

- tive of n . In these terms, no planar heteromorphic $2p_x-3d_x$ (xz) system can be aromatic. Therefore, no alternation effect analogous to the Hückel $4n + 2$ rule for planar p_x-p_x systems is to be expected. The argument is perhaps naïve, but the conclusion is identical with that reached in Craig's more rigorous analysis.^{23a} For detailed discussions and leading references on the possibility (or otherwise) of aromaticity in systems containing d orbitals see ref 23.
- (23) (a) D. P. Craig in "Theoretical Organic Chemistry", Kekulé Symposium, Butterworth, London, 1959, p 20; D. P. Craig and N. L. Paddock in "Nonbenzenoid Aromatics", Vol. 2, J. P. Snyder, Ed., Academic Press, New York, N.Y., 1971, p 273; (b) L. Salem, "The Molecular Orbital Theory of Conjugated Systems", W. A. Benjamin, New York, N.Y., 1966, p 158; M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969, p 430.
- (24) I. Gutman and N. Trinajstić, *Top. Curr. Chem.*, **42**, 49 (1973), and references cited therein. The graph-theoretic demonstration (the "loop rule") is, however, still restricted to Hückel topologies. It is difficult to see what graph-theoretic significance can be attached to the negative

- off-diagonal elements that necessarily occur in the topological matrix of a Möbius system.
- (25) For instance, Craig's rules,^{23a,29} which test for a totally symmetric VB ground state, are restricted to systems possessing a twofold axis that passes through at least two π centers. Many polycycles of interest, e.g., benzocyclobutadiene, are thereby excluded. Moreover, the rules refer only to Hückel topology.
- (26) D. P. Craig, *J. Chem. Soc.*, 3175 (1951); "Non-Benzenoid Aromatic Compounds", D. Ginsburg, Ed., Interscience, New York, N.Y., 1959, p 1.
- (27) The sign \sim is placed in the two-atom bridge of **41**, because this is common to the two Möbius circuits of the network but outside the six-atom Hückel circuit. Correct usage of the sign \sim is generally self-evident if it is thought of as denoting a nodal intersection or a negative overlap in the basis set of AO's.
- (28) E.g., R. Huisgen and H. Seidel, *Tetrahedron Lett.*, 3381 (1964); G. Quinkert, K. Opitz, W. W. Wiersdorff, and M. Finke, *ibid.*, 3009 (1965).
- (29) G. L. Closs and P. E. Pfeffer, *J. Am. Chem. Soc.*, **90**, 2452 (1968).
- (30) Reference 1a, p 76.
- (31) Reference 1a, p 79.
- (32) Reference 1a, p 107 ff.
- (33) H. E. Simmons and T. Fukunaga, *J. Am. Chem. Soc.*, **89**, 5208 (1967); R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, **89**, 5215 (1967).
- (34) M. J. Goldstein and R. Hoffmann, *J. Am. Chem. Soc.*, **93**, 6193 (1971).
- (35) M. J. Goldstein, *J. Am. Chem. Soc.*, **89**, 6357 (1967).
- (36) D. H. Rouvray, *Chem. Br.*, **10**, 11 (1974); *R. Inst. Chem. Rev.*, **4**, 173 (1971); A. T. Balaban, Ed., "Chemical Applications of Graph Theory", Academic Press, London, England, 1974.
- (37) A. Rassat, *C. R. Acad. Sci. Ser. C*, **274**, 730 (1972).

Perturbed [12]Annulenes. Derivatives of Dibenzo[*cd,gh*]pentalene¹

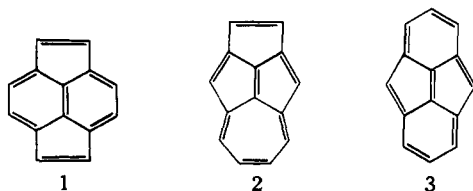
Barry M. Trost^{*2} and Philip L. Kinson³

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received August 13, 1974

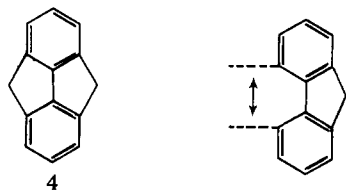
Abstract: The synthesis of 4,8-dihydrodibenzo[*cd,gh*]pentalene from 4,5-methylenephenanthrene is reported. The key step involves a ring contraction of the diazo ketone from 4,5-methylene-9,10-phenanthraquinone which is complicated by an unusual addition of the intermediate ketocarbene to the aromatic solvent. This dihydrodibenzopentalene derivative serves as the precursor of three derivatives of dibenzo[*cd,gh*]pentalene, dibenzo[*cd,gh*]pentaleno-4,8-quinone, dibenzo[*cd,gh*]pentaleno-4,8-semiquinone anion, and dilithium dibenzo[*cd,gh*]pentalenide. The properties of these derivatives support the utilization of the peripheral electronic model which describes the dibenzopentalene system as a perturbed [12]annulene. The use of pentafluorophenylcopper in a decarboxylation of a benzhydryl carboxylic acid is described.

The concept of antiaromaticity, founded in molecular orbital theory, remains an important challenge in organic chemistry.⁴ While various monocyclic [4 n]annulenes have been made, all the members except for $n = 1$ suffer from sufficiently gross molecular distortions from the required symmetrical planar structure to make them invalid tests of the model.⁵ Studies on the cyclobutadiene system have been somewhat perplexing. Infrared studies suggest a square planar structure for the parent system,⁶ while 1,2-diphenylcyclobutadiene^{7a} and "push-pull" cyclobutadienes^{7b} have been claimed to be rectangular structures that rapidly equilibrate by bond shift. A paramagnetic ring current has been claimed for tri-*tert*-butylcyclobutadiene.⁸ Electrochemical studies of substituted derivatives suggest substantial electronic destabilization. The dehydro[12]annulenes,^{9a} which should exhibit greater molecular planarity than the parent [12]annulene,^{9b} do exhibit properties of a paramagnetic

system. More pertinent work lies in the very recent reports of 1,3,5-tri-*tert*-butylpentalene and 1,6- and 1,7-bridged methano[12]annulenes for which NMR data suggest substantial paramagnetic contributions to the proton chemical shifts.¹⁰ We initiated a series of studies directed toward the three isoelectronic hydrocarbons **1–3** since we felt that these would be unusually good models for the planar [12]annulene with minimum bond alternation (the structural requirements for antiaromaticity).¹¹ As a criterion for the success of our peripheral electronic model, we took the splitting between the HOMO and LUMO. For the antiaromatic [12]annulene system, these orbitals are degenerate, and the molecule is a ground-state triplet. Therefore, the success of these structures in serving as models for the antiaromatic [12]annulene system requires a minimum perturbation from the triplet ground state. Calculations support this contention. PPP-SCF calculations indicate the lowest lying triplet state of pyracylene **1** is approximately 2.05 eV above the ground state, while that for dibenzo[*cd,gh*]pentalene (**3**) is only 0.32 eV. Compound **2** falls in between. Indeed, the spectroscopic and chemical properties of pyracylene are quite abnormal and can be best interpreted in terms of a perturbed [12]annulene.¹¹ In this paper, we wish to report our studies directed toward the dibenzopentalene system **3**.



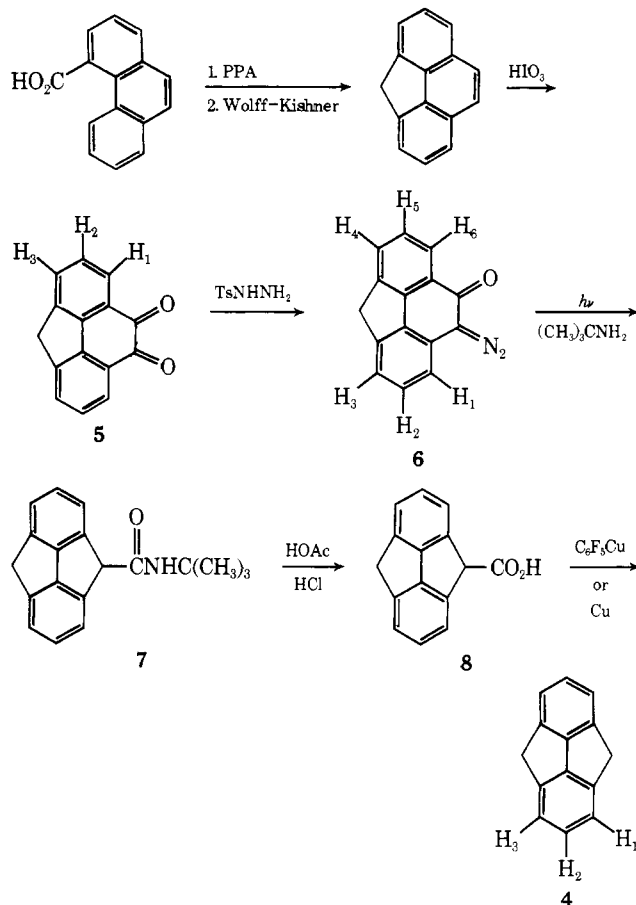
The synthetic challenge of this molecule lies in its high strain energy. We can consider the extent of the problem by examining 4,8-dihydrodibenzo[*cd,gh*]pentalene (**4**), a logical precursor to **3**, in relation to fluorene. In essence, we are bridging C-4 and C-5 of fluorene, a distance of 3.31 Å, by a single carbon atom.¹² The fact that the distance to be bridged is greater than the total length of two carbon-carbon σ bonds indicates that **4** will be terribly strained. Based



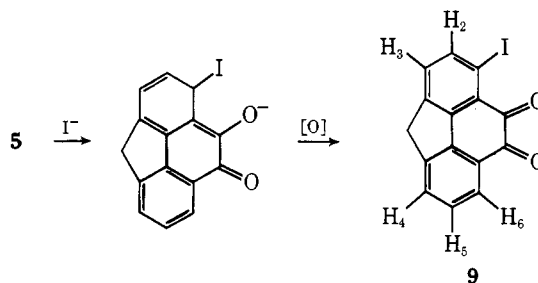
upon the X-ray structure subsequently obtained, we have verified this expectation and derive a strain energy of 66 kcal/mol.¹³ This high strain energy indicates that the synthetic step creating this ring system must possess sufficient driving force to overcome the developing strain energy. We therefore turned to the Wolff rearrangement, a highly successful approach to strained hydrocarbons, as the key reaction.¹⁴

Synthesis of 4,8-Dihydrodibenzo[*cd,gh*]pentalene. 4,8-Dihydrodibenzo[*cd,gh*]pentalene (**4**) was prepared as outlined in Scheme I. 4,5-Methylenepheneanthrene, available

Scheme I. Synthesis of 4,8-Dihydrodibenzo[*cd,gh*]pentalene



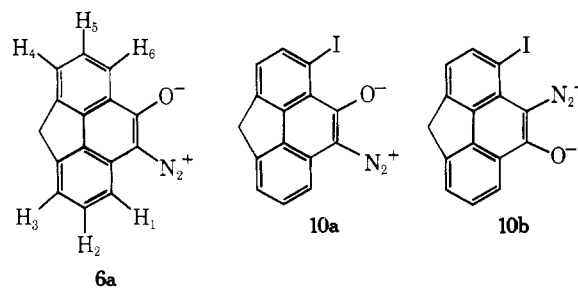
by slightly improved procedures over those of Newman^{15a} and of Medenwald^{15b} from 1,2-dihydrophenanthrene-4-carboxylic acid,¹⁶ was oxidized to its quinone **5**, utilizing iodic acid.¹⁷ A major by-product is the iodinated quinone **9**, mp 252° dec, which could be separated from **5** only with great difficulty. It can be envisioned to arise by conjugate addi-



tion of iodide formed as a by-product from the iodic acid followed by oxidation of the intermediate adduct. Using 1 equiv of iodic acid in acetic acid gave a 21% yield of **9** in addition to a 36% yield of the desired quinone. Utilizing 3.7 equiv of iodic acid and a tenfold dilution of the reaction mixture with dioxane dramatically decreases the yield of **9** (2%) while increasing the yield of quinone **5** to 63%.

