

prepared above was added to 2.50 g (16.4 mmol) of 5 in 50 mL of petroleum ether, and the solution was stirred for 16 h at room temperature under a nitrogen atmosphere. Upon cooling the solution to -78°C , pale yellow crystals were obtained which were collected by filtration. This material was recrystallized from petroleum ether at -78°C to give 1.2 g (30%) of 14: mp $87-89^{\circ}\text{C}$; IR (Nujol) 1690, 1655, 1600, 1280 cm^{-1} ; NMR (CDCl_3) δ 1.88 (3 H, s), 1.70-2.10 (2 H, m), 2.10-2.60 (8 H, m), 3.10-3.35 (2 H, m), 3.96 (3 H, s); mass spectrum, m/z 246 (M^+).

Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_3$: C, 73.17; H, 7.32. Found: C, 73.23; H, 7.41.

cis-6,7-Cyclopenteno-1,4,5,8,9,10-hexahydro-1,4-dihydroxy-2-methoxy-3-methylnaphthalene (15). A solution of 150 mg (0.64 mmol) of 14 in 20 mL of anhydrous ether was slowly added to a stirred suspension of 28 mg (0.73 mmol) of lithium aluminum hydride in 25 mL of ether at -60°C . The mixture was stirred for 1.5 h after the addition was complete, and 40 mL of ethyl acetate was added, followed by 2 mL of water. The solution was allowed to warm to room temperature, extracted with ethyl acetate, dried, and evaporated at 20°C . The residual oil was washed with petroleum ether to yield 108 mg (68%) of unstable 15: IR (Nujol) 3500, 3000, 1680, 1630 cm^{-1} . This material was used immediately for conversion to 16.

6,7-Cyclopenteno-5,8-dihydro-2-methoxy-3-methylnaphthalene (16). A solution of 928 mg (3.7 mmol) of 15 in 20 mL of pyridine at 0°C was slowly added to 6.00 g (40 mmol) of phosphorus oxychloride. After addition was complete, the solution was heated at 65°C for 18 h. The excess phosphorus oxychloride was destroyed by careful addition of water at 0°C , and the mixture was extracted with three 50-mL portions of ether. The ether extract was washed with 1 N hydrochloric acid until acidic and then with aqueous sodium bicarbonate and dried. Removal of the solvent in vacuo left a colorless solid, which was chromatographed on alumina (elution with hexane) to give 434 mg (55%) of 16: IR (CCl_4) 1500, 1235, 1205, 1090 cm^{-1} ; NMR (CDCl_3) δ 1.80-2.20 (2 H, m), 2.19 (3 H, s), 2.22-2.50 (4 H, m), 3.31 (4 H, s) 3.80 (3 H, s), 6.60 (1 H, s), 6.91 (1 H, s).

Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}$: C, 84.07; H, 8.47. Found: C, 83.91; H, 8.58.

6,7-Cyclopenteno-1,4,5,8-tetrahydro-2-methoxy-3-methylnaphthalene (17). To a solution of 198 mg (0.93 mmol) of 16 in 100 mL of dry tetrahydrofuran was added 80 mL of distilled ammonia, followed by 100 mg (14.9 mmol) of lithium. After 10 min, 2 mL of 100% ethanol was added, and after a further 15 min the solution became colorless, and the ammonia was allowed to evaporate. To the residue was added 50 mL of water, and the mixture was extracted with four 100-mL portions of ether. The extract was evaporated, and the residue was chromatographed on alumina. Elution with hexane gave 172 mg (86%) of 17: IR (CCl_4) 1200, 1165, 1135 cm^{-1} ; NMR (CDCl_3) δ 1.65 (3 H, s), 1.70-2.10 (2 H, m), 2.10-2.40 (4 H, m), 2.45-2.80 (8 H, two broad singlets of 4 H each), 3.52 (3 H, s), mass spectrum, m/z 216 (M^+).

Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{O}$: C, 83.33; H, 9.25. Found: C, 83.33; H, 9.36.

Methyl 3,5,9,11,13-Pentaoxotetradecanoate (18). A stream of ozone was passed through a solution of 216 mg (1.0 mmol) of 17 in 150 mL of methylene chloride at -78°C until a light blue coloration persisted. Nitrogen was then passed through the solution for 1 h to remove excess ozone, and the solution of ozonide was reduced with hydrogen over 30 mg of 10% palladium-on-charcoal at room temperature for 3 h. The solution was filtered, and the solvent was evaporated to leave 131 mg (42%) of 18 as a light yellow oil: IR (neat) 3500 (broad), 1730 cm^{-1} ; NMR (CDCl_3) complex with singlets at δ 3.67 and 3.80 (1:3); UV (ethanol) λ_{max} 298 and 358 nm (shoulder); mass spectrum, m/z 312.120 (calcd for $\text{C}_{15}\text{H}_{20}\text{O}_7$, 312.121).

