

SYNTHESES AND PROPERTIES OF TETRAAZAAZULENOCORONANDS
AND OCTAAZAAZULENOCRYPTAND¹

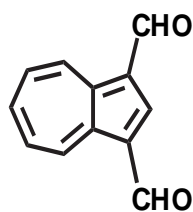
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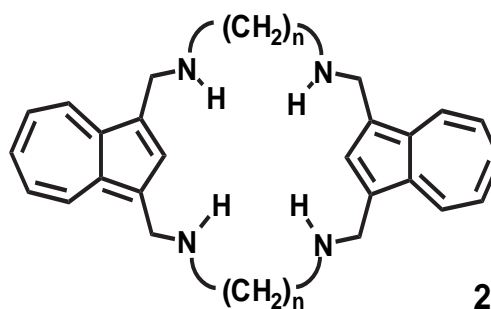
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Abstract - Treatment of 1,3-diformylazulene (**1**) with 1.2 equiv. of α,ω -alkanediamines (**3** and **4**) and tris(2-aminoethyl)amine (**5a**) in ethanol for 24 h at room temperature gave tetraazaazulenocoronands (**2** and **9**) and octaazaazulenocryptand (**10**) in one-pot procedure in good yields.

Recently, Nozoe *et al.* reported² the synthesis and the complexation of macrocycles having aminotropone units. On the other hand, Lohr *et al.* reported³ the synthesis of the macrocyclic polyethers azulenes,



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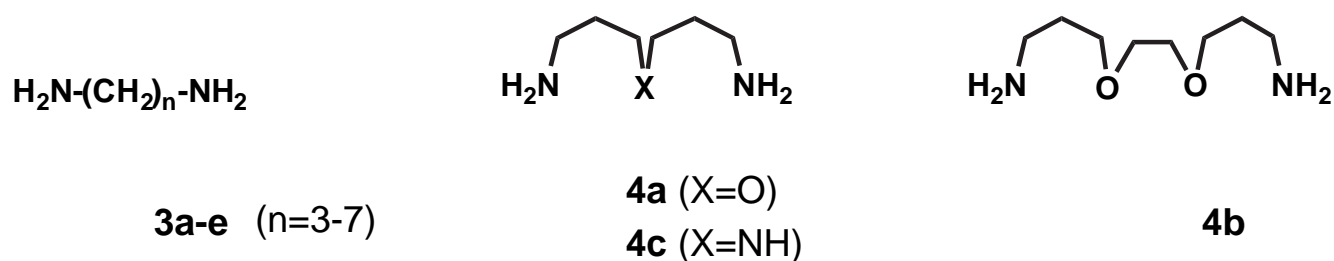


2a-e (n=3-7)

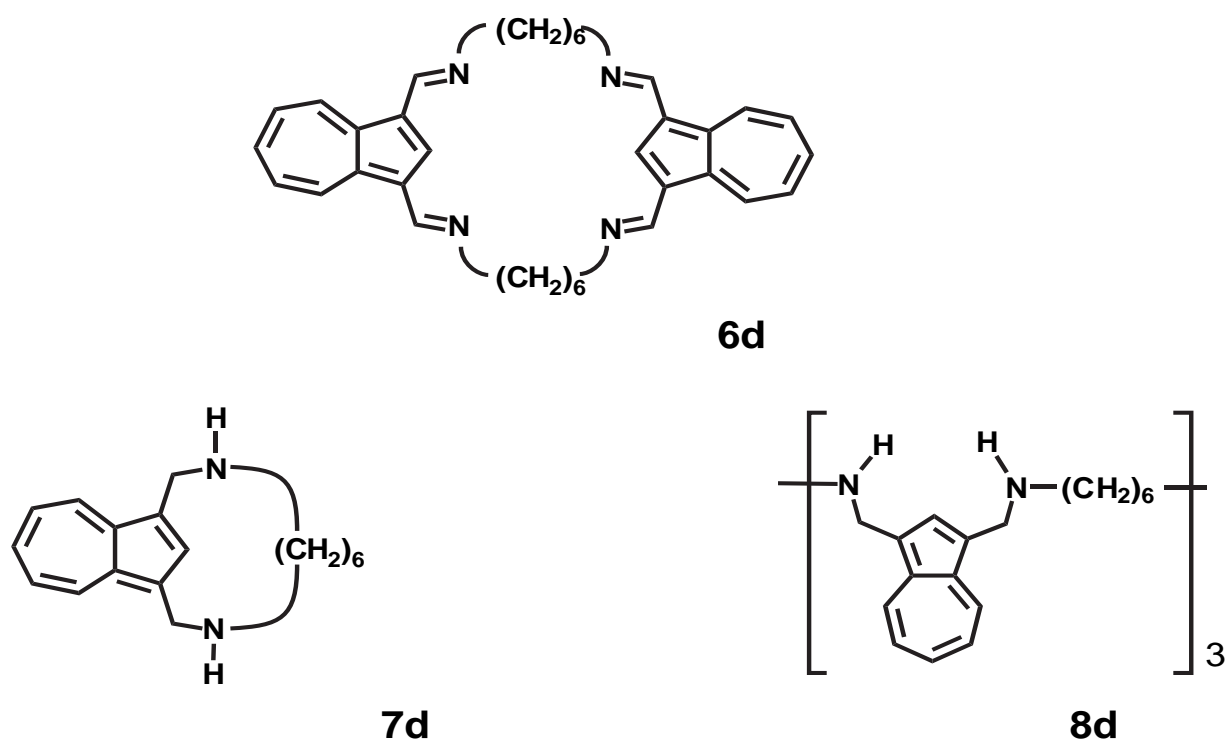
[†]Dedicated to Professor Shô ITÔ on the occasion of his 77th birthday.