The structure of **5** is clearly supported by its spectral properties. In addition to a single carbonyl stretch at 1680 cm⁻¹ in its infrared spectrum¹⁸ (cf. 1680 cm⁻¹ for 9,10-phenanthraquinone), the proton NMR spectrum¹⁹ shows an ABC pattern for the aromatic protons (δ_A 7.84, δ_B 7.75, δ_C 7.39, $J_{AB} = J_{BC} = 8.0$ Hz; $J_{AB} = 1.5$ Hz with $H_A = H_1$, $H_B = H_3$, and $H_C = H_2$) and a singlet (δ 4.03) broadened by allylic coupling for the methylene protons. Insolubility and difficulty in purifying **9** led to its full characterization after conversion to its diazo ketone. The gross structure was clearly supported by a carbonyl frequency¹⁸ at 1680 cm⁻¹ and proton NMR absorptions relative to trifluoroacetic acid at 3.48–3.64 ppm (H_3 , H_4 , H_6) and 3.94–4.12 (H_2 , H_5) and a singlet at 7.54 for the methylene group. It was best to take the mixture of **5** and **9** directly on to the next step.

Treatment of this mixture in ethanol with *p*-toluenesulfonylhydrazine led directly to a mixture of the diazo ketones **6** and **10** which were easily separated by column chromatography on silica gel.²⁰ The mass spectrum of diazo ketone **6** shows in addition to an appropriate molecular ion,

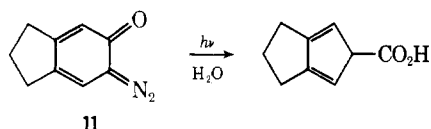


fragment ions for loss of nitrogen (m/e 204), carbon monoxide (m/e 176), and acetylene (m/e 150) with appropriate metastable ions at m/e 179.4, 151.8, and 127.8.²¹ The low-energy carbonyl band in the infrared spectrum¹⁸ (1632 cm⁻¹) indicates a substantial contribution to the structure from the dipolar form **6a**. The most significant feature of the proton NMR spectrum¹⁹ is the appearance of a doublet ($J = 7.6$ Hz) at δ 7.98 and one at δ 7.73 ($J = 7.6$ Hz) corresponding to H_1 and H_6 . The tentative relative assignment of the absorption at lowest field to H_1 is based on an anticipated greater deshielding of the proton ortho to the positive nitrogen. In the diazo ketone from 9,10-phenanthraquinone, the corresponding protons appear at δ 8.15 and 7.75.

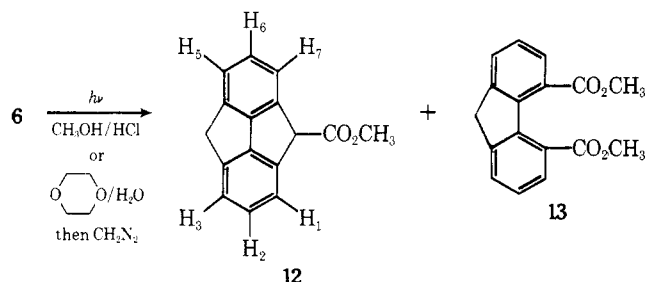
Comparison of these data with those for **10** confirms the structural assignment of the latter. The mass spectrum indicated a molecular formula of $C_{15}H_7N_2OI$ as well as a peak at m/e 332 for loss of acetylene, and peaks at m/e 330, 302, and 175 for successive loss of nitrogen, carbon monoxide, and iodide. The NMR spectrum¹⁹ is most pertinent in confirming the position of the iodine. Only a single doublet for

1 H at low field (δ 8.04, J = 7.6 Hz) is observed indicating that either H₁ or H₆ of **6** is replaced by iodide. This fact establishes structure **9** for the quinone rather than a different positional isomer. Furthermore, if the relative assignments of H₁ and H₆ is accepted, the presence of only a single doublet at δ 8.04 allows **10a** to be assigned to the diazo ketone rather than **10b**. This assignment also agrees with the one that would be made on the assumption that the tosylhydrazine reacts at the less hindered carbonyl group of **9**.

As anticipated, the Wolff rearrangement of **6** proved most troublesome.²² The successful ring contraction of diazo ketone **11** in water suggested these conditions for the

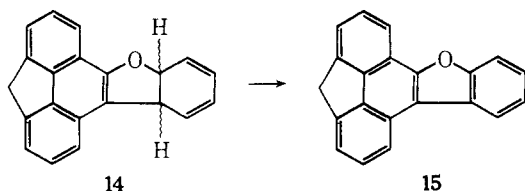


ring contraction.²³ Irradiation of **6** at 3500 Å in aqueous dioxane (for solubility) or in 1.6% hydrochloric acid in methanol led to a very complex mixture of products from which a 0.3% yield of methyl 4,8-dihydrodibenzo[*cd,gh*]pentalene-4-carboxylate (**12**) and, in the former case, a 4.4%



yield of dimethyl fluorene-4,5-dicarboxylate (**13**) were the only ones identified. Mass spectrometry established the formula of **12** as C₁₆H₁₂O₂ and showed fragmentation ions at m/e 204 and 176 with metastable peaks at m/e 176.3 and 151.8 for successive loss of methanol and carbon monoxide. The NMR spectrum¹⁹ exhibited an ABC pattern (H_A = H₃, H_B = H₁, H_C = H₂) with H_A at δ 7.48, H_B at δ 7.36, and H_C at δ 7.20 (J_{AC} = J_{BC} = 7.6 Hz; J_{AB} = 1.5 Hz) for the aromatic protons and singlets at δ 5.38, 4.21, and 3.72 for the methine, methylene, and methyl ester, respectively. Compound **13** was identified by its spectral properties (see Experimental Section).

The disappointingly low yield led to an extensive search for improved reaction conditions. Photolysis of **6** at 3500 Å in benzene containing *tert*-butylamine affords a complex mixture of products from which a 2% yield of *N-tert*-butyl-4,8-dihydrodibenzo[*cd,gh*]pentalene-4-carboxamide (**7**) and a 20% yield of 1a,5a-dihydro(4,5-methylene-9,10-phenanthra)[*d*]benzo[*b*]furan (**14**) have been isolated by pre-



parative thick-layer chromatography.

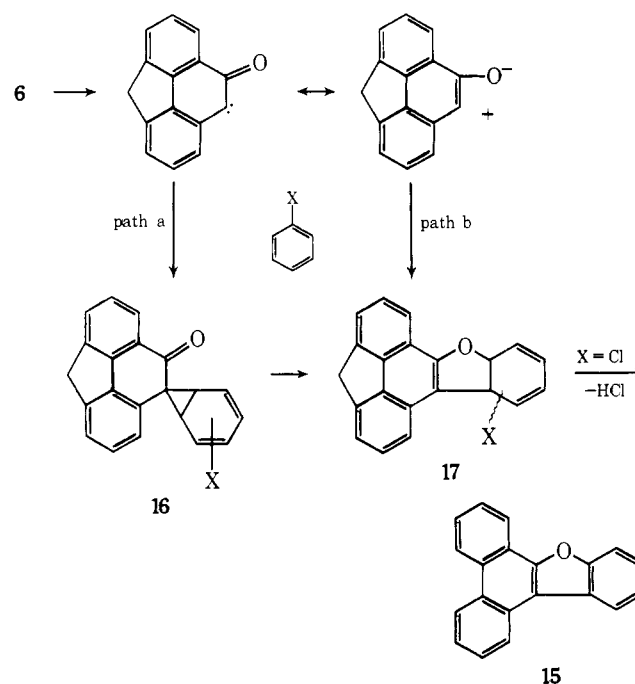
The amide **7** was not obtained pure. The material upon hydrolysis did lead to pure carboxylic acid. Nevertheless, the spectral properties of the crude material did confirm the structural assignment. Thus, the presence of the amide was clearly indicated by infrared bands at 3425, 1670, and 1587 cm⁻¹.¹⁸ The mass spectrum showed a molecular ion at m/e 277.1469 (calcd for C₁₉H₁₉NO, 277.1469) and fragment

ions at m/e 220, 178, and 176 corresponding to loss of isobutylene, *tert*-butyl isocyanate, and *tert*-butylformamide, respectively. Because of the impurities, the aromatic region of the NMR spectrum was an uninterpretable multiplet at δ 7.12–8.08.¹⁹ The methine and methylene protons appear as broadened singlets at δ 5.28 and 4.30, respectively. The amide proton appears as a broad singlet at δ 3.97 and the *tert*-butyl group as a singlet at δ 1.21.

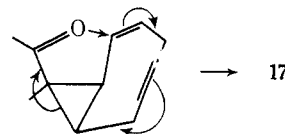
The structure of **14**, mp 42.5–46.0°, rests on its spectral properties, its aromatization with DDQ to **15**, and its mode of formation. Mass spectrometry establishes the formula as C₂₁H₁₄O. The fact that this spectrum consists of almost only two peaks, the molecular ion (base peak) and the M⁺ – 2 ion, indicates a polycyclic polyunsaturated molecule. The infrared spectrum²⁴ shows no carbonyl group and a strong band at 1216 cm⁻¹ for an ether linkage. The NMR spectrum²⁴ is rather complex, presumably because the compound is a mixture of diastereomers. However, multiplets at δ 4.93–5.42 and 6.04–6.95 indicate the presence of nonaromatic vinyl protons and the bridgehead methine hydrogens. Upon aromatization with DDQ, these signals disappear. The spectrum now only shows an aromatic multiplet and a methylene singlet in the ratio of 5:1. The lack of any methylene signal except for the 4,5-methylene bridge (δ 3.50) suggests the dihydro isomer depicted rather than alternative ones (all of which must have a methylene group).

Two likely mechanisms for the formation of dihydrobenzofuran **14** are shown in Scheme II. The ketocarbene may

Scheme II. Addition of **6** to Aromatics



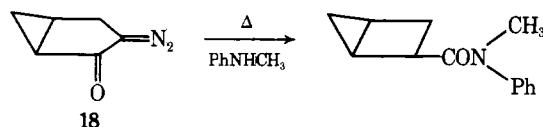
react with solvent either in carbene fashion (path a) to form a cyclopropane followed by rearrangement to the dihydrofuran or by direct dipolar cycloaddition (path b) to **17** (X =



H). The rearrangement of acylcyclopropanes to dihydrofurans is preceded.²⁵ In the case of **16**, an eight-electron process depicted below is also possible. If concerted, orbital symmetry requires an odd number of inversions in the cyclic array of orbitals.

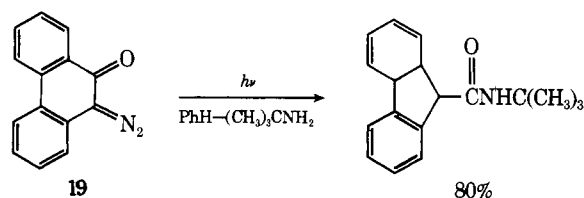
Decreasing the nucleophilicity of the aromatic solvent should increase the yield of the desired product at the expense of **14**; whereas, electron-donating groups should give opposite results. In qualitative agreement with this supposition, toluene decreases the yield of **7** to 1%, and chlorobenzene and hexafluorobenzene increase the yield to 3 and 5%, respectively. In chlorobenzene, the product corresponding to **17**, X = Cl, is not isolated. Aromatization by elimination of hydrogen chloride leads directly to the benzofuran **15**.

In the ring contraction of **18**, thermal decomposition suc-



ceeded where photolytic methods gave poor results.²⁶ However, refluxing a solution of **6** in *N*-methylaniline led to no ring contraction where less than 1% would have been detectable.

The low yields in the ring contraction of **6** to **7** is in stark contrast to the normal success of this approach to strained rings. To determine whether electronic or steric factors were involved, the diazo ketone **19** was rearranged under



conditions identical with those employed for **6**. Obtention of an 80% yield of ring-contracted product suggests that the low yields in the case of **6** arise from the steric constraints imposed upon the system.²² Furthermore, the fact that polycyclic hydrocarbons of considerably higher strain energy than the dihydrodibenzopentalene ring system (such as the propellanes) are synthesized by such approaches indicates that the limiting factor is the amount of strain introduced in the rearrangement and not the total strain energy of the product. Thus, the limit for the Wolff rearrangement is on the order of the difference in strain energies of the 4,5-methylenephenanthrene and dihydrodibenzopentalene systems which is approximately 50 kcal/mol.

