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NMR STUDIES OF 2-ARYL DERIVATIVES OF BENZIMIDAZOLE, BENZIMIDAZOLIUM ION, AND BENZIMIDAZOLINE

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Abstract – A series of 2-arylbenzimidazoles, 2-aryl-1,3-dimethylbenzimidazolium iodides, and 2-aryl-1,3-dimethylbenzimidazolines were prepared and their NMR spectra were examined. The substituent parameters were calculated for 2-benzimidazolyl, 2-benzimidazoliumyl, and 2-benzimidazolinyl groups on the chemical shifts of the protons and the carbons of benzene ring. The 2-benzimidazoliumyl group was found to cause a significant up-field shift of the *ipso*-carbon signal and down-field shift for the *ortho*- and *para*-carbon signals. On the other hand, the 2-benzimidazolyl and the 2-benzimidazolinyl groups cause down-field shift of the *ipso*-carbon signals but cause almost negligible change on the other carbon signals.

INTRODUCTION

Benzimidazole has been one of the subjects that are widely investigated. Countless reports on physical properties, biological activities, reactions, and synthesis of benzimidazole and its derivatives can be found in literature.[1]

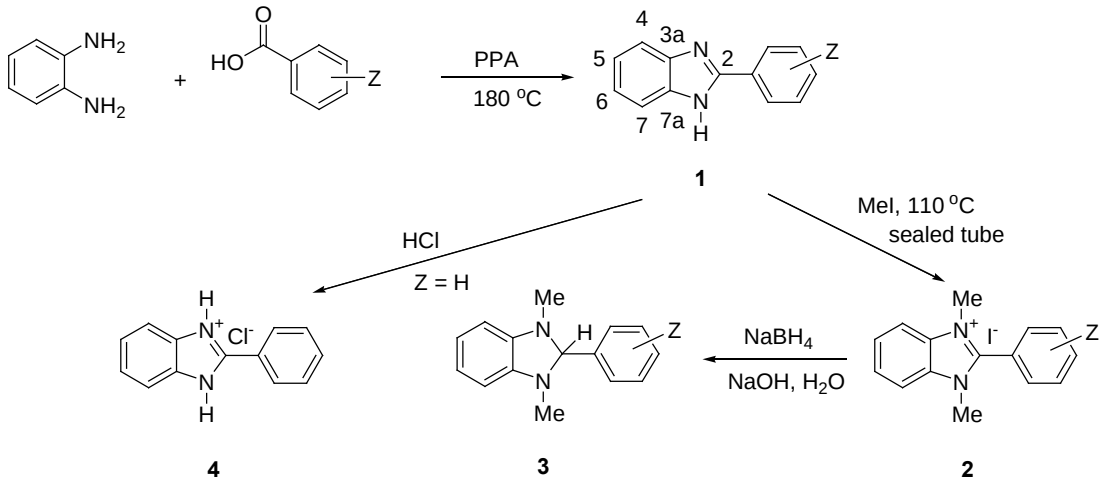
We have been interested in 2-arylbenzimidazolium ions and 2-arylbenzimidazolines because they are the mimics of NAD^+ and NADH, respectively.[2] In the course of our extensive investigation on the hydride transfer reaction between the benzimidazolium ions and the benzimidazolines, we came to observe striking phenomena in their NMR chemical shifts. This paper is to report the effects of benzimidazole, benzimidazolium ion, and benzimidazoline rings as substituents on the ^1H and ^{13}C NMR chemical shifts of benzene.

RESULTS AND DISCUSSION

The synthesis of 2-arylbenzimidazoles (**1**) have been investigated for more than a century. New and modified methods have been reported frequently in recent years.[3] Our preparation of **1** was based on the

method of Craig *et al.* with a slight modification.[4] The synthesis of 1,3-dimethyl-2-arylbenzimidazolium ions (**2**), and 1,3-dimethyl-2-arylbenzimidazolines (**3**) are summarized in Scheme 1.

