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PREPARATION AND STRUCTURE OF BICYCLOALKANE-CONDENSED ARYLDIAZIRIDINES ACCOMPANIED BY PYRIMIDINES

Pál Sohár,[a] Antal Csámpai,[a] Reijo Sillanpää,[b] Ferenc Fülöp[c] and Géza Stájer*[c]

[a]Research Group for Structural Chemistry and Spectroscopy (at present: Protein Modelling Group), Hungarian Academy of Sciences Institute of Chemistry, Loránd Eötvös University, P.O. Box 32, H-1518 Budapest, Hungary
[b]Department of Chemistry, University of Jyväskylä, P.O. Box 35, 40351 Jyväskylä, Finland
[c]Institute of Pharmaceutical Chemistry, University of Szeged, P.O. Box 427, H-6701 Szeged, Hungary. E-mail: stajer@pharm.u-szeged.hu

Dedicated to Prof. Heinrich Wamhoff on the ocasion of his 70th birthday

Abstract – Di-*exo*- and di-*endo*-2-aminonorbornane/enemethanamines **1–3**, di-*exo*-oxanorbornene derivative **4** and *cis*-cyclohexane and *trans*-4-cyclohexene analogues **5**, **6** were reacted with *p*-chlorobenzaldehyde in the presence of *N*-bromosuccinimide in dichloromethane. *Via* the reactions of **1–6**, condensed diaziridines **7–12** accompanied by pyrimidine derivatives **13–16** were prepared after isolation with column chromatography. The mechanisms proposed for alternative transformations were supported by DFT calculations. The structures of the new compounds were proved by IR and NMR spectroscopy and, for **7**, **9** and **12**, also by means of X-ray crystallography.

INTRODUCTION

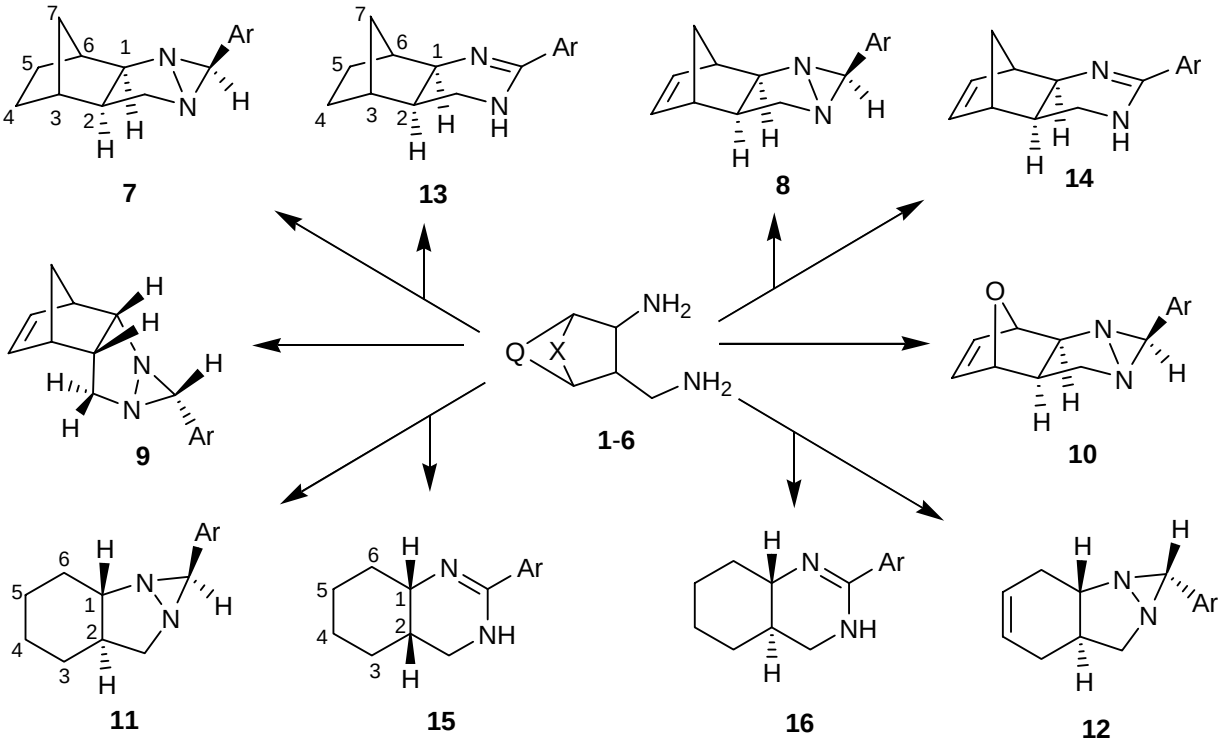
Earlier, the reactions with levulinic acid of di-*exo*-3-aminobicyclo[2.2.1]heptane- and hept-5-ene-2-methanamines, prepared by the reduction of aminocarboxamides, were used to obtain pyrrolo-quinazolinone or pentacyclic dipyrrolodiazepine derivatives.[1] The cyclization of amines with aldehydes or ketones to diaziridines,[2–7] and the chemistry of these strained molecules, have been well

studied.[8–15] The diaziridines play important role in the syntheses of various drugs[16–18] and in cancer research.[19-22]

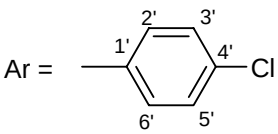
This paper presents a facile preparation of polycondensed diaziridines from (bi)cycloalkan/enes carrying amino- and aminomethyl groups in adjacent positions.

