Send Orders for Reprints to reprints@benthamscience.ae

The Open Organic Chemistry Journal, **2015,** *9,* **1-8** **1**

Open Access

Synthesis and Characterization of New Compounds in the Series 1-alkyl-4-[2-aryl-1-diazenyl]piperazines

Erin MacLeod and Keith Vaughan*

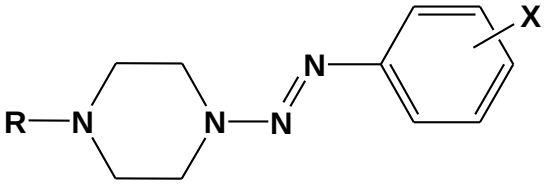
Department of Chemistry, Saint Mary's University, Halifax, N.S., Canada

Abstract: 24 New triazenes derived from the 1-alkylpiperazines have been synthesized. Each 1-alkylpiperazine was treated with a diazonium salt solution to produce the new triazenes, which have been characterized by proton and carbon-13 NMR spectroscopy, IR spectroscopy and by mass spectrometric analysis. Assignment of the chemical shifts to specific protons and carbons in the piperazine ring was facilitated by comparison with the chemical shifts in the previously reported 1-methyl-4-[2-aryl-1-diazenyl]piperazines (**1**).

Keywords: 1-Alkylpiperazine, aryldiazenyl, diazonium coupling, piperazine, triazene.

INTRODUCTION

In a previous report [1] a series of 1-methyl-4-[2-aryl-1-diazenyl]piperazines (**1**) were synthesized and characterized. In this paper, we now report the formation of 24 new triazenes derived from 1-alkylpiperazines, namely the 1-ethyl series (**2**), the 1-hydroxyethyl series (**3**), the 1-butyl series (**4**) and the 1-iso-propyl series (**5**).



1 R = -Me
2 R = -Et
3 R = -CH_2CH_2OH
4 R = -Bu
5 R = -*i*-Pr

This paper is the latest chapter in an extensive study of the synthesis of N-aryldiazenylpiperazines and the structural characterization of these triazenes. In Part I of this series [1], the diazonium coupling reaction of 1-methylpiperazine was explored in order to synthesize the 4-methyl-1-(2-aryldiazen-1-yl-)piperazines (**1**). "The structure of one compound, namely methyl 4-{(E)-2-(4-methylpiperazino)-1-diazenyl} benzoate, in this series has been verified by X-ray crystallography [2], which showed that the piperazine ring adopts a normal chair conformation." In the process of characterizing these triazenes by NMR spectroscopy, the chemical shift parameters "of the protons and carbons in the piperazine ring were clearly established and verified by some classical 2D NMR work" [1, 2]. "This data was used to advantage in the characterization of 4-methyl-1-[aryldiazenyl]-homopiperazines (**6**), which have been described, along with the 1,4-di-(2-aryldiazen-1-yl) diazepanes" (**7**), in Part II of this series [3]. The bis-triazenes (**7**) were obtained by reaction of homopiperazine with the diazonium salt in 1:2 molar proportion.

This bis-diazotization strategy was subsequently explored with piperazine itself and the synthesis of a series of 1,4-di-(2-aryldiazen-1-yl-)-piperazines (**8**) was described in Part III of this series [4]. "The bis-triazenes of type **8** were characterized by a range of spectroscopic techniques and the data was compared with some previously published work [5] in which several of the bis-aryldiazenyl-piperazines had already been described." Subsequently, we extended the study of bis-triazenes to the 1,4-di-[2-aryl-1-diazenyl]-2-methylpiperazines (**9**), which were prepared by diazonium coupling to 2-methylpiperazine [6], and then to the 1,4-di-[2-aryl-1-diazenyl]-2,6-dimethylpiperazines (**10**) [7].

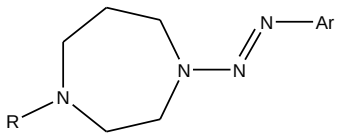
"The work described in this paper is a logical extension of our previous study [1] of the synthesis of the 1-methyl-4-[2-aryl-1-diazenyl]piperazines" (**1**).

