

THE SYNTHESIS OF [15]ANNULENONE 4,7:10,13-DIOXIDES AND AROMATIC 4,7:10,13-DIOXIDO[15]ANNULENIUM CATIONS

NOVEL 14π 'ODD' ANNULENE SYSTEMS¹

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Abstract—2,15 - Dimethoxycarbonyl - [15]annulenone 4,7:10,13 - dioxide (14) has been prepared by the condensation of *cis* - α,β - bis(5 - formyl - 2 - furyl)ethylene (13) with dimethyl acetonedicarboxylate. Treatment of 14 with conc H_2SO_4 led to 4,7:10,13 - dioxido[15]annulenone 2,15 - dicarboxylic acid anhydride (17), which was subsequently converted to the corresponding dicarboxylic acid (18) by dilute KOH. Decarboxylation of 18 gave rise to two isomeric [15]annulenone 4,7:10,13 - dioxides, i.e., the tri-*cis* isomer (7) and the mono - *trans* - di - *cis* isomer (8).

Regarding to the ring current effects, the proton chemical shifts of these [15]annulenones were compared with those of a reference model, 4,7:10,13 - dioxido - cyclopentadecaheptaene (2.4.6.8.10.12.14) (3). Both of the parent [15]annulenones (7 and 8) have been interpreted as nondiatropic, while the anhydride (17) has been shown to be diatropic, sustaining an induced diamagnetic ring current. The enforced planarity and symmetrical geometry of the anhydride have been discussed. As expected, when 7, 8, 14, 17 and 18 were dissolved in CF_3COOH or conc H_2SO_4 , completely delocalized [15]annulenium cations were produced, all of which proved to be diatropic. Three possible geometrical isomers of these 14π cations were established experimentally.

Advances in annulene chemistry² have now extended to 'odd' annulenes,³ and a rich variety of such compounds belonging to $[4n + 1]$ - and $[4n + 3]$ annulenes^{4a-d} have been prepared and studied extensively in the light of the Hückel rule. However, the synthesis of 'odd' annulenes should be expected to involve considerable experimental difficulties due to the presence of steric interactions of the internal hydrogens,⁵ as was observed in 'even' annulenes. All the planar and nearly planar 'odd' annulenes obtained so far are limited to bridged or

dehydroannulenes, suggesting that the existence of these compounds may be due to the presence of some appropriate bridges or acetylenic bonds.‡

On this basis, utilization of furan rings to make up a planar 'pseudo monocyclic'⁶ conjugated system was expected to be promising. Thus, [18]annulene trioxide (2), prepared by Badger *et al.*⁷ could be visualized as a bridged [18]annulene, in which three O atoms of the furan rings eliminate the inner H—H repulsion⁵ of carbocyclic [18]annulene itself (1),⁸ and becomes diatropic. However, it could be predicted that the incorporation of furan rings is best suited for the synthesis of the unexplored medium ring-sized 'odd' annulenes, in which the H—H repulsion of the inner hydrogens would become serious with decreasing ring size. None of these compounds had been obtained, until we began our attack on this field.