The crude amide **7** was hydrolyzed to the acid **8** by refluxing in acetic acid–aqueous hydrochloric acid. Decarboxylation occurred by heating this acid in a sublimator at 290° to give **4** in 36% yield. However, a substantial improvement in the yield of **4** (to 85%) was effected by employing copper–bronze or pentafluorophenylcopper in hot quinoline.^{27,28} The use of the soluble copper catalyst led to a more rapid decarboxylation.

4,8-Dihydrodibenzo[*cd,gh*]pentalene (**4**) was purified by sublimation or preparative TLC followed by recrystallization from methanol to give colorless crystals, mp 137.5–138.3°. The structure was fully confirmed by its spectral properties and X-ray crystallography. Its NMR spectrum²⁴ shows a triplet (*J* = 0.7 Hz) for the methylene groups (δ 4.13) and an A₂B pattern for the aromatic protons (δ_A = 7.17, δ_B = 6.98; *J*_{AB} = 7.6 Hz). The mass spectrum was most interesting. Sixty-four percent of the total ion current was borne by the ions at *m/e* 178, 176, 89, and 88 corresponding to the molecular ions and doubly charged molecular ions of **4** and dibenzo[*cd,gh*]pentalene. The facility to form the dibenzopentalene system under electron impact suggests that some degree of stability is associated with the peripheral 10 π -electron dication system.

The unusual geometry of **4** was clearly indicated by its X-ray structure as summarized in Figure 1.¹³ As pointed

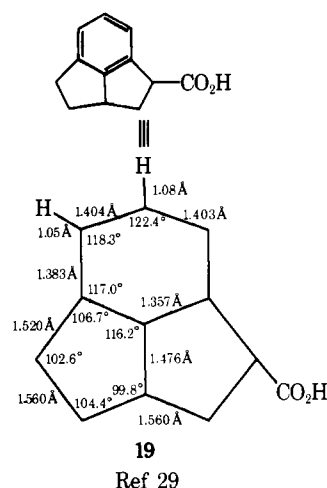
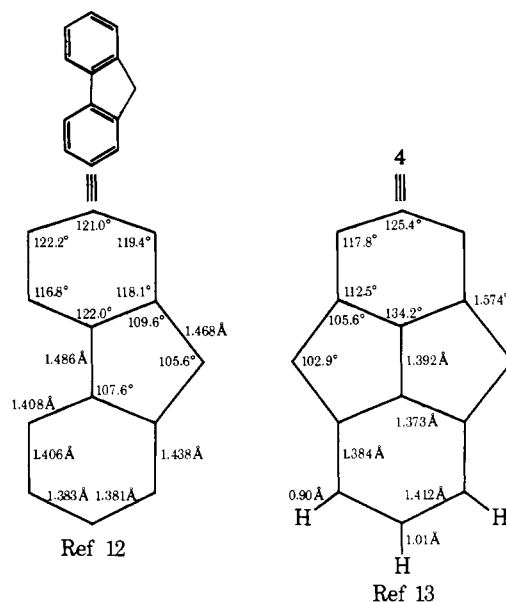
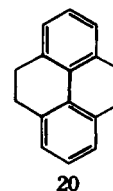


Figure 1. Structures of 4,8-dihydrodibenzo[*cd,gh*]pentalene and related systems.

out previously, the molecule is planar with a central-bond length of only 1.39 Å (cf. the C₁₅–C₁₆ bond of pyrene of 1.42 Å). A further unusual feature is the shortening of the aromatic C–H bonds compared with the corresponding C–H bond lengths in **19** indicating greater *s* character especially in the C–H bonds on C-1, C-3, C-5, and C-7. This is also reflected by the downfield chemical shift of H₁, H₃, H₅, and H₇ of **4** relative to the comparable protons of **20** (δ

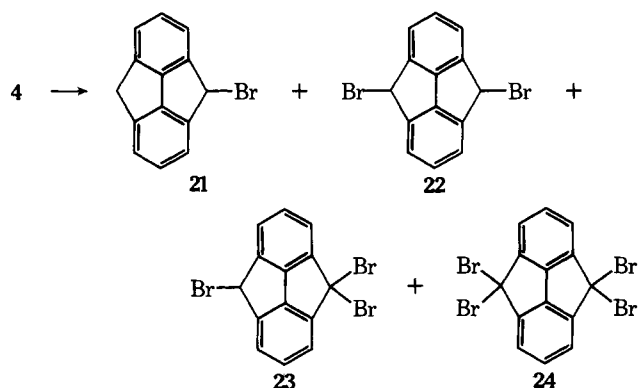


6.99) which would not be strained. On the basis of its geometry, the strain energy of **4** was calculated to be 66 kcal/mol.¹³

Synthesis of Dibenzo[*cd,gh*]pentalene-4,8-quinone. A series of four brominated derivatives **21–24** of 4,8-dihydrodibenzo[*cd,gh*]pentalene was prepared to provide functionality for formation of the dibenzopentalene system including the parent, fully unsaturated hydrocarbon. Photochemical bromination of **4** resulted in successive substitution of bromine for benzylic hydrogen depending upon the number of

Table I. Bromination of 4

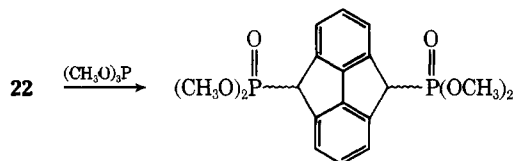
Equiv of Br ₂	% 21	% 22	% 23	% 24
1.5	58	24		
2.0		64		
4.2			25	53



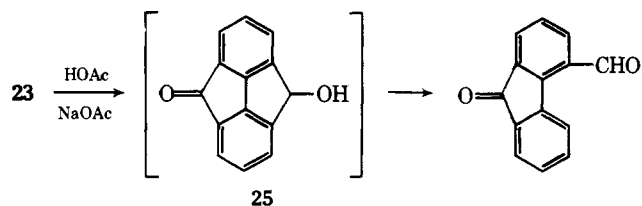
equivalents of bromine employed (see Table I). The spectroscopic properties allow the assignments of structures as shown.

The monobromide **21** has been tentatively assigned on the basis of its NMR spectrum. In addition to an ABC pattern in the NMR spectrum for the aromatic protons (δ 7.36, 7.28, and 7.15; $J_{AC} = J_{BC} = 7$ Hz; $J_{AB} = 1.5$ Hz), two broad singlets appear at δ 6.25 and 4.23 in the ratio of 1:2. The chemical shifts and couplings are consistent with the monobromide. Unfortunately, too little material was obtained pure for full characterization.

The remaining structures are more secure. The molecular formula for dibromide **22** was established as C₁₄H₈Br₂ by high resolution mass spectroscopy. The presence of ions at m/e 334, 336, and 338 in the approximate ratio of 1:2:1 confirms the presence of two Br. Peaks at m/e 257, 255, and 176 (base peak) correspond to successive loss of bromine atoms to afford the dibenzopentalene radical cation. Its NMR spectrum¹⁹ shows the aromatic protons as an A₂B pattern ($\delta_A = 7.41$, $\delta_B = 7.17$; $J_{AB} = 6.7$ Hz) and the methine protons as a broad singlet at δ 6.20. While the NMR spectrum did not show any evidence of a mixture of geometric isomers, the stereochemistry or stereochemical purity has not been established. Further characterization was provided by reaction of **22** with trimethyl phosphite.



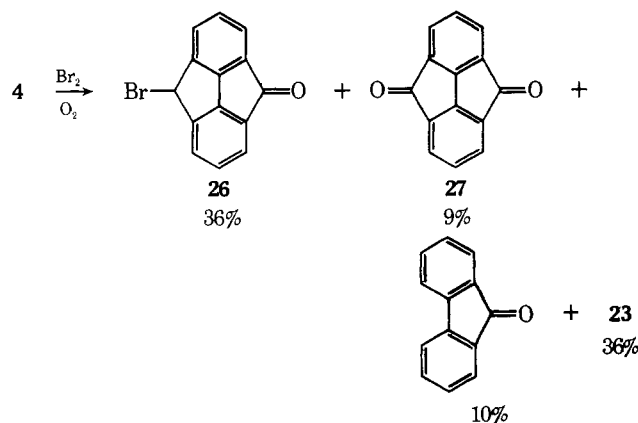
Mass spectrometry confirmed a formula of C₁₄H₇Br₃ for **23** including a molecular ion region containing ions of m/e 412, 414, 416, and 418 in the ratio of 1:3:3:1. This spectrum included peaks for successive loss of bromine atoms with reasonably intense ions at m/e 254 and 256 corresponding to the radical cation of 4-bromodibenzo[*cd,gh*]pentalene. Like the other unsymmetrically substituted derivatives of this system, the aromatic region in the proton NMR spectrum¹⁹ appears as an ABC pattern with $\delta_A = 7.44$, $\delta_B = 7.37$, and $\delta_C = 7.24$ ($J_{AC} = J_{BC} = 7.0$ Hz; $J_{AB} = 1.5$ Hz). The methine hydrogen appears as a broad singlet at δ 6.15. An attempt to prepare the hydroxy ketone **25**, a tautomer of 4,8-dihydroxydibenzo[*cd,gh*]pentalene, by solvolysis of **23** in buffered acetic acid³⁰ produced 4-formylfluorenone. The presumed intermediate **25** suffers ring cleavage to relieve



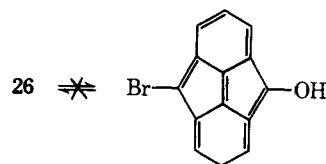
the high strain energy of the dibenzopentalene ring system.

The formula of **24** as C₁₄H₆Br₄ was confirmed by mass spectrometry (see Experimental Section). It is interesting to note that fairly intense ions corresponding to the radical cation of 4,8-dibromodibenzo[*cd,gh*]pentalene (m/e 332, 334, and 336) appear. As expected for the symmetrically substituted system, the aromatic protons in the NMR spectrum¹⁹ appear as an A₂B pattern ($\delta_A = 7.42$, $\delta_B = 7.29$; $J_{AB} = 7.4$ Hz).

Bromination of **4** in the presence of oxygen leads to oxidation of the methylene groups to ketones in addition to bromination. The presence of a ketone in **26** is indicated by

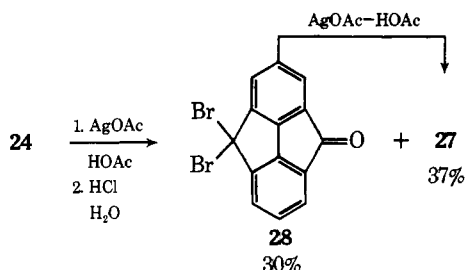


an ir band at 1724 cm⁻¹ (cf. fluorenone at 1720 cm⁻¹). The appearance of the aromatic protons in the NMR spectrum as an ABC pattern indicates asymmetric substitution of the methylene groups of the dihydrodibenzopentalene system. The molecular formula is established by high-resolution mass spectrometry which also shows fragmentation by loss of carbon monoxide (m/e 242 and 244) and Br (m/e 191, base peak). Compound **26** is a tautomer of 4-bromo-8-hy-



droxydibenzo[*cd,gh*]pentalene. As expected, there is no evidence that tautomerization occurs. The most exciting compound is the diketone **27** since it represents a fully unsaturated derivative of the desired dibenzopentalene system. It was characterized subsequently (vide infra). Such oxidation accompanying bromination is not unusual. Under similar conditions, fluorene is converted to fluorenone in 91% yield. Capture of the radicals that are intermediates in the bromination by oxygen to form peroxides which ultimately cleave to ketones rationalizes the results.³¹

A more convenient synthesis of the quinone is from the tetrabromide **24**. Solvolysis of this bromide in acetic acid in the presence of silver acetate leads to the diketone **27** in addition to the partially hydrolyzed compound **28**. Exposure of the latter compound to the same reaction conditions does convert it to **27**. Buffered aqueous acetic acid, conditions which convert 9,9-dibromofluorene to fluorenone in quantitative yield, only causes decomposition of **28**. The structure



of **28** is further confirmed by its spectroscopic properties (see Experimental Section).