DISCUSSION

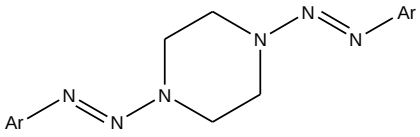
The reaction of a diazonium salt with 1-ethylpiperazine proceeded smoothly to afford good to excellent yields of the 1-ethyl-4-[2-aryl-1-diazenyl]piperazine series (**2**). Yields and physical data of these compounds are shown in Table **1**. The compounds of series **2** are low-melting point solids, which have high solubility in a range of solvents, making it difficult to achieve purification by recrystallization in all cases. Some success was achieved with hexanes or ethyl acetate/hexanes mixture. The IR data show the presence of the aryl substituent functional group absorptions, as well as the appropriate OOP bands for the particular substituent in the benzene ring. The ^{1}H NMR data for series **2a-2i** are presented in Table **2**. The spectra of compounds **2a-2g** show the typical signals for an AA'BB' pattern of a *p*-disubstituted

*Address correspondence to this author at the Department of Chemistry, Saint Mary's University, Halifax, N.S., Canada; Tel: (902)-420-5650; Fax: (902)-496-8104; E-mail: keith.vaughan@smu.ca

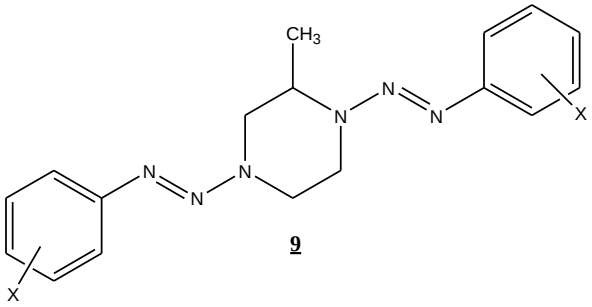
1874-0952/15 **2015 Bentham Open**



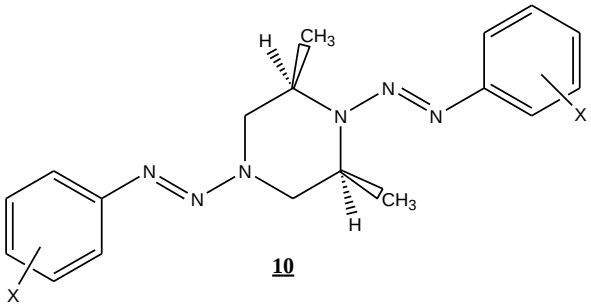
6 **R = Me**
7 **R = Ar-N=N-**



8



9



10

benzene derivative, whereas the *o*-bromo-derivative (**2h**) shows four unique chemical shifts in the aromatic region as expected with multiplicity of a doublet of doublets or doublet of triplets. The 3-pyridyl analogue (**2i**) also shows a pattern of four unique aromatic hydrogen atoms. All compounds in the series show the typical signals for the *N*-ethyl group. i.e. a 2-proton quartet at *ca.* 2.48 and a 3-proton triplet at *ca.* 1.11 ppm . The protons in the piperazine ring appear as 4-proton triplets at *ca.* 2.6 and 3.8, with a coupling constant J_{ab} = *ca.* 5 Hz.

