mL, 103 mmol) was added at 0 °C to a stirred solution of the sulfone 4 (17.7 g, 50 mmol) in dry THF (100 mL) under argon. After 30 min, HMPTA (5 mL) and γ-butyrolactone (4.3 g, 50 mmol) were added at -78 °C. The reaction mixture was stirred for 3 h and then allowed to reach room temperature and quenched with aqueous NH_4Cl. The organic phase was extracted with ethyl acetate, washed with brine, dried over Na_2SO_4, and evaporated in vacuo. The crude residue was chromatographed on a silica gel column, eluting with hexane–ethyl acetate (70:30), to separate the unreacted sulfone 4 (3.56 g, 20%) and then the sulfone **5** (12.1 g, 28.3 mmol, 55%): IR (neat) 3400 (m), 1720 (s), 1310 (s), 1070 (s), 1030 cm^{-1} (s); NMR δ 7.5–8.0 (m, 5 H, aromatic), 4.6 (s, 1 H, OCHO), 4.15 (t, 1 H, $CHSO_2$), 3.2–4.0 (m, 6 H, CH_2O), 2.9 (m, 2 H, $CH_2C{=}O$), 2.5 (s, 1 H, OH), 1.0–2.1 (m, 20 H); mass spectrum, *m/e* 339 (M^+ - THPO), 197 (339 - H - $PhSO_2$). Anal. Calcd for $C_{23}H_{36}O_6S$: C, 62.71; H, 8.24; S, 7.26. Found: C, 62.86; H, 8.24; S, 7.21.

1-Hydroxy-12-[(tetrahydro-2*H*-pyran-2-yl)oxy]dodecan-4-one (6). Aluminum amalgam (10 g of Al, 0.37 mol), prepared according to Corey,[8] was added to the solution of sulfone **5** (10.7 g, 25 mmol) in THF–H_2O (9:1, 600 mL), and the mixture was stirred at reflux for 3 h and then cooled and filtered. The solid phase was washed with THF. Most of the solvent was removed in vacuo, ether was added, the aqueous phase was separated, and the organic phase was dried over Na_2SO_4 and concentrated. The crude product **6** was purified by chromatography on a silica gel column, using hexane–ether (7:3), to obtain 6.75 g (22.5 mmol, 85%): IR (neat) 3400 (m), 1715 (s), 1135 (s), 1120 (s), 1075 (s), 1030 cm^{-1} (s); NMR δ 4.6 (s, 1 H, OCHO), 3.1–4.0 (m, 6 H, CH_2O), 2.1–2.8 (m, 5 H, OH and $CH_2C{=}O$), 1.1–2.0 (m, 20 H); mass spectrum, *m/e* 299 (M^+ - H), 283 (M^+ - OH), 199 (M^+ - THPO). Anal. Calcd for $C_{17}H_{32}O_4$: C, 67.96; H, 10.74. Found: C, 68.05; H, 10.72.

4-Oxo-12-[(tetrahydro-2*H*-pyran-2-yl)oxy]dodecanal (7). Pyridinium chlorochromate on alumina[10] (57 g, 45 mmol) was added to a solution of **6** (4.5 g, 15 mmol) in CH_2Cl_2 (80 mL) distilled from P_2O_5. After the mixture was stirred for 3 h at room temperature, the solvent was evaporated, ether was added, and the solid phase was filtered and washed with ether. The organic phase was concentrated and the residue was chromatographed on a silica gel column, eluting with hexane–ether (7:3), to obtain the pure compound **7** (3.0 g, 10 mmol, 67%): IR (neat) 1720 (s), 1030 cm^{-1} (s); NMR δ 9.8 (s, 1 H, CHO), 4.55 (s, 1 H, OCHO), 3.1–4.0 (m, 4 H, CH_2O), 2.2–2.9 (m, 6 H, $CH_2C{=}O$), 1.2–2.0 (m, 18 H); mass spectrum, *m/e* 298 (M^+), 255 (M^+ - CH_2CHO), 197 (M^+ - THPO). Anal. Calcd for $C_{17}H_{30}O_4$: C, 68.42; H, 10.13. Found: C, 68.70; H, 10.10.

