2 H), 2.15 (m, 2 H), 2.09–1.91 (m, 3 H), 1.80–1.70 (m, 2 H), 1.46 (dm, $J = 8.0$ Hz, 1 H), 1.31 (d, $J = 8.0$ Hz, 1 H), 1.22–1.08 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 214.72, 162.89, 148.55, 56.56, 54.40, 54.14, 42.07, 41.89, 39.23, 39.13, 26.59, 26.54; MS m/z (M^+) calcd 174.1045, obsd 174.1048.

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.66; H, 8.11.

The mother liquor from above was concentrated, and the residue was subjected to MPLC on silica gel (elution with 5% ether in petroleum ether) to give in turn **44**, **33**, and **43**.

For **33**: a colorless oil, bp 70–75 °C at 0.7 Torr; IR ($CHCl_3$, cm^{-1}) 2980, 2930, 2880, 1735; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.15 (s, 1 H), 3.09 (s, 2 H), 3.00 (s, 1 H), 2.15 (s, 1 H), 1.95 (d, $J = 8.9$ Hz, 1 H), 1.85 (dd, $J = 16.6, 2.8$ Hz, 1 H), 1.67–1.50 (m, 3 H), 1.40 (d, $J = 6.9$ Hz, 1 H), 1.14 (d, $J = 8.2$ Hz, 1 H), 0.94–0.85 (m, 1 H), 0.71–0.63 (m, 1 H); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 213.52, 158.68, 146.30, 55.04, 50.37, 49.25, 43.10, 42.53, 39.64, 34.96, 24.78, 24.02; MS m/z (M^+) calcd 174.1045, obsd 174.1038.

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.77; H, 8.11.

For **43**: colorless liquid, bp 70 °C at 0.5 Torr; IR ($CHCl_3$, cm^{-1}) 3010, 2970, 2935, 2915, 2885, 2870, 1740; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.39 (d, $J = 3.1$ Hz, 1 H), 3.01 (d, $J = 3.1$ Hz, 1 H), 2.84 (d, $J = 3.7$ Hz, 1 H), 2.35 (s, 1 H), 2.16–2.12 (m, 1 H), 2.03–1.95 (m, 3 H), 1.82 (dm, $J = 9.5$ Hz, 1 H), 1.89–1.79 (m, 1 H), 1.76–1.70 (m, 2 H), 1.61 (d, $J = 10.2$ Hz, 1 H), 1.39–1.34 (m, 1 H); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 216.95, 169.35, 112.46, 60.51, 60.05, 60.78, 41.48, 30.50, 38.98, 28.71, 31.40, 23.50; MS m/z (M^+) calcd 174.1045, obsd 174.1064.

For **44**: colorless liquid, bp 70 °C at 0.5 Torr; IR ($CHCl_3$, cm^{-1}) 2970, 2930, 2870, 1730; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.79 (d, $J = 2.0$ Hz, 1 H), 3.15 (s, 1 H), 2.75 (d, $J = 2.9$ Hz, 1 H), 2.56 (d, $J = 4.0$ Hz, 1 H), 2.18 (dm, $J = 8.7$ Hz, 1 H), 2.04–2.00 (m, 3 H), 1.80 (d, $J = 8.6$ Hz, 1 H), 1.81–1.70 (m, 1 H), 1.76–1.59 (m, 1 H), 1.52 (d, $J = 9.9$ Hz, 1 H), 1.45–1.27 (m, 2 H); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 215.30, 159.46, 122.07, 73.80, 52.15, 42.86, 42.01, 39.77, 38.32, 35.76, 31.81, 23.96; MS m/z (M^+) calcd 174.1045, obsd 174.1064.

Cleavage of *syn*-Sesquinorbornen-4-one. Ketone **32** (500 mg, 2.87 mmol) in dry tetrahydrofuran (2 mL) was added to freshly prepared LDA at −78 °C as above. Ethyl nitrite (220 mg, 2.93 mmol) was later introduced. After quenching of the reaction mixture with brine, the products were extracted into chloroform and subjected to chromatography on silica gel (sequential elution with 2:8, 2:7, and 7:3 ether–petroleum ether) gave in order 130 mg (26%) of recovered **32**, 440 mg (62%) of **45**, and 50 mg (9%) of **46**.

