

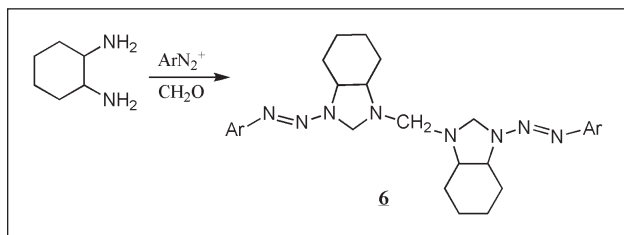
Synthesis and Characterization

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Reaction of diazonium salts with solutions of 1,2-diaminocyclohexane mixed with formaldehyde affords the 1-[2-aryl-1-diazenyl]-3-({3-[2-aryl-1-diazenyl]perhydrobenzo[d]imidazol-1-yl)methyl}perhydrobenzo[d]imidazoles (**6**), a new series of bis-triazenes with different connectivity than any previous type of bis-triazene reported. The products have been characterized principally by NMR and IR spectroscopy, elemental analysis and unequivocally by X-ray crystallography. The methylene protons of the perhydroimidazole rings are diastereotopic giving rise to a doublet of doublets pattern in the ^1H NMR spectra. However, detailed analysis of the NMR spectra shows that there is more than one set of doublet-of-doublet signals, suggesting the presence of different rotameric forms of the products. The ^{13}C NMR spectral assignments were assisted by COSY and DEPT experiments with selected compounds.

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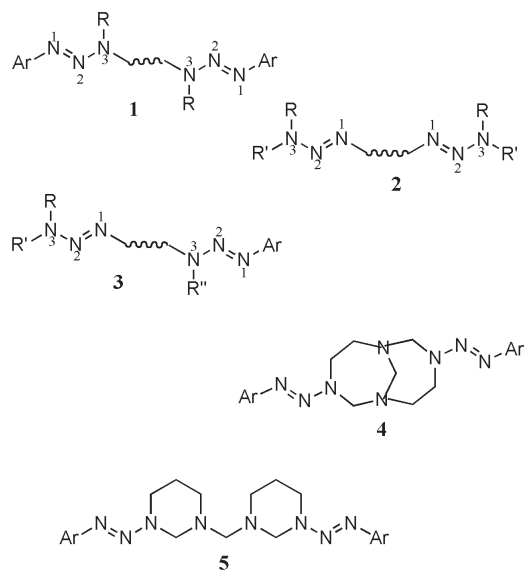
Introduction.

A triazene is any molecule containing three contiguous nitrogen atoms with one N=N double bond, *i.e.* N=N-N. Triazenes have been studied extensively as versatile tools for organic synthesis [1], as multifunctional linkers in the solid-phase synthesis of heterocyclic libraries [2], as anti-tumour agents [3], specifically recently in the treatment of brain tumours [4] and in natural product synthesis [5]. Recent progress in the synthesis of bis-triazenes has been reviewed [6] and the variety of known bis-triazenes can be described by the general structures **1** and **2** (Scheme 1). In bis-triazenes of type **1** the triazenes are linked at N-3 of each triazene unit through the spacer [7,8], whereas in bis-triazenes of type **2** the spacer is attached at N-1 of each triazene unit [9]. Mixed bis-triazenes of type **3**, where a triazene is linked at N-1 *via* a spacer to N-3 of a second triazene, are at present unknown.

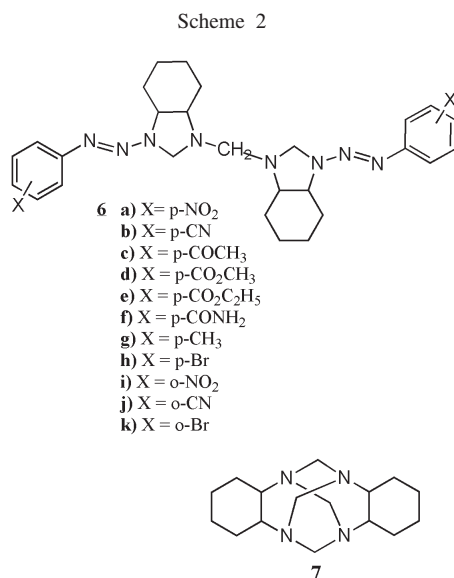
Among the bis-triazenes of type **1**, there is a series of 3,8-di-(2-aryl-1-azeny)-1,3,6,8-tetraazabicyclo[4.4.1]undecanes (**4**), which arise from diazonium coupling with a mixture of 1,2-ethylenediamine and formaldehyde [8]. When this approach was extended to the analogous reaction with 1,3-diaminopropane and formaldehyde, a different mode of molecular scaffolding resulted in the formation of the linear bicyclic bis-triazene series, the 1-[2-aryl-1-diazenyl]-3-(3-[2-aryl-1-diazenyl]hexahydro-1-pyrimidinylmethyl)hexahydropyrimidines (**5**) [10]. The different molecular architecture present in molecules of types **4** and

