

THE SYNTHESIS OF 6,7-BENZO-4,9-OXIDO[11]-ANNULENONE AND AROMATIC 6,7-BENZO-4,9-OXIDO[11]ANNULENYL CATIONS¹

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Abstract—The titled annulenone **6**, the first benz-annulated 11-membered fully conjugated ketone, has been prepared by the aldol type condensation of 3-benzoxepin-2,4-dialdehyde **3** and dimethyl acetone-dicarboxylate. Some evidence for the nonaromatic character of **6** could be obtained from the NMR and IR spectra as well as protonation behaviour of **6**.

The NMR spectrum of **6** in conc H₂SO₄ confirmed the presence of an aromatic 1-hydroxy-6,7-benzo-4,9-oxido[11]annulenyl cation **7**. 6,7-Benzo-4,9-oxido-1-hydroxy-1-homo[10]annulene **11** was prepared by the NaBH₄ reduction of **6**. The treatment of **11** with CF₃COOH regenerated another completely delocalized [11]annulenyl cation **12**. The pK_R⁺ of **12** was obtained as -4.1, spectrophotometrically. The electronic spectra of these novel cations (**7** and **12**) were found to be similar to those of 4,5-(2',3'-naphtho)tropylium cations (**13a** and **13b**), respectively.

According to Sondheimer's classification,^{3a,b} "annulenones"^{3c} (fully conjugated monocyclic ketones) **1a** and **1b** are interesting class of compounds belonging to "odd numbered annulenes". If planar, [4n + 3]annulenones **1a** are expected to be diatropic,^{3a} and [4n + 1]annulenones **1b** are expected to be paratropic.^{3a} Cyclopropenones,⁴ cyclopentadienones⁵ and tropone⁶ are well known members

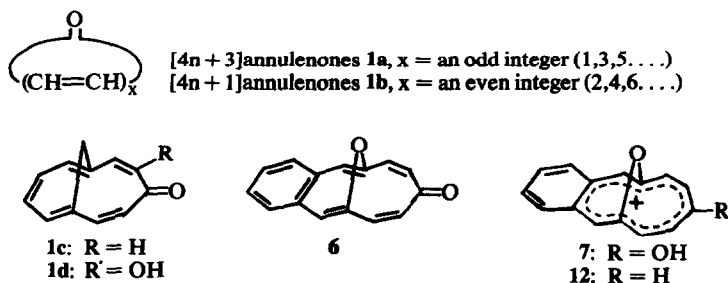
representing [3]-, [5]- and [7]annulenones, respectively. In recent years, [9]-,⁷ [11]-,^{8,9} [13]'^{3c,10} [15]-^{11,12} and [17]-^{13,14} annulenones have been reported. Nonalternant polycyclic ketones such as benzocycloheptatriene-4'-ones **10**¹⁵ and 5-H-cyclopenta[cd]phenalen-5-one¹⁶ may also enter into the same category, since these compounds are considered as [11]- and [13]-annulenones in which zero bridges hold the perimeter in a rigid geometry. However, only a few [4n + 3]annulenones **1a** have been found to be diatropic in their ground states.†