For **45**: colorless oil; IR ($CHCl_3$, cm^{-1}) 3580, 3300, 3005, 2970, 2875, 1730; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (br s, 1 H), 7.39 (d, $J = 7.5$ Hz) and 6.74 (d, $J = 6.7$ Hz tota 1 H), 4.19 and 4.18 (2 q, $J = 7.1$ Hz, total 2 H), 3.90–3.7 and 3.25–3.15 (m, 2 H), 2.95 (d, $J = 1.2$ Hz, 1 H), 2.84 (d, $J = 1.2$ Hz, 1 H), 2.72–2.53 (m, 1 H), 2.40–2.21 (m, 1 H), 1.71 (AB q, $J = 12.6$ Hz, 2 H), 1.59 (dm, $J = 8.2$ Hz, 1 H), 1.4–1.1 (m, 1 H), 1.29 (t, $J = 7.1$ Hz, 3 H), 0.99–0.92 (m, 2 H); ^{13}C NMR (20 MHz, $CDCl_3$) ppm (major isomer) 173.82, 153.54, 151.13, 149.63, 60.49, 49.60, 45.63, 41.24, 41.11, 40.45, 35.69, 25.23, 22.40, 14.09; MS m/z (M^+) calcd 249.1365, obsd 249.1373.

Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.45; H, 7.68. Found: C. 67.65; H, 7.68.

For **46**: yellow crystals, mp 127 °C dec (from ether–petroleum ether); IR ($CHCl_3$, cm^{-1}) 3570, 3300, 3010, 2970, 2920, 2870, 1745, 1655, 915; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.5 (br s, 1 H), 4.13 (s, 1 H), 3.23 (d, $J = 0.8$ Hz, 1 H), 3.05 (s, 1 H), 2.99 (s, 1 H), 2.37 (AB q, $J = 9.5$ Hz, 2 H), 1.91–1.84 (m, 2 H), 1.66 (d, $J = 8.2$ Hz, 1 H), 1.44 (d, $J = 8.2$ Hz, 1 H), 1.33–1.19 (m, 2 H); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 198.05, 160.39, 155.32, 155.12, 55.64, 52.56, 51.93, 42.20, 42.07, 40.23, 26.54, 26.40; MS m/z (M^+) calcd 203.0946, obsd 203.0976.

Anal. Calcd for $C_{12}H_{1N}O_2$: C, 70.92; H, 6.45. Found: C, 70.78; H, 6.57.

Cleavage of *anti*-Sesquinorbornen-4-one. Analogous treatment of **33** (570 mg, 3.27 mmol) afforded 430 mg (53%) of **47** in addition to 90 mg of impure keto oxime. For **47**: colorless oil; IR ($CHCl_3$, cm^{-1}) 3580, 3300, 2970, 2870, 1725, 1190; ^{1}H NMR (300 MHz, $CDCl_3$) δ (major isomer) 7.76 (br s, 1 H), 7.29 (d, $J = 8.4$ Hz, 1 H), 4.12 (dq, $J = 7.2, 1.5$ Hz, 2 H), 3.64–3.58 (m, 2 H), 2.92 (s, 1 H), 2.84 (s, 1 H), 2.62 (dt, $J = 13.9, 5.3$ Hz, 1 H), 2.37 (dt, $J = 13.9, 2.8$ Hz, 1 H), 1.73–1.65 (m, 4 H), 1.27 (t, $J = 7.2$ Hz, 3 H), 1.00 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm (major isomer) 173.42, 153.73, 151.86, 149.33, 60.61, 51.78, 47.34, 42.89, 41.73, 41.09, 36.05, 26.40, 26.00, 14.16; MS m/z (M^+) calcd 249.1365, obsd 249. 1361.

Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.45; H, 7.68. Found: C, 67.53; H, 7.66.

Acknowledgment. We thank the National Institute of Health (Grant CA-12115) for financial support and Dr. Judith Gallucci, Haibing Deng, and Anthony Blackburn (The Ohio State University) for the X-ray crystallographic analyses.