RESULTS AND DISCUSSION

When refluxed in dichloromethane with *p*-chlorobenzaldehyde and *N*-bromosuccinimide (NBS), di-*exo*-3-aminobicyclo[2.2.1]heptane-2-methanamine **1**, di-*exo*- and di-*endo*-3-aminobicyclo[2.2.1]hept-5-ene-2-methanamines **2** and **3** (obtained from the appropriate carboxamides [23] by LAH reduction in THF), di-*exo*-3-amino-7-oxabicyclo[2.2.1]hept-5-ene-2-methanamine **4**,[1] *cis*-2-amino-1-aminomethylcyclohexane **5** and *trans*-2-amino-1-aminomethylcyclohex-4-ene **6** furnished the corresponding teracyclic and tricyclic diaziridino[1,2-*a*]pyrazoles (**7**–**12**, Scheme 1) in low to moderate yields (18-38%, Table 1). Besides these and compounds **13**–**16**, the other products were not identified.



1	di-*exo*	CH_2-CH_2	CH_2
2	di-*exo*	CH=CH	CH_2
3	di-*endo*	CH=CH	CH_2
4	di-*exo*	CH=CH	O
5	*cis*	CH_2-CH_2	—
6	*trans*	CH=CH	—



The numbering shown is used for the interpretation of NMR data.

Reagents: 4-Cl-C_6H_4CHO, NBS, DCM

Scheme 1

Table 1. Physical and analytical data on compounds (**7-16**)

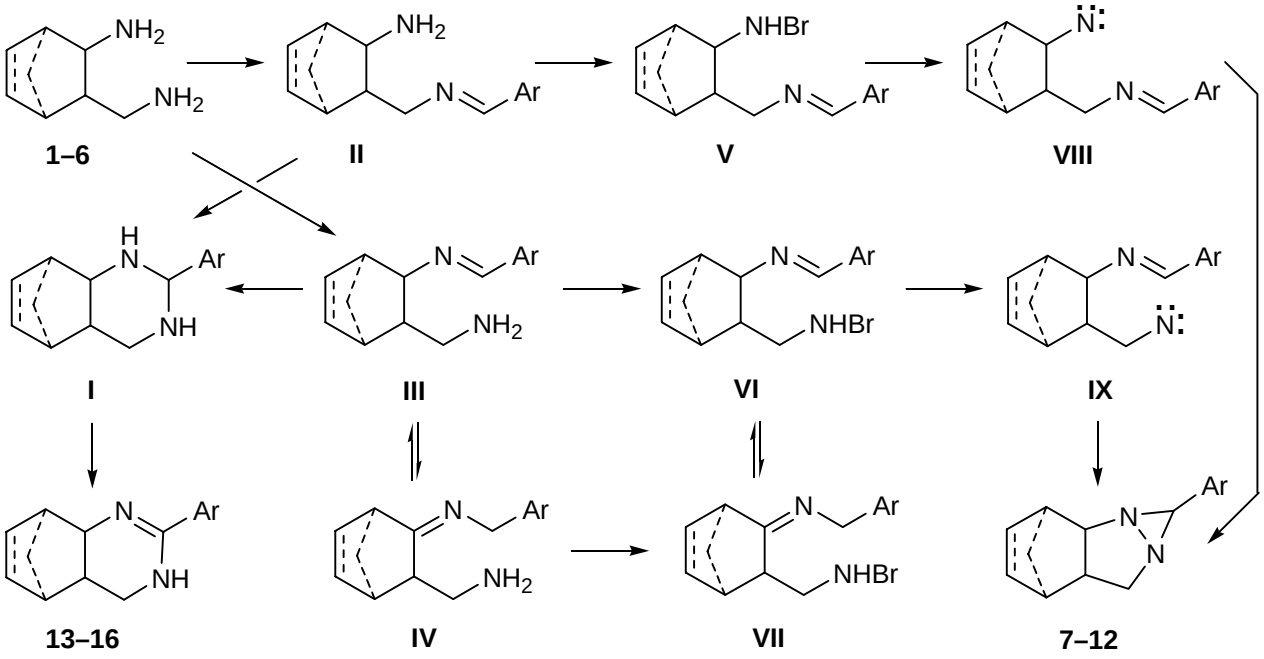
Compd.	mp °C	Yield %	Formula	Analysis					
				Found %			Calcd %		
				C	H	N	C	H	N
7	77-78[a]	38	$C_{15}H_{17}ClN_2$	69.30	6.71	10.90	69.09	6.57	10.74
8	65-67[b]	21	$C_{15}H_{15}ClN_2$	69.28	5.94	10.60	69.63	5.84	10.83
9	109-111[b]	34	$C_{15}H_{15}ClN_2$	69.44	5.57	10.98	69.63	5.84	10.83
10	121-123[b]	28	$C_{14}H_{13}ClN_2O$	64.25	5.13	10.48	64.50	5.03	10.74
11	98-99[b]	25	$C_{14}H_{17}ClN_2$	67.41	6.48	10.92	67.60	6.89	11.26
12	104-106[b]	18	$C_{14}H_{15}ClN_2$	67.87	5.53	11.50	68.15	6.13	11.35
13	166-168[c]	20	$C_{15}H_{17}ClN_2$	69.35	6.69	10.96	69.09	6.57	10.74
14	288-290[d]	21	$C_{15}H_{15}ClN_2$	69.87	5.91	11.07	69.63	5.84	10.83
15	269-270[d]	15	$C_{14}H_{17}ClN_2$	67.81	6.61	11.45	67.60	6.89	11.26
16	338-339[e]	25	$C_{14}H_{15}ClN_2$	67.96	5.97	11.42	68.15	6.13	11.35