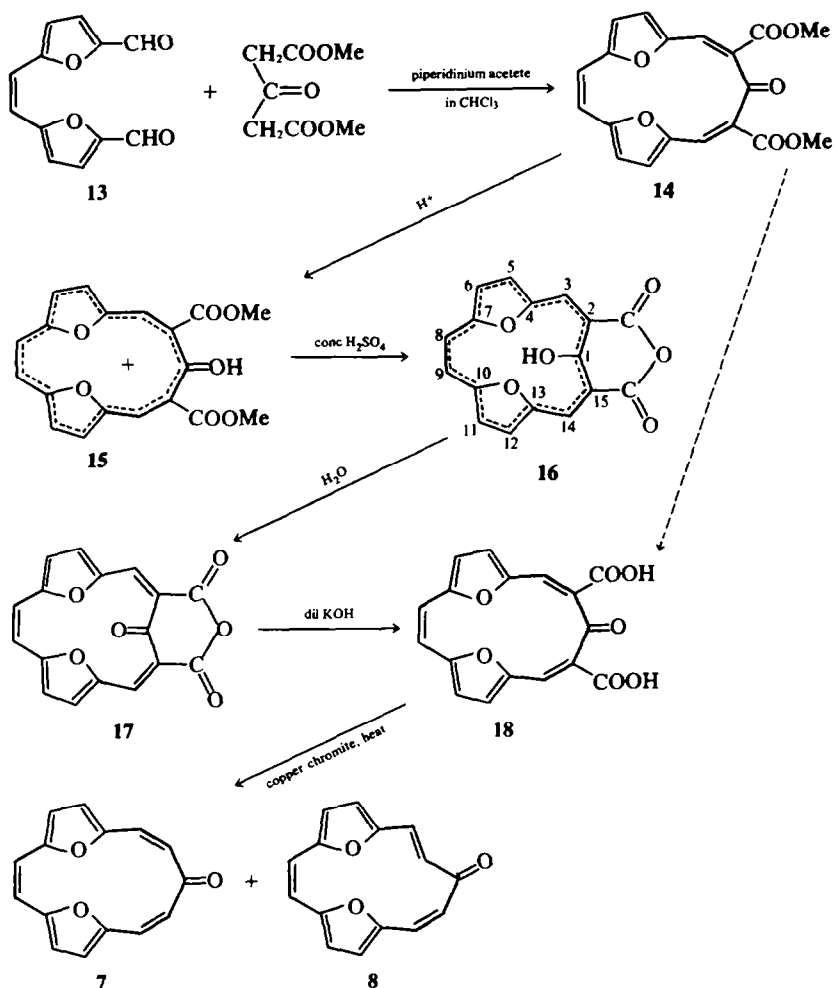
As anticipated, several kinds of [15]-⁹ and [16]annulenes¹⁰ containing two furan rings (3-6) have been successfully prepared. It is of interest to find out that the presence of furan rings does not disturb the π electron distribution which extends to the periphery of the pseudomonocyclic conjugated systems thus prepared. Indeed, the ring current effects are a sharp reverse showing that these are paramagnetic in the case of 4^9 (16π) and 6^{10} (16π), and diamagnetic in the case of 2^7 (18π) and 5^9 (14π), respectively.§

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‡Attempts to obtain [13]- and [17]annulenes by the catalytic hydrogenation of the corresponding dehydro[13]- and dehydro[17]annulenes have not been successful so far: see F. Sondheimer, Refs 2b and 4h. For bridged [11]annulenes, see E. Vogel *et al.*, Refs 4b and 4c, and H. Ogawa, Refs 4d and 4e.

§Bridged [17]annulenes containing 5-membered heterocyclic rings have been prepared by T. M. Cresp and M. V. Sargent, see Refs 4o and 4p. For larger macrocyclic annulenes containing furan or thiophene rings, see, M. J. Broadhurst, R. Grigg, and A. W. Johnson, *J. Chem. Soc. (C)*, 3681 (1971); A. W. Johnson, *The Chemistry of Non-benzenoid Aromatic Compounds* p. 195. Butterworths, London (1971).



SCHEME 1

The direct hydrolysis of the diester (14) with 20% KOH aq gave the corresponding dicarboxylic acid (18) in a poor yield (3%), presumably due to the occurrence of a side reaction which leads to a Michael-type H₂O addition to the C=C double bond. A more excellent pathway became evident. This involves the conversion of the diester (14) to the anhydride (17), followed by a mild alkaline hydrolysis of 17 to give the dicarboxylic acid (18) in an almost quantitative yield. The anhydride formation could be best monitored by the colour change. On dissolving the diester (14) in conc H₂SO₄, a beautiful blue colour developed, and the solution became gradually purple, and finally red, indicating a complete conversion of the protonated diester (15) to the protonated anhydride (16). Other standard methods for the hydrolysis were no more successful.

The decarboxylation of the dicarboxylic acid (18) was carried out in quinoline in the presence of copper chromite to give two isomeric [15]annulenone dioxides (7 and 8). These compounds only differ in one of the double bonds adjacent to the carbonyl group. The tri-*cis*-[15]annulenone 4,7:10,13-dioxide (7) was obtained as orange yellow prisms (20%), m.p. 158–60° (M⁺, *m/e* 238), which decomposed gradually in the solid state on exposure to light and air. The 2,3-*trans*-8,9:14,15-di-*cis* isomer (8) (M⁺, *m/e* 238) was isolated as a reddish oil (10%) from the well separated upper band of the same chromatogram. The spectral data of these isomers were very similar (see experimental), and the allocation of the stereochemistry rests upon the NMR spectra obtained from the corresponding protonated species 20 and 21 (see, Fig 2 and later discussion). The formation of the mono-*trans* isomer

