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SYNTHESES AND PROPERTIES OF TETRAAZAAZULENOCORONANDS AND OCTAAZAAZULENOCRYPTAND[1]

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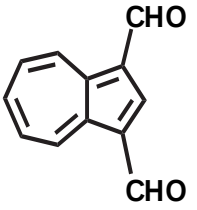
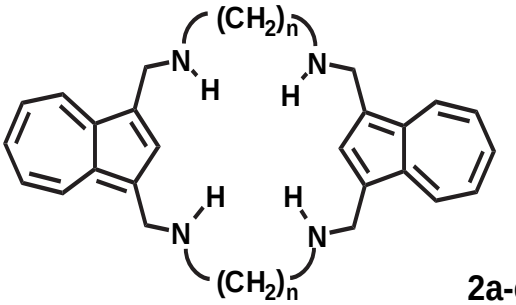
Abstract - Treatment of 1,3-diformylazulene (**1**) with 1.2 equiv. of α,ω-alkanediamines (**3** and **4**) and tris(2-aminoethyl)amine (**5a**) in ethanol for 24 h at room temperature gave tetaraazaazulenocoronands (**2** and **9**) and octaazaazulenocryptand (**10**) in one-pot procedure in good yields.

Recently, Nozoe *et al.* reported[2] the synthesis and the complexation of macrocycles having aminotropone units. On the other hand, Lohr *et al.* reported[3] the synthesis of the macrocyclic polyethers azulenes,



1

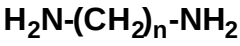


2a-e (n=3-7)

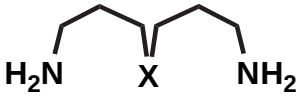
†Dedicated to Professor Shô ITÔ on the occasion of his 77th birthday.

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.

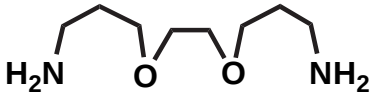
α,ω-Alkanediamines used in this study are diamines (**3a-e**, n=3-7), diamines having hetero atoms in methylene chain (**4a-c**), and tris(2-aminoethyl)amines (**5a**,**b**).



3a-e (n=3-7)

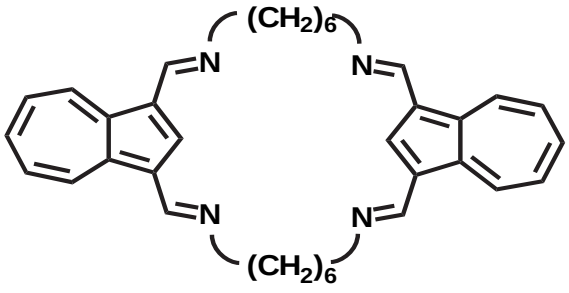


4a (X=O)
4c (X=NH)

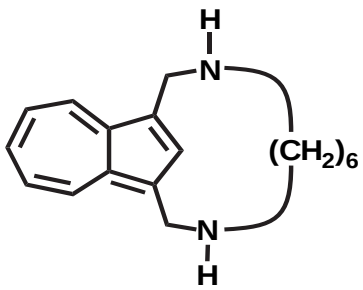


4b

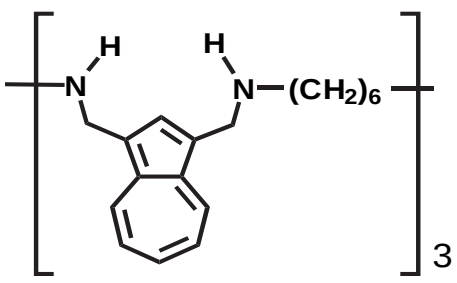
A typical experimental procedure is described for the reaction of **1** with **3d**: A mixture of 1,3-diformylazulene (**1**, 100 mg) and 1,6-hexamethylenediamine (**3d**, 80 mg) in ethanol (200 mL) was stirred for 24 h at room temperature. To the mixture, $NaBH_4$ (100 mg) was added and then stirred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



6d



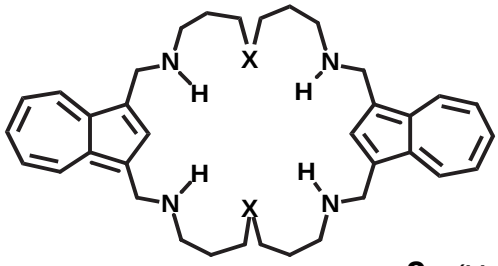
7d



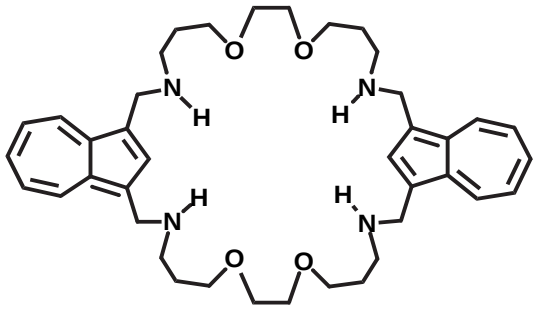
8d

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**).