Supplementary Material Available: X-ray data for **21** and **31**; ^{1}H NMR, ^{13}C NMR, and mass spectra of **20**, **21**, **23**, **43**, **44**, and **45**; and tables of final positional parameters anisotropic thermal parameters, bond lengths, bond angles, intramolecular distance, and torsion angles for **21** and **31** (38 pages). Ordering information is given on any current masthead page.

Crystal and Molecular Structure of *cis*-1,4,9,10-Tetramethyl-9,10-dihydroanthracene-9,10-diol

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The title compound (*cis*-**2**) was found to crystallize independently from a mixture of the three possible stereoisomers. An X-ray structure determination showed that individual molecules of *cis*-**2** have a shallow boat geometry; the dihedral angle between the least-squares planes of the aromatic rings is 165.3°. The molecules of *cis*-**2** exist in infinite hydrogen-bonded chains with a stepped sheet structure and a short hydrogen bond distance of ca. 1.7 Å.

Much effort has been devoted to establishing the preferred geometries of 9,10-dihydroanthracenes (DHA's) in solution and in the solid state.[1] In general, X-ray crystallographic analyses have demonstrated that 9-substituted

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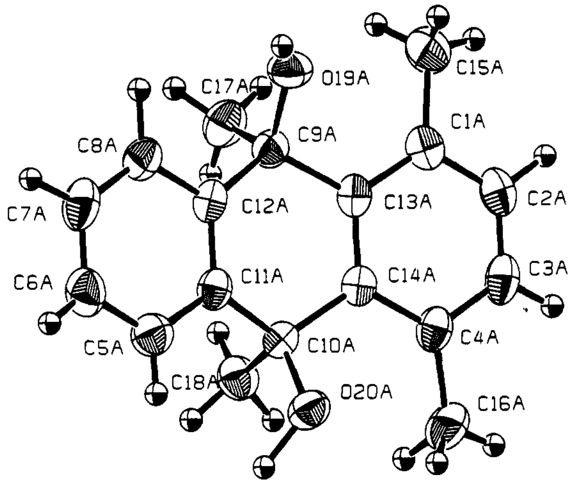
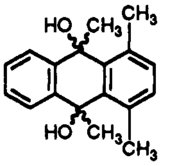


Figure 1. ORTEP drawing for *cis*-2 showing the crystallographic numbering system.

and *cis*-9,10-disubstituted DHA's, like DHA itself, have boat-shaped central rings and when substituents are present they are in the pseudoaxial positions. A limited number of examples suggest that trans-9,10-disubstituted, 9,9-disubstituted, and 9,9,10,10-tetrasubstituted DHA's, where all four substituents are large, are roughly planar.[2-5] However, hydroxyl groups probably have little effect on the degree of folding of the central ring; *cis*-9,10-dipropyl-9,10-dihydroanthracene-9,10-diol (1) has a boat geometry with the propyl groups pseudoaxial both in solution[6] and in the solid state.[5] Few diols like 1 have been subjected to X-ray crystal structure determination though they are of some interest with respect to intermolecular hydrogen bonding and complexation of other hydroxylic compounds. In preparing 1,4,9,10-tetramethyl-9,10-dihydroanthracene-9,10-diol (2) as a synthetic intermediate, we observed that it crystallized in two distinct habits under certain conditions. Since 2 has three stereoisomeric forms, a meso compound (*cis*-2) and a *d*,*l* pair (*trans*-2), it appeared likely that the diastereomers of 2 had crystallized independently, possibly providing an opportunity to determine the molecular and crystal structure of a 9,9,10,10-tetrasubstituted DHA having peri substituents.



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Recrystallization of 2[7-9] by vapor diffusion (benzene/petroleum ether) yielded a mixture of needles and prisms which were separated physically and gave different melting points. The structure of one of the prisms was determined by X-ray crystallography to be *cis*-2. This crystal had a triclinic cell[10,11] and, upon successful solution and refinement of the structure by direct methods[12,13] ($R = 0.054$), the space group was determined to be $P\bar{1}$. Figure 1 is an ORTEP[14] drawing of the refined structure showing the crystallographic numbering system. There are four molecules in the unit cell and two (designated A and B) in the asymmetric unit, and these have nearly identical molecular parameters.

