Methano-Bridged 14π-Electron Aromatic Annulenes. 2. 5-Methoxy-7,12-methano-6-azabenz[10]annulene and the Benzenesulfonate Ester of 5-Hydroxy-7,12-methano-6-azabenz[10]annulene

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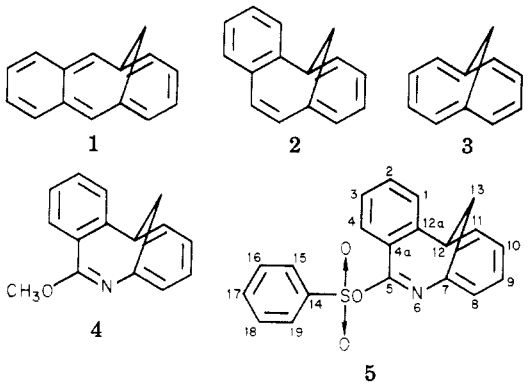
Received February 2, 1981

The syntheses of 5-methoxy-7,12-methano-6-azabenz[10]annulene (**4**) and the benzenesulfonate ester of 5-hydroxy-7,12-methano-6-azabenz[10]annulene (**5**) are described. Compounds **4** and **5** were shown to be delocalized aromatic systems as evidenced by their ^{13}C and ^{1}H NMR chemical shifts. Ester **5** was prepared by Beckmann rearrangement of **7a** (which was available from anion **6** by treatment with *tert*-butyl nitrite). Hydrolysis of **5** with potassium hydroxide followed by alkylation with trimethyloxonium tetrafluoroborate gave the benz[10]annulene **4**.

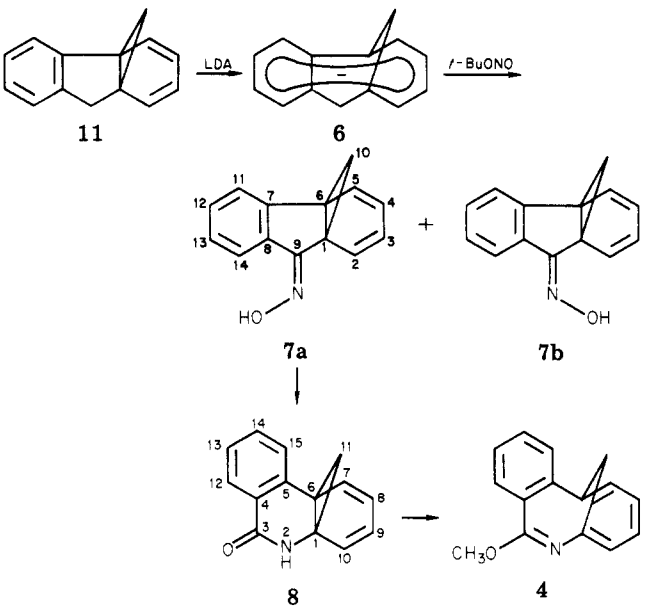
Introduction

Recently Vogel and Schäfer reported the syntheses of the first mono methano-bridged, uncharged 14π-annulenes, 3,4-benzo-1,6-methano[10]annulene (**1**)[2] and 2,3-benzo-1,6-methano[10]annulene (**2**).[3] Proton NMR analysis showed them to be delocalized aromatic systems, although **2** exhibited some bond localization as compared to the parent 10π-system, 1,6-methano[10]annulene (**3**).[4] In connection with a study on the physiological properties of methano-bridged, nitrogen-containing heterocycles, we undertook the synthesis of 5-methoxy-7,12-methano-6-azabenz[10]annulene (**4**) in order to develop a methodology for the construction and manipulation of complex methano-bridged heterocycles. In this paper, we present our methodology for the construction of the 7,12-methano-6-azabenz[10]annulene system and the syntheses of azabenz[10]annulenes **4** and **5**. These two compounds, viewed as aza analogues of 2,3-benzo-1,6-methano[10]annulene, also were of interest with respect to charge delocalization.

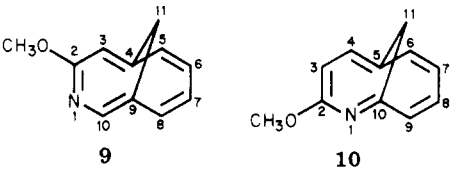


We recently reported the preparation of the 1,6-methanofluorenyl anion **6**[5] and its subsequent reaction with various electrophiles. It seemed likely that anion **6** should react with *tert*-butyl nitrite to give a mixture of oximes, **7a,b**. Separation of the oximes and Beckmann rearrangement of the anti isomer **7a** would give lactam **8**,

Scheme I



which could be transformed to **4** by using standard procedures (Scheme I). This sequence of reactions has been used by Lipa and Helmkamp[6,7,13] to construct the 4,9-methano-1-aza[10]annulene (**9**) and the 5,10-methano-1-aza[10]annulene (**10**) backbones from the appropriate ketones.



