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^{13}C NMR SPECTRA OF N-SUBSTITUTED AZIRIDINES[1]

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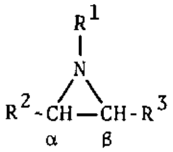
Abstract---- The ^{13}C chemical shifts for the cis- and trans-N-substituted diphenyl, dibenzoyl, aroylaryl, and arylcyanoaziridines (1--8) have been reported (Table 1, 2, and 3). The differences of ^{13}C chemical shifts between the cis and trans isomers and the effects of N- and ring C-substituents, and of the para-substituted groups of phenyl or benzoyl group upon the chemical shifts of the ring carbons are described. The chemical shifts of the ring carbons are qualitatively discussed in terms of steric compression effects.

The ^{13}C NMR technique has been valuable for the structural investigation of small ring compounds.[2] Indeed, systematic ^{13}C NMR studies of N-unsubstituted[3] and N-substituted[4] aziridines have been reported. In this note, we describe the results of ^{13}C NMR spectral measurements of thirty-nine cis- and trans-N-substituted aziridines (1--8),[5] which would complement the recent report of Cromwell and Kingsbury et al.,[4] who have studied, from the ^{13}C NMR spectral data of a number of N-substituted 2-aroylaziridines, the effect of three-ring to carbonyl hyperconjugation, the effect of the nitrogen lone pair on J_{C-H} values and the carbonyl group, and the steric compression effect in these systems. In addition to the last effect, we will briefly deal with the substituent (on the phenyl ring) effects upon the chemical shifts of the ring carbons.

The ^{13}C chemical shifts for the aziridines (1--8) are given in Table 1--3. The assignments were made by considering signal multiplicities from off-resonance decoupling experiments or from coupled spectra, coupling constants (J_{C-H}), line intensities, and the chemical shifts of N-unsubstituted aziridines.[3a] The aromatic and cyclohexyl carbons were assigned by chemical shift comparison with the substituted benzenes[6,7] and N-alkylcyclohexylamines,[8] and by means of their characteristic intensities. The ^{13}C NMR spectra of the aziridines (1--4) were simple and easily assigned as they have same substituents on the α and β carbons (hereafter designated as C-α and C-β). The assignments of C-α and C-β of the benzoyl aziridines (6) were established by comparison of the substituent



1	(cis and trans)	$R^1=R^2=R^3=C_6H_5$
2	(cis and trans)	$R^1=C_6H_{11}$, $R^2=R^3=C_6H_5$
3	(cis and trans)	$R^1=C_6H_5CH_2$, $R^2=R^3=C_6H_5$
4	(cis and trans)	$R^1=C_6H_{11}$, $R^2=R^3=C_6H_5CO$
5	(cis)	$R^1=CH_3$, $R^2=C_6H_5CO$, $R^3=C_6H_5$
6a	(cis and trans)	$R^1=C_6H_{11}$, $R^2=C_6H_5CO$, $R^3=C_6H_5$
6b	(cis and trans)	$R^1=C_6H_{11}$, $R^2=p\text{-}CH_3OC_6H_4CO$, $R^3=C_6H_5$
6c	(cis and trans)	$R^1=C_6H_{11}$, $R^2=p\text{-}CH_3C_6H_4CO$, $R^3=C_6H_5$
6d	(cis and trans)	$R^1=C_6H_{11}$, $R^2=p\text{-}ClC_6H_4CO$, $R^3=C_6H_5$
6e	(cis and trans)	$R^1=C_6H_{11}$, $R^2=p\text{-}NO_2C_6H_4CO$, $R^3=C_6H_5$
6f	(cis and trans)	$R^1=C_6H_{11}$, $R^2=C_6H_5CO$, $R^3=p\text{-}CH_3OC_6H_4$
6g	(cis and trans)	$R^1=C_6H_{11}$, $R^2=C_6H_5CO$, $R^3=p\text{-}CH_3C_6H_4$
6h	(cis and trans)	$R^1=C_6H_{11}$, $R^2=C_6H_5CO$, $R^3=p\text{-}ClC_6H_4$
7a	(cis and trans)	$R^1=C_6H_{11}$, $R^2=CN$, $R^3=C_6H_5$
7b	(cis)	$R^1=C_6H_{11}$, $R^2=CN$, $R^3=p\text{-}CH_3OC_6H_4$
7c	(cis and trans)	$R^1=C_6H_{11}$, $R^2=CN$, $R^3=p\text{-}CH_3C_6H_4$
7d	(cis and trans)	$R^1=C_6H_{11}$, $R^2=CN$, $R^3=p\text{-}ClC_6H_4$
7e	(cis and trans)	$R^1=C_6H_{11}$, $R^2=CN$, $R^3=o\text{-}ClC_6H_4$
8a	(cis)	$R^1=C_6H_5CH_2$, $R^2=CN$, $R^3=C_6H_5$
8b	(cis)	$R^1=C_6H_5CH_2$, $R^2=CN$, $R^3=p\text{-}CH_3OC_6H_4$
8c	(cis)	$R^1=C_6H_5CH_2$, $R^2=CN$, $R^3=p\text{-}CH_3C_6H_4$
8d	(cis)	$R^1=C_6H_5CH_2$, $R^2=CN$, $R^3=p\text{-}ClC_6H_4$
8e	(cis)	$R^1=C_6H_5CH_2$, $R^2=CN$, $R^3=o\text{-}ClC_6H_4$