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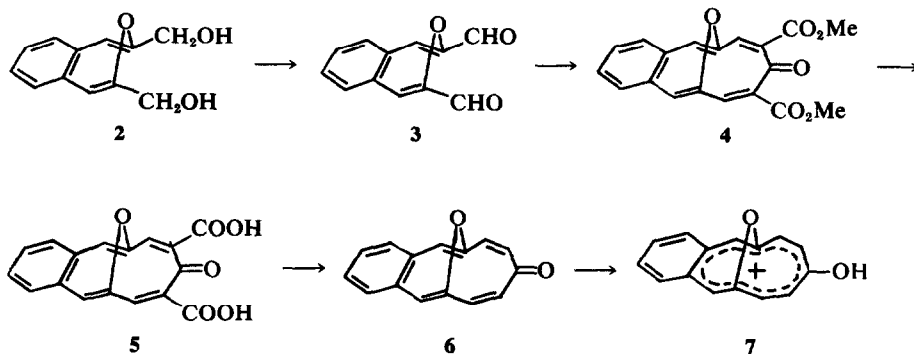
†Although tropone was initially regarded as an aromatic annulenone, its aromatic character has been seriously questioned by Bertelli.⁶ On the other hand, tropolone is an aromatic hydroxy[7]annulenone. 4,9-Methano[11]annulenone **1c** is not diatropic,⁸ but some derivatives of benzocycloheptatriene-4'-one **10** are proved to be diatropic by physical criteria.¹⁵ Tetramethylene-2,6,8,14-tetrahydro[15]annuleneone is diatropic.¹¹ Recently reported keto-phlorins, which were obtained as porphin oxydation products [A. H. Jackson, G. W. Kenner, and K. M. Smith, *J. Chem. Soc. (C)*, 302 (1968); P. S. Clezy, A. J. Liepa, and G. A. Smythe, *Aust. J. Chem.* **23**, 603 (1970)], are considered as aza[19]annulenones.

Very recently, 4,9-methano[11]annulenone **1c**⁸ and 2-hydroxy-4,9-methano[11]annulenone **1d**⁹ have been reported by Vogel *et al.* We now describe the synthesis of 6,7-benzo-4,9-oxido[11]annulenone **6**, together with aromatic 6,7-benzo-4,9-oxido[11]annulenyl cations **7** and **12**.

The starting material was 3-benzoxepin-2,4-dialdehyde **3**, which was prepared by oxidation of 2,4-bis(hydroxymethylene)-3-benzoxepin **2**. Despite a report¹⁷ to the contrary, the oxidation afforded the dialdehyde **3** in 50% yield. The con-



SCHEME 1



SCHEME 2

condensation of 3 with dimethyl acetonedicarboxylate in the presence of piperidinium acetate gave 6,7-benzo-2,11-dicarbomethoxy-4,9-oxido[11]annulenone 4 in 55% yield. The structure was assigned on the basis of elemental analysis and spectral properties. The mass spectrum of 4 exhibited a molecular ion peak at m/e 338, together with other fragment ions at m/e 310, 279, 251. The alkaline hydrolysis of 4 yielded the corresponding dicarboxylic acid 5 in 97% yield, as yellow prisms, which decomposed at 210–230° on an attempted mp determination to give the annulenone 6. A pyrolysis of 5 followed by the spontaneous sublimation yielded an analytically pure sample of annulenone 6, m.p. 225°, lemon yellow needles. The annulenone 6 was also prepared in 80% yield by the copper chromite catalysed decarboxylation of 5. The structural assignment was based on the following spectroscopic evidence. The NMR spectrum shows 4H quartet at τ 3.09 and 3.90 ($J = 11$ Hz), due to the pairs of the newly introduced *cis*-olefinic protons, 2H singlet at τ 3.28 due to the H-5, H-8 protons, and 4H multiplet at τ 2.3–2.7 due to the benzenoid protons. The mass spectrum exhibited a strong molecular ion at m/e 222, and a next highest peak at m/e 194 ($M-28$). The occurrence of ($M-CO$) ion can be commonly detected in similarly disposed carbonyl compounds such as tropone,¹⁹ tropolone, benzocycloheptatriene-4'-ones 10,¹⁵ and 4,9-methano[11]annulenone 1c.⁸ The annulenone 6 is a thermally stable compound, and can be kept for long time when pure. As seen from Fig 1, the UV spectrum is very similar to that given by 4,5-(2',3'-naphtho)-tropone 8.²⁶

Annulenone 6 being a derivative of [11]annulenone ($n = 2$ member in $[4n + 3]$ annulenone), may sustain a diamagnetic ring current in an applied magnetic field due to the cyclic delocalization of the carbonyl positive charge. According to the aromatic ring current concept,¹⁸ the observable down field shifts of all the ring protons provide a criterion for such an induced ring current, when these shifts are compared with those of suitable models in which there is no ring current. For comparative purposes

