4 : 7,10 : 13-Diepoxy-1-aza[16]annulene and 3 : 6,9 : 12,15 : 18-Triepoxy-2-chloro-1-aza-[18]annulene as the First Examples of Oxygen-bridged Aza-[4*n*]- and -[4*n* + 2]-annulenes

Haru Ogawa,*[a] Megumi Kumemura,[a] Taiji Imoto,[a] Izumi Miyamoto,[b] Hidefumi Kato,[b] and Yōichi Taniguchi[b]

[a] *Faculty of Pharmaceutical Sciences, Kyushu University 62, Fukuoka 812, Japan*
[b] *Kurume Technical College, General Chemistry, Komorino, Kurume 830, Japan*

The title compounds were prepared by the Beckmann rearrangement of diepoxy[15]- and triepoxy[17]-annulenone oximes (**2**) and (**11**), respectively; 4 : 7,10 : 13-diepoxy-1-aza[16]annulene (**5**) exists as two tautomers, the keto form (**5a**) and the dipolar form (**5b**), forming a paratropic 16π system; 3 : 6,9 : 12,15 : 18-triepoxy-2-chloro-1-aza-[18]annulene (**12**) proved to be strongly diatropic (18π).

Since the report by Badger *et al.* of a triepoxy[18]annulene[1] as the first oxygen-bridged [18]annulene, recent progress in annulene chemistry has allowed the characterization of a host of aza-annulenes.[2] However, except for one example of an oxygen-bridged aza[15]annulene,[3] neither aza[4*n*]- nor aza[4*n*+2]-annulenes belonging to this class have hitherto been reported, although a comparison of the properties of these compounds with those of other aza-annulenes would provide a useful insight into the question of heteroaromaticity and ring current. We now report the preparation of the title compounds as the first 'oxygen-bridged aza-annulenes' of this type.

The ring expansion of annulenone oxime by Beckmann rearrangement is the most straightforward methodology for obtaining aza-annulenes.[2a,4—6] On refluxing diepoxy[15]annulenone (**1**)[7] with a 5 molar excess of $NH_2OH{\cdot}HCl$ for 3 h in EtOH, the Michael addition of NH_2OH took place concurrently with oxime formation to give three products (Scheme 1). These were separated by column chromatography (SiO_2, CH_2Cl_2–EtOH) and characterized (in the sequence of the elution); oxime (**2**) [m.p. 180 °C (n-hexane–benzene), orange prisms, *m/z* 253 (M^+), 8.5%], an isoxazoline derivative (**3**) [m.p. 145—146 °C (n-hexane), yellow prisms, *m/z* 253 (M^+), 18%], and a hydroxylamine adduct (**4**) [m.p. 173—174 °C (benzene), *m/z* 286 (M^+), 57.8%], respectively. Both (**3**) and (**4**) could be converted into oxime (**2**) in satisfactory yields, when dissolved in tetrahydrofuran (THF) and refluxed for 4 h with a small amount of conc. HCl. [Refluxing (**4**) (100 mg) in THF (3 ml) with 5—6 drops of conc. HCl for 4 h gave (**3**) (24%) and (**2**) (12%); refluxing (**3**) (100 mg) in THF (3 ml) with 5—6 drops of conc. HCl gave (**2**) (35%)]. A facile Beckmann rearrangement occurred when (**2**) was treated with an excess of tosyl chloride in pyridine at room temperature. The diepoxy[16]aza-annulene (**5**)† was obtained in 60% yield [m.p. 168—170 °C (EtOH), violet prisms, *m/z* 253 (M^+)]. Surprisingly, the electronic spectrum of (**5**) displayed absorptions typical of the isoelectronic diepoxy[16]annulenes (**6**)[8]