2-[7-[(Tetrahydro-2*H*-pyran-2-yl)oxy]heptyl]cyclopent-2-en-1-one (8). The γ-keto aldehyde **7** (2.53 g, 8.5 mmol) was added to 1% aqueous NaOH (100 mL) and the mixture was stirred at 70 °C for 1 h. The organic phase was extracted with ether, dried (Na_2SO_4), and evaporated. The crude residue was chromatographed on a silica gel column, eluting with hexane–ether (8:2), to obtain the pure cyclized compound **8** (1.43 g, 5.1 mmol, 60%): IR (neat) 1710 (s), 1630 (m), 1130 (s), 1070 (s), 1030 cm^{-1} (s); NMR δ 7.4 (s, 1 H, vinylic), 4.6 (s, 1 H, OCHO), 3.3–4.0 (m, 4 H, CH_2O), 2.0–2.8 (m), 6 H, $CH_2C{=}O$), 1.2–1.8 (m, 16 H); mass spectrum, *m/e* 280 (M^+), 179 (M^+ - THPO). Anal. Calcd for $C_{17}H_{28}O_3$: C, 72.82; H, 10.06. Found: C, 72.80; H, 10.07.

2-(6-Carboxyhexyl)cyclopent-2-en-1-one (9). Aqueous 8 N chromic acid[16] was slowly nadded to a solution of compound **8** (1.29 g, 4.6 mmol) in acetone (10 mL), freshly distilled from $KMnO_4$, under stirring. When the reaction was complete, 2-propanol (1 mL) was added, and the solid was filtered and washed with acetone. Most of the solvent was evaporated in vacuo, aqueous 10% NaOH was added, and the neutral organic materials were extracted with ether. The aqueous phase was acidified with HCl, and the organic acids were extracted with ethyl acetate. The organic phase was dried (Na_2SO_4) and concentrated. The acid **9** was isolated by preparative TLC on silica gel, eluting with hexane–ethyl acetate (1:1), collecting 0.676 g of product (3.2 mmol, 70%): mp, 37–38 °C (lit.[4a] mp 37–38 °C); IR (Nujol mull) 1735 (s), 1710 (s), 1670 (s), 1620 (s), 1220 (s), 1165 cm^{-1} (s); NMR δ 10.9 (s, 1 H, CO_2H), 7.3 (s, 1 H, vinylic), 2.0–3.0 (m, 8 H), 1.5–2.0 (m, 8H); mass spectrum, *m/e* 210 (M^+), 192 (M^+ - H_2O). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.41; H, 8.61.

Registry No. **2** (R = H), 96-48-0; **4**, 79918-30-2; **5**, 79918-31-3; **6**, 79918-32-4; **7**, 79918-33-5; **8**, 79918-34-6; **9**, 5239-43-0; 1,8-octanediol, 629-41-4; 1,8-diiodooctane, 24772-63-2; 8-iodo-1-octanol, 79918-35-7; 2-(8-iodooctan-1-oxy)tetrahydropyran, 53596-83-1; 8-[(tetrahydropyran-2-yl)oxy]octane benzenesulfinate, 79918-36-8.

Homoallylic Coupling in 1,4-Dihydronaphthalenes. 3. Crystal Structure of 1,4-Dihydronaphthoic Acid

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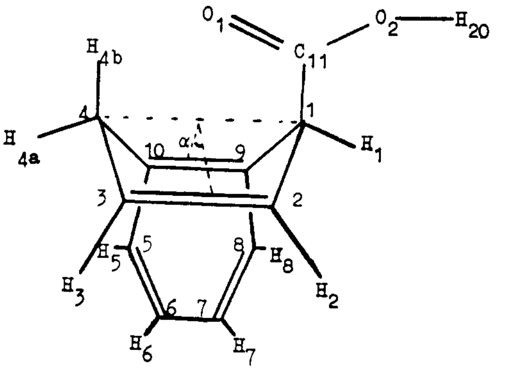
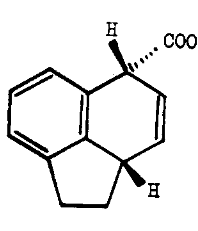
The precise conformations of simple dihydronaphthalenes in solution remain uncertain despite much discussion[1-9] of the interpretation of their solution NMR data. Marshall and co-workers originally suggested[1,2] that 1,4-dihydronaphthoic acid adopts a flattened boat geometry (1) in which the carboxyl group is placed pseudoaxially, whereas a more puckered conformation (α = ca. 150°) was initially suggested by Rabideau.[3] A subsequent study of ^{13}C–^{13}C and ^{13}C–^{1}H couplings about ^{13}C-labeled dihydro aromatic acids provided clear evidence that the conformation of 1 lies somewhere between the effectively planar 1,4-dihydrobenzoic acid and the highly puckered (α = 145°) 9,10-dihydroanthroic acid.[4] In the meantime, we had prepared a rigid, highly puckered dihydronaphthalene (2)[5] and had determined its conformation (α = 146.5°) by X-ray crystallography.[6] This work clearly established a



(1)



(2)

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‡ Bedford College.

