the sulfenyl chloride had not disappeared. The mixture was then filtered, the solvent removed under vacuum, and the solid product recrystallized from *n*-hexane. During each recrystallization, some insoluble bis-4-nitrophenyl disulfide had to be removed before crystallization was allowed to proceed.

General procedure for the preparation of 2,4-dinitrophenyl aryl disulfides. One-hundredth mole of 2,4-dinitrobenzenesulfenyl chloride, freshly recrystallized from carbon tetrachloride (m.p. 98°) was dissolved in 100 ml. of hot, dry ether and placed in a three necked flask fitted with a thermometer, dropping funnel, and a reflux condenser, the top of which was protected with a calcium chloride drying tube. To this solution was added dropwise 0.01 mole of the arenethiol in 30 ml. of dry ether. In the case of β-naphthlenethiol, 140 ml. of dry ether was required because of the insolubility of this compound in ether. After the thiol addition was complete, the mixture was refluxed for an additional 2 hr. During this time evolution of hydrogen chloride was observed. The solution was then allowed to stand overnight without heating. The solvent was then removed and the product recrystallized from a mixture of ethanol and benzene.

4-Nitrophenyl methyl sulfide was prepared by reducing bis-4-nitrophenyl disulfide to the thiol according to the procedure of Zincke[22] as reported above. The thiol was then methylated with dimethyl sulfate in alkali. The product was recrystallized from 95% ethanol to give light yellow needles, m.p. 71–72°. The reported melting point[26] is 72.°

BLOOMINGTON, IND.

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[26] K. Brand and K. W. Kranz, *J. prakt. Chem.*, (2) **115**, 143 (1927).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Ultraviolet Spectra of Triptycene Derivatives

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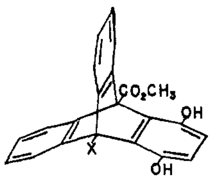
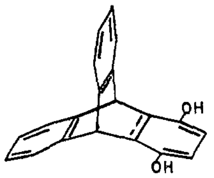
The preparation and ultraviolet spectra of several bridgehead derivatives of 2,5-dihydroxytriptycene are reported. It is shown that these spectra can be successfully interpreted by the model previously developed for triptycene. The bridgehead substituents have a negligible effect on the spectra.

Recently a model was developed for the interpretation of the ultraviolet spectrum of triptycene.[2] According to this model the triptycene spectrum is essentially that of an *o*-substituted benzene which, however, has been slightly displaced by interaction of the weak transition dipoles. An extension of this model to triptycenes which are substituted in one of the rings suggests that their ultraviolet spectra should be approximately the sum of the bands found in the three separate chromophores. This is only an approximation since weak interactions similar to those in triptycene should occur in such derivatives. The particular triptycene derivatives to be considered in this paper are methyl 2,5-dihydroxy-1-triptoate, Ia, methyl 6-methyl-2,5-dihydroxy-1-triptoate, Ib, methyl 6-bromo-2,5-dihydroxy-1-triptoate, Ic, as well as the simpler 2,5-dihydroxtriptyrene, II. With these molecules it should be possible to not only test the extension of the spectral model but also to determine what effect, if any, the isolated bridgehead substituents have on the spectra.

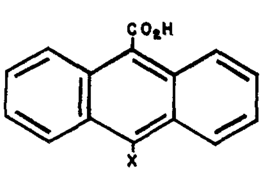


Ia X=H
Ib X=CH$_3$
Ic X=Br



II

Preparation of 6-bridgehead derivatives. The 6-bridgehead derivatives were prepared from the appropriately substituted anthroic acids by the same sequence employed by Bartlett and Greene[3] for Ia. Accordingly, 9-anthroic acid, IIIa, was synthesized in 80% yield by the metallation of 9-bromoanthracene with phenyllithium followed by reaction of the organometallic intermediate with carbon dioxide.



IIIa X=H
IIIb X=CH$_3$
IIIc X=Br

This method in our hands proved to be superior to that of the Latham, May, and Mosettig procedure[4] which gave 9-anthroic acid in 62% yield by reaction of oxaylyl chloride with anthracene. The substituted acids, IIIb and IIIc, were prepared by the procedure of Mikhaĭlov and Bronovitskaya.[5] This involved the preparation of the organo lithium

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[1] Based in part on the Ph.D. dissertation of A. C. Craig, Dept. of Chemistry, Cornell University, 1959.

[2] C. F. Wilcox, Jr., *J. Chem. Phys.*, in press; Dr. Edel Wasserman has informed us that he has carried out an excition treatment of triptycene (Ph.D. dissertation, Harvard, 1958). We would like to acknowledge an enlightening discussion of this treatment with Dr. Wasserman.

