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Carbon-13 Chemical Shifts of Polychlorobicyclo[2.2.1]heptene Derivatives

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Synopsis. The ^{13}C chemical shifts of 5-substituted polychlorobicyclo[2.2.1]heptene derivatives were determined. The chlorine, 5-*endo* and 5-*exo* substituent effects on the chemical shifts were discussed. The differences in the C_3 and C_7 chemical shifts are shown to be helpful for the identification of the *endo* and *exo* isomers. A possible operation of the interaction of pi electrons with a carbon-chlorine dipole is also discussed.

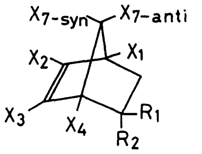
Because of their rigid molecular structures and fixed geometry, bicyclo[2.2.1]heptene derivatives have been extensively investigated by means of the ^{1}H and ^{13}C nuclear magnetic resonance methods.[1-3] The polar substituent effect on the ^{1}H and ^{13}C chemical shifts has been actively discussed as well as the molecular geometry effect on spin-coupling phenomena. Some chlorine nuclear quadrupole resonance (NQR) spectra of chlorobicyclo[2.2.1]heptenes were measured, and the ^{35}Cl NQR frequencies were discussed in terms of the charge density on the chlorine atoms.[4,5] However, the ^{13}C chemical shifts of chlorobicyclo[2.2.1]heptenes seem to have been reported only sporadically. In connection with our research project concerning high-pressure Diels-Alder reactions, we wish to report here some results of the systematic ^{13}C NMR examination of 5-substituted polychlorobicyclo[2.2.1]heptenes. The assignment of the C_5-*endo* and *exo* isomers by means of the ^{13}C NMR spectra is one of the purpose of the present investigation. Discussion will also be focused on the evidence of the interaction of the pi-electrons with a carbon-chlorine dipole.

Results and Discussion

The compounds employed in this work were synthesized by the usual Diels-Alder reactions and are listed in the Scheme. The proton chemical shifts of the compounds have been given elsewhere.[6] All the compounds gave nicely resolved ^{13}C NMR spectra. In most instances, the assignment of the signals to specific carbons was straightforward on the basis of the earlier results,[1-3] together with off-resonance decoupled spectra. In some cases, however, the assignment was made by using the substituent parameters of Lippmaa *et al.*[1]

Substituent Effect. The introduction of chlorine atoms onto C_1, C_4, and C_7 induced a pronounced paramagnetic effect on the substituted atoms and the neighbors. However, the chlorine atoms on C_2 and C_3 exerted a diamagnetic influence on the shifts of the substituted sp^2 carbon atoms.

For compounds **1** and **1′**, three carbons are in γ-positions with respect to the 5-substituent, and the orientation of the substituent affects the shieldings of the γ-carbon atoms (C_1, C_3, and C_7). The steric perturbation caused by the 5-substituent can be anticipated at C_3 by the *endo* 5-substituent, and at C_7 by the *exo* one. Thus, for each *endo* isomer, the C_3 resonance appeared at a higher field than the C_3 of the corresponding *exo* isomer. This shielding effect of the *endo* 5-substituent decreased with the increase in the numbers of the chlorine substituents. On the contrary, the C_7 nuclei were indeed shielded by the *exo* 5-substituent, while the *endo* 5-substituent appeared to cause a slight deshielding of the C_7 atoms.[7] These effects increased in the presence of the chlorine substituents (except for **5′**). These differences, which are real but small, may provide an approach for the assignment of the *endo-exo* isomer pairs.



	X_1	X_2	X_3	X_4	X_7 (*syn*)	X_7 (*anti*)	R_1	R_2
1n	H	H	H	H	H	H	H	CO_2Me
1x	H	H	H	H	H	H	CO_2Me	H
2n	Cl	Cl	Cl	Cl	H	H	H	CO_2Me
2x	Cl	Cl	Cl	Cl	H	H	CO_2Me	H
3n	Cl	Cl	Cl	Cl	H	Cl	H	CO_2Me
4n	Cl	Cl	Cl	Cl	Cl	H	H	CO_2Me
4x	Cl	Cl	Cl	Cl	Cl	H	CO_2Me	H
5n	Cl	Cl	Cl	Cl	Cl	Cl	H	CO_2Me
1′n	H	H	H	H	H	H	H	CN
1′x	H	H	H	H	H	H	CN	H
2′n	Cl	Cl	Cl	Cl	H	H	H	CN
2′x	Cl	Cl	Cl	Cl	H	H	CN	H
5′n	Cl	Cl	Cl	Cl	Cl	Cl	H	CN
5′x	Cl	Cl	Cl	Cl	Cl	Cl	CN	H

Scheme 1.

