Chemical Shift Anisotropy in (1R)-(+)Camphor and (+)-Nopinone: Geometrical Effects

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Abstract: *Camphor and nopinone are two important building blocks in assymmetric synthesis. They are also convenient models to probe current theories on anisotropy effects and their relative contributions to hydrogen chemical shifts. We have thus calculated geometries and chemical shifts for camphor and nopinone and compared them with experimental data. It is clear that, besides the respective distance between the hydrogen nucleus and the carbonyl group, their relative geometry influences considerably the magnetic field felt by that nucleus.*

Camphor[1,2] **(1)** and nopinone[2] **(2)** are two important building blocks in assymmetric synthesis. They are also convenient models to probe current theories[3,4] on anisotropy effects and their relative contributions to hydrogen chemical shifts. We have thus calculated geometries and chemical shifts for 1 and 2 and compared them with observed values.[1,2] It is clear that, besides the besides the distancefrom the hydrogen nucleus to the carbonyl group, 1 and 2 relative geometriesinfluence considerably the magnetic field felt by that nucleus.

(1R)-(+)Camphor, (+)-nopinone, spectra were acquired in a 5 mm o.d. tube using $CDCl_3$ as solvent and TMS as reference on a Varian Unity Plus 300MHz spectrometer (299.96 MHz for ^{1}H and 75.43MHz for ^{13}C) at 303K. Chemical shifts were calculated using Gaussian 98 program with GIAO method and B3LYP/6-31G(d,p) basis set and CHARGE program for hydrogen chemical shifts.

As observed for camphor[1], ^{13}C and ^{1}H chemical shifts in the vicinity of the carbonyl group show the largest deviation between observed and calculated chemical shifts (Tables 1 and 2). Hydrogen chemical shifts calculated by the CHARGE program are closer to the observed values than to those by Gaussian 98.

The effect of the carbonyl group on methyl and methylene hydrogens in its vicinity is evaluated by comparison. For **1**, H_{3a} and H_{3e} are almost equally deshielded (0.4 – 0.5 ppm) relative to H_{5a} and H_{5e}, respectively, while for **2** this effect is ca 0.6 ppm for H_{3a} relative to H_{4a} and ca 0.2 for H_{3e} relative to H_{4e}. In terms of methyl groups, 1 shows a difference of ca between the two methyl groups, (IC) and this difference increases to almost 0.5 ppm in **2**. The shorter average distance from the *syn*

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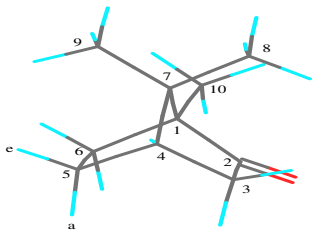
methyl group on **2** could partially account for its larger shielding relative to the *anti* methyl group as compared to **1**. But this cannot be the whole picture. For **2**, H_{3e} is closer to the carbonyl group, but is relatively less deshielded than H_{3a}, while for **1** H_{3e} and H_{3a} are relatively equally distant from the carbonyl group and almost equally deshielded. These observations may be rationalized by the O-C_2-C_3-H_3 dihedral angles. While for **1** they are approximately 60^0, for **2** they are 70^0 for $H_{3a,}$ and 40^0 for $H_{3e.}$ Thus, there must be an angular component to the anisotropy of the carbonyl group although it may not correspond to the model proposed by McConnel.[5]



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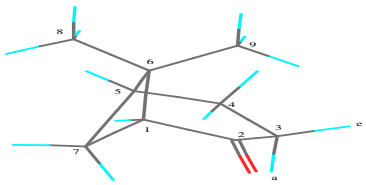

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Table 1. Observed and calculated Hydrogen Chemical Shift of **1** and **2**.

H	CAMPHOR (1)					NOPINONE (2)				
	Obs ppm	**Calc. CHARGE**	**Δ**	**Calc. Gaussian**	**Δ**	**Obs ppm**	**Calc. CHARGE**	**Δ**	**Calc. Gaussian**	**Δ**
H_1	---	---	---	---	---	2.65	2.61	0.04	2.48	0.17
H_{3a}	1.84 (d)	1.83	0.01	1.36	0.48	2.48	2.40	0.08	2.49	-0.01
H_{3e}	2.35 (dt)	2.52	-0.17	2.33	0.02	2.34	2.13	0.21	2.18	0.21
H_4	2.09 (t)	2.15	-0.06	2.01	0.08	---	---	---	---	---
H_{4a}	---	---	---	---	---	1.89	1.97	-0.1	1.92	0.05
H_{4e}	---	---	---	---	---	2.11	2.39	-0.28	2.00	0.11
H_5	---	---	---	---	---	2.24	2.29	-0.05	2.23	0.01
H_{5a}	1.34 (m)	1.41	-0.07	1.31	0.03	---	---	---	---	---
H_{5e}	1.95 (m)	2.05	-0.10	2.05	-0.10	---	---	---	---	---
H_{6a}	1.41 (m)	1.68	-0.27	1.43	-0.02	---	---	---	---	---
H_{6e}	1.67 (m)	1.94	-0.27	1.81	-0.14	---	---	---	---	---
H_{7a}	---	---	---	---	---	1.59	1.75	-0.16	1.60	-0.01
H_{7e}	---	---	---	---	---	2.48	2.14	0.34	2.42	0.06
H_{11}	0.84 (s)	1.03	-0.19	1.45	-0.61	1.33	1.00	0.33	1.01	0.32
H_{12}	0.84 (s)	1.03	-0.19	0.55	0.29	1.33	1.00	0.33	1.67	-0.34
H_{13}	0.84 (s)	1.03	-0.19	0.89	-0.05	1.33	1.00	0.33	1.04	0.29
H_{14}	0.96 (s)	0.95	0.01	0.94	0.02	0.86	0.94	-0.08	0.81	0.05
H_{15}	0.96 (s)	0.95	0.01	0.80	0.16	0.86	0.94	-0.08	0.92	-0.06
H_{16}	0.96 (s)	0.95	0.01	0.91	0.05	0.86	0.94	-0.08	1.05	-0.19
H_{17}	0.91 (s)	0.96	-0.05	1.24	-0.33	---	---	---	---	---
H_{18}	0.91 (s)	0.96	-0.05	0.91	0.00	---	---	---	---	---
H_{19}	0.91 (s)	0.96	-0.05	0.89	0.02	---	---	---	---	---

Table 2. Observed and Calculated Carbon-13 Chemical Shift of **1** and **2**.

C	CAMPHOR (1)			NOPINONE (2)		
	Obs. ppm	Calc. ppm	Δ	Obs. ppm	Calc. ppm	Δ
C_1	57.2	61.1	3.9	57.3	54.5	2.9
C_2	218.8	209.5	9.3	214.0	180.3	33.7
C_3	42.8	43.9	1.1	32.1	33.9	1.8
C_4	42.6	46.2	3.6	20.7	24.1	3.4
C_5	26.6	29.8	3.2	39.8	42.8	3.0
C_6	29.5	32.4	2.9	40.5	45.3	4.8
C_7	46.3	50.9	4.6	24.6	27.5	2.9
C_8	19.3	21.2	1.9	25.3	26.1	0.8
C_9	18.7	20.5	1.8	21.5	22.4	0.9
C_{10}	8.8	12.5	3.7	---	---	---

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