however, the azaazulenocoronands is still unknown. Tetraazaazulenocoronands are expected to have a larger cavity and better complexation toward the transition metal ions. In this communication, we wish to report a one-pot procedure of novel tetraazaazulenocoronands (**2** and **9**) and octaazaazulenocryptand (**10**) *via* compound (**6d**) or its analog from 1,3-diformylazulene (**1**) and α,ω -alkanediamines (**3** and **4**) or tris(2-aminoethyl)amine (**5a**) under high dilution condition.

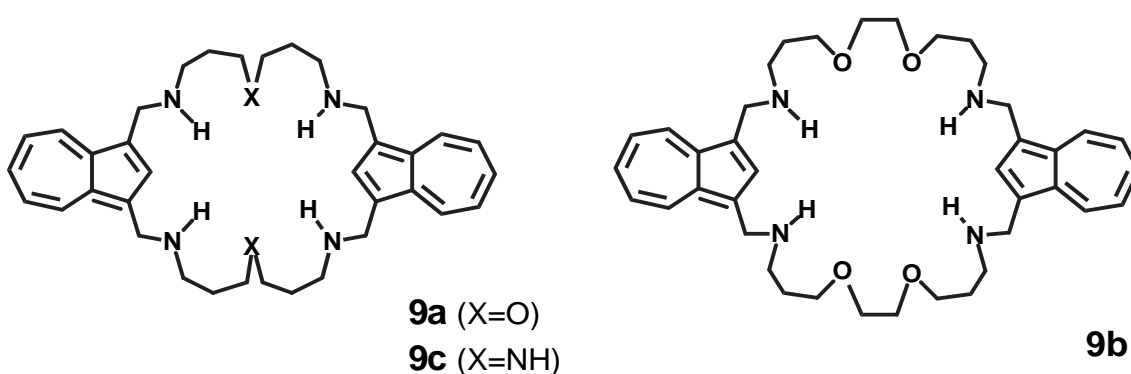
α,ω -Alkanediamines used in this study are diamines (**3a-e**, $n=3-7$), diamines having hetero atoms in methylene chain (**4a-c**), and tris(2-aminoethyl)amines (**5a,b**).