Extension of the diazonium coupling reaction to 1-(2-hydroxyethyl)-piperazine resulted in excellent yields of the 1-(2-hydroxyethyl)-4-[2-aryl-1-diazenyl]piperazine series (**3**). Yields and physical data of these compounds are shown in Table **3**. The compounds of this series have higher melting points than those of series **2**, and they were consequently much easier to recrystallize. The ^{1}H NMR data for series **3a-3i** are presented in Table **4**. The spectra of compounds **3a-3g** show the typical signals for an AA'BB' pattern, and the *o*-bromo- and 3-pyridyl derivatives displayed aromatic signals similar to those of **2h** and **2i**. The protons in the piperazine ring appear as 4-proton triplets at *ca.* 2.68 and 3.85, with a coupling constant J_{ab} = *ca.* 5.1 Hz. All compounds in the series show the typical signals for the methylene groups of the 2-hydroxyethyl moiety, i.e. a 2-proton triplet at *ca.* 2.64 and a 2-proton triplet at *ca.* 3.68 ppm . The proton of the OH group appears in the range 1.3-1.8 ppm, with the exception of the signal at 4.82 ppm in the 3-pyridyl derivative (**3i**).

Further extension of the diazonium coupling reaction to 1-butylpiperazine resulted in excellent yields of the 1-butyl-4-[2-aryl-1-diazenyl]piperazine series (**4**). Yields and physical data of these compounds are shown in Table **5**. The ^{1}H NMR data for series **4a-4d** are presented in Table **6**. The spectra of compounds **4a-4d** show the typical signals for an AA'BB' pattern of a p-substituted aryl ring The protons in the piperazine ring appear as 4-proton triplets at *ca.* 2.6 and 3., with a coupling constant J_{ab} = *ca.* 5.1 Hz. All compounds in the series show the typical signals for the butyl group: a 2-proton triplet at *ca*. 2.4, a 2-proton pentet at *ca.* 1.52, a 2-proton pentet at *ca.* 1.35 and a 3-proton triplet at. 0.94 ppm. The coupling constants within the butyl group are in the range *J* = *ca.* 7.5 Hz.

Two compounds of the 1-isopropyl-4-[2-aryl-1-diazenyl]piperazine series (**5**) have been synthesized. Physical data are reported in Table **7** and ^{1}H NMR data are shown in Table **8**. The spectroscopic data are similar to the data of series **2**, **3** and **4** and are consistent with the structures **5a** and **5b**. As a final proof of structure, all of the new compounds reported here have been analyzed by high resolution mass spectrometry to confirm the molecular formulas of each compound. The results for all series are tabulated in Table **9**.

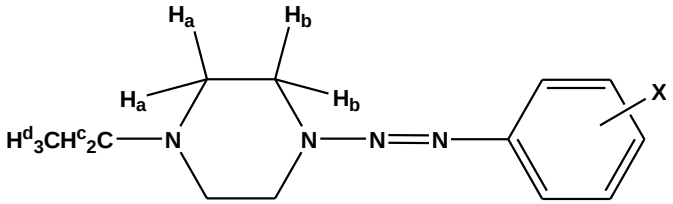
It is relevant to the present work that the medicinal chemistry of piperazine derivatives has attracted considerable interest. Research on arylpiperazines is quite extensive due to their biological applications. They are especially known for their high affinity toward serotonin receptors, chiefly 5-HT1A receptors. Many common anxiolytics and antidepressants incorporate arylpiperazines.[1] It is believed that arylpiperazine agonist or antagonist activity comes from either its coplanarity or perpendicular conformation, respectively, of the aryl ring with the piperazine N1 nitrogen. The possibility of combining the structural unit of a triazene with that of a piperazine raises interesting questions like what biological activities might be generated from such a marriage.

Table 1. Physical data of 1-ethyl-4-[2-aryl-1-diazenyl]piperazines.

Compound #	X	Yield	m.p. (°C) (a)	Crystal Appearance	IR (cm^{-1})
2a	p-CN	84%	57-59	Glassy sheets Dark Brown	2217.3 (CN) 845.4 (OOP)
2b	p-CO_2Me	76%	84-85	Amorphous orange	1715.4 (C=O) 865/733 (OOP)
2c	p-NO_2	60%	87-89	Medium sized orange needles	1511/ 1333 (NO_2)
2d	p-CH_3	38%	53-54	Amorphous Red/Orange	820.5 (OOP)
2e	p-Br	94%	60-61	Amorphous Dark Orange	616.9 (C-Br) 834.5 (OOP)
2f	p-CH_3O	26%	44-47	Amorphous Red	1251.1 (CH_3O) 830.2 (OOP)
2g	p-CH_3CO	72%	51-52	Amorphous Red	1678.4 (C=O) 842.1 (OOP)
2h	o-Br	94%	Oil	Dark Amber oil	648.0 (C-Br)
2i	pyr	quantitative	Oil	Red oil	1670/1574 (C=N)

