Synthesis and Characterization of 7,16-Bis(phenylazo)tetraaza[14]annulenes

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The diazo coupling reaction between a tetraaza[14]annulene (**1**) and a series of 4-substituted phenyldiazonium tetrafluoroborates yielded the corresponding 7,16-disubstituted products. Mass spectra indicate the presence of molecular ion peaks that substantiate the 7,16-disubstituted products (**4**); the lack of olefinic proton signals corresponding to the 7,16- position in the ^{1}H nmr spectra of **4** also show that diazo coupling has taken place. Analysis of signals corresponding to the methyl groups of **4** in their ^{1}H and ^{13}C nmr spectra indicate that the imine-bis-hydrazone form is present for compounds that do not contain *p*-methoxyphenyl groups. However, analysis of methyl signals in the nmr specta of compounds **4** containing *p*-methoxyphenyl groups show that the bis-azo form and the imine-bis-hydrazone form are present through tautomerism. Complexation with nickel(II) ion induces the formation of the bis- azo structure.

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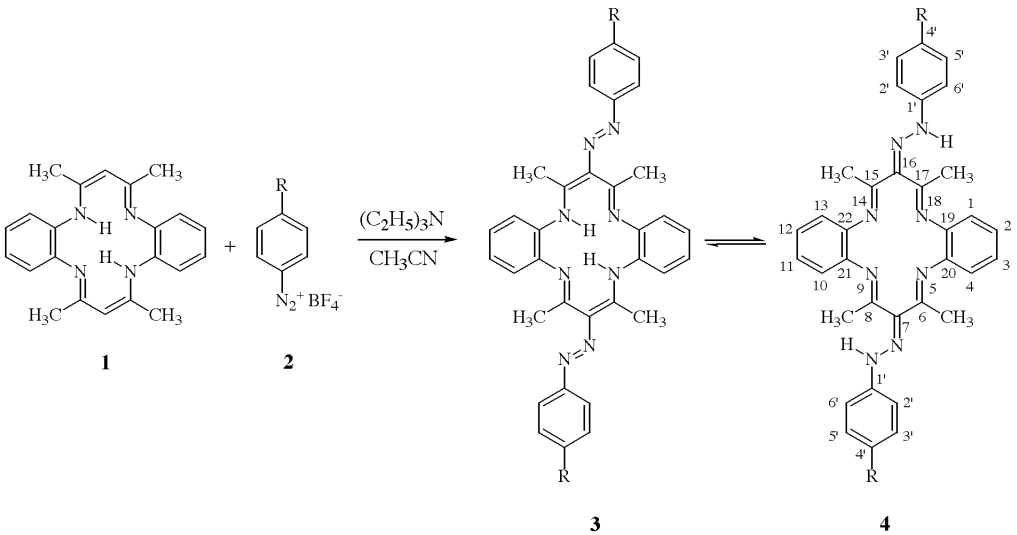
Introduction.

In previous papers we have reported the replacement reaction of tetraaza[14]annulene nickel(II) complex (**Ni-1**) with acid chlorides [1], the substitution reaction of complex **Ni-1** with 4-substituted benzyl bromides [2] and the diazo coupling reaction of complex **Ni-1** with 4-substituted phenyldiazonium salts [3]. However, examples of the diazo coupling reaction between a tetraaza[14]annulene (**1**) and phenyldiazonium salts are rare because of a tendency to decompose in the presence of acids. Dabrowiak *et al.*, presented the diazo coupling reaction of compound **1** with 4-chlorophenyldiazonium hexafluorophosphate alone [4]. We have also studied the reactivity of the 7,16-positions of compound **1**, which is free from a metal ion, with various electrophilic reagents [5].

Scheme 1



1 **2** **3** **4**

2-H	3-H	4-H	R = H
2-NO_2	3-NO_2	4-NO_2	R = NO_2
2-Cl	3-Cl	4-Cl	R = Cl
2-CH_3	3-CH_3	4-CH_3	R = CH_3
2-OCH_3	3-OCH_3	4-OCH_3	R = OCH_3

In the present work, we report the results of the reactivity of the 7,16-positions of compound **1**, namely 5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*]-[1,4,8,11]tertraazacyclotetradecine, with a series of 4-substituted phenyldiazonium salts. We have also characterized the spectral properties of the present products by mass, vibrational, electronic and nmr spectroscopy. The characteristic behavior has been discussed in reference to complex **Ni-1**.

