34405-42-0; **4**, 34405-43-1; **5**, 122-09-8; **5** HCl, 1197-21-3; **6**, 5531-33-9.

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## The Conformation of 1,4-Dihydro-1-naphthoic Acid. II. The Nuclear Magnetic Resonance Spectrum of the Heptadeuterio Analog

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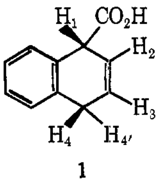
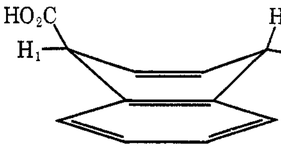
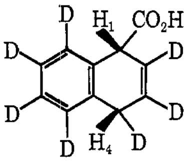
We previously reported[1] that the pmr spectrum of 1,4-dihydro-1-naphthoic acid (**1**) argued for a puckered conformation of the dihydro ring with the carboxylate group in the pseudoaxial position (see **2**) and that all nmr parameters of **1** could be determined from this study except the homoallylic coupling constants $J_{14}$ and $J_{14'}$. We now wish to report the determination of these homoallylic parameters from the pmr spectrum of the heptadeuterio analog **3** and to present a more complete analysis of the conformation of **1**.



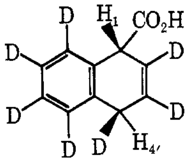
**1**



**2**



**3a** (cis)



**3b** (trans)

The heptadeuterio compound **3** was synthesized in a three-step sequence from perdeuterionaphthalene (see Experimental Section). The deuterium-decoupled pmr spectrum of **3** demonstrated an approximate 50:50 mixture of the *cis*- and *trans*-dihydro epimers (**3a** and **3b**) from the approximately equal areas corresponding to $H_4$ and $H_{4'}$. The $H_4$ and $H_{4'}$ signals were split into doublets, directly giving $J_{14} = J_{\text{cis}} = 3.84$ Hz and $J_{14'} = J_{\text{trans}} = 4.36$ Hz.[2] Since for the proposed conformation of **1** it is to be expected[3] that $J_{14}, > J_{14'}$ these newly determined parameters are consistent with our previous contention that the carboxylate group was pseudoaxial.[1]

This completion of the determination of the pmr parameters for **1** allows a fuller analysis of the conformation of **1**. The similar values of $J_{14}$ and $J_{14'}$ strongly suggest the dihydro ring is nearly flat.[4] Furthermore, a closer inspection of the previously determined parameters[1] of **1** also indicates the dihydro ring is not strongly puckered. First, if the dihydro ring of **1** were a true boat, the dihedral angle involving $H_3$ and $H_{4'}$ would be near 90° and $J_{34'}$ should be much less than the observed value of 2.44 Hz.[6] Second, the allylic coupling constants allow the calculation[5] that the dihedral angle involving $H_2$ and $H_4$ is much larger than 0°.[7] Third, the absolute value of $J_{44'}$[1] is suspiciously large for a highly puckered system,[8] and is much more consistent with a nearly planar ring. Thus, it appears that the conformation of **1** is a "flattened boat" in which the dihydro ring is only slightly puckered and that the pmr data for **1** lead to conclusions consistent with work for other 1,4-cyclohexadienes, in which it has been proposed that this system is planar or only slightly puckered.[9]

### Experimental Section

Nmr spectra were recorded on a JEOL PS-100 spectrometer, using tetramethylsilane as the internal standard and deuteriochloroform as the solvent. Deuterium-decoupling was done with a JEOL deuterium radiofrequency oscillator JNM-RH-D, in conjunction with a JEOL heteronuclear decoupler JNM-SD-HC. Melting points were determined by a Thomas-Hoover melting point apparatus. All deuterated compounds were analyzed by pmr and were found to have a minimum isotopic purity of 98%.

**Naphthalene-$d_8$** (minimum isotopic purity of 98%) was purchased from Diaprep, Inc., Atlanta, Ga.

**1-Bromonaphthalene-$d_7$** was synthesized from naphthalene-$d_8$ in the fully developed bromination procedure[10] to give a 62% yield (9.78 g), bp 95–112° (0.5 mm) [lit.[10] bp 132–135° (12 mm), 1-bromonaphthalene].

**1-Naphthoic acid-$d_7$** was synthesized from the bromo precursor by the usual Grignard procedure[11] to give an 88% yield (7.37 g), mp ($H_2O$) 155–159° (lit.[12] mp 159–160°, 1-naphthoic acid).

**2,3,4,5,6,7,8-Heptadeuterio-1,4-dihydro-1-naphthoic acid (3)** was prepared by the Birch reduction of the perdeuterionaphthoic precursor in the previous manner[1] to give a 73% yield (1.79 g), mp (hexane) 86–88° (lit.[13] mp 86°, **1**).

**Registry No.**—**1**, 5111-73-9; **3a**, 34405-19-1; **3b**, 34405-20-4.

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[1] J. L. Marshall and T. K. Folsom, *J. Org. Chem.*, **36**, 2011 (1971).

[2] The methine signal ($H_1$) was also split into a doublet with $J_{\text{obsd}} = 4.1$ Hz, but resolution was not sufficient to distinguish the two $J$ values.

[3] M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960); M. Barfield, *ibid.*, **48**, 4463 (1968).

[4] The Barfield INDO treatment[5] predicts that, for a flat dihydro ring, $J_{14'}/J_{14} = 1.12$ and that this ratio increases with increased puckering to 3.3 for a true boat (S. Sternhell, private communication). The determined ratio is actually 1.14.

[5] M. Barfield, *J. Amer. Chem. Soc.*, **93**, 1066 (1971).

[6] K. L. Williamson and W. S. Johnson, *ibid.*, **83**, 4623 (1961); M. Karplus, *J. Chem. Phys.* **30**, 11 (1959); S. Sternhell, *Quart. Rev., Chem. Soc.*, **23**, 236 (1969); A. A. Bothner-By, S. Castellano, S. J. Ebersole, and H. Gunther, *J. Amer. Chem. Soc.*, **88**, 2466 (1966).

[7] It can be predicted[5] from the pmr data[1] of 1,4-dihydro-1-naphthoic acid that the dihedral angle involving $H_2$ and $H_4$ is ∼52° and that involving $H_2$ and $H_4$ is ∼68°.

[8] M. Barfield and D. M. Grant, *J. Amer. Chem. Soc.*, **85**, 1899 (1963).

[9] H. Oberhammer and S. H. Bauer, *ibid*, **91**, 10 (1969); M. J. Bennett, J. T. Purdham, S. Takada, and S. Masamune, *ibid.*, **93**, 4063 (1971); R. J. Jandacek and S. H. Simonsen, *ibid*, **91**, 6663 (1969).

[10] H. T. Clarke and M. R. Brethen, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1932, p 121.

[11] J. L. Marshall, K. C. Erickson, and T. K. Folsom, *J. Org. Chem.*, **35**, 2038 (1970).

[12] A. A. Morton, J. B. Davidson, T. R. P. Gibb, Jr., E. L. Little, E. F. Clarke, and A. G. Green, *J. Amer. Chem. Soc.*, **64**, 2250 (1942).

[13] K. Von Auwers and K. Moller, *J. Prakt. Chem.*, **109**, 144 (1925).