

Synthesis of a Derivative of Triangulene; the First Non-Kekulé Polynuclear Aromatic¹

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The first synthesis of a non-Kekulé polynuclear aromatic, a trioxy derivative of triangulene, has been achieved through a two-electron reduction of tetrabutylammonium 4,8-dioxo-4*H*,8*H*-dibenzo[*cd,mn*]pyren-12-olate **14**. The single crystal X-ray diffraction structure of this precursor shows it to be essentially planar with a three-fold axis of symmetry. The trioxytriangulene produced when it is reduced also possesses a three-fold axis of symmetry and it has a triplet ground state. The powder ESR spectrum obtained is that for a uniaxial system fitted using the parameters $|D/hc| = 0.0064 \text{ cm}^{-1}$, $|E/hc| = 0.0000 \text{ cm}^{-1}$. It is stable at room temperature but very sensitive to air oxidation.

π -Biradicals² are characterised by a pair of singly occupied π -molecular orbitals. They are of many different structural types and there is no wholly satisfactory way in which they can be classified. However, it is possible to distinguish three main families:³ the non-Kekulé polyenes,⁴ the non-Kekulé quinodimethanes,⁵ and the non-Kekulé polynuclear aromatics.⁶⁻¹² Several members of the non-Kekulé polyene and the non-Kekulé quinodimethane families have been synthesised and the chemistry of the simpler members of each group is quite well understood. However, the non-Kekulé polynuclear aromatics have proved impossible to obtain and they remain uncharacterised. The simplest non-Kekulé polynuclear aromatics are shown in Table 1. The first member of the family **1** is usually known as triangulene [systematic (IUPAC) name 4*H*,8*H*-dibenzo[*cd,mn*]pyrene] or as Clar's Hydrocarbon and it is typical of the group as a whole. Like the other members of the group it is a system which contains an even number of π -electrons but, despite this, the topology of the system means that it is impossible to write a resonance structure in which each π -electron is paired with one on a neighbouring carbon. Hückel Molecular Orbital calculations support the simple picture of a biradical structure and yield a pair of degenerate non-bonding singly occupied π -molecular orbitals [Fig. 1(a)]. Since these are non-disjoint¹³ (they are co-extensive,¹⁴ they share atoms in common) the biradical should have a triplet ground state.

Synthesis of non-Kekulé polynuclear aromatics was first attempted by Clar and co-workers.⁶⁻⁸ Although they were successful in making several precursors with the correct carbon skeleton, the last stage of the synthesis, conversion into the non-Kekulé polynuclear aromatic itself, always failed. They concluded that such systems were intrinsically unstable. Aspects of the problem have since been investigated by other groups and the most significant success has been in the production of the dianion of triangulene (in which both ψ_{11} and ψ_{12} are doubly occupied)¹¹ and several related closed-shell dianion and dication species.¹² We now report the first successful synthesis of an open-shell non-Kekulé polynuclear aromatic, the triplet trioxy derivative of triangulene **5** [Fig. 1(b)].¹ The method employed is shown in Scheme 1. The initial stages are based mostly on very old work by Weiss and Korczyn.⁹ The important differences between our approach and previous routes lie in the separation and purification steps (the second step using hydrazine, the sixth step using potassium carbonate-ethanol), in the final reduction step and in the production of the tetrabutylammonium salt. The nature of the product from the first step of the reaction sequence has been the cause of some debate and confusion.^{7,9,15} In the 1920s Weiss and Korczyn concluded that the reaction of the Grignard reagent **6** with phthalic anhydride gave the phthalide (3*H*-benzofuran-1-one)

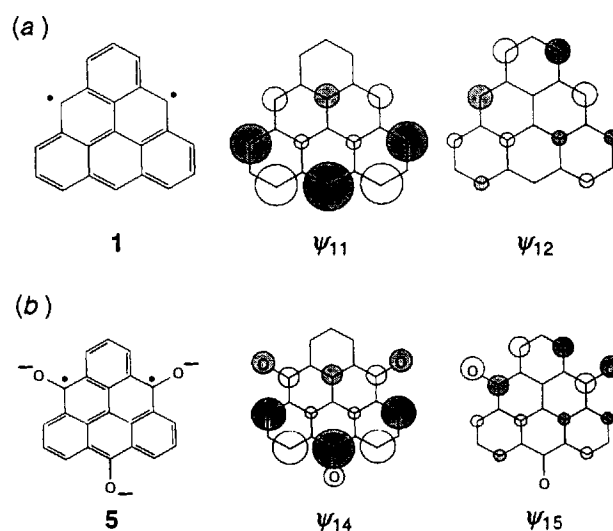


Fig. 1 A comparison of the structures and singly-occupied molecular orbitals for triangulene **1** and its trioxy derivative **5**