[3] P. D. Bartlett and F. D. Greene, *J. Am. Chem. Soc.*, **76**, 1088 (1954).

[4] H. G. Latham, Jr., E. L. May, and E. Mosettig, *J. Am. Chem. Soc.*, **70**, 1079 (1948).

[5] B. N. Mikhaĭlov and V. P. Bronovitskaya, *Zhur. Obshceĭ. Khim.*, **22**, 157 (1952).

derivative of 9,10-dibromoanthracene followed either by carbonation to give IIIc or reaction with methyl iodide followed by a second carbonation reaction to give IIIb. All three acids were converted into their methyl esters with diazomethane.

The Diels-Alder adducts of the esters with *p*-benzoquinone were obtained by refluxing a benzene solution of the ester with *p*-benzoquinone under a nitrogen atmosphere for twenty-four to forty-eight hours. It is interesting to observe that, although the unsubstituted and methyl substituted adducts were formed in 58% and 65% yields, respectively, the bromo derivative was obtained in only 9–16% yield even when the quinone-ester ratio was increased threefold. Since the bromine and methyl groups have comparable size, this poorer adduction would appear to be related to either the electron withdrawing properties of the bromine atom or the loss of the bromine to ring delocalization energy in going to the adduct. Similar deleterious effects of *meso*-bromine substituents on Diels-Alder adduction of other anthracene derivatives with quinone have been observed by Theilacker and co-workers.[6]

The adducts were isomerized in hydrochloric acid-glacial acetic acid media to give the desired hydroquinones in good yield. As additional support for these structures, it can be pointed out that the three hydroquinones were easily oxidized in 72% to 85% yields with sodium bromate in acid solution into the corresponding quinones.

Infrared spectra. In the preceding reactions, the significant changes in molecular structure were reflected remarkably well by the infrared spectra. The anthroate esters had absorption near 5.80 μ typical of methyl esters of aromatic acids.[7] The benzoquinone adducts had two prominant bands at 5.72 and 5.95 μ. The shorter wave-length band is characteristic of saturated methyl esters,[8] while the longer wave-length band corresponds to α,β-unsaturated ketone absorption.[9] The related hydroquinones, Ia, Ib, Ic, all showed broad absorption at 2.90–3.00 μ and the ester carbonyl absorption was shifted to longer wave-lengths (5.77–5.80 μ). This would suggest, as Bartlett and Greene already have pointed out[3] for Ia, that in these hydroquinones a hydrogen bond is formed between the phenolic 2-hydroxy group and the carbonyl oxygen of the ester. Upon oxidation of the hydroquinones to the quinones, the ester carbonyl absorption returned to its normal position and typical quinoid bands appeared at 5.99–6.05 μ.[10]

Ultraviolet spectra. The ultraviolet spectra of alcoholic solutions of methyl 2,5-dihydroxy-1-triptoate and its 6-methyl and 6-bromo derivatives are presented in Table I along with the maxima of triptycene, 2,5-dihydroxy triptycene, and *o*-xylohydroquinone. Examination of the data in Table I yields several striking comparisons. First, the triad of bands in the ultraviolet spectrum of triptycene show up in remarkably constant positions in the four dihydroxytriptycenes. This constancy can be explained by an analysis almost identical to that developed for the ultraviolet spectrum of triptycene. This approach is based on the Longuet-Higgins and Murrell[12] model for electronic spectra which treats π-electron transitions in terms of local and charge-transfer excitations. In triptycene the longest wave length 279 mμ band is associated[2] with the doubly degenerate antisymmetrical combinations of the local $\alpha(^1L_b)$-bands, $1/\sqrt{6}\ (2\theta_\alpha\text{-}\phi_\alpha\text{-}\Omega_\alpha)$ and $1/\sqrt{2}\ (\phi_\alpha\text{-}\Omega_\alpha)$, where the symbols θ_α, ϕ_α and Ω_α each represent a local α transition on the θ, ϕ or Ω- benzene ring. In triptycene these transitions are bathochromically shifted relative to the symmetrical combination, $1/\sqrt{3}\ (\theta_\alpha + \theta_\alpha + \Omega_\alpha)$, by the combined effect of neighboring ring and substituent induced mixing of higher energy transitions. This difference in behavior between the symmetric and antisymmetric combinations can be arrived at by imagining that initially the benzene rings are isolated so that each contributes an absorption spectrum characteristic of an isolated benzene ring. Then when the interaction terms are included these local transitions mix and give rise to displaced maxima. However, because the α-transitions have two components of the transition dipole which to a first approximation act in directions these interaction terms essentially cancel for triptycene. What little shift is observed can be ascribed largely to the presence of substituents (the two bridgehead C—H groups) which perturb the α-transitions so that the components of the oppositely acting dipoles are no longer exactly equal. These perturbed transitions interact in such a way as to shift the antisymmetrical combinations to longer wave lengths.