Results

Anion **6** was prepared from diene **11** and treated with *tert*-butyl nitrite to give a mixture of oximes **7a** and **7b** in a ratio of 2:1, respectively (see Scheme I). Assignment of **7a** and **7b** as the anti and syn oximes, respectively, followed from observations by Phillips[8] and Crawford[9a]

(1) Address correspondence to this author. Present address: Fluorochem Inc., 680 S. Ayon Ave., Azusa, CA 91702.
(2) Schäfer, R., Ph.D. Thesis, Universitat Köln, 1974.
(3) Tanimoto, S.; Schäfer, R.; Ippen, J.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 613.
(4) Vogel, E.; Roth, H. D. *Angew. Chem.* **1964**, *76*, 145.
(5) Hunadi, R. J.; Helmkamp, G. K. *J. Org. Chem.* **1978**, *43*, 1586. (b) Hunadi, R. J. *Diss. Abstr. Int. B.* **1978**, *38*, 2672-B.
(6) Lipa, W. J. Ph.D. Thesis, University of California, Riverside, CA, 1977.
(7) Lipa, W. J.; Crawford, H. T.; Radlick, P. C.; Helmkamp, G. K. *J. Org. Chem.* **1978**, *43*, 3813.
(8) Phillips, W. D. *Ann. N.Y. Acad. Sci.* **1958**, *70*, 817.

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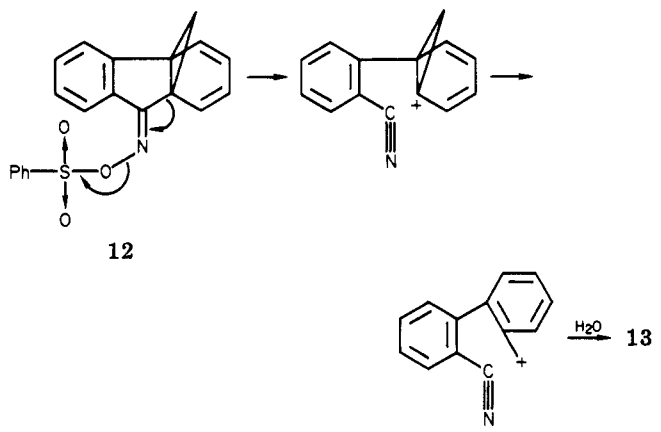
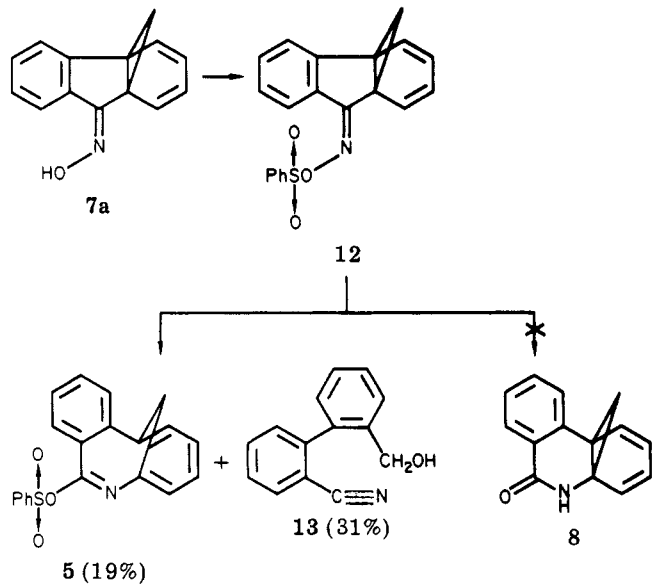
Scheme II

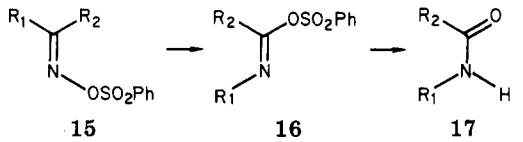


Scheme III

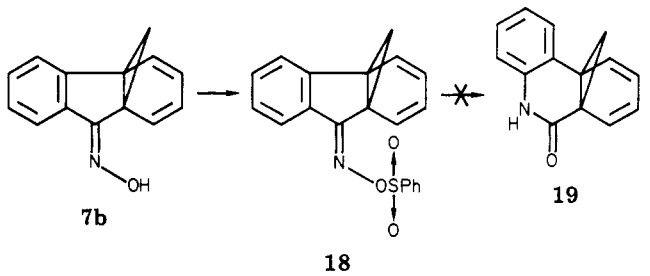


that the protons of nitrosoamines, alkyl nitrites, and aldoximes which were syn to the oxygen atom (H-14 in **7a** and H-2 in **7b**) were shifted downfield in the proton NMR spectrum relative to the proton in the anti isomer (H-2 in **7a** and H-14 in **7b**) by 20–40 Hz.