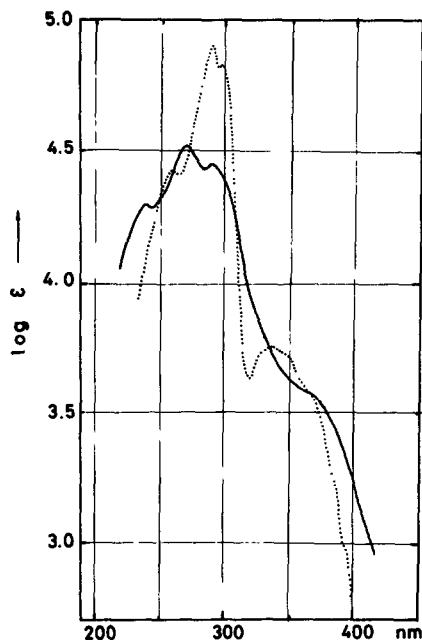
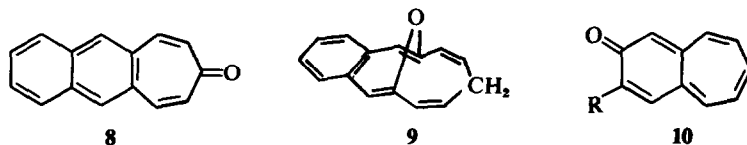


Fig 1. Electronic spectra of 6,7-benzo-4,9-oxido[11]annulenone 6 (— in MeOH) and 4,5-(2',3'-naphtho)tropone 8 (····· in EtOH). The spectrum of 8 was reproduced on the basis of the original spectrum, reported by G. Naville, H. Strauss and E. Heilbronner.²⁶

we chose two models, *i.e.*, 6,7-benzo-4,9-oxido-1-homo[10]annulene 9,²⁰ and 4,9-methano[11]annulenone 1c.⁸ The former which was obtained by a double Wittig reaction of 3 and trimethylene-bis(triphenylphosphonium bromide),²¹ is expected to have no ring current, because homoaromatic cyclic delocalization is of no importance in neutral molecules.²² The polyenone character of the latter compound 1c was firmly established by an analysis of the NMR coupling constants,⁸ as well as by X-ray analysis.²³

The annulene protons of 6 have each shifted to the down-field by $\sim \tau$ 0.6, as compared with those of model 9. However, the NMR spectrum of 6 also



exhibits closely similar chemical shifts with those of the latter model 1c.⁸ Therefore, it should be noted that the shifts of the H-2, H-11 and H-3, H-10 protons to a lower field are not connected directly with the ring current, but with local diamagnetic anisotropy due to the C=O group [Fig 2a and 2d, Table 1].

Further support for the nonaromatic character of 6 can be obtained from the C=O frequency, which is well correlated with the bond order of the C=O group. Compound 6 shows a strong absorption at 1642 cm⁻¹, which was compared with 1582 cm⁻¹ for tropone (CH₂Cl₂), 1582 cm⁻¹ for 5-hydroxy-benzocycloheptatriene-4'-one 10 (R=OH)¹⁵ (CHCl₃), and 1607 cm⁻¹ for 4,9-methano[11]annulenone 1c⁸ (neat). The relatively high frequency of 6 indicated that 6 does not sustain a substantial degree of single bond character in the C=O group. On this basis, we may infer that bond orders of the >C=O group in

these [11]annulenones decrease in the order of 10 (R=OH) > 1c > 6.

The nonaromatic character present in the 6,7-benzo-4,9-oxido[11]annulenone 6 is also evidenced by the fact that the protonation of this compound by CF₃COOH occurs on the C=O oxygen. As in unsaturated ketones, the NMR spectrum recorded in CF₃COOH was not much altered except that all the observable peaks become broad,²⁴ and no remarkable down-field shifts were observed [Fig 2b]. Thus, all the physical evidence discussed leads to a conclusion that 6,7-benzo-4,9-oxido[11]annulenone 6 possesses no appreciable degree of aromatic character, in spite of its small deviation from planarity, and of its eliminated mobility.