effects on chemical shifts of the aziridines (**6a**--**h**) with those of the chalcones[9] as shown in Figure 1 and 2; the upfield resonances of ring carbons of the trans-benzoyl aziridines (**6a**--**h**) and the downfield resonances of those of the cis-isomer were attributed to C-β, since their variation patterns with the substituents are similar to those of C-β resonances of the chalcones. These assignments are in accord with those based upon qualitative considerations of long-range ^{13}C-H couplings of **6a** and **6b**.[4] In the cyanoaziridines (**7**) and (**8**), the signal at the higher field can be attributed to C-α bonded to a cyano group (Figure 3) based on the empirical rule that substitution with cyano group results in a shielding of the carbon, while substitution with phenyl group causes a deshielding.[6] In the trans-cyanoaziridines (**7**), pairs of the signals were observed for C-β and cyclohexyl N-methine, cyano, and phenyl carbons, whereas, in the cis-isomer, they appeared only at C-α.[10] This phenomenon is possibly due to the presence of two conformational

Table 1 C-13 NMR data of 1 ~ 4 (ppm from TMS)

Compd. No.	cis/trans	ring-C	N-Substituent[a]					C-Substituents[b]				
			C-1	C-2	C-3	C-4	-$\underline{C}H_2$-	C-1'	C-2'	C-3'	C-4'	$\underline{C}$=O
1	cis	49.0	154.5	119.8	129.1	122.7		135.9	127.8	127.8	126.9	
	trans	50.0	148.2	120.8	128.6	121.8		136.4	128.2	127.3	127.4	
2	cis	48.1	68.8	32.4	24.5	26.4		137.4	128.0	127.6	126.3	
	trans	46.3[c]	58.6	(32.3 33.2	(24.3 24.8	26.1		140.2	128.0	128.0	127.1	
3	cis	49.3	139.0	127.9	127.6	126.5	64.9	136.4	127.9	127.6	126.9	
	trans	48.2[c]	129.7	128.2	127.8	127.4	56.2	139.6	126.5	128.2	126.4	
4	cis	48.4	69.9	32.3	24.7	25.7		136.5	128.4	128.4	133.2	193.3
	trans	46.2	58.8	(32.6 33.0	(24.4 24.7	25.7		(136.2 137.3	128.7	128.7	133.7	(193.1 194.7

[a] Phenyl-C of 1, cyclohexyl-C of 2 and 4, and benzyl-C of 3.

[b] Phenyl-C.

[c] Center of the broad signals.