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Table I. Observed and Calculated ^1H NMR Coupling Constants for 1,4-Dihydronaphthoic Acid (1)

	J, Hz				J, Hz		
atoms	obsd[a]	calcd[b,d]	calcd[c,d]	atoms	obsd[a]	calcd[b,d]	calcd[c,d]
1,2	4.6	4.3	5.1	2,4a	−1.2	0.6	−1.4
1,3	−1.2	−0.6	−1.4	2,4b	−3.0	−2.6	−3.1
1,4a	3.8			3,4a	4.6	4.3	5.1
1,4b	4.4			3,4b	2.4	2.7	3.3
2,3	9.6			4a,4b	−21.9		

[a] See references 1 and 2. [b] References 5, 11, and 12. [c] Reference 4. [d] Assumes α = 169.2°.

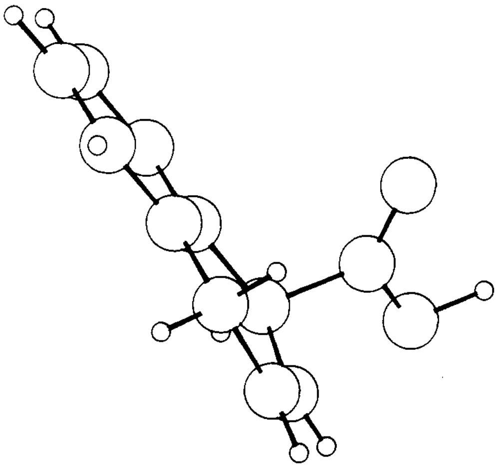

Figure 1. Solid-state geometry of 1,4-dihydronaphthoic acid (1) showing the "flattened boat" conformation.

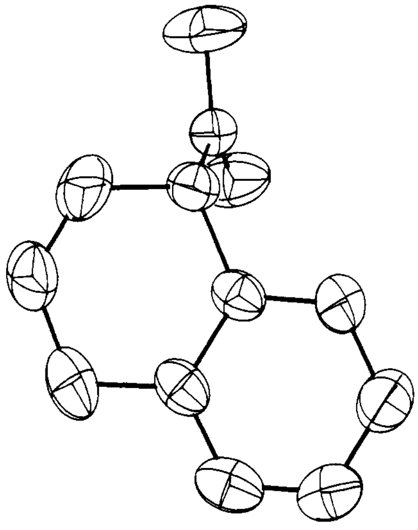

Figure 2. Carbon and oxygen skeleton of 1,4-dihydronaphthoic acid (1): thermal ellipsoids represents 50% probability surfaces.

Table II. Bond Angles (Degrees) about 1,4-Dihydronaphthoic Acid (1) with Estimated Standard Deviations in Parentheses

C(2)-C(1)-C(9)	111.3 (2)	C(7)-C(8)-C(9)	119.8 (2)
C(2)-C(1)-C(11)	104.7 (2)	C(1)-C(9)-C(8)	117.5 (2)
C(9)-C(1)-C(11)	115.1 (2)	C(1)-C(9)-C(10)	125.3 (2)
C(1)-C(2)-C(3)	121.8 (3)	C(8)-C(9)-C(10)	117.2 (2)
C(2)-C(3)-C(4)	128.3 (2)	C(4)-C(10)-C(5)	118.1 (2)
C(3)-C(4)-C(10)	111.9 (2)	C(4)-C(10)-C(9)	119.9 (2)
C(6)-C(5)-C(10)	120.4 (2)	C(5)-C(10)-C(9)	122.0 (2)
C(5)-C(6)-C(7)	117.3 (2)	C(1)-C(11)-O(1)	121.8 (2)
C(6)-C(7)-C(8)	123.4 (3)	C(1)-C(11)-O(2)	115.2 (2)
O(1)-C(11)-O(2)	123.1 (2)		

model for a highly puckered dihydronaphthalene ring and consequently supported the view that 1 adopts a more planar geometry than 2 in solution. At the same time, Rabideau analyzed in detail the ^1H NMR spectra of several other dihydronaphthalenes and was able to demonstrate unequivocally that bulky C-1 substituents increase ring puckering, thereby minimizing steric interaction with the peri proton H-8.[7] There seems to be general agreement that 1,4-dihydronaphthoic acid (1) is "somewhat puckered but not truly boat shaped",[8] but its exact geometry remains undefined.[9]