Crystallization solvent: [a]hexane; [b]Petroleum ether (bp. 40-60 °C); [c]EtOAc–Et_2O; [d]EtOH; [e]Et_2O.

The relatively low yields (Table 1) may be attributed to the competitive formation of the saturated condensed pyrimidines **13**–**16** separated by column chromatography. The preparations of diaziridines intermolecularly from monoamines, *e.g.* primary aliphatic amines with carbonyl compounds and *N*-chlorosuccinimide or NaOCl in aqueous alkaline medium are likewise known.[9,12–15,24,25] However, the present report is the first description of the simultaneous formation of isomeric pyrimidines **13**–**16**. The attempt to transform **11** to a pyrimidinone with a *cis* (**15**) or *trans* (**16**) structure by refluxing in CH_2Cl_2 was unsuccessful suggesting that the diaziridines **7**–**12** are not intermediates of **13**–**16**, but are formed in alternative reaction pathways (Scheme 2).

It should also be pointed out that under the applied conditions *cis*-cyclohexanediamine **5** undergoes epimerisation affording the *trans*-condensed cyclohexane **11**. We have observed analogous *cis*–*trans* isomerizations taking place *via* reversible protonation-deprotonation.[26]

Considering the experimental observations, three competitive transformations can be taken into account (Scheme 2). In the first, the NBS-mediated oxidation of the primarily formed cyclic aminal **I** gives condensed pyrimidinones **13-16** as final products. On the other hand, when *N*-bromination of the two alternative amino-imines **II** and **III** preceeds their ring closure to **I**, the resulted *N*-bromoamines **V** and **VI** undergo 1,1-dehydrobromination to give the nitrenes **VIII** and **IX**, respectively, which cyclize irreversibly into the same diaziridine product **7–12**. The *cis–trans* isomerization may take place through the Schiff-base intermediates **III** and **VI** by reversible 1,3-hydrogen migrations **III** ⇆ **IV** and **VI** ⇆ **VII**. In intermediates **II** and **V**, such process does not cause a change in the *cis* or *trans* annelation. The complexity of the reaction is even more complicated because the intermediary nitrenes can attack on two diastereomeric faces of the (*E*)-arylmethylimine.



Scheme 2

The results of a comparative DFT analysis of ammonia and bromoamine support this view (Table 2), and represents that the functional groups are present in the assumed intermediates. The computations were carried out at B3LYP/6-311+G(2d,p) level of theory[27] by Gaussian program package.[28] In both cases, the geometry optimization was followed by calculation of the energy and the local population (Σc^2 on a particular atom) of the frontier molecular orbitals (FMO's).[29,30] Electronic chemical potential[31] [$\mu = (E_{HOMO} + E_{LUMO})/2$] and atomic charges (natural-[32] and Merz-Kollman,[33] resp.) are listed in Table 2. In our proposed mechanism, the μ values represent electron donor proporties,[31] *i.e.* the net charges and HOMO population on the nitrogen atoms clearly show that ammonia is more nucleophilic than the bromoamine. It means that the conversion of amine intermediates **II** and **III** prefer cyclization to the perhydropyrimidine **I**, while bromoamines **V** and **VI** show more pronounced tendency to undergo HBr-elimination affording nitrene intermediates.