Table 2 C-13 NMR data of 2-benzoylaziridines 5 and 6 (ppm from TMS)

Compd.	cis	Ring-C		Cyclohexyl-C				Benzoyl-C					Phenyl-C				
No.	trans	α	β	C-1	C-2	C-3	C-4	C=O	C-1'	C-2'	C-3'	C-4'	C-1"	C-2"	C-3"	C-4"	Sub.[c]
5	cis	51.1	52.4	47.3[a]				193.2	136.8	128.4	128.0	133.0	134.9	128.0	127.9	127.3	
6a	cis	49.8	49.3	69.1	31.9 32.3	24.6	26.0	193.5	137.1	128.3	128.0	132.7	135.6	127.8	127.5	127.2	
	trans	47.3	48.6	57.9	32.8 33.2	24.4 24.7	26.1	194.9	138.2	128.7	128.4	133.3	139.5	128.4	127.4	126.5	
6b	cis	49.8	48.9	69.2	31.9 32.3	24.6	26.1	191.9	130.4	130.4	113.5	163.2	135.9	127.8	127.5	127.1	55.4
	trans	47.0	47.8	58.0	32.7 33.2	24.4 24.7	26.1	192.9	131.3	130.7	113.8	163.6	139.5	128.2	127.3	126.5	55.4
6c	cis	49.8	49.1	69.2	31.9 32.3	24.6	26.1	192.9	134.7	128.2	129.0	143.5	135.7	127.8	127.5	127.1	21.6
	trans	47.1	48.1	57.9	32.7 33.2	24.3 24.6	26.0	194.2	135.7	128.5	129.3	144.1	139.4	128.2	127.3	126.5	21.7
6d	cis	49.8	49.1	69.0	31.9 32.3	31.9	26.0	192.5	135.4	129.5	128.6	139.1	135.4	127.8	127.4	127.3	
	trans	47.1	48.6	57.9	32.7 33.1	24.3 24.6	26.0	193.5	136.4	129.7	129.0	139.7	139.1	128.3	127.4	126.4	
6e	cis	50.2	49.6	68.8	31.9 32.3	24.5	25.9	192.3	————[b]								
	trans	47.3	49.3	58.0	32.4 33.0	24.2 24.5	25.9	193.5	————[b]								
6f	cis	49.9	48.9	69.1	31.8 32.3	24.5	26.1	193.6	137.3	128.6	128.2	132.6	129.8	128.2	113.4	158.8	55.3
	trans	46.9	48.4	57.9	32.7 33.2	24.3 24.7	26.1	195.0	138.2	128.6	128.2	133.0	133.0	127.6	113.7	159.0	55.3
6g	cis	49.9	49.3	69.2	31.9 32.3	24.6	26.1	193.5	137.2	128.3	128.1	132.7	127.5	128.6	128.6	136.8	21.1
	trans	47.1	48.6	57.9	32.7 33.1	24.3 24.6	26.1	195.0	138.2	128.6	128.2	133.0	137.0	129.0	126.4	136.4	21.1
6h	cis	49.8	48.5	68.9	31.8 32.2	24.4	26.0	193.1	137.0	128.3	128.0	132.9	134.2	128.9	128.0	132.9	
	trans	47.3	47.6	57.8	32.7 33.1	24.3 24.6	26.0	194.5	138.1	128.6	128.4	133.3	138.1	128.4	127.8	133.3	

[a] N-Methyl-C.

[b] Not assigned as the spectra were measured without isolation of cis and trans isomers.

[c] Methyl- or methoxy-C.

Table 3 C-13 NMR data of 2-cyanoaziridines 7 and 8 (ppm from TMS)