The gross geometry of the individual molecules of *cis*-2 is, as expected, a "butterfly" or boat conformation with the 9,10-methyl groups in the pseudoaxial positions. The dihedral angle between the least-squares planes of the aromatic rings is 165.3°; a value substantially larger than for any *cis*-9,10-dialkyl-9,10-dihydroanthracene or for 1 (149°), the only other *cis*-diol for which X-ray crystal structure data is available.[5] The shallow boat geometry forces expansion of the endocyclic carbon bond angles at the 9- and 10-positions to 113.8° compared to 111° for 1. The other angles about C9 and C10 in *cis*-2 are essentially at the tetrahedral value, suggesting little steric interaction involving the peri methyl groups. However, the peri methyl groups are bent away (bond angle 126°) from the central ring, and the HCH angles of both types of methyl groups show substantial distortion from tetrahedral geometry (largest angle 113°, smallest angle 94°). This geometry corresponds very closely to the global minimum located by molecular mechanics procedures using the MMX force field.[15] In a comparison of the calculated geometry with the crystal structure geometry, the root mean square deviation of all carbon atoms was only 0.069 Å.

One other feature of the crystal structure of *cis*-2 is striking and significant. The distance between one of the hydroxyl hydrogens of one molecule of the asymmetric unit and the nearest oxygen of the second molecule is only ca 1.7 Å, a compelling indication of an intermolecular hydrogen bond. Hence *cis*-2 exists in infinite chains of hydrogen-bonded molecules with a stepped sheet structure illustrated by the stereo PLUTO drawing in Figure 2 that shows the two molecules of the asymmetric unit. That view also highlights a difference in the rotational states

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(10) $C_{36}H_{40}O_4$, FW 536.71 (two molecules), dimensions (mm) 0.600 × 0.500 × 0.600. One reflection was used for the unit cell determination; ω scan peak width at half-height 0.29. $V = 1383.1$ (4) Å^3, Z value = 2, $D_{\text{calc}} = 1.289$ g/cm^3, $F_{000} = 576$, $\mu_{(\text{Mo K}\alpha)} = 0.77$ cm^{-1}.

(11) Mo Kα ($\lambda = 0.71069$ Å), 23 °C, 6° take-off angle, $\omega - 2\theta$ scan, scan rate 8°/min, scan width $(1.78 + 0.30 \tan \theta)°$, $2\theta_{\max}$ (50°), Lorentz polarization and absorption corrections, secondary extinction (0.56453×10^{-5}).

(12) All calculations were performed using the TEXSAN, TEXRAY Structure Analysis Package, version 2.1, of Molecular Structure Corporation, The Woodlands, TX, and the SHELXTL program package.[13] Full-matrix least-squares refinement, $\Sigma w(|F_o| - |F_c|)^2$, $4F_o^2/\sigma^2(F_o^2)$, p factor (0.03), 3159 observations ($I > 3.00\sigma(I)$), 522 variables, reflection parameter ratio (6.05), R_w 0.068, goodness of fit 2.78, max shift/error in final cycle (0.18), maximum peak in final diff. map (0.25 e$^-$/Å), minimum peak in final diff. map (−0.21 e$^-$/Å^3)). The non-hydrogen atoms were refined anisotropically and the hydrogens were refined isotropically.

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(15) We used the MMX88 force field in the computer program PCMODEL. Comparisons of experimental and calculated geometries were done using the computer program PCDISPLAY. Both programs are available from Serena Software, P.O. Box 3076, Bloomington, IN 47402-3076. The calculated minimum for *trans*-2 is a near-planar geometry with a "chairlike" distortion having a heat of formation 1.4 kcal/mol higher than that of *cis*-2.

