Notes

Conformation of 1-Phenyl-1,4-dihydronaphthalene

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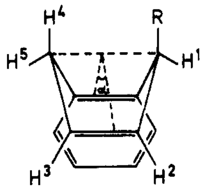
The molecular geometry of 1,4-dihydronaphthalenes has been the subject of several investigations employing NMR spectroscopy[1] and force-field calculations.[2-5] In most studies based on the interpretation of NMR spectra some ambiguity remains due to the uncertainty of the correlation between the homoallylic coupling constants ($^5J_{1,4(\text{trans})}$ and $^5J_{1,4(\text{cis})}$ and the folding angle α as defined in formula A.

A



From force-field calculations it was concluded that 1,4-dihydronaphthalene possesses a planar configuration, but the energy required for nonplanar distortion is small. Substitution at C(1) results in optimum conformations that are not planar. The distortion increases with the steric bulk of the substituent (Table I). The conformation with the substituent in a pseudoaxial (pa) position is much more stable than that with a pseudoequatorial (pe) substituent. Very recently an X-ray analysis of 1,4-dihydronaphthoic acid (2) has been reported.[4] The cyclohexadiene part of this molecule was found to adopt a boat structure with the folding angle α = 169.2° and the carboxylic group occupying a pseudoaxial position. This structure corresponds to the "flattened boat" structure proposed by Marshall[5] and the "somewhat puckered but not truly boat-shaped" structure proposed by Rabideau[6] for this compound.

Previously, we observed[7] that the fraction of 1-phenyl-1,2-dihydronaphthalene having the phenyl group in the pa position is 0.44, in contrast to the marked preference of nonaromatic substituents at C(1) for the pa position.[8]

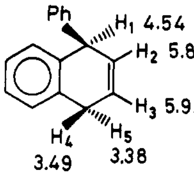
The preference for the pe position of the phenyl group might be due to π-stacking of the phenyl group and the aromatic part of the dihydronaphthalene. When we isolated 1-phenyl-1,4-dihydronaphthalene (1) as a photoproduct from 1-phenyl-benzobicyclo[3.1.0]hex-2-ene,[9] it was of interest to investigate whether the conformation of this compound also deviates from that generally observed for 1-alkyl-1,4-dihydronaphthalenes.

The 500-MHz ^{1}H NMR spectrum of 1 was recorded in $CDCl_3$ solution resonances were assigned by selective ^{1}H-decoupling experiments. Coupling constants and chemical shift values were obtained by means of computer simulations of the experimental spectrum. The chemical shifts are given in formula B. The coupling constants are summarized in Table II, together with corresponding J values for some closely related compounds.

Table I

substituent	calcd folding angle α, deg
H	180^a
CH_3	164^a
t-C_4H_9	149^a

^{a} Reference 3.



B

From the data in Table II the conformational resemblance of 1 and 2 is evident. In comparison with $^5J_{\text{cis}}$ (pa–pa) of 5 (8.5 Hz) and $^5J_{\text{cis}}$ (pe–pe) of 4 (1.8 Hz), $^5J_{\text{cis}}$ values of both 1 and 2 have an intermediate value.

Valuable information can be derived from the allylic couplings $^4J_{1,3}$, $^4J_{2,4}$, and $^4J_{2,5}$. The relative large values of $J_{1,3}$ in 5 and $J_{2,4}$ in 5 and 6 (ca. 3 Hz) show that in these rigid molecules the axially oriented C–H bonds at C(1) or C(4) are almost parallel with the π-orbitals of the olefinic bond;[11] concurrently the small values of $J_{1,3}$ in 4 and 6 and of $J_{2,5}$ in 4 ($\leq$1 Hz) point out that the pe protons of these compounds are nearly in the plane of the double bond.