Compd. No.	cis/trans	Ring-C		Cyclohexyl- or Benzyl-C						Phenyl-C				
		α	β	C-1	C-2	C-3	C-4	-$\underline{C}H_2$-	-$\underline{C}$≡N	C-1'	C-2'	C-3'	C-4'	Sub.[a]
7a	cis	(31.4 31.6	45.9	68.4	32.0	24.0	25.9		117.1	134.6	128.3	128.3	127.1	
	trans	34.0	(52.2 52.8	60.9 62.2	32.1	24.6	25.6		(120.3 121.8	161.0	(136.3 137.3	(128.6 130.1	(127.0 127.8	
7b	cis	(31.3 31.6	45.6	68.5	32.1	24.1	25.9		117.3	126.7	128.3	113.9	159.7	55.3
7c	cis	(31.4 31.6	45.8	68.5	32.1	24.0	25.9		117.2	131.6	127.0	129.1	138.0	21.2
	trans	34.0	(52.1 52.7	60.4 61.7	32.1	24.5	25.6		(120.6 122.2	161.1	(126.5 127.6	129.3	(133.4 134.4	21.4
7d	cis	(31.5 31.6	45.1	68.3	32.0	24.0	25.8		116.8	133.2	128.6	128.6	134.1	
	trans	34.0	(52.3 52.9	61.3 62.9	32.0	24.6	25.5		121.6	(159.9 160.3	(134.6 136.2	128.4	(128.9 129.2	
7e	cis	(30.9 31.7	43.9	68.1	32.1	24.0	25.8		116.8	132.5	(133.7 129.0	(129.3 126.9	129.0	
	trans	34.1	(52.4 53.0	61.4 63.1	31.9	24.6	25.5		(119.9 120.8	(158.6 159.2	(135.0 130.5	(130.9 127.0	130.1	
8a	cis	32.6	46.8	136.5	128.6	127.8	127.2	63.3	116.6	133.8	128.4	128.4	127.7	
8b	cis	32.6	46.6	136.7	128.6	127.8	127.6	63.4	116.8	125.9	128.3	114.0	141.5	55.2
8c	cis	32.6	46.9	136.7	128.6	127.7	127.1	63.5	116.6	130.9	127.9	129.1	138.2	21.2
8d	cis	32.6	46.0	136.4	128.6	128.6	127.1	63.2	116.4	132.5	128.6	128.6	134.3	
8e	cis	32.1	44.8	136.5	128.6	128.0	127.8	63.2	116.3	133.9	(131.8 129.5	(128.8 126.9	129.1	

[a] Methyl- or methoxy-C.

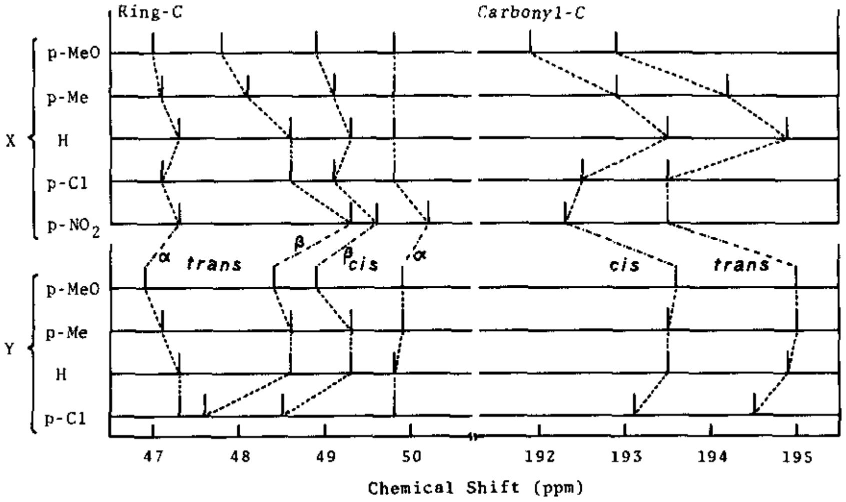
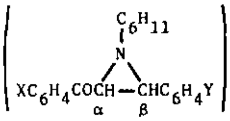


Figure 1. Substituent effects of X and Y in 2-aroyl-3-aryl-1-cyclohexylaziridines 6a-h



$\left(XC_6H_4CO\underset{\alpha}{C}H-\underset{\beta}{C}HC_6H_4Y,\ N\text{-}C_6H_{11}\right)$

on the ^{13}C chemical shifts of the ring (α and β) and carbonyl carbons.