The quinone **27** has a molecular formula of $C_{14}H_6O_2$ as established by high-resolution mass spectroscopy. In addition, fragmentation with sequential loss of carbon monoxide is indicated by ions at m/e 178 and 150 with appropriate metastable transitions at m/e 153.8 and 126.4. As expected for the symmetrical structure, the proton NMR¹⁹ shows an A_2B pattern with $\delta_A = 7.47$, $\delta_B = 7.20$, and $J_{AB} = 7.3$ Hz. Two carbonyl absorptions at 1751 and 1709 cm^{-1} arise as a result of vibrational coupling.

Structure of 4,8-Dibenzo[cd,gh]pentalenoquinone. 4,8-Dibenzo[cd,gh]pentalenoquinone (**27**) is the first neutral, fully conjugated derivative of dibenzopentalene. The infrared frequency for the unperturbed carbonyl group is associated with several factors such as strain, dipole interactions, and inductive and conjugative interactions. To determine the frequency in cases with vibrational coupling, Davison suggests utilizing the simple average which would be 1730 cm^{-1} for **27**.³² On the other hand, Yates suggests that, in cases of unequal intensities of the coupled bands as for dibenzocyclooctatetraenoquinone, the value of the uncoupled carbonyl vibrational frequency is the weighted average.³³ For **27**, the frequency would be 1736 cm^{-1} . While several reasons for the somewhat higher energy of this band compared with those of fluorenone (1720 cm^{-1}) and 4,5-phenanthrylene ketone (1716 cm^{-1}) can be envisioned, the X-ray structures of **4** compared with those of fluorenone suggest that differences in the bond lengths of the aryl-carbonyl C-C bond necessitate decreased conjugation of the carbonyl group of **4** with the aromatic rings compared with fluorenone. A similar effect is seen in comparing 9-anthrone (1656 cm^{-1}) and benzophenone (ir 1675 cm^{-1}) where nonplanarity of the benzene rings is associated with decreased conjugation and a higher carbonyl frequency.

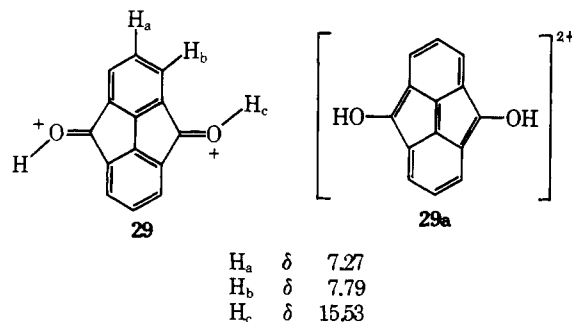
The ultraviolet spectrum of dibenzo[cd,gh]pentalenoquinone provides additional support for the presence of long bonds α to the carbonyl groups. Fluorenone exhibits an $n \rightarrow \pi^*$ transition at 370 nm ($\log \epsilon$ 2.5) and 4,5-phenanthrylene ketone at 372 nm ($\log \epsilon$ 2.8); whereas, the quinone **27** exhibits a $n \rightarrow \pi^*$ transition at 357 nm ($\log \epsilon$ 2.95). Normally a bathochromic shift is observed in going from a monoketone such as 9-anthrone (λ 368 nm; $\log \epsilon$ 1.7) to a related p -quinone such as anthraquinone (λ 405 nm; $\log \epsilon$ 1.7). The hypsochromic shift of **27** reflects decreased interaction between the carbonyl groups and the benzene rings.

Studies have shown that the NMR chemical shift of the $C=O^+H$ protons of protonated quinones and ketones can be used as a measure of the degree of delocalization of the positive charge over the molecule.³⁴ Treatment of **27** with a 10% solution of antimony pentafluoride in fluorosulfonic acid at -78° affords a solution of bis-protonated quinone **29**. Pouring this solution onto ice allows recovery of starting quinone. Comparison of the hydroxyl protons of **29** relative to that of bis-protonated 9,10-anthraquinone (δ 13.80) and 1,4-naphthoquinone (δ 14.58) indicates a large downfield shift in **29**. Combined with a relatively small downfield shift of the ring protons of **29**, these data indicate poor delocalization of excess positive charge. Delocalization of charge

Table II. Hückel and McLachlan Calculations for Dibenzo[cd,gh]pentalenoquinone Radical Anion

h	k	k_α^a	Spin density ^b			Hückel energy	
			ρ_1	ρ_4	ρ_0	E_9	E_{10}
1.0	0.9	1.0	0.2067	0.1728	0.0578	-0.0542	0.2152
0.8	0.8	1.0	0.2024	0.1706	0.0667	-0.0538	0.2059
0.8	1.6	1.0	0.1796	0.0766	0.1107	0.3222	0.5192
1.2	1.6	1.0	0.1936	0.1063	0.0836	0.2291	0.4453
1.6	1.6	1.0	0.2043	0.1296	0.0630	0.1480	0.3852
1.6	0.8	1.0	0.2218	0.2012	0.0210	-0.2226	0.1226
1.0	0.10	1.0	0.2030	0.1611	0.0681	0.0000	0.2541
1.0	1.0	0.8	0.1693	0.2093	0.0835	0.1126	0.3143
1.6	1.2	0.8	0.1791	0.2226	0.0579	0.0930	0.3115
Exptl			0.1780		0.0791		

^a k_α is the k for the bonds α to the carbonyls. ^b Negative spin densities are predicted for all other atoms.



(represented by resonance form **29a**) might have been anticipated to be unusually extensive since **29a** represents a 10π -electron peripheral system. The most reasonable explanation for the absence of such a phenomenon may be associated with unusually long bonds α to the carbonyl groups.

Further insight into this system can be gleaned from dibenzopentalenosemiquinone radical anion. Hückel calculations, which predict zero spin density of the odd electron on the central vinyl unit, suggest that the dibenzopentalenosemiquinone radical anion will closely resemble a [12]annulosemiquinone radical anion. The ESR spectrum of the radical anion **30**, generated electrolytically in DMSO containing tetra-*n*-butylammonium perchlorate, exhibits splitting constants of 4.540 (4 H) and 0.917 G (2 H). Reference to the McConnell relationship with $Q = 25.5 \pm 1.5$ G/e indicates that the spin density on C_1 is 0.178 ± 0.010 , and that the spin density on C_2 is 0.036 ± 0.002 . Examination of Hückel and McLachlan calculations indicates that the odd electron is in the orbital designated ψ_{10} (as opposed to ψ_9). ψ_{10} remains higher in energy than ψ_9 in spite of large variations in the parameters utilized for oxygen (see Table II). A modification wherein the $C_{3a}-C_4$, C_4-C_{4a} , $C_{7a}-C_8$, and C_8-C_{8a} bonds are assigned a lower overlap integral to take into account their unusual length is seen to improve agreement between calculations and experiment. It is important to note that the spin density of 0.178 on C_1 indicates that 70% of the odd electron density resides at these positions.

The g factors of semiquinone radical anions also contribute to our understanding of the electron distribution.³⁵ Such anions possessing no halogen atoms usually have g factors in the narrow range of 2.0044 ± 0.0004 , while hydrocarbon radical anions have g values in the range of 2.0026 ± 0.0001 . The g factor of **30**, 2.0035, is unusually low, a fact which suggests that the spin density on the oxygen atoms is unusually low. Utilizing the empirical relationship developed previously³⁵ which relates the oxygen spin density to the half-wave potential of the quinone (vide infra) and the Hückel energy of the hydrocarbon radical anion related to the semiquinone indicates a spin density on each oxygen of

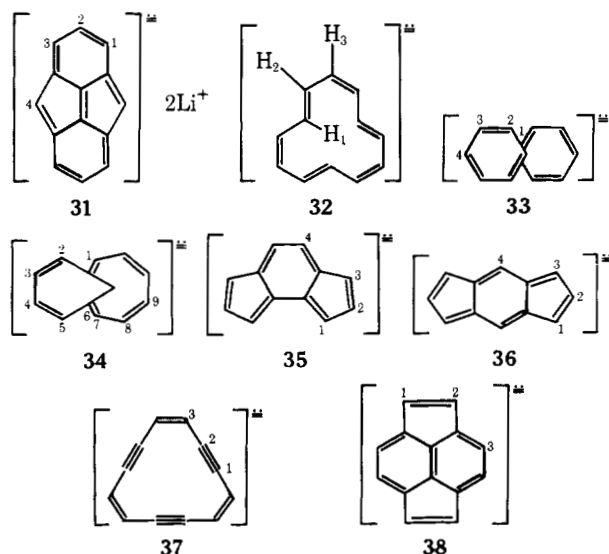
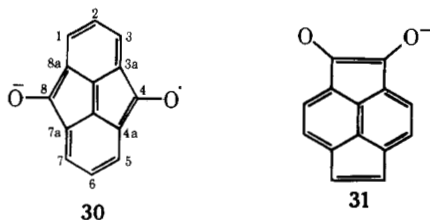


Figure 2. Structures of dilithium dibenzo[cd,gh]pentalenide and related dianions.

0.0791 in good agreement with McLachlan calculations. As in the case of pyraclosemiquinone anion **31**, the carbon framework serves as an unusually good electron-acceptor system. This result suggests that some destabilization is associated with a 12π -electron periphery that formally exists in **30**, and that increased electron density alleviates some of the destabilizing interactions. The higher oxygen spin density of **30** compared with that of **31** may be associated with



decreased efficiency of electron delocalization as a result of increased bond length of the $C_{3a}-C_4$, C_4-C_{4a} , $C_{7a}-C_8$, and C_8-C_{8a} bonds.

Utilizing the above oxygen spin density, an additional 16% of the odd electron density resides on these atoms. Calculations (see Table II) indicate that the remaining 14% is distributed between the two carbonyl carbons, and that little, if any, is on the vinyl cross-link. These results strongly support the view that dibenzopentalenosemiquinone radical anion closely resembles [12]annulene semiquinone radical anion.

Insight into relative thermodynamic stability can be obtained from polarographic data.³⁶ The half-wave potential is related to the amount of work required to convert a molecule to its radical anion. Dibenzopentalenoquinone **27** exhibits two polarographic reduction waves in DMSO. The first is a reversible one-electron wave at -0.895 V vs. SCE ($E_{1/2} - E_{3/4} = 62$ mV; $i_d = 0.027$ μ A) and the second an irreversible wave at -1.630 V ($E_{1/2} - E_{3/4} = 90$ mV; $i_d = 0.041$ μ A). If electronic stabilization were associated with the dibenzosemiquinone radical anion, the reduction potential of dibenzopentalenoquinone would approximate or be more positive than that of 9,10-anthraquinone (-0.784 V). The substantially more negative (by 0.228 V) reduction potential of **27**, which also may be taken as a reflection of the difference in thermodynamic stability between dibenzopentalene and anthracene, is evidence for electronic destabilization in the dibenzopentalene system.

Dilithium Dibenzo[cd,gh]pentalenide. Much effort has been expended on the conversion of 4,8-dihydrodibenzo[cd,gh]pentalene (**4**), its dianion (vide infra), and its various brominated derivatives to dibenzo[cd,gh]pentalene (**3**). This effort has not been successful. The polarogram of **22** shows two weak waves at -1.017 and -1.237 eV vs. SCE (cf. pyracylene at -1.056 and -1.635 eV)¹¹ which do disappear with time. Nevertheless, the species responsible for these waves remains elusive. For example, attempts to carry out polarographic reductions of the dibromo derivatives in an ESR cavity to detect the radical anion of **3** failed to reveal the presence of any radical species. Application of similar methods to the generation of pyracylene and its derivatives was successful.¹¹ The failure to observe dibenzopentalene or dibromodibenzopentalene in the above reactions suggests that electronic destabilization, which results in kinetic instability, may be associated with the dibenzopentalene ring system.

If that supposition be true, conversion of the 12π -electron periphery of dibenzopentalene to a 14π -electron periphery should result in a stable "aromatic" system. Treatment of **4** in THF- d_8 with *n*-butyllithium in hexane at -78° followed by warming to room temperature affords a solution of dilithium dibenzo[cd,gh]pentalenide (**31**) (see Figure 2). Inverse addition of the dianion solution to D_2O produces recovered **4** with 99% d_2 (mass spec) incorporation in the 4,8 positions (NMR).