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Registry No. 4, 6971-52-4; 5, 2207-57-0; 6, 95274-99-0; 7, 95275-00-6; 8, 95275-02-8; 9, 95275-03-9; 10, 95275-01-7; 12, 95275-05-1; 13, 20968-70-1; 14, 95275-06-2; 15, 95275-07-3; 16, 95275-08-4; 17, 95275-09-5; 17 (ozonide), 95275-11-9; 18, 95275-10-8; 1,2-bis((dimethylamino)methyl)cyclopentane, 95275-04-0; 2,6-dihydroxytoluene, 608-25-3; 2,3-dimethylbutadiene, 513-81-5.

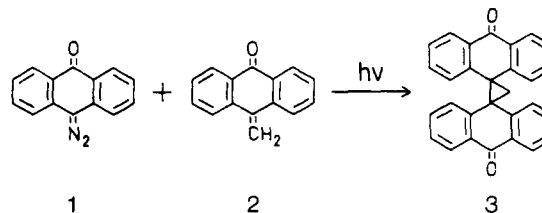
Formation of 6(2H)-Aceanthrylenones and Their Photochemical Conversion into Aceanthrylenes

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The photochemical decomposition of 10-diazoanthrone (1) in the presence of methyleneanthrone (2) gives the spiro-substituted anthrone 3, which, in refluxing solvents



under nitrogen, had been found to be converted into the aceanthrylenone derivative 4.¹ The apparently facile formation of 4 from 3 is intriguing insofar as it seems to involve the spontaneous loss of two hydrogen atoms. In conjunction with the present study dealing with the previously unnoticed photosensitivity of 4, we have also investigated its formation from 3.

Freshly prepared solutions of spirocyclopropane anthrone 3 in benzene or methylene chloride under nitrogen assume a transient red color which originates from a broad absorption around 500 nm. These red solutions give rise to a multiline ESR spectrum which may be attributable to biradical 5 (cf. Figure 1). Chemical evidence for the actual presence of 5 was obtained by trapping with molecular oxygen which gave peroxide 6 in 79% yield.²

The electron spectral changes associated with the disappearance of absorption around 500 nm under nitrogen are probably explicable by a homolytic rearrangement of 3 resulting in the formation of the hydroxy-substituted aceanthrene 7, which is reversibly converted into its keto tautomer 8. Treatment of the reaction mixture with acetic anhydride/pyridine affords the acetate 9 whose electronic absorption spectrum (see Experimental Section) supports the suggested formation of 7.

Upon exposure to oxygen, 7/8 in methylene chloride solution is converted into the hydroperoxide 10, which gives the 6(2H)-aceanthrylenone 4 by treatment with trifluoroacetic acid.³ More conveniently, however, 4 can be obtained by stirring a suspension of 3 in benzene under argon in the presence of a hydrogen acceptor such as DDQ or silver oxide (see Scheme I). Consequently, the previously^{1a} noted conversion of 3 into 4 under nitrogen is presumably due to the inadvertent presence of some oxidant.

Oxidation product 4 forms colorless crystals (mp $321-322^{\circ}\text{C}$ (lit.^{1a} mp $303-304^{\circ}\text{C}$) and exhibits a UV absorption in solution around 360 nm which we find to be characteristic of the 6(2H)-aceanthrylenone chromophore (see Experimental Section). The compound attracted our at-

(1) (a) Nakazawa, S.; Hirakawa, K.; Fujimori, S.; Iwazaki, K. *J. Chem. Soc., Perkin Trans. 1* 1979, 2052. (b) More recently, structure 3 has been assigned tentatively, and probably erroneously, to a compound that has a melting point of 240°C and is stable in solution: Zitzmann Suits, J.; Applequist, D. E.; Swart, D. J. *J. Org. Chem.* 1983, 48, 5120.

(2) Analogous peroxides have been obtained in the autoxidation of bis(phenols) (Colgate, S. M.; Hewgill, F. R. *Aust. J. Chem.* 1980, 33, 351). We are indebted to Dr. F. R. Hewgill of the University of Western Australia for recording the ESR spectrum shown in Figure 1.

(3) For an analogous reaction of TFA with an anthronyl hydroperoxide, see: Becker, H.-D.; Sanchez, D. *J. Org. Chem.* 1979, 44, 1787.