Treatment of the anti oxime **7a** with sodium hydroxide and benzenesulfonyl chloride gave the benzenesulfonate ester **12** in essentially quantitative yield. After ester **12** was refluxed in aqueous acetone, two compounds were isolated by chromatography. The lower R_f material, which was assigned the structure **13**, is the product arising from an abnormal Beckmann rearrangement. A proposed pathway is shown in Scheme II. The higher R_f material was identified as the benzenesulfonate ester imidate **5** and not the expected lactam **8** (see Scheme III). It has been shown by Oxley and Short[10] that the Beckmann rearrangement of benzenesulfonate esters of oximes proceeds through the imine **16**. In the case of **5**, the hydrolysis to **8** did not occur due to either the stability of the aromatic 14π system or the resistance of the imine to hydrolysis in the absence of acid or base.



When the syn oxime **7b** was treated with sodium hydroxide and benzenesulfonyl chloride, the benzenesulfonate ester **18** was obtained in essentially quantitative yield. This ester proved to be resistant to attempted Beckmann rearrangement. Only starting material was obtained when ester **18** was refluxed in aqueous acetone (40 h) or treated with 2,6-lutidene in refluxing aqueous dioxane (17 h).[9b]

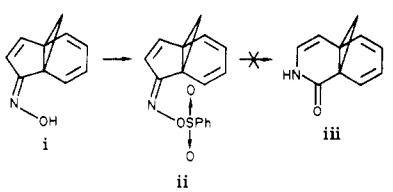


Treatment of the benzenesulfonate ester **5** with potassium hydroxide resulted in the formation of norcaradiene lactam **8** in 77% to nearly quantitative crude yields (the cycloheptatrienyl lactam **20** was not formed[11a]). Subsequent reaction of the lactam **8** with trimethyloxonium tetrafluoroborate[11b] gave the desired imino ether **4** in 34% yield. The structure of **4** was verified by ^1H and ^{13}C NMR spectroscopy (proton NMR data are given in Table I).

Discussion

Comparison of the proton NMR spectrum of ester **5** with that of 2,3-benzo-1,6-methano[10]annulene (**2**) indicates that both systems are similar with respect to charge delocalization. Consequently ester **5** can be considered a delocalized aromatic system (the chemical shift positions of C-8 and C-11 are reversed in **5** as compared to the analogous protons in **2**; protons H-11b and H-11a of **2** are found at δ 1.38 and −0.06, respectively, as compared to δ 1.27 and 0.25 for H-13b and H-13a of **5**; $J_{11a,11b}$ for **2** is 9 Hz, $J_{13a,13b}$ for **5** is 9.37 Hz). The effects of benzoannelation can be ascertained by comparison of ester **5** with a suitable

(9) (a) Crawford, H. T. Ph.D. Thesis, University of California, Riverside, CA, 1974. (b) Crawford[9a] also observed that syn oxime i did not undergo Beckmann rearrangement while the corresponding anti oxime did rearrange. Although a phenyl group is usually a good migrating group in Beckmann rearrangements, the failure of the syn oxime **7b** to undergo rearrangement may be due to structural or electronic factors inherent to the tricyclo[4.3.1.0^{1,6}]decane skeleton.



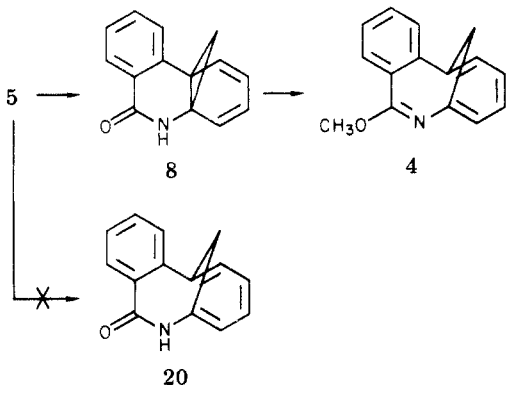
(c) The assignment of H-11b and H-11a in structure **21** was accomplished by the inspection of the long-range coupling constants. H-11b appears as a doublet of triplets due to W coupling with H-6 and H-9 while H-11a appears as a double doublet due to W coupling with H-4.[9a] Similarly, H-11b of **5** is a broadened doublet due to W coupling with H-8 and H-11, and H-11a is a sharp doublet due to the absence of protons in the heterocyclic ring.

(10) Oxley, P.; Short, W. F. *J. Chem. Soc.* **1948**, 1514.

(11) (a) Since 1,6-methano-7,8,9,10-tetrahydronaphthalene exists solely as the cycloheptatriene structure, one would expect the hydrolysis of ester **5** to give cycloheptatriene **20**. In contrast, Lipa, Helmkamp, and Vogel have shown that this is not always true for lactams incorporated into the 4,9-methano-1-aza[10]annulene and 5,10-methano-1-aza[10]annulene systems.[7,13,14] Apparently, in some cases, the lactam functionality imposes structural constraints upon the skeleton which favor the norcaradiene form. (b) Paquette, L. A.; Berk, H. C.; Ley, S. V. *J. Org. Chem.* **1975**, *40*, 902.