Results and Discussion.

Diazo Coupling Reaction of Tetraaza[14]annulene (**1**) with Five Phenyldiazonium Salts.

Synthesis of compounds **4-H**, **4-NO_2**, **4-Cl**, **4-CH_3** and **4-OCH_3** is shown in Scheme 1. The diazo coupling reaction of compound **1** with five phenyldiazonium salts, in a 1:3-5 molar ratio and in the presence of triethylamine, was achieved in acetonitrile at room temperature to give the corresponding 7,16-disubstituted products in 22-48 % yields. A 1:2 molar ratio of the reagents generated a mixture of the 7-substituted and 7,16-disubstituted compounds. Separation of the mixture was hardly carried out by column chromatography. The reaction between compound **1** and the phenyldiazonium salts having electron withdrawing group substituted at the 4 position of phenyl groups gave a better yield than those with electron donating group at the same positions, indicating that the reaction is sensitive to electronic effects resulting from the 4-substituent.

These reactions show that the olefinic carbons at the 7-and 16-positions in compound **1** are susceptible to electrophilic substitution. This is in contrast to the olefinic carbon at the 3-position of 2,4-pentanedione diimine, which is free from a metal, and does not undergo an electrophilic substitution reaction [6]. The analytical data for compounds **4-H**, **4-NO_2**, **4-Cl**, **4-CH_3** and **4-OCH_3** are collected in Table 1.

Table 1

Analytical Data for Tetraaza[14]annulenes

Compound	Empirical Formula	Elemental Analyses Calcd./Found % C	H	N
4-H	$C_{34}H_{32}N_8$	73.89	5.84	20.27
		73.39	6.11	19.85
4-NO_2	$C_{34}H_{30}N_{10}O_4$	63.54	4.71	21.79
		63.42	4.77	21.55
4-Cl	$C_{34}H_{30}N_8Cl_2$	65.70	4.86	18.03
		65.59	5.18	17.79
4-CH_3	$C_{36}H_{36}N_8$	74.46	6.25	19.29
		74.21	6.34	19.09
4-OCH_3	$C_{36}H_{36}N_8O_2$	70.57	5.92	18.29
		70.86	5.98	18.10

Mass Spectra.

The EI mass spectra of compounds **4-H**, **4-NO_2**, **4-Cl**, **4-CH_3** and **4-OCH_3** reveal the presence of a molecular ions $M^{+\bullet}$ with m/z 552, 642, 620 (^{35}Cl), 580 and 612, respectively. An excellent agreement is found between the calculated and observed isotopic distributions. In their EI spectra the molecular ion peaks are not the base peaks due to extensive fragmentation. However, in their FAB mass spectra $[M+1]^+$ ions at 553, 643, 621 (^{35}Cl), 581 and 613, respectively, are observed as base peaks due to soft ionization.

Infrared Spectra.

A strong band due to the C=N stretching mode is observed at 1610 cm^{-1} in ir spectrum of compound **1**. The band shifts significantly to higher frequency upon diazo coupling and is observed at 1620 cm^{-1} [7]. Compound **1** shows an extremely weak band at 3060 cm^{-1} corresponding to the N-H stretching mode of the intramolecular hydrogen bond. The weak intensity of this band for compound **1** may be due to the structural nature of the macrocycle, which is nearly planer. However, a medium absorption band at about 3320 cm^{-1} corresponding to the N-H stretching mode is observed for all 7,16-disubstituted products [8]. This characteristic band greatly increases in intensity upon formation of the 7,16-disubstituted products, and may result from the imine and hydrazone functional groups. Moreover, compound **4-NO_2** indicates strong bands at 1540 and 1330 cm^{-1} corresponding to the NO_2 stretching modes [9]. Characteristic ir bands are listed in Table 2.