If planar, the basicity of a [4n+3]annulenone is dominated by the ease with which it reversibly adds a proton to form a delocalized hydroxy[4n+3]annulenylium cation. A completely delocalized 1-hydroxy[11]annulenylium cation 7 was not regenerated until concentrated H₂SO₄ was used for the protonating acid. Thus, upon treatment with H₂SO₄, the annulenone exhibited a deep red-green colouration, and the electronic spectrum in 85% H₂SO₄ exhibited a spectacular change exhibiting maxima at 243 nm (ε 15,500), 265 (16,000), 345 (44,200) and 480 (14,500). As seen from Fig 3, the electronic spectrum is very similar to that of 1-hydroxy-4,5-(2',3'-naphtho)-tropylium cation 13a,²⁶ which has a geometrically similar perimeter with 7. The NMR spectrum of 6 in H₂SO₄ gave the most striking spectral evidence for the formation of the aromatic 1-hydroxy[11]annulenylium cation 7, showing a large down-field shifts of all the annulene protons. The spectrum consisted of 4H multiplet at τ 1.10 (benzenoid protons), complex 2H multiplet at τ 1.3-1.6 (H-5, H-8 protons), and 4H broadened AB quartet at τ 0.78 and 2.05 (J = 11 Hz) assignable to the H-2, H-11 and H-3, H-10 protons, without changing the *cis* coupling constants [Fig 2c). The consistency of the *cis* coupling constants were also found both in the protonated and ordinary spectra of 4,9-methano[11]annulenone 1c.⁸

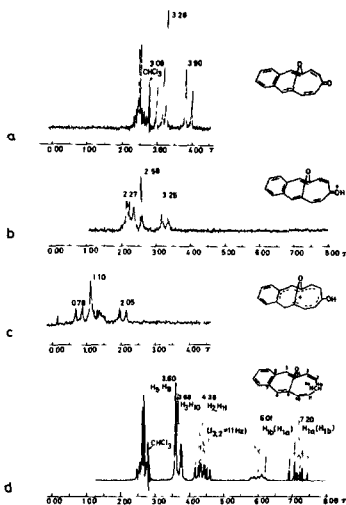


Fig 2. NMR spectra of 6,7-benzo-4,9-oxido[11]annulenone 6 [(a) in CDCl₃; (b) in CF₃COOH, and (c) in conc H₂SO₄] and 6,7-benzo-4,9-oxido-1-homo[10]annulene 9 in CDCl₃ [60 MHz].

Table 1. Chemical shifts of compounds 6, 9, and 1c, at 60 MHz (τ values)

Compound	H-2, H-11	H-3, H-10	H-5, H-8	H-6, H-7	benzenoid H
6	3.90 (J = 11 Hz)	3.09 (J = 11 Hz)	3.28	—	2.3-2.7
9	4.38 (J = 11 Hz)	3.68 (J = 11 Hz)	3.60	—	2.4-2.8
1c ⁸	3.98 (J = 12.2 Hz)	2.82 (J = 12.2 Hz)	3.1	2.79	—
Δ[9-6]	0.48	0.59	0.32		
Δ[1c-6]	0.08	-0.27	-0.50		