Table 2. HOMO and LUMO energies, electronic chemical potential (μ), atomic charges (ρ),[a] HOMO electron densities (Σc^2_{HOMO}) and LUMO electron deficiency on the relevant atoms.[b]

	E_{HOMO} (eV)	E_{LUMO} (eV)	μ (eV)	ρ(NBO) on N/C=N[c]	ρ(NBO) on Br	ρ(MK) on N/C=N[c]	ρ(MK) on Br	Σc^2_{HOMO} on N[b]	Σc^2_{HOMO} on Br
NH_3	−7.43	0.30	−3.57	−1.053	–	−0.960	–	0.471	–
NH_2Br	−7.25	−2.02	−4.64	−0.849	0.128	−0.614	−0.041	0.217	0.466
H_2C=NH	−7.62	−0.91	−4.27	−0.020	–	0.215	–	0.585	–

[a]natural (NBO) and Merz-Kollman (MK), resp.; [b]Σc^2_{LUMO} on the imino-C in H_2C=NH; [c]Charge on N for NH_3 and NH_2Br and on the carbon atom of imino group in H_2C=NH.

STRUCTURE

The IR, ^{1}H and ^{13}C NMR spectroscopic data proving the presumed structures of the new compounds are given in Tables 3 and 4. For comparison of the NMR data, the numbering in Scheme 1 is used in these Tables and through this discussion.

Table 3. Characteristic IR frequencies[a] and ^{1}H-NMR data[b] on compounds (**7-16**)

	$\gamma C_{Ar}H$ band	NCH_2[c]		$CH_2(7)$[d]	H-1[e]	H-2[f]	H-3[g]	H-4,5[h]	H-6[i]	CH[j]	H-2′,6′	H-3′,5′
				cyclohexane/ene or norbornane/ene/oxanorbornene moiety						*s* (1H)	*p*-chlorophenyl[k]	
7	803	2.93,	3.62	1.13,[l] 1.59	3.54	2.40	2.09	1.08,[l] 1.47 1.10,[l] 1.52	2.56	2.70	7.24	7.28
8		2.96,	3.57	1.65, 1.88	3.87	~2.66[l]	~2.66[l]	6.14, 6.21	3.20	2.91	7.29	7.33
9	803	2.82,[l]	3.33	1.46, 1.60	4.48	3.09	2.83[l]	6.34, 6.41	3.22	2.80[l]	7.19	7.25
10	814	3.19,	3.62	–	4.00	2.66	4.69	6.39	5.15	2.80	7.25	7.28
11	811	2.83,	3.29	–	3.41	2.45	~1.58,[l] 1.66	1.12, ~1.58[l] 1.18, 1.41	1.08, 1.90	3.78	7.28	7.33
12	813	~2.6,[l]	3.69	–	~2.72[m]	~2.72[m]	2.00, 2.28	5.66	2.32, ~2.6[l]	3.66	7.22	7.28
13	832	2.87,	3.43	0.95, 1.57	3.15	1.84	2.22	1.16,[l] 1.44 1.16,[l] 1.46	1.94	–	7.78	7.42
14	837	3.14,	3.55	1.10, ~1.47[l]	3.47	2.26	2.12	~1.24,[m] ~1.47[l] ~1.24,[m] 1.54	~2.5[n]	–	7.85	~7.68
15	834	3.20,	3.60	–	3.54	~1.88[l]	~1.88,[l] 2.35	5.69	2.10, 2.55	–	7.77	7.70
16	831	3.32,	3.52	–	3.81	2.13	1.34,[l] 1.68[m]	1.42 1.34,[l] 1.68[m]	1.68[m] 1.94	–	7.79	7.68

[a]In KBr discs (cm^{-1}). Further IR bands: νNH: ~ 3115 (**13**, **16**), 3500-2500, very broad (**14**); [b]In $CDCl_3$ (**7-10**, **12**) or DMSO-d_6 solution (**11**, **13-16**) at 500 MHz. Chemical shifts in ppm (δ_{TMS} = 0 ppm), coupling constants in Hz. For the numbering, see in the Scheme 1. Further ^{1}H-NMR signals: NH, s (1H): ~6.85 broad (**13**), ~10.2 very broad (**14**), 9.92 (**16**), ~10.0 broad (**15**); [c]2×*dd* (2×1H) ^2J = 11.9 ± 0.1 (**7-10**), 13.7 ± 0.3 (**13-16**), 9.5 (**12**), ^3J (upfield dd): 4.9 ± 0.3 (**7-10**), 10.8 (**15**), 6.8 (**13**), 5.2 (**14**), 4.7 (**16**), ^3J (downfield dd): 9.3 ± 0.2 (**7-10**), 7.5 (**13**), 7.9 (**14**), 4.5 (**15**, **16**), t+dd (**11**), *J* = 11.6 and 8.0, *?* + dd (**12**), *J* = 9.5 and 6.4; [d]*AB*-type spectrum, 2×d (2×1H), *J* = 10.5 (**7**, **14**), 9.3 (**8**), 8.7 (**9**), 9.9 (**13**). Due to long-range couplings, further split to 2×md (**7**), td (up- and downfield d for **8**, **9**, resp., by ~1.7 Hz); [e]d, *J* = 7.1 (**7**), 6.8 (**8**), 6.5 (**10**), 8.0 (**13**, **14**), dd, *J* = 8.8, 4.1 (**9**), m with unresolved lines (**11**, **12**, **16**), dt, *J* = 10.5, 10.5, 5.4 (**15**), C–CH_2–C group, qi (2H); [f]m (1H); [g]d (H), *J* = 3.8 (**7**), 3.5 (**13**), s (1H, **10**), 2×m (2H, **11**, **12**, **15**, **16**); [h]4×m (4×1H) for **7**, **11**, **13**, **14**, **16**, 2×dd (2×1H), *J* = 5.7, 3.3 (**8**, **9**), ~s (2H) for **10**, **12**, **15**; [i]d (H), *J* = 4.1 (**7**), >2 (**13**), s (1H) for **8-10,** 2×m (2H, **11**, **12**, **15**, **16**); [j]Diaziridine ring; [k]*AA´BB´*-type spectrum, 2×~d (2×2H), *J* = 8.5±0.1; [l]Overlapping signals; [n]Hidden by the solvent signal.