(8) can be explained by the thermal isomerization of the tri-*cis* isomer (7).*

DISCUSSION

A. Substituted [15]annulenones and [15]annulenium ions

The compounds 14, 17 and 18 being considered as bridged [15]annulenones, if planar, may sustain induced diamagnetic ring current due to the polarization of the carbonyl groups. This would shift the outer protons to lower field, and the inner protons to higher field.^{2b}

Suitable models lacking a ring current are necessary to examine the ring current. Evidently, 4,7:10,13 - dioxido - cyclopentadecaheptaene (2.4.6.8.10.12.14) (3)⁹ is a suitable model for the comparison[†]

The differences in chemical shifts obtained from 14, 17 and 18, as compared with the cyclic model (3), are given in Table 1.

The observed downfield shifts [$\Delta\tau$ 0.3–0.54 for 14, see Table 1, (entry G), and $\Delta\tau$ 0.46–0.85 for 18 (entry I)] are obviously too small to provide clear-cut evidence indicating that both 14 and 18 sustain a diamagnetic ring current.

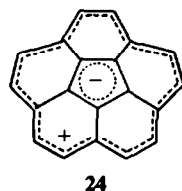
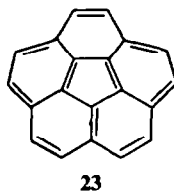
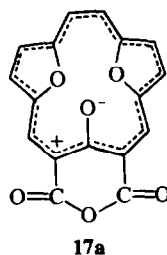
On the other hand, when the diester (14) was dissolved in CF_3COOH , a deep blue colour developed, and the NMR spectrum (CF_3COOH) proved to be strongly diatropic, exhibiting all the outer protons at low field (τ 1.48–2.38, see entry B). The diamagnetic shifts clearly indicate the expected formation of the [15]annulenium ion (15) [$\Delta\tau$ 1.22–1.45, see entry H].

It is significant that proton resonances of the anhydride (17) are considerably deshielded (see, entry D and J), while 14 and 18 are not. The observed downfield shift ($\Delta\tau$ 1.35–1.70, see entry J) clearly supports that the anhydride (17) is diatropic in the ground state. An interesting feature of the anhydride (17) was also revealed by the largest

downfield shift in its protonated species 16 ($\Delta\tau$ 1.93–2.02, see entry K).

It is of interest that the anhydride ring of 17 plays an important role in the presence of the diatropic ring current. Inspection of molecular models suggests that the fused anhydride ring not only changes the parent geometry (i.e., structure 14→16), but also reinforces the new periphery by its 6-membered ring. As a consequence, the enforced planarity of 17 permits the cyclic delocalization of π bonds against the energetically unfavoured geometry caused by the proximity of the inside O atoms.

The diatropic character of 17 is appreciated when the structure 17a is compared with that of corannulene, dibenzo[ghi,mno]fluoroanthene (23),¹² whose dipolar structure (24) contains two concentrically charged systems,—cyclopentadecaheptaenyl cation and cyclopentadienyl anion. The structural similarity between these 15-membered systems is shown below.



The electronic spectrum of the protonated anhydride (16) is remarkable for its very sharp absorptions (prominent peaks at 383 (ϵ 154,000) and 392.5 nm (112,000) in H_2SO_4), as well as its spectral shape which is similar to that of the all-*cis* [15]annulenium tetrafluoroborate (5).⁹

The corannulene type geometry of 16 is more favourable for the demonstration of an induced diamagnetic ring current in the disubstituted [15]annulene systems than the geometry of the all-*cis*-annulenium ion (15), based on the larger downfield shift (in NMR) and on the observed higher intensities (in electronic spectrum) (Fig 1).

B. Parent [15]annulenones and [15]annulenium ions

The NMR spectra (CDCl_3) of 7 showed the signals of the ten outer protons at the ordinary olefinic region [τ 2.7–3.1, see Fig 2a]. The nine outer pro-

*The ready interconversion of one geometrical isomer to another is well documented in the annulene and dehydroannulene series [see, Ref 2a and J. F. M. Oth, G. Anthoine, and J. M. Gilles, *Tetrahedron Letters*, 6265 (1968)].