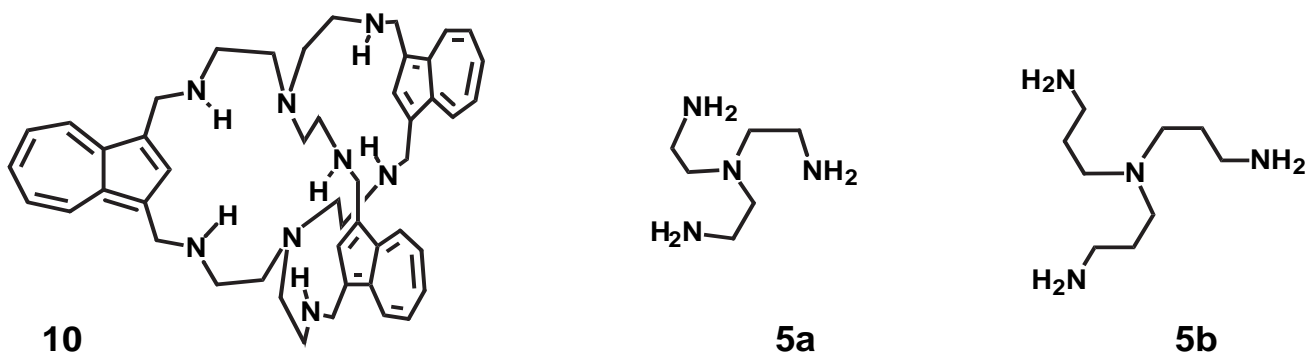
A typical experimental procedure is described for the reaction of **1** with **3d**: A mixture of 1,3-diformylazulene (**1**, 100 mg) and 1,6-hexamethylenediamine (**3d**, 80 mg) in ethanol (200 mL) was stirred for 24 h at room temperature. To the mixture, NaBH_4 (100 mg) was added and then stirred for 6 h at room temperature. After concentration *in vacuo*, the residue was purified through a silica gel column



with NaCl aq-MeOH as an eluent, giving **2d** as blue oil (75 % yield), two by-products, monomer (**7d**, trace) and trimer (**8d**, trace), and high absorptive unknown compound. The structure of **2d** was deduced from inspection of the spectroscopic data as well as elemental analysis. Compound (**2d**) showed a UV spectrum similar to that of azulene and a molecular ion peak at m/z 537 (MH^+) in the FAB-MS spectrum. In the 1H NMR spectrum of **2d**, there are the three sets of the adjacent methylene protons at δ 1.30, 1.49, and 2.63 and one set of an isolated methylene proton at δ 4.23, respectively. Also, the signals at 7.06 (t), 7.52 (t), and 8.29 (d) are assigned for protons at the 5, 7-positions, the 6-position, and 4, 8-positions, respectively, by their coupling constants of $J=9.8$ Hz, indicating symmetrical structure. A similar reaction of **1** with **4a-c**, which having hetero atoms in methylene chains, afforded the corresponding tetraazaazelenocoronands (**9a-c**).



The reaction of **1** with tris(2-aminoethyl)amine (**5a**) gave octaazaazulenocryptand (**10**) together with insoluble solid. Compound (**10**) showed a UV spectrum similar to that of azulene and a molecular ion peak at m/z 749 (MH^+) in the FAB-MS spectrum. In the 1H NMR spectrum of **10**, there are the three



sets of the adjacent methylene protons at δ 2.61, 2.77, and 3.94 and one set of an isolated methylene proton at δ 4.23, respectively. Also, the signals at 7.01 (t), 7.48 (t), and 8.18 (d) are assigned for protons

at the 5, 7-positions, the 6-position, and 4, 8-positions, respectively, by their coupling constants of $J=9.8$ Hz, indicating symmetrical structure.

Properties and yields of **2a-e**, **9a-c**, and **10** obtained by this one-pot procedure are shown in Table 1.

Table. 1 Properties and yields of **2a-e**, **9a-c**, and **10** obtained by this one-pot procedure.

Reagents	Products	Yield (%)	Color	FAB-MS (MH ⁺)
3a (n=3)	2a ⁴	56	Blue oil	453
3b (n=4)	2b ⁵	50	Blue oil	481
3c (n=5)	2c ⁶	45	Blue oil	509
3d (n=6)	2d ⁷	75	Blue oil	537
3e (n=7)	2e ⁸	70	Blue oil	565
4a	9a ⁹	15	Blue oil	569
4b	9b ¹⁰	80	Blue oil	657
4c	9c ¹¹	20	Blue oil	595
5a	10 ¹²	12	Blue oil	749

In contrast, similar treatment of tris(2-aminopropyl)amine (**5b**) gave a blue insoluble solid without the corresponding cryptand.

As mentioned above, compounds (**2d**, **9a-e**, and **10**) in methanol solution are stable to acidic conditions (6N-HCl) but were decolorized slowly by air at room temperature and were decomposed under alkaline conditions (6N-NaOH) to give a dark-brown or almost black insoluble solid.

The complexation of these compounds with metal ions is in progress.

