

Original Research Article

Synthesis of Nonsymmetric Dibenzoyldihydromonobenzotetraazacyclo[14]annulenes as Transition Metal Hosts: X-ray Structure of 13,14-Benzo-3,10-di(*p*-chlorobenzoyl)-5,8-dihydro-2,4,9,11-tetramethyl-1,5,8,12-tetraazacyclotetradeca-1,3,9,11-tetraene

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Abstract

13,14-Benzo-5,8-dihydro-2,4,9,11-tetramethyl-1,5,8,12-tetraazacyclotetradeca-1,3,9,11-tetraene and 13,14-benzo-3,10-di(*p*-[X]benzoyl)-5,8-dihydro-2,4,9,11-tetramethyl-1,5,8,12-tetraazacyclotetradeca-1,3,9,11-tetraene, wherein X = CH₃, H, Cl, NO₂ and OCH₃, were synthesized and characterized. IR spectra of the benzoylated compounds showed an intense band assigned to the stretching modes of C=O in the region 1632 ~ 1638 cm⁻¹. Hammett plot of the energies of $\pi \rightarrow \pi^*$ for the compounds was linear with a positive slope (+0.923). ¹H NMR signals exhibited a deshielding effect due to benzoyl groups, while methyl protons only exhibited the shielding effect by the magnetic anisotropy of the group. The substituent effect on ¹³C NMR was similar to that on proton NMR. The cyclic voltammograms of the compounds mostly showed two one-electron irreversible oxidation peaks and one or two reduction waves between -0.280 and -2.500 V depending on the substituents. Hammett plots of 1st and 2nd oxidation potentials ($E_{\text{op}(1)}$ and $E_{\text{op}(2)}$) were linear with slopes of +0.036 and +0.045, respectively. The structure of the compound **4** (monoclinic, C2/c, $a = 26.0059$ (19), $b = 6.9058$ (5), $c = 33.082$ (2), $\beta = 109.5930^\circ$, $Z = 8$) was determined using X-ray diffraction method.

Introduction

Although much attention has been paid to the spectroscopic and electrochemical properties of transition metal complexes with tetraaza[14]annulene ligands, there have been few studies of ligands as free bases, except for symmetrical dibenzotetraaza[14]annulenes [1–10]. The reactivities of such compounds were also studied and reported by Sakata *et al.* [11, 12] and Dabrowiak *et al.* [13]. However, until now the reactions of asymmetrical free base, monobenzotetraaza[14]annulene have scarcely been studied irrespective of their substituents.

In this paper, we attempted to synthesize a new asymmetrical free base ligands, dihydromonobenzotetraaza[14]annulenes with *p*-substituted benzoyl group through demetallation process, wherein the substituents were CH₃, H, Cl, NO₂ and OCH₃. The transition metal complexes with the free base ligands will be used in the oxidation and reduction of some substrates such as styrene derivatives or simple inorganic compounds. The compounds synthesized were characterized by means of

elemental analyses, infrared, electronic, ¹H NMR and ¹³C NMR spectra and cyclic voltammetry. The crystal structure of the compound, 13,14-benzo-3,10-di(*p*-chlorobenzoyl)-5,8-dihydro-2,4,9,11-tetramethyl-1,5,8,12-tetraazacyclotetradeca-1,3,9,11-tetraene, was identified by X-ray diffraction analysis.

Experimental

Materials and measurements

Ni(OAc)₂ · 4H₂O, 1,2-phenylenediamine, 1,2-diaminoethane, 2,4-pentandione, and *p*-substituted benzoyl chloride (substituents = CH₃, H, Cl, NO₂ and OCH₃) were purchased from Aldrich. Solvents such as methanol, ethanol and dichloromethane were refluxed over calcium hydride under nitrogen, and checked for purities by GC just before use. Dimethylsulfoxide (DMSO) was purchased from Merck and used without further purification. Tetraethylammonium perchlorate (TEAP) used as a supporting electrolyte was prepared and purified by the method described in the literature [14].

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Elemental analyses of the complex and the free-based ligands prepared were carried out on a Carlo-Ebra, EA 1108 instrument. Infrared spectra were recorded on a Matteson Instruments, Inc. Galaxy 7020 A using KBr Pellets. ^1H NMR (300 MHz) spectra were recorded on a Bruker instrument at room temperature and chemical shifts in CDCl_3 were given in ppm relative to tetramethylsilane as an internal reference. Electronic absorption spectra were obtained on a Shimadzu UV-265 spectrophotometer.

Cyclic voltammetry was performed using a Bioanalytical System (BAS) CV-50W electrochemical analyzer and a C2 cell stand at room temperature. A three-electrode system composed of a glassy carbon electrode as a working electrode, Ag/Ag^+ (0.01 M AgNO_3 in 0.1 M TEAP-DMSO solution) as a reference electrode, and a platinum wire as an auxiliary electrode for the electrochemical measurement was used.