†In order to obtain another 2,15-disubstituted model, NaBH_4 reduction of the diester (14) was carried out, but the reduction occurred preferentially at the double bond adjacent to the ester carbonyl group to give 2,3 - dihydro-2,15 - dimethoxycarbonyl[15]annulenone 4,7:10,13 - dioxide (22), and no 1-hydroxy derivative of 14 was obtained.

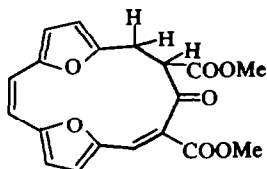


Table 1. NMR chemical shifts of **14**, **17** and **18** compared with the model **3** *

entry	A	B	C	D	E	F	G	H	I	J	K
	14	15	18	17	16	3	Δ 3-14	Δ 3-15	Δ 3-18	Δ 3-17	Δ 3-16
Solvent	CDCl ₃	CF ₃ COOH	d ₆ -DMSO	d ₆ -DMSO	CF ₃ COOH	CDCl ₃	—	—	—	—	—
H-3, H-14	2.27	1.48	2.31	1.43	0.73	3.50	(1.23)	(2.02)	(1.19)	(2.07)	(2.77)
H-furan	3.04	2.17	2.77	2.00	1.53	3.46	0.42	1.29	0.69	1.46	1.93
H-furan	2.81	1.90	2.50	1.65	1.22	3.35	0.54	1.45	0.85	1.70	2.13
H-8, H-9	3.30	2.38	3.14	2.25	1.58	3.60	0.30	1.22	0.46	1.35	2.02

*Proton chemical shifts represent τ , TMS being used as internal standard.

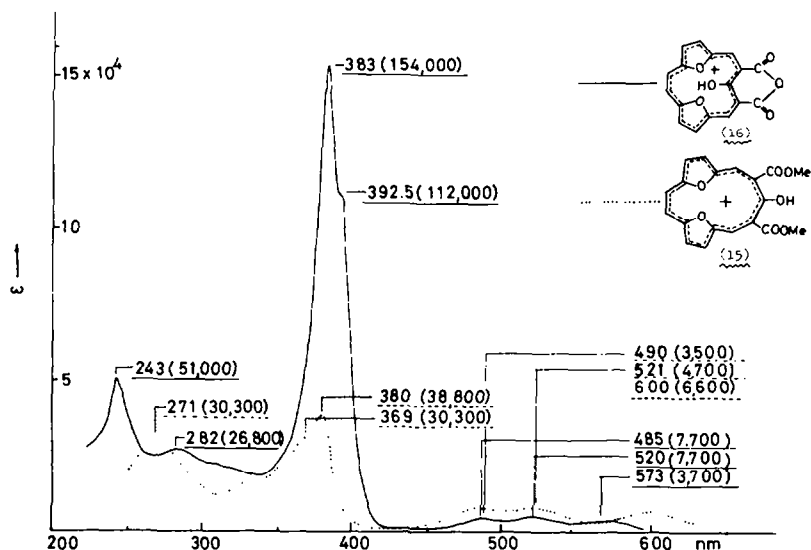


Fig 1. Electronic spectra of the corresponding [15]annulenium cations derived from 4,7:10,13-dioxido [15]annulenone-2,15-dicarboxylic acid anhydride (17) (solid line, in conc. H_2SO_4) and 2,15-dimethoxycarbonyl [15]annulenone 4,7:10,13-dioxide (14) (dotted line, in CF_3COOH).

tons and one inner proton of 8 resonated at nearly the same region [τ 2.65–3.15, Fig 2b]. Consequently these parent [15]annulenones (7 and 8) possess no substantial diamagnetic ring current. We consider, the nondiatropic character of 7 and 8 may be ascribed to their nonplanarity. As the delocalization energy of the $[4n+3]$ annulenone decreases with increasing ring size, a planar geometry is essential for

the occurrence of a diamagnetic ring current, otherwise any gain in delocalization energy counterbalances the consequent angle strain.

On the other hand, the annulenones (7 and 8) can be expected to be potential precursors of the corresponding [15]annulenium cations (20 and 21), respectively.

