

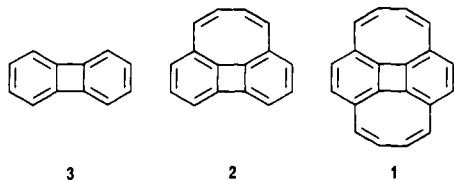
Dicyclooctabiphenylene. Synthesis and Properties¹

Charles F. Wilcox, Jr.,* and Erik N. Farley

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14853.
Received March 12, 1984. Revised Manuscript Received July 5, 1984

Abstract: The synthesis and properties of the "antiaromatic" hydrocarbon dicycloocta[1,2,3,4-def:1',2',3',4'-jkl]biphenylene (**1**) are described. The observed electronic and ¹H NMR spectra of **1** agree well with previous predictions. The series of polycycles consisting of biphenylene (**3**), cycloocta[def]biphenylene (**2**), and dicycloocta[def:ijkl]biphenylene (**1**) is examined in terms of resonance energy and qualitative aromaticity models.

Of the multitude of known polycyclic π hydrocarbons, relatively few contain multiple [4*n*]-membered rings, even though the two-dimensional polyfusion of [4]- and [8]- π rings is geometrically feasible. Although the theoretical reasons for the scarcity of [4*n*]-fused polycycles are well-known, it would be highly desirable to have a broader range of these elusive systems for experimental study. We have thus been led to prepare² a series of unusual polycyclic hydrocarbons related to biphenylene (**3**).³ Molecules in this series exhibit a striking range of physical properties. In the present work, we report more fully the synthesis and properties of the coronoid hydrocarbon dicycloocta[def:ijkl]biphenylene (**1**)^{2e} and discuss the completed series of hydrocarbons **3**, **2**, and **1**.



Experimental Section

Calculations. The iterative Hückel calculations reported here use a variable β technique similar to that described earlier.^{2c,d,4a,b5} The iterative relationships used were:

$$\text{bond length/order: } R_{ij} = 1.504 - (0.167)P_{ij}$$

$$\beta/\text{bond length: } \beta_{n+1} = \beta_n \exp[3.80(1.393 - R_{ij})]$$

The McWeeny-Hückel ring current calculations⁶ assume regular polygonal ring areas with sides of unit benzenoid bond length and give values relative to benzene. Chemical shift calculations⁷ use an in-plane

segmented (Biot-Savart)⁸ geometric model calibrated to benzenoid⁹ and biphenylenoid² chemical shifts using the iterative McWeeny-Hückel ring currents.

General. ¹H NMR spectra were recorded on Varian EM-390 or Bruker WM-300 spectrometers with Me₄Si as an internal reference in the solvent indicated. UV-vis electronic spectra were taken with either a Cary 219 or a Cary 15 spectrophotometer. Melting points were determined with a MEL-TEMP and are uncorrected. Acetone, Me₂SO, and DMF were dried over 4-Å molecular sieves before use; THF was freshly distilled from sodium/benzophenone ketyl.

2,5-Dimethylisonitrosoacetanilide (5). A 36-L Pyrex kinetics bath, equipped with a mechanical stirrer and steam heated by copper immersion coils, was charged with 24 L of water and 6.81 kg of anhydrous Na₂SO₄, and then 432 g (2.61 mol) of chloral hydrate was added and stirred to dissolution. A mixture of 303 mL (2.43 mol) of 2,5-dimethylaniline (**4**), 210 mL of concentrated HCl, and 1200 mL of water was then added. A solution of 528 g (7.60 mol) of hydroxylamine hydrochloride in 1.5 L of water was added next, and the resulting chalky mixture was stirred and heated for 1.5 h to give brownish flakes of product. The mixture was cooled to ambient temperature and the supernatant removed by siphoning. Suction filtration of the remaining solids gave **5** as tan flakes, which were air dried until slightly moist and used directly in the following step.

3,6-Dimethylisatin (6). A mixture of 975 mL of 96% sulfuric acid and 200 mL of water in a 4-L Erlenmeyer flask was stirred magnetically in an ice bath. A thermometer was suspended in the solution, and the crude isonitrosoacetanilide **5** was added so that the temperature remained at 45–60 °C as the solids dissolved slowly to give a deep purple solution. When all of compound **5** had been added, the temperature was raised to 80 °C by a hot plate, causing the mixture to become thick and reddish-orange. The mixture was heated for 1 h and then cooled slightly and poured into 7 L of crushed ice. The resulting orange precipitate of isatin **6** was suction filtered, dried to a moist red-orange solid, and used directly in the next step.

3,6-Dimethylanthranilic Acid (7). A 4-L Erlenmeyer flask equipped with a magnetic stirrer was charged with 450 g of NaOH and 2 L of water. A thermometer was suspended in the flask, and all of the isatin **6** was added at about 70 °C to give a purple-black solution. Hydrogen peroxide (30%) was then added by pipet, keeping the reaction temperature below 100 °C. The addition was discontinued when acidified reaction samples showed no orange precipitate of isatin on a spotting plate (~150 mL of H₂O₂ added). The brownish reaction mixture was then carefully acidified with concentrated HCl. After the ensuing evolution of CO₂ (pH ~7) had subsided, the dark insoluble impurities congealed as a hard tar and were removed manually. Further acidification gave a slight precipitate (pH ~5) which redissolved and was replaced by a much thicker precipitate of the anthranilic acid **7** (pH ~4). The volume of precipitate was maximized by pH adjustment, and the mixture was cooled on ice with stirring. Suction filtration and air drying gave **7** as a slightly yellow-orange powder, 183.5 g (46% overall yield from **4**) after

(1) Taken in part from: Farley, E. N. Ph.D. Thesis, Cornell University, Ithaca, NY, 1984.

(2) (a) Wilcox, C. F., Jr.; Uetrecht, J. P.; Grohman, K. K. *J. Am. Chem. Soc.* **1972**, *94*, 2532. (b) Wilcox, C. F., Jr.; Uetrecht, J. P.; Grantham, G. D.; Grohmann, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 1914–1920. (c) Wilcox, C. F., Jr.; Grantham, G. D. *Tetrahedron* **1975**, *31*, 2889–2895. (d) Obendorf, S. K.; Wilcox, C. F., Jr.; Grantham, G. D.; Hughes, R. E. *Tetrahedron* **1976**, *32*, 1327–1330. (e) Wilcox, C. F. Jr.; Farley, E. N. *J. Am. Chem. Soc.* **1983**, *105*, 7191–7192. (f) Wilcox, C. F., Jr.; Farley, E. N. *J. Org. Chem.*, in press.

(3) The chemistry of biphenylene and related compounds has been reviewed: (a) Cava, M. P.; Mitchell, M. J. "Cyclobutadiene and Related Compounds"; Academic Press: New York and London, 1967; Chapter 10, pp 255–316. (b) Barton, J. W. In "Nonbenzenoid Aromatics"; Snyder, J. P., Ed.; Academic Press: New York and London, 1969; Vol. 1, Chapter 2, pp 32–62.