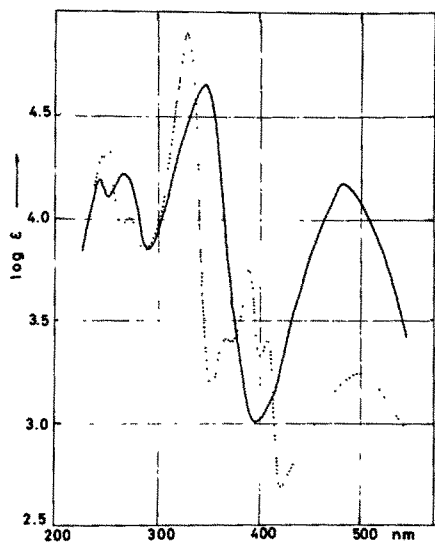


Fig 3. Electronic spectra of 6,7-benzo-4,9-oxido[11]-annulenyl cation 7 (in 85% H_2SO_4) and 1-hydroxy-4,5-(2',3'-naphtho)tropylium cation 13a (in 70% H_2SO_4). The spectrum of 13a was reproduced on the basis of the original spectrum, reported by G. Naville, H. Strauss and E. Heilbronner.²⁶

Attempts were made to prepare another aromatic 6,7-benzo-4,9-oxido[11]annulenyl cation. The NaBH_4 reduction of 6 afforded a cyclic alcohol 11 in 88% yield, yellow needles, m.p. 193° , as a sole product. The structural assignment of 11 was based on spectral and analytical data. The mass spectrum showed an expected molecular ion at m/e 224. The IR spectrum exhibited a max at 3360 cm^{-1} , due to the OH group. The NMR spectrum (CDCl_3) exhibited 2H AB system at τ 3.65 and 4.55 ($J = 11\text{ Hz}$), another 2H AB system at τ 3.69 and 4.48 ($J = 11\text{ Hz}$), 2H singlet at τ 3.37, and 1H-multiplet at τ 4.20, and 1-H broadened signal at τ 5.20, which was exchangeable with D_2O (OH proton) (Fig 4). The UV spectrum in ethanol was almost superimposable with that of 6,7-benzo-4,9-oxido-1-homo[10]annulene 9,²⁰ showing a main max at 262 nm (ϵ 88,800).

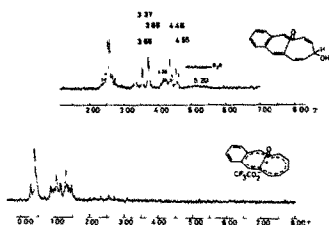
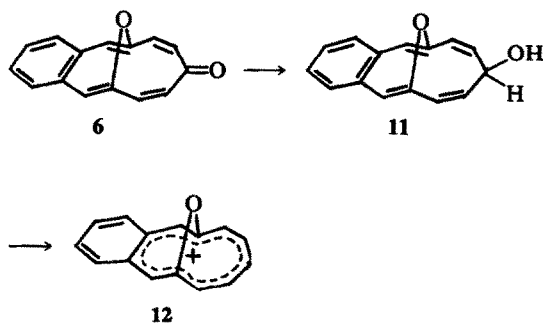


Fig 4. NMR spectra of 6,7-benzo-4,9-oxido-1-hydroxy-1-homo[10]annulene 11 (in CDCl_3) and 6,7-benzo-4,9-oxido[11]annulenyl cation 12 (in CF_3COOH) [60 MHz].



SCHEME 3

According to the method,²⁶ compound 11 was treated with CF_3COOH or 70% HClO_4 , which resulted in an immediate colour change, and the electronic spectrum of the deep green solution was characterized by new bands at 245 nm (ϵ 13,100), 289 (28,900), 352.5 (64,800), 450 (42,000), 475.5 (5,600), together with a series of fine bands at 570 nm (ϵ 2,690), 582 (2,620), 595 (2,950) and 610 (3,460), suggesting the formation of an aromatic [11]annulenyl cation 12 (Fig 5). The longest wavelength band (610 nm) shifted *ca* 350 nm bathochromically as compared with the maximum of its conjugated base 11. The band at 610 nm almost coincided with the longest wavelength band of 4,5-(2',3'-naphtho)tropylium cation 13b, manifesting the close relationship between 12 and 13b. The NMR spectrum of 12 in CF_3COOH is just as convincing as the electronic spectrum in affirming an aromatic benz-annelated 10π annulenyl cation,