We have now completed a single-crystal X-ray structure determination of 1. In the solid state, it adopts a boat geometry with α = 169.2° and the carboxyl substituent in a pseudoaxial position (Figures 1 and 2). This conformation closely corresponds to the "flattened boat" proposed by Marshall.[10] We have used the crystallographic geometry to predict values for proton–proton couplings about the dihydroaromatic ring. A comparison of the computed and experimental values (Table I) shows good agreement for the vicinal and allylic couplings, particularly since no allowance has been made for substituent effects. It is significant that the flattened boat conformation is entirely consistent with a marked difference in the magnitudes of the pseudoaxial and pseudoequatorial vicinal couplings, a feature that has previously caused controversy in the interpretation of the ^1H NMR data.[3]

The significance of the homoallylic couplings $J_{1,4a}$ and $J_{1,4b}$ about 1 is uncertain because it is not yet possible to make satisfactory theoretical predictions of these quantities in a dihydronaphthalene skeleton, and further experimental data would be helpful. Rabideau[7] has reiterated earlier views[11] that, in principle, homoallylic coupling constants, or their ratios ($^5J_{cis}/^5J_{trans}$), should provide a particularly sensitive probe into the conformations of dihydroaromatic rings. He has interpreted these data in terms of two conformational types: either "highly puckered" or "less puckered (but not planar)",[7] corre-

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(10) Marshall calculates[4] couplings for a "flattened boat" geometry having a degree of puckering (α) of ca. 167° (N.B. the angle α used in ref 4 *does not correspond with* the angle α used in the present work; great care should be taken to avoid any confusion). Marshall also refers[4] to a "true boat" for which α = ca. 140°.

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Table III. Bond Lengths (Å) in 1,4-Dihydronaphthoic Acid (1) with Estimated Standard Deviations in Parentheses

C(1)-C(2)	1.395 (3)	C(11)-O(1)	1.167 (2)
C(1)-C(9)	1.491 (3)	C(11)-O(2)	1.302 (3)
C(1)-C(11)	1.471 (3)	C(1)-H(1)	0.997 (24)
C(2)-C(3)	1.294 (4)	C(2)-H(2)	0.891 (31)
C(3)-C(4)	1.451 (4)	C(3)-H(3)	0.960 (35)
C(4)-C(10)	1.408 (3)	C(4)-H(4a)	0.952 (33)
C(5)-C(6)	1.288 (4)	C(4)-H(4b)	1.032 (30)
C(5)-C(10)	1.378 (3)	C(5)-H(5)	0.971 (30)
C(6)-C(7)	1.355 (4)	C(6)-H(6)	1.000 (30)
C(7)-C(8)	1.357 (3)	C(7)-H(7)	0.925 (34)
C(8)-C(9)	1.308 (3)	C(8)-H(8)	0.932 (29)
C(9)-C(10)	1.365 (3)	O(2)-H(20)	1.007 (44)

sponding to Marshall's "true boat" and "flattened boat", respectively.[4] We have now established the solid-state geometries of a representative dihydronaphthalene from each of these limiting cases.

Experimental Section

1,4-Dihydronaphthoic acid was prepared as previously described[1] and crystallized from ethanol.

Crystal data: $C_{11}H_{10}O_2$; $M_r = 174$; $a = 5.566$ (1), $b = 6.146$ (1), $c = 29.170$ (4) Å; $\beta = 86.48$ (1)°; $V = 817.1$ Å^3; $D_c = 1.2$, $D_m = 1.2$ (by floatation); monoclinic, space group $P2_1/c$; $Z = 4$; λ(Mo Kα) = 0.71069 Å.

Initial survey photographs exhibited the systematic absences $0kl$ with $l = 2n + 1$ and $h00$ with $h = 2n + 1$ with no general conditions, indicating the space group $P2_1/c$ with b unique. A selected crystal (0.8 × 0.4 × 0.4 mm) was then mounted on an Enraf-Nonius CAD-4F four-circle diffractometer. An approximate orientation matrix was derived from the coordinates of 21 reflections observed on a rotation photograph; these reflections were automatically centered. The orientation matrix and cell parameters were optimized by a least-squares refinement using the angular coordinates of 25 reflections with $16 < \theta < 18°$.

Automatic data collection by using bisecting geometry yielded 2468 reflections. Four absorption curves were also collected. After application of Lorentz and polarization corrections, the data were merged to give 1371 independent structure amplitudes with $I > 3\sigma(I)$, where I is the final intensity and $\sigma(I)$ is the standard deviation derived from counting statistics.