The NMR spectrum of the dianion proved most interesting. It exhibits an essentially first-order spectrum (see Table III). Most significant is the great similarity in NMR chemical shifts to the [12]annulene dianions **32**–**37** suggesting similar electron distributions.³⁷

Plotting the NMR chemical shift of the protons of rigid polycyclic dianions **35**, **36**, and **38** vs. the Hückel charge density of the corresponding carbon atom in which the excess charge is restricted to the periphery of the molecule reveals a reasonably good straight line even without correcting for differential ring-current effects (see Figure 3). Utilizing this correlation, excellent correlation of the charge densities for **31** with calculated values are observed (see Table IV). Obtention of charge densities from the proton chemical shifts after correcting for ring current contributions also leads to similar results.³⁸

The close similarity of the proton chemical shifts of **31** to those of **32**–**38** and the excellent agreement of the experimentally derived and theoretically calculated charge densities provide strong evidence that all the excess negative charge resides on the periphery of the molecule with effectively little, if any, charge delocalized over the central double bond. Obviously, strong support for the description of the dibenzopentalene system on the basis of the peripheral electronic model derives therefrom.

Experimental Section

General. Melting points are uncorrected. NMR spectra were recorded on Varian A-60, A-60-A, and HA-100 NMR spectrometers. Time average NMR spectra were recorded on a Varian HA-100 NMR spectrometer with a Varian C-1024 time averaging computer. Infrared spectra were recorded on a Beckman IR8 recording infrared spectrometer. Ultraviolet spectra were determined on a Cary Model 15 recording spectrophotometer. Mass spectra and exact mass determinations were obtained on an AEI MS 902 mass spectrometer at 70 eV ionizing voltage. ESR spectra were obtained on a Varian E3 EPR spectrometer. Polarographic data were obtained on a Sargent Model XV polarograph equipped with a Sargent Model A IR compensator.

Columns used in column chromatography were slurry packed in the solvent specified and allowed to stand 24 hr before use. Eluents were deaerated. Preparative thick-layer chromatography was performed on 20×20 or 20×40 cm plates of silica gel PF254

Table III. NMR Parameters of **31** and Related Dianions

Dianion	δ_1	δ_2	δ_3	δ_4	δ_{7-9}	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$
31	6.25	6.67	6.25	5.34		7.1	7.1	
32	-4.60	6.98	6.23			14.0	7.2	
33		7.16	6.28	6.41			8.4	10.7
34		7.56	6.51		5.5		8.3	8.5
35	5.84	6.06	5.92	6.85		2.1	3.1	
36	5.65	6.50		7.40				
37			6.74					
38	6.00		6.75					

Table IV. Charge Densities in **31**

Position	δ	Experimental		HMO	SCF
		Method A ^a	Method B ^b		
4	5.340	1.34	1.30	1.33	1.29
1	6.245	1.16	1.18	1.16	1.18
2	6.670	1.06	1.11	1.04	1.06

^a Obtained utilizing the correlation in Figure 2. ^b Obtained utilizing the ring-current correction.

(Brinkman Instruments) activated at 100° for 1 hr and stored in a dry box prior to use unless otherwise stated. All reactions were run under nitrogen, heated with oil baths, and stirred magnetically unless otherwise stated.

Preparation of 4,5-Methylenephenanthrene-9,10-quinone (5).

Method A. 4,5-Methylenephenanthrene-9,10-quinone (5) and 1-Iodo-4,5-methylenephenanthrene-9,10-quinone. 4,5-Methylenephenanthrene (826 mg, 4.65 mmol) was dissolved in 27.2 ml of glacial acetic acid and warmed to just below reflux. A solution of iodic acid (780 mg, 1.0 mol equiv) in 3.1 ml of water was added dropwise, and heating was continued with distillation of the iodine-acetic acid mixture at a rate of 7.8 ml/hr. An additional 7.8 ml of acetic acid was added at the end of 1 hr, and the distillation continued at the same rate for an additional 1.5 hr. The mixture was cooled, poured into 31 ml of water, and allowed to crystallize. The orange crystalline product was filtered and washed with water, aqueous sodium carbonate solution, aqueous sodium thiosulfate solution, and again with water. After air drying, 1.18 g of material was obtained. Extraction of the filtrate with chloroform followed by rotary evaporation of the solvent afforded an additional 0.164 g of material. The combined materials were dissolved in 125 ml of chloroform and applied to a column of silica gel (300 g, slurry packed in benzene). Elution with 1% ethyl acetate-benzene and then 2% ethyl acetate-benzene afforded 316 mg, 21% yield, of 1-iodo-4,5-methylenephenanthrene-9,10-quinone, mp 252° dec (producing purple vapors). The spectral properties are reported in the results and discussion section. It was further characterized after conversion to its corresponding diazo ketone. Further elution of the column with 2% ethyl acetate-benzene, followed by rotary evaporation of the solvent, afforded 341 mg, 36% yield, of 4,5-methylenephenanthrene-9,10-quinone, mp 260° dec, after recrystallization from diglyme (lit.³⁹ mp 240–241°). The NMR and ir spectral data are reported in the results and discussion sections. Mass spec: 220 (97), 192 (100), 164 (89), 163 (74); uv^{40} (log ϵ): 246 sh (4.17), 255 sh (4.31), 260 (4.35), 278 (4.26), 328 (3.68), 434 (3.33); mol wt 220.0534 (calcd for C₁₅H₈O₂, 220.0534).

Method B. 4,5-Methylenephenanthrene-9,10-quinone (5). 4,5-Methylenephenanthrene (5.00 g, 26.3 mmol) was dissolved in 1350 ml of dioxane, and 150 ml of glacial acetic acid and the resulting solution were warmed to 90°. A solution of 17 g (96.8 mmol) of iodic acid in 125 ml of deionized water was added rapidly and the mixture refluxed for 8 hr. The reaction mixture was cooled and the solvent removed on a rotary evaporator. The residue was taken up in dichloromethane and extracted with water. The water layer was washed with dichloromethane, and the organic layers were combined. The solvent was removed on a rotary evaporator. The crude quinone mixture was dissolved in dichloromethane and chloroform and applied to a column of silica gel (600 g). The column was eluted with chloroform until the iodine had been removed from the column, and then with 5% ethyl acetate in chloroform until the quinone had been removed from the column. Removal of the solvent from the eluate on a rotary evaporator, followed by vacuum

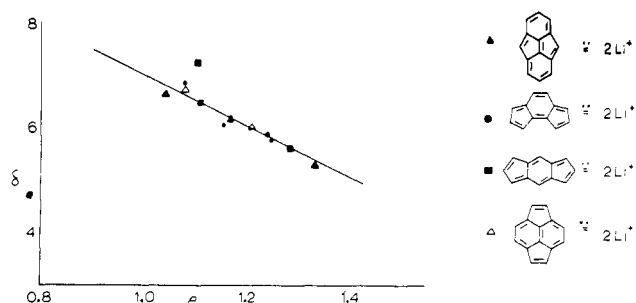


Figure 3. Correlation of charge densities (abscissa) and NMR proton shifts (ordinate) of perturbed [12]annulene dianions.

drying, afforded 3.97 g, 69% yield of 4,5-methylenephenanthrene-9,10-quinone as a deep reddish-brown powder containing (based on separation of the two materials after conversion to the diazo ketone) 2% of 1-iodo-4,5-methylenephenanthrene-9,10-quinone. The crude quinones were redissolved in 1:3 chloroform-benzene and applied to a column of 300 g of activity V Woelm alumina packed with benzene. Elution of the column with 25% chloroform in benzene followed by rotary evaporation of the solvent afforded 3.62 g, 63% yield, of the quinones as a bright-orange powder which was used in subsequent reactions.

Preparation of 9-Diazo-10-keto-4,5-methylenephenanthrene (16) and 1-Iodo-9-diazo-10-keto-4,5-methylenephenanthrene (10). 4,5-Methylenephenanthrene-9,10-quinone (3.972 g, 17.1 mmol) (containing 2% of iodoquinone) and *p*-toluenesulfonylhydrazine (3.70 g, 19.9 mmol) were refluxed in 35 ml of 95% ethanol for 20 min. After cooling, the resultant crystals were filtered, taken up in 1:10 chloroform-dichloromethane, and applied to a column of 500 ml of silica gel packed with dichloromethane. Elution with 3 l. of dichloromethane afforded visual separation of the bands on the column. The column was then eluted with 1:1 dichloromethane in chloroform to afford 141 mg, 2.2% yield, of 1-iodo-9-diazo-10-keto-4,5-methylenephenanthrene, mp 195° dec (turns brown at 185°) after recrystallization from chloroform. Spectral data: NMR¹⁹ δ 8.04–7.08 (5 H, m), 4.00 (2 H, s); ir¹⁸ 2105, 2092, 1632, 1613 cm⁻¹; mass spec (calcd for C₁₅H₇N₂OI, 357.9605) 357.9605, 358 (14), 330 (20), 203 (12), 175 (23), 85 (52), 83 (100); uv^{40} (log ϵ) 252 (4.50), 278 (4.08), 346 (3.53), 373 sh (3.65), 386 (3.82), 407 (3.78). Further elution of the column with 1:1 chloroform in dichloromethane afforded 2.521 g, 60% yield, of 9-diazo-10-keto-4,5-methylenephenanthrene, mp 180–181° dec, after recrystallization from ethanol. Spectral data: NMR¹⁹ δ 7.99–7.02 (6 H, m), 5.98 (2 H, s); ir¹⁸ 2100, 2080, 1632, 1610 cm⁻¹; mass spec (calcd for C₁₅H₈N₂O, 232.0637) 232.0637, 232 (23), 204 (84), 176 (100); uv^{40} (log ϵ) 247 (4.71), 251 (4.69), 264 (4.39), 306 (3.58), 329 sh (3.60), 342 (3.72), 276 (3.86), 394 (3.84).

Photolyses of 9-Diazo-10-keto-4,5-methylenephenanthrene (6).

Method A. *N*-tert-Butyl-4,8-dihydrodibenzo[*cd,gh*]pentalene-4-carboxamide (7) and 1a,5a-Dihydro(4,5-methylene-9,10-phenanthra)-[*d*]benzo[*b*]furan (14). Benzene (2.7 l.) and freshly distilled *tert*-butylamine (80 ml) were placed in a 3-l. spherical Pyrex photolysis apparatus equipped with a nitrogen bubble tube and an internal water jacket (room temperature water) and deaerated for 30 min. 9-Diazo-10-keto-4,5-methylenephenanthrene (512 mg, 2.20 mmol) was added, and deaeration continued for an additional hour. The solution was then irradiated for 1 hr in a Srinivasan-Griffin photochemical reactor using 3500-Å bulbs. Infrared monitoring of the disappearance of bands at 2100 and 2080 cm⁻¹ (for the diazo ketone) in a series of aliquots indicates that 96% of the diazo ketone reacts in 1 hr under these conditions. The solvent was removed on a rotary evaporator. The products from 12 such photolyses were combined. The combined material was applied to eight 20 × 40 cm preparative thick-layer plates and eluted twice with dichloromethane. Two regions of the plates were taken and are described below. The material was removed from the silica gel with chloroform and the chloroform removed on a rotary evaporator. Region 1, *R_f* 0.08–0.20, 690 mg of 20% pure product (NMR), 2% yield, was identified on the basis of spectral data as *N*-tert-butyl-4,8-dihydrodibenzo[*cd,gh*]pentalene-4-carboxamide as listed in the results and discussion section. It was carried on to **4** without further puri-

fication. Region 2, R_f 0.76–1.00, was divided in half, and one-half was reapplied to two preparative thick-layer plates and eluted once with pentane, affording two major bands at R_f 0.40 and 0.75. The band R_f 0.75 was removed with chloroform and afforded, after removal of solvent on a rotary evaporator and vacuum drying, 750 mg, 20% yield, of a semicrystalline material, mp 42.5–46.0°. This material, on the basis of spectral data and its subsequent transformation on treatment with dichlorodicyanobenzoquinone to 4,5-methylene-9,10-phenanthra[*d*]benzo[*b*]furan, has been tentatively assigned the structure 1a,5a-dihydro(4,5-methylene-9,10-phenanthra)[*d*]benzo[*b*]furan. Spectral data: NMR¹⁹ δ 7.78–6.95 (9 H, m), 6.95–6.04 (2 H, m), 5.42–4.93 (1 H, m), 3.50 (2 H, bs); ir²⁴ 3063, 2906, 1321, 1216, 1131, 904, 711 cm⁻¹; mass spec (calcd for C₂₁H₁₄O, 282.1045) 282.1045, 282 (100), 281 (30), 280 (63), 279 (27), 254 (5), 253 (15), 252 (10), 251 (7), 250 (11); uv⁴⁰ (log ϵ) 241 sh (4.49), 251 sh (4.61), 256 (4.71), 258 (4.71), 280 sh (4.15), 300 (4.11), 311 (4.14), 327 (3.92), 351 (2.94).