(4) (a) Coulson, C. A.; Mallion, R. B. *J. Am. Chem. Soc.* **1976**, *98*, 592–598. (b) Gomes, J. A. N. F.; Mallion, R. B. *J. Org. Chem.* **1981**, *46*, 719–727. (c) Mallion, R. B. *Pure Appl. Chem.* **1980**, *52*, 1541–1548. (d) Haigh, C. W.; Mallion, R. B. *Prog. Nucl. Magn. Reson. Spectrosc.* **1980**, *13*, 303–344.

(5) (a) Figeys, H. P. *Tetrahedron Lett.* **1966**, 4625–4630. (b) Figeys, H. P. *Chem. Commun.* **1967**, 495–496. (c) Figeys, H. P.; Defay, N.; Martin, R. H.; McOmie, J. F. W.; Ayres, B. E.; Chadwick, J. B. *Tetrahedron* **1976**, *32*, 2571–2578.

(6) McWeeny, R. *Mol. Phys.* **1958**, *1*, 311–321.

(7) Wilcox, C. F., Jr.; Rigos, A. A., manuscript in preparation. These calculations follow the strategy of Haigh, Mallion, and Armour^{7a} with the parametric scheme $\delta_{\text{pred}}(\text{CCl}_4) = 1.404(H'/H'_{\text{benzene}}) + 5.92$. See also ref 7b,c. (a) Haigh, C. W.; Mallion, R. B.; Armour, E. A. G. *Mol. Phys.* **1970**, *18*, 751–766. (b) Memory, J. D.; Wilson, N. K. "NMR of Aromatic Compounds"; Wiley: New York, 1982; Chapter 3, pp 40–68. (c) Mallion, R. B. *J. Chem. Phys.* **1981**, *75*, 793–797.

(8) (a) Mallion, R. B. *Mol. Phys.* **1973**, *25*, 1415–1432. (b) Haddon, R. C. *Tetrahedron* **1972**, *28*, 3613–3633, 3635–3655.

(9) Haigh, C. W.; Mallion, R. B. *Mol. Phys.* **1970**, *18*, 737–750.

drying in a vacuum over P_2O_5 . Crude **7** could be used in subsequent diazotization reactions with excellent results.

3,6-Dimethylbenzenediazonium 2-Carboxylate (8) and 1,4,5,8-Tetramethylbiphenylene (9). **Warning:** *Diazonium Carboxylates such as 8 are known to be explosive and should be handled only with the utmost care and proper safety equipment.* We have found this material to be more sensitive to thermal decomposition than other diazonium carboxylates; it will decompose readily when inadequate stirring or large-scale or excessively rapid diazotization produces too large a temperature rise. While, in our hands, the decomposition of the suspended diazonium carboxylate was gentle, there is significant potential for violent eruption of suspensions or detonation of the filtered solid. *We recommend that only experienced workers should undertake this large-scale preparation, and then only in full awareness of the danger.* Preparations on any scale should adhere to all precautions given here and elsewhere.¹⁰

A 2-L three-necked flask was equipped with a mechanical stirrer, an addition funnel, an immersion thermometer and an ice-salt bath. Dimethylantranilic acid **7**, 165.2 g (1.0 mol), and 1.25 L of dry THF were added and stirred for 0.5 h or until the solution temperature had minimized (< -10 °C). Beyond this point, safety shields were used for all manipulations. To the cold solution was added 25 mL (0.34 mol) of trifluoroacetic acid, and the mixture was again stirred to lower the temperature. The addition funnel was charged with 200 mL (1.42 mol) of isoamyl nitrite, which was then added slowly over 1.5 h, keeping the reaction temperature below -5 °C. The reaction mixture was stirred for an additional 1.5 h, during which time the red precipitate of diazonium carboxylate **8** appeared. The product was suction filtered on a large, well-secured Büchner funnel (**No Frits!**) with use of cold (-20 °C) THF streamed from a plastic squirt bottle as an aid in manipulation (**No Spatulas!**). During the suction filtration some gas evolved from the filtrate (**Danger!**). All glassware was placed in a bucket of water after use, and spills or splashes of **8** were neutralized with water. The collected product was washed with cold THF (<50 mL) until the filtrate clarified and then with cold (-20 °C) 1,2-dichloroethane (1,2-DCE) also dispensed from a squirt bottle. While being careful not to let the product dry out or warm up, the filter funnel was removed and carefully inverted in a beaker containing 100 mL of cold 1,2-DCE. More cold solvent was then squirted into the bottom of the funnel until the solids loosened and slid into the beaker. The funnel was rinsed, the filter paper removed with forceps, and the beaker of slurred product swirled cautiously in an ice bath to break up any clumps. (**Warning:** *The product must be kept cold at this point. Gas evolution from the solid indicates the need for immediate cooling!*) The product may be kept for up to 0.5 h without trouble if it is kept cold, but it is best used quickly; it should not be warmed or stored.

The slurry was carefully added, with the aid of a bent teaspoon and a squirt bottle of cold 1,2-DCE, to 17.5 L of stirred refluxing 1,2-DCE in a 36-L Pyrex bath. After the smooth but vigorous evolution of gas had ceased, the resulting red-black solution was allowed to cool and was then concentrated by distillation. Ethylene glycol was added to the residue and the mixture distilled through a short path. When no more needles of tetramethylbiphenylene (**9**) were seen to distill, the distillate was cooled on ice and suction filtered and the collected solid washed well with cold methanol and air dried. The pale yellow solid was dried in a vacuum desiccator to yield 14.38 g (13.8%) of **9**: mp 231–233 °C (lit.^{11a} mp 228.5–229.0 °C); ¹H NMR (300 MHz, CCl_4) δ 6.30 (4 H, s), 2.12 (12 H, s); ¹H NMR (300 MHz, $CDCl_3$) δ 6.43 (4 H, s), 2.14 (12 H, s); mass spectrum m/e 208.1249, calcd 208.1252 for $C_{16}H_{16}$.

1,4,5,8-Tetrakis(bromomethyl)biphenylene (10). A 3-L three-necked flask with a reflux condenser and a drying tube was charged with 13.54 g (0.065 mol) of tetramethylbiphenylene (**9**), 47.39 g (0.266 mol) of *N*-bromosuccinimide, and 2 L of CCl_4 (dried over $MgSO_4$). The mixture was heated to reflux, 10–20 mg of dibenzoyl peroxide was added, and a incandescent floodlight was shone on the mixture to initiate reaction. When the NBS had been replaced by buoyant succinimide, a distillation head was attached and the solvent was removed under an aspirator vacuum with heating. The residue was washed by trituration with 275 mL of acetone in small portions, leaving a greenish-yellow insoluble product which was dried under reduced pressure. The product **10** was collected as a greenish-yellow powder, 23.55 g (69.16%): mp 244–248 °C (with some decomposition); ¹H NMR (300 MHz, Me_2SO-d_6) δ 6.27 (4 H, s), 3.93 (8 H, s); mass spectrum m/e 518.7595, calcd 518.7596 for $C_{16}H_{11}^{79}Br_4$, and 527.7602, calcd 527.7596 for $C_{16}H_{12}^{81}Br_4$.