7.^{9,15} Reinvestigating the reaction in the 1950s Clar concluded that their product also contained significant amounts of the diketone **8**.⁷ In our experience an almost equal mixture of products **7** and **8** (along with a little of the 3:1 adduct **9**) is always obtained. Whereas the reaction can be carried out on a large scale, the chromatographic separation of the phthalide **7** can only be performed efficiently on a small scale. Hence, this does not appear to be a promising starting point for a multi-step synthesis. Alternative routes to the phthalide **7** were explored, but none proved satisfactory.¹⁶ However, we eventually found that if the crude mixture of **7-9** is treated with hydrazine, the by-products **8** and **9** are converted into soluble derivatives and the less soluble phthalide can be separated directly, in good purity, and on a large scale. The ready availability of the pure phthalide **7** now obviates the need for the longer routes to compound **12** developed by Clar.⁷ Reductive opening of the γ -lactone ring and oxidation of the aromatic methyl substituents of the intermediate **10** was achieved by the method of Weiss and Korczyn without difficulty yielding the tricarboxylic acid **11**.⁹ Treatment of this acid with concentrated sulfuric acid and dilution of the mixture with water according to the Clar-Weiss-Korczyn procedure yields a black powder which gives a satisfactory combustion analysis. Because this material is virtually insoluble in all common organic solvents further purification by crystallisation or chromatography is impossible. However, it is very slightly soluble in dimethyl sulfoxide and, although previous workers had identified the powder as the

Table 1 The four simplest representatives of the family of non-Kekulé polynuclear aromatics 1-4 compared to isomeric Kekulé (classical) structures^a

Formula	Kekulé	Non-Kekulé
C ₂₂ H ₁₂		
C ₂₄ H ₁₄		
C ₂₆ H ₁₆		
C ₂₆ H ₁₆		

^a Note that for a Kekulé system with $2n$ π -electrons there are n fully occupied π -bonding orbitals, n vacant antibonding orbitals, and a singlet ground state. For the corresponding non-Kekulé system there are $n-1$ bonding orbitals, $n-1$ vacant antibonding orbitals and a degenerate pair of half-occupied non-bonding orbitals. Depending on the form of these orbitals such non-Kekulé systems may possess either a singlet or triplet ground state.¹³

pure diketophenol **12**, the ¹H NMR spectrum in [²H₆]-DMSO suggests that it is actually quite impure. This impression is reinforced by the IR spectrum (Nujol mull) which, as well as peaks attributable to the desired ketone, always shows a strong absorption $\nu_{\text{C=O}}$ ca. 1780 cm⁻¹. This latter suggests that the impurity might be a γ -lactone, presumably arising through the oxidation of the methanetriyl carbon in the strongly acid reaction medium. When this black powder is refluxed with potassium carbonate-ethanol the impurity is removed. We assume that the lactone is hydrolysed and the salt produced preferentially dissolved in the ethanol. An insoluble bright blue powder, the potassium salt **13** remains, which is now

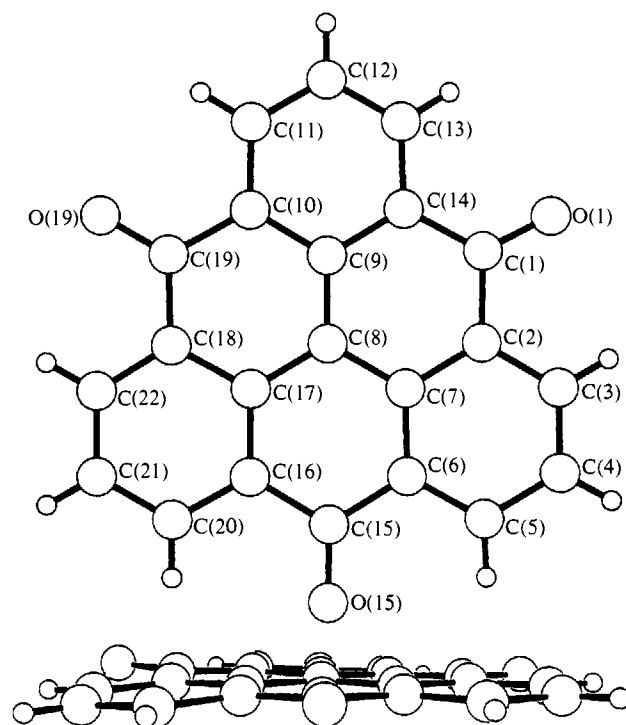
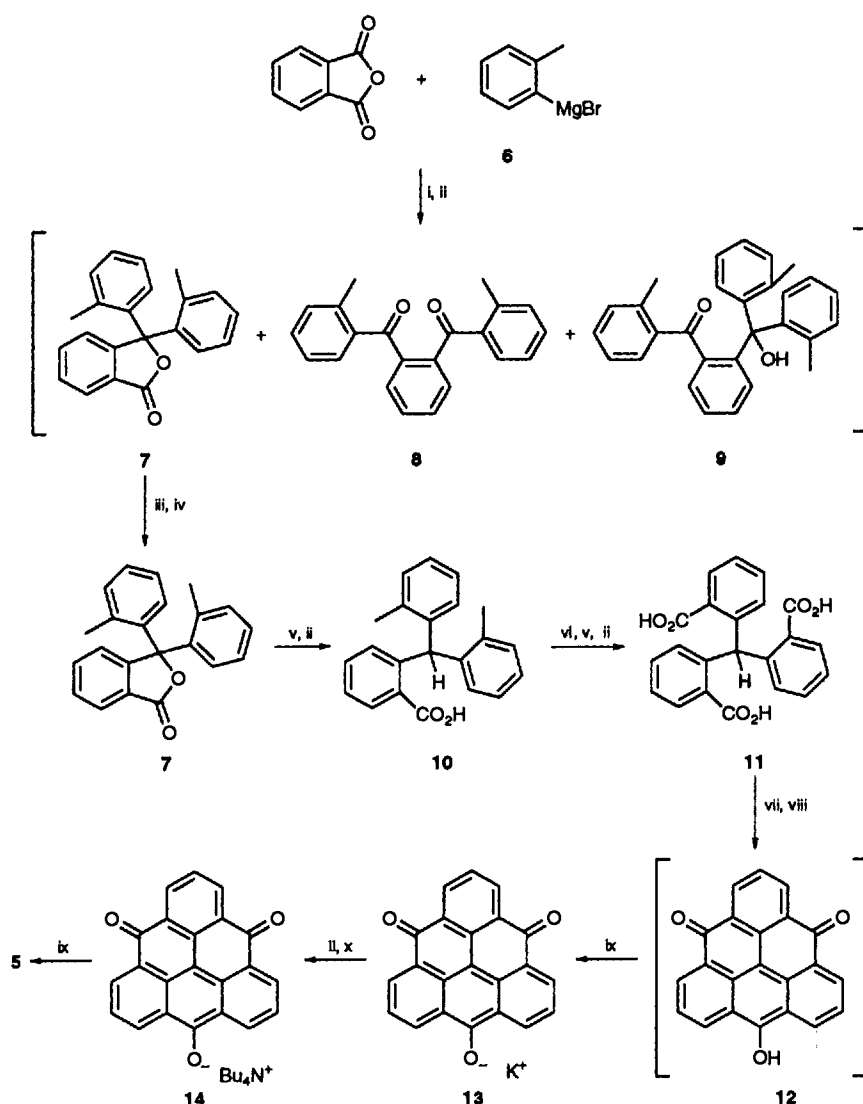