Recrystallization solvent = hexanes or hexanes/ethyl acetate mixture

Table 2. ^{1}H NMR chemical shift data (ppm) in $CDCl_3$ of the 1-ethyl-4-[2-aryl-1-diazenyl]piperazines.



Compound #	X	Aromatic	H_a	H_b	H_c	H_d	X
2a	p-CN	7.75, 7.72, 7.56, 7.53	3.88 (t, 4H) J = 5.0	2.59 (broad s, 4H)	2.46 (q, 2H) J = 6.7	1.10 (t, 3H)	n/a
2b	p-CO_2Me	8.00, 7.98, 7.45, 7.44	3.86 (t, 4H) J = 5.4	2.58 (t, 4H) J = 4.9	2.47 (q, 2H) J = 7.2	1.11 (t, 3H) J = 7.2	3.87 (s, 3H)
2c	p-NO_2	8.17, 8.15, 7.48, 7.47	3.94 (broad s, 4H)	2.63 (broad s, 4H)	2.52 (q, 2H) J = 7.2	1.13 (t, 3H) J = 7.2	n/a
2d	p-CH_3	7.36, 7.34, 7.15, 7.13	3.79 (t, 4H) J = 5.2	2.59 (t, 4H) J = 5.2	2.48 (q, 2H) J = 7.2	1.13 (t, 3H) J = 7.2	2.33 (s, 3H)
2e	p-Br	7.44, 7.42, 7.31, 7.29	3.81 (t, 4H) J = 5.3	2.58 (t, 4H) J = 5.3	2.48 (q, 2H) J = 7.2	1.12 (t, 3H) J = 7.2	n/a
2f	p-CH_3O	7.41, 7.39, 6.88, 6.86	3.75 (t, 4H) J = 5.2	2.58 (t, 4H) J = 5.3	2.47 (q, 2H) J = 7.2	1.12 (t, 3H) J = 7.2	3.79 (s, 3H)

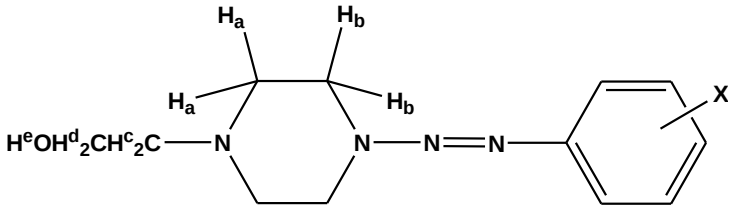
Table 2. Contd…..

Compound #	X	Aromatic	H_a	H_b	H_c	H_d	X
2g	p-CH_3CO	7.91, 7.90, 7.46, 7.44	3.86 (t, 4H) J = 5.3	2.58 (t, 4H) J = 5.0	2.47 (q, 2H) J =7.2	1.10 (t, 3H) J = 7.2	2.55 (s, 3H)
2h	o-Br	7.57 (1H, dd) 7.41(1H, dd) 7.23(1H, dt) 7.00(1H, dt)	3.89 (t, 4H) J = 4.9	2.60 (t, 4H) J = 5.1	2.49 (q, 2H) J = 7.2	1.12 (t, 3H) J = 7.2	n/a
2i	pyr	8.64(1H, d) 8.35(1H, dd) 7.67(1H, dt) 7.20(1H, dd)	3.82 (t, 4H) J = 5.3	2.56 (t, 4H) J = 5.2	2.45 (q, 2H) J = 7.2	1.09 (t, 3H) J = 7.2	n/a

Table 3. Physical data of 1-(2-hydroxyethyl)-4-[2-aryl-1-diazenyl]piperazines.