In 1 and 2 the allylic couplings have intermediate values; therefore, all protons at C(1) and C(4) must have a gauche orientation relative to the π-orbitals of the C(2)–C(3) bond. The small difference between $J_{2,4}$ and $J_{2,5}$ of 1 demonstrates that the relative orientations of both C–H bonds at C(4) with respect to the π-orbitals of the C(2)–C(3) bond are very alike. This points to a rather planar conformation for the cyclohexadiene ring. The slightly smaller values of $J_{1,3}$ and $J_{2,5}$ relative to $J_{2,4}$ indicate that H(1) and H(5) are pseudoequatorial protons. Consequently the phenyl substituent occupies a pa position.

For a further study of the geometry of 1, the vicinal

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(1) P. W. Rabideau, *Acc. Chem. Res.*, **11**, 141 (1978).

(2) K. B. Lipkowitz, P. W. Rabideau, D. J. Raber, L. E. Hardee, P. v. R. Schleyer, A. J. Kos, and R. A. Kahn, *J. Org. Chem.*, **47**, 1002 (1982).

(3) D. J. Raber, L. E. Hardee, P. W. Rabideau, and K. B. Lipkowitz, *J. Am. Chem. Soc.*, **104**, 2843 (1982).

(4) A. K. Cheethan, M. C. Grossel, and D. James, *J. Org. Chem.*, **47**, 566 (1982).

(5) (a) J. L. Marshall and T. K. Folson, *J. Org. Chem.*, **36**, 2011 (1971); (b) J. L. Marshall, A. M. Ihrig, and P. N. Jenkins, *ibid.*, **37**, 1863 (1972); (c) J. L. Marshall, L. G. Faehl, C. R. McDaniel, and N. D. Ledford, *J. Am. Chem. Soc.*, **99**, 321 (1977).

(6) P. W. Rabideau, J. W. Paschal, and L. E. Patterson, *J. Am. Chem. Soc.*, **97**, 5700 (1975).

(7) J. J. M. Lamberts and W. H. Laarhoven, *Recl. Trav. Chim. Pays-Bas*, **102**, 181 (1983).

(8) M. J. Cook and N. L. Dassanyake, *J. Chem. Soc., Perkin Trans. 2*, 1901 (1972).

(9) J. J. M. Lamberts and W. H. Laarhoven, *J. Org. Chem.*, **48**, 2202 (1983).

(10) P. W. Rabideau, E. G. Burkholder, M. J. Yates, and J. W. Paschal, *J. Am. Chem. Soc.*, **99**, 3596 (1977).

(11) (a) S. Sternhall, *Q. Rev.*, **23**, 236 (1969); (b) L. M. Jackman and S. Sternhall in "Applications of NMR Spectroscopy in Organic Chemistry", 2nd ed., Pergamon Press, New York, 1969, p 316.

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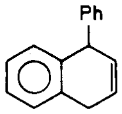
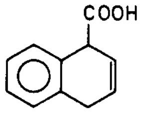
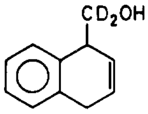
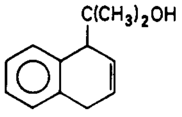
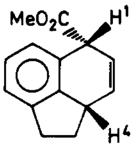
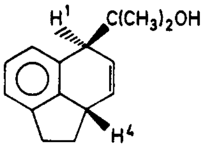
Table II. Coupling Constants of 1-Substituted 1,4-Dihydronaphthalenes[a]

	$J_{1,2}$	$J_{1,3}$	$J_{1,4}$ (*trans*)	$J_{1,5(4)}$ (*cis*)	$J_{2,3}$	$J_{2,4}$	$J_{2,5}$	$J_{3,4}$	$J_{3,5}$	$J_{4,5}$	ref
1. 	3.75	1.3	4.9	4.6	10.4	2.0	1.6	2.95	3.75	22.5	
2. 	4.6	1.2	4.4	3.8	9.6	3.0	1.2	2.4	4.6	21.9	*b*
3. 	3.8	≤1	3.7	3.5	9.9			2.1	3.7	21.0	*c*
4. 	5.2	≤1	3.0	1.8	9.6	2.0	≤1	2.0	5.0	20.5	*c*
5. 	1.6	2.8		8.5	9.6	3.1		1.4			*c*
6. 	5.0	≤1	3.2		9.5	2.8		1.2			*c*

[a] The signs of the coupling constants are not determined. [b] Reference 5. [c] Reference 10.