Table 2

Characteristic IR Absorption Bands for Tetraaza[14]annulenes [a]

Compound	IR Band (cm^{-1}) ν N-H	ν C=N
1	3060	1610
4-H	3327	1625
4-NO_2	3301	1620
4-Cl	3307	1625
4-CH_3	3318	1622
4-OCH_3	3330, 3062	1625

[a] Measured by the potassium bromide disk method at room temperature.

Electronic Spectra.

For Compound **1**, a very intense absorption band at 29000 cm^{-1} is observed, in the visible range, which can be reasonably attributed to a $\pi \rightarrow \pi^*$ transition in the macrocycle [5]. On the other hand, compounds **4-H**, **4-NO_2**, **4-Cl**, **4-CH_3** and **4-OCH_3** exhibit two bands in the 25000-34000 cm^{-1} region, and can be assigned to $\pi \rightarrow \pi^*$ transitions because of the large molar extinction coefficients. In

other words, for the diazo coupling products the absorption is split into two bands, where one shifts to lower energy and the other to higher energy. The $\pi \rightarrow \pi^*$ transitions for the compounds are compiled in Table 3.

Table 3

Electronic Absorption Bands for Tetraaza[14]annulenes [a]

Compound	Transition energy in cm^{-1} (ε)
1	29000(47800)
4-H	27200(39000), 34000(11400)
4-NO_2	25300(61300), 33700(8870)
4-Cl	27300(46600), 33300(8850)
4-CH_3	26900(42000), 33300(22900)
4-OCH_3	26700(41900), 32300(24000)

[a] Measured in chloroform at room temperature.

NMR Spectra.

The olefinic proton signals (4.86 ppm in compound **1**) at the 7- and 16-positions are not observed upon diazophenylation (compounds **4**). The amine proton signals show upfield shifts relative to compound **1** by 1.29-1.72 ppm on diazophenylation with the exception of the **4-OCH_3** compounds. The magnitude of upfield shifts for compounds **4-H** and **4-CH_3** is larger than that observed for compounds **4-Cl** and **4-NO_2**. This results from the electronic effect of a 4-substituent in the phenyl group.

The proton nmr data for compound **4-Cl** in four solvents are listed in Table 5. The amine proton signal reveals the upfield shift by 0.70 ppm which is dependent on solvent effect. Nevertheless, the amine proton signal of compound **1** only exhibits a very small shift in each solvent because of intramolecular hydrogen bonds [10]. This shows that the 7,16-disubstituted product is not the bis azo form **3** but is the imine-bis-hydrazone form **4**.

The proton signals of the methyl groups at the 6-, 8-,15- and 17-positions for compound **1** are equivalent and singlets. On the other hand, the methyl protons of compounds **4-H**, **4-NO_2**, **4-Cl** and **4-CH_3** are nonequivalent and two singlets of equal intensity are observed with downfield shifts of 0.07-0.40 ppm, relative compound **1**, due to diazophenylation. The downfield shifts indicate that the methyl groups are within the anisotropic deshielding zone of the benzene rings of the substituted phenyl groups. This observation is inconsistent with the bis azo form **3** but consistent with imine-bis-hydrazone form **4**.

The aromatic protons at the 2-, 3-, 11- and 12-positions in the macrocyclic skeleton, with the exception of compound **4-OCH_3**, couple with the adjacent two aromatic protons, and the signals are also split into two triplets of equal intensity. This results because the aromatic protons experience anisotropic effects from the benzene rings in the substituted phenyl groups to different extents. On the other hand, the aromatic protons at the 1-, 4-, 10- and 13-positions are observed as two doublets of equal

Table 4

^{1}H NMR Data and Their Assignments for Tetraaza[14]annulenes [a]