The treatment of 7 or 8 with CF_3COOH or conc

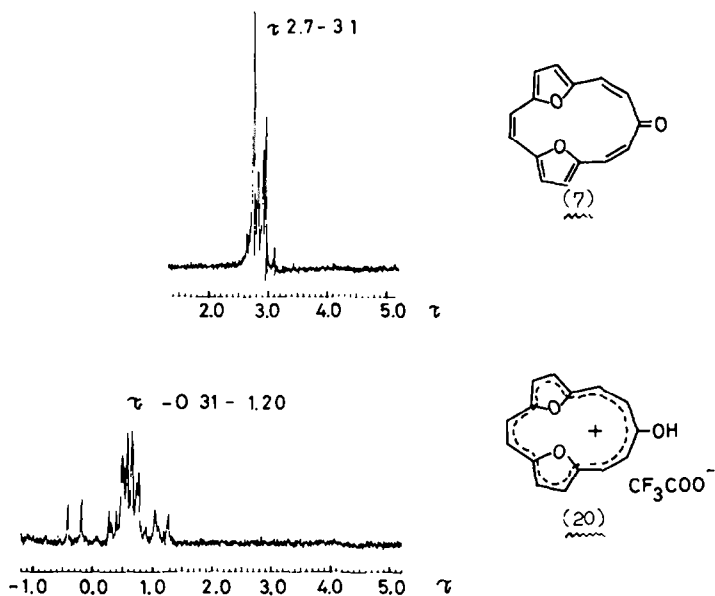


Fig 2a. NMR spectra of (7) in CDCl_3 (upper spectrum) and (20) in CF_3COOH (lower spectrum) at 25°C [60 MHz].

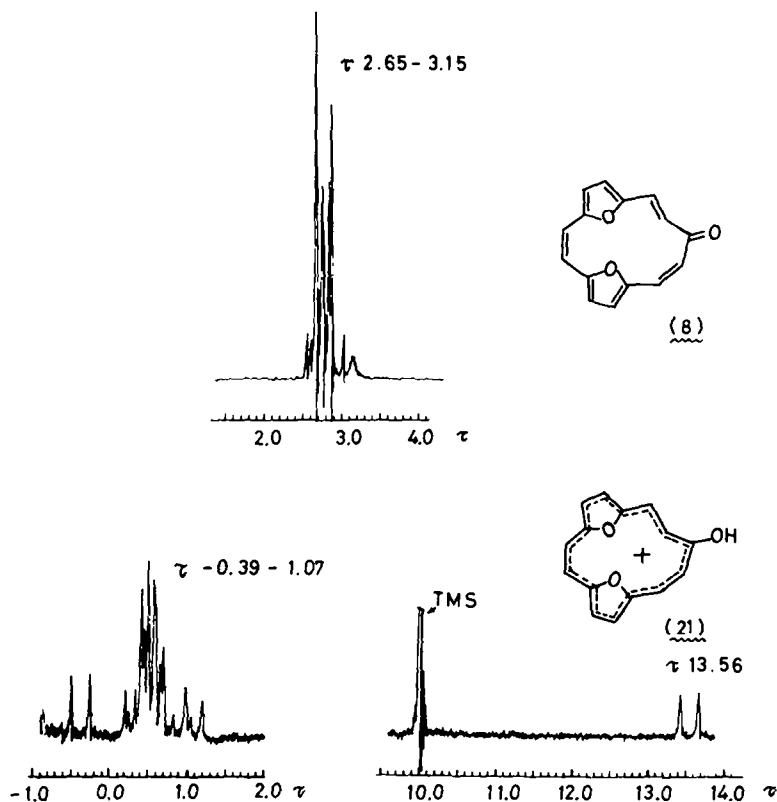


Fig 2b. NMR spectra of (8) in CDCl₃ (upper) and (21) in CF₃COOH (lower) at 25°C [60 MHz].

H₂SO₄ gave deep reddish orange solutions, which are characteristic for these protonated species.

The ten outer protons of **20** and nine outer protons of **21** were now deshielded at τ -0.31-1.20 and τ -0.39-1.07, respectively (Fig 2). In sharp contrast, the one inner proton of **21** was extraordinarily shielded, and appeared at τ 13.56 (doublet, J = 15 Hz) at 25°, and τ 13.43 at 60°. This high-field resonance and the area integration were exactly what we expected for **21**.