Compound #	X	Yield %	m.p. (°C)	Solvent	Recovery %	Crystal Appearance	IR (cm^{-1})
3a	p-CN	88	157-159	Ethanol	78	Peach glassy sheets	2219 (CN) 851 (OOP)
3b	p-CO_2Me	93	92-93	Ethyl Acetate	49	Small needles yellow/ brown	1720 (C=O) 862/774 (OOP)
3c	p-NO_2	62	102-103	Methanol	66	Amorphous brown	1509/ 1338 (NO_2) 853 (OOP)
3d	p-CH_3	83	69-71	Cyclohexane	84	Peach coloured sheets	823 (OOP)
3e	p-Br	85	97-99	Cyclohexane	45	Light yellow amorphous	636 (C-Br) 830 (OOP)
3f	p-CH_3O	74	61-62	Cyclohexane	20	Light brown sheets	1161/1250 (C-O) 832 (OOP)
3g	p-CH_3CO	96	91-93	Ethyl Acetate	41	Orange amorphous	1674 (C=O) 851 (OOP)
3h	o-Br	100	26-27	n/a	n/a	Orange amorphous	649/689 (C-Br)
3i	pyr	86	Oil	n/a	n/a	Red spikes growing up vial	1665/1589 (C=N)

Table 4. ^{1}H NMR chemical shift data (ppm) in $CDCl_3$ of the 1-(2-hydroxyethyl)-4-[2-aryl-1-diazenyl]piperazines.



Compound #	X	Aromatic	H_a	H_b	H_c	H_d	H_e	X
3a	p-CN	7.63, 7.60, 7.51, 7.47	3.91 (t, 4H) J = 5.4	2.67 (t, 4H) J = 5.6	2.65 (t, 2H) J = 5.4	3.69 (t, 2H) J = 5.3	1.8 (s, 1H) v. broad	n/a

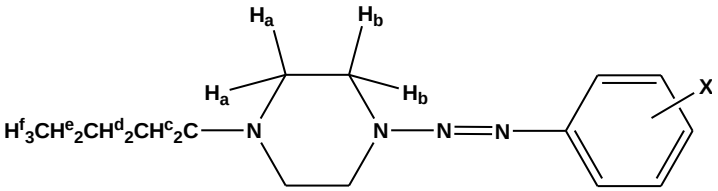
Table 4. Contd…..

Compound #	X	Aromatic	H_a	H_b	H_c	H_d	H_e	X
3b	p-CO_2Me	8.04, 8.00, 7.49, 7.45	3.88 (t, 4H) J = 5.5	2.67 (t, 4H) J = 5.6	2.64 (t, 2H) J = 5.4	3.68 (t, 2H) J = 5.4	1.76 (broad s, 1H)	3.90 (s, 3H)
3c	p-NO_2	8.23, 8.20, 7.55, 7.51	3.96 (broad t, 4H) J = 3.8	2.68 (broad t, 4H) J = 5.0	2.66 (broad t, 2H)	3.72 (broad t, 2H) J = 5.0	1.3 (broad s, 1H)	n/a
3d	p-CH_3	7.36, 7.33, 7.17, 7.13	3.79 (t, 4H) J = 5.3	2.68 (t. 4H) J = 5.4	2.63 (t, 2H) J = 5.6	3.67 (t, 2H) J = 5.3	1.66 (broad s, 1H)	2.34 (s, 3H)
3e	p-Br	7.47, 7.44, 7.33, 7.30	3.82 (t, 4H) J = 5.3	2.68 (t, 4H) J = 5.1	2.64 (t, 2H) J = 5.1	3.68 (t, 2H) J = 5.1	1.65 (broad s, 1H)	n/a
3f	p-CH_3O	7.43, 7.40, 6.90, 6.87	3.76 (t, 4H) J = 5.3	2.67 (t, 4H) J = 5.5	2.63 (t, 2H) J = 5.4	3.67 (t, 2H) J = 5.3	1.76 (v. broad s, 1H)	3.82 (s, 3H)
3g	p-CH_3CO	7.97, 7.94, 7.51, 7.47	3.89 (t, 4H) J = 5.1	2.69 (t, 4H) J = 5.3	2.64 (t, 2H) J = 5.4	3.69 (t, 2H) J = 5.1	1.7 (broad s, 1H)	2.59 (s, 3H)
3h	o-Br	7.59(1H, dd) 7.42(1H, dd) 7.26(1H, dt) 7.02(1H, dt)	3.89 (t, 4H) J = 4.9	2.69 (t, 4H) J = 5.13	2.64 (t, 2H) J = 5.4	3.68 (t, 2H) J = 5.0	1.77 (broad s, 1H)	n/a
3i	pyr	8.60(1H, d) 8.29(1H, dd) 7.66(1H, dt) 7.18(1H, dt)	3.77 (t, 4H) J = 5.0	2.58 (t, 4H) J = 5.0	2.55 (t, 2H) J = 5.0	3.65 (t, 2H) J = 6.3	4.82 (s, 1H)	n/a