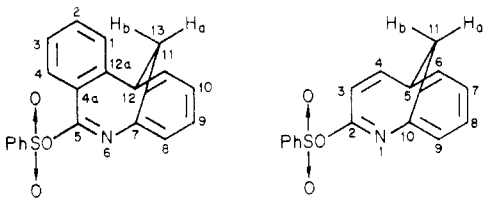
(12) Schäfer-Ridder, M.; Wagner, A.; Schwamborn, M.; Schreiner, H.; Devrout, E.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 853.

(13) Lipa, W. J.; Helmkamp, G. K., unpublished work.



8 4 20

10π system. Since the benzenesulfonate ester of 2-hydroxy-5,10-methano-1-aza[10]annulene (**21**) has been prepared by Crawford,[9a] we can assess the relative degree of aromaticity in **5** by comparing the chemical shifts of the bridge protons with those of **21**.

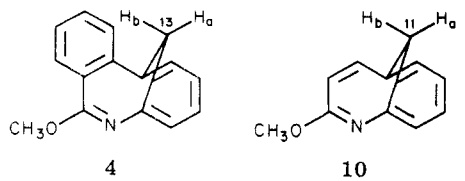


5 21

As shown by Vogel,[14] the chemical shifts of the bridge protons reflect the presence and degree of aromaticity in methano-bridged systems. Protons H-11b and H-11a of **21** were found at δ −0.16 and 0.48 ($J_{11a,11b}$ = 9 Hz).[9c] Since H-13b and H-13a in **5** were found at δ 1.27 and 0.25, respectively, it can be seen that there has been a significant weakening of the diamagnetic ring current caused by benzoannelation. This is the same type of effect observed by Vogel[3] when 1,6-methano[10]annulene (**3**) was benzoannelated at the 2,3-position to produce 2,3-benzo-1,6-methano[10]annulene (**2**). Since δ (H-13a) is much greater than δ (H-13b) in **5** as compared to **21**, it is possible that there is double bond fixation as drawn for **5**.

Additional evidence regarding the structure of **5** can be procured from its UV and ^{13}C NMR spectra. The UV spectrum shows λ_{max} 255 nm (ϵ 36 320), 296 (14 680), 340 (sh, 4930), 384 (6220), indicative of a 14π heteroaromatic system with a shift toward longer wavelengths as compared to 5,10-methano-1-aza[10]annulene.[12] In the ^{13}C NMR spectrum, the bridge carbon C-13 is found at δ 38.44, which is typical of a carbon located over an aromatic ring (the C-11 shift of 1,6-methano[10]annulene is δ 34.8,[15] while that of the norcaradiene lactam **8** is δ 25.37).

We also can ascertain the effects of benzoannelation on annulene **4** by comparing it to 2-methoxy-5,10-methano-1-aza[10]annulene (**10**) prepared independently by Vogel[12]



4 10

and Lipa[13] (see Table I). In **10**, the proton shifts of H-11b and H-11a are δ 0.22 and 0.40, respectively, as compared to δ 1.65 and 0.32 for H-13b and H-13a of **4** ($J_{11a,11b}$ for **4** is 9.37 Hz, $J_{13a,13b}$ for **10** is 9.0 Hz). These chemical shifts suggest that there is even more double bond fixation in **4** than ester **5** since H-13b has moved further downfield. It is possible that the electronic effects caused by the benzenesulfonate ester in **5** are responsible for this change. The shifts of the remaining protons in **10** are similar to those of **4**, indicating that, except for more double bond fixation, the charge delocalization over both systems (**4** and **5**) is similar.

Again, additional information concerning the aromaticity of **4** can be gained from the examination of the ^{13}C NMR and UV spectra of this compound. As with ester **5** the ^{13}C NMR shift of C-13 of **4**, i.e., δ 39.26, is typical for a carbon located over an aromatic ring. The UV spectrum of **4** shows λ_{max} 253 nm (ϵ 29 810), 277 (sh, 13 310), 287 (sh, 12 290), and 370 (5570), which is similar to that of **5** and **10** except that in **10** the first band is at 236 nm with a lower extinction coefficient (ϵ 21 300). The last three bands of **4**, as compared to **5**, are shifted to lower wavelength, indicating that there is better delocalization in ester **5**. Nevertheless, the UV spectrum of azaannulene **4** is indicative of a heteroaromatic system.

Conclusions

We have shown that azabenzannulenes **4** and **5** are indeed aromatic systems and similar to the parent system 2,3-benzo-1,6-methano[10]annulene (**2**). This conclusion was reached after examination of ^{1}H and ^{13}C NMR as well as UV data. The data presented in this paper support the concept that benzoannelation tends to decrease the aromaticity of methano-bridged systems as judged by the chemical shifts of the bridge protons. Also it was shown that the C-13 NMR shift of the bridge carbon is a very useful tool in determining whether a system is in a norcaradiene or cycloheptatriene form.