ACKNOWLEDGMENTS

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4. **2a**: UV λ_{\max} (MeOH) 235 (log ϵ 4.35), 270 (4.67, sh), 278 (4.77), 290 (4.69, sh), 342 (3.81), 355 (3.66), 596 (2.67), 645 (2.55, sh), 685 nm (2.24, sh). IR (KBr) 3250 cm^{-1} (NH). ^1H NMR (500 MHz, CDCl_3) δ 1.74 (4H, m, $J = 6.2$ Hz, CH_2), 2.18 (4H, br, NH), 2.74 (8H, t, $J = 6.2$ Hz, NCH_2), 4.17 (8H, s, ArCH_2), 7.01 (4H, t, $J = 9.8$ Hz, H-5,7), 7.45 (2H, t, $J = 9.8$ Hz, H-6), 7.67 (2H, s, H-2), 8.26 (4H, d, $J = 9.8$ Hz, H-4,8). ^{13}C NMR (125.65 MHz, CDCl_3) δ 29.48 (t), 46.23 (t), 48.81 (t), 121.69 (d), 127.11 (s), 133.07 (d), 136.61 (s), 137.38 (d), 137.55 (d). *Anal.* Calcd for $\text{C}_{30}\text{H}_{36}\text{N}_4$: C, 79.61, H, 8.02; N, 12.38. Found: C, 80.30; H, 8.38; N, 11.33.
5. **2b**: UV λ_{\max} (MeOH) 235 (log ϵ 4.52), 270 (4.69, sh), 278 (4.88), 283 (4.82, sh), 343 (3.88), 360 (3.75), 595 (2.73), 645 (2.62, sh), 715 nm (2.01, sh). IR (neat) 3250 cm^{-1} (NH). ^1H NMR (500 MHz, CDCl_3) δ 1.55 (8H, m, CH_2), 1.71 (4H, br, NH), 2.67 (8H, m, NCH_2), 4.19 (8H, s, ArCH_2N), 7.06 (4H, t, $J = 9.8$ Hz, H-5,5',7,7'), 7.52 (2H, t, $J = 9.8$ Hz, H-6,6'), 7.82 (2H, s, H-2,2'), 8.30 (4H, d, $J = 9.8$ Hz, H-4,4',8,8'). ^{13}C NMR (125.65 MHz, CDCl_3) δ 27.90 (t, CH_2), 46.14 (t, CH_2), 49.54 (t, CH_2), 121.85 (d, C-5,7), 127.37 (s, C-1,3), 133.27 (d, C-4,8), 136.84 (s, C-3a,8a), 137.56 (d, C-6), 137.631 (d, C-2). *Anal.* Calcd for $\text{C}_{32}\text{H}_{40}\text{N}_4$: C, 79.96; H, 8.39; N, 11.66. Found: C, 81.02; H, 8.76; N, 10.23.