Compound	Methyl (6,8,15,17-CH_3)	Macrocycle (Aromatic)	Substituent (Aromatic)	Amine (N-H)	Substituent R: -CH_3; -OCH_3	Olefinic	Structure
1	2.12(s)	6.90(s)		12.59(s)		4.86(s)	
4-H	2.20(s)	6.82(d, J=7.4 Hz)	7.18(d, J=7.9 Hz)	10.88(s)			
	2.27(s)	7.13(t, J=7.4 Hz)	7.29(t, J=7.9 Hz)				
		7.17(t, J=7.4 Hz)	6.94(t, J=7.9 Hz)				
		6.91(d, J=7.4 Hz)					
4-NO_2	2.21(s)	6.84(d, J=7.6 Hz)	7.12(d, J=9.0 Hz)	11.30(s)			
	2.29(s)	7.20(t, J=7.6 Hz)	8.20(d, J=9.0 Hz)				
		7.24(t, J=7.6 Hz)					
		6.93(d, J=7.6 Hz)					
4-Cl	2.19(s)	6.81(d, J=7.6 Hz)	7.10(d, J=8.9 Hz)	10.95(s)			
	2.25(s)	7.13(t, J=7.6 Hz)	7.24(d, J=8.9 Hz)				
		7.18(t, J=7.6 Hz)					
		6.90(d, J=7.6 Hz)					
4-CH_3	2.19(s)	6.81(d, J=7.3 Hz)	7.08(s)	10.87(s)	2.70(s)		
	2.52(s)	7.11(t, J=7.3 Hz)					
		7.16(t, J=7.3 Hz)					
		6.90(d, J=7.3 Hz)					
4-OCH_3	2.19(s)	6.81(d, J=7.5 Hz)	6.86(d, J=8.6 Hz)	10.95(s)	3.78(s)		**4**
	2.25(s)	7.11(t, J=7.5 Hz)	7.12(d, J=8.6 Hz)				
		7.14(t, J=7.5 Hz)					
		6.90(d, J=7.5 Hz)					
	2.52(s)	7.17(s)	6.94(d, J=7.9 Hz)	14.29(s)	3.84(s)		**3**
			7.63(d, J=7.9 Hz)				

[a] Chemical shifts in ppm from internal TMS. Measured in chloroform-d at room temperature. Multiplicity of a proton signal is given in parentheses after δ-value; s=singlet, d=doublet, t=triplet.

Table 5

Solvent Effect for ^{1}H NMR Data of Tetraaza[14]annulene **4-Cl** [a]

Solvent	Methyl (6,8,15,17-CH_3)	Macrocycle (Aromatic)	Substituent (Aromatic)	Amine (N-H)
$CDCl_3$	2.19(s) 2.25(s)	6.81(d, J=7.6 Hz) 7.13(t, J=7.6 Hz) 7.18(t, J=7.6 Hz) 6.90(d, J=7.6 Hz)	7.10(d, J=8.9 Hz) 7.24(d, J=8.9 Hz)	10.95(s)
$(CD_3)_2CO$	2.15(s) 2.27(s)	6.89(d, J=7.3 Hz) 7.13(t, J=7.4 Hz) 7.17(t, J=7.3 Hz) 7.15(d, J=7.3 Hz)	7.31(m)	10.66(s)

[a] Chemical shifts in ppm from internal TMS. Measured at room temperature. Multiplicity of a proton signal is given in parentheses after δ-value; s=singlet, d=doublet, t=triplet, m=multiplet.