Method B. *N*-tert-Butyl-4,8-dihydrodibenzo[*cd,gh*]pentalene-4-carboxamide (7) and 4,5-Methylene-9,10-phenanthra[*d*]benzo[*b*]furan (15). 9-Diazo-10-keto-4,5-methylenephenanthrene (510 mg, 2.20 mmol) was dissolved in 1 l. of freshly distilled chlorobenzene in a 1-l. Pyrex photolysis apparatus equipped with a nitrogen bubble tube and an internal cooling jacket (room temperature water) and deaerated for 1 hr. Freshly distilled *tert*-butylamine (30 ml) was added, and the deaeration continued for an additional 30 min. The solution was then irradiated for 45 min in a Srinivasan-Griffin photochemical reactor using 3500-Å lamps. Infrared analysis of the disappearance of infrared bands at 2100 and 2080 cm⁻¹ in a series of aliquots indicates that 96% of the diazo ketone had reacted in this time. The solvent was removed on a rotary evaporator, and this material combined with that from three similar photolyses. The combined materials were dissolved in dichloromethane and extracted with water, and the dichloromethane was removed on a rotary evaporator. The material was applied to four 20 × 40 cm preparative thick-layer plates and eluted twice with dichloromethane. The region of R_f 0.08–0.20 was obtained, and the material was removed from the silica gel with chloroform. This material, 345 mg (containing 20% amide by NMR), 3% yield, was identified on the basis of spectral data and subsequent conversions as *N*-tert-butyl-4,8-dihydrodibenzo[*cd,gh*]pentalene-4-carboxamide.

In an identical experiment employing 426 mg of 9-diazo-10-keto-4,5-methylenephenanthrene, the material on the preparative thick-layer plates from R_f 0.85–1.00 was isolated and removed from the silica gel with chloroform. The chloroform was removed on a rotary evaporator. This material (259 mg, 50% yield) was identified on the basis of spectral data as 4,5-methylene-9,10-phenanthra[*d*]benzo[*b*]furan. The material was pure by NMR and thin-layer chromatography (R_f 0.85, dichloromethane eluent). Recrystallization from chloroform (1.5 ml) afforded 114 mg of material, mp 146.0–147.5°. Spectral data: NMR²⁴ δ 8.16–7.17 (10 H, m), 4.00 (2 H, s); ir²⁴ 1438, 1347, 1315, 1212, 1133, 1109 cm⁻¹; mass spec (calcd for C₂₁H₁₂O, 280.0888) 280.0888, 280 (100), 279 (31); uv⁴⁰ (log ϵ) 243 sh (4.58), 248 (4.67), 254 (4.68), 261 sh (4.65), 269 sh (4.55), 281 sh (4.17), 297 (4.12), 306 sh (4.16), 313 (4.33), 321 (4.24), 329 (4.45), 334 sh (3.88), 343 sh (3.44), 353 (3.47).

Method C. *N*-tert-Butyl-4,8-dihydrodibenzo[*cd,gh*]pentalene-4-carboxamide (7). The photolyses in which diethyl ether, toluene, and hexafluorobenzene were employed as solvents were carried out in the same manner as method B. The reaction mixture was cooled by means of the internal cooling jacket which was filled with Dry Ice-acetone. Yields of amide 7 for ether at room temperature (0.7%), toluene at -30° (1%), and hexafluorobenzene at room temperature (5%) as solvent were determined by isolation of crude *tert*-butylamide 7 by preparative thick-layer chromatography. The purity of the crude amide preparation was determined from the NMR integrals.

Method D. Methyl 4,8-Dihydrodibenzo[*cd,gh*]pentalene-4-carboxylate. 9-Diazo-10-keto-4,5-methylenephenanthrene (111 mg, 0.483 mmol) was dissolved in 1 l. of deaerated 1.6% methanolic HCl, placed in the apparatus described in method B, and irradiated for 2.5 hr with 3500-Å lamps. The solvent was removed on a rotary evaporator and the material combined with another batch obtained in the same manner. The combined material was applied to a preparative thick-layer plate and eluted once with chloroform, and the region of R_f 0.45–0.58 was removed, affording 7.7 mg of

material. This material and another 6.9 mg of material obtained in a similar manner were combined and rechromatographed (one elution with chloroform). The band of R_f 0.50, 2 mg, 0.3% yield, was removed and identified as methyl 4,8-dihydrodibenzo[*cd,gh*]pentalene-4-carboxylate on the basis of spectral data reported in the results section. Mass spec: 236 (100), 221 (15), 215 (15), 214 (9), 193 (21), 178 (28), 177 (51), 176 (10), 165 (20); mol wt 236.0884 (calcd for C₁₆H₁₃O₂, 236.0837).

Method E. Methyl 4,8-Dihydrodibenzo[*cd,gh*]pentalene-4-carboxylate (12) and Dimethyl Fluorene-4,5-dicarboxylate (13). 9-Diazo-10-keto-4,5-methylenephenanthrene (373 mg, 1.13 mmol) was dissolved in 380 ml of deaerated dioxane. This solution and 9.50 g of sodium carbonate in 95 ml of deaerated deionized water were placed in a quartz irradiation tube and deaerated for 30 min. The solution was irradiated at ambient temperature in a Srinivasan-Griffin photochemical reactor for 14 hr using 3500-Å lamps. Water (400 ml) and chloroform (300 ml) were added and the layers separated. The aqueous layer was acidified with concentrated hydrochloric acid and extracted with ethyl acetate. The ethyl acetate was removed on a rotary evaporator. The residue was taken up in 10 ml of ethyl acetate and treated with an excess of ethereal diazomethane. After 5 min, the solvent was removed on a rotary evaporator and the material applied to a preparative thick-layer plate. The plate was eluted twice with chloroform affording two major bands. The material was removed from the silica gel with chloroform. Band 1, R_f 0.88, 3 mg, 0.3% yield, was identified on the basis of mass-spec and thin-layer comparison as crude methyl 4,8-dihydrodibenzo[*cd,gh*]pentalene-4-carboxylate.

Band 2, R_f 0.37, 17.2 mg, 4.4% yield, was identified on the basis of spectral data as dimethyl fluorene-4,5-dicarboxylate. The material was recrystallized from methanol, affording material of mp 153–154°. Spectral data: NMR²⁴ δ 7.74, 7.55, 7.28 (6 H, ABC pattern broadened by allylic couplings, $J_{ac} = J_{bc} = 7.6$ Hz; $J_{ab} = 1.5$ Hz), 3.85 (2 H, s), 3.73 (6 H, s); ir²⁴ 1721 cm⁻¹; mass spec 282 (100), 251 (71), 250 (60), 223 (39); uv⁴⁰ (log ϵ) 242 (4.32), 268 (3.84), 277 (3.84), 309 sh (3.92), 324 (4.08); mol wt 282.0892 (calcd for C₁₇H₁₄O₄, 282.0892).

Dehydrogenation of 1a,5a-Dihydro(4,5-methylene-9,10-phenanthra)[*d*]benzo[*b*]furan (14). Under nitrogen, 1a,5a-dihydro(4,5-methylene-9,10-phenanthra)[*d*]benzo[*b*]furan (375 mg, 1.33 mmol) and dichlorodicyanobenzoquinone (332 mg, 1.46 mmol) in xylene (20 ml) were heated under reflux for 19 hr. The solvent was distilled and the remaining material taken up in ethyl acetate (100 ml) and washed with 3 × 70 ml portions of 10% aqueous potassium hydroxide and potassium chloride solution. The solvent was removed on a rotary evaporator. The material was applied to a preparative thick-layer plate and eluted with 1:1 pentane-dichloromethane, affording one band of R_f 0.85. This band was removed with chloroform and afforded, after vacuum drying, 135 mg, 36% yield, of (4,5-methylene-9,10-phenanthra)[*d*]benzo[*b*]furan, mp 146–148° (recrystallized from CHCl₃), identical with respect to spectral data, thin layer, and mixture melting point with the product obtained in the chlorobenzene photolysis.

Preparation of 4,8-Dihydrodibenzo[*cd,gh*]pentalene-4-carboxylic Acid (8). Crude *N*-tert-butyl-4,8-dihydrodibenzo[*cd,gh*]pentalene-4-carboxamide (690 mg, 20% pure by NMR, 0.5 mmol) was dissolved in 40 ml of glacial acetic acid and heated to 80° to effect solution. Hydrochloric acid (20 ml, 20% aqueous solution) was added slowly which caused some precipitation from the reaction mixture. The mixture was heated at reflux for 8.5 hr. The solvent was distilled. The last traces of solvent were removed under vacuum (20 mm). The residue was dissolved in 50 ml of dichloromethane and extracted with 100 ml of 10% aqueous potassium carbonate. The layers were carefully separated, and the aqueous layer was washed with another portion of dichloromethane. Ethyl acetate (50 ml) was added and the basic layer obtained. The ethyl acetate layer was washed with 10% aqueous potassium carbonate and that added to the basic layer. The basic layer was acidified with 45 ml of concentrated aqueous hydrochloric acid and extracted twice with ethyl acetate, and the solvent was removed on a rotary evaporator. Vacuum drying afforded 94 mg, 85% yield, of 4,8-dihydrodibenzo[*cd,gh*]pentalene-4-carboxylic acid. Recrystallization from benzene-hexane afforded material of mp 222.0–223.5°. Spectral data: NMR¹⁹ δ 10.40 (1 H, bs), 7.44, 7.35, 7.17 (6 H, ABC pattern broadened by allylic coupling with methine and methylene protons, $J_{ac} = J_{bc} = 7.6$ Hz; $J_{ab} = 1.5$ Hz), 5.57 (1 H, s), 4.31 (2

H, s); ir^{18} 1703 cm^{-1} ; mass spec 222 (92), 205 (6), 204 (4), 194 (15), 193 (22), 192 (19), 178 (100), 176 (59), 165 (59), 83 (78); uv^{40} ($\log \epsilon$) 267 (4.34), 274 sh (4.31), 298 sh (3.12), 317 (2.82); mol wt 222.0689 (calcd for $\text{C}_{15}\text{H}_{10}\text{O}_2$, 222.0681).

Preparation of 4,8-Dihydrodibenzo[*cd,gh*]pentalene (4). Method A. Pentafluorophenylcopper-Quinoline. Under nitrogen, a solution of 4,8-dihydrodibenzo[*cd,gh*]pentalene-4-carboxylic acid (94 mg crude material, 82% pure by NMR, 0.35 mmol) and pentafluorophenylcopper^{27b} (9.5 mg, 0.041 mmol) in freshly distilled deaerated quinoline (5 ml) was heated with swirling in a metal bath at 220–225° for 3 min. Bubbling occurred during the first minute. While the mixture was cooling, water (1 ml) was added. The material was taken up in ether and extracted with 20% aqueous hydrochloric acid (100 ml), 10% aqueous hydrochloric acid (100 ml), water (50 ml), and twice with 10% aqueous potassium hydroxide (50 ml). The ether was removed on a rotary evaporator. The material was applied to a 20 × 40 cm preparative thick-layer plate and eluted twice with pentane. Removal of the band of R_f 0.49 afforded 50 mg (85% yield) of 4,8-dihydrodibenzo[*cd,gh*]pentalene, mp 137.5–138.3° after recrystallization from methanol. For the NMR and mass spectral data, see section on results. Ir^{24} 3049, 2915, 1449, 1408, 1042, 696 cm^{-1} . Uv^{40} ($\log \epsilon$): 267 (4.31), 274 sh (4.29), 296 sh (3.00), 308 sh (2.61); mol wt 178.0783 (calcd for $\text{C}_{14}\text{H}_{10}$, 178.0783).