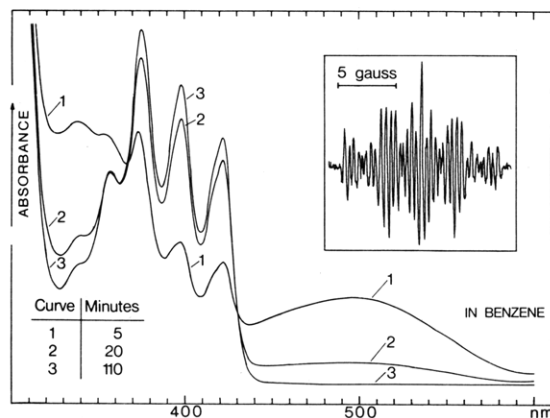
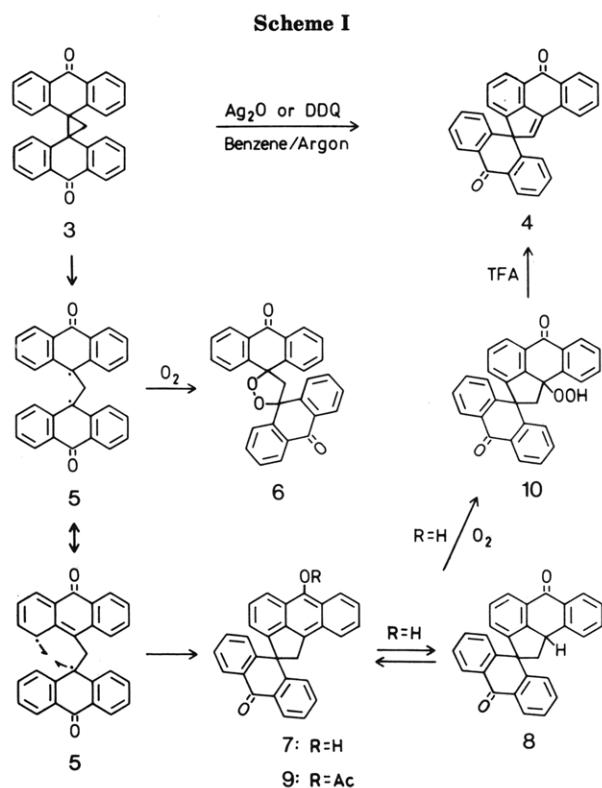


Figure 1. Electron spectral changes and ESR spectrum (insert) associated with the spontaneous isomerization of 3.



tion because of its photosensitivity: adsorbed on silica gel coated TLC plates, nonfluorescent 4 is readily converted into a fluorescent product upon exposure to daylight. When a solution of 4 (50 mg) in methylene chloride (75 mL) under nitrogen is irradiated through Pyrex (125-W high-pressure mercury lamp), the solution first turns red within 1 min, and after 5 min the solution has turned yellow (see Figure 2). Subsequent treatment of the irradiated, air-sensitive solution with acetic anhydride/pyridine regenerates the red color, and conventional workup then affords in 82% yield a dark-red crystalline compound for which UV/vis, IR, ^1H NMR, and high-resolution mass spectroscopic data are in agreement with the aceanthrylene derivative 11. The red color of 11 is characteristic of the

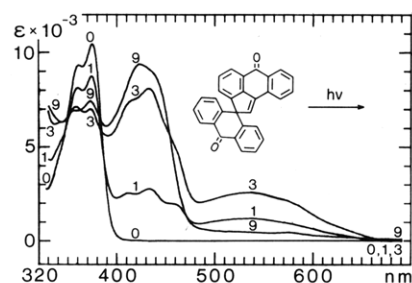
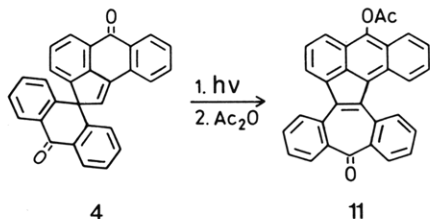
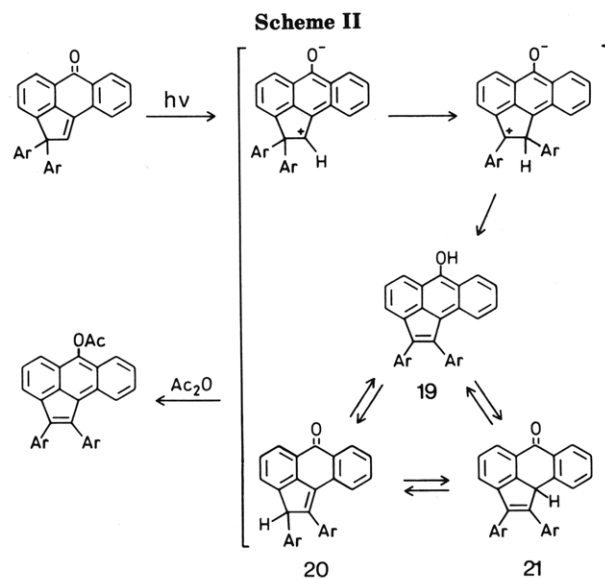
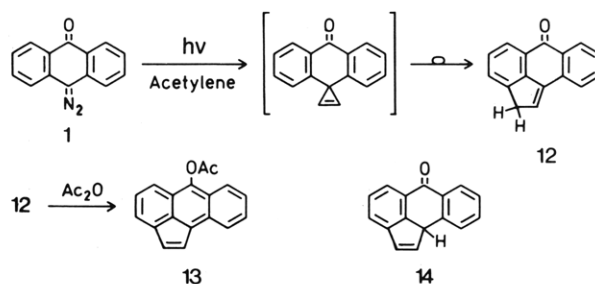