Fig. 2 X-Ray diffraction derived structure of the salt **14** (omitting the tetrabutylammonium counter ion) viewed perpendicular to and edge-on to the molecular plane

spectroscopically pure (¹H and ¹³C NMR spectra in [²H₆]-DMSO and IR in Nujol mull) and gives a fairly satisfactory combustion analysis. It is, however, still non-crystalline and insoluble in most organic solvents. It has a solubility of only 1-2 mg cm⁻³ in DMSO and DMF. It is therefore converted into its tetrabutylammonium salt **14**, which, being crystalline, soluble in most organic solvents and spectroscopically pure, proves a much more tractable substrate for further studies. Elemental analysis shows this salt to be a hemihydrate.

Simple resonance theory leads to the expectation that the anionic nucleus of the salt **14** will be symmetric. Also, polyaryl systems such as this one should be almost planar. These two expectations are largely confirmed by the X-ray crystal structure (Fig. 2). Some problems were experienced with this crystal-structure determination, arising from the fact that the half water of crystallisation is statistically (randomly) distributed, which causes a subtle form of disorder (it should be noted that the final *R*-value is quite high). Table 2 lists several very short contacts between the water molecule and several of the surrounding atoms indicating that it is strongly involved in hydrogen bonding. The molecule, which was refined with an occupancy factor of 0.5, occupies only half of the unit cells within the crystal. The strong hydrogen bonding only occurs in half unit cells within the crystal. If the hydrogen bonding causes slight displacement of anion then the structure solution obtained is the statistical average of the two positions. The displacement must be very small since it proved impossible to resolve the disorder. Data collection at low temperature was not possible since the crystal undergoes a phase transition at approximately 5 °C. Attempts to grow anhydrous crystals and crystals containing 1 equiv. of water both proved unsuccessful. The anion is essentially planar and as the edge-on view in Fig. 2 shows the only significant deviations from planarity are for atoms C(20), C(21) and C(22). Although it is clear from models that such distortions from planarity relieve the unfavourable *peri* interactions between the α -hydrogens and the oxygens they must also result in some loss of conjugation. The fact that this portion of the molecule is closest



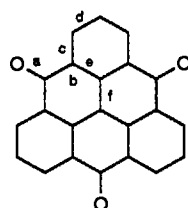
Scheme 1 Reagents and conditions: i, reaction in dry Et₂O; ii, HCl, H₂O; iii, NH₂NH₂, H₂O; iv, filter; v, Na–Hg; vi, KMnO₄, H₂O; vii, conc. H₂SO₄; viii, H₂O; ix, K₂CO₃, EtOH; x, Bu₄N⁺ OH⁻; xi, Na–K, DMF, 10⁻⁵ mmHg

to the water of hydration [O(1W)–O(15), 260 pm; O(1W)–H(20), 225 pm] is probably the significant factor and it suggests that the distortion is related to the interaction with the water. The distribution of the chains of the tetrabutylammonium ion and the positions of neighbouring molecules also contribute to the low-symmetry nature of the environment of each anion. Despite this these anions are close to being three-fold symmetric. The mean carbon–carbon bond lengths and standard deviation for bonds related by the approximate C₃ axis are shown in Fig. 3 which also displays the Hückel molecular orbital derived bond orders. The correlation of carbon–carbon bond orders and bond lengths is within the normal error limits and the Coulson equation is obeyed.¹⁷ The carbon–oxygen bond length of 124 pm is a little greater than the normal C=O bond length found in ketones and may be compared with the C=O bond length in *p*-benzoquinone (122 pm). It is considerably shorter than the C–O bond length in the phenoxide ions (average 130 ± 4 pm for 79 phenoxides in the Cambridge structural data base; excluding picrate salts).