Table 5. Physical data of 1-butyl-4-[2-aryl-1-diazenyl]piperazines.

Compound #	X	Yield %	m.p. (°C)	Solvent	Recovery %	State of Crystal	IR
4a	p-CN	24	41-42	n/a	n/a	Amorphous light brown	2216.6 (CN) 846.8 (OOP)
4b	p-CO_2CH_3	67	82-83	Ethanol	26	White glassy, possibly in sheets	1718.9 (C=O) 865 (OOP)
4c	p-Br	86	52-54	Ethanol	20	Some white and some brown sheets	637 (C-Br) 834 (OOP)
4d	p-CH_3O	14	30-32	n/a	n/a	Amorphous copper colour	1246 (CH_3O) 836 (OOP)

Table 6. ^{1}H NMR chemical shift data (ppm) in $CDCl_3$ of 1-butyl-4-[2-aryl-1-diazenyl]piperazines.

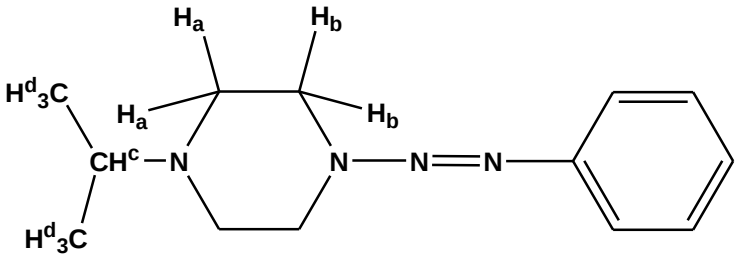


Compound #	X	Aromatic	H_a	H_b	H_c	H_d	H_e	H_f	X
4a	p-CN	7.63 7.59 7.50 7.47	3.90 (t, 4H) J = 5.3	2.59 (t, 4H) J = 4.9	2.42 (t, 2H) J = 7.5	1.52 (p, 2H) J = 7.8	1.37 (p, 2H) J = 7.3	0.94 (t, 3H) J = 7.0	n/a
4b	p-CO_2Me	8.03 8.00 7.49 7.45	3.88 (t, 4H) J = 5.5	2.60 (t, 4H) J = 5.1	2.42 (t, 2H) J = 7.6	1.52 (p, 2H) J = 7.6	1.35 (p, 2H) J = 7.3	0.94 (t, 3H) J = 7.3	3.90 (s, 3H)
4c	p-Br	7.47 7.43 7.33 7.29	3.81 (t, 4H) J = 5.0	2.59 (t, 4H) J = 5.0	2.41 (t, 2H) J = 7.5	1.52 (p, 2H) J = 7.5	1.36 (p, 2H) J = 7.5	0.94 (t, 3H) J = 7.5	n/a
4d	p-CH_3O	7.43 7.39 6.90 6.87	3.75 (t, 4H) J = 5.0	2.59 (t, 4H) J = 5.0	2.41 (t, 2H) J = 7.5	1.52 (p, 2H) J = 7.5	1.36 (p, 2H) J =7.5	0.94 (t, 3H) J = 7.5	3.81 (s, 3H)

Table 7. Physical data of 1-isopropyl-4-[2-aryl-1-diazenyl]piperazines.