Experimental Section

Spectra were obtained as follows: 60-MHz NMR spectra on Varian A-60, A-60D, T-60, or EM-360 spectrometer; 90-MHz ^{1}H NMR and 22.63-MHz ^{13}C NMR spectra on a Brüker HX-90 FT multinuclear spectrometer; infrared spectra on a Perkin-Elmer Model 137 spectrometer; ultraviolet spectra on a Cary-14 spectrometer; mass spectra on a Finnigan mass spectrometer. High-resolution mass spectra were recorded on a AEI MS-9 spectrometer (University of California, Los Angeles). Melting points, obtained on a Thomas-Hoover capillary melting point apparatus, are uncorrected. Since elemental compositions were determined by high-resolution mass spectroscopy, the chemical purity of new compounds was established by spectroscopic and chromatographic techniques (details regarding this data are given in each case).

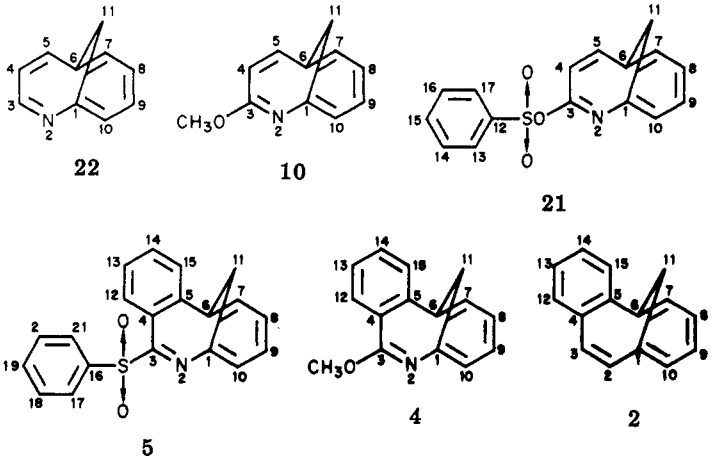
Grace-Davison grade 62 neutral silica gel, EM precoated PLC plates (silica gel 60 F-254), and 0.25-mm plates (EM silica gel 60 F-254) were used for preparative-scale chromatography. Analytical thin-layer chromatography was performed with EM precoated TLC sheets (silica gel F-254, 0.25 mm on plastic support).

Tetrahydrofuran was redistilled from potassium benzophenone ketyl under nitrogen just prior to use; hexane and methylene chloride were distilled; all other solvents were used as obtained from Mallinckrodt.

***anti*-9-Oximino-1,6-methanofluorene (7a) and *syn*-9-Oximino-1,6-methanofluorene (7b).** To a stirred solution of 702 mg (3.90 mmol) of diene **11** in 30 mL of tetrahydrofuran under argon were added successively 1.4 mL (9.75 mmol) of diisopropylamine and 1.4 mL (3.90 mmol) of HMPA via syringe. This solution was cooled to 0 °C and 5.0 mL (7.80 mmol) of 1.56 M *n*-butyllithium/hexane solution was added (via syringe). Stirring at 0 °C was continued for 25 min after which 789 mg (7.80 mmol) of *tert*-butyl nitrite in 5 mL of tetrahydrofuran was added via syringe. This solution was stirred at 0 °C for 75 min and at room temperature for 30 min. Saturated ammonium chloride solution

(14) (a) Vogel, E. *Spec. Publ.-Chem. Soc. No. 21*, 113–47. (b) Vogel, E. *Robert A. Welch Found. Proceed.* **1968**, *12*, 215.
(15) Günther, H.; Schmickler, H.; Jikeli, G. *J. Magn. Reson.* **1973**, *11*, 344.

Table I. ^{1}H NMR Data for Methano-Bridged Annulenes[a]



22 10 21 5 4 2

proton	22[c,g]	10[d,g,h]	21[d,i]	5[e]	4[e]	2[f,j]
2						7.33 (J = 11.05)
3	8.23 (d, J = 6.3)					7.04 (J = 11.05)
4	6.50 (dd, J = 9.0, J' = 6.3)	6.06 (d, J = 10.2)	6.29 (d, J = 9.5)			
5	7.38 (d, overlapped with H-7)	7.47 (d, J = 10.2)	7.56 (d, J = 9.5)			
7	6.60-7.20 (m)	6.70-7.30 (m)	6.92 (m)	6.52 (m)	6.57 (m)	7.34
8	6.60-7.20 (m)	6.70-7.30 (m)	6.92 (m)	7.04 (m)	7.00 (m)	7.26
9	6.60-7.20 (m)	6.70-7.30 (m)	6.92 (m)	7.04 (m)	7.00 (m)	7.26
10	7.38 (d, overlapped with H-5)	6.70-7.30 (m)	7.58 (m)	7.29 (m)	7.19 (m)	6.99
11	−0.40 and 0.65 (AX system, J = 8.4)	0.22 and 0.40 (AB system, J = 9.0)	−0.16 and 0.48 (dt, J = 9, J' = ~2; dd, J = 9, J' = ~2)	0.25 and 1.27 (d, J = 9.37)	0.32 and 1.65 (d, J = 9.09)	−0.06 and 1.38 (d, J = 9.0)
12				8.21 (m)	8.19 (dd, J = 7.92, J' = 1.76)	7.85
13			8.05 (m)	7.58 (m)	7.59[b] (dt, J = 7.18, J' = 1.76)	7.55
14			7.58 (m)	7.58 (m)	7.41[b] (dt, J = 7.47, J' = 1.76)	7.50
15			7.58 (m)	8.44 (m)	8.49 (dd, J = 7.77, J' = 1.91)	8.34
16			7.58 (m)			
17			8.05 (m)	8.21 (m)		
18				7.58 (m)		
19				7.58 (m)		
20				7.58 (m)		
21				8.21 (m)		
OCH_3		4.00 (s)			4.05 (s)	