Synthesis

13,14-Benzo-5,8-dihydro-2,4,9,11-tetramethyl-1,5,8,12-tetraazacyclotetradeca-1,3,9,11-tetraene (1)

This compound was prepared and purified by the previously published methods [15].

13,14-Benzo-3,10-di(p-methyl benzoyl)-5,8-dihydro-2,4,9,11-tetramethyl-1,5,8,12-tetraazacyclotetradeca-1,3,9,11-tetraene (2)

Compound **1** (0.296 g, 0.001 mol) was dissolved in benzene (50 cm^3) containing triethylamine (0.203 g, 0.002 mol) and the corresponding *p*-methylbenzoyl chloride (0.002 mol) in benzene (30 cm^3) was added using a dropping funnel. The mixture was heated under reflux for 4 h with stirring and bubbling nitrogen gas to protect against moisture. Then the reaction mixture stood for around 24 h at room temperature and filtered. The filtrate was evaporated to dryness under reduced pressure and the resulting solid was recrystallized from a 1:2 mixture of dichloromethane and methyl alcohol. Yield 0.149 g (28%). Anal. Calcd. (%) for $\text{C}_{34}\text{H}_{36}\text{N}_4\text{O}_2$ (**2**): C, 76.66; H, 6.68; N, 10.52; Found: C, 76.64; H, 6.60; N, 10.55. IR (KBr disc, cm^{-1}): $\nu(\text{C}=\text{C})$, 1572; $\nu(\text{C}=\text{N})$, 1605; $\nu(\text{C}=\text{O})$, 1632; $\nu(\text{aromatic})$, 735 and 850. UV-vis: λ_{max} (nm) and ε_{max} ($\text{M}^{-1}\text{ cm}^{-1}$) in chloroform 320 and 38,000. The color was brown. EIMS: m/z 532 $[\text{M}]^+$.

13,14-Benzo-3,10-di(p-[X]benzoyl)-5,8-dihydro-2,4,9,11-tetramethyl-1,5,8,12-tetraazacyclotetradeca-1,3,9,11-tetraene: X = H (3), Cl (4), NO₂ (5) and OCH₃ (6)

The compounds **3**, **4**, **5** and **6** were prepared from reactions of the compound **1** (0.001 mol) with triethylamine (0.002 mol) and the corresponding *p*-Xbenzoyl chloride (0.002 mol) in benzene according to the procedures described above. For $\text{C}_{32}\text{H}_{32}\text{N}_4\text{O}_2$ (**3**): Yield 0.151 g (30%). Anal. Calcd. (%): C, 76.16; H, 6.39; N, 11.10; Found: C, 76.01; H, 6.39; N, 11.13. IR (KBr disc, cm^{-1}): $\nu(\text{C}=\text{C})$, 1562; $\nu(\text{C}=\text{N})$, 1591; $\nu(\text{C}=\text{O})$, 1638; $\nu(\text{aromatic})$, 723 and

850. UV-vis: λ_{max} (nm) and ε_{max} ($\text{M}^{-1}\text{ cm}^{-1}$) in chloroform 319 and 32,000. The color was yellow. EIMS: m/z 504 $[\text{M}]^+$. For $\text{C}_{32}\text{H}_{30}\text{N}_4\text{O}_2\text{Cl}_2$ (**4**): Yield 0.201 g (35%). Anal. Calcd. (%): C, 67.02; H, 5.28; N, 9.77; Found: C, 67.20; H, 5.18; N, 9.75. IR (KBr disc, cm^{-1}): $\nu(\text{C}=\text{C})$, 1553; $\nu(\text{C}=\text{N})$, 1586; $\nu(\text{C}=\text{O})$, 1633; $\nu(\text{aromatic})$, 748 and 858. UV-vis: λ_{max} (nm) and ε_{max} ($\text{M}^{-1}\text{ cm}^{-1}$) in chloroform 318 and 31,000. The color was light red. EIMS: m/z 572 $[\text{M}]^+$. For $\text{C}_{32}\text{H}_{30}\text{N}_6\text{O}_6$ (**5**): Yield 0.107 g (18%). Anal. Calcd. (%): C, 64.64; H, 5.09; N, 14.13; Found: C, 64.32; H, 5.11; N, 14.01. IR (KBr disc, cm^{-1}): $\nu(\text{C}=\text{C})$, 1554; $\nu(\text{C}=\text{N})$, 1597; $\nu(\text{C}=\text{O})$, 1634; $\nu(\text{NO}_2)$, 1345; $\nu(\text{aromatic})$, 748 and 855. UV-vis: λ_{max} (nm) and ε_{max} ($\text{M}^{-1}\text{ cm}^{-1}$) in chloroform 302 and 47,500. The color was orange. EIMS: m/z 594 $[\text{M}]^+$. For $\text{C}_{34}\text{H}_{36}\text{N}_4\text{O}_4$ (**6**): Yield 0.152 g (27%). Anal. Calcd. (%): C, 72.31; H, 6.43; N, 9.92; Found: C, 72.28; H, 6.39; N, 9.90. IR (KBr disc, cm^{-1}): $\nu(\text{C}=\text{C})$, 1575; $\nu(\text{C}=\text{N})$, 1602; $\nu(\text{C}=\text{O})$, 1638; $\nu(\text{aromatic})$, 745 and 852. UV-vis: λ_{max} (nm) and ε_{max} ($\text{M}^{-1}\text{ cm}^{-1}$) in chloroform 321 and 39,500. The color was yellow. EIMS: m/z 564 $[\text{M}]^+$.