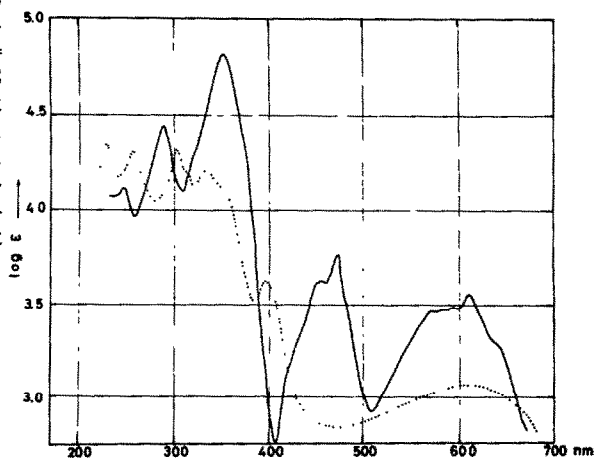
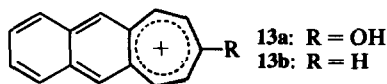


Fig 5. Electronic spectra of 6,7-benzo-4,9-oxido[11]-annulenyl cation 12 (— in 70% perchloric acid) and 4,5-(2',3'-naphtho)tropylium cation 13b (····· in 70% H_2SO_4). For the sake of comparison, the spectrum of 13b was reproduced on the basis of the original spectrum, which was reported by G. Naville, H. Strauss and E. Heilbronner.²⁶



which showed all the signals at the low field at τ 0.3–1.5 (Fig 4).

The ionic stability of 12 is expected to be greatly reduced by benzannellation, as in the case of benzannulated tropylium ions.²⁶ As expected, the pK_R^+ value of 12 was obtained as -4.1 spectrophotometrically by the use of Deno's function $Co = pK_R^+ - \log [R^+]/[ROH]$.²⁵ A comparison of this value with that of 4,9-methano[11]annulenyl cation³ and 1,2:4,5-dibenz-tropylium cation²⁶ shows that ionic stability of 12 is far less than that of the former ($+6.2$) and is comparable to that of the latter (-3.7).

EXPERIMENTAL

General procedures. M.p.s were determined on a Yanagimoto hot-stage apparatus and are uncorrected. IR spectra were measured on a Koken model 301 spectrophotometer; only significant maxima are reported. Electronic spectra were determined on a Hitachi Perkin-Elmer model 139 spectrophotometer. NMR spectra were measured on a Nihondenshi 60 MHz spectrometer, TMS being used as an internal standard. Mass spectra were determined on a Nihondenshi MS OSG spectrometer operating at 70 eV.

2,4-Bis(hydroxymethylene)-3-benzoxepin 2. This alcohol was prepared by LAH reduction of dimethyl-3-benzoxepin-2,4-dicarboxylate,²⁷ essentially as described,¹⁷ m.p. 89–91°. Electronic spectrum (EtOH), 238 nm (ϵ 37,200) and 285 (1,200); NMR spectrum ($CDCl_3$), 4H multiplet at τ 3.04 (benzenoid), 2H singlet at 4.23 (benzylic), 4H singlet at 5.90 (methylene), and 2H singlet at 6.05 (hydroxyl, disappears on addition of D_2O).

2,4-Bis(formyl)-3-benzoxepin 3. MnO_2 (48 g),²⁸ was added to a soln of 2 (2.7 g) in chloroform (500 ml), and the mixture was stirred at room temp for 10 hr. MnO_2 was removed by filtration and washed well with hot chloroform. The solvent was evaporated under reduced pressure, and the reddish crystalline residue was recrystallized from CCl_4 to give the dialdehyde (1.3 g, 50%), red prisms, m.p. 132–3°; IR spectrum (Nujol), band at 1688 ($\nu C=O$), 1650, 1630, 1442, 1175, and 990 cm^{-1} ; NMR spectrum ($CDCl_3$), 4H multiplet centered at τ 2.60–3.00 (benzenoid), 2H singlet at 3.60 (benzylic), and 2H singlet at 0.94 (aldehydic); electronic spectrum, λ max (EtOH) 258 nm (ϵ 25,000) and 276 (sh) (18,300); mass spectrum, peak at 200 (M^+). (Found: C, 72.08; H, 4.13. Calc. for $C_{12}H_8O_3$: C, 71.99; H, 4.03.)