1,4,5,8-Tetrakis(triphenylphosphoniummethyl)biphenylene Tetrabromide (11). A 1-L three-necked flask, equipped with a mechanical stirrer and steam heating, was charged with 21.93 g (0.042 mol) of tetrabromide **10**, 110 g (0.42 mol) of PPH_3 , and 500 mL of DMF. After 4.5 days, heating was discontinued and the mixture cooled to room temperature. The yellow precipitated product was suction filtered, washed repeatedly with dry ether, air dried, and placed in a vacuum desiccator.

Phosphonium salt **11** was obtained as a yellow crystalline powder, 52.14 g (79.18%): mp >400 °C dec; ¹H NMR (300 MHz, Me_2SO-d_6) δ 7.21–7.29 (12 H, m), 6.94–7.09 (48 H, m), 5.22 (4 H, s), 3.92 (8 H, d, $J = 14.7$ Hz).

Glyoxal Monomer.¹² A 1-L round-bottomed flask was connected through a U-shaped glass adapter with a loosely filled sidearm drying tube (alumina) to a 250-mL round-bottomed flask. The 1-L flask was charged with 20 g each of P_2O_5 and glyoxal trimer dihydrate. The reactants were mixed well by shaking, and the receiver flask was immersed in a dry ice/isopropyl alcohol bath at -80 °C. The reactants were warmed gently with a heat gun and then heated more strongly at one edge of the powder to initiate the exothermic decomposition of the mixture. (**Safety Shield!**) Green gaseous glyoxal monomer condensed as light green needles in the receiver flask, which was then removed and evacuated at -80 °C until the pressure remained relatively constant (about 1 mmHg). The vacuum was broken and 150 mL of THF was added to the flask, which was then sealed with a septum and allowed to warm to ambient temperature. The solution could be stored for 2 or 3 months at 0 °C, but it gave the best results when recently prepared.

1,4,5,8-Tetravinylbiphenylene (13). A 500-mL three-necked flask, equipped with magnetic stirring, rubber septa, and a nitrogen inlet tube, was charged with 0.67 g (0.43 mmol) of tetraphosphonium salt **11** and 100 mL of Me_2SO . After being flushed with nitrogen with stirring, 4.5 mL of 0.45 M dimethyl potassium in Me_2SO was injected into the reaction mixture to give a black solution. The ylide solution was stirred for 1 h; meanwhile, a 500-mL round-bottomed flask containing 10 g of formaldehyde trimer was connected through a glass adapter and Tygon tubing to 15 cm of 7-mm-o.d. glass tubing. The flask was flushed with nitrogen, the end of the glass tube was introduced below the surface of the ylide solution, and the trimer was warmed with a heat gun to evolve formaldehyde gas. (**Safety Shield!**) The resulting bright yellow solution containing suspended formaldehyde polymers was poured into a separatory funnel with 50% saturated brine (100 mL) and CH_2Cl_2 (100 mL). The layers were separated, and the aqueous layers was washed with CH_2Cl_2 (2 × 75 mL). The combined organic layers were washed with water (4 × 150 mL) and brine (150 mL). The solution was dried over $MgSO_4$, filtered, and evaporated to give a yellow solid. The residue was chromatographed on silica gel (Davison, 60–200 mesh) with CCl_4 . A fast, yellow, UV-fluorescent band was collected as a single fraction and evaporated to yield feathery, bright-yellow crystals of tetravinylbiphenylene (**13**), 75.3 mg (69%): decomposed without melting; ¹H NMR (300 MHz, $CDCl_3$) δ 6.96 (4 H, s), 6.81–6.72 (4 H, d of d, $J_1 = 17.57$ Hz, $J_2 = 10.97$ Hz) centered 6.76, 5.69–5.62 (4 H, d of d, $J_1 = 17.56$ Hz, $J_3 = 0.94$ Hz) centered 5.65, 5.36–5.32 (4 H, d of d, $J_2 = 10.93$ Hz, $J_3 = 0.83$ Hz) centered 5.34; mass spectrum m/e 256.1241, calcd 256.1252 for $C_{20}H_{16}$.

Dicycloocta[1,2,3,4-def:1',2',3',4'-jkl]biphenylene (1). A 500-mL round-bottomed flask, equipped with magnetic stirring, was charged with 2.00 g (1.27 mmol) of tetraphosphonium salt **11** and 200 mL of Me_2SO . The flask was sealed with a rubber septum, flushed with argon, and stirred under argon for 1 h to dissolve the salt. Potassium *tert*-butoxide, 0.62 g (5.52 mmol), was added to the flask, turning the reaction mixture jet black with the appearance of some fine black suspension. A solution of glyoxal in THF (25 mL) was added slowly dropwise by syringe, decolorizing the reaction mixture with the formation of red polymers. More glyoxal solution (10 mL) was added, and the resulting solution was stirred for 0.5 h and then poured into a separatory funnel with water (500 mL) and CH_2Cl_2 (200 mL). The organic layer was drained, and the aqueous layer was extracted further with CH_2Cl_2 (2 × 150 mL). The combined organic layers were washed with water (4 × 500 mL) and brine (500 mL). The orange CH_2Cl_2 solution was drained, dried with $MgSO_4$, filtered, and evaporated under a vacuum to a small quantity of dark orange-brown oil which solidified momentarily. This solid was quickly treated with CS_2 (3 × 5 mL), grinding well with a spatula each time to extract the product. The resulting red-brown solution was chromatographed on silica gel (Woelm, 32–63 μm), eluting with CS_2 . The steel blue product band eluted first and was collected as a single fraction of 39 mL.

Solutions of **1** were stored in the dark at -30 °C and were kept dilute unless otherwise necessary. Solid **1** formed deep blue-black microcrystals which decomposed within seconds of solvent evaporation, but could be transferred to other solvents by rapid redissolution.

Proton NMR sometimes showed the product to contain a trace of 7,8-dimethylcycloocta[def]biphenylene (**14**), which followed directly behind **1** during chromatography. This hydrocarbon, occurring as an oil or a waxy red solid, could be separated from decomposed solutions of **1** by hexane chromatography on silica gel.

A 5-mL aliquot of solution was evaporated (with decomposition) and weighed, 0.5 mg. This extrapolated to give, for the reaction, 3.2 mg (1%) of **1** and 0.7 mg (1/4%) of **14**, based upon the relative NMR ratios.