Method B. Copper-Quinoline.^{27a,41} Under nitrogen, crude 4,8-dihydrodibenzo[*cd,gh*]pentalene-4-carboxylic acid (72 mg, 82% pure by NMR, 0.27 mmol), benzoic acid (15 mg), copper powder (300 mg), and freshly distilled deaerated quinoline (3 ml) were heated under reflux for 60 min. After cooling, the material was dissolved in ether, filtered through sintered glass, and extracted twice with 10% aqueous hydrochloric acid. The solvent was removed on a rotary evaporator. The material was applied to a 20 × 40 cm preparative thick-layer plate and eluted twice with Skelly B (hexanes). Removal of the band of R_f 0.56 afforded 38 mg (85% yield) of 4,8-dihydrodibenzo[*cd,gh*]pentalene, mp 137.5–138.5° (methanol), identical with respect to spectral data, mixture melting point, and thin-layer behavior with the above sample.

Method C. Thermal Decarboxylation.^{41b} Under nitrogen, 4,8-dihydrodibenzo[*cd,gh*]pentalene-4-carboxylic acid (15 mg of material, 75% pure by NMR, 0.051 mmol) was heated to 290°, during which time 12 mg sublimed. This material was applied to a 20 × 20 cm preparative thin-layer plate and eluted once with chloroform, and the material of R_f 0.70 was removed with chloroform. Resublimation afforded 4 mg, 36% yield, of 4,8-dihydrodibenzo[*cd,gh*]pentalene identical with respect to spectral data and thin-layer behavior with the above sample.

Bromination of 4,8-Dihydrodibenzo[*cd,gh*]pentalene. Method A. 4,8-Dibromo-4,8-dihydrodibenzo[*cd,gh*]pentalene (22). 4,8-Dihydrodibenzo[*cd,gh*]pentalene (14.9 mg, 0.084 mmol) was dissolved in deaerated carbon tetrachloride (0.5 ml) in a flame-dried flask. A solution of bromine (26.9 mg, 0.168 mmol, 2.00 mol equiv) in deaerated carbon tetrachloride (2.58 ml) was added to the rapidly stirred solution in portions of 1.00, 1.00, and 0.58 ml. After each addition, the mixture was irradiated with a no. 2 photoflood lamp held 10 cm from the reaction vessel for periods of 15, 15, and 120 sec, respectively. The solvent was removed on a rotary evaporator. The crude dibromide was recrystallized from carbon tetrachloride (1 ml) and carbon tetrachloride-hexane (1 ml, 0°) to afford in two crops 18 mg, 64% yield, of 4,8-dibromo-4,8-dihydrodibenzo[*cd,gh*]pentalene, mp 245° dec.⁴² After elution with Skelly B (hexane) four times, this material exhibited a single spot of R_f 0.25 on PF-254 silica gel. The material was identified on the basis of the following spectral data: NMR^{19} δ 7.410, 7.173, 6.200 (A_2BX pattern, $J_{ab} = 7.6$, $J_{ax} = 2.5$, $J_{bx} = 0.0$ Hz); ir^{18} 2923, 1128, 976 cm^{-1} ; mass spec 338 (5), 336 (10), 334 (6), 257 (28), 255 (28), 176 (100), 150 (20), 88 (26); uv^{40} ($\log \epsilon$) 246 (4.34), 291 (3.73); mol wt 333.8985 (calcd for $\text{C}_{14}\text{H}_8\text{Br}_2$, 333.8994).

Method B. 4-Bromo-4,8-dihydrodibenzo[*cd,gh*]pentalene (21) and 4,8-Dibromo-4,8-dihydrodibenzo[*cd,gh*]pentalene (22). 4,8-Dihydrodibenzopentalene (11.1 mg, 0.062 mmol) was dissolved in deaerated carbon tetrachloride (2.5 ml) in a flame-dried flask. A solution of bromine (15 mg, 0.94 mmol) in deaerated carbon tetrachloride (1.65 ml) was added to the rapidly stirred solution in portions of 0.50, 0.50, 0.50, and 0.15 ml. After each addition, the mixture was irradiated with a no. 2 photoflood lamp held 30 cm from the flask for periods of 5, 10, 10, 10, and 60 sec, respectively. The

solvent was removed on the rotary evaporator. The crude bromides were applied to a 20 × 40 cm preparative thick-layer plate and eluted four times with pentane, affording four bands. These bands were removed from the silica gel with chloroform. Band 1, R_f 0.70, contained too little material to work with and was not examined further. Band 2, R_f 0.49, 5.5 mg, 34% yield, was identified tentatively as 4-bromo-4,8-dihydrodibenzo[*cd,gh*]pentalene. For the spectral data, see section on results. Band 3, R_f 0.40, 8.8 mg, 24% yield each of two materials; was identified on the basis of its NMR and thin-layer behavior as an approximately 1:1 mixture of 4,8-dibromo-4,8-dihydrodibenzo[*cd,gh*]pentalene and 4-bromo-4,8-dihydrodibenzo[*cd,gh*]pentalene. Band 4, R_f 0.01–0.06, was a crystalline yellow material and was not examined further.

Method C. 4,4,8,8-Tetrabromo-4,8-dihydrodibenzo[*cd,gh*]pentalene (24) and 4,4,8-Tribromo-4,8-dihydrodibenzo[*cd,gh*]pentalene (23). Dihydrodibenzopentalene (7.5 mg, 0.042 mmol) was dissolved in deaerated carbon tetrachloride (0.5 ml) in a flame-dried flask. A solution of bromine (28.4 mg, 0.18 mmol, 4.2 mol equiv) in deaerated carbon tetrachloride (2.3 ml) was added to the rapidly stirred solution in portions of 0.5, 0.5, 0.5, and 0.8 ml. After each addition, the solution was irradiated with a no. 2 photoflood lamp held 60 cm from the reaction vessel for periods of 5, 10, 30, and 120 sec, respectively. The bromine color had disappeared approximately half way through each irradiation period. The solvent was removed on a rotary evaporator, and the crude bromides were applied to a 20 × 40 cm preparative thick-layer plate. The plate was eluted four times with Skelly B (hexanes), affording two clearly separated major bands in addition to the origin. Traces of material appeared between the origin and the lower band. The materials were removed from the silica gel with chloroform. Band 1, R_f 0.50, was identified as 4,4,8,8-tetrabromo-4,8-dihydrodibenzo[*cd,gh*]pentalene (11.0 mg, 53% yield). This material was recrystallized from 9:1 CDCl_3 - Me_4Si (0.3 ml) at -10° , affording 8 mg of material, mp 258° dec.⁴² The material recovered from the mother liquor darkened rapidly at 240° and melted with decomposition at 250°. Spectral data: NMR^{19} δ 7.423, 7.294 (A_2B pattern, $J_{ab} = 7.4$ Hz); ir^{18} 2901, 2849, 1451, 1404, 1044, 986, 659 cm^{-1} ; mass spec 498 (3), 496 (17), 494 (20), 492 (14), 490 (3), 417 (30), 415 (86), 413 (84), 411 (29), 336 (37), 334 (65), 332 (32), 256 (17), 254 (22), 174 (100), 167 (41), 87 (75); uv^{40} ($\log \epsilon$) 258 (4.24), 300 (3.64). mol wt 493.7166 (calcd for $\text{C}_{14}\text{H}_6\text{Br}_4$, 493.7166). Band 2, R_f 0.38, was identified as 4,4,8-tribromo-4,8-dihydrodibenzo[*cd,gh*]pentalene (4.3 mg, 25% yield), mp 148–155°. The NMR spectral data are included in the section on results. Other spectral data: ir^{18} 2915, 2841, 1733, 1558, 1453, 1404, 1143, 981, 657, 641 cm^{-1} ; mass spec 418 (2), 416 (6), 414 (6), 412 (2), 337 (32), 335 (62), 333 (30), 256 (43), 254 (40), 191 (22), 175 (54), 175 (48), 175 (42), 80 (100); uv^{40} ($\log \epsilon$) 255 (4.28), 295 (3.79); mol wt 413.8080 (calcd for $\text{C}_{14}\text{H}_7\text{Br}_3$, 413.8080).

Synthesis of 4,8-Dibenzo[*cd,gh*]pentalenoquinone (27). Method A. Silver Acetate Hydrolysis of 4,4,8,8-Tetrabromo-4,8-dihydrodibenzo[*cd,gh*]pentalene (24). Under nitrogen and in the dark, 4,4,8,8-tetrabromo-4,8-dihydrodibenzo[*cd,gh*]pentalene (15 mg, 0.03 mmol), silver(I) acetate (100 mg, 0.60 mmol), and glacial acetic acid (1.5 ml) were stirred at room temperature for 48 hr. Another 1.5 ml of glacial acetic acid was added, and stirring continued for another 45 hr. Concentrated aqueous hydrochloric acid (85 μL) and water (750 μL) were added, and the mixture was stirred for an additional 22 hr. After filtration of the solids and washing the precipitate with chloroform, the filtrate was concentrated in vacuo on a rotary evaporator. The residue was applied to a 20 × 20 cm preparative thick-layer plate of air-dried silica gel G (not activated) and eluted twice with 6% dichloromethane in pentane and once with 50% dichloromethane in pentane to afford three bands in addition to the origin.

Band 1, R_f 0.31, 3.2 mg, 30% yield, was identified as 4-keto-8,8-dibromo-4,8-dihydrodibenzo[*cd,gh*]pentalene, mp 163–168°. Spectral data: NMR^{24} δ 7.49, 7.34, and 7.20 (ABC pattern, $J_{ac} = J_{bc} = 7.0$ Hz; $J_{ab} = 1.5$ Hz); mass spec 352 (5), 350 (10), 348 (5), 271 (45), 269 (45), 206 (100), 192 (80), 191 (50), 164 (80), 163 (86), 150 (90); uv^{40} ($\log \epsilon$) 265 sh (4.11), 272 (4.16), 278 sh (4.13); for infrared spectral data, see section on results; mol wt 349.8767 (calcd for $\text{C}_{14}\text{H}_6\text{Br}_2\text{O}$, 349.8767).

Band 2, R_f 0.21, 0.6 mg, was not examined further. Band 3, R_f 0.14, 2.3 mg, 37% yield, was identified as 4,8-dibenzo[*cd,gh*]pentalenoquinone, mp 254–258°, on the basis of its spectral proper-

ties. For ir and NMR data, see section on results. Other spectral data: mass spec 206 (100), 178 (16), 150 (84), 75 (25); uv^{40} (log ϵ) 254 sh (4.10), 261 (4.23), 268 (4.23), 278 sh (3.85), 312 sh (3.10), 357 (2.95); mol wt 206.0368 (calcd for $C_{14}H_6O_2$, 206.0368).

Method B. Silver Acetate Hydrolysis of 4-Keto-8,8-dibromo-4,8-dihydrodibenzo[cd,gh]pentalene (28). 4-Keto-8,8-dibromo-4,8-dihydrodibenzo[cd,gh]pentalene (4 mg, 0.011 mmol), silver(I) acetate (18 mg, 0.054 mmol), and glacial acetic acid (1 ml) were stirred in the dark for 25.5 hr. Concentrated hydrochloric acid (15 μ l.) and water (250 μ l.) were added, and the mixture was stirred in the dark for an additional 11 hr at room temperature. After filtration of the precipitate and washing the latter with chloroform, the combined filtrates were concentrated in vacuo. The residue was applied to a 20 \times 20 cm preparative thick-layer plate and eluted twice with 6% dichloromethane in pentane. Two bands were obtained.

Band 1, R_f 0.49, 1.3 mg, 33% yield, was identified by comparison of spectral data and thin-layer behavior with an authentic sample as 4-keto-8,8-dibromo-4,8-dihydrodibenzo[cd,gh]pentalene, mp 163–168°.