Compound #	X	Yield %	m.p. (°C)	State of Crystal	IR
5a	p-CN	84	57-59	Amorphous light brown	2221.2 (CN) 846.9 (OOP)
5b	p-CO_2Me	85	61-62	Amorphous red/ brown	1716.6 (C=O) 821.2 (OOP)

Table 8. ^{1}H NMR chemical shift data (ppm) in $CDCl_3$ 1-isopropyl-4-[2-aryl-1-diazenyl]piperazine.



Compound #	X	Aromatic	H_a	H_a	H_c	H_d	X
5a	p-CN	7.62 7.59 7.50 7.46	3.89 (t, 4H) J = 5.0	2.68 (t, 4H) J = 5.0	2.82 (septet , 1H) J = 6.3	1.08 (d, 6H) J=6.5	n/a
5b	p-CO_2Me	8.01, 7.99 7.46, 7.45	3.86 (t, 4H) J = 5.2	2.67 (t, 4H) J = 5.0	2.81 (septet, 1H) J = 6.6	1.075 (d, 6H) J = 6.8	3.89 (s, 3H)

Table 9. High Resolution Mass Spectrometric Analysis of the 1-alkyl-4-[2-aryl-1-diazenyl]piperazines.

Compound #	Formula	Calculated Mass	Found
2a	$C_{13}H_{18}N_5$	244.1562	244.1557
2b	$C_{14}H_{20}N_4O_2$	276.1586	276.1601
2c	$C_{12}H_{17}N_5O_2$	263.1382	263.1400
2d	$C_{13}H_{20}N_4Na$	255.1580	256.1603
2e	$C_{12}H_{18}N_4Br$	297.0709	297.0703
2f	$C_{13}H_{20}N_4NaO$	271.1529	271.1527
2g	$C_{14}H_{21}N_4O$	261.1710	261.1708
2h	$C_{12}H_{18}N_4Br$	297.0709	297.0714
2i	$C_{11}H_{18}N_5$	220.1557	220.1565
3a	$C_{13}H_{17}N_5O$	259.1433	259.1431
3b	$C_{14}H_{20}N_4NaO_3$	315.1428	315.1438
3c	$C_{12}H_{18}N_5O_3$	280.1404	280.1404
3d	$C_{13}H_{20}N_4NaO$	271.1529	271.1517
3e	$C_{12}H_{17}N_4BrO$	312.0586	312.0597
3f	$C_{13}H_{20}N_4NaO_2$	287.1478	287.1462
3g	$C_{14}H_{20}N_4NaO_2$	299.1478	299.1470
3h	$C_{12}H_{18}N_4BrO$	313.0659	313.0661
3i	$C_{11}H_{18}N_5O$	236.1506	236.1504
4a	$C_{15}H_{21}N_5Na$	294.1689	294.1679
4b	$C_{16}H_{24}N_4NaO_2$	327.1791	327.1784
4c	$C_{14}H_{22}N_4Br$	325.1022	325.1015
4d	$C_{15}H_{25}N_4O$	277.2023	277.2033
5a	$C_{14}H_{20}N_5$	258.1713	258.1721
5b	$C_{15}H_{23}N_4O_2$	291.1816	291.1824

EXPERIMENTAL

The general techniques of measuring physical properties can be found in a number of our previous papers [1, 3, 4, 6, 7].