Since with each of the four dihydroxy triptycenes an analogous antisymmetrical α-transition, $1/\sqrt{2}\ (\theta_\alpha - \Omega_\alpha)$, arises and since the electron environments are so similar it is suggested that the local pertur-

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(6) W. Theilacker, U. Berger-Brose, and K. Beyer, *Ber.*, **93**, 1658 (1960).

(7) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1958, p. 182.

(8) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1958, p. 180.

(9) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1958, p. 136.

(10) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1958, p. 150.

(11) This sample was prepared by Mrs. Margaret McPhee Miano according to the method of O. H. Emerson and L. I. Smith, *J. Am. Chem. Soc.*, **62**, 141 (1940). This spectrum is consistent with that of L. Paolini and G. B. Marini-Bettolo, *Gazz. chim. ital.*, **87**, 395 (1957).

(12) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc. A.*, **68**, 601 (1955).

TABLE I

ULTRAVIOLET SPECTRA OF ALCOHOLIC SOLUTIONS OF 6-SUBSTITUTED 2,5-DIHYDROXY TRIPTYCENES AND RELATED COMPOUNDS

Compound	λ_{max} (log ϵ in parentheses)				
Methyl 2,4-dihydroxy-1-triptoate	254 (sh) (3.24)	263 (3.25)	271 (sh) (3.29)	277 (3.57)	302 (3.65)
Methyl 6-methyl-2,4-dihydroxy-1-triptoate		261 (3.29)	269 (3.27)	278 (3.38)	304 (3.65)
Methyl 6-bromo-2,4-dihydroxy-1-triptoate		260 (sh) (3.18)	269 (3.11)	277 (3.21)	308 (3.68)
2,4-Dihydroxytriptycene	256 (3.20)	263 (3.42)	272 (3.62)	279 (3.62)	300 (3.62)
Triptycene		264 (sh) (3.3)	271 (3.55)	279 (3.67)	
o-Xylohydroquinone[11]					294 (3.46)

bations should be similar to those found in triptycene. In support for this suggestion it can be argued that on the one hand various α-substituted alkyl benzenes show little variation in their α-band positions[13] and on the other hand the extra mixing induced by the additional pair of OH groups should be small because of their distance from the pair of non-substituted benzene chromophores. Theoretical estimation of this latter effect suggests less than 0.5 mμ additional shift.[14] For these reasons it is not too surprising that the triad of bands starting at 279 mμ shows up in all five molecules.

From the data in Table I it would appear that the bands near 300 mμ are to be associated with the 294 mμ band of 2,3-dimethyl-hydroquinone. These bands also have undergone a displacement but not in as constant a way as the transitions of the *o*-xylene chromophores. The exact positions of these 300 mμ bands are more difficult to account for since little is known of the energetics of the upper excited states and it is these details in conjunction with the degree of mixing with the ground state which determine the magnitude of shift from 294 mμ. There is an approximate empirical correlation, as might be expected, between the position of this band and the inductive nature of the bridgehead substituents as measured by the sum of the Taft σ^* parameters.[15] However, with the given groups this correlation might as easily be a trivial relationship between the size of the group and its ability to interfere with solvation of the hydroxy groups.

A further point to be made from the data in Table I and the foregoing analysis is that when weak substituents[16] such as —OH are attached to only one of the benzene rings the band sequence of 279 mμ, 271 mμ, etc., should appear. Since the present data demonstrate that bridgehead substituents have little effect on these bands in the case of a pair of —OH substituents it seems reasonable that this band system should be diagnostic for triptycenes with weak substituents in one ring. When strong substituents[16] like NH_2 are included the situation is no longer clear. The strong substituents introduce considerable amounts of local charge transfer states and these depending on the number and orientation of the substituents might mix with *o*-xylene transitions to produce abnormal shifts of the 279 mμ band sequence. Such special interaction if it occurred might be turned around and used as a new measure of strong and weak substituents and the degree of local charge-transfer mixing.