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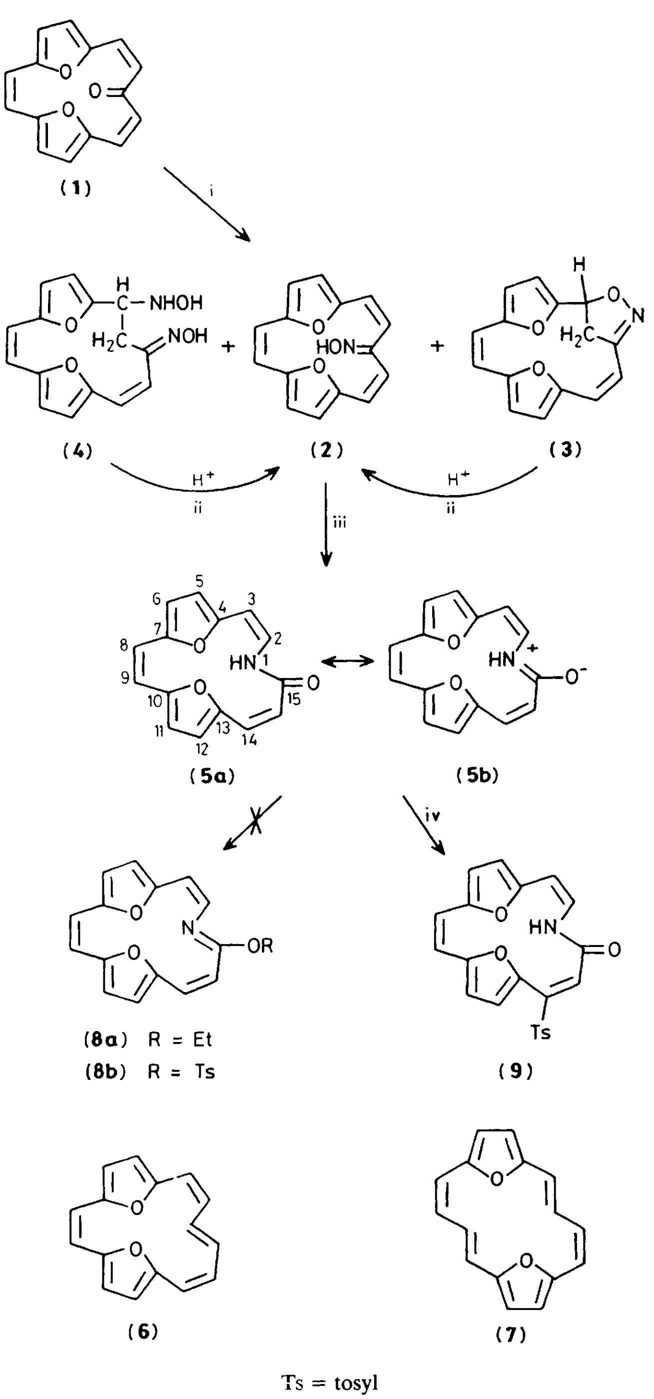
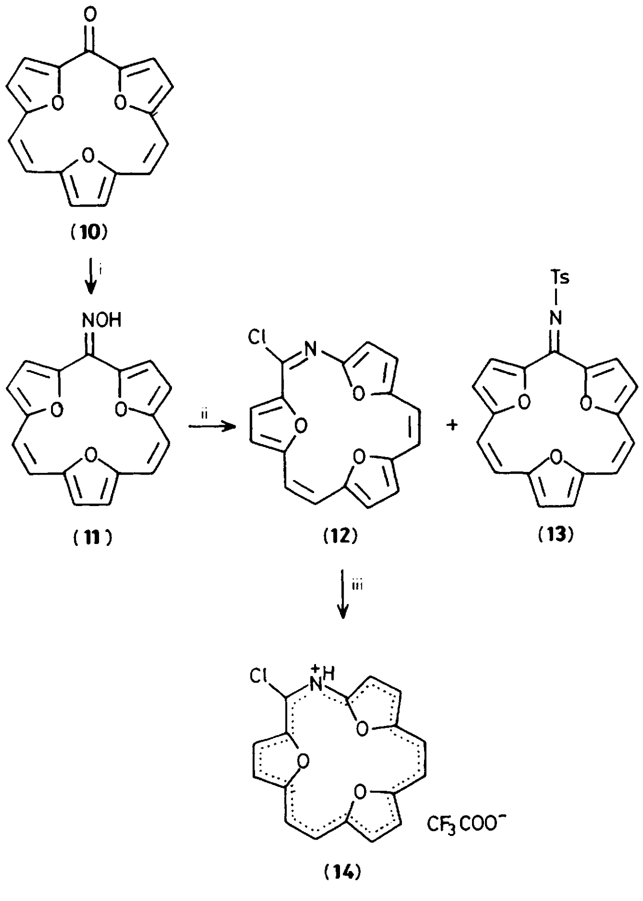
† *Selected spectral data:* (**5**) $\lambda_{max.}$ (KBr) 3390 (ν_{NH}), 1650 cm^{-1} ($\nu_{C=O}$); $\lambda_{max.}$ (CH_2Cl_2) 241 (ε 28 000 dm^3 mol^{-1} cm^{-1}), 280 sh (48 400), 290 (5 300), 301 (38 700), 322 sh (14 200), 348 sh (7 000), and 518 nm (800); ^1H n.m.r. ($CDCl_3$, 100 MHz), δ (Me_4Si) 4.50 (H-3, d, $J_{2,3}$ 10.0 H), 4.81 (H-8, d, $J_{8,9}$ 14.4 Hz), 4.81 (H-14, d, $J_{14,15}$ 14.4 Hz), 5.00 (H-9, d, $J_{8,9}$ 14.6 Hz), 5.39 (d, J_{furan} 3.6 Hz), 5.41 (H-15, d, $J_{14,15}$ 14.6 Hz), 5.60 (1H, d, J_{furan} 3.6 Hz), 5.64 (1H, d, J_{furan} 3.6 Hz), 5.80 (1H, d, J_{furan} 3.6 Hz), 6.12 (H-2, d.d, $J_{1,2}$ 11, and $J_{2,3}$ 10 Hz), and 15.89 (NH, 1H, br, $J_{1,2}$ 11 Hz). (**12**) $\lambda_{max.}$ (CH_2Cl_2) 336 sh (ε 95 400 dm^3 mol^{-1} cm^{-1}), 344 (179 800), 380 (3 300), 404 (5 400), 421 (13 200), 443 (5 700), 484 (1 500), 506 (1 200), 530 (2 600), 556 (1 200), and 580 (3 500); ^1H n.m.r. ($CDCl_3$, 400 MHz), 8.74 (1H, d, J 13.4 Hz), 8.76 (2H, d, J 4.2 and 4.0 Hz), 8.77 (1H, d, J 13.8 Hz), 8.79 (1H, d, J 13.4 Hz), 8.81 (1H, d, J 4.0 Hz), 8.85 (1H, d, J 4.0 Hz), 8.87 (1H, d, J 4.0 hz), 8.88 (1H, d, J 13.8 Hz), and 9.51 (1H, d, J 4.2 Hz). (**14**) ^1H N.m.r. ($CF_3CO_2D/CDCl_3$, 400 MHz) H_{furan}: 9.41 (1H, d, J 4.4 Hz), 9.45 (1H, d, J 4.4 Hz), 9.48 (1H, d, J 4.8 Hz), 9.55 (1H, d, J 4.4 Hz), 9.63 (1H, d, J 4.4 Hz), 10.15 (1H, d, J 4.8 Hz; H_{cis} 9.50 (2H, J 12.8 and J 12.8 Hz), 9.69 (1H, d, J 12.8 Hz), and 9.73 (1H, d, J 12.8 Hz).