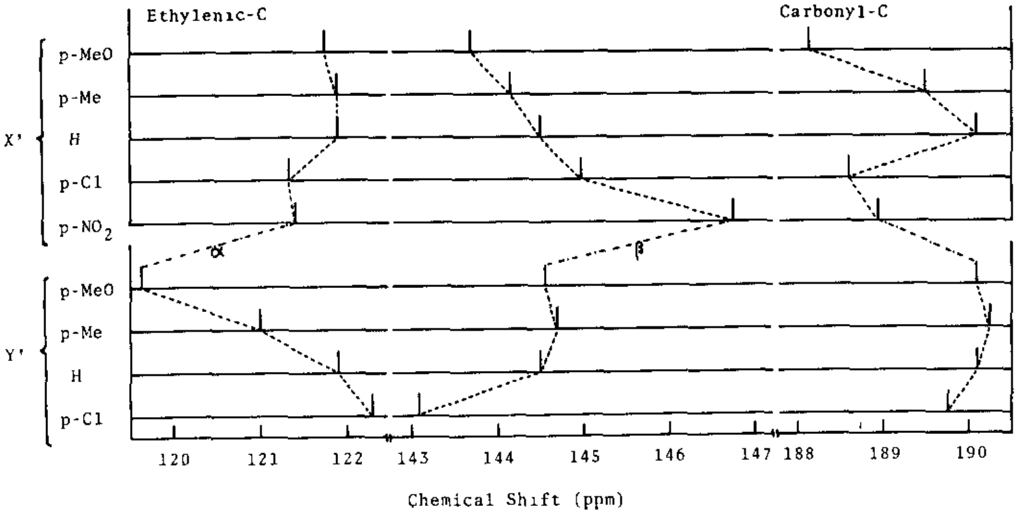


Figure 2. Substituent effects of X' and Y' in chalcones $X'C_6H_4COCH=CHC_6H_4Y'$ on the ^{13}C chemical shifts of the ethylenic (α and β) and carbonyl carbons.[9]

isomers which have different orientation of the cyclohexyl group on the nitrogen atom.

It is well documented that ^{13}C chemical shifts are influenced by steric interactions mostly arising from touching or overlapping of van der Waals radii of closely spaced substituents.[11] When two hydrogenated carbons are γ-gauche relative to each other, the steric compression effect on carbon shielding is generally observed.[12] Therefore, an analogous compression effect due to the steric interactions of the substituents R^1, R^2, and/or R^3 in the present aziridine systems would serve to shift the ring carbons upfield.[13] The values of the chemical shifts of the ring carbons for the *trans*-aziridines (1) and (7) are larger than those of the corresponding *cis* isomers, while in the aziridines (2--4) and (6), the ring carbon signals of the *cis* isomer were observed at lower field than those of the *trans* isomers. Therefore, it is speculated that, for 1 and 7, the *cis*-interaction of R^2 with R^3 predominates over the *syn*-interaction of R^1 with R^2 or R^3, and *vice versa* for 2--4 and 6. In the *trans*-aziridines (6), the C-α are more shielded than the C-β, whereas, in the *cis* isomers, were observed the opposite as shown in Figure 2, suggesting the *syn*-relation of the aroyl group (attached to C-α) with respect to the cyclohexyl group in the *trans*-isomers. Comparisons of the chemical shifts of the ring carbons of the *cis*-aziridines 1, 2, and 3, of 5 and 6a, and of 7 and 8 indicate that N-substitution with methyl, phenyl, benzyl, and cyclohexyl results in an increasing order of shielding of the ring carbons. Specifically, substitution of methyl with cyclohexyl group (5 and 6a) causes the upfield shifts at C-α (1.3 ppm) and C-β (3.1 ppm). At present, these shielding effects remain unexplained.

As shown in Figure 1 and 2, variations of the ring and carbonyl carbon chemical shifts in 6 with the *para*-substituents have a resemblance to those of the ethylenic and carbonyl carbons in the chalcones, though the substitution effects are smaller in the aziridines. While a pattern of substitution effects of the *cis*-cyanoaziridines (7) differs from that of the *trans* isomers (7) (Figure 3), the chemical shifts of the *cis* 7 varies in a similar fashion to those of the *cis* 8.

Finally, the coupling constants (J_{C-H}) of the ring carbons of 1--8 are summarized in Table 4. The J values of the *trans*-aziridines (1), (4), and (6) are larger than those of the corresponding *cis* isomers, whereas, in the case of 7, the J values of C-α of the *trans* isomers and of C-β of the *cis* isomers are larger than those of the corresponding *cis* and *trans* isomers, respectively. Particularly, the differences of the J values between C-α and C-β of the *trans*-aziridines (7) are remarkably large. A correlation of a carbon-proton coupling constant and an s character of the carbon hybrid orbital has been known,[14] thus suggesting that the C-α of the *trans*-aziridines (6) and (7) and the *cis*-aziridines (8) which have relatively large coupling constants are hyperconjugated or pseudoconjugated with the aroyl or cyano groups. The effect of three-ring to carbonyl hyperconjugation as well as the effect of the nitrogen lone pair on selected coupling constants have already been discussed.[4]