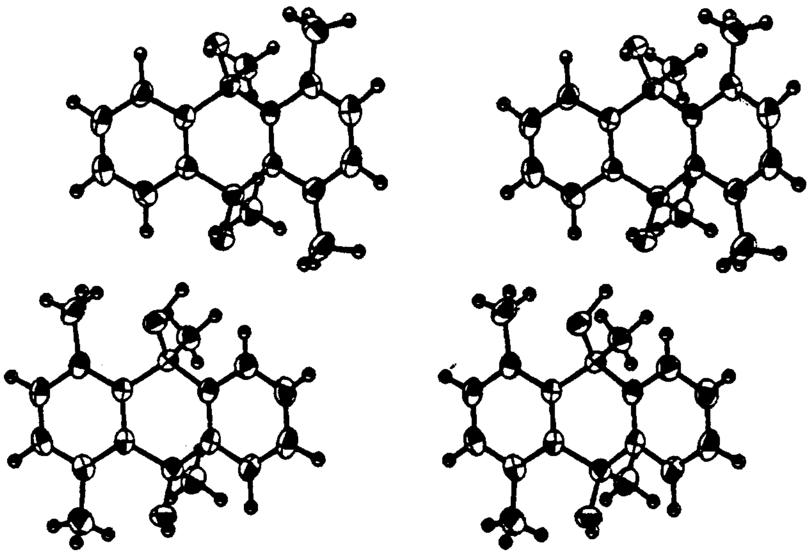

Figure 2. Stereo PLUTO drawing of the two molecules of *cis*-**2** in the asymmetric unit.

of the hydroxyl groups in molecules A and B. MacMillan et al. noted an oxygen–oxygen distance between molecules of the trans isomer of **1** of 2.814 Å that suggested the existence of a hydrogen bond there as well.[5] Also, Mak and co-workers have described *intermolecular* hydrogen bonds ((O···H–O distance 2.767 Å) in the crystal structure of a 1:1 molecular complex of *trans*-9,10-diphenyl-9,10-dihydroanthracene-9,10-diol with ethanol.[16] One is tempted to speculate that the near planar geometries in these latter two examples and the flattened boat geometry in *cis*-**2** are important in the occurrence of hydrogen-bonded structures in 9,10-dihydroanthracene-9,10-diols. In any case, the present work demonstrates unequivocally that short intermolecular hydrogen bonds can exist in such molecules and that these may lead to highly ordered networks of molecules in the solid state.

Experimental Section

The title compound was prepared from 1,4-dimethylanthraquinone via a Barbier synthesis, taking no precautions to prevent equilibration of geometric isomers upon work up.[7,8] Following dry-column flash chromatography[9] on Florisil, the ^{1}H NMR spectrum at 100 MHz (Bruker WP100SY spectrometer) in $CDCl_3$ solution appeared to be of a single diastereomer: δ 1.60 (s, 3 H), 1.73 (s, 1 H), 2.68 (s, 3 H), 7.09 (s, 1 H), 7.55 (m, 2 H). However, addition of 0.06–0.42 equiv of tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III) to a 0.04 M $CDCl_3$ solution of **2** yielded NMR spectra containing an additional set of peaks. Both sets of peaks were shifted downfield from the peaks in a sample containing no shift reagent, but all induced shifts were relatively small. At the highest shift reagent concentration, the 9,10-methyl protons appeared at δ 1.71 and 2.01, and the 1,4-methyl protons were at δ 2.73 and 2.91. The higher field signal for both sets of protons had the larger area (3:1 ratio), and this was true for the aryl proton peaks as well.

Single-Crystal X-ray Analysis. A mixture of needles (mp 191–2 °C, sealed tube) and prisms (mp 208–9 °C with changes in the physical appearance of the material at ca. 192 °C) of **2** was physically separated. Measurements were made at ambient temperature on a clear prism crystal of **2** on a Rigaku AFC6S diffractometer with graphite monchromated molybdenum Kα radiation. The crystal had cell dimensions, a = 10.665 (2) Å, b = 15.096 (2) Å, c = 9.582 (1) Å, α = 90.66 (1)°, β = 116.13 (1)°, and γ = 92.42 (1)°. Of the 5171 reflections collected, 4884 were unique. The structure was solved by direct methods.[12,13] Atom scattering factors were taken from Cromer and Waber.[17]

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Supplementary Material Available: Tables of crystallographic data for *cis*-**2** (16 pages); structure factor tables (33 pages). Ordering information is given on any current masthead page.

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