As shown in Fig. 1 the structure of triangulene **1** and its trioxo derivative **5** are fundamentally similar and, in particular, the form of the SOMOs (ψ_{11} and ψ_{12} for **1**, and ψ_{14} and ψ_{15} for **5**) is the same. Whereas it is still difficult to devise a synthesis of triangulene **1** itself, the trioxo derivative **5** should be obtained very simply by a two-electron reduction of the mono-anion **14**. This reaction is analogous to the known reduction of

phenalenone to the oxy-phenalenyl radical.¹⁸ We argued that, like the oxy-phenalenyl radical, the trioxo-triangulene **5** would be stable at room temperature. Cyclic voltammetry showed that the salt **14** underwent a reversible two-electron reduction, confirming that, under an argon atmosphere, the trioxo-triangulene is stable at room temperature for at least a few seconds. When generated under vacuum, it proved stable over many months! When the bright blue solution of the potassium salt **13**, or preferably the tetrabutylammonium salt **14**, in dimethylformamide is reduced with potassium or preferably sodium–potassium alloy under vacuum the blue colour is discharged and when the resulting brown–green solution is frozen the triplet spectrum of trioxo-triangulene is observed, $g = 2.0034$, $|D/hc| = 0.0064 \text{ cm}^{-1}$, $|E/hc| = 0.0000$. The zero value of $|E/hc|$ is consistent with a biradical that has three-fold symmetry (*i.e.* it is uniaxial) and the value of $|D/hc|$ is consistent with the proposed structure.^{1,3} Since the half-field $\Delta m = 2$ transition is very weak¹⁹ ‘Curie Law’ studies were based on the temperature dependence of the intensity of the $\Delta m = 1$ transition.† These confirmed that the biradical has the expected triplet ground state and that the spectrum does not arise by thermal population of a triplet species. It is one of only a handful

† Experiment by K. Sales and D. Oduwale, Queen Mary and Westfield College, London.



Bond	a	b	c	d	e	f
Number of symmetry (C_3) related bonds	3	6	6	6	6	3
Bond length/pm	123.6	147.4	140.0	137.4	142.4	141.9
Standard deviation	0.8	1.2	0.8	2.6	1.1	1.2
HMO bond order ($h_o = 1.0$)	1.47	1.51	1.56	1.67	1.52	1.52

Fig. 3 Bond-lengths and bond-orders for the salt 14

Table 2 Selected bond lengths (pm), angles ($^\circ$) and non-bonded contacts (pm) for compound 14 with e.s.d.s in parentheses

C(1)–O(1)	124.3(7)	C(2)–C(1)	145.9(9)
C(14)–C(1)	147.6(8)	C(3)–C(2)	139.7(8)
C(7)–C(2)	142.8(8)	C(4)–C(3)	137.3(9)
C(5)–C(4)	139.3(8)	C(6)–C(5)	139.6(8)
C(7)–C(6)	141.5(9)	C(15)–C(6)	148.1(9)
C(8)–C(7)	142.9(8)	C(9)–C(8)	140.1(9)
C(17)–C(8)	142.6(9)	C(10)–C(9)	144.3(9)
C(14)–C(9)	141.1(9)	C(11)–C(10)	139.0(11)
C(19)–C(10)	147.0(10)	C(12)–C(11)	135.2(11)
C(13)–C(12)	138.8(9)	C(14)–C(13)	139.5(10)
C(15)–O(15)	122.5(9)	C(16)–C(15)	149.5(10)
C(17)–C(16)	141.0(10)	C(20)–C(16)	141.6(9)
C(18)–C(17)	143.9(9)	C(19)–C(18)	146.0(11)
C(22)–C(18)	140.7(11)	C(19)–O(19)	123.9(8)
C(21)–C(20)	140.5(11)	C(22)–C(21)	133.2(13)
C(2)–C(1)–O(1)	121.4(6)	C(14)–C(1)–O(1)	121.6(7)
C(14)–C(1)–C(2)	116.9(6)	C(3)–C(2)–C(1)	119.9(6)
C(7)–C(2)–C(1)	120.7(6)	C(7)–C(2)–C(3)	119.4(7)
C(4)–C(3)–C(2)	121.9(6)	C(5)–C(4)–C(3)	119.4(6)
C(6)–C(5)–C(4)	120.7(7)	C(7)–C(6)–C(5)	120.4(6)
C(15)–C(6)–C(5)	118.3(7)	C(15)–C(6)–C(7)	121.3(6)
C(6)–C(7)–C(2)	118.2(6)	C(8)–C(7)–C(2)	119.9(7)
C(8)–C(7)–C(6)	121.9(6)	C(9)–C(8)–C(7)	120.8(6)
C(17)–C(8)–C(7)	118.7(7)	C(17)–C(8)–C(9)	120.5(6)
C(10)–C(9)–C(8)	121.8(7)	C(14)–C(9)–C(8)	121.0(6)
C(14)–C(9)–C(10)	117.2(8)	C(11)–C(10)–C(9)	120.0(7)
C(19)–C(10)–C(9)	119.1(9)	C(19)–C(10)–C(11)	120.8(7)
C(12)–C(11)–C(10)	121.5(7)	C(13)–C(12)–C(11)	120.1(9)
C(14)–C(13)–C(12)	121.0(8)	C(9)–C(14)–C(1)	120.7(7)
C(13)–C(14)–C(1)	119.2(7)	C(13)–C(14)–C(9)	120.2(7)
O(15)–C(15)–C(6)	121.5(8)	C(16)–C(15)–C(6)	114.8(8)
C(16)–C(15)–O(15)	123.7(7)	C(17)–C(16)–C(15)	121.7(7)
C(20)–C(16)–C(15)	117.5(8)	C(20)–C(16)–C(17)	120.8(7)
C(16)–C(17)–C(8)	121.4(7)	C(18)–C(17)–C(8)	119.8(8)
C(18)–C(17)–C(16)	118.8(7)	C(19)–C(18)–C(17)	121.0(7)
C(22)–C(18)–C(17)	117.7(9)	C(22)–C(18)–C(19)	121.4(8)
C(18)–C(19)–C(10)	117.6(7)	O(19)–C(19)–C(10)	121.5(9)
O(19)–C(19)–C(18)	120.8(8)	C(21)–C(20)–C(16)	118.3(9)
C(22)–C(21)–C(20)	121.4(8)	C(21)–C(22)–C(18)	123.0(9)
O(1w) ... O(15)	259.9(10)	O(1w) ... H(20)	225.0(11)
O(1w) ... O(1 ^a)	270.6(10)	H(26c) ... O(19 ^b)	256.0(11)
O(1w) ... H(21 ^c)	246.8(11)	O(1w) ... H(27a ^d)	252.4(11)
O(1w) ... H(29a ^d)	239.5(11)		

