

Homoallylic Coupling in 1,4-Dihydronaphthalenes. Part 2.¹ Crystal Structure of *cis*-2a,5-Dihydro-5-acenaphthoic Acid

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The structure of the title compound (1) has been determined by direct methods from single-crystal X-ray diffractometer data. Crystals are triclinic, space group $P\bar{1}$, with $Z = 2$, in a cell with lattice parameters $a = 8.446(4)$, $b = 8.534(4)$, $c = 8.940(3)$ Å, $\alpha = 122.95(4)^\circ$, $\beta = 107.48(3)^\circ$, and $\gamma = 70.32(3)^\circ$. 2 534 independent reflections gave a final R of 0.057. The dihydronaphthalene ring adopts a highly puckered boat conformation. Good agreement is found between interproton couplings predicted from the crystallographic structure and the experimental values.

From a recent detailed study¹ of the n.m.r. spectrum of *cis*-2a,5-dihydro-5-acenaphthoic acid (1) it was concluded that in this compound the 1,4-dihydronaphthalene ring is held in a rigid and highly puckered boat conformation. A value of α ,† the angle of fold, of between 140 and 150° was suggested from the measured vicinal, allylic, and homoallylic couplings about the dihydrobenzene ring. However, it was not clear from the spectral data whether this ring was symmetrically puckered, or if there was twisting about the olefinic bond. In order to confirm our predictions and to establish the actual dihedral angles between the various interacting protons, information which would allow a direct comparison of the experimental and calculated^{2,3} coupling constants, we have now determined the crystal structure of this compound.

† The angle α is that between the planes defined by the double bonds of the dihydrobenzene ring, *i.e.* between the planes C(2a)–C(3)–C(4)–C(5) and C(2a)–C(1b)–C(5a)–C(5) (see ref. 1).

¹ M. C. Gossel and R. C. Hayward, *J.C.S. Perkin II*, 1976, 851, is regarded as Part 1.

² M. Barfield and S. Sternhell, *J. Amer. Chem. Soc.*, 1972, **94**, 1905.

³ M. Barfield, A. M. Dean, C. J. Fallick, R. J. Spear, S. Sternhell, and P. W. Westerman, *J. Amer. Chem. Soc.*, 1975, **97**, 1482.

The structures of several 1,4-dihydrobenzenes and analogous systems have previously been determined by X-ray crystallography. Cyclohexa-1,4-dienylglycine (2)⁴ and *anti*-1,2,4,5-tetraphenyl-3,6-dimethoxycarbonylcyclohexa-1,4-diene (3)⁵ have both been shown to contain a planar cyclohexadiene ring, in agreement with n.m.r. studies of several 1,4-dihydrobenzoic acids.⁶ However, these results need not reflect an inherent conformational preference since crystal lattice forces may dominate here. Indeed, whilst 9,10-dihydroanthracene is puckered, 9,10-dihydro-1,2,5,6-dibenzanthracene adopts a planar conformation in the crystal.⁷ 4'-Bromo-*trans*-1,4-dihydro-4-tritylbiphenyl (4a) has α 165°.⁸ The n.m.r. spectrum of the related compound (4b) also suggests a puckered cyclohexadiene ring (it is unlikely that variation of the substituent X should have

⁴ R. J. Jandacek and S. H. Simonsen, *J. Amer. Chem. Soc.*, 1969, **91**, 6663.

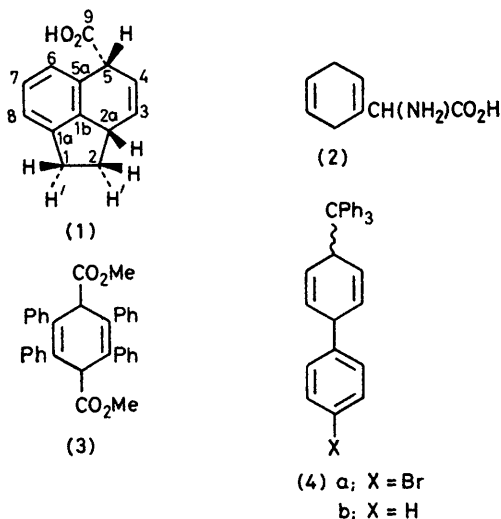
⁵ M. J. Bennett, J. T. Purdham, S. Takada, and S. Masamune, *J. Amer. Chem. Soc.*, 1971, **93**, 4063.