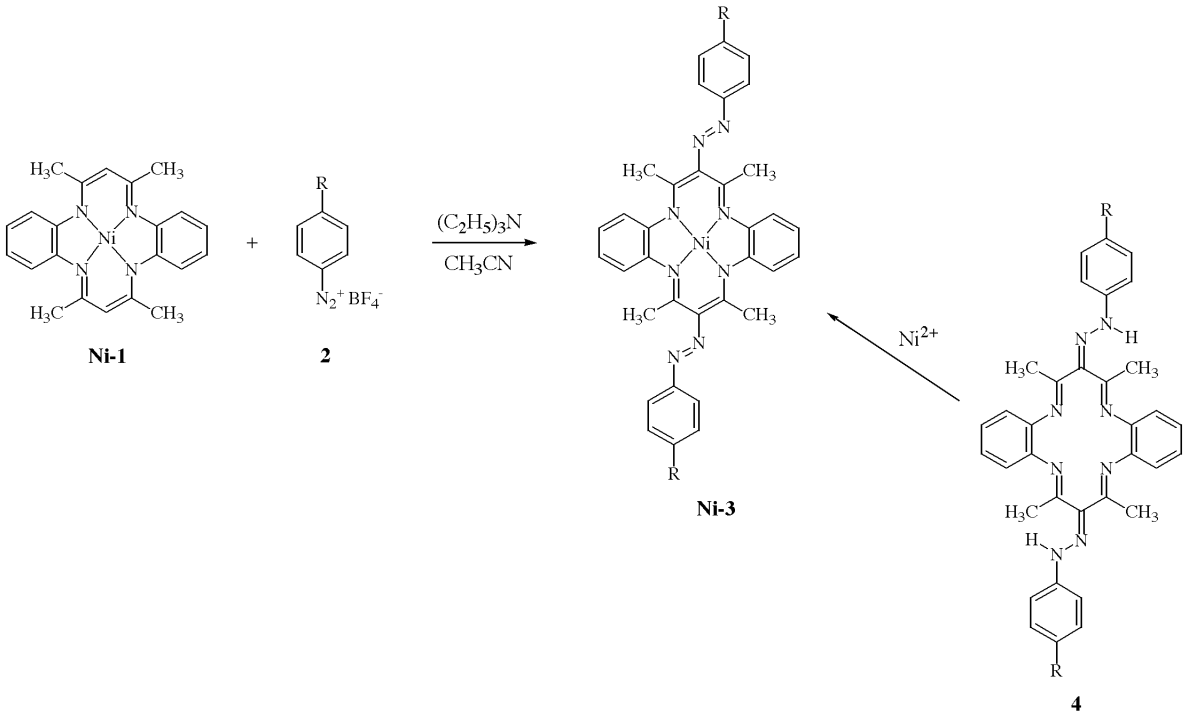
intensity, again due to anisotropic effects from the benzene rings in the substituted phenyl groups. These observations support the imine-bis-hydrazone form **4**.

In the 4-substituted phenyl groups, with the exception of compound **4-H** and **4-CH_3**, a nearly first-order A_2X_2 system is observed for the phenyl protons. In the 4-substituted phenyl groups of compound **4-CH_3**, the aromatic proton signals are observed as a singlet because their chemical shifts are the same by coincidence.

In compound **4-OCH_3**, the methyl proton signal of the macrocyclic skeleton is observed as three singlets. The proton signal of the 4-substituted methoxy group in the phenyl group is observed as two singlets, and the amine proton signal is observed as two singlets. The aromatic protons in the macrocyclic skeleton show a mixed spectra, that is, two triplets and two doublets due to the structural formula **4** (bis-hydrazone) and a singlet due to the structural formula **3** (bis-azo), judging from CH-cosy, NOESY and temperature variability experiments. These results indicate that hydrazone-azo tautomers occurs in compound **4-OCH_3**.

The diazo coupling reaction of complex **Ni-1** with phenyldiazonium salts gave the corresponding 7,16-bis-(phenylazo) products [3]. The complexation reaction of compounds **4-H**, **4-NO_2**, **4-Cl**, **4-CH_3** and **4-OCH_3** with nickel(II) acetate yield identical products with those obtained by the diazo coupling reaction of complex **Ni-1**. For the nickel(II) complexes only one methyl proton signal

Scheme 2



and two kinds of the aromatic proton signals are observed for the macrocyclic skeleton, respectively [3]. The data show that the complexation with a nickel ion results in the formation of azo- hydrazone tautomer exclusively.

The tautomeric equilibrium of the compounds is studied by ^{1}H-nmr spectra. As judged by the spectra the equilibriums, with the exception of compound **4-OCH$_3$** lie almost to the bis-hydrazone forms, whereas the nickel(II) complexes are all azo forms. For the **4-OCH$_3$** compound, the tautomers exist in a nearly 1:1 ratio. Though there is a possibility of both a anti- and syn-form, the products probably exist in the anti-forms due to steric hindrance between the methyl group and the phenyl group according to the Corey-Pauling Koltum model. Proton nmr data and their assignments for 7,16-disubstituted tetraaza[14]annulenes are summarized in Table 4.