Superscripted atoms are related to their reference atoms at (x, y, z) as follows: (a) $-0.5 - x, -0.5 + y, 0.5 - z$; (b) $0.5 + x, 1.5 - y, -0.5 + z$; (c) $-1.0 - x, 1.0 - y, 1.0 - z$; (d) $0.5 - x, -0.5 + y, 0.5 - z$.

of triplet-ground-state organic molecules that is stable at room temperature. Under vacuum, samples can be stored for many months without loss in the intensity of the ESR signal. It is, however, very sensitive to oxygen and once the sealed tube is

broken open the bright blue coloration of the ketone 14 is instantly restored.

For the first time it has been possible to make and to observe the ESR spectrum of an open-shell non-Kekulé polynuclear aromatic system, albeit of a derivative. Synthesis and spectroscopic observation of the parent hydrocarbons 1–4 remain a challenge. Although it is difficult to be sure whether the three oxygen substituents stabilise the triangulene nucleus³ the results obtained so far, and reported in this paper, seem to cast doubt on the current suggestion⁶ that non-Kekulé polynuclear aromatics are intrinsically highly unstable.

Experimental

Mps were determined either on a Reichart hot stage or in a Griffin melting point apparatus and are uncorrected. Samples for combustion analysis were routinely dried by heating at $65^\circ\text{C}/0.5\text{ mmHg}$ for 3 days.

UV–VIS spectra were recorded in ethanol solution using a Pye-Unicam PU8800 UV–VIS spectrophotometer. IR spectra were recorded as Nujol mulls on a Perkin-Elmer 1420 ratio recording spectrophotometer or a Philips PU 9706 spectrophotometer. Only significant or assignable absorbances are recorded.

NMR spectra were recorded on a General Electric QE300 or a Bruker AM400 instrument. Chemical shifts are given relative to tetramethylsilane, coupling constants J are given in Hz, and unless stated otherwise the solvent used was CDCl_3 .

Mass spectra were obtained on a VG Autospec instrument. All peaks $> 20\%$ of M^+ (and less intense peaks of particular significance) are reported.

Solvents were routinely purified according to the procedures recommended by Perrin.²⁰

Column chromatography on silica refers to the use of Merck Kieselgel 7731 Type 60 and thin layer chromatography to Merck Kieselgel 7730 GF254.

3,3-Di-*o*-tolyl-1,3-dihydro-2-benzofuran-1-one 7.—2-Bromotoluene (140 cm^3 , 199 g , 1.16 mol) was added dropwise over 30 min to a vigorously stirred refluxing suspension of magnesium (30 g , 1.25 mol) in diethyl ether (600 cm^3). The reaction mixture was refluxed for a further 3 h under an atmosphere of nitrogen. The resulting green solution was then pumped through PTFE tubing, using nitrogen pressure, onto a solution of phthalic anhydride (70 g , 0.47 mol) in benzene (1000 cm^3) at such a rate that only a gentle reflux of solvent was observed. The reaction mixture was then refluxed for a further 24 h, after which the mixture was pumped onto $2\text{ mol dm}^{-3}\text{ HCl}$ (1000 cm^3), again at such a rate that only a gentle reflux of solvent was observed. The organic phase was separated, washed with water ($3 \times 100\text{ cm}^3$), dried (MgSO_4) and filtered. The

solvent was evaporated to give a viscous orange-red gum, which was dissolved in ethanol (750 cm³), then refluxed with hydrazine hydrate (30 cm³) for 24 h. Thereafter the solution was reduced by evaporation to approximately 10% of the original volume and the resulting mixture filtered. The residue was washed with ethanol (3 × 50 cm³), then dried to yield the pure title compound **7** (55 g, 37%), mp 172–174 °C (from ethanol; lit.,⁷ 174 °C) (Found: C, 84.1; H, 5.8. C₂₂H₁₈O₂ requires C, 84.15; H, 5.7%; λ_{max}/nm 268 (ε/dm³ mol⁻¹ cm⁻¹ 1790); ν_{max}/cm⁻¹ 1775 (C=O) and 1610 (C=C); δ_H 2.15 (6 H, s, CH₃), 7.02 (2 H, d, *J* 7.0), 7.08 (2 H, t, *J* 7.0), 7.28 (2 H, t, *J* 7.0), 7.34 (2 H, d, *J* 7.0), 7.40 (1 H, d, *J* 9.2), 7.57 (1 H, t, *J* 9.2), 7.70 (1 H, t, *J* 9.2) and 7.95 (1 H, d, *J* 9.2); δ_C 21.5 (ArCH₃), 94.0, 125.1, 125.6, 126.4, 127.1, 128.5, 129.2, 132.8, 133.8, 137.1, 138.7 and 169.9 (C=O).