5 has been clearly established by X-ray crystallography; several examples of series **4** have been elucidated by X-ray structure determination [11]. The X-ray structure of an example of series **5** has been published recently [12]. Thus a cross-over in molecular engineering occurs when going from a 2-carbon spacer in the diamine to the 3-carbon spacer present in **5**. We now report that the reaction of dia-

Scheme 1



zonium salts with a mixture of 1,2-diaminocyclohexane and formaldehyde affords the 1-[2-aryl-1-diazenyl]-3-({3-[2-aryl-1-diazenyl]perhydrobenzo[*d*]imidazol-1-yl}-methyl)perhydro-benzo[*d*]imidazoles (**6**) (Scheme 2), which are linear bicyclic bis-triazenes analogous to those of series **5**. This paper describes the synthesis and characterization of this novel series of bis-triazenes (**6**).



EXPERIMENTAL

All reagents were reagent grade materials purchased from the Aldrich Chemical Co. Ltd., and were used without further purification. The 1,2-diaminocyclohexane was mainly the *trans* isomer (Aldrich 27,001-6). Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were obtained using nujol mulls, unless otherwise stated, on a Perkin Elmer 299 spectrophotometer. ¹H and ¹³C NMR spectra were obtained on a Bruker 250 MHz spectrophotometer at the Atlantic Regional Magnetic Resonance Centre at Dalhousie University in Halifax, Nova Scotia. Chemical shifts were recorded in CDCl₃ solutions at 20 °C, and are relative to TMS internal standard. Elemental analysis was carried out by the Canadian Microanalytical Laboratory, Delta, B.C., Canada

1,8,10,17-Tetraazapentacyclo[8.8.1.1^{8,17}.0^{2,7}.0^{11,16}]icosane (**7**).

A slurry of *N,N*-dimethylformamide (20.0 mL) and paraformaldehyde (3.00 g) was made and heated to 75 °C in a water bath. 1,2-Diaminocyclohexane (6.00 mL) was added dropwise over five minutes, keeping the temperature between 75 °C and 85 °C. The solution was stirred for twenty minutes at 85 °C, at which point the paraformaldehyde dissolved and a white precipitate began to form. The solution was stirred for an additional thirty minutes at 85 °C to ensure complete precipitation. The solution was cooled to room temperature and the white precipitate was isolated *via* vacuum filtration and left to dry. A second crop of large needle like crystals was obtained from the filtrate after two days. Yield 5.91 g, 87%. M.p. 195-198 °C (pet. Ether).

¹³C NMR (CDCl₃): 25.9 (C3, C4, C9, C10), 34.1 (C2, C5, C8, C11), 68.7 (C1, C6, C7, C12) and 71.7 (C13, C14, C15, C16) ppm. ¹H NMR (CDCl₃): 1.22 – 1.33 (m), 1.72 – 1.81 (m), 2.515 (br.d), 2.88 (s), 2.96 (s), 3.81 (d), 4.06(d) ppm. An X-ray crystallographic structure of compound **7** has been determined and full details have been published elsewhere [13].

Anal. Calcd. for C₁₆H₂₈N₄: C 69.5, H 10.2, N 20.3. Found: C 69.5, H 10.05, N 19.9%.

Tetrafluoroborate Diazonium Salts.