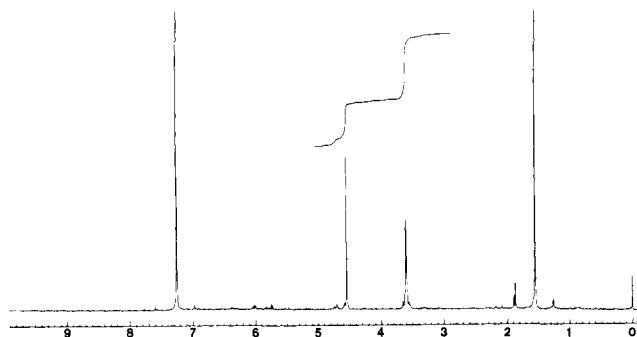


Figure 1. ^1H NMR spectrum of **1** in CDCl_3 (300 MHz). The peaks at δ 0.0, 1.5, and 7.3 are due to Me_4Si , H_2O , and CHCl_3 . The minor peaks at δ 1.9, 4.7, 5.8, and 6.0 are due to **14** and possibly some decomposition products.

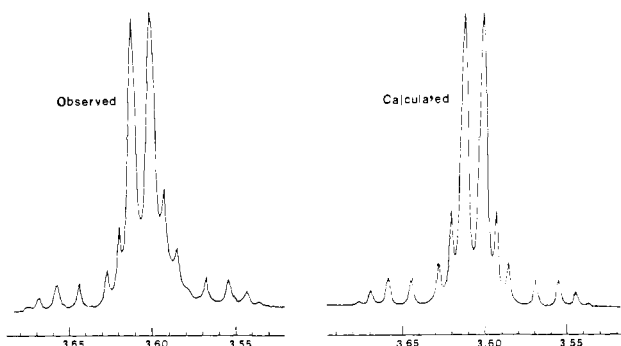
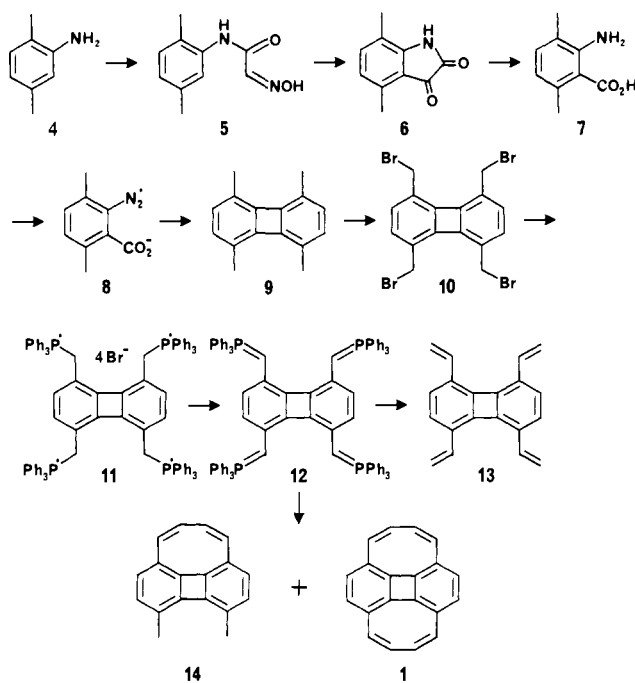


Figure 2. ^1H NMR spectra observed and calculated for the AA'BB' cycloocta spin system of **1**.

Scheme I



1: ^1H NMR (90 MHz, CS_2) δ 4.43 (4 H, s), 3.51 (8 H, m); ^1H NMR (300 MHz, CS_2) δ 4.41 (4 H, s), 3.40–3.55 (8 H, m) centered 3.48; ^1H NMR (300 MHz, CDCl_3) δ 4.55 (4 H, s), 3.54–3.68 (8 H, m), centered 3.61. The NMR spectrum of **1** in CDCl_3 is shown in Figure 1. LAOCOON III analysis¹³ of the AA'BB' cycloocta multiplet observed at δ 3.54–3.68 in the 300-MHz CDCl_3 spectrum gave $\delta_A = \delta_{A'} = 3.63$, $\delta_B = \delta_{B'} = 3.59$ and $J_{AB} = 13.83$ Hz, $J_{A'B'} = -0.58$ Hz, $J_{AA'} = 1.25$ Hz, $J_{BB'} = 10.07$ Hz (see Figure 2).

14: ^1H NMR (300 MHz, CDCl_3) δ 6.025–6.00 (2 H, d, $J = 8.283$ Hz) centered 6.0125, 5.75–5.73 (2 H, d, $J = 8.234$ Hz) centered 5.74, 4.51–4.77 (4 H, m, AA'BB') centered 4.64, 1.86 (6 H, s); mp 114–117 $^\circ\text{C}$; mass spectrum m/e 230.1105, calcd 230.1095 for $\text{C}_{18}\text{H}_{14}$.

Table I. Predicted Electronic Transitions for Polycycles^a

system	symmetry	transition (%)	E , eV	λ , nm	$\log \epsilon$
3	D_{2h}	6–7 (97) B_{1g}	3.24	382.7	forbidden
		6–8 (71) B_{3u}	3.72	333.3	3.63
2	C_{2v}	8–9 (99) B_1	2.37	523.2	0.79
		8–10 (80) B_1	2.97	417.5	1.62
1	D_{2h}	10–11 (95) B_{1g}	2.05	604.9	forbidden
		9–11 (93) B_{3u}	2.30	539.1	2.34

^aReference 19.

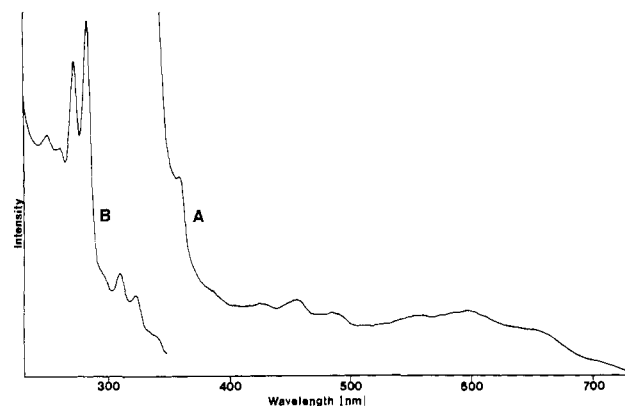


Figure 3. UV-vis spectrum of **1** in cyclohexane: spectrum A, 3.3×10^{-4} M; spectrum B, 3.3×10^{-5} M. Absorptivities of individual peaks are recorded in Table II.

Results

Hydrocarbon **1** was prepared by a "double" bis-Wittig¹⁴ synthetic approach similar to that used earlier² (Scheme I). Beginning with a large-scale modification of Gronowitz and Hansen's Sandmeyer-isatin synthesis,¹⁵ 3,6-dimethylantranilic acid (**7**) was prepared from commercial 2,5-dimethylaniline (**4**) in three steps and 46% overall yield. Aprotic diazotization of **7** by the method of Friedman and Logullo¹⁰ to give the diazonium carboxylate (**8**), followed by thermolysis in refluxing 1,2-dichloroethane, produced 1,4,5,8-tetramethylbiphenylene (**9**)¹¹ in 14% yield. Treatment of **9** with 4 equiv of NBS in CCl_4 gave a 69% yield of the tetrabromide (**10**), which was converted to the tetrakis(phosphonium) salt (**11**) in 79% yield. Solutions of **11** gave the tetrakis(ylide) **12** upon treatment with either dimethyl potassium or *t*-BuOK. Quenching with gaseous formaldehyde gave a 69% yield of 1,4,5,8-tetravinylbiphenylene (**13**); alternatively, treatment of **12** with monomeric glyoxal¹² produced the deep blue polycycle **1** and the dark red hydrolysis product¹⁶ **14** in yields of 1% and 1/4%, respectively.