Also isolated from the orange-red gum by column chromatography of a small portion on silica [light petroleum (bp 40–60 °C)–chloroform, 1:1] was *o*-[hydroxybis(*o*-tolyl)-methyl]phenyl(*o*-tolyl)methanone **9**, m.p. 120 °C (from CHCl₃; lit.,⁹ 124–126 °C); δ_H 1.25 (1 H, s, OH), 2.3 (3 H, s, CH₃), 2.5 (3 H, s, CH₃), 2.75 (3 H, s, CH₃), 7.15 (1 H, dd, *J* 7.9 and 2.0), 7.25 (1 H, dt, *J* 7.9 and 2.0), 7.45 (12 H, m), 7.75 (2 H, m) and 7.93 (1 H, dd, *J* 7.9 and 2.0); δ_C 19.8 (ArCH₃), 20.6 (ArCH₃), 21.3 (ArCH₃), 119.9, 122.2, 124.4, 125.1, 125.4, 125.8, 127.1, 127.5, 127.8, 129.2, 129.7, 130.4, 130.7, 131.3, 131.5, 135.7, 136.4, 137.2, 139.5, 140.9, 141.5, 145.2 and 198.5 (C=O); *m/z* 389 (M⁺, 50%), 298 (24, M⁺ – C₇H₇), 195 (20), 119 (100, M⁺ – C₇H₇ – CO), 91 (66, C₇H₇⁺) and 51 (26); the inequivalence of the three methyl resonances in this compound presumably results from hindered rotation; and di(*o*-tolyl)-*o*-phenylenedimethanone **8** mp 143–145 °C (from chloroform; lit.,⁷ 128–131 °C); λ_{max}/nm 244 (ε/dm³ mol⁻¹ cm⁻¹ 7410); δ_H 2.3 (6 H, s, CH₃), 7.12 (2 H, dt, *J* 1.0 and 7.5), 7.2 (4 H, m), 7.3 (2 H, dt, *J* 1.0 and 7.5) and 7.5 (4 H, m); δ_C 20.5 (ArCH₃), 125.0, 129.7, 130.7, 131.4, 137.1, 139.4, 140.8 and 198.3 (C=O); *m/z* 314 (M⁺, 87%), 223 (26, M⁺ – C₇H₇), 195 (100, M⁺ – C₇H₇ – CO), 165 (32), 119 (62), 105 (13, M⁺ – 2 × C₇H₇ – CO) and 91 (85, C₇H₇⁺).

*2-(Di-*o*-tolylmethyl)benzoic Acid 10.*⁹—Powdered 3% sodium amalgam (240 g) was added to a refluxing solution of 3,3-di-*o*-tolyl-1,3-dihydro-2-benzofuran-1-one **7** (30 g, 0.095 mol) in ethanol (600 cm³) over 4 h. The mixture was then refluxed for a further 24 h. Thereafter the ethanol was distilled from the reaction vessel and the residue boiled with water for 15 min. The aqueous phase was decanted from the vessel and the procedure then repeated a further five times. The combined aqueous fractions were acidified to pH 1 with 36% hydrochloric acid. The resulting slurry was filtered, and the residue washed with water. This residue was redissolved in 2 mol dm⁻³ aqueous sodium hydroxide, the solution filtered, and then reacidified with 36% hydrochloric acid. After cooling and filtration, the residue was washed with water (3 × 250 cm³) and dried to give the title compound **10** (29 g, 90%), mp 243–245 °C (from ethanol; lit.,⁹ 243 °C) (Found: C, 83.2; H, 6.35. C₂₂H₂₀O₂ requires C, 83.5; H, 6.3%; ν_{max}/cm⁻¹ 2500–3600 (OH), 1700 (C=O) and 1610 (C=C); δ_H ([²H₆]-DMSO) 2.2 (6 H, s, CH₃), 6.62 (2 H, d, *J* 8.0), 6.85 (1 H, d, *J* 7.0), 6.92 (1 H, s, CHAr₃), 7.0–7.2 (6 H, m), 7.26 (1 H, t, *J* 7.0), 7.33 (1 H, t, *J* 7.0) and 7.96 (1 H, dd, *J* 8.0, 1.0); δ_C ([²H₆]-DMSO) 19.4 (ArCH₃), 46.1 (CHAr₃), 125.5, 126.0, 126.1, 129.0, 130.1, 130.3, 131.2, 131.4, 137.0, 142.1 and 168.5 (C=O).