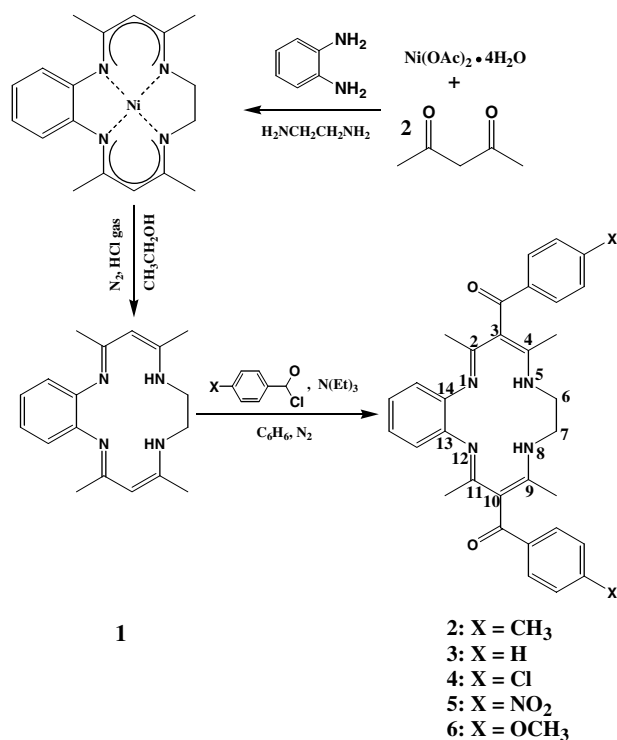
X-ray crystallographic analysis

Preliminary examination and data collection for crystal of the compound **4** were performed with Mo-K α radiation ($\lambda = 0.71073\text{ \AA}$) on an Enraf-Nonius CAD4 computer controlling a *k*-axis diffractometer equipped with a graphite crystal, incident-beam monochromator. Cell constants and orientation matrices for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections. The data were collected for Lorentz-polarization and absorption corrections were applied to the data. The structure was solved by direct methods using SHELXS-86 [16] and refined by full-matrix least-squares calculations with SHELXL-97 [17]. The final cycle of the refinement converged with $R = 0.0487$ and $wR = 0.1146$.

Results and discussions

Synthesis of nonsymmetric monobenzotetraazacyclo[14]annulenes

Compounds **1** ~ **6** were prepared according to the processes illustrated in Scheme 1. The reactions of **1** with *p*-substituted benzoyl chloride in a 1:2 molar ratio in the existence of triethylamine were carried out under refluxing benzene and then led to the corresponding 3,10-dibenzoylated products with a range of yields from 18 to 35%. Purification of the crude products was achieved by recrystallizing from mixtures of dichloromethane and methyl alcohol. Compound **1** underwent an electrophilic substitution reaction at the olefinic carbons of methine sites of its macrocyclic ring as the olefinic carbon of the 3-position in metal acetylacetonate [12, 18]. Elemental analyses given in the Experimental section were consistent with their formulations.



Scheme 1.

IR and electronic spectra

As described in the Experimental section, the stretching modes of the C=C and C=N bonds of compound **1** appeared at 1502 and 1562 cm^{-1} , respectively, while those of compounds **2** ~ **6** showed at around 1553 ~ 1575 and 1586 ~ 1605 cm^{-1} , respectively. The C=C and C=N stretching modes after benzylation moved to higher frequencies around 50 ~ 70 and 20 ~ 40 cm^{-1} , respectively, depending on the substituent of the benzoyl groups. The asymmetrical monobenzotetraazacyclo[14]annulenes with dibenzoyl groups typically exhibited a strong band attributed to the C=O stretching mode in the regions 1632 ~ 1638 cm^{-1} , reflecting successive benzylation.