6. **2c**: UV λ_{\max} (MeOH) 235 (log ϵ 4.41), 278 (4.92, sh), 290 (4.86, sh), 342 (3.95), 357 (3.80), 382 (2.63), 420 (1.95), 595 (2.75), 654 (2.62, sh), 725 nm (2.10, sh). IR (neat) 3250 cm^{-1} (NH). ^1H NMR (500 MHz, CDCl_3) δ 1.29 (4H, m, $J = 7.0$ Hz, CH_2), 1.48 (8H, m, $J = 7.0$ Hz, CH_2), 2.61 (8H, t, $J = 7.0$ Hz, NCH_2), 4.21 (8H, s, ArCH_2), 7.05 (4H, t, $J = 10$ Hz, H-5,7), 7.51 (2H, t, $J = 10$ Hz, H-6), 7.82 (2H, s, H-2), 8.29 (4H, d, H-4,8). ^{13}C NMR (125.65 MHz, CDCl_3) δ 25.17 (t, CH_2), 29.92 (t, CH_2), 46.14 (t, NCH_2), 49.27 (t, NCH_2), 121.84 (d), 127.18 (s), 133.23 (d), 136.86 (s), 137.61 (d), 137.69 (d). *Anal.* Calcd for $\text{C}_{34}\text{H}_{44}\text{N}_4$: C, 80.27; H, 8.79; N, 11.01. Found: C, 80.98; H, 9.14; N, 9.87.
7. **2d**: UV λ_{\max} (MeOH) 235 (log ϵ 4.41), 275 (4.73, sh), 279 (4.81, sh), 290 (4.75, sh), 243 (3.77), 358 (3.58), 585 (2.69), 650 (2.55, sh), 710 nm (2.07, sh). IR (neat) 3270 cm^{-1} (NH). ^1H NMR (500 MHz, CDCl_3) δ 1.30 (8H, m, CH_2), 1.49 (8H, m, CH_2), 1.77 (4H, br, NH), 2.63 (8H, t, $J = 7.0$ Hz, CH_2), 4.23 (8H, s, CH_2), 7.06 (4H, t, $J = 9.8$ Hz, H-5,7), 7.52 (2H, t, $J = 9.8$ Hz, H-6), 7.88 (2H, s, H-2), 8.29 (4H, d, $J = 9.8$ Hz, H-4,8). ^{13}C NMR (125.65 MHz, CDCl_3) δ 26.88 (t, CH_2), 29.80 (t, CH_2), 45.83 (t, CH_2), 49.01 (t, CH_2), 121.76 (d, C-5,7), 127.55 (s, C-1,3), 133.19 (d, C-4,8), 136.80 (s, C-3a, 8a), 137.41 (d, C-6), 137.60 (d, C-2). *Anal.* Calcd for $\text{C}_{36}\text{H}_{48}\text{N}_4$: C, 80.55; H, 9.10; N, 10.44. Found: C, 80.23; H, 9.43; N, 10.33.
8. **2e**: UV λ_{\max} (MeOH) 235 (log ϵ 4.09), 279 (4.79), 342 (3.55), 358 (3.27, sh), 598 (2.73), 624 (2.59, sh), 709 nm (2.09, sh). IR (KBr) 3300 cm^{-1} (NH). ^1H NMR (270 MHz, CDCl_3) δ 1.27 (4H, m, CH_2), 1.48 (8H, m, CH_2), 1.66 (12H, m, CH_2), 2.65 (8H, t, $J = 7.0$ Hz, NCH_2), 4.24 (8H, s, ArCH_2), 7.07 (4H, t, $J = 10$ Hz, H-5,7), 7.54 (2H, t, $J = 10$ Hz, H-6), 7.88 (2H, s, H-2), 8.31 (4H, d, $J = 10$ Hz, H-4,8). ^{13}C NMR (67.8 MHz, CDCl_3) δ 27.12 (t, CH_2), 29.33 (t, CH_2), 29.89 (t, CH_2), 40.18 (t,

