

NMR STUDIES OF BRIDGED RING SYSTEMS. XVIII. REMARKABLE STERIC γ EFFECT UPON ^{13}C CHEMICAL SHIFTS IN TRICYCLO[3.2.1.0^{2,4}]OCTENES AND ITS APPLICATION TO ^{13}C SIGNAL ASSIGNMENT OF 9-ISOPROPYLIDENEBENZONORBORNENE DERIVATIVES

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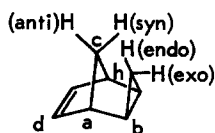
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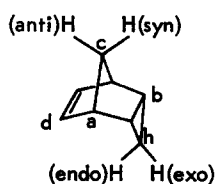
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In the course of NMR studies of anisotropic shielding effects exerted by a cyclopropane ring,¹ we have found that the $\text{H}_{\text{c(syn)}}$ signal in the ^1H NMR spectrum of tricyclo[3.2.1.0^{2,4-exo}]oct-6-ene (**2**) is only slightly shifted from the position of that in norbornene (**1**), contrary to the expectation that the ^1H signal should be shifted considerably upfield by the cyclopropane anisotropy.¹ This fact may result from the strong steric compression (van der Waals interaction)² between the $\text{H}_{\text{c(syn)}}$ and the $\text{H}_{\text{h(endo)}}$ of the cyclopropane



(2)



(3)

ring. Thus, we have examined the ^{13}C NMR spectra of **1**, **2**, tricyclo[3.2.1.0^{2,4-endo}]oct-6-ene (**3**), benzonorbornene (**4**), and benzotricyclo[3.2.1.0^{2,4-exo}]oct-6-ene (**5**), to find large upfield shifts associated with the strong steric γ effect³ expected for the C_{c} signal in **2** and the C_{d} signal in **3**. Further, we

describe an application of this effect to ^{13}C signal assignments of some 9-isopropylidenebenzonorbornene derivatives (**6-9**).

Table 1 lists the data obtained from natural-abundance ^1H -noise-decoupled ^{13}C FT NMR spectra in CDCl_3

at 15.1 MHz[†] together with the signal shift values due to introduction of a cyclopropane ring into the bicyclo-[2.2.1]heptane skeleton. The signals were assigned by using the single-frequency off-resonance ¹H-decoupling technique and known chemical-shift rules.³

As can be seen from Table 1, the C_c signal was shifted remarkably by -11.1 ppm from 1̄ to 2̄, whereas it moved downfield by +15.2 ppm from 1̄ to 3̄. Similarly, the C_d signal was shifted by -4.8 ppm from 1̄ to 3̄ and by +5.9 ppm from 1̄ to 2̄. These upfield shifts apparently due to the steric γ-effects³ become much more conspicuous when the spectra of 2̄ and 3̄ are directly compared; the steric effects upon the C_c and the C_d signals amount to -26.3 and -10.7 ppm, respectively.[‡] A similar steric γ shift of -12.1 ppm was also observed on the C_c signal from 4̄ to 5̄.

In comprehensive ¹³C NMR studies on a number of norbornane and norbornene derivatives already reported,⁴⁻⁷ various effects of several substituents on chemical shifts were examined in detail. The largest γ-effect reported for a methyl substitution is -7.7 ppm on the C₆ signal by a C₂(endo)-methyl substituent in norbornane.^{4,7} Thus, it should be emphasized that the steric γ shifts presented here are extraordinarily large. The shifts observed for the C_c signal obviously result from the strong steric interaction of H_{c(syn)} with H_{h(endo)}; that observed for the C_d signal can be attributed to the steric repulsion between the π electrons and H_{h(endo)}, as suggested previously.⁴

Table 2 lists the ¹H NMR data[†] on 1̄-5̄. The former compression effect is reflected in the slight differences in chemical shifts of H_{c(syn)} between 1̄ and 2̄ and between 4̄ and 5̄, as described earlier. However, the H_d signal in 3̄ seems not to suffer the steric compression shift from the H_{h(endo)}; this fact confirms that a direct interaction between the H_d and the H_{h(endo)} is not required to produce the upfield shift of the C_d signal mentioned above. The H_{c(syn)} signals have been reported to be much less shielded (+0.45 ppm) by an aziridine and an oxirane ring introduction into 1̄.⁸ These larger shifts are due to not only the steric compression of the hetero atoms but also to other deshielding effects arising from their lone-pair electrons.⁸ Other signal shifts

[†] The ¹³C FT NMR spectra were taken with a Varian NV-14 FT spectrometer in the CDCl₃-locked mode at 15.1 MHz. Sample concentrations were about 1 M in CDCl₃ containing TMS as an internal reference. The ¹H NMR spectra were recorded on a Varian HA-100 spectrometer in the frequency-swept and TMS-locked mode at 100 MHz. Sample concentrations were about 0.5 M in CCl₄. The ¹H spectra were analyzed using an LAOCN 3 computer program. The chemical shifts are expressed by δ and an upfield shift has a negative value. Accuracies are within ±0.1 and -0.01 ppm for ¹³C and ¹H chemical shifts, respectively.