The absorption maxima of **20** appeared at $\lambda_{\max}^{\text{CF}_3\text{COOH}}$ 237 (14,800), 260 (17,000), 337 (97,000), 358 (87,000), 476 (17,000) and 496 nm (19,000).⁹ Electronic spectra of these cations (**20** and **21**) are similar to that of the [15]annulenium tetrafluoroborate (**5**),⁹ (λ_{\max} 30% H₂SO₄ 331 (110,000), 345 (108,000), 481 (8,260), and 503 (8,420)),⁹ confirming both of these [15]annulenium ions (**20** and **21**) are completely delocalized ions.

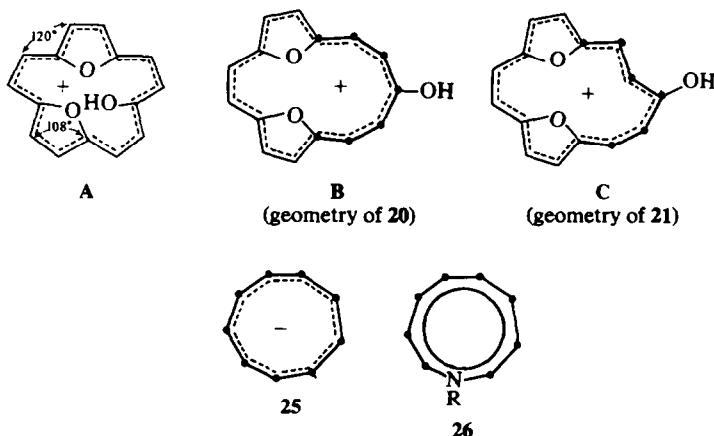
C. Geometry of bridged [15]annulenium ions

Another interesting facet of the annulenium cations is their geometrical variance. Three kinds of geometry shown below could be capable of existence in bridged [15]annulenium ions, all of them

proved to be diatropic, and, therefore, are considered to be planar.

The highly symmetrical geometry of Fig A (geometry of **6**) is also considered to be more stable than that of **20**. This is understood, if one assumes that the furan rings are regular pentagons, and that all of the C=C bonds of Fig A are equivalent in length. From the construction A, five outside-, and ten inside bond angles of this 15-membered ring system are only restricted to two kinds of strain-free bond angles, i.e. 120° and 108°, respectively (see constructions A). It may be also interesting to know that geometry A is not very different from that of [16]annulene dioxide (**6**), whose periphery is considered to be reasonably coplanar, based on its strong paratropic character. Geometry B (geometry of **20**) is similar in part to that of aromatic cyclononatetraenide (**25**)¹⁴ or aromatic azonides (**26**).¹⁵ Prototype geometry of C (geometry of **21**) can be found also in the partial geometry of mono-*trans* isomers of 9- or 10-membered annulenes.¹⁶

We consider, such isomeric transformations may occur in other annulene systems as a consequence of some chemical changes or introduction of certain substituents.



EXPERIMENTAL

General procedures. M.p.s determined on a Yanagimoto hot-stage microscope and have been uncorrected. Electronic spectra were determined on a Hitachi-Perkin-Elmer model 139 spectrophotometer. IR spectra were recorded on a Koken DS-301 spectrophotometer. NMR spectra were taken on a Nihondenshi H-60 spectrometer, and recorded in τ values relative to TMS at 10:00 as internal standard. For column chromatography, Marinckrodt Silic AR (200–325 mesh) was used.

cis- α,β -Bis(5-formyl-2-furyl)ethylene (13). The yield of the *cis* dialdehyde (13)¹¹ was increased to 30%, when anhyd DMF was used as solvent. The *cis* isomer (13) was separated from the *trans* isomer by repeated extraction of the product (a mixture of *cis*-*trans* isomers) with boiling CCl₄, since the *trans* isomer was extremely insoluble in the usual organic solvents. Other reaction conditions and procedure were essentially the same with our previous method,¹¹ except that 13 was finally recrystallized from acetonitrile. The analytically pure sample of 13 melted at 123–125° as reddish orange needles.