- NCH₂), 49.58 (t, ArCH₂), 121.82 (d, C-5,7), 127.37 (s, C-1,3), 133.23 (t, C-4,8), 136.84 (s, C-3a,8a), 137.61 (d, C-2,6). *Anal.* Calcd for C₃₈H₅₂N₄: C, 80.80; H, 9.28; N, 9.92. Found: C, 81.45; H, 9.16; N, 9.39.
9. **9a**: UV λ_{max} (MeOH) 202 (log ϵ 4.43), 206 (4.47), 235 (4.52), 278 (4.81), 287 (4.74, sh), 341 (4.11), 356 (3.87), 594 (2.73), 648 nm (2.53, sh). IR (neat) 3300 cm⁻¹ (NH). ¹H NMR (500 MHz, CDCl₃) δ 1.74 (8H, m, $J=6.7$ Hz, CH₂), 2.20 (4H, br, NH), 2.70 (8H, t, $J=6.7$ Hz, NCH₂), 3.46 (8H, t, $J=6.7$ Hz, OCH₂), 4.07 (8H, s, ArCH₂N), 7.02 (4H, t, $J=10$ Hz, H-5,7), 7.50 (2H, t, $J=10$ Hz, H-6), 7.87 (2H, s, H-2), 8.22 (4H, d, $J=10$ Hz, H-4,8). ¹³C NMR (125.65 MHz, CDCl₃) δ 29.65 (CH₂), 46.21 (ArCH₂), 47.75 (N-CH₂), 69.83 (OCH₂), 121.84 (C-5,7), 127.28 (C-1,3), 133.35 (C-4,8), 136.84 (C-3a,8a), 137.55 (C-6), 137.60 (C-2). *Anal.* Calcd for C₃₆H₄₈N₄: C, 76.02; H, 8.51; N, 9.85. Found: C, 76.44; H, 8.56; N, 9.36.
10. **9b**: UV λ_{max} (MeOH) 203 (log ϵ 4.32), 235 (4.46), 278 (4.83), 289 (4.75, sh), 342 (3.81), 357 (3.59), 594 (2.73), 640 (2.70, sh), 705 nm (2.08, sh). IR (neat) 3350 cm⁻¹ (NH). ¹H NMR (500 MHz, CDCl₃) δ 1.71 (8H, m, $J=6.5$ Hz, CH₂), 2.35 (4H, br, NH), 2.73 (8H, t, $J=6.5$ Hz, NCH₂), 3.46 (8H, t, $J=6.5$ Hz, OCH₂), 3.49 (8H, s, OCH₂), 4.17 (8H, s, ArCH₂), 7.02 (4H, t, $J=10$ Hz, H-5,7), 7.49 (2H, t, $J=10$ Hz, H-6), 7.89 (2H, s, H-2), 8.28 (4H, d, $J=10$ Hz, H-4,8). ¹³C NMR (125.65 MHz, CDCl₃) δ 29.64 (CH₂), 46.10 (ArCH₂), 47.17 (N-CH₂), 69.89 (OCH₂), 70.10 (OCH₂), 121.76 (C-5,7), 127.25 (C-1,3), 133.23 (C-4,8), 136.86 (C-3a,8a), 137.48 (C-6), 137.85 (C-2). *Anal.* Calcd for C₄₀H₅₆N₄: C, 73.14; H, 8.59; N, 8.53. Found: C, 73.77; H, 8.83; N, 7.65.
11. **9c**: UV λ_{max} (MeOH) 203 (log ϵ 4.42), 236 (4.40), 278 (4.75), 288 (4.65, sh), 346 (3.71), 360 (3.51), 425 (2.08, sh), 590 nm (2.67). IR (neat) 3250 cm⁻¹ (NH). ¹H NMR (500 MHz, CDCl₃) δ 1.62 (8H, m, $J=6.7$ Hz, CH₂), 2.18 (6H, s, NMe), 2.33 (8H, t, $J=6.7$ Hz, NCH₂), 2.38 (4H, br, NH), 2.67 (8H, t, $J=6.7$ Hz, NCH₂), 4.11 (8H, s, ArCH₂), 7.04 (4H, t, $J=10$ Hz, H-5,5',7,7'), 7.51 (2H, t, $J=10$ Hz, H-6,6'), 7.88 (2H, s, H-2,2'), 8.25 (4H, d, $J=10$ Hz, H-4,4',8,8'). ¹³C NMR (125.65 MHz, CDCl₃) δ 27.05 (t, CH₂), 42.49 (t, CH₂), 46.15 (q, CH₃), 48.54 (t, CH₂), 56.26 (t, CH₂), 121.90 (d, C-5,7), 127.03 (s, C-1,3), 133.35 (d, C-4,8), 136.89 (s, C-3a,8a), 137.62 (d, C-6), 137.75 (d, C-2). *Anal.* Calcd for C₃₈H₅₈N₆: C, 76.21; H, 9.76; N, 14.03. Found: C, 78.60; H, 9.56; N, 11.84.
12. **10**: UV λ_{max} (MeOH) 204 (log ϵ 4.58), 207 (4.56, sh), 214 (4.53, sh), 236 (4.62), 278 (4.98), 291 (4.95, sh), 345 (4.03), 360 (3.89), 595 (2.84), 640 (2.75, sh), 707 nm (2.27, sh). IR (neat) 3250 cm⁻¹ (NH). ¹H NMR (500 MHz, CDCl₃) δ 2.61 (12H, m, CH₂N), 2.75 (4H, br, NH), 2.77 (12H, m, CH₂N), 3.94 (12H, s, ArCH₂), 7.01 (6H, t, $J=10$ Hz, H-5,7), 7.48 (3H, t, $J=10$ Hz, H-6), 7.89 (3H, s, H-2), 8.18 (6H, d, $J=10$ Hz, H-4,8). ¹³C NMR (125.65 MHz, CDCl₃) δ 45.81 (t, CH₂), 48.30 (t, CH₂), 55.18 (t, CH₂), 121.67 (d, C-5,7), 127.18 (s, C-1,3), 133.03 (d, C-4,8), 136.52 (s, C-3a,8a), 137.38 (d, C-2,6). *Anal.* Calcd for C₄₈H₆₀N₈: C, 76.97; H, 8.07; N, 14.96. Found: C, 79.55; H, 8.78; N, 11.67.