Figure 2. Electronic absorption spectrum of 4 (1.7×10^{-3} M in methylene chloride (curve 0), and the spectral changes observed after 1, 3, and 9 min of irradiation through Pyrex under nitrogen (cf. Experimental Section).

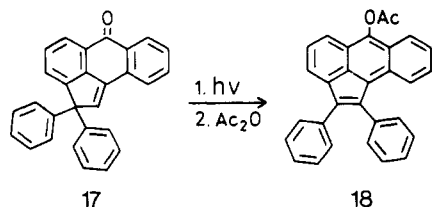
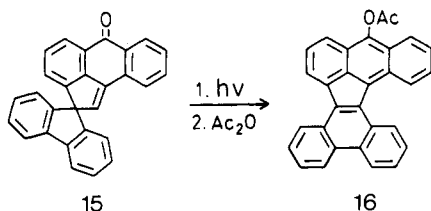


aceanthrylene chromophore, as is apparent from a comparison of its electronic absorption spectrum with that of the parent aceanthrylene⁴ and its 6-acetoxy derivative 13.



The synthesis of 13 for that purpose involved the preparation of the heretofore unknown 6(2*H*)-aceanthrylenone 12 which was obtained by photochemical decomposition of 10-diazoanthrone (1) in the presence of acetylene. The electronic absorption spectrum of 12 reveals the 6(2*H*)-aceanthrylenone chromophore, and its ^1H NMR spectrum clearly rules out the conceivable isomer structure 14.

We have found that the photochemical isomerization of 4 by 1,2-aryl migration is not uniquely associated with its spiro-anthranyl substitution, but other 2,2-diaryl 6(2*H*)-aceanthrylenones isomerize in similar fashion. Thus, the spiro-fluorenyl-substituted aceanthrylenone 15 and 2,2-diphenyl-6(2*H*)-aceanthrylenone (17) in methylene chloride solution also rearrange photochemically, and in situ acetylation of the photoproducts affords the aceanthrylene



derivatives 16 and 18 in 59% and 92% yield, respectively. Whether the aryl migration proceeds by an ionic mechanism as outlined in Scheme II or involves radical intermediates has not been investigated. Nor do we have structural proof for the conceivable oxygen-sensitive photoproducts in solution, i.e., the formally interconvertible hydroxy-substituted aceanthrylene 19, the 6(2*H*)-aceanthrylenone 20, and its isomer 21. The absorption spectral changes associated with the isomerization of 4 suggest the primary formation of the 6-hydroxyaceanthrylene chromophore and its subsequent light-induced ketonization. In the case of the photochemical isomerization of 17, however, there are hardly any color changes noticeable during the irradiation, indicating the primary formation of the 6-hydroxyaceanthrylene chromophore to be of minor importance.

Experimental Section

Melting points were determined on a hot-stage microscope and are uncorrected. Infrared spectra, in KBr pellets, were recorded on a Perkin-Elmer 197 Infrared Spectrophotometer. ¹H NMR spectra were recorded on a Bruker 270 instrument using CDCl₃ as solvent, and chemical shifts are given in parts per million downfield from Me₄Si. Electronic absorption spectra were taken on a Varian Cary 210 spectrophotometer. High-resolution mass spectra were obtained on an AEI MS 902 instrument. The ESR spectrum was recorded at room temperature in xylene under argon with a Varian V4500 instrument. Elemental analyses were performed by NOVO Microanalytical Laboratory, Bagsvaerd, Denmark.

Photochemical Reactions. Irradiations were carried out in a water-cooled Pyrex immersion well apparatus at about 12 °C, using a Philips HPK 125-W high-pressure mercury lamp. Photochemical isomerizations were performed under nitrogen or argon.