EXPERIMENTAL

9-Anthroic acid (IIIa). A. The procedure of Latham, May, and Mosettig[4] was followed to give a 62% yield of a yellow powder, m.p. 209.5–215°. A small portion was recrystallized from dilute ethanol to yield pale yellow needles, m.p. 221–222°; reported, 208–212°.

B. Twenty grams (0.075 mole) of 9-bromoanthracene was added to an ethereal solution of 7 g. (0.085 mole) of freshly prepared phenyllithium and the solution was stirred under nitrogen for 45 min. at 25–35°. The reaction was cooled and then poured over a large excess (*ca.* 200 g.) of Dry Ice. The resultant slurry was allowed to stand for 20 min. after which time 500 ml. of ether and 500 ml. of water were added and the system allowed to stand overnight. The layers were separated and the ether layer then was extracted with 10% aqueous sodium carbonate solution. The carbonate extract was combined with the original aqueous layer and neutralized with 10% sulfuric acid to precipitate 12.6 g. (75.5%) of a light yellow powder, m.p. 217–218°. From the ether layer there was obtained 2.5 g. of starting material so that on the basis of consumed material the conversion to 9-anthroic acid was 80%.

9-Bromo-10-methylanthracene. This was prepared by the procedure of Mikhailov and Bronvitshaya[5] from 9,10-dibromoanthracene in 98% crude yield. Recrystallization from 95% ethanol afforded long yellow needles, m.p. 163–164°; reported m.p. 170–173°.

Anal. Calcd. for $C_{15}H_{11}Br$: C, 66.44; H, 4.09; Br 29.47. Found: C, 66.66; H, 4.17; Br 29.36.

9-Methyl-10-anthroic acid (IIIb). This was prepared from 9-bromo-10-methylanthracene by the procedure of Mikhailov

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[13] F. A. Matsen, Technique of Organic Chemistry, Vol. IX, Chemical Applications of Spectroscopy, A. Weissberger, Ed., Interscience Publishers, Inc., New York, 1956, p. 677.

[14] This calculation was made using theoretically evaluated penetration integrals. While the exact number is not significant the order of magnitude probably is.

[15] Chapter 13 by R. W. Taft, Jr. in M. S. Newman, *Steric Effects in Organic Chemistry*, John Wiley and Sons, Inc., New York, N. Y., 1956.

[16] J. N. Murrell, *Proc. Phys. Soc.* (*London*), **68**, 969 (1955).

and Bronvitshaya[5] in 82% crude yield. Recrystallizations from ethanol yielded very bright yellow plates, m.p. 225–226°; reported 217–219°.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.33; H, 5.12; Neut. Equiv., 236. Found: C, 81.13; 81.19; H, 5.21, 5.13; Neut. Equiv., 233, 244.

9-Bromo-10-anthroic acid (IIIc). This was prepared from 9,10-dibromoanthracene by the procedure of Mikhailov and Bronvitshaya[5] in 73% yield. Recrystallization from 75% ethanol–25% benzene gave a fluffy yellow solid, m.p. 267–268°; reported 265–267°.

Anal. Calcd. for $C_{15}H_9O_2Br$: C, 59.82; H, 3.01; Br 26.54; Neut. Equiv., 301. Found: C, 60.09; 60.02; H, 3.09, 3.08; Br, 26.48, 26.63; Neut. Equiv., 286, 299.

Methyl esters. A. *Methyl 9-anthroate.* The acid (IIIa), 9.3 g. (0.042 mole) in ether, was esterified with an ethereal solution of diazomethane (0.068 mole) prepared from *N*-methyl-*N*-nitrosourea. After evaporation of the ether 7.6 g. (78%) of ester, m.p. 105–108°, was obtained. Recrystallization from ethanol gave pale yellow needles, m.p. 110–111°; reported 113°.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.33; H, 5.12. Found: C, 80.23, 81.51; H, 5.15, 5.17.

B. *Methyl 9-methyl-10-anthroate.* In the same manner as in part A there was obtained a 35% yield of methyl ester which when purified melted at 162–163°.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.57; H, 5.64. Found: C, 82.00, 80.17; H, 5.78, 5.77.

C. *Methyl 9-Bromo-10-anthroate.* In the same manner as in part A there was obtained an 85% yield of methyl ester which when purified melted at 109–110°.

Anal. Calcd. for $C_{16}H_{11}C_2Br$: C, 60.97; H, 3.52; Br, 25.36. Found: C, 60.71; H, 3.37; Br 25.32.