Band 2, R_f 0.18, 1.5 mg, 64% yield, was identified by comparison of spectral data and thin-layer behavior with an authentic sample as 4,8-dibenzo[cd,gh]pentalenoquinone, mp 254–258°.

Method C. Bromine and Oxygen Oxidation of 4,8-Dihydrodibenzo[cd,gh]pentalene (4). 4,8-Dihydrodibenzo[cd,gh]pentalene (22.6 mg, 0.127 mmol) was dissolved in carbon tetrachloride (10 ml). With oxygen bubbling through the solution, bromine (65 mg, 0.41 mmol) as a solution in carbon tetrachloride (2.5 ml) was added in five portions with 30-sec irradiations (no. 2 photoflood lamp held 15 cm from the reaction vessel) after each addition. The solvent was removed on a rotary evaporator and the material applied to a 20 \times 20 cm preparative thick-layer plate. The plate was eluted twice with 50% dichloromethane in pentane. Three major bands were obtained.

Band 1, R_f 0.85, 19.0 mg, 36% yield, was identified on the basis of NMR and thin-layer comparison with an authentic sample as 4,4,8-tribromo-4,8-dihydrodibenzo[cd,gh]pentalene. Band 2, R_f 0.47, 13.2 mg, 36% yield, was identified on the basis of spectral data as 4-keto-8-bromo-4,8-dihydrodibenzo[cd,gh]pentalene. Spectral data: NMR²⁴ δ 7.42, 7.32, 7.13 (ABC pattern $J_{ac} = 7.0$, $J_{bc} = 6.0$, $J_{ab} = 1.5$ Hz); ir^{18} 1724 cm^{-1} ; mass spec 272 (30), 270 (32), 206 (15), 192 (53), 191 (100), 164 (45), 163 (85), 150 (12), 81.5 (42); uv^{40} (log ϵ) 264 sh (4.06), 268 (4.08); mol wt 269.9681 (calcd for $C_{14}H_7BrO$, 269.9681).

Band 3, R_f 0.32, 4.9 mg, was identified on the basis of spectral data and thin-layer comparison with authentic material as an approximately 1:1 mixture of fluorenone and 4,8-dibenzo[cd,gh]pentalenoquinone. This band was reapplied to a 20 \times 20 cm preparative thick-layer plate of air-dried silica gel G, and eluted three times with 5% dichloromethane in pentane. This afforded fluorenone (2.7 mg, R_f 0.12, 10% yield if from the dihydrodibenzopentalene) and 4,8-dibenzo[cd,gh]pentalenoquinone (2.5 mg, 9% yield, R_f 0.04, mp 254–258°).

Bisprotonation of 4,8-Dibenzo[cd,gh]pentalenoquinone. 4,8-Dibenzo[cd,gh]pentalenoquinone (3.19 mg, 0.015 mmol) was placed in an NMR tube and immersed in liquid nitrogen (–196°). A 10% solution of antimony pentafluoride in fluorosulfonic acid (0.5 ml) was added such that the materials did not mix (the acid solution freezes on the side of the tube). The materials were mixed at –78° using a glass rod, and the NMR spectrum of the resultant dark solution of bisprotonated 4,8-dibenzopentalenoquinone was determined using dichloromethane ($\delta \equiv 5.30$) as an internal standard: NMR (δ , –80°) 15.53 (2 H, s), 7.79, 7.27 (6 H, A₂B pattern showing viscosity broadening); (–40°) =O⁺H not observed, 7.79, 7.30 (6 H, A₂B pattern, $J_{ab} = 7.5$ Hz). The solution was cooled from –40 to –78° and poured onto ice. Chloroform was added to dissolve the organic materials. The chloroform layer was separated and washed with water and the solvent removed on a rotary evaporator. The residue was shown to be identical with respect to infrared spectrum, color, and thin-layer comparison (R_f 0.06, two elutions with 50% dichloromethane in hexane, R_f 0.22, two elutions with benzene) with an authentic sample of 4,8-dibenzo[cd,gh]pentalenoquinone.

Polarographic Reduction of 4,8-Dibenzo[cd,gh]pentalenoquinone. Polarography of a deaerated solution of 4,8-dibenzo[cd,gh]pentalenoquinone (3.3 mg, 5.3×10^{-4} M) in 30 ml of DMSO (distilled from calcium hydride) containing 0.100 M tetra-*n*-but-

ylammonium perchlorate as supporting electrolyte shows a reversible ($E_{1/4} - E_{3/4} = 62$ mV) one-electron wave ($i_d = 0.027$ μ A) at –0.895 V vs. SCE. A second irreversible wave ($E_{1/4} - E_{3/4} = 90$ mV, $i_d = 0.041$ μ A) is observed at –1.630 V vs. SCE. The counter electrode was a mercury pool. A drop time of 7.2 sec and a mercury head of 50 cm were employed. The temperature was 21°. The reference SCE was immersed in the electrolyte solution and separated from the sample solution by a sintered glass frit.

ESR Spectrum of 4,8-Dibenzo[cd,gh]pentalenoquinone Radical Anion (30). Electrolytic reduction of a deaerated solution of 3.3 mg of 4,8-dibenzo[cd,gh]pentalenoquinone (5.34×10^{-4} M) in 30 ml of DMSO (distilled from calcium hydride) containing 0.100 M tetra-*n*-butylammonium perchlorate as supporting electrolyte was performed in a Varian electrolytic cell at 25° using a mercury pool cathode and platinum wire anode. The observed line width was 50 mG. The g factor of the radical anion was determined by measuring the difference in field strength between the centerline of 30 and the centerline of samples of benzosemiquinone radical anion⁴³ (2.0046) in small capillaries strapped to each face of the electrolytic cell. The line width of the benzosemiquinone radical anion signal was 75 mG, indicating homogeneity of the field.

Sodium Acetate Hydrolysis of 4,4,8-Tribromo-4,8-dihydrodibenzo[cd,gh]pentalene. Under nitrogen, 4,4,8-tribromo-4,8-dihydrodibenzo[cd,gh]pentalene (4.0 mg, 0.096 mmol) was refluxed for 13 hr in a solution of 570 mg of sodium acetate in 1.7 ml of 60% aqueous acetic acid. Concentrated hydrochloric acid (1.4 ml) was added and the material partitioned between dichloromethane (25 ml) and water (25 ml). Rotary evaporation of the solvent from the dichloromethane layer afforded 3.1 mg of material. This material was applied to a preparative thick-layer plate and eluted once with dichloromethane. Two major yellow bands were observed. One at R_f 0.06, 0.7 mg, was not examined further. The other R_f 0.25, 0.9 mg, was identified as 4-formylfluorenone, 45% yield, mp 155–163°, on the basis of the following spectral data. Spectral data: NMR¹⁹ δ 10.44 (1 H, s), 8.45 (1 H, d, $J = 7.0$ Hz), 8.04–7.33 (7 H, m); ir^{24} 1725 cm^{-1} ; mass spec metastable peaks at 155.8, 154.18, 128.4, 127.4, 208 (100), 207 (37), 180 (77), 179 (3), 152 (32), 151 (41), 150 (25); uv^{40} (log ϵ) 227 (4.21), 242 sh (4.07), 251 (4.24), 259 (4.40), 269 (4.00), 278 (3.98), 309 (3.39), 332 (3.12), 348 (2.94); mol wt 208.0524 (calcd for $C_{14}H_8O_2$, 208.0524).

Preparation of Dilithium Dibenzo[cd,gh]pentalenide (31). With rigid exclusion of moisture and oxygen, 4,8-dihydrodibenzo[cd,gh]pentalene (5.5 mg, 0.031 mmol) was dissolved in freshly distilled (from LAH) THF-*d*₈ (0.3 ml) in an NMR tube and cooled to –78°. *n*-Butyllithium (100 μ l., 1.94 M, 0.39 mmol) in hexane was added, causing a precipitate to form. After warming to room temperature, a pale-yellow solution was obtained and the NMR of the dilithium dibenzo[cd,gh]pentalenide solution determined. Nearly quantitative crystallization of the dianion can be effected by cooling the solution to –10° (NMR). The dianion solution showed no signs of decomposition over a period of 2 hr at 39°. Inverse addition of the dianion-containing solution by syringe to rapidly stirred D₂O (10 ml, 99.8% dec) followed by extraction after 1 min with dichloromethane afforded 4,8-dideuterio-4,8-dihydrodibenzo[cd,gh]pentalene (99% *d*₂ incorporation) containing 1% monodeuterated material. Spectral data: NMR²⁴ δ 7.21, 7.03 (6 H, A₂B pattern broadened by allylic coupling, $J_{ab} = 7.6$ Hz), 4.13 (2 H, 1:1, t, $J_{HD} = 2.3$ Hz); mass spec 180 (100), 179 (15), 178 (18). The 12-eV mass spectrum showed *m/e* (rel %) 179 (1.2), 180 (100), 181 (16), and 182 (2) from which was calculated the % *d* incorporation.

Preparation of Tetramethyl 4,8-Dihydrodibenzo[cd,gh]pentalenyl-4,8-bisphosphonate. 4,8-Dibromo-4,8-dihydrodibenzo[cd,gh]pentalene (3.75 mg, 0.0112 mmol) and 1.5 ml of freshly distilled trimethyl phosphite were heated under reflux for 4.0 hr. The excess trimethyl phosphite was removed on a rotary evaporator and the crystalline residue subjected to 0.5 mm of pressure for 15 min at room temperature, affording 4.6 mg of material. This material was taken up in 4 drops of chloroform and caused to crystallize by the addition of 14 drops of hexane, affording 2.9 mg, 70% yield, of tetramethyl 4,8-dihydrodibenzo[cd,gh]pentalenyl-4,8-bisphosphonate as a powder, mp 238–240°. Spectral data: NMR¹⁹ δ 7.61, 7.32 (6 H, A₂B pattern, $J_{ab} = 7.3$ Hz), 5.14 (1 H, d, $J = 7$ Hz), 3.63, 3.59 (12 H, two doublets, intensity ratio 2:1, $J = 11.2$ Hz); ir^{18} 3003, 2967, 2857, 1449, 1404, 1246, 1204, 1057,

1035 cm^{-1} ; mass spec 394 (100), 176 (27), 109 (24); uv^{40} ($\log \epsilon$) 269 (4.15), 273 sh (4.14), 289 sh (3.22), 365 (2.84), 382 (2.88).

Brominative Decarboxylation⁴⁴ of Fluorene-9-carboxylic Acid. Fluorene-9-carboxylic acid (1.00 mmol), red mercuric oxide (120 mg, 0.55 mmol), and 10 ml of deaerated bromotrichloromethane were placed in a flame-dried flask. Bromine (160 mg, 1.00 mmol) in 10 ml of deaerated bromotrichloromethane was added dropwise to the stirred solution over 30 min. The mixture was irradiated for 1.5 hr with a no. 2 photoflood lamp placed 8 cm from the flask, cooled, and filtered. The solvent was removed on a rotary evaporator. The crude material was applied to a preparative thick-layer plate and eluted once with 1:1 dichloromethane-pentane, affording two bands. Band 1, R_f 0.80, 51 mg, 21% yield, was identified as 9-bromofluorene on the basis of its NMR and thin-layer comparison spot. Band 2, R_f 0.27, 30 mg, mp 140–145° (hexane), was not investigated further.

Brominative Oxidation of Fluorene. Fluorene (166 mg, 1.00 mmol) was dissolved in 75 ml of carbon tetrachloride. A solution of bromine (336 mg, 2.1 mmol) in carbon tetrachloride (25 ml) was added dropwise over 10 min to the rapidly stirred solution while bubbling oxygen through the solution and irradiating with a no. 2 photoflood lamp held 60 cm from the reaction vessel. The solvent was removed on a rotary evaporator. The material was applied to a 20 × 20 cm preparative thick-layer plate and eluted once with dichloromethane. Two major bands were observed. The first, R_f 0.90, 77 mg, was not examined further. The second, R_f 0.52, 163 mg, was identified as fluorenone (91% yield) by color, thin-layer, and NMR comparison with authentic material.

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