The desired aryl amine (0.020 mol) was dissolved in 15 mL of 4 *M* HCl with stirring and heating if necessary. The solution was cooled to 0 °C using an ice-salt bath and diazotized with dropwise addition of NaNO₂ (1.47 g) in 3 mL deionized water, keeping the temperature between 0 °C and 5 °C. This solution was stirred for sixty minutes at 0 °C. 50% Aqueous HBF₄ (6.83 g) was added to a solution of NaOH (1.11 g) in 4 mL of deionized water. The resulting NaBF₄ solution was added dropwise to the diazotized aryl amine, keeping the temperature between 0 °C and 5 °C. A precipitate usually formed immediately. The solution was left to stir for an additional fifteen minutes to ensure complete precipitation. The precipitates were isolated *via* vacuum filtration and dried. The product was used without further purification in methods C and D.

1-[2-Aryl-1-Diazenyl]-3-({3-[2-aryl-1-diazenyl]perhydrobenzo[*d*]imidazol-1-yl}methyl) perhydrobenzo[*d*]imidazoles (**6**).

General Procedure.

Method A.

The desired aryl amine (0.008 mol) was dissolved in 25 mL of 2 *M* HCl with stirring and heating if required. The solution was cooled to 0 °C using an ice-salt bath. The solution was diazotized by adding NaNO₂ (0.69 g) in 5 mL of deionized water dropwise, keeping the temperature between 0 °C and 5 °C. The resulting solution was left to stir for thirty minutes. A solution of 2.6 mL of 50% 1,2-diaminocyclohexane-50% deionized water in 20 mL of 37% formaldehyde was prepared and stirred at 0 °C for thirty minutes in an ice-salt bath. This solution was then added to the diazotized aryl amine solution dropwise, keeping the temperature between 0 °C and 5 °C. The resulting solution was left to stir for thirty minutes at 0 °C, then basified to pH 8 using a saturated NaHCO₃ solution. The product precipitated out of solution upon pH adjustment and was isolated by vacuum filtration and then washed with de-ionized water. A variety of recrystallisation methods were used with various solvents in attempts to purify the crude solids. Physical data for the products are shown in Table 1.

Method B.

1,8,10,17-Tetraazapentacyclo[8.8.1.1^{8,17}.0^{2,7}.0^{11,16}]icosane (**7**) (1.71 g) was dissolved in 15 mL 37% formaldehyde with gentle heating and the solution was cooled to 0 °C using an ice-salt bath while stirring for thirty minutes. The resulting solution was then slowly added to the diazonium salt solution (0.008 mol) dropwise, keeping the temperature between 0 °C and 5 °C, and then left to stir for thirty minutes at 0 °C before being basified to pH 8 using a saturated NaHCO₃ solution. The solid, which precipitated out, was isolated and analyzed as in Method A.

Method C.

The tetrafluoroborate diazonium salt of the desired aryl amine (0.008 mol) was stirred with 25 mL of 2 *M* HCl to form a suspen-

sion. The suspension was cooled to 0 °C using an ice-salt bath. A solution of 50% 1,2-diaminocyclohexane-50% deionized water (0.005 mol) was added to 20 mL 37% formaldehyde at 0 °C and stirred for thirty minutes. This solution was added to the tetrafluoroborate diazonium salt suspension, keeping the temperature between 0 °C and 5 °C. The resulting solution was left to stir for ninety minutes. Any insoluble material was removed *via* vacuum filtration. The filtrate was basified to pH 8 using a saturated NaHCO₃ solution. The solid that precipitated out was isolated and analyzed as in Method A.

Method D.

1,8,10,17-Tetraazapentacyclo[8.8.1.1^{8,17}.0^{2,7}.0^{11,16}]jicosane (7) (1.38 g) was dissolved in 15 mL of 37% formaldehyde with gentle heating and stirring. The resulting solution was cooled to 0 °C with an ice-salt bath and left to stir for thirty minutes. This

solution was then added to the tetrafluoroborate diazonium salt suspension dropwise, keeping the temperature between 0 °C and 5 °C. The solution was left to stir for ninety minutes. Any insoluble material was removed *via* vacuum filtration and the filtrate was basified to pH 8 using a saturated NaHCO₃ solution. The resulting solid was isolated and analyzed as in Method A.

Discussion.