Carbon-13-nmr data and their assignments for 7,16-disubstituted tetraaza[14]annulenes are compiled in Table 6. Compounds **4-H**, **4-Cl** and **4-CH$_3$** are too insoluble to give satisfactory ^{13}C-nmr spectra. The carbon signals of the methyl groups at the 6-, 8-, 15- and 17-positions for compound **1** are equivalent and singlets. On the other hand, the methyl carbon signals of compounds **4-NO$_2$**, **4-Cl** and **4-CH$_3$** except for compounds **4-H** and **4-OCH$_3$** are nonequivalent and observed as two singlets. One signal of the methyl carbons shows a upfield shift by 6.1-6.3 ppm, but the other signal indicates a downfield shift by 2.5 ppm. This shows that the methyl groups are divided into two kinds and that the compounds are bis-hydrazone forms. The olefinic carbon signals at the 7,16-positions show large downfield shifts of 15.3-17.1 ppm. The off-resonance decoupling carbon signal of compounds **4-NO$_2$**, **4-Cl** and **4-CH$_3$** is a singlet because there is no proton at these positions on diazophenylation. The olefinic and aromatic carbon signals at the 6-, 8-, 15-, 17-, 19-, 20-, 21-, 22-, 2-, 3-, 11- and 12-positions exhibit slight downfield shifts. For the aromatic carbon signals at 1-, 4-, 10- and 13-positions slight upfield shifts are observed. Carbon signals for the phenylazo groups are observed in the 21-155 ppm range.

For compound **4-OCH$_3$** signals correspondint to three kinds for the methyl groups are observed. The aromatic carbons in the macrocyclic skeleton and the substituted phenyl groups exhibit the mixed spectra of bis-hydrazone (**3**) and bis-azo (**4**) as judged by CH-cosy and variable temperature experiments. This result is in agreement with that of the corresponding proton nmr spectrum.

Consequently, electronic effect are related to the position of equilibrium between tautomers. Furthermore, strong electron donating groups at the 4-position of the phenyl group cause a shift to the azo form.

Table 6

Carbon-13 Data and Their Assignments for Tetraaza[14]annulenes [a]

Compound	6,8,15,17 CH_3	C(6) C(8) C(15) C(17)	C(19) C(20) C(21) C(22)	C(2) C(3) C(11) C(12)	C(1) C(4) C(10) C(13)	C(7) C(16)	C(1')	C(2')	C(3')	C(4')	4-CH_3 4-OCH_3	Structure
1	20.8	158.4	138.1	122.7	122.5	97.7						
4-H				118.6	121.1			116.1	129.5	124.7		
				125.8	126.1							
4-NO$_2$	14.7	164.7	142.0	124.5	119.7	137.3	148.5	113.0	126.0	144.3		
	23.3	169.2	141.7	125.4	129.1							
4-Cl	14.5	164.6	142.1	124.1	119.7	137.8		114.8	129.2	126.3		
	23.3	169.2	142.5	124.8	120.1							
4-CH$_3$	14.5	164.6	141.1	123.8	119.7	138.0		113.7	129.7	130.9	20.7	
	23.3	169.1	142.7	124.5	120.1							
4-OCH$_3$	14.5	164.6	138.0	124.5	119.8	137.4	140.1	114.8	114.6	154.8	55.6	**4**
	23.3	169.2	142.7	123.8	120.1							
	19.8	163.0	129.2	125.0	125.0	117.9	148.2	122.4	114.0	159.3	55.5	**3**

[a] Chemical shifts in ppm from internal TMS. Measured in chloroform-d at room temperature.

EXPERIMENTAL

Elemental analyses were determined with a Yanaco CHN corder MT-3. EI mass spectra were carried out with a JEOL JMS-SX 102A gas chromatograph-mass spectrometer at 40 eV using a direct inlet system. FAB mass spectra were taken on a JEOL JMS-DX 300 gas chromatograph-mass spectrometer in a magic bullet matrix using xenon in the fast atom beams. Infrared spectra in the 400-4000 cm^{-1} region were recorded on a Heschel FT/IR-410 spectrophotometer at room temperature as potassium bromide disks. Electronic spectra covering the 12500-40000 cm^{-1}

range were obtained with a Shimadzu UV 200S double beam spectrophotometer for chloroform solutions at room temperature. Proton and carbon-13 nmr spectra were measured with a JEOL JNM-A500 spectrometer in chloroform-d, acetone-d_6, acetonitrile-d_3 and dimethyl sulfoxide-d_6 at room temperature. Chemical shifts are given in ppm relative to tetramethylsilane as an internal reference standard. All melting points were performed with a Yanaco MP-500D micro melting point apparatus (hot-plate type).