Scheme 1



Z: **a**, *m*-F; **b**, *m*-Cl; **c**, *m*-Br; **d**, *m*-Me; **e**, *p*-F; **f**, *p*-Cl; **g**, *p*-Br; **h**, *p*-Me; **i,** H

Several years ago we reported the prohibited tautomerism in unsubstituted 2-phenylbenzimidazole (**1i**).[5] Now we have found that the tautomerism of the proton at N-1 to N-3 does not take place in all the *m*- and *p*-substituted 2-phenylbenzimidazoles (**1a-h**) in DMSO-d_6 solution. This is evidenced by the appearance of seven ^{13}C NMR signals for the benzimidzole skeleton. It is known that benzimidazole itself tautomerizes in solution showing only four ^{13}C NMR signals.[6]

The NMR spectra of **1**, **2**, and **3** have been obtained in 0.1 *M* concentration at 25 °C. The assignments of the ^{1}H and ^{13}C NMR signals were made by ^{1}H-^{1}H COSY and ^{1}H-^{13}C HETCOR spectroscopy. *Meta*- and *para*-fluorophenyl derivatives (**1-3a** and **1-3e**) were investigated using the ^{19}F-^{13}C coupling constants for definite assignments. The observed coupling constants (i.e., for **1a**: ^{1}J = 244.8, ^{2}J = 20.5 and 24.3, ^{3}J = 8.6 and 9.2, ^{4}J = 2.7 Hz; for **1e**: ^{1}J = 250.2, ^{2}J = 22.2, ^{3}J = 9.3, ^{4}J = 4.0 Hz) are very close to the values for fluorobenzene.[7]

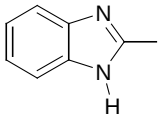
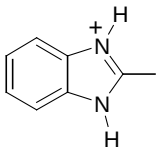
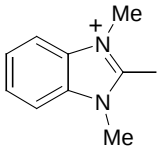
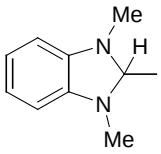
Once the accurate chemical shift assignments are made for **1a-i**, the effect of 2-benzimidazolyl group on the chemical shift of the ring-protons and the ring-carbons in benzene can be calculated by following the additivity rule and using the values listed in literature.[8] Similarly, the effects of 2-benzimidazoliumyl and 2-benzimidazolinyl groups were also calculated, and the results are listed in Table 1.

One of the striking observations is the shielding effect of 1,3-dimethylbenzimidazolium-2-yl group on the *ipso*-C, causing an up-field shift of 6.1 ppm. Although the positive charge may be delocalized mostly on the two N atoms through resonance, the imidazole ring is positively charged. The positively charged group is expected to deshield a neighboring nucleus and a down-field shift should be the result. For

example, the $(CH_3)_3N^+-$ group causes a down-field shift of the *ipso*-C signal by 19.5 ppm.[9] Substituents such as vinyl, phenyl, and carbonyl that have an sp^2-hybridized carbon atom usually cause a down-field shift of the *ipso*-C signal of the benzene ring.[9]

There are many examples of substituents that cause a down-field shift of the *ipso*-C and a simultaneous up-field shift of *ortho*-C signals (i. e., F−). On the other hand, less than ten examples of substituents that cause the opposite effect have been reported, and they are HC≡C−, $N\equiv N^+-$, Br−, I−, CN−, NCS−, CF_3CO-, NC−, and H_3Si- groups.[9] Among these only HC≡C−, Br−, and CF_3CO- show comparable magnitudes of shift of the *ipso*-C signal to the benzimidazolium-2-yl group, as shown in Table 1. But, *meta*- and *para*-Cs do not show similar trends in either magnitude or direction.

Table 1. Calculated Substituent Parameters for Benzimidazolyl, Benzimidazoliumyl, and Benzimidazolinyl Groups on the Chemical Shifts of the Protons and Carbons of Benzene Ring

Substituent	*o*-H	*m*-H	*p*-H	*i*-C	*o*-C	*m*-C	*p*-C
	1.00	0.37	0.33	3.3	-0.8	0.05	0.05
	0.30	0.18	0.19	-3.5	5.1	3.3	7.3
	0.78	0.64	0.73	-6.1	4.45	1.2	4.2
	0.11	-0.10	0.26	12.8	1.6	0.8	1.7
F—[a]	-0.26	0.00	-0.20	34.8	-13.0	1.6	-4.4
Br—[a]	0.18	-0.08	-0.04	-5.8	3.2	1.6	-1.6
HC≡C—[a]	0.15	-0.02	-0.01	-6.2	3.6	-0.4	-0.3
CF_3CO-[a]	-	-	-	-5.6	1.8	0.7	6.7
N≡C—[a]	0.36	0.18	0.28	-15.7	3.6	0.7	4.3
$N\equiv N^+-$[a]	-	-	-	-12.7	6.0	5.7	16.0
ClCO—[a]	0.84	0.22	0.36	4.7	2.7	0.3	6.6
ClO_2S-[a]	0.76	0.35	0.45	15.6	-1.7	1.2	6.8
Me_3N^+-[a]	0.69	0.36	0.31	19.5	-7.3	2.5	2.4

[a] From reference 9.