⁶ M. C. Gossel and M. J. Perkins, *J.C.S. Perkin II*, 1975, 1544.

⁷ J. Iball and D. W. Young, *Acta Cryst.*, 1958, **11**, 476.

⁸ D. J. Atkinson and M. J. Perkins, *Tetrahedron Letters*, 1969, 2335.

a significant effect on the conformation here). However, the observation⁹ that vicinal and allylic couplings are not identical in the *cis*- and *trans*-isomers of (4b) suggests that the conformations of these may not be



identical, making comparison of crystallographic and n.m.r. data difficult.

The present study is the first in which a 1,4-dihydrobenzene or 1,4-dihydronaphthalene ring is held in a rigid conformation* thus removing any ambiguities in the comparison of its solid-state structure and its spectroscopic properties.

EXPERIMENTAL

cis-2a,5-Dihydro-5-acenaphthoic acid was prepared as previously described¹ and crystallised from acetonitrile.

TABLE 1

Fractional atomic co-ordinates for carbon and oxygen atoms, with estimated standard deviations in parentheses

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
C(5a)	0.969 8(1)	0.596 5(2)	0.358 2(1)
C(5)	0.789 4(2)	0.575 7(2)	0.330 9(2)
C(4)	0.733 9(2)	0.438 7(2)	0.135 0(2)
C(3)	0.840 1(2)	0.290 9(2)	0.029 5(2)
C(2a)	0.026 5(2)	0.253 0(2)	0.097 0(2)
C(2)	0.157 2(3)	0.169 8(2)	-0.030 6(2)
C(1)	0.316 2(3)	0.246 7(3)	0.093 9(2)
C(1a)	0.241 4(2)	0.435 8(2)	0.245 4(2)
C(8)	0.308 1(2)	0.595 5(2)	0.373 1(2)
C(7)	0.204 2(2)	0.755 6(2)	0.491 7(2)
C(6)	0.036 3(2)	0.758 4(2)	0.484 2(2)
C(1b)	0.076 4(2)	0.437 7(2)	0.243 7(1)
C(9)	0.665 1(1)	0.765 9(2)	0.401 5(2)
O(1)	0.670 5(1)	0.861 4(2)	0.574 4(1)
O(2)	0.564 6(1)	0.823 4(2)	0.299 9(1)

Crystal Data.—C₁₃H₁₂O₂, Triclinic. *M* = 200.24, *a* = 8.446(4), *b* = 8.534(4), *c* = 8.840(3) Å, α = 122.95(4)°, β = 107.48(3)°, γ = 70.32(3)°, *U* = 503.5 Å³, *D*₀ = 1.31 g cm⁻³ (by flotation), *Z* = 2, *D*_c = 1.32 g cm⁻³. Mo-*K*_α radiation, λ = 0.710 69 Å, μ(Mo-*K*_α) = 0.7 cm⁻¹. Space group P1̄.

* 1,4-Bridged structures, e.g. norbornadiene, are more difficult to study because the small pseudo-equatorial-pseudo-equatorial coupling present, and the possibility of further coupling pathways through the σ framework.

⁹ L. Benati, M. Tiecco, A. Tundo, and F. Taddei, *J. Chem. Soc. (B)*, 1970, 1443.