Scheme 1. *Reagents and conditions:* i, excess of $NH_2OH{\cdot}HCl$, reflux, 3 h, EtOH; ii, aq. THF, reflux, 4 h, dilute HCl; iii, TsCl–pyridine, room temp.; iv, excess of TsCl–$CHCl_3$, reflux, 4 h.



Scheme 2. *Reagents and conditions:* i, excess of $NH_2OH{\cdot}HCl$, reflux, 3 h, EtOH; ii, TsCl–Et_3N–C_6H_6, room temp.; iii, CF_3CO_2H.

[$\lambda_{max.}$ 548 nm (in n-hexane)] and (7)[9] [530 nm (in n-hexane)], exhibiting $\lambda_{max.}$ at 518 nm (in CH_2Cl_2). We therefore assumed that a delocalized 16π conjugation was able to exist *via* the 'amide linkage.' The ^1H n.m.r. data of (**5**) confirmed this; of the ten annulene protons, nine resonated at δ 4.50—5.85, and the NH proton, which is located inside the ring, resonated at extremely low field (δ 15.9). This showed that (**5**) is clearly paratropic and that the observed high field resonances are comparable with those of (**6**) [δ 3.51—4.95] and (**7**) [δ 4.00—5.00]. This proves convincingly that the keto form (**5a**) and the dipolar form (**5b**) exist as tautomers in order for a delocalized cyclic perimeter to develop as a consequence of the two oxygen bridges. The attempted *O*-alkylation of (**5**) by $[Et_3O]^+BF_4^-$ failed to give the 2-ethoxy-diepoxy[16]annulene (**8a**).

The prolonged refluxing of (**5**) with an excess of tosyl chloride in $CHCl_3$ gave a Friedel–Craft type substitution product (**9**)[10] in 4% yield [m.p. 149—151 °C (EtOH), blue prisms, m/z 407 (M^+)] instead of the expected *O*-tosylate (**8b**). Compound (**9**) proved to be paratropic.

Treatment of triepoxy[17]annulenone (**10**)[11] with $NH_2OH{\cdot}HCl$ gave the oxime (**11**) [m.p. 228—230 °C (EtOH)] in almost quantitative yield as shown in Scheme 2. Treatment of (**11**) with an excess of tosyl chloride in Et_3N–C_6H_6 and the subsequent chromatographic separation (SiO_2, CH_2Cl_2) gave two products: triepoxy-2-chloroaza[18]annulene (**12**)† [m.p. 219—221 °C (benzene–n-hexane), m/z 311 (M^+), 8.0%, from the fast moving band] and triepoxy[17]annulenone *N*-sulphonylimine (**13**) [m.p. 200—202 °C, green prisms (EtOH), m/z 431 (M^+), from the later green band, 15.3%]. That (**13**) possesses a 17-membered skeleton was confirmed by the presence of a paramagnetic ring current, exhibiting resonances for all the outer annulene protons at δ 4.70—5.57 (8H), except for two protons, which resonated at δ 7.01. Conversely, the ^1H n.m.r. data (400 MHz in $CDCl_3$) of (**12**) were entirely consistent with the aromatic structure, exhibiting one furan proton at δ 9.51 (J = 4.0 Hz) and the other nine protons in a very narrow downfield region (δ 8.74—8.88). The observed downfield shifts were comparable with those reported earlier for the triepoxy[18]annulene [δ 8.86 and 8.66 in $CDCl_3$].[1] On protonation (CF_3CO_2D), (**12**) gave the violet cation (**14**)† showing further downfield shifts (δ 9.41—10.15), in agreement with an earlier case where a non-bridged aza[18]annulene[2b] was protonated. The ^1H n.m.r. spectra of (**12**) and (**5**) were not temperature-dependent.

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