Synthesis of the Phenyldiazonium Salts.

Phenyldiazonium tetrafluoroborate (**2-H**), 4-nitrophenyldiazonium tetrafluoroborate (**2-NO_2**), 4-chlorophenyldiazonium tetrafluoroborate (**2-Cl**), 4-methylphenyldiazonium tetrafluoroborate (**2-CH_3**) and 4-methoxyphenyldiazonium tetrafluoroborate (**2-OCH_3**) are new. The preparative procedures for compounds **2-H**, **2-NO_2**, **2-Cl**, **2-CH_3** and **2-OCH_3** have been reported [3].

Synthesis of the 7,16-Bis(phenylazo)tetraaza[14]annulenes.

5,14-Dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]-tetraazacyclotetradecine (**1**).

The synthetic procedure for compound **1** has been described previously [11].

7,16-Bis(phenylazo)-6,8,15,17-tetramethyldibenzo[*b*,*i*]-[1,4,8,11]tetraazacyclotetradecine (**4-H**).

To an acetonitrile solution (10 ml) of compound **1** (100 mg) was added dropwise an acetonitrile solution (5 ml) containing diazonium salt **2-H** (214 mg). After addition of triethylamine (1 ml), the reaction solution was stirred at room temperature for 18 hours. The crystalline solid was recovered by filtration, thoroughly washed with water and recrystallized from ethyl acetate to obtain 40 mg of fine yellow crystals (25 %), mp 237.8-240.1° dec; ir: ν C-H 3052, 2965, 2921, δ C-H 768, 750, 687 cm^{-1}; ms: m/z (relative intensity) 553 (27.1), 552 (68.1), 460 (100), 443 (37.6), 354 (29.1), 328 (68.1), 301 (61.4), 299 (74.2), 275 (60.6), 133 (41.9).

7,16-Bis(4-nitrophenylazo)-6,8,15,17-tetramethyldibenzo[*b*,*i*]-[1,4,8,11]tetraazacyclotetradecine (**4-NO_2**).

This was prepared from diazonium salt **2-NO_2** (205 mg), compound **1** (111 mg) and triethylamine (1 ml) in acetonitrile (15 ml), following the above procedure, and thoroughly washed with water and recrystallized from ethyl acetate to give 100 mg of fine yellow crystals (48 %), mp 285.4-285.7° dec; ir: ν C-H 3070, 2970, 2925, δ C-H 845, 745 cm^{-1}; ms: m/z (relative intensity) 643 (2.1), 642 (4.6), 620 (20.9), 521 (38.3), 504 (45.8), 494 (42.1), 474 (41.6), 384 (33.0), 369 (37.5), 335 (34.3), 309 (30.2), 134 (91.1), 108 (100).

7,16-Bis(4-chlorophenylazo)-6,8,15,17-tetramethyldibenzo[*b*,*i*]-[1,4,8,11]tetraazacyclotetradecine (**4-Cl**).

This compound was prepared from diazonium salt **2-Cl** (251 mg) and compound **1** (100 mg) in acetonitrile (15 ml) containing triethylamine (1 ml), following the above procedure, to yield 64 mg of fine yellow crystals (35 %), mp 239.0-242.6° dec; ir: ν C-H 3064, 3013, 2924, δ C-H 815, 755 cm^{-1}; ms: m/z (relative intensity) 622 (13.6), 620 (15.9), 512 (16.3), 494 (38.5), 477 (14.3), 362 (25.9), 335 (30.3), 309 (26.0), 127 (70.3), 108 (100); ^{1}H nmr (acetonitrile-d_3): 10.31 (s, 2H, -NH); (dimethyl sulfoxide-d_6): 10.25 (s, 2H, -NH).