6,7-Benzo-4,9-oxido-2,11-dicarbomethoxy[11]annulene 4. A soln of 3 (300 mg, 1.5 mM) and dimethyl acetonedicarboxylate (392 mg, 2.25 mM) in chloroform (50 ml) was added slowly to a vigorously stirred soln of piperidinium acetate (prepared from 1 g of piperidine and 1 g AcOH) in chloroform (300 ml) over a period of 3 hr. The mixture was stirred for an additional 1 hr, and then washed with water, dried (Na_2SO_4), and evaporated under reduced pressure. Crystallization from dichloroethane gave 4 (277 mg, 55%) as yellow needles, m.p. 285°; homogenous on TLC; IR spectrum (KBr), bands at 1703, 1690 ($\nu C=O$ ester), 1650 cm^{-1} ($\nu C=O$ ketone); electronic

spectrum, λ max dichloroethane) 302 nm (ϵ 51,500); mass spectrum, peaks at m/e 338 (M^+), 310 ($M-CO$), 279 ($M-COOMe$), and 251 ($M-CO-COOMe$); NMR spectrum ($CDCl_3$), 2H singlet at τ 2.28 (H-3, H-10), another 2H singlet at 3.05 (H-5, H-8), 4H multiplet centered at 2.48 (benzenoid), and 6H singlet at 6.15 (carbomethoxy). (Found: C, 67.35; H, 4.15. Calc. for $C_{19}H_{14}O_6$: C, 67.45; H, 4.17%.)

6,7-Benzo-4,9-oxido[11]annulene 2,11-dicarboxylic acid 4. The diester 4 (800 mg) was mixed with dioxane (40 ml), water (48 ml) and KOH (2.1 g). The mixture was stirred vigorously under N_2 at 80–90° for 2 hr, and evaporated almost to dryness under reduced pressure. Acidification by conc HCl afforded crude crystals of 5, which were recrystallized from DMF/ CH_3CN (1:3) to give 5 (310 mg, 97%) as yellow prisms, which decomposed at ca 210° on an attempted m.p. determination: IR spectrum (KBr), bands at 1692 ($\nu C=O$ carboxylic acid) and 1653 cm^{-1} ($\nu C=O$ ketone); λ max (MeOH) 293 nm (ϵ 43,300); mass spectrum, peaks at m/e 222 ($M-2CO_2$) and 194 ($M-2CO_2-CO$); NMR spectrum (deutro DMF), 2H singlet at τ 2.70 (H-3, H-10), 2H singlet at 2.46 (H-5, H-8), 4H multiplet at τ 2.1–2.6 (benzenoid), and 2H broadened signal centered at 4.00 (carboxylic acid, disappears on addition of D_2O). (Found: C, 65.80; H, 3.11. Calc. for $C_{17}H_{10}O_6$: C, 65.81; H, 3.25%.)

6,7-Benzo-4,9-oxido[11]annulene 6

Method A. The acid 5 (10 mg) was placed on a sublimation dish (8 mm in diam and 5 mm in ht) and heated on a hot-stage (220°). With the evolution of CO_2 needle crystals of 6 were attached to the cold surface of the cover glass. The repeated sublimation conducted yielded 56.3 mg of an analytically pure sample (from 158 mg of 5, 50.6%), m.p. 225°; IR spectrum (KBr), bands at 1642 ($\nu C=O$ ketone), 1600, 1135, 1115, 1000 and 900 cm^{-1} ; λ max (MeOH) 238 nm (ϵ 9,900), 269 (32,900) and 289 (28,000) (Fig 1); NMR spectrum ($CDCl_3$, Fig 2a), 4H AB system at τ 3.09 and 3.90 ($J = 11$ Hz), 4H multiplet at 2.30–2.70 (benzenoid), and 2H singlet at 3.28 (H-5, H-8); mass spectrum, peaks at m/e 222 (M^+) and 194 ($M-28$). (Found: C, 81.00; H, 4.34. Calc. for $C_{15}H_{10}O_2$: C, 81.06; H, 4.54%.)