For **7**–**12**, the diaziridine ring is confirmed by the presence of the diaziridine-H (original formyl-H) singlet in the ^{1}H NMR spectrum. The chemical shifts of this hydrogen (2.70–3.78 ppm) and the corresponding carbon (55–80 ppm) are rather small, referring to the strong shielding of these atoms, which is again characteristic for strained three-membered ring systems.[35a] For an open-chain N–CH–N-type moiety, much larger shifts would be expected.[35b] The assignments of the ^{1}H and ^{13}C NMR signals were proved by HMQC and HMBC measurements, the former confirming the direct bonding between these H's and C's and the HMBC cross-peaks indicating the topology **I** (Figure 1).

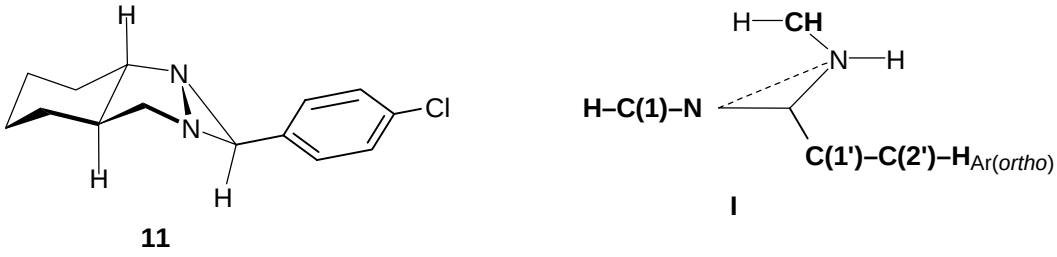


Figure 1

One of the methylene-H's (1-H and 1'-H) or the *ortho* H's on the benzene ring give cross-peaks to the diaziridine-C and the diaziridine-H gives cross-peaks to the CH_2, C-1 and C_{Ar}-2',6'. The presence of the two nitrogens was confirmed by {N,H}-HMBC measurements for **7**, **9**, **12** (and **14**). The two nitrogen shifts are 122 and 129 (**7**), 122 and 127 (**9**) and 124 and 129 ppm (**12**), values expected for sp^3 N atoms. From the above shifts and the fact that no NH bands and signals are present in the IR and ^{1}H NMR spectra, the diaziridine structure follows straightforwardly. The stereostructures of these compounds were proved by DIFFNOE experiments.[35c, 36] For **7**, **8** and **10**, the sterically close arrangement of H-1 and the diaziridine-H was proved by the mutual response of the other signal when one of them was irradiated. This means the *endo* position of the diaziridine-H (and also the three-membered ring), in accordance with the X-ray results (Figure 2).