Dicyclooctabiphenylene (**1**) is unstable as the solid, but can be observed momentarily as blue-black crystals before decomposing to a light yellowish insoluble polymer. This decomposition is concentration dependent and is manageably slow in dilute solutions (see Experimental Section). No dimers could be detected by NMR or TLC in the decomposition products of either solid or dissolved **1**. The exclusion of light and/or oxygen had no effect on the rate of decomposition of solutions as judged by decolorization and NMR, and did not prevent the decomposition of solid

(10) (a) Logullo, F. M.; Seitz, A. M.; Friedman, L. *Org. Synth.* **1968**, *48*, 12–17. (b) Logullo, F. M. Ph.D. Dissertation, Case Institute of Technology, Cleveland, OH, 1965.

(11) (a) Hart, H.; Teuerstein, A.; Babin, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 903–906. (b) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1977**, *99*, 6045–6049. (c) Hart, H.; Jiang, J. B.-C.; Sasaoka, M. *J. Org. Chem.* **1977**, *42*, 3840–3845.

(12) The procedure given here simplifies an earlier adaptation^{2b} of the original preparation: Harries, C.; Temme, P. *Chem. Ber.* **1907**, *40*, 165–172.

(13) (a) Bothner-By, A. A.; Castellano, S. M. In "Computer Programs for Chemistry"; Detar, D. F., Ed.; W. A. Benjamin: New York, 1968; Vol. 1. (b) Bothner-By, A. A.; Castellano, S. *QCPE* **1967**, *10*, 111, LAOCN3.

(14) Vollhardt, K. P. C. *Synthesis* **1975**, 765–780.

(15) Gronowitz, S.; Hansen, G. *Ark. Kemi* **1967**, *27*, 145–151.

Table II. UV-vis Spectra for Selected Polycycles

1 ^a		2 ^b		14 ^c	
λ , nm	log ϵ	λ , nm	log ϵ	λ , nm	log ϵ
208 (?)	5.16	225	4.35	226	4.49
249	4.29	258	3.86	233 s	4.45
260	4.27	268	3.94	257	4.36
271	4.42	280	4.10	271 s	4.11
282	4.47	292	4.30	282 s	4.02
294 s	3.94	305	4.31	297	3.98
309	3.94	327	2.91	310	3.80
322	3.84	342	3.05	324 s	3.05
338 s	3.55	360	3.17	336	2.89
358	3.23	378	3.17	343 s	2.82
386 s	2.86	402	3.07	351	2.73
425	2.80	410	3.05	362	2.74
456	2.82	431	3.02	382	2.64
484	2.74	440	3.05	408	2.36
557	2.74	463	3.00	418	2.41
596	2.77	478	2.81	447	2.50
648 s	2.64	512	2.69	475	2.43
702 s	2.17	557	2.42	511	2.00
		621	1.63	553	1.59
				617	0.77

1 ^d		3 ^e		13 ^f	
λ , nm	log ϵ	λ , nm	log ϵ	λ , nm	log ϵ
388	2.99	249	5.00	224	4.62
423	2.81	330	3.95	232	4.61
455	2.84	343	3.90	254	4.69
484	2.80	356	4.00	262	4.69
523 s	2.64	368	3.35	283 s	4.68
567	2.70	374	2.84	295	4.76
608	2.71	379	2.52	304 s	4.69
660 s	2.59	385	2.40	384 s	3.86
		392	2.34	407	3.9
				431	3.89

^aThis work. Solvent: cyclohexane. Shoulders denoted by "s".
^bReference 2b. Solvent: cyclohexane. ^cThis work. Solvent: cyclohexane.
^dThis work. Solvent: carbon disulfide. ^eReference 37. Solvent: hexane. (0-0) origin and (0-1) hot band not recorded here; see ref 22. ^fThis work. Solvent: cyclohexane.

1. This is in contrast to the known sensitivity of **2** to photooxidative polymerization in solution.¹⁷ The addition of excess bromine in CCl₄ to **1** caused immediate decolorization, giving a greenish-yellow solid which appeared (TLC, NMR, MS) to be a very complex mixture of bromine addition products. While no individual products could be identified, the color, NMR, and mass spectrum of the mixture suggested the addition of 1-2 equiv of Br₂ to each of the cycloocta rings. Moreover, the mass spectrum showed an efficient loss of halogen typical of polyhalohydrocarbons,¹⁸ with a total halogen loss peak observed at *m/e* 252. High-resolution mass spectrometry of this peak gave a mass value in acceptable accord with the proposed formula (obsd 252.0928, calcd 252.0939 for C₂₀H₁₂).

The UV-vis spectra of cyclooctannellated biphenylenes have been studied theoretically by a number of workers.^{19,20} The calculated spectral data for **1**, **2**, and **3** by Vogler and Ege^{19,21} are shown in Table I; the observed spectral data for **1**, **2**, **3**, **13**, and **14** are given in Table II. The spectrum of **1** (see Figure 3), like that of **2**, shows considerable vibrational fine structure in the visible

(16) Shechter et al. have reported a similar hydrolysis of a benzylic phosphonium salt with either dimethyl sodium or *n*-BuLi. Use of *t*-BuLi in THF precluded hydrolysis: Card, P. J.; Friedli, F. E.; Shechter, H. *J. Am. Chem. Soc.* **1983**, *105*, 6104-6114. However, *n*-BuLi/THF reduced the yield of **2** markedly from that for Me₂SO solutions.^{2a,b}

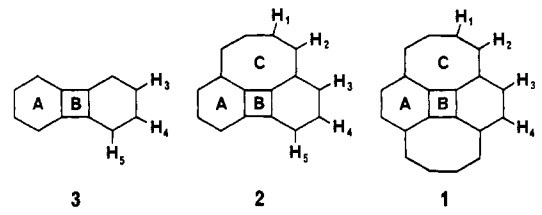
(17) Wilcox, C. F., Jr.; Utrecht, J. P., unpublished results.

(18) McLafferty, F. W. "Interpretation of Mass Spectra"; University Science Books: Mill Valley, CA, 1980; pp 226-228.

(19) Vogler, H.; Ege, G. *J. Am. Chem. Soc.* **1977**, *99*, 4599-4604.

(20) Favini, G.; Gamba, A.; Pitea, D. *Z. Phys. Chem. (Wiesbaden)* **1977**, *105*, 135-146.