The up-field shift of the *ipso*-C signal by Br is explained by heavy atom shielding while the similar phenomenon by HC≡C− or N≡C− is believed to be the result of the anisotropy effect of triple bond.[10] The only example of the up-field shift of the *ipso*-C signal by a substituent having an sp^2-hybridized carbon is the trifluoroacetyl group. It is conceivable that the strong electron-withdrawing property of the trifluoromethyl group may induce the lone-pair electrons on the O atom to move toward the C atom so that the C=O double bond becomes close to a triple bond (C≡O). This should enhance the *s* character of the carbonyl carbon (i.e., from sp^2 to *sp*), which, in turn, generates the anisotropy effect as if it is an alkynyl carbon.

The magnitudes of the up-field shift of *ipso*-C signal caused by N≡C− (− 15.7 ppm) and N≡N^+− (− 12.7 ppm) are much greater than for the other substituents except the I− group.[9] This can also be explained by the increasing anisotropy effect due to the movement of the lone-pair electron on N atom toward the C or N atom, which should make the *s* character of the these atoms far greater than a normal *sp*-hybridized C of alkynyl group.

In order to examine the effect of the methyl groups in **2** on the chemical shift, we prepared 2-phenylbenzimidazolium chloride (**4**), obtained its NMR spectra under the same conditions, and compared the spectra with those of **2i**. To our surprise, the chemical shift value of C-2 of **4** (150.31 ppm) was very close to that of **2i** (150.76 ppm). But the *ipso*-C signal is shifted to down-field by 3.50 ppm. The signal which corresponds to C-3a/7a is shifted most down-field by 3.57 ppm and the other ^{13}C NMR signals are all shifted to same direction by 1.25-2.30 ppm The ^{1}H NMR spectrum of **4** also shows an interesting deviation. The signal corresponding to H-4/7 is shifted to down-field by 0.13 ppm, but other signals are all shifted to up-field by 0.37-0.44 ppm. These findings are consistent with the predominant paramagnetic shielding term that may be the major factor affecting the ^{13}C NMR chemical shift.

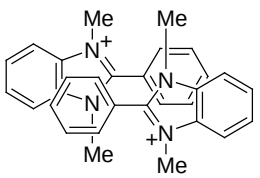
Then, a question may arise: why the *ipso*-Cs of the phenyl groups in **2** show an up-field shift with significant magnitude (− 6.1 ppm) whereas those of **1** show a down-field shift with a relatively small magnitude (+ 3.3 ppm)? The benzimidazole and phenyl rings in **1** may lie nearly in the same plane because there is no significant steric hindrance between the two rings. The electronic effect of the benzimidazole ring is both electron-withdrawing by the inductive effect and electron-releasing by the mesomeric effect. The two effects may offset one another, if not completely, and the result is small deviation in the ^{13}C NMR chemical shift values of the phenyl rings (− 0.8 for *o*-C, 0.05 for *m*- and *p*-C).

In case of the benzimidazolines (**3**) the two rings are not coplanar. The effect of the benzimidazolin-2-yl group may mostly originate from the sp^3-hybridized carbon atom bearing two electronegative N atoms. Therefore, the phenyl C signals are shifted to down-field and only the *ipso*-C signal is shifted the most (+ 12.8 ppm).