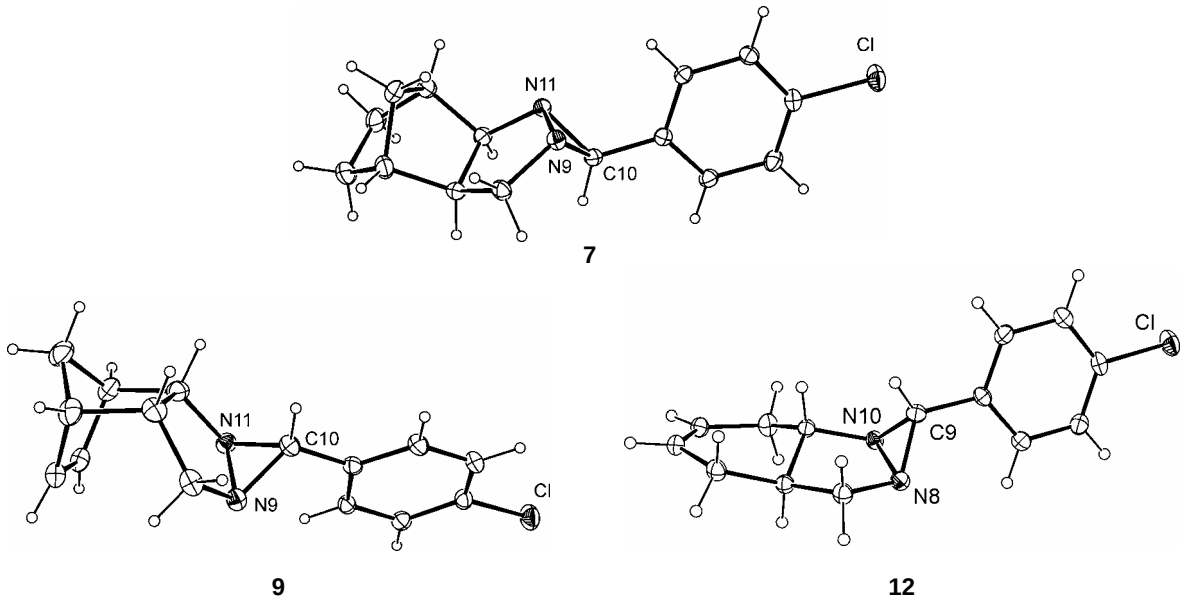


Figure 2. ORTEP structures of diaziridines **7**, **9** and **12**

As observed earlier,[37, 38] the di-*endo* annelation of the hetero ring to the norbornane/ene moiety results in a double doublet split of the 1-H signal, while for di-*exo* annelation a double split of this signal is characteristic, *i.e.* the 1-H,6-H dihedral angle is ~90°, while for di-*endo* derivatives it is ~30°. Thus, the dd of 1-H confirms the unaltered di-*endo* configuration of the starting diamine in **9**. As 1-H and the diaziridine-H give a mutual NOE, the *exo* orientation of the diaziridine-H is unquestionable. The

corresponding structure of **9**, depicted in the Scheme 1, was confirmed by X-ray study (Figure 2). This structure is plausible, because it is sterically more favoured as compared with the analogous di-*endo* arrangement of the diaziridine ring.

Table 4. ^{13}C-NMR chemical shifts[a] on compounds (**7-16**)[b]

	CH[c]	NCH_2	C-1	C-2	C-3	C-4	C-5	C-6	CH_2(7)	C-1′	C-2′,6′	C-3′,5′	C-4′
			cyclohexane/ene, norbornane/ene or oxanorbornene group[d]							*p*-chlorophenyl group			
7	64.8	61.4	77.4	51.5	42.2	27.1	26.4	41.6	32.8	136.2	128.84[e]	128.91[e]	134.7
8	65.8	59.6	78.0	50.4	47.2	139.3	136.9	47.5	43.4	136.2	128.86[e]	128.90[e]	134.7
9	64.8	58.1	79.2	51.5[f]	46.2	137.0	135.7	48.0	51.5[f]	136.3	128.8	128.9	134.6
10	64.0	58.5	77.4	47.8	83.0	137.7	136.2	82.7	–	135.6	129.0	128.9	134.9
11	55.2	54.5	61.1	32.3	23.6	24.4	21.6	30.7	–	138.4	130.2	128.7	133.4
12	79.8	60.5	69.3	54.5	29.7	126.4[e]	126.9[e]	32.2	–	136.2	128.9	129.0	134.9
13	155.9	46.7	58.1	42.7	45.2	30.0	26.9	42.3	33.8	136.3	128.72[e]	128.78[e]	135.0
14	160.4	41.2	56.7	40.6	42.5	29.4	26.1	44.1	33.8	128.2	131.1	129.9	139.1
15	158.9	44.6	51.6	31.1	28.8[e]	126.5[g]	125.2[g]	31.2[e]	–	128.6	130.8	129.8	138.6
16	159.1	43.8	50.0	28.9	25.7	21.6	23.8	29.3	–	128.0	130.8	129.9	138.8

[a]In ppm (δ_{TMS} = 0 ppm) at 125.7 MHz. Solvent: $CDCl_3$ (**7-10** and **12**) or DMSO-d_6 (**11** and **13-16**); [b]Assignments were supported by DEPT, HMQC and HMBC measurements; [c]Diaziridine ring (**7-12**) or C=N (**13-16**); [d]For the numbering, see in the Scheme 1; [e,g]Interchangeable assignments; [f]Two overlapping lines.