[a] The numbering convention used in this table is based on the compounds being tricyclo[4.4.1.0^{1,6}]undecanes. Although this method does not conform to the Chemical Abstracts numbering convention, it offers the advantage that all six annulenes can be directly compared to one another since they are all numbered in the same fashion. Chemical shifts are in δ relative to Me_4Si; multiplicities and coupling constants, J and J', (in hertz) are given in parentheses. [b] Assignments can be interchanged. [c] 90-MHz spectrum run in CCl_4. [d] 60-MHz spectrum run in $CDCl_3$. [e] 90-MHz spectrum run in $CDCl_3$. [f] 100-MHz spectrum run in acetone-d_6. [g] Reference 12. [h] Reference 13. [i] Reference 9a. [j] Reference 3.

was added and the product was extracted into ether. The combined organics were washed successively with dilute hydrochloric acid, saturated sodium bicarbonate solution, and water. The ether extracts were dried over $MgSO_4$, filtered, and concentrated to yield 924 mg of a viscous orange oil (2:1 mixture of **7a** and **7b**). This crude product was chromatographed twice on silica gel to yield 138 mg (17%) of anti oxime **7a**, 257 mg (32%) of a mixture of **7a** and **7b**, and 182 mg (22%) of syn oxime **7b** (the first chromatography column was eluted with benzene and the second with 6% ether/94% hexanes, 71% total chromatographed yield).

7a: light-yellow oil; R_f 0.66 (50% ether/50% benzene); IR (film) 3.12 (OH), 3.28, 3.48, 6.09 (C=N), 6.27, 6.90, 10.55, 13.25, 14.01, 15.00 μm; NMR ($CDCl_3$/Me_4Si) δ 9.27–9.65 (br s, 1 H, OH), 8.35–8.67 (m, 1 H, H-14), 7.09–7.79 (m, 3 H, aromatic), 6.33 (unsymmetrical A_2B_2 pattern, 4 H, olefinic), 2.02 (d, J = 3.6 Hz, 1 H, H-10b), 0.59 (d, J = 3.6 Hz, 1 H, H-10a); mass spectrum, m/e (relative intensity) 209 (61), 192 (66), 191 (41), 165 (100); exact mass calcd for $C_{14}H_{11}NO$ 209.0840, found 209.0834.

7b: light-orange solid; mp 115.5–121.0 °C after sublimation (110 °C, 0.1 mm); R_f 0.66 (50% ether/50% benzene); IR (film) 3.22 (OH), 3.39, 3.60, 6.08 (C=N), 6.28, 6.82, 6.88, 9.99, 10.57, 13.14, 13.75, 14.09, 14.72 μm; NMR ($CDCl_3$/Me_4Si) δ 9.40–9.84 (br s, 1 H, OH), 7.02–7.85 (m, 5 H, aromatic and H-2), 6.41–6.80 (m, 1 H, vinyl), 6.24 (m, 2 H, vinyl), 2.20 (d, J = 3.6 Hz, 1 H, H-10b), 0.60 (d, J = 3.6 Hz, 1 H, H-10a); mass spectrum, m/e (relative intensity) 209 (15), 190 (16), 165 (18), 119 (94), 117 (100); exact mass calcd for $C_{14}H_{11}NO$ 209.0840, found 209.0835.