*2,2',2''-(Methanetriyl)tribenzoic Acid 11.*⁹—2-(Di-*o*-tolylmethyl)benzoic acid **10** (29 g, 0.092 mol) was added to a solution of sodium carbonate (60 g) in water (2250 cm³) and boiled until it had dissolved. Potassium permanganate (90 g, 0.057 mol) was added over 4 h. Nitrogen was bubbled through an air bleed to prevent bumping of the mixture while the reaction was boiled

for a further 24 h. Thereafter the reaction mixture was reduced to approximately 10% of its original volume and ethanol (500 cm³) was added. The mixture was set aside until all the purple coloration had been discharged, after which it was filtered through Celite, and the residue washed with hot ethanol (3 × 250 cm³). The combined filtrates were refluxed with 3% sodium amalgam (120 g) for 24 h. After being decanted from the mercury residues, the solution was reduced to approximately 10% of its original volume, acidified to pH 1 with 36% hydrochloric acid, cooled and filtered to yield the title compound **11** (18.5 g, 54%), mp 285–290 °C (from ethanol; lit.,⁹ 303 °C) (Found: C, 68.7; H, 4.1. C₂₂H₁₆O₆ 0.5 H₂O requires C, 68.6; H, 4.15%; λ_{max}/nm 274 (ε/dm³ mol⁻¹ cm⁻¹ 8670); ν_{max}/cm⁻¹ 2300–3300 (OH), 1700 (C=O) and 1610 (ArC=C); δ_H ([²H₆]-DMSO) 6.90 (3 H, d, *J* 8.0), 7.22 (3 H, t, *J* 8.0), 7.32 (3 H, t, *J* 8.0), 7.88 (3 H, d, *J* 8.0), 8.11 (1 H, s, CHAr₃) and 12.5 (3 H, s, OH); δ_C ([²H₆]-DMSO) 46.7 (CHAr₃), 125.9, 130.5, 130.7, 131.0, 131.4, 145.6 and 168.2 (C=O).

Potassium 4,8-Dioxo-4H,8H-dibenzo[cd,mn]pyren-12-olate 13.—2,2',2''-(Methanetriyl)tribenzoic acid **11** (30 g, 0.078 mol) was mixed with sulfuric acid (*d* 1.835; 500 cm³) and the mixture was heated to 120 °C for 2 h. The resulting blue solution was cooled and added to ice-cold water (1500 cm³) to give a thick blue-black emulsion. The solids were separated by centrifugation, washed on the centrifuge with water (3 × 100 cm³), transferred to a clean reaction vessel and refluxed for 24 h with potassium carbonate (11 g) in ethanol (500 cm³). After cooling, water (500 cm³) was added to the reaction mixture. The resulting blue suspension was filtered and the residue washed with water (3 × 250 cm³) and dried to yield the potassium salt **13** (20.7 g, 57%) (Found: C, 73.0; H, 3.0; K, 10.3. C₂₂H₉KO₃ requires C, 73.3; H, 2.5; K, 10.8%; λ_{max}(DMSO)/nm 580 (ε/dm³ mol⁻¹ cm⁻¹ 3120), 640 (3480), 644 (5160) and 680 (4860); ν_{max}/cm⁻¹ 1600 (C=O) and 1560 (ArC=C); δ_H ([²H₆]-DMSO) 7.5 (3 H, t, *J* 7.6, 2-, 6- and 10-H) and 8.74 (6 H, d, *J* 7.6, 1-, 3-, 5-, 7-, 9- and 11-H); δ_C ([²H₆]-DMSO) 99.9, 108.8, 120.2, 126.9, 132.8 and 180.5 (C=O).

The salt **13** could be methylated and acetylated but the resultant derivatives proved air sensitive. They could be obtained entirely free from impurities as judged by ¹H NMR spectroscopy, but analytical samples could not be obtained. Attempted crystallisation or repeated chromatography resulted in rapidly diminishing yields.

The salt **13** (37 mg, 0.1 mmol) was stirred with diazomethane solution (approx. 0.5 g in 40 cm³ diethyl ether) for 2 days. The mixture was evaporated to dryness and subjected to column chromatography on silica eluting with 0.25% v/v methanol-dichloromethane followed by preparative thin layer chromatography on silica eluting with the same solvent. Isolation of the purple band gave 12-methoxy-4H,8H-dibenzo[cd,mn]pyrene-4,8-dione as a red solid, 1.5 mg (4.4%); λ_{max}(CHCl₃)/nm 390 (ε/dm³ mol⁻¹ cm⁻¹ 11 000), 448 (15 400), 492 (21 100), 516 (22 500); ν_{max}/cm⁻¹ 1720 (C=O); δ_H 4.75 (3 H, s, OCH₃), 7.80 (1 H, t, *J* 6.5, 2-H), 7.92 (2 H, t, *J* 7.6, 8- and 10-H), 8.82 (2 H, d, *J* 7.6, 7- and 9-H), 8.84 (2 H, d, *J* 7.6, 5- and 11-H) and 9.00 (2 H, d, *J* 6.5, 1- and 3-H).

The salt **13** (50 mg, 0.14 mmol) was stirred with a mixture of acetic anhydride (10 cm³) and concentrated sulfuric acid (1 cm³) for 3 h. The mixture was added to water (20 cm³), and extracted with dichloromethane (10 × 50 cm³). The red solution was dried, filtered, and evaporated. Column chromatography and thin-layer chromatography using the same solvent system as before gave 12-acetoxy-4H,8H-dibenzo[cd,mn]pyrene-4,8-dione as a red solid (3.2 mg, 6.3%); λ_{max}(CHCl₃)/nm 396 (ε/dm³ mol⁻¹ cm⁻¹ 10 500), 436 (10 300), 480 (13 800), 510 (17 600) and 540 (12 000); ν_{max}/cm⁻¹ 1730 (C=O); δ_H 2.74 (3 H, s, CH₃), 7.81 (1 H, t, *J* 7.7, 2-H), 7.93 (2 H, t, *J* 8.0, 6- and 10-H), 8.45 (2 H, d,

J 8.0, 7- and 9-H), 8.82 (2 H, d, *J* 8.0, 5- and 11-H) and 8.98 (2 H, d, *J* 7.7, 1- and 3-H).