2,15-Dimethoxycarbonyl [15]annulenone 4,7:10,13-dioxide (14). A soln of 13¹¹ (2.0 g, 9.25 mM) and freshly distilled dimethyl acetonedicarboxylate (2.09 g, 12 mM) in dry CHCl₃ (50 ml) was slowly added through a peristaltic pump over a period of 3 h to a vigorously stirring soln of piperidine (5.0 g, 70 mM) and glacial AcOH (4.2 g, 70 mM) in dry CHCl₃ (200 ml) under reflux. After the addition, stirring was continued for 1 h. The dark-reddish soln was cooled, washed successively with water to remove the catalyst. The separated CHCl₃ layer was dried with Na₂SO₄ and evaporated to dryness *in vacuo* to afford a dark viscous residue, which was dissolved in a minimum amount of CHCl₃ and chromatographed on silica gel with CHCl₃. Evaporation of the earlier fractions, and when small amounts of CCl₄ was added, compound 14 crystallized as reddish purple prisms (700 mg, 21.5%), m.p. 170° (from CCl₄); IR spectrum (Nujol), bands at 1713 (ester >C=O), 1660 (ketone >C=O), 1613 cm⁻¹ (C=C); NMR spectrum (CDCl₃), 2H singlet at τ 3.30 (H-8, H-9 protons), 2H singlet at τ 2.27 (H-3, H-14 protons), two doublets at τ 3.04 and 2.81 with $J = 4$ Hz (furan protons), 6H singlet at τ 6.18 (carbomethoxy protons); mass spectrum, $M^+ m/e$ 354; electronic spectrum, λ_{max} (MeOH) 271 (ϵ 24,800), 334 (27,400) and 450 nm (5,050). (Found: C, 64.12; H, 4.10. Calcd for C₁₉H₁₄O₇: C, 64.40; H, 4.10%).

Further elution of the column with CHCl₃ furnished a reddish amorphous polymeric material, which did not show a definite m.p. In some experiments, the diester (14) was contaminated with this polymeric material, which was removed by repeated chromatography on silica gel (with CH₂Cl₂).

4,7:10,13-Dioxido[15]annulenone-2,15-dicarboxylic acid anhydride (17). Finely pulverized 14 (500 mg, 1.41 mM) was dissolved into conc H₂SO₄ (20 ml) at room temp. Instantaneously, a blue colour developed, but it turned gradually to purple on standing. The soln was allowed to stand 24 h at room temp with occasional shaking, and then quenched onto ice (200 g), and centrifuged. The crystals were washed several times with water, and recrystallized from acetonitrile. Compound 17 was obtained as scarlet prisms, m.p. 360°, in an almost quantitative yield; IR spectrum (KBr) bands at 1733, 1700 (>C=O ketone); electronic spectrum, λ_{max} (CH₂CN) 260 (ϵ 24,200), 355 (36,000), 490–500 (6,580) and 520 nm (7,700); NMR spectrum (d₆-DMSO), 2H singlet at τ 1.43 (H-3, H-14 protons), 2H singlet at τ 2.25 (H-8, H-9 protons), two 2H doublets each centered at τ 1.65 and 2.00 ($J = 4$ Hz, furan protons); mass spectrum, $M^+ m/e$ 308. (Found: C, 65.96; H, 2.44. Calcd for C₁₇H₆O₆: C, 66.24; H, 2.62%).

4,7:10,13-Dioxido[15]annulenone-2,15-dicarboxylic acid (18). The anhydride 17 (1.0 g, 3.24 mM) was dissolved in 3% KOH aq (100 ml), and treated with some active charcoal. The filtered soln was allowed to stand 1 h at room temp, and then acidified with dil HCl. The mixture was then extracted with a large amount of EtOAc, washed with water successively, and dried (Na₂SO₄). After removal of the solvent *in vacuo*, 18 crystallized as beautiful black prisms, m.p. 300° (without melting); electronic spectrum, λ_{max} (CH₂CN) 248 (ϵ 36,200), 256 (45,200), 267 (44,700), 330 (27,000) and 450 nm (4,600); IR spectrum (KBr), 1680, 1713 (>C=O carboxylic acid), 1660 cm⁻¹ (>C=O ketone); NMR spectrum (d₆-DMSO), 2H singlet at τ 3.14 (H-8, H-9 protons), 2H singlet at τ 2.31 (H-3, H-14 protons), two doublets centered at τ 2.77 and 2.50 (furan protons, $J = 4$ Hz) and 2H broadened singlet at τ 2.91 (carboxylic acid protons), which was exchangeable with D₂O. (Found: C, 62.31; H, 3.00. Calcd for C₁₇H₁₀O₇: C, 62.58; H, 3.09%).