The structure was solved by direct methods with MULTAN[13] and refined by least-squares[14] methods with the block-diagonal approximation to the full normal matrix. All the hydrogen atoms were evident from a difference Fourier synthesis, and the structure was further refined by full-matrix least-squares methods on a CDC 7600 computer. A three-term Chebyshev series was used as a weighting scheme[15] for the final cycles of refinement, which included the positional parameters and temperature factors (which were anisotropic for the carbon and oxygen atoms).

A comparison of F_{obsd} and F_{calcd} values showed that a correction for the effects of absorption was not necessary despite the rather large size of the crystal used, but one reflection having $F_{obsd} > 2200$ was excluded from the final cycles of refinement. A final R of 0.0484 ($R_w = 0.0676$) was obtained. Bond lengths and angles are presented in Tables II and III.

Registry No. 1, 5111-73-9.

Supplementary Material Available: Tables of atomic coordinates together with observed and calculated factors and thermal parameters for the carbon and oxygen atoms (12 pages). Ordering information is given on any current masthead page.

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Improved Syntheses of (±)-*trans*-9,10-Dihydroxy-9,10-dihydrobenzo[*a*]pyrene and of (±)-*trans*-1,2-Dihydroxy-1,2-dihydrodibenz[*a*,*h*]anthracene

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Non-K-region dihydro diols of polycyclic aromatic hydrocarbons (PAH) generated by the epoxide hydrolase mediated hydration of metabolically formed arene oxides play an important role in the metabolism of PAH.[1-6] They are precursors of dihydro diol epoxides some of which are considered ultimate carcinogenic metabolites of PAH.[7-10]

From the two most thoroughly tested carcinogenic unsubstituted PAH, benzo[*a*]pyrene and dibenz[*a*,*h*]anthracene (DBA), only the non-K-region dihydro diols with the olefinic bond in the bay region,[11] *trans*-7,8-dihydroxy-7,8-dihydrobenzo[*a*]pyrene and *trans*-3,4-dihydroxy-3,4-dihydrodibenz[*a*,*h*]anthracene, have been intensively studied.

The biological role of the non-K-region dihydro diols of these hydrocarbons, **6b** and **13b**, where the olefinic bond is not part of the bay region (in **13b** the position of the double bond is called the M region[12]) is much less well-known, although **6b** and **13b** are formed metabolically in considerable amounts.[13,14] The apparent lack of interest in the dihydro diols **6b** and **13b** stems partly from the fact that their syntheses described in the literature[10,15,16] are more difficult than those of the better studied isomers.[10,16-18]

We therefore devised improved synthetic pathways for **6b** and **13b** that resulted in a six-step synthesis of **6b** (Scheme I) and an eight-step synthesis of **13b** (Scheme II) starting with commercially available compounds.

For the synthesis of **6b**, 9,10-dihydrobenzo[*a*]pyren-7(8*H*)-one was transformed to **1**. McCaustland et al.[15] do not recommend the Huang-Minlon procedure[19] for this deoxygenation possibly because of azine formation; they used instead the more laborious Wolff–Kishner method as originally described for the synthesis of **1**.[20]

We found, however, that **1** can be prepared from 9,10-dihydrobenzo[*a*]pyren-7(8*H*)-one in very good yield if the Huang-Minlon procedure is slightly modified.

Dehydrogenation of **1** to **2** was achieved with DDQ according to Fu et al.[21] in 65% yield. Due to its tendency to aromatize **2** was never obtained free of benzo[*a*]pyrene. Since this hydrocarbon can be easily removed in the next step, no attempt was made to purify **2**.

The dehydrogenated mixture of hydrocarbons containing **2** was subjected to a Prêvost reaction with silver benzoate, yielding **3a** which was contaminated with a small amount of the cis isomer **4a**. McCaustland et al.[15] achieved the separation of the geometrical isomers on the level of the tetrahydro diols **3b** and **4b** by fractional crystallization. This method according to our own experience does not always work well. One recrystallization of the mixed dibenzoates **3a** and **4a** from $CHCl_3$–MeOH, however, furnished easily the *trans*-dibenzoate **3a** in 62% yield without a trace of **4a**. The purity was checked by TLC after methanolysis of **3a** and **4a**. It is interesting to note that the *trans*-dibenzoate **3a** has a higher mobility on silica gel

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† This study is part of the M.S. theses of G.S. and H.F.

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