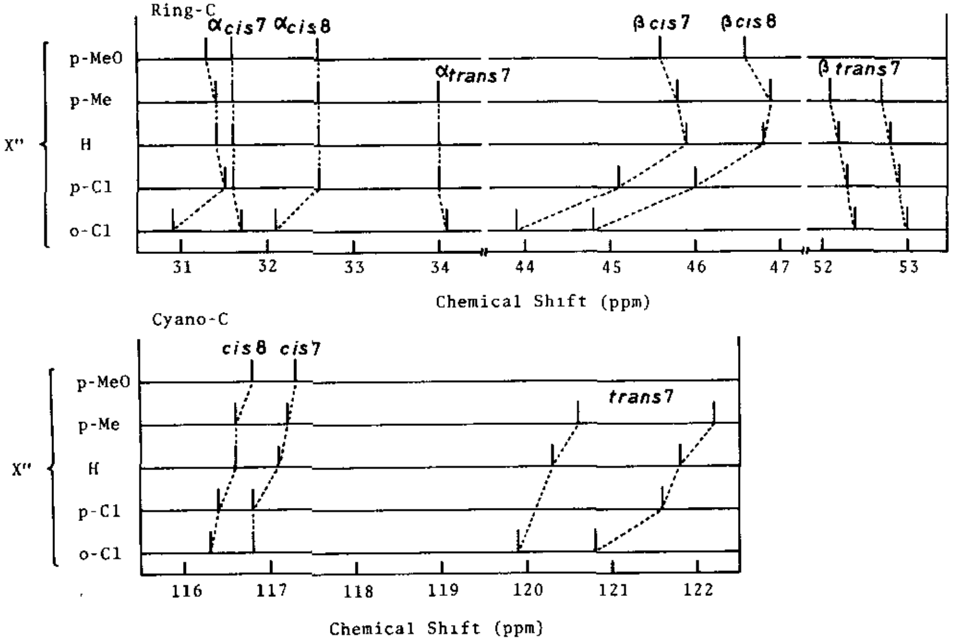
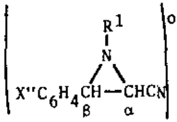


Figure 3. Substituent effects of X" in 1-cyclohexyl- and 1-benzyl-2-aryl-3-cyanoaziridines 7a-e and 8a-e



on the ^{13}C chemical shifts of the ring (α and β) and cyano carbons.

Table 4 Coupling constants (J_{C-H}) of the ring carbons in the N-substituted aziridines 1 ~ 8

Compd. No.	J_{C-H} (Hz) cis α			J_{C-H} (Hz) trans α	
1	165			168	
2	161			—	
3	165			—	
4	165			173	
5	165	164		—	
6a	164	167		175	164
6b	163	164		176	170
6c	164	166		173	167
6d	163	162		175	165
6e	—	—		—	—
6f	164	—		178	167
6g	161	162		176	166
6h	164	165		173	167
7a	179	165		194	132
7b	178	165		—	—
7c	179	167		192	140
7d	179	167		193	143
7e	182	171		185	129
8a	181	166		—	—
8b	178	168		—	—
8c	178	166		—	—
8d	178	170		—	—
8e	181	170		—	—

In conclusion, the ^{13}C NMR technique can be employed as an easy and reliable method of determing configuration of aziridines.

Recording of the Spectra----The ^{1}H noise decoupled and proton coupled spectra, as well as the signal frequency "off resonance" decoupled ^{13}C FT NMR spectra were measured using ca. 1.0 M solutions in $CDCl_3$ on a JEOL JNM FX-60 spectrometer (15.04 MHz). The solutions were kept in 10 mm tubes at 25 °C, and the deuterium signal of $CDCl_3$ was used as lock signal. The values of δC were referenced to internal tetramethylsilane and were accurate to ± 0.1 ppm. The reliability of the J_{C-H} values were ± 1.2 Hz.

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References and Notes

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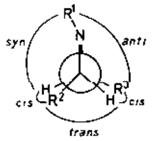
5. In this report, *cis* and *trans* shows a steric relation between the substituents R^2 and R^3, and *syn* and *anti* indicates that between R^1 and R^2 or R^3, as depicted in the following figure.



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13. Rigorously, the differences in chemical shifts observed should be explained as a combination of such effects as lone pair , hyperconjugation, and steric compression effects; these effects can not be unambiguously separated.

14. See ref. 11, p. 93ff.

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