[‡] Anisotropic shielding effects of the cyclopropane ring on C_c and C_d are expected to amount to only 1 ppm at the most in view of the size of the effects upon the protons in these compounds.¹

Table 1. ^{13}C NMR Data in CDCl_3

No.	Compound		C_a	C_b	C_c	C_d	C_e	C_f	C_g	C_h	C_i	C_j	
(1)		δ_{C}	41.8	24.6	48.5	135.2	-	-	-	-	-	-	
			42.2 ^a	25.5 ^a	48.8 ^a	135.5 ^a	-	-	-	-	-	-	-
			42.0 ^b	24.8 ^b	48.8 ^b	135.8 ^b	-	-	-	-	-	-	-
			41.6 ^c	24.6 ^c	48.5 ^c	135.2 ^c	-	-	-	-	-	-	-
(2)		δ_{C}	41.4	21.9	37.4	141.1	-	-	-	19.2	-	-	
		(2)-(1) $\Delta\delta(\text{ppm})$	-0.4	-2.7	-11.1	5.9	-	-	-	-	-	-	-
(3)		δ_{C}	42.3	12.3	63.7	130.4	-	-	-	17.1	-	-	
		(3)-(1) $\Delta\delta(\text{ppm})$	0.5	-12.3	15.2	-4.8	-	-	-	-	-	-	-
(4)		δ_{C}	43.7	27.1	49.2	-	147.9	125.4	120.3	-	-	-	
(5)		δ_{C}	42.8	20.5	37.1	-	151.5	124.8	120.6	14.9	-	-	
		(5)-(4) $\Delta\delta(\text{ppm})$	-0.9	-6.6	-12.1	-	3.6	-0.6	0.3	-	-	-	
(6)		δ_{C}	43.9	27.1	148.6	-	147.7	125.4	119.9	-	110.8	19.8	
(7)		δ_{C}	45.7	20.5	140.6	-	150.3	124.8	120.2	15.7	116.5	19.5	
		(7)-(6) $\Delta\delta(\text{ppm})$	1.8	-6.6	-8.0	-	2.6	-0.6	0.3	-	5.7	-0.3	
(8)		δ_{C}	50.8	-	161.9	142.9	152.6	124.4	120.8	-	102.2	18.9	
		(8)-(6) $\Delta\delta(\text{ppm})$	6.9	-	13.3	-	4.9	-1.0	0.9	-	-8.6	-0.9	
(9)		δ_{C}	52.3	-	160.1	-	149.5	125.1	121.1	-	107.7	19.3	
		(9)-(6) $\Delta\delta(\text{ppm})$	8.4	-	11.5	-	1.8	-0.3	1.2	-	-3.1	-0.5	

^a Concentrated solution in dioxane. Data cited in ref. 4 (relative to CS_2) are converted to the internal TMS scale using the relationship: $\delta(\text{TMS}) = 192.8 - \delta(\text{CS}_2)$. ^b Concentrated solution in CS_2 . See ref. 5. ^c Taken from ref. 7.

seen in 2, 3, and 5 result mostly from the cyclopropane anisotropy.¹

In the ¹³C NMR spectra of 6-9, differentiation of the C_c from the C_i signal was not easy. However, the effects of π-bonds,⁵ and particularly that of the cyclopropane ring, allow ready assignment of the signals as shown in Table 1. In this case, the upfield shift of -8.0 ppm of the C_c signal from 6 to 7 is smaller than that observed from 4 to 5; this fact may imply a weaker steric interaction between the π electrons of the isopropylidene group and the H_{h(endo)} in 7. Further, the C_c signals were inclined to be more easily saturated than the C_i signals in these spectra, a trend which is consistent with the assignments.³ It is interesting to note that the direction of shift of the C_c and C_i signals due to introduction of a cyclopropane or benzene ring, or a double bond into 6 are opposite to each other.

Table 2. ¹H NMR Data in CCl₄

No.	Compounds to be compared	H _a	H _{b(exo)}	H _{b(endo)}	H _{c(anti)}	H _{c(syn)}	H _d	H _{h(exo)}	H _{h(endo)}
(1) ^a	δ _H	2.83	1.57	0.94	1.32	1.07	5.93	-	-
(2)	δ _H	2.70	-	0.94	0.84	1.11	6.32	0.75	1.43
	(2)-(1) Δδ(ppm)	-0.13	-	0.00	-0.48	0.04	0.39	-	-
(3)	δ _H	2.73	1.29	-	1.67	1.76	5.64	0.54	0.34
	(3)-(1) Δδ(ppm)	-0.10	-0.28	-	0.35	0.69	-0.29	-	-
(4) ^a	δ _H	3.30	1.85	1.14	1.73	1.48	-	-	-
(5)	δ _H	3.16	-	0.98	1.18	1.44	-	0.74	1.37
	(5)-(4) Δδ(ppm)	-0.14	-	-0.16	-0.55	-0.04	-	-	-

^a Data taken from ref. 9.

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