After preliminary photography using oscillation, Weissenberg, and precession techniques, a selected crystal (ca. 0.8 × 0.6 × 0.5 mm) was set up on a Hilger and Watts PDP8-controlled four-circle diffractometer. Accurate cell parameters and orientation matrix were obtained by the least-squares refinement of the setting angles of 29 reflections. The intensity of each independent reflection

TABLE 2

Atomic co-ordinates and isotropic temperatures factor (Å)² for hydrogen atoms, with estimated standard deviations in parentheses

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{iso}
H(5)	0.791 (2)	0.521 (2)	0.404 (2)	0.025 (4)
H(4)	0.609 (3)	0.464 (3)	0.090 (3)	0.047 (5)
H(3)	0.204 (3)	0.793 (3)	0.095 (3)	0.046 (5)
H(2a)	0.052 (2)	0.164 (3)	0.147 (2)	0.032 (4)
H(2')	0.892 (3)	0.772 (3)	0.111 (3)	0.046 (6)
H(2)	0.810 (3)	0.981 (3)	0.097 (3)	0.055 (6)
H(1')	0.392 (3)	0.158 (3)	0.140 (3)	0.058 (6)
H(1)	0.373 (3)	0.268 (3)	0.029 (3)	0.061 (6)
H(8)	0.426 (3)	0.596 (3)	0.381 (3)	0.049 (6)
H(7)	0.752 (2)	0.128 (3)	0.420 (2)	0.033 (5)
H(6)	0.032 (2)	0.125 (3)	0.427 (2)	0.029 (4)
H(OH)	0.431 (3)	0.013 (4)	0.381 (4)	0.080 (8)

with θ < 30° was measured by an ω—2θ scan with ordinate analysis.¹⁰ Mo-*K*_α radiation from a graphite monochromator was used and 2 908 reflections measured. Lorentz and polarisation corrections were applied, together with an empirical absorption correction.¹¹ The structure was solved by direct methods by use of the program MULTAN.¹² Before refinement, reflections with *I* < 3σ(*I*), where σ is the standard deviation derived from the counting statistics, were rejected, to give a final set of 2 534 independent observed structure amplitudes. Refinement was carried out by full matrix least-squares calculations with individual anisotropic temperature factors in the form

TABLE 3

Bond lengths (Å), with estimated standard deviations in parentheses

C(1)—C(1a)	1.513 (2)	C(9)—O(1)	1.292 (2)
C(1)—C(2)	1.541 (3)	C(9)—O(2)	1.235 (1)
C(1a)—C(1b)	1.384 (2)		
C(1a)—C(8)	1.384 (2)	C(1)—H(1)	0.97(2)
C(2)—C(2a)	1.540 (2)	C(1)—H(1')	1.00(2)
C(2a)—C(1b)	1.500 (2)	C(2)—H(2)	1.06(2)
C(2a)—C(3)	1.498 (2)	C(2)—H(2')	1.00(2)
C(3)—C(4)	1.318 (2)	C(2a)—H(2a)	1.01(2)
C(4)—C(5)	1.518 (2)	C(3)—H(3)	0.98(2)
C(5)—C(5a)	1.524 (2)	C(4)—H(4)	1.00(2)
C(5)—C(9)	1.507 (2)	C(5)—H(5)	0.98(2)
C(5a)—C(6)	1.394 (2)	C(6)—H(6)	0.99(2)
C(5a)—C(1b)	1.385 (2)	C(7)—H(7)	0.98(2)
C(6)—C(7)	1.392 (2)	C(8)—H(8)	0.98(2)
C(7)—C(8)	1.392 (2)	O(1)—H(OH)	1.08(3)

$\exp[-2\pi^2(U_{11}ha^{*2} + U_{22}kb^{*2} + U_{33}lc^{*2} + 2U_{23}kblb^{*c*} + 2U_{31}hka^{*a*} + 2U_{12}hka^{*b*})]$. All the hydrogen atoms were located on an electron-density difference map. The co-ordinates and individual isotropic thermal factors of the hydrogen atoms were then refined. After the last two cycles of least-squares refinement of all the parameters a final *R* of 0.057 was obtained. Scattering factors of all the

¹⁰ H. C. Watson, D. M. Shotton, T. M. Cox, and H. Muirhead, *Nature*, 1970, 225, 806.

¹¹ A. C. T. North, D. C. Phillips, and F. S. Matthews, *Acta Cryst.*, 1968, A24, 351.