Chromatography. Chromatographic isolation of products always involved flash chromatography⁵ on silica gel with methylene chloride as eluant.

Starting Materials. 10-Diazoanthrone (1),⁶ 10-methyleneanthrone (2),⁷ and spiro[aceanthrylene-2(6*H*),9'-(9*H*)]fluorene-6-one (15)⁸ were prepared according to the literature. 2',2'-Diphenylspiro[anthracene-9(10*H*),1'-cyclopropan]-10-one was prepared as follows: A solution of 1 (0.55 g, 2.5 mmol) and 1,1-diphenylethene (0.51 g, 2.8 mmol) in benzene (75 mL) under nitrogen was irradiated for 15 min. The color of the solution changed from red-

brown to yellow. Vacuum evaporation of the solvent gave a residue from which the main product was isolated by chromatography (*R_f* 0.44); yield 0.73 g (78%) of colorless crystals (from methylene chloride/ethanol); mp 201–203 °C (depending on the rate of heating; lit. mp 206⁹ and 256–258 °C¹⁰); IR 1660 cm⁻¹ (CO); ¹H NMR δ 8.32 (“d”, 2 H, *J* = 8 Hz), 7.24 (“t”, 2 H, *J* = 7 Hz), 7.12–6.91 (m, 12 H), 6.57 (d, 2 H, *J* = 8 Hz), 3.00 (s, 2 H).

Dispiro[anthracene-9(10*H*),1'-cyclopropane-2',9''-(10'*H*)-anthracene]-10',10''-dione (3). A solution of 1 (180 mg, 0.82 mmol) and 2 (170 mg, 0.82 mmol) in benzene (75 mL) under nitrogen was irradiated for 10 min to give 3 as a yellow precipitate which was filtered off and washed with benzene: yield 148 mg (45%), mp 140 °C dec (lit.^{1a} mp 139–140 °C dec). Additional product 3 which had deposited on the walls of the irradiation apparatus and was difficult to remove mechanically, was dissolved in methylene chloride (70 mL) and converted into peroxide 6, which was isolated in 28% yield.

Spiro[aceanthrylene-2(6*H*),9'(10'*H*)-anthracene]-6,10'-dione (4). (A) **By Treatment of Hydroperoxide 10 with TFA.** Addition of TFA (1 mL) to a suspension of 10 (150 mg, 0.35 mmol) in chloroform (10 mL) gave a solution which, after 30 min, was concentrated (to 2 mL) and diluted with ethanol (10 mL) to give a precipitate of crude 4 (yield 115 mg, 83%). It was recrystallized from methylene chloride/methanol to give colorless crystals: mp 320–321 °C (lit.^{1a} 303–304 °C); IR 1645 cm⁻¹; ¹H NMR δ 8.57 (“d”, 1 H, *J* = 8 Hz), 8.45 (“d”, 2 H, *J* = 8 Hz), 8.17 (“d”, 1 H, *J* = 8 Hz), 7.97 (“d”, 1 H, *J* = 7 Hz), 7.74–7.63 (m, 2 H), 7.49–7.32 (m, 5 H), 7.17 (s, 1 H), 7.16 (“d”, 1 H, *J* = 8 Hz), 6.87 (“d”, 2 H, *J* = 8 Hz); UV (CH₂Cl₂) λ_{max} 260 nm (ε × 10⁻³, 26.8) sh, 270 (29.7), 300 (16.4) sh, 360 (9.4), 374 (10.5); high-resolution mass spectrum, *m/z* calcd for C₂₉H₁₆O₂ 396.1150, found 396.1145 (M⁺).

(B) **From 3 by Oxidation with DDQ.** DDQ (62 mg, 0.27 mmol) was added to a stirred suspension of 3 (100 mg, 0.25 mmol) in benzene (10 mL) under argon. After 6 h, precipitated DDQH₂ was removed by filtration. Vacuum evaporation of solvent from the filtrate gave 68 mg (68%) of colorless crystals (after chromatography and recrystallization from methylene chloride/ethanol), which were identical with 4 obtained according to A.

(C) **From 3 by Oxidation with Silver Oxide.** A suspension of 3 (170 mg, 0.43 mmol) and Ag₂O (0.7 g, 3 mmol) in benzene (200 mL) under argon was stirred vigorously for 2 h. Filtration through Celite, followed by vacuum evaporation of solvent from the filtrate gave a residue which was chromatographed. Recrystallization of the main fraction from methylene chloride/ethanol gave 133 mg (78%) of colorless crystals, identical with 4 obtained according to A.