The electronic absorption spectra of the compounds typically exhibited a very intense band at around 300 ~ 320 nm, which might be assigned to a $\pi \rightarrow \pi^*$ transitions within a macrocyclic ring. Compound **1** showed at 322 nm, while the band after benzylation was slightly shifted to a higher frequency with respect to the electron-withdrawing substituents. As illustrated in Figure 1, the Hammett plot of $1/\lambda_{\text{max}}$ against substituent constants ($2\sigma_p$; see reference [19]) was not good linearity. However, the values of $1/\lambda_{\text{max}}$ were gradually and positively dependent on the electron-withdrawing groups with the slope +0.923 (correlation coeff. 0.9440). It could be demonstrated from such results for asymmetrical dibenzoylated monobenzotetraaza[14]annulenes that the energies of $\pi \rightarrow \pi^*$ transition were correlated with inductive effects of the substituents on benzoyl group in order; $\text{NO}_2 > \text{Cl} > \text{H} > \text{CH}_3 > \text{OCH}_3$.

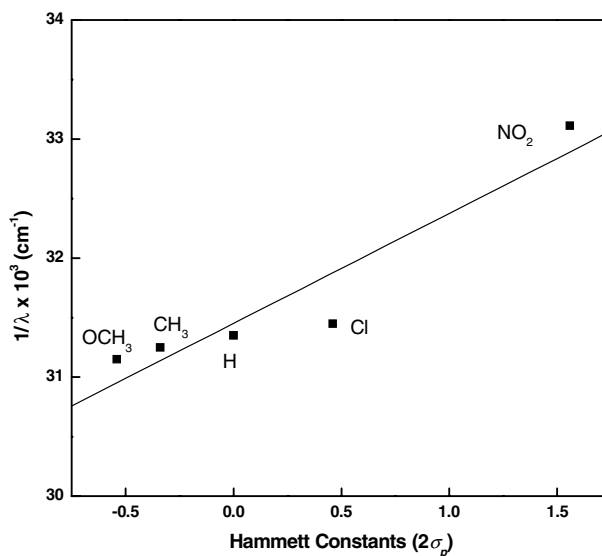


Figure 1. Correlation between the maximum energy of the $\pi \rightarrow \pi^*$ of the compounds **2** ~ **6** and Hammett parameters ($2\sigma_p$).

^1H and ^{13}C NMR spectra

^1H NMR data for asymmetrical free base, monobenzotetraaza[14]annulene and its dibenzoylated compounds prepared were presented in Table 1. Their assignments were made by comparing to their spectra with those of other tetraaza[14]annulenes [20, 21]. The proton signal of the methine sites of compound **1** appeared at 4.757 ppm, while those of compounds **2** ~ **6** disappeared because of the benzylation. The 5- and 8-amine proton peaks of the compounds were generally broad and moved to downfield by 1.036 ~ 1.432 ppm relative to that of compound **1**. For compounds **2** ~ **6**, the resonances of the 4- and 9-methyl protons were moved to upfield to a greater extent than that those of 2- and 11-methyl. This reflects the fact that the benzoyl groups might not be perpendicular but distorted on macrocycle ring plane. That is, the methyl groups are subjected to the shielding effect of substituted benzoyl group. The ethylene proton peaks for compounds **2** ~ **6** were also shifted to downfield by 0.121 ~ 0.206 ppm relative to that of **1**. The effects of the substituents on the resonances of amine and ethylene protons were examined by means of a Hammett plot. As shown in Figure 2, the relationship between $\Delta\rho$ ($\delta_X - \delta_H$; X = substituents) and $2\sigma_p$ was linearly and positively related with a slopes (ρ) of +0.185 (correlation coeff. 0.9973) for amine and +0.040 (correlation coeff. 0.9884) for ethylene proton, respectively. The $\Delta\rho$ values are similarly affected by the substituents on benzoyl group as the effect on $1/\lambda_{\text{max}}$ values.

^{13}C NMR data and their assignments for the compounds were also presented in Table 2. The carbon resonances of the **2** ~ **6** were appreciably shifted to the downfield (around 12 ~ 13 ppm) relative to that of **1**, indicating successive benzylation, except for the imine carbon because of its localizing effect. The carbon

Table 1. ^1H NMR data for the compounds **1** ~ **6**^a

No.	Methyl	Methine	Ethylene	X	Aromatic (macrocycle)	Aromatic (benzoyl)	N-H
1 ^b	1.972(s) 2.101(s)	4.757(s)	3.443(s)		6.945(m)		11.873(br)
2	1.754(s) 2.049(s)		3.574(s)	2.432(s)	6.811 ~ 6.982(m)	7.262(d) 7.849(d)	12.955(br)
3	1.725(s) 2.063(s)		3.580(s)		6.792 ~ 6.976(m)	7.458 ~ 7.937(m)	13.014(br)
4	1.728(s) 2.080(s)		3.594(s)		6.775 ~ 7.034(m)	7.432(d) 7.865(d)	13.075(br)
5	1.685(s) 2.165(s)		3.649(s)		6.769 ~ 7.060(m)	8.033(d) 8.305(d)	13.305(br)
6	1.779(s) 2.027(s)		3.564(s)	3.893(s)	6.820 ~ 6.974(m)	6.948(d) 7.935(d)	12.909(br)

^aChemical shifts in ppm from internal TMS; measured in chloroform-*d*; multiplicity of a proton signal is given in parentheses after δ value; singlet (s), doublet (d), broad (br), multiplet (m).