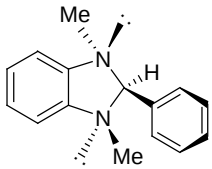
The signals corresponding to the *ortho*- and *para*-C of **2** are shifted to down-field significantly with similar magnitude (4.4 and 4.2 ppm, respectively) compared to those of **1** and **3**. This may be the results of the so called π polarization which may be initiated by the positively charged benzimidazolium substituent.[11]

The effect of the benzimidazol-2-yl, benzimidazolium-2-yl, and benzimidazolin-2-yl groups on the proton chemical shift of the benzene ring is also interesting. It is worthy to point out that the *ortho*-H in **1** is shifted to down-field by 1.00 ppm. Such a large shift cannot be found in literature to the best of our knowledge. The nitro ($-NO_2$) group has been known to cause the most down-field shift of the *ortho*-H by 0.95 ppm. Phenyloxycarbonyl ($-COOC_6H_5$) group is reported to be the second most effective substituent that causes down-field shift of the *ortho*-H signal by 0.90 ppm.[12] Chlorocarbonyl (ClCO−) and chlorosulfonyl (ClO_2S-) groups have comparable effects on *ortho*-H as the benzimidazolium-2-yl group has, but their effects on *meta*- and *para*-H are quite different as shown in Table 1. The large down-field shift of the *ortho*-H signal of **1** may be due to the diamagnetic anisotropy effect originated by the π electrons in the benzimidazole ring. However, the hydrogen bonding between N and *ortho*-H atoms should also contribute to the unusual magnitude of the shift.

In general, the electronic effect of a substituent decreases as the distance from it increases, as appeared in *meta*- and *para*-H signals of **1**. But the proton signals of **3** show quite a large irregularity (*o*-H 0.11, *m*-H − 0.10, *p*-H 0.26 ppm). All the proton signals of **2** show quite a down-field shift (*o*-H 0.78, *m*-H 0.64, *p*-H 0.73 ppm). Apparently, the electronic effect of the positively charged ring is propagated to the phenyl ring not only by through-bond transmission but also by through-space transmission. The two rings may stack on each other, as shown for **I**. Similar stacking should not be possible with the benzimidazoline (**3**) because C-2 is sp^3-hybridized. The *meta*-H of the phenyl ring may lie on the shielding region of the ring current effect produced by the benzene ring, as shown like **II**.



I



II

In conclusion, we report the benzimidazolium-2-yl group as a positively charged substituent that cause the up-field shift of the *ipso*-C signal of benzene ring. The benzimimidazol-2-yl group causes a down-field shift of the *ortho*-H signal of the benzene ring.

EXPERIMENTAL

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DPX-400 FT NMR spectrometer in the Central Lab of Kangwon National University at 400 MHz for ^1H and 100 MHz for ^{13}C and were

referenced to tetramethylsilane (TMS). The concentration of the solution was 0.10 M in DMSO-d_6. Each solution was prepared in a 1 mL cylindrical volumetrical flask by weighing the compound into the flask and filling with solvent containing 1%-TMS. A portion (0.6 mL) of the solution was transferred into an NMR tube and the spectrum was obtained at 20 ^{o}C, and the results are listed in Tables 2-7.

The benzimidazole derivatives **1**, **2**, and **3** are all known compounds.[13]

An Illustrative Procedure for the Preparation of 2-Arylbenzimidazoles: A mixture of *o*-phenylenediamine (2.06 g, 19.1 mmol), benzoic acid (2.30 g, 20.5 mmol), and polyphosphoric acid (5.52 g) was stirred in an oil bath at 180 ^{o}C for 1.5 h. The solution was cooled to rt. The pH was adjusted to 10 with 6%-NH_4OH. The tarry solid was collected by filtration, washed with NH_4OH solution, and recrystallized from EtOH to give **1i**.

An Illustrative Procedure for the Preparation of 2-Aryl-1,3-dimethylbenzimidazolium Iodides: A solution of sodium hydroxide (0.28 g, 7 mmol) in MeOH (7 mL) was prepared first in a pressure tube. **1i** (1.27 g, 6.54 mmol) and methyl iodide (6.75 g, 47 mmol) were added. The tube was sealed and was heated in an oil bath at 110 ^{o}C for 12 h. After cooling to rt, the mixture was suspended in acetone and filtered. The residue was dissolved in EtOH (200 mL) by heating, decolorized with charcoal, and recrystallized from EtOH to give **2i**.

An Illustrative Procedure for the Preparation of 2-Aryl-1,3-dimethylbenzimidazolium Iodides: $NaBH_4$ (0.35 g, 9.25 mmol) was added to a solution of **2i** (1.60 g, 4.57 mmol) in MeOH (30 mL). The mixture was stirred. Reaction took place immediately. After stirring for 30 min, the solvent was evaporated off and the residue was extracted with CH_2Cl_2. The extract was evaporated and the residue was recrystallized from EtOH -water (5:1 v/v) to give **3i**.