Reaction of a series of aqueous diazonium salts with a mixture of 1,2-diaminocyclohexane and formaldehyde (Method A) gives rise to products that have been characterized as the title compounds **6(a-j)** in moderate yields. Many of the products made by Method A had broad melting points and did not respond well to conventional attempts to purify them by recrystallization. Modified procedures were attempted in order to optimize yields and purity of the compounds. 1,2-Diaminocyclohexane reacts with formaldehyde to

Table 1
Physical and IR Spectroscopic Data of the 1-[2-Aryl-1-diazenyl]-3-({3-[2-aryl-1-diazenyl]perhydrobenzo[d]imidazol-1-yl)methyl}perhydrobenzo[d]imidazoles (**6**)

#	X	Method	Yield %	m.p. (°C)	IR (cm ⁻¹)	Recryst. Solvent
6a	<i>p</i> -NO ₂	A or B	44	221-223	1560, 1350 (NO ₂)	Hexanes/ Ethyl Acetate
		C	65		830(<i>p</i> -sub. OOP)	
6b	<i>p</i> -CN	A	56	209-211	2170 (CN)	Hexanes/ Ethyl Acetate
		B	37		785(<i>p</i> -sub.)	
6c	<i>p</i> -COCH ₃	A	48	187-188	1650 (C=O)	Hexanes/ Ethyl acetate/ Toluene
		D	40		820(<i>p</i> -sub.)	
6d	<i>p</i> -CO ₂ CH ₃	A	43	180-183	1690 (C=O)	Hexanes/ Ethyl acetate
		B	48		1240, 1130 (C-O) 850 (<i>p</i> -sub.)	
6e	<i>p</i> -CO ₂ Et	A	60	74-80	1710 (C=O)	
		C	20		1270, 1000 (C-O) 860 (<i>p</i> -sub)	
6f	<i>p</i> -CONH ₂	A	48	190-193	3280, 3140 (NH br.)	Hexanes/ Ethyl acetate
		B	43		1630 (C=O)	
		D	33		1580 (NH bend) 830 (<i>p</i> -sub.)	
6g	<i>p</i> -CH ₃	A	23	196-197	810 (<i>p</i> -sub)	Hexanes/ Ethyl acetate
6h	<i>p</i> -Br	A	51	200-201	810 (<i>p</i> -sub)	Hexanes/ Ethyl acetate
6i	<i>o</i> -Br	A	37	214-215	730 (<i>o</i> -sub)	Hexanes/ Ethyl acetate
6j	<i>o</i> -CN	A	55	88-92	2200 (CN)	
		B	66		745 (<i>o</i> -sub.)	

Table 2
Elemental Analysis Data of the 1-[2-Aryl-1-diazenyl]-3-({3-[2-aryl-1-diazenyl]perhydrobenzo[d]imidazol-1-yl)methyl}perhydrobenzo[d]imidazoles (**6**)

Compound #	X	Formula	Calculated			Found		
			C	H	N	C	H	N%
6a	<i>p</i> -NO ₂	C ₂₇ H ₃₄ N ₁₀ O ₄	57.6	6.1	24.9	57.43	6.05	24.17
6b	<i>p</i> -CN	C ₂₉ H ₃₄ N ₁₀	66.6	6.6	26.8	66.51	6.66	26.51
6c	<i>p</i> -COCH ₃	C ₃₁ H ₄₀ N ₈ O ₂	66.9	7.2	20.1	66.50	7.37	20.20
6d	<i>p</i> -CO ₂ Me	C ₃₁ H ₄₀ N ₈ O ₄	63.3	6.8	19.0	63.38	6.66	19.11
6e	<i>p</i> -CO ₂ Et	C ₃₃ H ₄₄ N ₈ O ₄	64.2	7.2	18.2	64.24	7.24	18.20
6g	<i>p</i> -CH ₃	C ₂₉ H ₄₀ N ₈	69.5	8.1	22.4	69.00	8.22	22.71
6h	<i>p</i> -Br	C ₂₇ H ₃₄ N ₈ Br ₂	51.4	5.4	17.8	51.45	5.51	17.29
6i	<i>o</i> -Br	C ₂₇ H ₃₄ N ₈ Br ₂	51.4	5.4	17.8	51.47	5.64	17.48

give the pentacycloicosane (**7**) [14]. In Method B, the arene diazonium chloride was allowed to react with **7** directly in aqueous solution; the same products were obtained as in Method A, occasionally in better yield. In Method D, the arene diazonium fluoroborate was suspended in hydrochloric acid and allowed to react with **7** in formaldehyde solution, and in Method C the diazonium fluoroborate was reacted with a mixture of the diaminocyclohexane and formaldehyde. In most cases, Method A gave the best yield of crude product, but did not always give the optimal purity. Yields and m.p.'s are given in Table 1. Elemental analysis results for the compounds of series **6** are given in Table 2.