(21) (a) Panciř, J.; Matoušek, I.; Zahradník, R. *Collect. Czech. Chem. Commun.* **1973**, *38*, 3039-3066. (b) Hochmann, P.; Zahradník, R.; Kvasnička, V. *Collect. Czech. Chem. Commun.* **1968**, *33*, 3478-3513.

Table III. Ring Currents,^a ¹H NMR Chemical Shifts,^b and "London" Contributions to Magnetic Susceptibility^c


	π system		
	3	2	1
Simple McWeeny Ring Current			
ring			
A	+0.270	-0.594	-4.185
B	-1.748	-1.263	-5.831
C		-2.637	-6.717
Iterative McWeeny Ring Current			
ring			
A	+0.608	+0.369	-0.091
B	-0.804	-0.745	-1.164
C		-0.706	-1.071
Gomes Circuit Ring Current			
ring			
A	+0.27	+0.10	-0.19
B	-1.79	-1.40	-1.39
C		-0.70	-0.88
Observed Chemical Shift			
proton			
1		4.61	3.63 ^d
2		4.74	3.59 ^d
3	6.73	5.83	4.55
4	6.73	6.21	4.55
5	6.62	6.05	
London Contribution to Magnetic Susceptibility			
	+0.906	-0.861	-4.610

^aBenzene = +1.00. This work, see text. ^bIn ppm (δ) downfield from Me₄Si: 300-MHz spectra taken in CDCl₃, Me₄Si internal reference. ^cBenzene = +1.000; ring area factors approximated as regular polygons of unit bond length. ^dThis assignment assumes a slightly paratropic ring current for the A ring of **1**.

region.^{2b} The spectrum of **1** is similar to those of other dicyclooctannellated biphenylenes,^{2f} and to a lesser degree that of **2**.

The longest wavelength band of **1** tails down to about 750 nm in cyclohexane and to about 770 nm in carbon disulfide. Spectra in cyclohexane show a very weak shoulder at 702 nm which is not visible in the CS₂ spectrum; the first peak common to both spectra occurs at 648 nm (660 nm in CS₂). The long-wavelength transition in **1** is predicted to occur at 605 nm, giving a discrepancy of 0.3 eV relative to the 702-nm shoulder, and less than half this value relative to the first common peak.

As noted by Vogler and Ege, the long-wavelength transition calculated for biphenylene (**3**) matches well with the observed λ_{\max} (~394 nm), while the energy of the comparable transition in **2** is calculated to be about 0.3 eV too high relative to the 621-nm λ_{\max} . We suggest that this discrepancy arises because the fitted transition of **2** and the 702-nm shoulder in **1** are in fact (1-0) hot bands, characteristic of molecules with forbidden or nearly forbidden long-wavelength transitions. In biphenylene, the longest wavelength transition observed (405 nm) has been identified as such a hot band.²² In any event, a discrepancy of 0.3 eV does not vitiate the identification of **1**, given the similar discrepancy found for **2**.

Prior to the synthesis of **1**, ring currents were calculated for **1**, **2**, and **3** with use of an iterative variant of the McWeeny theory.⁶ These values, along with the related quantity X_L , are shown in Table III.²³ With use of a Biot-Savart type single

(22) (a) Hochstrasser, R. M. *Can. J. Chem.* **1961**, *39*, 765-772. (b) Hochstrasser, R. M.; McAlpine, R. D. *J. Chem. Phys.* **1966**, *44*, 3325-3328.

Table IV. Resonance Energies (RE) and Resonance Energies per Electron (REPE) for Selected Hydrocarbons

method ^a (units)	compound			
	benzene	3	2	1
RE				
Hückel (β)	2.000	4.505	5.776	7.036
Hess-Schaad (β)	0.39	0.33	0.05	-0.24
Trinajstić-Aihara (β)	0.273	0.123	-0.147 ^b	-0.486
Randić (eV)	0.869	0.330 ^b	0.039	-0.627
Gomes (eV)	0.992	1.007	0.834 ^f	0.329
Dewar-DeLlano (eV)	0.869	1.346	1.26	1.17
REPE				
Hückel (β)	0.333	0.375	0.361	0.352
Hess-Schaad (β)	0.065	0.027	0.003	-0.012
Trinajstić-Aihara (β)	0.045	0.010	-0.009	-0.024
Randić (eV)	0.145	0.027	0.002	-0.031
Gomes (eV)	0.165	0.084	0.052	0.016
Dewar-DeLlano (eV)	0.145	0.112	0.079	0.059

^aNotes on methods: Hückel energies relative to ethylene. Hess-Schaad reference structures averaged over all Kekulé structures (ref 25a). Conjugated circuits methods include "dependent" circuits, but not disjoint circuits (ref 27 and 28). ^bMinor differences from published values appear to result from different enumerations of circuits or polynomial coefficients, but are not serious.

current geometric model⁸ correlating iterative McWeeny ring currents and observed proton chemical shifts (CCl₄) for both benzenoid⁹ and biphenylenic² hydrocarbons,⁷ it was predicted that **1** would exhibit notably paratropic proton chemical shifts of δ 3.7–3.8 (cycloocta) and δ 4.8 (benzenoid). These predictions compare well with the observed chemical shifts of **1** (CDCl₃) as shown in Table III (see also Figure 1). We feel that the small discrepancies are entirely satisfactory, given that no solvent corrections have been made and that the prediction involved a considerable extrapolation of the ring current/chemical shift model.

Discussion

The resonance energies (RE) of **1** and related systems calculated by a variety of available methods^{24–28} are presented in Table IV.

All of these schemes predict π electron stabilization to decrease in the order **3** > **2** > **1**, and all schemes except the crude ethylene-referenced Hückel model predict these compounds to have REPE^{25a} stabilizations less than that of benzene. Kinetic and thermodynamic instability must be distinguished,²⁹ but if the experimentally observed stability reflects overall π electron stabilization for this series, then the various schemes correctly predict the stability order. However, the schemes disagree as to whether the π electrons of **1** and **2** are stabilized relative to a comparable olefinic ("Dewar-type") reference system. Interestingly, the most sophisticated method (Dewar-DeLlano SCF)²⁴ predicts a moderately large and positive REPE for **1**; the only other method to

give a positive REPE is Gomes' conjugated circuit technique.²⁸ While such positive values might at first sight appear inconsistent with the "antiaromatic" behavior of compound **1**, it is important to recognize that the strong bond alternation of "antiaromatic" species can greatly modify the calculated physical properties. The localization of double bond character sharply reduces the negative REs calculated for antiaromatic systems; it is reasonable that the presence of benzenoid and other $[4n + 2]$ circuits could lead to net positive RE in **1**.