¹² G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, A27, 368.

atoms were taken from ref. 13. Atomic co-ordinates and isotropic thermal factors are given in Tables 1 and 2, bond lengths and angles in Tables 2 and 4 respectively. Final

TABLE 4
Bond angles ($^{\circ}$)

C(1a)-C(1)-C(2)	102.7(1)	C(4)-C(5)-C(9)	112.3(1)
C(1)-C(1a)-C(8)	131.5(1)	C(5a)-C(5)-C(9)	112.4(1)
C(1)-C(1a)-C(1b)	109.3(1)	C(5)-C(5a)-C(1b)	126.7(1)
C(8)-C(1a)-C(1b)	119.2(1)	C(5)-C(5a)-C(6)	115.9(1)
C(1)-C(2)-C(2a)	104.6(1)	C(6)-C(5a)-C(1b)	117.4(1)
C(2)-C(2a)-C(3)	120.0(1)	C(5a)-C(6)-C(7)	119.9(1)
C(2)-C(2a)-C(1b)	101.8(1)	C(6)-C(7)-C(8)	121.6(1)
C(3)-C(2a)-C(1b)	109.5(1)	C(1a)-C(8)-C(7)	118.6(1)
C(3)-C(4)-C(5)	123.0(1)	C(1a)-C(1b)-C(5a)	123.1(1)
C(4)-C(5)-C(5a)	110.7(1)	C(2a)-C(1b)-C(5a)	125.1(1)
C(5)-C(9)-O(1)	114.9(1)	C(5)-C(9)-O(2)	121.9(1)
O(1)-C(9)-O(2)	123.1(1)		

observed and calculated structure factors, and anisotropic thermal parameters for carbon and oxygen, are listed in Supplementary Publication No. SUP 21962 (23 pp., 1 microfiche).*

DISCUSSION

The structure of (1) is shown in Figures 1 and 2. There is remarkably little twisting about the double bond despite the considerable strain present in models of this compound. The actual ring-puckering angle α is

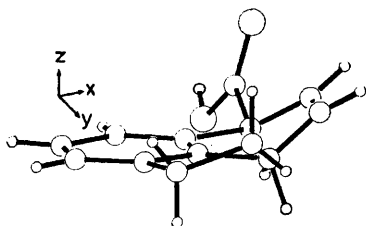


FIGURE 1 *cis*-2a,5-Dihydroacenaphthoic acid (1): a general view

found to be 146.5° , in very close agreement with the previous estimate.¹ The C(2a)-H and C(5)-H bonds are nearly parallel, a situation predicted⁶ to be the most favourable for homoallylic coupling. A projection along the C(5)-C(4) bond reveals that the C(5)-H bond has a dihedral angle of 90° ($\phi_{3,5}$) with respect to the carbon-carbon double bond C(3)-C(4), and of 83° ($\theta_{4,5}$) with respect to the C(4)-H bond where θ defines the dihedral angle between vicinal C-H bonds and ϕ is used to relate the protons H-2a and H-5 to the π -bond. This latter parameter was used by Barfield and co-workers^{2,3} when calculating allylic and homoallylic coupling constants. From a projection along C(2a)-C(3) the corresponding angles are found to have values of 82° ($\phi_{2a,4}$) and 105° ($\theta_{2a,3}$).

Vicinal coupling between a methylene and a vinylic proton (e.g. $J_{2a,3}$ and $J_{4,5}$) varies as $\cos^2 \theta$ ¹⁴⁻¹⁶ having a minimum value of ca. 1.8 Hz. The values of $J_{2a,3}$ and $J_{4,5}$ observed in the n.m.r. spectrum of (1) are

* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1976, Index issue.

¹³ D. T. Cromer and J. B. Mann, Los Alamos Scientific Laboratory Report LA 3816, 1967.