1-Alkyl-4-[2-aryl-1-diazenyl]piperazine

General Procedure

The aromatic primary amine (0.01mol) was dissolved in 10 mL of 3 mol/L HCl and 5 mL of water, with the aid of heat if necessary. The resulting solution was cooled in an ice/salt bath to 0°C. The solution was diazotized with a solution of sodium nitrite (0.011mol, 0.76g) in water 10mL, while maintaining that the temperature did not exceed 5°C, and then stirred for 30 min in the cold, after which, the 1-alkylpiperazine (0.10 mol) in 2 mL water was added drop wise while still keeping the temperature below 5°C. The solution was neutralized with a saturated aqueous solution of sodium bicarbonate, and then left to stir in the cold for a further 30 min until precipitation was deemed complete. The solid product was separated by suction filtration, dried, and recrystallized from an appropriate solvent. In some cases the product was an oil, in which case separation was achieved with an extraction performed with dichloromethane.

CONCLUSION

The results reported here provide a comprehensive account of the synthesis and characterization of the 1-ethyl (**2**), 1-(2-hydroxyethyl) (**3**), 1-butyl (**4**) and 1-isopropyl-4-[2-aryl-1-diazenyl]piperazines (**5**). This will prove to be a valuable resource of data for structure elucidation of related compounds.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

ACKNOWLEDGEMENTS

The authors are grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC) for a Discovery Grant to the principal author (KV). We are also grateful to the Faculty of Graduate Studies and Research at Saint Mary's University for a Summer Research Award (2010). We are also grateful to the Atlantic Region Magnetic Resonance Centre at Dalhousie University for providing NMR spectra, and to Dalhousie University for providing mass spectral data. In particular, we would like to thank Dr. Mike Lumsden for assistance with the NMR spectral data, and Mr. Xiao Feng for assistance with mass spectra.

REFERENCES

[1] Little, V.R.; Vaughan, K. Synthesis and characterization of a series of 1-methyl-4-[2-aryl-1-diazenyl]piperazines and a series of ethyl 4-[2-aryl-1-diazenyl]-1-piperazinecarboxylates. *Can. J. Chem.*, **2004**, *82*, 1294-1303.

[2] Little, V.R.; Jenkins, H.; Vaughan, K. An x-ray crystallographic study of the related triazenes, 1,4-di[(*E*)-2-(2-nitrophenyl)-1-diazenyl]piperazine and methyl 4-{(E)-2-(4-methylpiperazino)-1-diazenyl}benzoate. *J. Chem. Cryst*., **2008**, *38*, 447-452.

[3] Moser, S.L.; Vaughan, K. Synthesis and characterization of a series of 4-methyl-1-2-aryl-1-diazenyl]-1,4-diazepanes and 1,4-di-[2-aryl-1-diazenyl]-1,4-diazepanes. *Can. J. Chem*., **2004**, *82*, 1725-1735.

[4] Little, V.R.; Tingley, R.; Vaughan, K. Triazene derivatives of [1,x]-diazacycloalkanes. Part III. Synthesis and characterization of a series of 1,4-di[2-aryl-1-diazenyl]piperazines. *Can. J. Chem*., **2005**, *83*, 471-476.

[5] Yanarates, E.; Disli, A.; Yildirir. Y. New N,N'-bis-[substituted phenylazo]piperazines and their cleavage reactions in acetic acid. *Org. Prep. Proc. Int*., **1999**, *31*, 429-433.

[6] Hunter, N.; Tingley, R.; Peori, M.B.; Vaughan, K. Triazene derivatives of [1,x]-diazacycloalkanes. Part VIII. Synthesis and characterization of a series of 1,4-di[2-aryl-1-diazenyl]-2-methylpiperazines. *Can. J. Chem.*, **2007** *85*, 189-196.

[7] Hunter, N.; Vaughan, K. Triazene derivatives of [1,x]-diazacycloalkanes. Part IX. Synthesis and characterization of a series of 1,4-di[2-aryl-1-diazenyl]-2,6-dimethylpiperazines. *Can. J. Chem*., **2010,** *88*, 344-351.

Received: August 12, 2014 Revised: December 08, 2014 Accepted: December 11, 2014