^bRef. 17.

signals of these asymmetrical free-based tetraaza[14]-annulenes generally were shifted to upfield comparing to those of nickel(II) complexes with these free bases [21]. These results might be attributed to the abundant electron density of free base ligands obtained by demetallating tetraaza[14]annulene nickel(II) complex.

Cyclic voltammograms

Redox potentials of the compounds measured in TEAP-DMSO (0.1 M) solutions vs. Ag/Ag^+ (0.01 M) at 25 °C and sweep rates of 100 mVs^{-1} were listed in Table 3 and

the cyclic voltammograms in the potential range from +1.10 to -3.00 V vs. Ag/Ag^+ were shown in Figure 3. Compound **1** showed only two irreversible oxidation peaks at +0.168 and +0.577 V. After dibenzoylation, the voltammograms exhibited two irreversible oxidation peaks and one or two reduction ones in the ranges of +0.280 to +0.870 V and -1.200 to -2.500 V, respectively, as illustrated in Figure 3. The oxidation potentials of compounds **4** and **5** with the electron-withdrawing substituents of the benzoyl group were shifted to high voltage comparing to compound **1**. The reduction peaks might be attributed to benzoyl groups because there could not be any wave for compound **1** around the potential (Figure 3). The substituent effect on the oxidation potentials was also examined by means of a Hammett plot. As shown in Figure 4, the relationships between the 1st and 2nd oxidation potentials ($E_{\text{op}(1)}$ and $E_{\text{op}(2)}$) and $2\sigma_p$ were linearly and positively related with slopes of +0.036 (correlation coeff. 0.9520) for the first oxidation potential and +0.045 (correlation coeff. 0.9750) for the second oxidation potential, respectively. The observation reflects that the electron density of the oxidation sites is considerably affected by the substituent on the benzoyl group.

Crystal structure of compound **4**

The molecular structure of 13,14-benzo-3,10-di(*p*-chlorobenzoyl)-5, 8-dihydro-2, 4, 9, 11-tetramethyl-1,5,8,12-tetraazacyclotetradeca-1,3,9,11-tetraene was illustrated in Figure 5. Crystal data and refinement parameters were listed in Table 4. The selected bond distances and angles were presented in Table 5. The compound **4** adopting a saddle-shaped conformation was tilted to opposite sides of the plane defined by four nitrogen atoms. The distortion from planarity might be owing to steric interactions of β -substituents (two methyl groups) with the *o*-phenyl ring, which in general exhibited for the

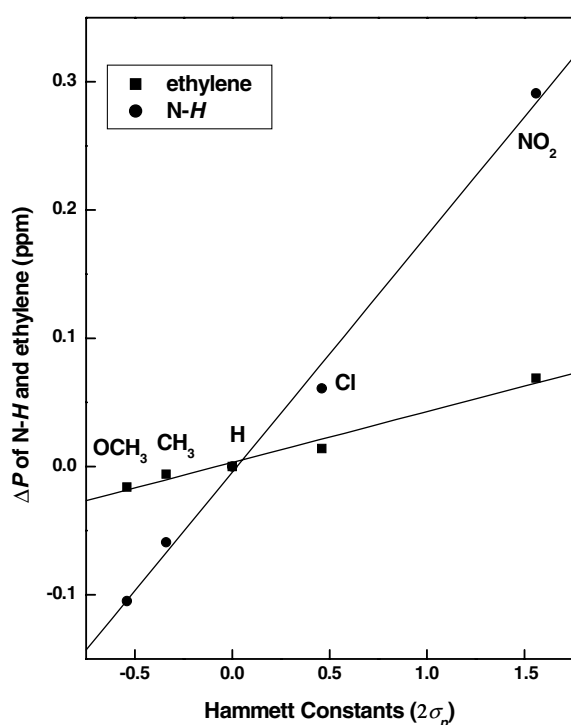


Figure 2. Correlation between the ΔP of the compounds **2** ~ **6** and Hammett parameters ($2\sigma_p$). $\Delta P = \delta_X - \delta_H$; X = substituents).