Table III. Torsion Angles of Compounds 1–6

angle	1	2	3	4	5	6
$H^1C^1C^2H^2$	54	49	54	46	69	47
$H^3C^3C^4H^4$	60	64	67	68	71	73
$H^3C^3C^4H^5$	56	51	57	49		

coupling constants $J_{1,2}$, $J_{3,4}$, and $J_{3,5}$ were analyzed with use of a generalized Karplus equation.[12]

The vicinal couplings of $^3J_{3,5}$ and $^3J_{3,4}$ (in 1–4), $^3J_{1,2}$ (in 1, 3–5), $^3J_{3,4}$ (in 5 and 6), and $^3J_{1,2}$ (in 2) were plotted as a function of the H–H torsion angle.

In Table III the torsion angles of the compounds 1–6 are given as estimated from these plots. Because in all compounds $J_{2,3}$ has the normal value for a torsion-free ethylenic bond, the torsion angles of 1 suggest again a cyclohexadiene ring, which is even more flattened than in 2. The folding angle α must be larger than 170°. In a planar molecule 1 with the angles $H^3C^3C^4H^4$ and $H^3C^3C^4H^5$ both 60° the calculated coupling constants are $J_{3,4} = 2.97$ and $J_{3,5} = 3.20$. It is of interest to note that from the differences between the homoallylic couplings of 2 and 3 it was concluded that 3 adapts a more puckered conformation than 2, whereas the present results point to quite the contrary.

The ^{1}H NMR spectrum of 1 appeared to be temperature independent over a temperature range of about 100 °C (50 to −45 °C), so the inferred near planarity is most probably not the result of averaging of nonplanar conformers.

The nearly planar geometry of 1 could certainly not be expected from the data given in Table I, and the result becomes the more unexpected, because 1-*tert*-butyl-1,4-dihydronaphthalene was more recently reported to have a twisted cyclohexadiene ring.[13] Models show, however, that in the conformation as derived from our study, the interactions between the ortho protons of the phenyl substituent, even a freely rotating one, and both the peri H and H(4) remain small.

The present results are in line with the small space demanding properties of phenyl groups observed in several other cases.[7,14–18]

Experimental Section

1-Phenyl-1,4-dihydronaphthalene was obtained as a product from the irradiation of 1-phenylbenzobicyclo[3.1.0]hex-2-ene.[9] The 500-MHz ^{1}H NMR spectrum of 1 in $CDCl_3$ was recorded by using a Bruker WH-500 spectrometer interfaced to an Aspect-2000 computer. The vicinal couplings as a function of the torsion angles were computed by using the Pascal computer program CAGPLUS.[19]

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Registry No. 1, 13387-49-0.

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(12) C. A. G. Haasnoot, F. A. A. M. de Leeuw, and C. Altona, *Tetrahedron*, **36**, 2783 (1980).

(13) N. L. Holy, H. P. Vail, A. H. Nejad, S. J. Huang, J. L. Marshall, O. Saracoglu, and C. R. McDaniel, *J. Org. Chem.*, **45**, 4271 (1980).

(14) P. W. Rabideau and R. G. Harvey, *J. Chem. Soc., Chem. Commun.*, 1005 (1969).

(15) A. W. Brinkman, M. Gordon, R. G. Harvey, P. W. Rabideau, J. W. Stothers, and A. L. Ternay, *J. Am. Chem. Soc.*, **22**, 5912 (1970).

(16) W. H. Laarhoven, W. H. M. Peters, and A. H. A. Tinnemans, *Tetrahedron*, **34**, 767 (1978).

(17) P. H. G. op het Veld and W. H. Laarhoven, *J. Chem. Soc., Perkin Trans. 2*, 915 (1978).

(18) A. H. A. Tinnemans and W. H. Laarhoven, *Tetrahedron*, **35**, 1537 (1979).

(19) C. A. G. Haasnoot, Abacus Program Library, no ABA037, Bruker Spectrospin AG, Fällandde, Switzerland.