Because of signal overlaps, the *trans* annelation of the six-membered ring in cyclohexane/ene **11** and **12** cannot be determined directly. Nevertheless, the downfield position of the C-1 line (61.1 and 69.3 ppm) makes the *cis* annelation improbable. On the other hand, NOE was observed between 2-H and the diaziridine-H in **11**. Assuming a *trans* annelation, this result suggests the structure depicted in Figure 1 and Scheme 1, and thus the sterically close di-*endo* arrangement, *cis* to the pyrazole ring of 2-H and the diaziridine-H. For **12**, it is not possible to clarify the stereostructure from the NMR data or by using the DIFFNOE technique, because 1-H and 2-H, and similarly the *equatorial* methylene-H of the NCH_2 group and the diaziridine-H, give overlapping signals. The X-ray data indicate a different structure from that for **11**: the diaziridine-H is *cis* to 1-H in the pyrazole ring. In accordance, in **12**, 1-H is more shielded due to anisotropic shielding of the three-membered ring.[35d] Additionally, a very strong field effect[35e, 39] was found for **11** in accord with the crowded structure (cf. Fig. 1): upfield shifts of the lines of the diaziridine, NCH_2, C-1 and C-2 by 24.6, 6.0, 8.2 and 22.2 ppm were observed.

The structures of pyrimidines **13**–**16** are obvious from the shifts (153.5–160.4 ppm) of the C=N carbon [instead of the line of diaziridine C(sp^3) between 55.2 and 79.8 ppm in 7–12] and the absence of the diaziridine-H singlet in the ^{1}H NMR spectra. For 15, the *cis* annelation is probable from the different half-signal-widths of 1-H and 2-H (~12 and 18 Hz) and the upfield shifts (by 11.1 and 3.4 ppm) of the C-1 and C-2 lines relative to those measured for **11**. The sum of the carbon shifts of the cyclohexane is larger by 14.4 ppm in **11** than in **15**, which supports the change in the annelation in the former from *cis* to *trans*.[35f]

CONCLUSION

The method described in this paper provides an easy route for the preparation of liphophilic (bi)cyclic diaziridines of potential biological interest and the theoretically supported mechanism explains the processes proceeding in two directions. Since the oxidative cyclization of ethylenediamine with aldehydes conducted under the same conditions afforded only dihydroimidazoles without contamination of strained diaziridino[1,2-*a*]diazetidines,[40] it seems that the formation of condensed diaziridines must be taken into account in case of propylenediamine-type precursors. The currently used methods, *e.g.* synthesis from amines, carbonyl compounds and NaOCl in water,[13, 24] or the similar application of NBS for the intramolecular oxidative cycloamination of olefins with aziridines,[41] are sometimes cumbersome, especially when the starting diamines are poorly soluble or insoluble in water, and hence they result in low yields. Our simple preparation procedure leads to cycloalkane-condensed diaziridines with chiral centres. The theoretical results may serve as useful informations to be considered in the development of analogous propylenediamine-based syntheses of pyrazolo-condensed diaziridines. A disadvantage here is the column chromatographic purification and the separation from pyrimidines.

EXPERIMENTAL

IR spectra were run in KBr disks with a Bruker IFS-55 FT-spectrometer controlled by Opus 3.0 software. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 solution in 5 mm tubes at RT, on a Bruker DRX-500 spectrometer at 500.13 (^{1}H) and 125.76 (^{13}C) MHz, with the ^{2}H signal of the solvent as the lock and TMS as the internal standard. The standard Bruker microprogram NOEMULT to generate NOE[42] and to get DIFFNOE spectra[35c, 36] was used with a selective pre-irradiation time. DEPT spectra[43] were run in a standard manner,[44] using only a $\Theta = 135°$ pulse to separate the CH/CH_3 and CH_2 lines phased "up" and "down", respectively. The HMQC[45, 46] and HMBC[47, 48] spectra were obtained by using the standard Bruker pulse programs COSY-45, INV4GSSW and INV4GSLRNDSW.

Di-*exo*-3-(*p*-chlorophenyl)-2,4-diazatetra-cyclo[6.2.1.1^{2,4}.0]undecane (7), 3-(*p*-chlorophenyl)-2,4-diazatetracyclo[6.2.1.1^{2,4}.0]undec-9-ene (8), di-*endo*-3-(*p*-chlorophenyl)-2,4-diazatetracyclo-[6.2.1.1^{2,4}.0]undec-8-ene (9), di-*exo*-3-(*p*-chloropheny)-2,4-diaza-11-oxatetracyclo[6.2.1.1^{3,5}.0]-undec-8-ene (10), *trans*-(3-*p*-chlorophenyl)-2,4-diazatricyclo[4.4.1.0.0^{2,4}]decane (11), *trans*-3-(*p*-chlorophenyl)-2,4-diazatricyclo[4.1.0.0^{2,4}]dec-8-ene (12), di-*exo*-3-(*p*-chlorophenyl)-2,4-diaza-tricyclo[6.2.1.0]undec-2-ene (13), di-*exo*-3-(*p*-chlorophenyl)-2,4-diazatricyclo[6.2.1.0]undeca-2,8-diene (14), *cis*-3-(*p*-chlorophenyl)-2,4-diazabicyclo[4.4.0]dec-2-ene (15), *trans*-3-(*p*-chloro-phenyl)-2,4-diazabicyclo[4.4.0]deca-2,8-diene (16). General procedure.