Attempted Preparation of 3-aza-2-oxo-4,5-benzotricyclo[4.4.1.0^{1,6}]undeca-4,7,9-triene (19) (Preparation of the Benzenesulfonate Ester of *syn*-9-Oximino-7,8-benzotricyclo[4.3.1.0^{1,6}]deca-2,4,7-triene (18)). To a 0 °C stirred solution of 54 mg (0.258 mmol) of the syn oxime **7b** in 10 mL of tetrahydrofuran under nitrogen were added successively 0.19 mL (0.387 mmol) of 8.05% aqueous sodium hydroxide and 76 mg (0.430 mmol) of benzenesulfonyl chloride in 3 mL of tetrahydrofuran. After being stirred for 1 h at 0 °C, the solution was allowed to warm to room temperature and stirred at this temperature for 5 h. Approximately 10 mL of water was added and the organics were extracted into methylene chloride and washed with water (twice) and saturated sodium chloride solution. Drying over

$MgSO_4$ followed by filtration and concentration gave 100 mg of **18** and benzenesulfonyl chloride (essentially a quantitative yield of **18**). Recrystallization of **18** from 30% ether/70% hexanes gave a light-yellow, crystalline solid: mp 170–172 °C dec; IR (KBr) 6.16 (C=N), 6.33, 7.38 (O=S=O), 8.46 (O=S=O), 9.17, 11.87, 12.41, 13.77, 14.03, 14.65, 14.94 μm; NMR ($CDCl_3/Me_4Si$) δ 8.10 (m, 2 H), 6.87–7.87 (m, 8 H), 6.44–6.87 (m, 1 H), 5.85–6.21 (m, 2 H), 2.16 (d, J = 4 Hz, 1 H), 0.60 (d, J = 4 Hz, 1 H).

The crude benzenesulfonate ester **18** (100 mg, 0.258 mmol) was dissolved in 16 mL of acetone. To this solution was added 16 mL of distilled water and the mixture was refluxed under nitrogen for 10 h. The solution was cooled to room temperature and the organics were extracted into methylene chloride and washed with water. The methylene chloride extracts were dried over $MgSO_4$, filtered, and concentrated to give 78 mg (87%) of recovered **18** as evidenced by proton NMR ($CDCl_3/Me_4Si$) analysis. Refluxing the ester (78 mg) in 45% aqueous acetone for an additional 40 h gave 60 mg (68%) of recovered starting material **18**.

Benzenesulfonate Ester of 5-Hydroxy-7,12-methano-6-azabenz[10]annulene (5). A 0 °C stirred solution of 100 mg (0.478 mmol) of anti oxime **7a** in 10 mL of tetrahydrofuran under nitrogen was treated successively with 0.36 mL (0.798 mmol) of 8.05% aqueous sodium hydroxide and 138 mg (0.782 mmol) of benzenesulfonyl chloride dissolved in 5 mL of tetrahydrofuran. Stirring was continued at 0 °C for 1 h and at room temperature for 5 h. After the addition of ~5 mL of water, the reaction mixture was extracted into methylene chloride and washed with water and saturated sodium chloride solution. The extracts were dried, filtered, and concentrated to yield 184 mg (110% crude yield, contains benzenesulfonyl chloride) of **12** as a light-brown solid: IR (film) 6.19 (C=N), 7.33 (O=S=O), 8.54 (O=S=O) μm; NMR ($CDCl_3/Me_4Si$) δ 7.91–8.35 (m, 3 H), 7.04–7.86 (m, 6 H), 6.23–6.73 (m, 2 H), 5.75–6.15 (m, 2 H), 1.94 (d, J = 4 Hz, 1 H), 0.52 (d, J = 4 Hz, 1 H).

A mixture of 184 mg (0.478 mmol) of crude **12**, 17 mL of acetone and 16 mL of water was heated to vigorous reflux under nitrogen for 9 h. After cooling to room temperature, the reaction mixture was extracted with methylene chloride and washed with water. Drying over $MgSO_4$ followed by filtration and solvent removal gave 102 mg of a viscous oil. This crude material was subjected to preparative thick-layer chromatography, eluting with 30% ethyl acetate/70% hexanes (after the plate was run up four times, two major bands were obtained). There was isolated 31 mg (19%) of **5** as a light-tan solid: mp 83–85 °C dec (sealed capillary) after recrystallization from hexanes and diethyl ether; R_f 0.40 (30% ethyl acetate/70% hexanes); IR (film) 6.28 (C=N), 6.35, 6.95, 7.31 (O=S=O), 8.25 (O=S=O), 8.39, 8.51, 8.58, 9.79, 12.38, 13.16, 13.74, 14.61 μm; 90-MHz NMR data are given in Table I; ^{13}C NMR ($CDCl_3/Me_4Si$) δ 148.18 (s), 143.59 (s), 138.50 (s), 134.59 (d), 131.19 (d), 129.65 (d, 3 C), 129.46 (d, 2 C), 127.52 (d), 126.77 (d), 126.61 (d), 125.55 (d), 125.10 (d), 117.12 (s), 107.03 (s), 103.96 (s), 38.44 (t); mass spectrum, m/e (relative intensity) 349 (7), 208 (62), 180 (73), 152 (62), 77 (100); UV (THF) 255 (ε 36 320), 296 (14 680), 340 (sh, 4930), 384 nm (6220); exact mass calcd for $C_{20}H_{15}NO_3S$ 349.0772, found 349.0786; exact mass calcd for $C_{14}H_{10}N$ (loss of benzenesulfonate ester) 192.0813, found 192.0809.