¹⁴ S. Sternhell, *Quart. Rev.*, 1969, **23**, 236, and references therein.

very close to this minimum, but allowance must be made for substituent effects. Using the foregoing values of ϕ , allylic couplings of $J_{2a,4} -3.29$ and $J_{3,5} -3.20$ Hz are predicted from INDO calculations,³ results which agree very well with the experimental observations (-3.22 and -3.09 Hz respectively). The structure of the five-membered ring agrees well with previous observations.¹ For example, the dihedral angle $\theta_{1',2}$ of 92° leads to negligible coupling between H-1' and H-2. $\theta_{1,2}$ and $\theta_{1',2'}$ are both ca. 31° ; accordingly $J_{1,2}$ and $J_{1',2'}$ are of similar magnitude.

In *cis*-3a,6-dihydroindane-6-carboxylic acid (5) a homoallylic coupling of 11.4 Hz is observed.¹ In view of

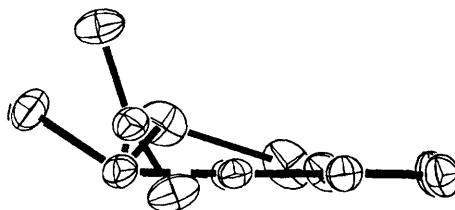
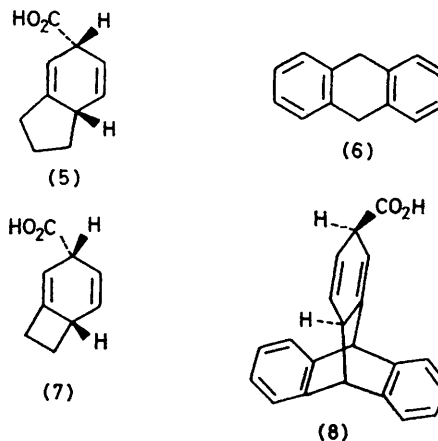


FIGURE 2 Compound (1): carbon skeleton, showing the angle of fold of the dihydronaphthalene ring

the similar substitution pattern about the dihydrobenzene ring in both (1) and (5) it is not unreasonable to expect the value of α to be similar for these two structures (though there will be a slight effect arising from the change in length of the aromatised double bond and in the hybridisation at C-1). If it is assumed that each interaction pathway in (5) is identical, then a coupling constant of ca. 5.7 Hz should be observed through the isolated double bond of (1), thus leaving a value of 2.7 Hz for that through the aromatic ring



here. This agrees quite well with the value of 4.8 Hz estimated⁶ for homoallylic coupling between pseudoaxial protons in 9,10-dihydroanthracene (6), where there are two aromatic interaction pathways; both n.m.r. spectroscopic⁶ and X-ray crystallographic studies¹⁷ of (6) suggest that it adopts a highly puckered

¹⁵ E. W. Garbisch, *J. Amer. Chem. Soc.*, 1964, **86**, 5561.

¹⁶ G. V. Smith and H. Kriloff, *J. Amer. Chem. Soc.*, 1963, **85**, 2016.

¹⁷ W. G. Ferrier and J. Iball, *Chem. and Ind.*, 1954, 1296.

boat conformation with α ca. 145° . For dihedral angles ϕ of 90° and 83° between the double bond and H-2a and H-5 respectively, a homoallylic coupling constant of 5.1 Hz is predicted from the semi-empirical calculations of Barfield and Sternhell.² This is slightly lower than the value estimated for coupling through the double bond in (1). Indeed, whilst the calculated maximum for homoallylic coupling is 10.5 Hz,⁶ values of 12.0 Hz have been observed in (7)¹⁸ and (8).¹⁹ The considerably

reduced magnitude of homobenzylic coupling [ca. 2.5 Hz in (1) and (6)] has been noted elsewhere in *ortho*-disubstituted aromatic systems²⁰ and presumably reflects reduced π -electron bond order in aromatic systems.

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¹⁸ M. C. Gossel and R. C. Hayward, unpublished results.

¹⁹ P. W. Rabideau, J. W. Paschal, and L. E. Patterson, *J. Amer. Chem. Soc.*, 1975, **97**, 5700.

²⁰ L. M. Jackman and S. Sternhell, 'Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon Oxford, 1969, p. 331.