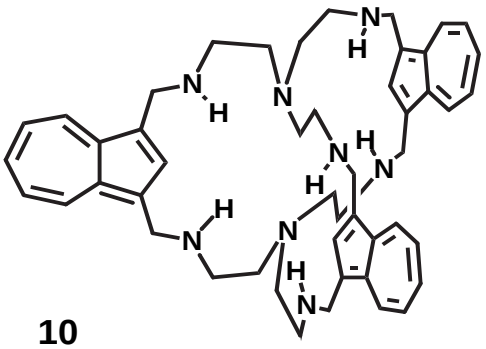


9a (X=O)
9c (X=NH)

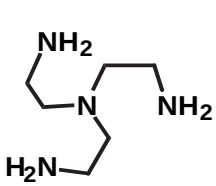


9b

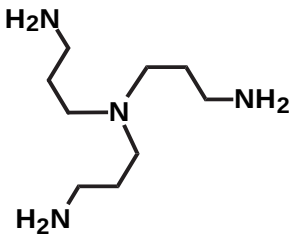
The reaction of **1** with tris(2-aminoethyl)amine (**5a**) gave octaazaazulenocryptand (**10**) together with insoluble solid. Compound (**10**) showed a UV spectrum similar to that of azulene and a molecular ion peak at m/z 749 (MH^+) in the FAB-MS spectrum. In the ^1H NMR spectrum of **10**, there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



10



5a



5b

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

We thank Professor Klaus Hafner (Technische Hochschule Darmstadt) for his very generous gift of a large amount of azulene. We also thank Mr. Hitoshi Fukada for the elemental analysis, Mr. Hideyuki Mitsuhashi for the measurement of the MS spectra (Analytical Center of Josai Univ.).

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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). ^{1}H 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 $C_{30}H_{36}N_4$: 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 452), 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). ^{1}H 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, $CDCl_3$) *d* 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 $C_{32}H_{40}N_4$: C, 79.96; H, 8.39; N, 11.66. Found: C, 81.02; H, 8.76; N, 10.23.
6. **2c:** UV λmax (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). ^{1}H 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 $C_{34}H_{44}N_4$: C, 80.27; H, 8.79; N, 11.01. Found:C, 80.98; H, 9.14; N, 9.87.
7. **2d**: UV λmax (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). ^{1}H 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=7.0Hz,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 $C_{36}H_{48}N_4$: C, 80.55; H, 9.10; N, 10.44. Found: C, 80.23; H, 9.43; N, 10.33.
8. **2e**: UV λmax (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). ^{1}H 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,

NCH_2), 49.58 (t, $ArCH_2$), 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 $C_{38}H_{52}N_4$: C, 80.80; H, 9.28; N, 9.92. Found: C, 81.45; H, 9.16; N, 9.39.

9. **9a**: UV λmax (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, $CDCl_3$) δ 1.74 (8H, m, *J*=6.7 Hz, CH_2), 2.20 (4H, br, NH), 2.70 (8H, t, *J* = 6.7 Hz, NCH_2), 3.46 (8H, t, *J*=6.7 Hz, OCH_2), 4.07 (8H, s, $ArCH_2N$), 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). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 29.65 (CH_2), 46.21 ($ArCH_2$), 47.75 (N-CH_2), 69.83 (OCH_2), 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 $C_{36}H_{48}N_4$: C, 76.02; H, 8.51; N,9.85. Found: C, 76.44; H, 8.56; N, 9.36.
10. **9b**: UV λmax (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, $CDCl_3$) δ 1.71 (8H, m, *J* = 6.5 Hz, CH_2), 2.35 (4H, br, NH), 2.73 (8H, t, *J* = 6.5 Hz, NCH_2), 3.46 (8H, t, *J* = 6.5 Hz, OCH_2), 3.49 (8H, s, OCH_2), 4.17 (8H, s, $ArCH_2$), 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). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 29.64 (CH_2), 46.10 ($ArCH_2$), 47.17 (N-CH_2), 69.89 (OCH_2), 70.10 (OCH_2), 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 $C_{40}H_{56}N_4$: C, 73.14; H, 8.59; N, 8.53. Found: C, 73.77; H, 8.83; N, 7.65.
11. **9c**: UV λmax (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, $CDCl_3$) δ 1.62 (8H, m, *J* = 6.7 Hz, CH_2), 2.18 (6H, s, NMe), 2.33 (8H, t, *J* = 6.7 Hz, NCH_2), 2.38 (4H, br, NH), 2.67 (8H, t, *J* = 6.7 Hz, NCH_2), 4.11 (8H, s, $ArCH_2$), 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'). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 27.05 (t, CH_2), 42.49 (t, CH_2), 46.15 (q, CH_3), 48.54 (t, CH_2), 56.26 (t, CH_2), 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 $C_{38}H_{58}N_6$: C, 76.21; H, 9.76; N, 14.03. Found: C, 78.60; H, 9.56; N, 11.84.
12. **10**: UV λmax (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, $CDCl_3$) δ 2.61 (12H, m, CH_2N), 2.75 (4H, br, NH), 2.77 (12H, m, CH_2N), 3.94 (12H, s, $ArCH_2$), 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). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 45.81 (t, CH_2), 48.30 (t, CH_2), 55.18 (t, CH_2), 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 $C_{48}H_{60}N_8$: C, 76.97; H, 8.07; N, 14.96. Found: C, 79.55; H, 8.78; N, 11.67.