Table 2. ^{1}H NMR Chemical Shift Values (δ) of Benzimidazoles in DMSO-d_6

	1a	**1b**	**1c**	**1d**[a]	**1e**	**1f**	**1g**	**1h**[b]	**1i**
N-H	13.06	13.03	13.04	12.94	12.97	12.99	13.02	12.87	13.00
4-H	7.69	7.68	7.69	7.20	7.20	7.19	7.21	7.18	7.21
5-H	7.22	7.21	7.20	7.20	7.20	7.19	7.21	7.18	7.21
6-H	7.24	7.25	7.25	7.21	7.21	7.23	7.22	7.20	7.23
7-H	7.60	7.54	7.55	7.68	7.55	7.54	7.55	7.65	7.64
2'-H	7.99	8.22	8.37	8.06	8.25	8.19	7.76	8.08	8.24
3'-H					7.39	7.63	8.13	7.35	7.55
4'-H	7.33	7.57	7.69	7.28					7.48
5'-H	7.59	7.59	7.52	7.42	7.39	7.63	8.13	7.35	7.55
6-'H	8.05	8.14	8.69	8.01	8.25	8.19	7.76	8.08	8.24

[a]3'-CH_3: δ 2.40. [b]4'-CH_3: δ 2.36

Table 3. ^{13}C NMR Chemical Shift Values (ppm) of Benzimidazoles in DMSO-d_6

	1a	**1b**	**1c**	**1d**[a]	**1e**	**1f**	**1g**	**1h**[b]	**1i**
2-C	150.54	150.23	149.95	151.92	150.98	150.66	150.75	151.94	151.82
3a-C	135.50	135.50	135.50	135.54	135.61	135.52	135.55	135.49	135.74
4-C	122.50	122.48	122.47	122.19	122.29	122.36	122.40	122.14	122.25
5-C	119.64	119.60	119.60	119.37	119.40	119.47	119.50	119.25	119.41
6-C	123.48	123.50	123.49	123.02	123.09	123.30	123.32	122.90	123.10
7-C	112.07	112.04	112.04	111.85	111.90	111.93	111.98	111.75	111.92
7a-C	144.20	144.15	144.15	144.36	144.34	144.23	144.26	144.35	144.28
1'-C	133.04	132.70	132.91	130.65	127.36	129.54	129.91	127.98	130.73
2'-C	113.59	129.39	126.52	127.58	129.29	129.58	128.88	126.94	127.01
3'-C	163.02	134.29	122.79	138.71	116.54	128.64	132.51	130.07	129.50
4'-C	117.14	130.08	132.96	131.02	163.63	135.00	123.80	140.12	130.39
5'-C	131.68	131.49	131.72	129.83	116.54	128.64	132.51	130.07	129.50
6'-C	123.07	125.53	125.89	124.15	129.29	129.58	128.88	126.94	127.01

[a]3'-CH_3: δ 21.59. [b]4'-CH_3: δ 21.52

Table 4. ^{1}H NMR Chemical Shift Values (δ) of Benzimidazoliums in DMSO-d_6

	2a	**2b**	**2c**	**2d**[a]	**2e**	**2f**	**2g**	**2h**[b]	**2i**	**4**
CH_3	3.91	3.92	3.92	3.90	3.89	3.91	3.89	3.89	3.89	-
4/7-H	8.16	8.17	8.17	8.12	8.14	8.16	8.13	8.13	8.13	8.26
5/6-H	7.78	7.80	7.80	7.74	7.75	7.77	7.76	7.75	7.74	7.30
2'-H	7.79	8.06	8.21	7.76	8.04	7.89	7.88	7.81	7.95	7.56
3'-H					7.67	7.99	8.02	7.61	7.81	7.44
4'-H	7.73	7.93	8.06	7.68					7.85	7.45
5'-H	7.87	7.82	7.75	7.65	7.67	7.99	8.02	7.61	7.81	7.44
6-'H	7.84	7.88	7.95	7.76	8.04	7.89	7.88	7.81	7.95	7.56