7,16-Bis(4-methylphenylazo)-6,8,15,17-tetramethyldibenzo[*b*,*i*]-[1,4,8,11]tetraazacyclotetradecine (**4-CH_3**).

Diazonium salt **2-CH_3** (288 mg) and compound **1** (101 mg) were treated in acetonitrile (15 ml) containing triethylamine (1 ml) following the above procedure. The product was obtained as fine yellow crystals. The yield was 45 mg (26 %), mp 236.8-237.8° dec; ir: ν C-H 3060, 3019, 2970, 2720, δ C-H 809, 755 cm^{-1}; ms: m/z (relative intensity) 581 (6.4), 580 (14.9), 472 (46.2), 368 (19.4), 353 (42.9), 340 (20.3), 313 (24.6), 289 (20.7), 236 (24.4), 108 (100).

7,16-Bis(4-methoxyphenylazo)-6,8,15,17-tetramethyldibenzo-[*b*,*i*][1,4,8,11]tetraazacyclotetradecine (**4-OCH_3**).

Diazonium salt **2-OCH_3** (212 mg) and compound **1** (102 mg) were reacted in acetonitrile (15 ml) containing triethylamine (1 ml) as described above to afford 40 mg of fine yellow crystals (22 %), mp 219.7-221.5° dec; ir: ν C-H 3063, 2987, 2963, 2929, δ C-H 835, 740 cm^{-1}; ms: m/z (relative intensity) 613 (10.1), 612 (23.9), 504 (64.5), 474 (66.4), 422 (42.9), 367 (100), 356 (89.7), 305 (77.5), 250 (50.5), 214 (61.7), 108 (71.8).

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REFERENCES AND NOTES

[1a] K. Sakata and T. Hori, *Synth. React. Inorg. Met.-Org. Chem.*, **20**, 263 (1990); [b] K. Sakata and A. Ueno, *Synth. React. Inorg. Met.-Org. Chem.*, **21**, 729 (1991); [c] K. Sakata and M. Itoh, *J. Heterocyclic Chem.*, **29**, 921 (1992); [d] K. Sakata, Y. Saitoh, K. Kawakami, N. Nakamura and M. Hashimoto, *Synth. React. Inorg. Met.-Org. Chem.*, **25**, 1279 (1995); [e] K. Sakata, K. Koyanagi and M. Hashimoto, *J. Heterocyclic Chem.*, **32**, 329 (1995); [f] K. Sakata, M. Shimoda and M. Hashimoto, *J. Heterocyclic Chem.*, **33**, 1593 (1996).

[2] K. Sakata, M. Hashimoto, T. Hamada and S. Matsuno, *Polyhedron*, **15**, 967 (1996).

[3] K. Sakata, J. Yamashita, M. Hashimoto, T. Moriguchi and A. Tsuge, *Inorg. Chim. Acta*, **281**, 190 (1998).

[4] D. P. Fisher, F. C. McElroy, D. J. Macero and J. C. Dabrowiak, *Inorg. Nucl. Chem. Lett.*, **12**, 435 (1976).

[5] K. Sakata, H. Tagami and M. Hashimoto, *J. Heterocyclic Chem.*, **26**, 805 (1989).

[6a] J. Feldman, S. J. McLain, A. Parthasarathy, W. J. Marshall, J. C. Calabrese and S. D. Arthur, *Organometallics*, **16**, 1514 (1997); [b] P. L. Holland and W. B. Tolman, *J. Am. Chem. Soc.*, **121**, 7270 (1999).

[7] R. H. Wiley and G. Irick, *J. Org. Chem.*, **24**, 1925 (1959).

[8] D. Hadzi and J. Jan, *Spectrochim. Acta*, **23A**, 571 (1967).

[9] R. M. Silverstein, G. C. Bassler and T. C. Morrill, Spectrometic Identification of Organic Compounds, 5th Ed, Wily, New York, 1991.

[10] M. Hashimoto and K. Sakata, *Anal. Sci.*, **11**, 631 (1995).

[11] K. Sakata, F. Yamaura and M. Hashimoto, *Synth. React. Inorg. Met.-Org. Chem.*, **20**, 1043 (1990).