Although it will be shown here that the spectroscopic data of compounds **6a-j** are consistent with the assigned structures, the solution of the structural problem was obtained unequivocally from X-ray crystallography of the *p*-methyl-(**6g**) and *p*-cyano-(**6b**) compounds. Full details of the X-ray crystal structure of **6b** has been published [15] and the X-ray structure of **6g** will be published elsewhere [16].

The IR spectra of all the products were recorded as nujol mulls to verify the presence of the functional group in the aryl moiety. The OOP CH bending vibration bands were recorded to verify the position of substitution in the benzene rings (see Table 1).

Details of the ^1H NMR spectra of the compounds of series **6** are given in Table 3; the carbon and hydrogen atom labels relevant to the data presentation are shown in Figure 1. The aromatic protons are clearly defined, as AA'BB' systems when the substituent is *para*. The protons in the aromatic substituent (X) are clearly evident when present. The homotopic protons of the linking methylene group (H_a, H_b) appear as a singlet at *ca.* 3.45 ppm. The protons at the extremities of the cyclohexane ring ($\text{H}_i, \text{H}_j, \text{H}_k, \text{H}_l$) appear predictably as a complex multiplet at *ca.* 1.2 – 1.6

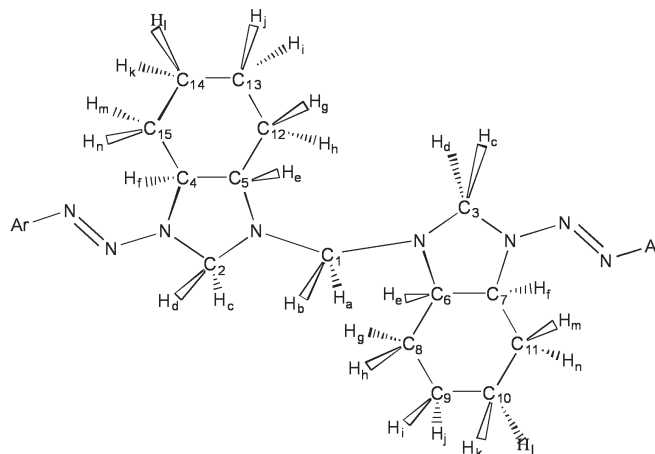


Figure 1. Carbon and Hydrogen atom labels for NMR interpretation.

ppm, and the adjacent protons ($\text{H}_g, \text{H}_h, \text{H}_m, \text{H}_n$) also as a multiplet at *ca.* 1.9 – 2.3 ppm. The two protons, H_e , appear at *ca.* 2.5 – 2.6 ppm in various forms, sometimes as a clean, but broad, doublet, and at other times as a doublet of triplets or as a doublet of doublets or as a broad multiplet. The two protons, H_f , are evident at *ca.* 3.4 – 3.5 ppm, partially hidden by the singlet of H_a, H_b , but usually evident as a broad multiplet. The most interesting feature of the ^1H NMR spectra is the more complex signal pattern arising from the diastereotopic protons of the two equivalent methylene groups, H_c and H_d , which appear as a doublet of doublets (“dd’s”) at *ca.* 5.05 ppm and 4.0 ppm. The coupling constant, J_{cd} ,

Table 3

^1H NMR Chemical Shift Data(ppm) in of the 1-[2-Aryl-1-diazenyl]-3-({3-[2-aryl-1-diazenyl]perhydrobenzo[d]imidazol-1-yl)methyl}perhydrobenzo[d]imidazoles (**6**) relative to TMS (1%) at 22 °C in CDCl_3