There was also obtained 31 mg (31%) of the nitrile alcohol **13** as a light-yellow oil: R_f 0.12 (30% ethyl acetate/70% hexanes); IR (film) 3.03 (OH), 3.41, 3.55, 3.61, 4.58 (CN), 6.32, 6.85, 7.00, 13.08 μm; NMR ($CDCl_3/Me_4Si$) δ 7.14–7.91 (m, 8 H), 4.51 (br s, 2 H), 1.98 (br s, 1 H); mass spectrum, m/e (relative intensity) 209 (31), 180 (100), 77 (27); exact mass calcd for $C_{14}H_{11}NO$ 209.0840, found 209.0834.

2-Aza-3-oxo-4,5-benzotricyclo[4.4.1.0^{1,6}]undeca-4,7,9-triene (8). To a solution of 20 mg (0.058 mmol) of ester **5** in 10 mL of anhydrous methanol was added 96 mg (1.68 mmol) of potassium hydroxide. The solution was stirred under nitrogen at the reflux temperature for 70 min. After the solution cooled to room temperature, saturated ammonium chloride solution and methylene chloride were added. The organic layer was washed twice with saturated ammonium chloride solution, dried over $MgSO_4$, filtered, and evaporated. Preparative thin-layer chromatography of the residue yielded 7.2 mg (60%) of **8** as a light-yellow oil which subsequently solidified: mp 135.5–139.5 °C; R_f 0.18 (20% ethyl acetate/80% methylene chloride); IR (film) 3.27 (NH), 3.41, 3.52, 6.02, 6.25 (C=O), 6.87, 7.24, 13.23, 13.52, 13.88 μm; 90-MHz NMR ($CDCl_3/Me_4Si$) δ 8.87 (dd, J = 7.77 Hz, J' = 1.61 Hz, 1 H, H-15), 8.73 (br s, 1 H, NH), 8.35 (dd, J = 7.69 Hz, J' = 1.39 Hz, 1 H, H-12), 8.06 (td, J = 7.44 Hz, J' = 1.51 Hz, 1 H, H-13 or H-14), 7.83 (td, J = 7.40 Hz, J' = 1.61 Hz, 1 H, H-14 or H-13), 7.20 (m, 1 H, H-10), 6.66 (m, 3 H, H-7,8,9), 1.73 (d, J = 5.35 Hz, 1 H, H-11b), 0.64 (d, J = 5.35 Hz, 1 H, H-11a); ^{13}C NMR ($CDCl_3/Me_4Si$) δ 163.12 (s), 142.19 (s), 132.33 (d), 130.14 (d), 126.53 (s), 126.39 (d), 126.26 (d), 124.99 (d), 123.62 (d), 122.11 (d), 121.59 (d), 58.64 (s), 48.56 (s), 25.37 (t); UV (THF) 236 (ε 12 320), 254 (sh, 9070), 333 nm (sh, 1790); exact mass calcd for $C_{14}H_{11}NO$ 209.0840, found 209.0834.

5-Methoxy-7,12-methano-6-azabenz[10]annulene (4). A mixture of 20 mg (0.096 mmol) of lactam **8**, 58 mg (0.383 mmol) of trimethyloxonium fluoroborate, and 5 mL of methylene chloride was stirred under nitrogen at room temperature for 10 h. To this was added 10 mL of aqueous potassium carbonate, and stirring was continued for an additional 15 min. The organic material was extracted into methylene chloride, washed once with water, and dried over $MgSO_4$. Evaporation of the solvent left 15 mg (71%) of a green oil which was purified by preparative thin-layer chromatography on silica gel. Elution with 10% ethyl acetate/90% hexanes yielded 7 mg (34%) of **4** as a light-yellow oil: R_f 0.48 (10% ethyl acetate/90% hexanes); IR (film) 3.47, 3.55, 3.68, 6.30, 6.35 (C=N), 7.78, 8.10, 8.13, 9.25, 13.78, 13.83 μm; 90-MHz NMR ($CDCl_3/Me_4Si$) data are given in Table I; ^{13}C NMR ($CDCl_3/Me_4Si$) δ 129.66 (d), 129.04 (d), 126.72 (d), 125.48 (d), 124.75 (d), 124.16 (d), 123.32 (d), 114.56 (d), 110.68 (s), 105.42 (s), 53.95 (q), 39.26 (t) (other 3 quarternary carbons not observed); UV (THF) 253 (ε 29 810), 277 (sh, 13 310), 287 (sh, 12 290), 370 nm (5570); exact mass calcd for $C_{15}H_{13}NO$ 223.0997, found 223.0984.

Acknowledgment. We gratefully acknowledge financial support of this work by the National Institute of Health (Pharmacology Toxicology Program) through Research Grant GM MH 20602.

Registry No. 4, 65487-66-3; **5**, 65487-65-2; **7a**, 77495-68-2; **7b**, 77495-69-3; **8**, 77495-70-6; **11**, 19540-84-2; **12**, 77495-71-7; **13**, 77495-72-8; **18**, 77495-73-9.