Method B. A mixture of 5 (300 mg), 7 ml quinoline, and copper chromite²⁹ (300 mg) was heated in an oil bath with stirring. When the temp reached 150°, CO_2 was evolved at a moderate rate, and the reaction was complete in 1 hr. Near the end of the reaction, the heat was increased to about 220°. After cooling, the catalyst was filtered off, and washed with chloroform. The dark reddish quinoline soln was combined with the chloroform extracts, and acidified with HCl. The chloroform layer was then washed well with water, dried, and evaporated. The residue was chromatographed on silica gel. Elution of the column with chloroform and crystallization from CCl_4 yielded 6 (150 mg, 80%) as lemon yellow needles, mp 225–7°; a mixed m.p. test showed that the product was identical with the authentic sample, which was obtained by the method A.

6,7-Benzo-4,9-oxido-1-hydroxy-1-homo[10]annulene 11. $NABH_4$ (132 mg, 3.5 mM) was added to a soln of 6 (170 mg, 0.766 mM) in EtOH (30 ml), and the mixture was refluxed on a water bath for 10 hr. After cooling, AcOH was added until the soln was acidic. The EtOH was evaporated under reduced pressure, and the residue was diluted with chloroform, and washed with water. The organic layer was dried, evaporated to a brown residue and chromatographed on silica gel. Elution with chloro-

form and crystallization from CCl_4 gave 11, as nearly colourless fine needles, m.p. 191–194° (150 mg, 88%); homogeneous on TLC; mass spectrum, molecular ion peak at m/e 224; electronic spectrum (EtOH) 262 nm (ϵ 88,800); NMR spectrum (Fig 4). (Found: C, 80.33; H, 5.44. Calc. for $\text{C}_{15}\text{H}_{12}\text{O}_2$: C, 80.33; H, 5.39%).

Protonation of 6,7-benzo-4,9-oxido[11]annulenone 6. A soln of 6 in 85% H_2SO_4 gave reddish green soln, which showed new bands at 243 nm (ϵ 15,500), 265 (16,000), 345 (44,200) and 480 (14,500) [Fig 3]. The NMR spectrum in conc H_2SO_4 [Fig 2c] exhibited 4H multiplet at τ 1.1, 2H multiplet at 1.3–1.6, 4H AB system centered at τ 0.78 and 2.05 ($J = 11$ Hz); the NMR spectrum of 6 in CF_3COOH (Fig 2b).

6,7-Benzo-4,9-oxido[11]annulenyl cation 12. When 11 was dissolved in 70% perchloric acid, a reddish green colour was immediately developed, and the electronic spectrum showed maxima at 245 nm (ϵ 13,100), 289 (28,900), 352.5 (64,800), 450 (4,200), 475.5 (5,600), 570 (2,690), 582 (2,620), 595 (2,950) and 610 (3,460) [Fig 5]; the NMR spectrum, see the Discussion and Fig 4.

Measurement of pK_R^+ of 12. The measurements were essentially based on the procedure reported.²⁵ Compound 11 which was not converted to 12 was assumed to exist as the free alcohol. This assumption was found to be reasonable, when independent concentrations of 11 and 12 were evaluated spectrophotometrically. The optical densities of 12 were measured at a stoichiometric concentration of 11 (1.56×10^{-5} M) with changing H_2SO_4 concentrations (30–40%). The λ max of 12 in 40% H_2SO_4 was the same as that in 85% H_2SO_4 .

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