Three classification schemes that have been introduced in an attempt to extend the Hückel $[4n + 2]$ rule and make it quantitative are the following: the periphery model,^{30–32} the conjugated circuit theory,^{27,28} and the algebraic structure count model.³³ The periphery model³⁰ has been extended by Rabinovitz to include semiperipheral and local circuits based upon the concept of the *priority of aromatic delocalization*.³² As applied to the present hydrocarbon series, the simple perimeter model correctly rationalizes the paratropicity and instability of **3** ($[12] \pi$) and **1** ($[16] \pi$), but fails to account for the properties of **2** ($[14] \pi$), which lie between those of **3** and **1**. While Rabinovitz' principle of aromatic priority explains the relatively low "antiaromaticity" of biphenylene (**3**) as being due to the priority of weakly coupled benzenoid circuits,^{32b} it does not explain the substantial paratropicity of **2**, assuming the priority of either the $[14] \pi$ periphery or the two benzenoid circuits.

The conjugated circuit approach^{27,28} seems to provide a good qualitative explanation of the behavior of the present series of polycycles (see Table IV). The Gomes circuit-based ring current formalism also gives currents that compare fairly well with those from the iterative McWeeny results. The Gomes ring currents (see Table III) are of the same sign and relative magnitude as the iterative values, and are more reasonable than the non-iterated McWeeny results. Benzenoid diatropism in the series **3**, **2**, **1** is seen to decrease as the further annelation of $[4n]$ component rings introduces a relatively greater number of large $[4n]$ conjugated circuits spanning benzenoid rings, culminating in the essentially atropic benzenoid rings of **1**.

The "algebraic structure count" (ASC) model, i.e., parity-signed Kekulé structures, first applied to π systems by Dewar and Longuet-Higgins,³⁴ has been extended as a tool for the prediction of polycycle properties on the basis of the absolute sum of the signed Kekulé structures.³³ As applied to the present series of polycycles, the ASC analysis correctly orders the resonance energy, diatropicity, and stability; the ASCs of the series **3**, **2**, and **1** are in fact **3**, **2**, and **1**.

The chemical instability and extreme paratropicity of **1**, in conjunction with the predominantly $[4n]$ circuit enumeration and several calculations of negative RE, would seem to suggest that the system is (to some degree) "antiaromatic". Standing in contrast to these points are the positive Dewar-DeLlano and Gomes REs calculated for the molecule. While a negative RE cannot be rejected in the absence of thermochemical data, a positive RE is less of a contradiction than might appear at first. Aihara has shown³⁵ how relative circuit areas can lead to situations (e.g., butalene and bicyclo[6.2.0]decapentaene) where X_L and RE

(23) (a) Application of Flygare's^{23b} localized magnetic susceptibility scheme results in a prediction that X_{zz} is unusually small ($-14 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$); with a slightly different assignment of $X_L(\text{benzene})$ it would even be paramagnetic. (b) Schmalz, T. G.; Norris, C. L.; Flygare, W. H. *J. Am. Chem. Soc.* **1973**, *95*, 7961–7967.

(24) (a) Dewar, M. J. S.; DeLlano, C. R. *J. Am. Chem. Soc.* **1969**, *91*, 789–795. (b) DeLlano, C. R. Ph.D. Dissertation, University of Texas at Austin, Austin, TX, 1968.

(25) (a) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 305–310. (b) Schaad, L. J.; Hess, B. A., Jr. *Pure Appl. Chem.* **1982**, *54*, 1907–1114.

(26) (a) Aihara, J.-i. *J. Am. Chem. Soc.* **1976**, *98*, 2750–2758. (b) Gutman, I.; Milun, M.; Trinajstić, N. *J. Am. Chem. Soc.* **1977**, *99*, 1692–1704. (c) Aihara, J.-i. *J. Am. Chem. Soc.* **1977**, *99*, 2048–2053.

(27) (a) Randić, M. *Chem. Phys. Lett.* **1976**, *38*, 68–70. (b) Randić, M. *J. Am. Chem. Soc.* **1977**, *99*, 444–450. (c) Randić, M. *Tetrahedron* **1977**, *33*, 1905–1920. (d) Randić, M. *Pure Appl. Chem.* **1980**, *52*, 1587–1596. (e) Randić, M. *Pure Appl. Chem.* **1983**, *55*, 347–354. (f) Randić, M. *Mol. Phys.* **1977**, *34*, 849–856. (g) Randić, M. *Int. J. Quantum Chem.* **1980**, *17*, 549–586.

(28) (a) Gomes, J. A. N. F.; D. Phil. Thesis, Oxford University, Oxford, England, 1976. (b) Gomes, J. A. N. F.; Mallion, R. B. *Rev. Port. Quim.* **1979**, *21*, 82–89. (c) Gomes, J. A. N. F. *Theor. Chim. Acta* **1981**, *59*, 333–356.

(29) Aihara, J.-i. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1935–1943.

(30) (a) Platt, J. R. *J. Chem. Phys.* **1954**, *22*, 1448–1458. (b) Wagnière, G.; Gouterman, M. *Mol. Phys.* **1962**, *5*, 621–627. (c) Müllen, K. *Helv. Chim. Acta* **1978**, *61*, 2307–2317.

(31) (a) Trost, B. M.; Bright, G. M. *J. Am. Chem. Soc.* **1967**, *89*, 4244–4245. (b) Trost, B. M.; Bright, G. M. *J. Am. Chem. Soc.* **1969**, *91*, 3689–3690. (c) Trost, B. M.; Bright, G. M.; Frihart, C.; Brittelli, D. *J. Am. Chem. Soc.* **1971**, *93*, 737–745.

(32) (a) Minsky, A.; Meyer, A. Y.; Hafner, K.; Rabinovitz, M. *J. Am. Chem. Soc.* **1983**, *105*, 3975–3981. (b) Rabinovitz, M.; Willner, I.; Minsky, A. *Acc. Chem. Res.* **1983**, *16*, 298–304.

(33) (a) Wilcox, C. F., Jr. *Tetrahedron Lett.* **1968**, 795–800. (b) Wilcox, C. F., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 2732–2736. (c) Gutman, I.; Trinajstić, N.; Wilcox, C. F., Jr. *Tetrahedron* **1975**, *31*, 143–146. (d) Wilcox, C. F., Jr.; Gutman, I.; Trinajstić, N. *Tetrahedron* **1975**, *31*, 147–152. (e) Wilcox, C. F., Jr. *Croat. Chem. Acta* **1975**, *47*, 87–94.

(34) Dewar, M. J. S.; Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1952**, *214*, 482–493.