#	X	Aromatic (8H)	X	H_a, H_b (2H)	H_c, H_d (4H)	H_e (2H)	H_f (2H)	$\text{H}_g, \text{H}_h, \text{H}_m, \text{H}_n$ (8H)	$\text{H}_i, \text{H}_j, \text{H}_k, \text{H}_l$ (8H)
6a	<i>p</i> -NO ₂	7.51 (d, J = 15Hz) 8.21 (d, J=15Hz)	-	3.48(s)	5.05(d), 4.08(d) 4.97(d), 4.21(d) 4.12(d), 3.76(d)	2.57(br d.)	3.50(br.m) (5 lines)	1.90-2.39(m) (20 lines)	1.24-1.60(m) (18 lines)
6b	<i>p</i> -CN	7.12 (d, J = 7.5Hz) 7.32 (d, J = 7.5Hz)	-	3.43(s)	5.00(d), 4.03(d) 4.92(d), 4.14(d) 4.12(d), 3.70(d)	2.54(br. d)	3.39(br. m)	1.87-2.32(m)	1.23-1.58(m) (14 lines)
6c	<i>p</i> -COCH ₃	7.48 (d, J = 7.5Hz) 7.93 (d, J = 7.5Hz)	2.60(s) (6H)	3.45(s)	5.04(d), 4.05(d) 4.96(d), 4.09(d)	2.58(d)	3.51(d)	1.80-2.35(m)	1.21-1.65(m)
6d	<i>p</i> -CO ₂ CH ₃	7.45 (d, J = 5.0Hz) 8.00 (d, J = 5.0Hz)	3.89(s) (6H)	3.45(s)	5.05(d), 4.07(d) 4.06(d), 4.20(d)	2.57(dd)	3.40(dd)	1.93-2.32 (m) (20 lines)	1.25-1.63(m) (24 lines)
6e	<i>p</i> -CO ₂ Et	7.46 (d, J = 5.4Hz) 7.95 (d, J = 5.4Hz)	1.40(t) 4.13(q)	3.41(s)	5.05(d), 4.10(d) 4.87(d), 4.11(d)	2.60(d)	3.45(d)	1.79-2.37(m)	1.20-1.65(m)
6f	<i>p</i> -CONH ₂	7.48 (d, J = 5.0Hz) 7.79 (d, J = 5.0Hz)	-	3.47(s)	5.05(d), 4.07(d) 4.97(d), 4.20(d)	2.58(br. d)	3.50(br. p)	1.91-2.32(m)	1.24 -1.56(m)
6g	<i>p</i> -CH ₃	7.12 (d, J = 7.5Hz) 7.32 (d, J = 7.5Hz)	2.33(s)	3.43(s)	5.00(d), 4.03(d) 4.92(d), 4.15(d) 4.82(d), 4.52(d)	2.54(br. d)	3.39(m) partially hidden	1.88-2.24(m)	1.17-1.60(m)
6h	<i>p</i> -Br	7.28 (d, J = 9.0Hz) 7.42 (d, J = 9.0Hz)	-	3.43(s)	4.99(d), 4.01(d) 4.91(d), 4.14(d)	2.52(br. d)	3.39(m) partially hidden	1.91-2.30(m)	1.20-1.57(m)
6i	<i>o</i> -Br	7.13-7.26(m)	-	4.06(s)	5.24(d), 4.78(d) 4.45(d), 4.36(d)	2.65(dt)	3.09(dt)	1.70-2.10(m)	1.20-1.60(m)
6j	<i>o</i> -CN	7.15-7.65(m)	-	3.45(s)	5.07(d), 4.09(d) 4.97(d), 4.25(d)	2.50(br. m)	3.50(m)	1.86-2.39(m)	1.25-1.61(m)

is in the range 8.0-10.0 Hz; whereas the coupling constant, J_{ef} , has a much wider variance from 7.3-11.9 Hz.

An interesting feature of these spectra is the fact that these dd's are doubled in most of the molecules and even tripled in a few. The most intense set of doublets occurs at *ca* 5.05 ppm and 4.0 ppm consistently; the second set of doublets occurs at *ca* 5.0 ppm and 4.2 ppm. When the minor doublets are evident, the dd's are seen at *ca*. 4.1 ppm and 3.7 ppm. The interpretation of these observations is that the hindered rotation around the N2-N3 triazine bonds, due to its partial double bond character [17], gives rise to a set of rotamers. In these rotamers, the CH_cH_d group is either *syn* or *anti* to the aryldiazenyl group, giving rise to different chemical shielding parameters and the observed different chemical shift for the dd's. Since there are two triazine units in the molecules of series **6**, there are potentially three rotamers, which could be designated as *anti-anti*, *syn-syn* or *syn-anti*, which accounts for the maximum three sets of dd's in the spectra of **6a**, **6b** and **6g**.