4',5'-Dioxadispiro[anthracene-9(10*H*),1'-cyclopentane-3',9''-(10'*H*)-anthracene]-10',10''-dione (6). Addition of 3 (200 mg, 0.5 mmol) to methylene chloride (200 mL) under oxygen at 0 °C gave a yellow solution which decolorized within 20 min. After 1 h, the solution was concentrated to a volume of 10 mL and diluted with diethyl ether (15 mL) to give 171 mg (79%) of colorless crystals: mp >190 °C dec; IR 1670 cm⁻¹ (CO); ¹H NMR δ 8.21 (“d”, 4 H, *J* = 8 Hz), 8.12 (“d”, 4 H, *J* = 8 Hz), 7.66 (“t”, 4 H, *J* = 8 Hz), 7.47 (“t”, 4 H, *J* = 8 Hz), 3.42 (s, 2 H); UV (CH₂Cl₂) λ_{max} 277 nm (ε × 10⁻³, 25.4), 350 (0.6) sh. Anal. Calcd for C₂₉H₁₆O₄: C, 80.92; H, 4.21. Found: C, 80.57; H, 4.14.

6-AcetoxySpiro[aceanthrylene-2(1*H*),9'(10'*H*)-anthracene]-10'-one (9). A solution of 3 (100 mg, 0.25 mmol) in methylene chloride (100 mL) under a stream of nitrogen was prepared and kept at 0 °C for 5 min. When the temperature was raised to 25 °C the yellow solution gradually became red and eventually yellow again with 3 h. Addition of acetic anhydride (5 mL) and pyridine (10 drops) under nitrogen, followed by vacuum evaporation of solvents gave a solid residue from which 9 was isolated by chromatography. Recrystallization from methylene chloride/ethanol gave 70 mg (63%) of yellow crystals: mp 260–290 °C dec (lit.^{1a} 288–289 °C); IR 1775 cm⁻¹ (OAc), 1665 (CO); ¹H NMR δ 8.42 (“d”, 2 H, *J* = 8 Hz), 8.13 (d, 1 H, *J* = 9 Hz), 7.92 (d, 1 H, *J* = 8 Hz), 7.76 (d, 1 H, *J* = 9 Hz), 7.64–7.33 (m, 7 H), 6.84 (“d”, 2 H, *J* = 8 Hz), 6.76 (d, 1 H, *J* = 7 Hz), 4.40 (s, 2 H), 2.69 (s, OAc); UV (cyclohexane) λ_{max} 254 nm (ε × 10⁻³, 91) sh, 262

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(132), 291 (6.8), 304 (5.9), 330 (1.9)sh, 345 (3.9), 362 (7.5), 382 (11.6), 398 (6.7) sh, 404 (10.5).

1,10b-Dihydro-10b-hydroperoxy Spiro[aceanthrylene-2-(6H),9'(10'H)-anthracene]-6,10'-dione (10). A solution of 3 (200 mg, 0.5 mmol) in methylene chloride (200 mL) was prepared at 0 °C under nitrogen and was kept under nitrogen at 25 °C for 3 h. The yellow solution gradually became red and subsequently yellow again. Oxygen was then bubbled through the solution for 2 h to give a colorless crystalline precipitate when part of the solvent was evaporated in vacuo. The crystals were filtered off and washed with methylene chloride: yield 120 mg (56%); mp >200 °C dec; IR 3160 cm⁻¹ (OOH), 1675 and 1645 (CO); ¹H NMR δ 8.40–8.29 (m, 3 H), 8.13 ("d", 1 H, *J* = 8 Hz), 7.65 (d, 1 H, *J* = 8 Hz), 7.60–7.35 (m, 8 H), 7.20 ("d", 1 H, *J* = 8 Hz), 6.58 ("d", 1 H, *J* = 7 Hz), 3.37 and 3.14 (AB system, *J* = 15 Hz), the hydroperoxy H was not discernible; UV (CH₂Cl₂) λ_{max} 275 nm (ε × 10⁻³, 25.3), 357 (0.5), 374 (0.5) sh. Anal. Calcd for C₂₈H₁₈O₄: C, 80.92; H, 4.21. Found: C, 80.29; H, 4.12.