(35) (a) Aihara, J.-i. *J. Am. Chem. Soc.* **1979**, *101*, 558–560. (b) Haddon, R. C. *J. Am. Chem. Soc.* **1979**, *101*, 1722–1728. (c) Aihara, J.-i. *Pure Appl. Chem.* **1982**, *54*, 1115–1128.

have the same sign (diatropic "antiaromatics") as opposed to the normal negative proportionality. In the case of **1**, the Trinajstić-Aihara RE is strongly negative and the "London" susceptibility contribution positive (paramagnetic), as expected for an "antiaromatic" species. However, bond alternation in **1** presumably enables the system to attain a positive RE, but does not change the sign of X_L . This is in contrast to bicyclo[6.2.0]-decapentaene, where stabilizing distortions increase the diatropicity but are probably insufficient to change the sign of the RE.³⁶

Summary. The polycyclic hydrocarbon dicycloocta[def: jkl]-biphenylene (**1**) has been prepared and its physical properties examined. The ¹H NMR spectrum of **1** shows a marked ring current paratropism as predicted by McWeeny ring current theory; the UV-vis spectrum agrees well with a previous prediction by Vogler and Ege. Various resonance energy calculations for the related polycycles **3**, **2**, and **1** disagree considerably as to the sign and magnitude of RE in **1**, though all of the schemes predict the

stability sequence (**3** > **2** > **1**) correctly. Of the current classification schemes for polycycles, the periphery model succeeds for **1** and **3**, but fails for **2**, while both the conjugated circuit theory and the algebraic structure count correctly describe the complete series.

Acknowledgment is made to the National Science Foundation Instrumentation Program for support of the Cornell Nuclear Magnetic Resonance Facility, and especially for Equipment Award CHE-7904825 (Bruker WM300 NMR spectrometer).

Registry No. **1**, 64074-44-8; **2**, 36230-20-3; **3**, 259-79-0; **4**, 95-78-3; **5**, 15540-89-3; **6**, 15540-90-6; **7**, 15540-91-7; **8**, 68596-88-3; **9**, 63548-78-7; **10**, 87729-44-0; **11**, 87739-06-8; **13**, 87729-46-2; **14**, 92096-48-5; HONH₂·HCl, 5470-11-1; PPh₃, 603-35-0; HC(O)C(O)H, 107-22-2; HCHO, 50-00-0; chloral hydrate, 302-17-0; glyoxal trimer dihydrate, 40094-65-3.

(36) Aihara, J.-i. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1245-1246.

(37) Clar, E. P.; Pickett, L. W.; Voris, D. *J. Am. Chem. Soc.* **1941**, *63*, 3231-3232.

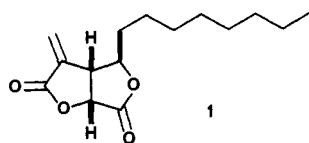
Synthetic Studies of the Furan-Carbonyl Photocycloaddition Reaction. A Total Synthesis of (±)-Avenaciolide

Stuart L. Schreiber*¹ and Amir H. Hoveyda

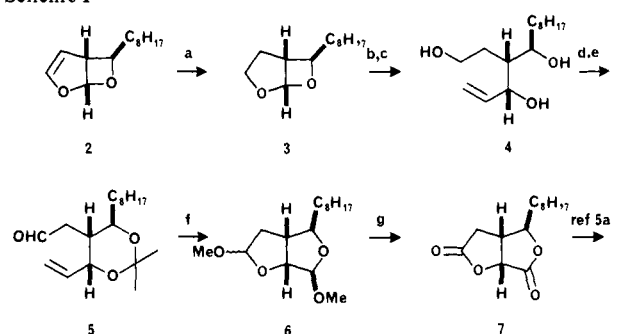
Contribution from the Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut 06511. Received March 26, 1984

Abstract: The Paternò-Büchi photocycloaddition of furan and nonanal serves as an entry point for a new synthesis of the antifungal mold metabolite avenaciolide (**1**). The method of "ancillary stereocontrol" is employed to complete the stereospecific synthesis.

The furan-carbonyl photocycloaddition reaction provides a method for the addition of an enolate equivalent (furan) to an aldehyde which allows access to threo-aldol products.² Furthermore, the dihydrofuran photoadduct can be converted to a variety of functionalized systems with a high degree of stereochemical control.² Recently, we described the application of this method in a short synthesis of the highly congested mycotoxin asteltoxin.³ Herein, we report on the efficient preparation of the antifungal metabolite (±)-avenaciolide^{4,5} (**1**) which also employs



Scheme I^a



^a (a) H₂, Rh/Al₂O₃, EtOAc, 97%; (b) 0.1 N HCl, THF (1:4), 96%; (c) CH₂=CHMgBr, THF, room temperature, 80%, (5:1); (d) acetone, CuSO₄, *p*-TSOH, 85%; (e) PCC, NaOAc, CH₂Cl₂, 91%; (f) O₃, MeOH, -78 °C, then Me₂S, room temperature, then K₂CO₃, then HCl, 31%; (g) MCPBA, BF₃·OEt₂, CH₂Cl₂, 80%.

the furan-carbonyl photocycloaddition reaction as the springboard for the synthesis.⁶ Our synthesis illustrates another key feature of the reaction: *multigram quantities of materials can be easily prepared in high yield and with complete stereochemical control so that its use as the first step in a synthesis design can be recommended.*

Photocycloaddition of nonanal (32.7 g) in furan (350 mL) with a Hanovia 450-W lamp equipped with a Vycor filter for 20 h

(6) For related studies, see: Zamojski, A.; Kozluk, T. *Tetrahedron* **1983**, *39*, 805.

(1) Searle Scholar, 1982-1985.

(2) (a) Schreiber, S. L.; Hoveyda, A. H.; Wu, H.-J. *J. Am. Chem. Soc.* **1983**, *105*, 660. (b) Schreiber, S. L.; Satake, K. *J. Am. Chem. Soc.* **1983**, *105*, 6723.

(3) Schreiber, S. L.; Satake, K. *J. Am. Chem. Soc.* **1984**, *106*, 4186.

(4) Isolation and structure determination: (a) Brookes, D.; Tidd, B. K.; Turner, W. B. *J. Chem. Soc.* **1963**, 5385. (b) Ellis, J. J.; Stodola, F. H.; Vesonder, R. F.; Glass, C. A. *Nature (London)* **1964**, *203*, 1382. (c) Brookes, D.; Sternhell, S.; Tidd, B. K.; Turner, W. B. *Aust. J. Chem.* **1967**, *18*, 373.

(5) Previous syntheses: (a) Parker, W. L.; Johnson, F. J. *Am. Chem. Soc.* **1969**, *91*, 7208. (b) Parker, W. L.; Johnson, F. J. *Org. Chem.* **1973**, *38*, 2489. (c) Herrmann, J. L.; Berger, M. H.; Schlessinger, R. H. *J. Am. Chem. Soc.* **1973**, *95*, 7923. (d) Herrmann, J. L.; Berger, M. H.; Schlessinger, R. H. *Ibid.* **1979**, *101*, 1544. (e) Anderson, R. C.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1975**, *97*, 3870. (f) Ohru, H.; Emoto, S. *Tetrahedron Lett.* **1975**, 3657. (g) Sakai, T.; Horikawa, H.; Takeda, A. *J. Org. Chem.* **1980**, *45*, 2039. (h) Murai, A.; Takahashi, K.; Takatsura, H.; Masamune, T. *J. Chem. Soc., Chem. Commun.* **1981**, 221. (i) Kido, F.; Tooyama, Y.; Noda, Y.; Yoshikoshi, A. *Chem. Lett.* **1983**, 881.