Tetrabutylammonium 4,8-Dioxo-4H,8H-dibenzo[cd,mn]-pyren-12-olate 14.—Concentrated hydrochloric acid (20 cm³) was added to the potassium salt **13** (2 g) in water (300 cm³) and the mixture gently warmed. After 2 h the resulting precipitate was filtered off and washed. The precipitate was added to a solution of 1 mol dm⁻³ aqueous tetrabutylammonium hydroxide (10 cm³). The reaction mixture was stirred for 1 h, after which the precipitated solid was once again filtered off, dried *in vacuo*, and transferred to the thimble of a Soxhlet extraction apparatus. Continuous extraction with dichloromethane and evaporation of the solution gave the crystalline bright blue tetrabutylammonium salt (1.3 g, 57%), which decomposed before melting (Found: C, 79.4; H, 8.1; N, 2.5. C₃₈H₄₅O₃N·0.5H₂O requires C, 79.7; H, 8.1; N, 2.5%; $\delta_{\text{H}}([^2\text{H}_6\text{O}]\text{-DMSO})$ 1.1 (12 H, t, *J* 7.0, CH₃), 1.45 (8 H, m, CH₂), 1.7 (8 H, m, CH₂), 3.3 (8 H, m, CH₂), 7.7 (3 H, t, *J* 7.6, 2-, 6- and 10-H) and 8.74 (6 H, d, *J* 7.6, 1-, 3-, 5-, 7-, 9- and 11-H).

Various attempts to explore the chemistry of compound **14**, involving heating the salt in solution, resulted in formation of the hydroxy compound **12** and the corresponding *O*-butyl derivative. Clearly, the anion **13** is capable of acting both as a base and a nucleophile towards the tetrabutylammonium counter ion. This phenomenon was also observed when an attempt was made to obtain a mass spectrum from this salt. As well as a base peak at *m/z* 142 (100% Bu₂N=CH₂⁺) strong peaks were observed at *m/z* 322 (46%, **10**⁺) and at 378 (6%, *O*-butyl derivative of **10**⁺). Presumably these two last mentioned materials arose from thermolysis in the port of the spectrometer.

X-Ray Crystallographic Analysis of Compound 14.—All crystallographic measurements were carried out at ambient temperature on a Stoe STAD14 diffractometer operating in the ω - θ scan mode using graphite-monochromated Cu-K α radiation ($\lambda = 154.185$ pm) and an on-line profile fitting method.²¹ The data-set was not corrected for absorption.

The structure was solved by direct methods using SHELXS-86²² and was refined by full-matrix least squares using SHELX-76.²³ All non-hydrogen atoms were refined with anisotropic displacement parameters, including a water solvate molecule which was refined with an occupancy factor of $\frac{1}{2}$. All hydrogen atoms were constrained to calculated positions (C-H = 96 pm) and were assigned an overall isotropic thermal parameter. The weighting scheme $w = [\sigma^2(F_o)]^{-1}$ was used. The final difference map was flat and displayed no features of chemical significance (maximum and minimum residual electron densities, 0.54 and -0.36 eÅ⁻³). An ORTEP²⁴ drawing of the anion of compound **14** is given in Fig. 2.

Crystal data. C₃₈H₄₅NO₃·0.5H₂O, 0.6 × 0.4 × 0.2 mm, *M* = 572.79 (includes hemihydrate), monoclinic, space group *P*2₁/*n*, *a* = 957.54(4), *b* = 1875.49(12), *c* = 1775.81(6) pm, $\beta = 97.018(4)^\circ$, *U* = 3.1718(3) nm³, *Z* = 4, *D*_x = 1.20 mg m⁻³, $\mu = 0.557$ nm⁻¹, *F*₀₀₀ = 1236.

Data collection. Each scan was divided into 30 steps, scan width and step sizes were calculated from a learnt profile, scan speeds 0.5–1.5 s⁻¹ depending on fast pre-scan, 4.0 < 2θ < 130.0°. 5521 Observed reflections, 3548 of which were unique and 3548 with *F*_o > 4.0 $\sigma(F_o)$.

Structure refinement. Number of parameters = 402, *R* = $\Sigma |F_o| - |F_c| / \Sigma |F_o| = 0.0881$, *R*_w = 0.0886, maximum $\Delta/\sigma = 0.10$ [in *y/b* of C(26)].

Supplementary data, which include hydrogen coordinates and all thermal parameters together with complete bond

lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre and are available on request.†

Reduction of the Salts 13 and 14.—Reduction and ESR spectroscopy studies were carried out using a two-chamber cell and vacuum line system of the type previously described.²⁵ A small pellet of sodium and a roughly equal pellet of potassium were added to the 'anion-generation' chamber, the cell attached to the vacuum line and evacuated. The mixture was melted using a small flame. Once cool the cell was detached from the line, the salt (**13** or **14**, *ca.* 5 mg) and dry, distilled *N,N*-dimethylformamide (*ca.* 2 cm³) were rapidly added and the cell re-attached to the line. After 3 freeze-pump-thaw cycles the cell was evacuated (*ca.* 10⁻⁵ mmHg), sealed and detached from the line. Once the solution had turned from bright blue to brown-green it was filtered into the ESR tube and the spectrum determined in the usual way.

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† For full details of the deposition scheme, see 'Instructions for Authors (1995)', Issue 1.

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