylamine was stirred at a temperature and for time given in Table V. After cooling 10 ml of ether was added to the solution, the crystals precipitated were collected by filtration and washed with ether. The crude product (**5**, **Q** = dialkylamino) was subjected to dry-column flash chromatography on Aluminium oxide 60 G (eluents: dichloromethane, followed by a 50:1 mixture of dichloromethane and methanol). The appropriate fractions were evaporated *in vacuo* to dryness, the residue was triturated with ether and collected by filtration (Table V, for their spectral data see Table VI).

#### Acknowledgement.

The authors wish to express their thanks to Mrs. Sándorné Sólyom and Mrs. Mónika Mezóvári for recording the ir spectra, to Mrs. Magdolna Nagy, Mr. Attila Fürjes and Dr. István Kövesdi for recording the nmr spectra, to Mr. Kálmán Újszászy, Mr. András Dobó, Dr. Éva Szabó and Dr. Péter Slégel for recording the ms spectra, to Miss Zsófia Kárpáti for recording the uv spectra, to Mrs. Magdolna Hirkóné-Csík for performing the elemental analyses and to Mrs. Erika Korenné-Ausländer, Mrs. Tünde Jenei and Miss Erika Kurunczi for technical assistance.

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[6] If the brown solution obtained crystallised the crystals were collected by filtration and chromatographed on a Kieselgel 60 H column (eluents: chloroform and 50:1 to 19:1 mixtures of chloroform and methanol) to yield the corresponding 2-Q-cycloalka[d][1,2,4]triazolo[1,5-a]pyrimidin-5( $\omega$ H)-one (1) by-product. Its amount does not exceed 5 %.

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