Table 2. ^{13}C NMR data for the compounds **1** ~ **6**^a

No.	Methyl	Methine	Ethylene	X	Aromatic (macrocycle)	Aromatic (benzoyl)	C–N & C=N	C=O
1	19.602	97.904	46.423		121.059		159.094	
	20.890				121.831		160.275	
					138.344			
2	17.218	109.892	43.801	21.603	122.011	129.194	157.837	198.100
	21.522				123.143	129.372	164.237	
					139.030	139.257		
						142.178		
3	17.387	109.915	43.822		122.202	128.552	160.472	198.309
	21.957				123.351	129.272	164.707	
					139.295	132.265		
						141.859		
4	17.396	109.520	43.784		122.220	128.838	160.775	196.790
	22.072				123.547	130.617	164.626	
					139.144	138.577		
						140.292		
5	17.639	109.439	43.623		122.350	123.838	162.522	195.285
	22.913				124.049	129.922	165.467	
					138.910	147.460		
						149.725		
6	17.235	109.876	44.043	55.450	122.140	113.743	159.367	197.469
	21.328				123.126	131.604	163.752	
					139.322	134.371		
						163.153		

^aChemical shifts in ppm from internal TMS; measured in chloroform-*d* at room temperature.

Table 3. Redox potential (E_{op} and E_{rp}) data for the compounds **1** ~ **6**

Comp.	E_{op} , V		E_{rp} , V	
	0 → +1	+1 → +2	0 → -1	-1 → -2
1	+0.170	+0.580		
2	+0.310	+0.800	-2.470	
3	+0.310	+0.800	-2.370	
4	+0.340	+0.820	-2.230	-2.420
5	+0.370	+0.860	-1.270	-1.810
6	+0.290	+0.750	-2.530	

derivatives of symmetrical dibenzotetraaza[14]annulene ligands [22–25]. The hydrogen bond distances and angles were presented in Table 6. The molecule had two N–H···N hydrogen bonds in the central tetraaza part of the molecule. The two H-atoms [H(2N) and H(3N)] also participated weak interactions with the N1 and N4 atoms, respectively. The N(2)–H(2N) and N(3)–H(3N) distances (both 0.85(3) Å) were roughly 0.3 Å shorter than those of symmetry dibenzotetraaza[14] annulene [23, 25]. The amino hydrogens showed not *trans* but *cis* (the nitrogen of ethylene group) to each other in the macrocycle. The imino C=N bonds [N(1)–C(7) = 1.297 Å and N(4)–C(14) = 1.304 Å] were about 0.03 Å shorter than the amino type [N(2)–C(9) = 1.324 Å and N(3)–C(12) = 1.326 Å]. The C–N–C average angles (about 122.45°) of imino type exhibited typical sp^2 character. The ethylene of between N(2) and N(3) on the macrocycle ring impressively exhibited two conformations N(2)C(10A)C(11A)N(3) and N(2)C(10B)

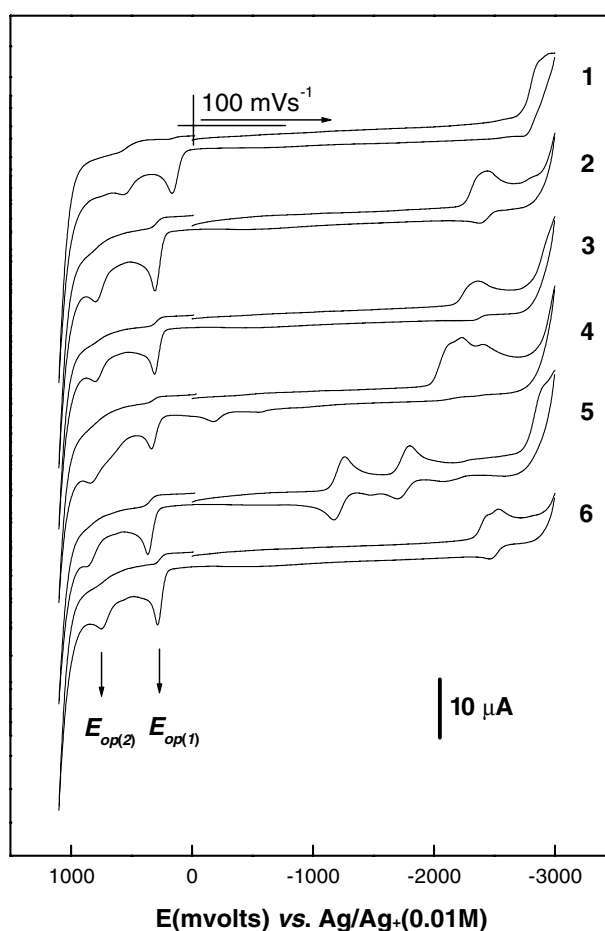


Figure 3. Cyclic voltammograms of compounds **1** ~ **6** in 0.1 M TEAP-DMSO solutions vs. Ag/Ag⁺ in [comp] = 1.0×10^{-3} M and at 25°.