8-Acetoxy-17H-3,4:6,7-dibenzocyclohept[1,2-a]aceanthrylen-17-one (11). A solution of 4 (50 mg, 0.13 mmol) in methylene chloride (75 mL) under argon was irradiated for 4–5 min. Addition of acetic anhydride (5 mL) and pyridine (5 drops) under argon followed by vacuum evaporation of solvents after 50 min gave a red residue from which 45 mg (82%) of dark-red crystals were isolated by chromatography: mp 278–286 °C dec (recrystallized from methylene chloride/ethanol); IR 1765 cm⁻¹ (OAc), 1665 (CO); ¹H NMR δ 8.16–8.05 (m, 4 H), 7.97 (d, 1 H, *J* = 8 Hz), 7.96–7.78 (m, 3 H), 7.71–7.36 (m, 7 H), 2.66 (s, OAc); UV (cyclohexane) λ_{max} 241 nm (ε × 10⁻³, 58.4), 256 (53.7), 266 (53.6), 300 (18.4)sh, 342 (5.8), 361 (7.9), 378 (10.2), 405 (7.0), 428 (9.6), 453 (8.1), 499 (2.7); high-resolution mass spectrum, *m/z* calcd for C₃₁H₁₈O₃ 438.1257, found 438.1317 (M⁺).

6(2H)-Aceanthrylenone (12). A solution of 1 (0.44 g, 2 mmol) in benzene (250 mL) was irradiated while acetylene was passed through the solution. The irradiation was terminated after 15 min when the color of the solution had changed from red-brown to yellow. The solvent was removed by vacuum evaporation to give a crude product, which showed three spots on TLC (SiO₂/CH₂Cl₂). The main product 12 (*R_f* 0.33) was isolated by chromatography and subsequent crystallization from methylene chloride/ethanol: yield 147 mg (34%) of colorless crystals; mp 180 °C dec (red melt; repeated chromatography and recrystallization from methylene chloride/*n*-hexane did not change the melting point); ¹H NMR δ 8.48 ("d", 1 H, *J* = 8 Hz), 8.15 (d, 1 H, *J* = 8 Hz), 8.02 (d, H, *J* = 8 Hz), 7.75 (d, 1 H, *J* = 7 Hz), 7.67 ("t", 1 H, *J* = 7 Hz), 7.56 ("t", 1 H, *J* = 8 Hz), 7.50 (t, 1 H, *J* = 8 Hz), 7.31 (t, 1 H, *J* = 2 Hz), 3.81 (d, 2 H, *J* = 2 Hz, irradiation at 3.81 leads to a singlet at 7.31); IR 1650 cm⁻¹ (CO); UV (CH₂Cl₂) λ_{max} 254 nm (ε × 10⁻³, 7.4), 285 (15.7), 349 (6.5), 364 (7.4); high-resolution mass spectrum, *m/z* calcd for C₁₆H₁₀O 218.0732, found 218.0726 (M⁺).

6-Aceanthrylenol Acetate (13). A solution of 12 (50 mg, 0.23 mmol), acetyl chloride (0.18 g, 2.3 mmol), and pyridine (0.1 g, 1.26 mmol) in methylene chloride (10 mL) was stirred under argon at room temperature for 3 days. The dark-red solution was diluted with methylene chloride, then washed with water, and dried over MgSO₄. Vacuum evaporation of solvents gave a red residue from which 13 was isolated by chromatography (*R_f* 0.60): yield 17 mg (28%) of red crystals from methylene chloride/ethanol; mp >130 °C dec; IR 1770 cm⁻¹ (OAc); ¹H NMR δ 8.23 ("d", 1 H, *J* = 9 Hz), 8.01 ("d", 1 H, *J* = 8 Hz), 7.87 (d, 1 H, *J* = 9 Hz), 7.75 (d, 1 H, *J* = 7 Hz), 7.62–7.42 (m, 4 H), 7.08 (d, 1 H, *J* = 5 Hz, a singlet is discernible at 7.52 (1 H) on irradiation at 7.08), 2.62 (s, OAc); UV (cyclohexane) λ_{max} 240 nm (ε × 10⁻³, 37.9), 256 (52.3), 348 (3.8), 365 (6.8), 383 (4.4), 402 (5.2), 418 (3.7), 425 (3.9); high-resolution mass spectrum, *m/z* calcd for C₁₈H₁₂O₂ 260.0837, found 260.0891 (M⁺).

Phenanthro[9,10-a]aceanthrylen-8-ol Acetate (16). Spiro[aceanthrylene-2(6H),9'-[9H]fluorene]-6-one (15) (50 mg, 0.14 mmol) in methylene chloride (75 mL) under argon was irradiated for 4 min. Addition of acetic anhydride (5 mL) and pyridine (5 drops) under argon followed by vacuum evaporation of solvent after 30 min gave a mixture of unchanged starting material and the acetylated photoproduct 16, which was isolated by chromatography. Yield 33 mg (59%) of brown crystals from methylene chloride/ethanol: mp dec >237 °C; IR 1760 cm⁻¹ (OAc); ¹H NMR

δ 8.81–8.67 (m, 5 H), 8.50 (d, 1 H, *J* = 7 Hz), 8.07 ("d", 1 H, *J* = 9 Hz), 7.91 ("d", 1 H, *J* = 9 Hz), 7.72–7.46 (m, 7), 2.65 (s, OAc); UV (cyclohexane) λ_{max} 259 nm (ε × 10⁻³, 97.9), 322 (14.3), 336 (14.8), 361 (6.7), 380 (8.6), 392 (5.8), 411 (7.1), 434 (12.3), 461 (12.6), 518 (3.0); high-resolution mass spectrum, *m/z* calcd for C₃₀H₁₈O₂ 410.1306, found 410.1313 (M⁺).