Diels-Alder adducts with p-benzoquinone. A. *Methyl 2,5-diketo-2,5,15,16-tetrahydro-1-triptoate.* This adduct was prepared by the method of Bartlett and Greene[3] except that the reaction was carried out under a nitrogen atmosphere. The product, obtained in 58% yield, melted at 199–200°; reported, 199–201°.

B. *Methyl 6-methyl-2,5,16,16-tetrahydro-1-triptoate.* This was prepared in 65% yield in a manner similar to that of A above except that the mixture was refluxed for only 24 hr. When the reflux time was extended to 44 hr., the yield was increased to 84%. The product melted at 196.5–197°.

Anal. Calcd. for $C_{23}H_{18}O_4$: C, 77.08: H, 5.06. Found: C, 76.81; H, 5.00.

C. *Methyl 6-bromo-2,4-diketo-2,5,15,16-tetrahydro-1-triptoate.* When the method described in part A above was applied to the bromo ester only a 4% yield was obtained. Substitution of *p*-xylene for benzene as solvent gave only intractable tars plus a trace of starting material. When the mole ratio of *p*-benzoquinone to ester was increased from 3:1 to 10:1 the yield using benzene as a solvent was 17% in one run and 10% in another run. The purified product melted at 211–211.5°.

Anal. Calcd. for $C_{22}H_{15}O_4Br$: C, 62.43; H, 3.57. Found C, 62.87, 62.99; H, 3.53, 3.61.

Conversion of the keto form to the hydroquinone. A. *Methyl 2,5-dihydroxy-1-triptoate.* The procedure of Bartlett and Greene was followed to obtain a 97% yield of fine colorless needles which sintered at 265° and melted at 272–273°; reported 265–266°.

B. *Methyl 6-methyl-2,4-dihydroxy-1-triptoate.* The procedure in part A was followed to obtain a 95% yield of fine colorless needles which melted at 274–275°.

Anal. Calcd. for $C_{23}H_{28}O_4$: C, 77.08; H, 5.06. Found: C, 77.52; H, 5.22.

C. *Methyl 6-bromo-2,5-dihydroxy-1-triptoate.* The procedure in part A was followed to obtain a 97% yield of fluffy off-white needles which melted at 286–287°.

Anal. Calcd. for $C_{22}H_{15}O_4Br$: C, 62.43; H, 3.57. Found C, 62.83; H, 3.77.

Oxidation of the triptycenehydroquinones to the triptycenequinones. A. *Methyl 2,4-diketo-2,5-dihydro-1-triptoate.* The procedure of Bartlett and Greene was followed to obtain a 72% yield of quinone which melted at 221–224°; reported 225°.

B. *Methyl 6-methyl-2,5-diketo-2,5-dihydro-1-triptoate.* In the same manner as in part A the methylhydroquinone was oxidized in 85% yield to the quinone which melted at 249–250°.

Anal. Calcd. for $C_{23}H_{16}O_4$: C, 77.51; H, 4.53. Found: C, 75.88; H, 4.57.

C. *Methyl 6-bromo-2,5-diketo-2,5-dihydro-1-triptoate.* The bromohydroquinone was oxidized by the method of part A in 85% yield to the quinone which melted at 265.5–266°.

Anal. Calcd. for $C_{22}H_{13}O_4Br$: C, 62.72; H, 3.13; Br, 18.97. Found C, 62.68; H, 3.21; Br, 19.52.

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[CONTRIBUTION NO. 120 FROM THE INSTITUTO DE QUÍMICA DE LA UNIVERSIDAD NACIONAL AUTÓNOMA DE MÉXICO]

The Intensity of the Carbonyl Band in the Infrared Spectra of Methyl Benzoates

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Received September 28, 1960

The quantitative infrared spectra of *meta* and *para* substituted methyl benzoates were measured, and it was found that the changes of the integrated absorption intensity (*A*), were in full agreement with the theoretical values. No linear relation was found when plotting *A vs.* Hammett σ values.

In the study of absorption intensities of infrared bands it is now customary to report not only their frequency but also their intensity. Cole,[1] Jones,[2] Brown,[3] and others, have shown that the empirical application of the infrared data is useful for structural studies of simple and complex organic molecules. Some values of infrared intensities are reported in the literature, but much work has to

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(1) A. R. W. Cole, G. T. A. Muller, D. W. Thornton, and R. S. L. Willix, *J. Chem. Soc.*, 1218 (1959).

(2) R. N. Jones, D. A. Ramsay, D. S. Keir, and K. Dobriner, *J. Am. Chem. Soc.*, **74**, 80 (1952).

(3) T. L. Brown, *J. Am. Chem. Soc.*, **80**, 794 (1958).