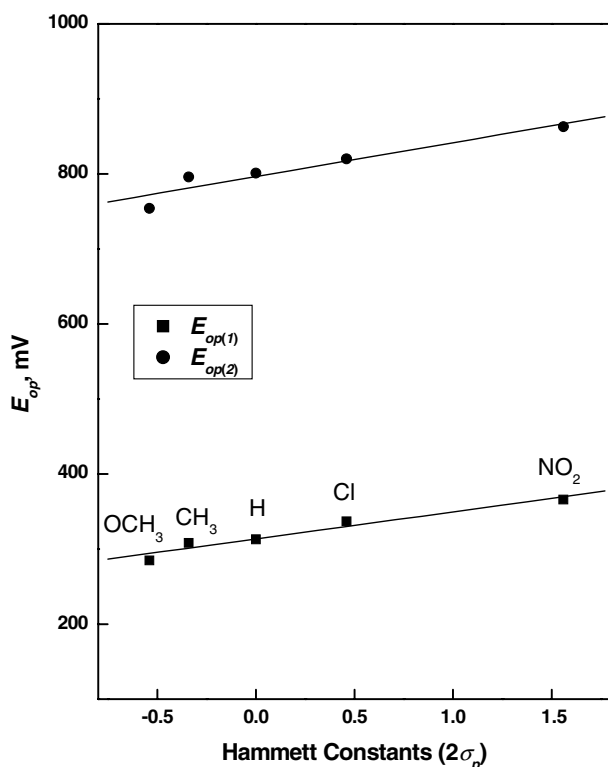


Figure 4. Hammett plot of the 1st and 2nd oxidation potentials of the compound **2** ~ **6**, $E_{op(1)}$ and $E_{op(2)}$ vs. $2\sigma_p$.

Table 4. Crystal data and structure refinement for compound **4**

Empirical formula	$C_{32}H_{30}Cl_2N_4O_2$
Formula weight	573.50
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	$a = 26.0059(19)$ Å $\alpha = 90^\circ$, $b = 6.9058(5)$ Å $\beta = 109.5930^\circ$, $c = 33.082(2)$ Å $\gamma = 90^\circ$.
Volume	$5597.2(7)$ Å ³
Z	8
Density (calculated)	1.361 Mg m ⁻³
Absorption coefficient	0.270 mm ⁻¹
$F(000)$	2400
Crystal size	$0.50 \times 0.25 \times 0.25$ mm ³
θ range for data collection	1.31 – 28.32°
Index ranges	$-34 \leq h \leq 28$ $-8 \leq k \leq 9$ $-28 \leq l \leq 43$
Reflections collected	16,910
Independent reflections	6688 [$R(\text{int}) = 0.0332$]
Completeness to $\theta = 28.32^\circ$	96.1%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9357 and 0.8770
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6688/0/460
Goodness-of-fit on F^2	1.024
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0487$, $wR2 = 0.1146$
R indices (all data)	$R1 = 0.0904$, $wR2 = 0.1318$
Largest diff. peak and hole	0.462 and -0.399 e. Å ⁻³