The difference in the intensities of the double doublets assigned to H_c and H_d indicates that the rotamers are not observed in equal amounts. Although we have no immediate way of assigning the chemical shifts of the H_c , H_d signals to a specific rotamer at this time, it is possible to derive an approximate measure of the % amounts of the three forms from the relative heights of the signals. Table 4 shows the results of this analysis.

A COSY spectrum of the *o*-cyano-derivative (**6j**) gives additional evidence for the presence of rotamers. The doublet at 5.07 ppm correlates with the doublet at 4.09 ppm, and 4.97 ppm corre-

lates with 4.25 ppm, but there is no cross-correlation indicating that these doublet of doublets arise from separate molecules. A HETCOR spectrum of **6j** provided evidence for the ^{13}C NMR assignments listed in Table 5. For example, the proton signal at 3.45 ppm (H_a , H_b) correlates with the carbon signal at 71.1 ppm (C_1) in the spectrum of **6j**; assignments for **6b**, **6c**, **6d** and **6g** were made by reference to **6j** and by comparison with the previously reported ^{13}C spectra of the bis-triazene series (**4**) [8]. Unequivocal confirmation of these assignments was obtained from a DEPT experiment with

Scheme 3

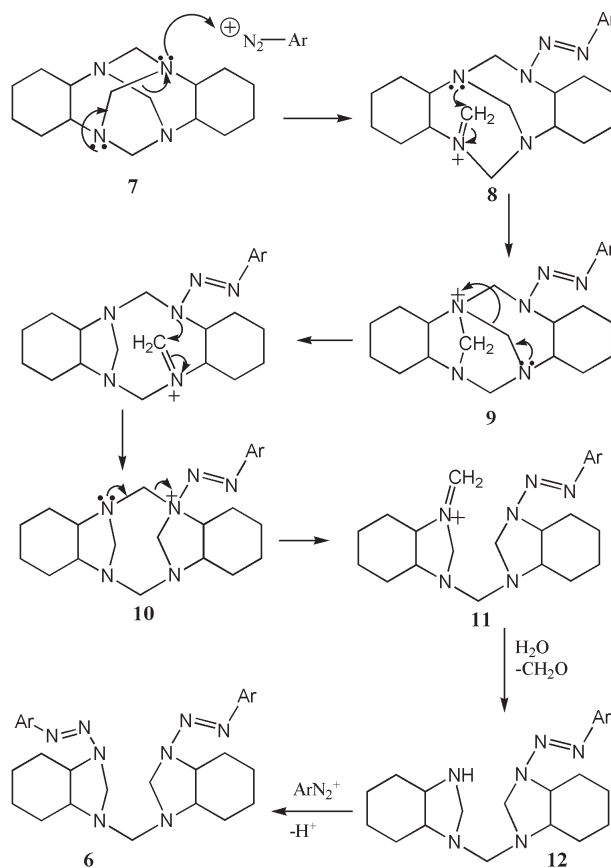


Table 4

Compound	X	% Major Rotamer (5.05/4.05ppm)	% Middle Rotamer (4.97/4.2 ppm)	% Minor Rotamer (4.1/3.7ppm)
6a	<i>p</i> -NO ₂	67	25	8
6b	<i>p</i> -CN	65	23	12
6c	<i>p</i> -COCH ₃	74	26	-
6d	<i>p</i> -CO ₂ Me	94	6	-
6e	<i>p</i> -CO ₂ Et	70	30	-
6f	<i>p</i> -CONH ₂	78	22	-
6g	<i>p</i> -CH ₃	69	21	10
6h	<i>p</i> -Br	71	29	-
6i	<i>o</i> -Br	71	29	-
6j	<i>o</i> -CN	60	40	-

Table 5

^{13}C NMR Chemical Shift Data(ppm) of the 1-[2-Aryl-1-diazenyl]-3-({3-[2-aryl-1-diazenyl]perhydrobenzo[d]imidazol-1-yl)methyl}perhydrobenzo[d]imidazoles (**6**) Relative to TMS (1%) at 22 °C in CDCl₃