A mixture of *p*-chlorobenzaldehyde (1.4 g, 1 mmol) and diamine (1.05 mmol): di-*exo*-2amino-bicyclo[2.2.1]heptane-3-methanamine **1** (1.5 g), di-*exo*-2-aminobicyclo[2.2.1]hept-5-ene-3-methanamine **2** (1.5 g), di-*endo*-2-aminobicyclo[2.2.1]hept-5-ene-3-methanamine **3** (1.5 g), di-*exo*-2-amino-7-oxabicyclo[2.2.1]hept-5-ene-3-methanamine **4** (1.5 g), *cis*-2-amino-1-aminomethylcyclohexane **5** (1.5 g) or *trans*-2-amino-1-aminomethyl-4-cyclohexene **6** (1.4 g) in dichloromethane (20 mL) was stirred at 0 °C for 20 minutes, and NBS (1.5 g, 1.05 mol) was then added. The solution was allowed to warm to room temperature and was stirred overnight. By the addition of NaOH solution (10%), the mixture was made alkaline, extracted with CH_2Cl_2 (3 × 10 mL), dried over Na_2SO_4 sicc. and evaporated to dryness. The residue was chromatographed on an alumina column (Al_2O_3 basic) and eluted with petroleum ether (bp 40-70°C) for diaziridines **7–12** (monitoring by TLC, aluminium sheets, Silica gel F_{254}, development with iodine vapour or/and UV light at 254 nm). Data of the products are listed in Table 1.

For pyrimidines **13**–**16**, the elution was performed with EtOH.

X-Ray crystallographic study: Crystallographic data were collected at 173 K with a Nonius-Kappa CCD area detector diffractometer, using graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å). The data were collected by φ and ω rotation scans and processed with the DENZO-SMN ν0.93.0 software package.[49] Selected bonding parameters for diaziridines 7, 9 and 12 are listed in Table 5.

Crystal data for **7**: M_r = 260.76, monoclinic, space group $P2_1/c$ (no. 14), a = 10.8439(5), b = 10.3266(6), c = 11.9825(5) Å, β = 99.701(3)°, V = 1322.62(11) Å^3, T = 173 K, Z = 4, μ(Mo-K_α) = 0.282 mm^{-1}, 2602 unique reflections (R_{int} = 0.0346), which were used in the calculations. The final $wR(F^2)$ was 0.1106 (all data).

Crystal data for **9**: M_r = 258.74, monoclinic, space group $P2_1/a$ (no. 14), a = 12.0060(8), b = 9.0980(5), c = 12.9489(9) Å, β = 115.797(3)°, V = 1273.46(14) Å^3, T = 173 K, Z = 4, μ(Mo-K_α) = 0.272 mm^{-1}, 2460 unique reflections (R_{int} = 0.0331), which were used in the calculations. The final $wR(F^2)$ was 0.1276 (all data).

Crystal data for **12**: M_r = 246.73, triclinic, space group *P-1* (no. 2), a = 6.0825(4), b = 9.6876(9), c = 11.1491(10) Å, α = 76.439(3), β = 76.874(4), γ = 80.249(5)°, V = 617.26(9) Å^3, T = 173 K, Z = 2, μ(Mo-K_α) = 0.288 mm^{-1}, 2400 unique reflections (R_{int} = 0.0319), which were used in the calculations. The final $wR(F^2)$ was 1343 (all data).

Table 5. Selected bond lengths (Å) and torsion angles (°) for **7, 9** and **12**

Distances	**7**	**9**	**12**[a]	Torsion angles	**7**	**9**	**12**[a]
N(9)-N(11)	1.511(3)	1.512(3)	1.544(3)	C(8)-N(9)-N(11)-C(2)	–0.7(3)	–0.8(2)	–2.1(3)
N(9)-C(8)	1.483(3)	1.487(4)	1.499(4)	N(9)-N(11)-C(2)-C(1)	–1.6(3)	–1.7(2)	26.2(3)
N(9)-C(10)	1.453(3)	1.474(4)	1.447(4)	N(11)-C(2)-C(1)-C(8)	3.2(3)	3.4(2)	–40.3(3)
N(11)-C(2)	1.486(3)	1.470(4)	1.493(4)	C(2)-C(1)-C(8)-N(9)	–3.7(3)	–4.0(3)	38.7(3)
N(11)-C(10)	1.460(3)	1.460(4)	1.460(4)	C(1)-C(8)-N(9)-N(11)	2.8(3)	3.1(3)	–22.8(3)

[a]for **12** N(9) = N(8), N(11) = N(10), C(8) = C(7) and C(10) = C(9)

The structures were solved by direct methods by use of the SIR92 program,[50] and full-matrix, least-squares refinements on F^2 were performed by use of the SHELXL-97 program.[51] In all cases, the hydrogen atoms were included at fixed distances with the fixed displacement parameters from their host atoms. Figures were drawn with ORTEP-3 for Windows.[52] The deposition numbers CCDC 609482-609484 contain the supple-mentary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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