2,15-Dimethoxycarbonyl-2,3-dihydro[15]annulenone 4,7:10,13-dioxide (22). To a soln of 14 (341 mg, 0.96 mM) in MeOH (25 ml) NaBH₄ (10.9 mg, 0.288 mM, 15% excess) was added portionwise at room temp. The reddish soln of

14 turned to yellow rapidly. After 30 min, TLC examination showed that no starting material was present. The mixture was acidified with AcOH, and then poured into water (ca 100 ml), and extracted with EtOH. Evaporation of the solvent *in vacuo* afforded reddish orange prisms, m.p. 155–6° (150 mg, 43%), mass spectrum, $M^+ m/e$ 356; IR spectrum (KBr), bands at 1753 (nonconjugated ester $>C=O$), 1713 (conjugated ester $>C=O$), 1690 cm^{-1} (ketone $>C=O$); electronic spectrum, λ_{max} (MeOH) 290 (15,900) and 425–440 nm (5,700); NMR spectrum ($CDCl_3$), two 3H singlets at τ 6.30 and 6.24 (Me protons), 2H multiplets centered at ca τ 6.50 overlapping with the carbomethoxymethyl signals (methylene protons), and an AB system at τ 3.80 and 4.16 (the *cis* olefinic protons at H-8 and H-9), three doublets each centered at τ 3.19 (1H), 3.53 (2H) and 3.78 (1H) due to the furan protons ($J = 4$ Hz), and a 1H singlet at τ 2.50 (H-14 proton). (Found: C, 63.75; H, 4.69. Calcd for $C_{15}H_{16}O_5$: C, 64.04; H, 4.53%).

Decarboxylation of 4,7:10,13-dioxido[15]annulene-2,15-dicarboxylic acid (18). A mixture of 18 (666 mg; 1.74 mM), quinoline (15 ml) and copper chromite (prepared according to Lazier and Arnold¹⁷) was heated at 170° for 15 min. The evolution of CO_2 ceased within 5 min. After cooling, excess dil HCl was added, and the resulting suspension was extracted with $CHCl_3$ several times. The filtered $CHCl_3$ extracts were combined, and washed successively with dil HCl, water, and finally NaHCO₃ aq, and dried (Na_2SO_4). The soln was concentrated *in vacuo*, and the resulting residue was dissolved in a minimum amount of $CHCl_3$ and chromatographed on a column of silica gel (3 cm \times 11 cm) with chloroform. Two well separated bands developed. The eluate was collected as soon as it become coloured. The first band fractions were evaporated to give 7, which was recrystallized from CCl_4 , as yellow prisms, m.p. 158–160° (83 mg, 20%); IR spectrum (KBr), bands at 1653, 1641 ($>C=O$), 1613, 1603 cm^{-1} ($>C=C$); electronic spectrum, λ_{max} (MeOH) 232 (ϵ 21,700), 245 sh (19,900), 318 (39,200), 390 sh (5,000), 405 (5,350), 450 sh (4,200), 465 (4,500) and 495 nm (3,600); λ_{max} (cyclohexane) 230 (ϵ 22,600), 255 sh (14,000), 310 (38,800), 395 sh (8,000), 405 (8,300), 445 sh (4,600) and 475 sh nm (2,100); mass spectrum, $M^+ m/e$ 238, with other fragment ions at 210, 181 and 153; NMR spectrum of 7, see Fig 2a. (Found: C, 75.50; H, 4.31. Calcd for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23%). Compound 7 becomes brown on standing in light and air.

Compound 8 was obtained as a reddish oil from the upper band of the same chromatogram (40 mg, 10%), which was homogeneous on TLC; IR spectrum ($CDCl_3$), bands at 1658 ($>C=O$), 1621 and 1601 cm^{-1} ; electronic spectrum, λ_{max} (MeOH) 232 (14,800), 316 (27,300), 400 (4,450), 440 (3,300), 465 (3,300) and 500 sh nm (2,700); mass spectrum $M^+ m/e$ 238; NMR spectrum of this compound, see Fig 2b. Found: C, 75.31; H, 4.21. Calcd for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23%).

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