[a]3'-CH_3: δ 2.10. [b]4'-CH_3: δ 2.10

Table 5. ^{13}C NMR Chemical Shift Values (ppm) of Benzimidazoliums in DMSO-d_6

	2a	**2b**	**2c**	**2d**[a]	**2e**	**2f**	**2g**	**2h**[b]	**2i**	**4**
CH_3	33.31	33.33	33.39	33.50	33.45	33.47	33.38	33.39	33.48	-
2-C	149.37	149.35	149.20	150.85	150.07	149.84	150.00	151.05	150.76	150.31
3a/7a-	132.18	132.20	132.17	132.18	132.20	132.23	132.23	132.23	132.19	135.76

C										
4/7-C	114.01	113.99	113.98	113.94	113.97	113.99	113.95	113.93	113.95	116.03
5/6-C	127.32	127.34	127.30	127.11	127.19	127.21	127.24	127.11	127.14	128.39
1'-C	123.36	123.49	122.90	121.37	117.94	120.34	120.67	118.54	121.46	124.96
2'-C	118.52	130.95	133.65	134.09	134.45	133.46	133.43	131.26	131.36	133.59
3'-C	162.32	134.56	123.65	139.60	117.41	130.18	133.09	130.55	129.96	131.84
4'-C	120.68	133.51	136.35	131.47	165.06	138.56	127.70	143.83	133.46	135.76
5'-C	132.50	131.98	132.07	128.45	117.41	130.18	133.09	130.55	129.96	131.84
6'-C	128.46	130.17	130.55	129.88	134.45	133.46	133.43	131.26	131.36	133.59

[a]3'-CH_3: δ 21.49. [b]4'-CH_3: δ 21.81

Table 6. ^{1}H NMR Chemical Shift Values (δ) of Benzimidazolines in DMSO-d_6

	3a	**3b**	**3c**	**3d**[a]	**3e**	**3f**	**3g**	**3h**[b]	**3i**
CH_3	2.25	2.24	2.26	2.22	2.24	2.24	2.24	2.22	2.24
2-H	4.68	4.67	4.68	4.57	4.65	4.65	4.64	4.57	4.61
4/7-H	6.39	6.39	6.40	6.37	6.39	6.39	6.39	6.37	6.38
5/6-H	6.23	6.23	6.24	6.20	6.23	6.23	6.23	6.20	6.21
2'-H	7.12	7.35	7.50	7.13	7.37	7.34	7.28	7.19	7.30
3'-H					7.04	7.27	7.41	7.01	7.20
4'-H	7.26	7.25	7.41	7.08					7.22
5'-H	7.03	7.24	7.19	7.00	7.04	7.27	7.41	7.01	7.20
6-'H	7.15	7.27	7.33	7.09	7.37	7.34	7.28	7.19	7.30

[a]3'-CH_3: δ 2.10. [b]4'-CH_3: δ 2.10

Table 7. ^{13}C NMR Chemical Shift Values (ppm) of Benzimidazolines in DMSO-d_6

	3a	**3b**	**3c**	**3d**[a]	**3e**	**3f**	**3g**	**3h**[b]	**3i**
CH_3	33.67	33.67	33.68	33.62	33.55	33.58	33.60	33.51	33.57
2-C	92.89	92.84	92.78	93.58	92.90	92.84	92.91	93.57	93.72
3a/7a-C	142.29	142.27	142.25	142.46	142.35	142.31	142.32	142.46	142.43
4/7-C	106.44	106.45	106.44	106.27	106.37	106.40	106.41	106.24	106.28
5/6-C	119.72	119.74	119.73	119.54	119.64	119.67	119.68	119.50	119.55
1'-C	142.57	142.17	142.40	139.30	135.55	138.43	138.86	136.27	139.27
2'-C	115.53	129.83	132.72	130.48	131.19	130.98	131.32	129.09	129.14
3'-C	162.78	133.75	122.32	138.20	116.86	129.05	131.99	129.56	128.97

4'-C	116.74	128.78	131.65	129.59	163.17	134.30	122.99	139.14	129.79
5'-C	131.04	130.98	131.27	128.83	116.86	129.05	131.99	129.56	128.97
6'-C	125.33	127.96	128.35	126.40	131.19	130.98	131.32	129.09	129.14

[a]3'-CH_3: δ 21.53. [b]4'-CH_3: δ 21.39

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