2,2-Diphenyl-6(2H)-aceanthrylenone (17). 2',2'-Diphenylspiro[anthracene-9(10H)-1'-cyclopropan]-10-one (0.72 g, 1.9 mmol; cf. Starting Materials paragraph) under argon was dissolved in refluxing xylene (50 mL) to give a colorless solution. Refluxing was continued for 3 h, as the color of the solution eventually became light-yellow. The solvent was removed by vacuum distillation, and the residue was dissolved in benzene (50 mL) under argon. Silver oxide (2 g) was suspended in the solution and the suspension was stirred vigorously for 16 h under argon. Workup by filtration through Celite, followed by vacuum evaporation of solvent, gave a residue from which 17 was isolated by chromatography (*R_f* 0.37): yield 0.51 g (71%) of colorless crystals which, according to ¹H NMR analysis, contained a trace of an impurity believed to be 1,10b-dihydro-2,2-diphenyl-6(2H)-aceanthrylenone. An analytically pure sample was prepared as follows. A solution of impure 17 (200 mg) in acetic anhydride (5 mL) and pyridine (5 drops) under argon was refluxed for 5 min. Vacuum evaporation of solvents gave a residue from which 170 mg (85%) of colorless crystals were isolated by chromatography and subsequent crystallization from methylene chloride/ethanol: mp 204–206 °C (depending on the intensity of the the inspection light of the hot-stage microscope; lit.⁸ yellow micro crystals, mp 224–225 °C); IR 1660 cm⁻¹ (CO); ¹H NMR δ 8.48 ("d", 1 H, *J* = 8 Hz), 8.14 ("d", 1 H, *J* = 8 Hz), 8.02 ("d", 1 H, *J* = 8 Hz), 7.73–7.47 (m, 5 H; a singlet is discernible at 7.50, 1 H), 7.34–7.24 (m, 10 H); UV (CH₂Cl₂) λ_{max} 284 nm (ε × 10⁻³, 14.6), 296 (14.0), 308 (11.1) sh, 360 (8.0) sh, 372 (9.0); high-resolution mass spectrum, *m/z* calcd for C₂₈H₁₈O 370.1358, found 370.1363 (M⁺).

1,2-Diphenyl-6-aceanthrylenol Acetate (18). A solution of 17 (50 mg, 0.14 mmol) in methylene chloride (75 mL) was irradiated for 5 min. Addition of acetic anhydride (5 mL) and pyridine (5 drops) under argon followed by vacuum evaporation of solvents after 30 min gave a red residue from which 51 mg (92%) of dark-red crystals were isolated by chromatography; mp 210–214 °C (recrystallized from methylene chloride/ethanol); IR 1765 cm⁻¹; ¹H NMR δ 8.01 ("d", 1 H, *J* = 8 Hz), 7.93 ("d", 1 H, *J* = 9 Hz), 7.80 ("d", 1 H, *J* = 7 Hz), 7.73 ("d", 1 H, *J* = 9 Hz), 7.64–7.58 (m, 1 H), 7.52–7.21 (m, 12 H), 2.64 (s, OAc); UV (cyclohexane) λ_{max} 238 nm (ε × 10⁻³, 37.2), 261 (66.9), 357 (5.3), 374 (7.8), 396 (6.2), 414 (7.7), 436 (5.9), 498 (2.6); high-resolution mass spectrum, *m/z* calcd for C₃₀H₂₀O₂ 412.1464, found 412.1457 (M⁺).

Lanthanide Tetrakis(β-diketonates) as Effective NMR Shift Reagents for Organic Salts

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Introduction

Lanthanide-induced shifts have been reported for organic salts in the presence of lanthanide tris(β-diketonates).¹⁻⁵ Substrates include ammonium,¹⁻⁵ phosphonium,⁵ sulfonium,⁵ and oxonium⁴ cations. This is a rather unexpected occurrence, and the most likely explanation is that the anion of the organic salt complexes with the lanthanide tris chelate. An ion pair then forms between the organic cation and the anionic lanthanide

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