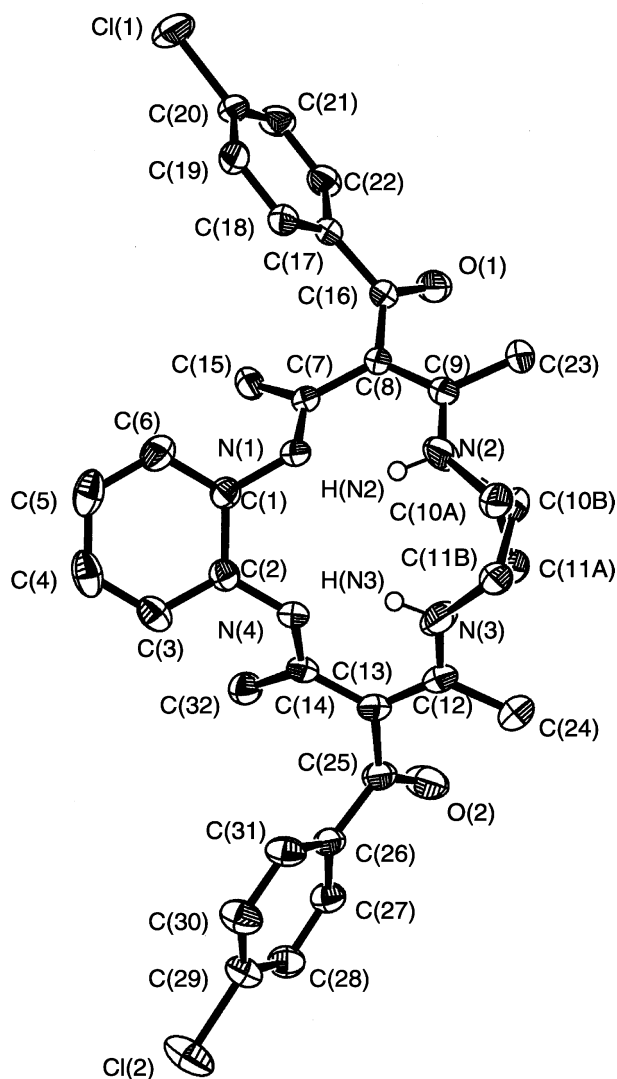


Figure 5. Crystal structure of 13,14-benzo-3,10-di(*p*-chlorobenzoyl)-5,8-dihydro-2,4,9,11-tetramethyl-1,5,8,12-tetraazacyclotetradeca-1,3,9,11-tetraene.

C(11B)N(3) as shown in Figure 5. Thus, the angles of amine type had two kinds of C(9)–N(2)–C(10A) $137.6(3)^\circ$ and C(9)–N(2)–C(10B) $114.4(3)^\circ$ (or C(12)–N(3)–C(11A) $116.3(3)^\circ$ and C(12)–N(3)–C(11B) $135.3(3)^\circ$) as first example for tetraazaannulene compounds. On the other hand, the angles of C(10A)–N(2)–C(10B) and C(11A)–N(3)–C(11B) were $37.0(2)^\circ$ and $35.3(2)^\circ$, respectively. These results indicate that the π -electrons are highly localized on the macrocycle ring compared with tetraaza[14]annulene metal complexes [23, 26].

Supplementary material

Crystallographic data for the structural analysis have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number CCDC 222448. Copies of this information can be obtained free of charge via E-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>; Tel: +44-1223-336031; Fax: +44-1223-336033.

Table 5. The selected bond distances [Å] and angles [°] for compound 4

N(1)–C(1)	1.417(2)	N(1)–C(7)	1.297(2)
N(2)–C(9)	1.324(4)	N(3)–C(12)	1.326(3)
N(4)–C(2)	1.410(2)	N(2)–C(10A)	1.489(5)
N(4)–C(14)	1.304(2)	N(2)–C(10B)	1.563(5)
C(7)–C(8)	1.465(3)	N(3)–C(11A)	1.572(6)
C(8)–C(9)	1.395(3)	N(3)–C(11B)	1.466(6)
C(12)–C(13)	1.394(3)	C(10A)–C(11A)	1.511(10)
C(13)–C(14)	1.460(3)	C(10B)–C(11B)	1.507(10)
C(1)–C(2)	1.407(3)	O(1)–C(16)	1.227(3)
C(7)–C(15)	1.504(3)	Cl(1)–C(20)	1.733(2)
C(9)–C(16)	1.477(3)	C(9)–C(23)	1.501(4)
C(16)–C(17)	1.503(3)		
C(1)–N(1)–C(7)	121.37(17)	N(2)–C(9)–C(8)	120.6(2)
C(2)–N(4)–C(14)	123.54(17)	N(3)–C(11A)–C(10A)	103.9(5)
N(1)–C(7)–C(8)	119.65(18)	N(3)–C(11B)–C(10B)	104.3(6)
N(3)–C(12)–C(13)	120.6(2)	N(4)–C(14)–C(13)	120.18(19)
N(1)–C(1)–C(2)	119.42(17)	N(4)–C(2)–C(1)	118.82(17)
C(7)–C(8)–C(9)	121.98(19)	C(8)–C(7)–C(15)	118.10(18)
C(12)–N(3)–C(11A)	116.3(3)	C(7)–C(8)–C(16)	119.09(18)
C(12)–N(3)–C(11B)	135.3(3)	C(8)–C(16)–O(1)	123.13(19)
C(9)–N(2)–C(10A)	137.6(3)	C(8)–C(16)–C(17)	118.91(18)
C(9)–N(2)–C(10B)	114.4(3)	C(19)–C(20)–Cl(1)	119.00(19)
N(2)–C(10A)–C(11A)	100.1(5)	C(8)–C(9)–C(23)	123.2(2)
N(2)–C(10B)–C(11B)	103.8(5)	C(11A)–N(3)–C(11B)	35.3(2)
C(10A)–N(2)–C(10B)	37.0(2)		

Table 6. Hydrogen bond distances [Å] and angles [°] for compound 4

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
N(3)–H(3N)...N(4)	0.85(3)	1.88(3)	2.600(3)	141(3)
N(2)–H(2N)...N(1)	0.85(3)	1.90(3)	2.587(3)	136(3)

Symmetry transformations used to generate equivalent atoms.

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