#	X	C ₁	C ₂ , C ₃	C ₄ , C ₇	C ₅ , C ₆	C ₁₁ , C ₁₅	C ₈ , C ₁₂	C ₉ , C ₁₃	C ₁₀ , C ₁₄	Aromatic	X
6b	<i>p</i> -CN	71.2	70.2	66.8	65.8	29.2	28.4	23.9	24.3	154.9, 133.1 121.0	109.7 (CN)
6c	<i>p</i> -COCH ₃	71.0	69.9	66.8	65.8	28.8	28.5	23.9	24.3	154.8, 134.2 129.6, 120.4	197.5(C=O) 26.6 (CH ₃)
6d	<i>p</i> -CO ₂ CH ₃	71.0	70.1	67.05	66.0	29.1	28.7	24.2	24.5	154.9, 130.8 127.1, 120.5	167.3 (C=O) 52.2 (O-CH ₃)
6g	<i>p</i> -CH ₃	71.2	70.2	66.7	65.6	29.2	28.7	24.0	24.4	148.8, 135.5 129.4, 120.5	21.1 (CH ₃)
6h	<i>p</i> -Br	[a]	[a]	[a]	65.8	29.1	28.6	24.1	24.5	131.9, 122.3	-
6j	<i>o</i> -CN	71.1	70.2	67.8	66.1	29.0	28.7	24.2	24.7	133.4, 133.2 125.2, 118.3	118.0 (CN)

[a] not resolved.

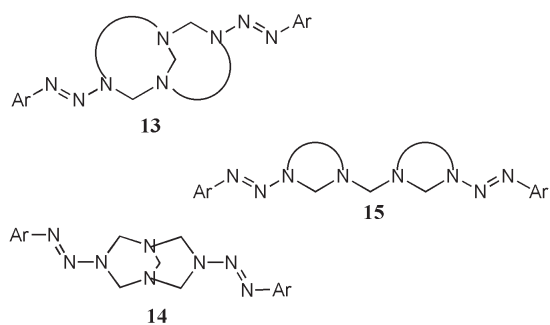
the *p*-acetyl-derivative (**6c**). In the DEPT spectrum: (a) the carbonyl signal at 197.5 ppm is inverted; (b) the aromatic quaternaries at 154.8 ppm and 134.2 ppm are inverted, but the signals at 129.6 ppm and 120.4 ppm are not; (c) the methyl carbon at 26.6 ppm is not inverted; (d) the signals assigned to the methylene carbons C1, C2, C3, and C8 through C15 are all inverted; (e) signals of the methine carbons C4, C5, C6 and C7 are not inverted.

A possible mechanism for the formation of the bis-triazenes (**6**) from the tetraazapentacycloicosane (**7**) is shown in Scheme 3. Initial attack by a diazonium ion at any one of the four equivalent nitrogen atoms initiates a ring opening to give the methyleneiminium cation (**8**), which then undergoes ring-closure to give the quaternary ammonium species (**9**) in which one of the imidazolidine rings has been created. Further ring opening and re-closure completes the second imidazolidine ring in **10**, which ring-opens again to give another methyleneiminium ion (**11**). Hydrolysis of **11** and loss of a molecule of formaldehyde gives the secondary amine (**12**) which is set-up for the final diazonium coupling reaction to give the observed product (**6**).

Conclusion.

The structure of the series of new bis-triazenes (**6**) described in this paper has been clearly established by X-ray crystallography of two examples. NMR correlation of chemical shifts with the remainder of the series gives unequivocal identification. One of the principal conclusions of this work is that there are two distinct types of oligomer produced by the interaction of a diazonium salt with a mixture of formaldehyde and a bis-primary amine. The bridged bicyclic type of bis-triazene is exemplified by the general structure (**13**) (Scheme 4). The known examples of this type are the bis-triazenes (**4**) which arise from ethylene diamine [8] and the bis-triazenes of type (**14**), which are produced from ammonia/formaldehyde mixtures [18]. The alternate type of molecular geometry is the linear bicyclic structure (**15**). The title compounds (**6**) reported here represent examples of bis-triazenes of type **15** and are analogous to the linear bicyclic hexahydropyrimidines (**5**) derived from 1,3-diaminopropane [10]. Further work is under way to delineate the structural requirements for formation of bis-triazenes of type **13** or **14**.

Scheme 4



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