Pi Electron-Dipole Interaction. The observed high-field shifts of the C_2 and C_3 carbons of the polychloro derivatives can be explained in terms of the electromeric effect of the chlorine atoms.[8] Particularly, the pentachloro derivative with the *anti* chlorine atom on C_7(**3n**) exhibited both the C_2 and C_3 signals at lower fields than the corresponding 7-syn-Cl isomer (**4n**) did. In contrast, the C_7 of **3n** was observed at a higher field than that of **4n**. Because the usual inductive and electromeric effects of the chlorine atom are expected to be quite similar for **3n** and **4n**, and because the double-bond anisotropy can not explain the difference in the bridged methylene ^{13}C chemical shifts of these compounds, this observation implies the operation of some sort of charge delocalization from the double bond to the C_7 carbon atom of the *anti* isomer(**3n**). The high solvolytic reactivity of *anti*-7-norbornenyl chloride has been interpreted in terms of pi-participation. In this connection, Chihara[4] reported the ^{35}Cl NQR frequencies of *anti*-7-

TABLE 1. CARBON-13 CHEMICAL SHIFTS OF BICYCLO[2.2.1] HEPTENE DERIVATIVES(ppm from TMS)

Compound	C_1	C_2	C_3	C_4	C_5	C_6	C_7	CO_2–CH_3	
1n	42.7	137.5	132.7	45.7	43.2	29.4	49.7	173.6	51.1
1x	41.8	138.1	135.9	46.6	42.8	30.4	46.5	175.2	51.3
2n	69.3	134.5	131.5	72.2	54.0	41.8	63.9	169.2	52.4
2x	68.8	136.3	133.8	72.4	51.9	43.6	57.9	170.8	52.4
3n	72.5	133.4	130.7	75.1	51.1	38.5	77.7	169.0	52.5
4n	73.8	131.6	128.6	76.6	50.9	39.0	80.6	168.6	52.8
4x	73.3	133.3	130.8	76.9	50.0	40.8	76.3	170.4	52.9
5n	78.6	132.5	129.7	81.0	50.5	38.3	102.7	168.3	52.7
								CN	
1′n	42.5	138.7	133.0	45.8	27.1	32.5	48.6	122.1	
1′x	42.0	138.1	134.4	47.6	27.4	32.3	47.4	122.2	
2′n	68.6	135.5	132.2	71.4	41.0	43.6	61.5	116.4	
2′x	68.4	136.2	132.2	71.4	39.5	44.2	59.5	117.0	
5′n	78.2	133.6	130.6	80.5	38.3	40.5	100.7	115.2	
5′x	78.3	133.8	131.7	79.7	36.9	39.0	100.2	114.7	

and *syn*-7-norbornenyl chlorides. The results clearly showed that the s-character of the carbon orbital in the C–Cl bond of the latter was larger than that of the former. This conclusion agrees with the ^{13}C chemical shifts and $J_{^{13}C-H}$ values of the C_7 carbon atoms.[9,10] Since this pi-participation involves the transfer of the charge from the double bond to the polarized C_7–Cl bond, this participation may be inhibited by the chlorine substituents on C_2 and C_3, which make the double bond less nucleophilic. The difference in the ^{13}C chemical shift of C_7 between **3n** and **4n** is 2.9 ppm, whereas that between *anti*-7- and *syn*-7-norbornenyl chlorides is 5.4 ppm;[10] this indicates a weaker pi-participation for the 2,3-dichlorinated derivative, **3n**.

Experimental

All the ^{13}C NMR spectra were recorded on a JEOL PS-100 FT spectrometer. The chemical shifts were recorded in ppm from TMS. The compounds employed in this work were prepared from the corresponding dienes and methyl acrylate or acrylonitrile by the Diels-Alder reaction. The details were reported elsewhere.[6] Each isomeric adduct was obtained by preparative glc using a Yanagimoto GCG-3 or a Shimadzu GC-6A gas chromatograph.

References

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6) K. Seguchi, A. Sera, and K. Maruyama, *Bull. Chem. Soc. Jpn.*, **49**, 3558 (1976).

7) The reported chemical shifts for bicyclo[2.2.1]heptene: C_1, 41.8; C_2, 135.2; C_5, 24.6; C_7, 48.5 ppm.[3]

8) G. Miyajima and K. Takahashi, *J. Phys. Chem.*, **75**, 331 (1971).

9) The ^{13}C–H coupling constants were found to be 175 and 166 Hz for **3n** and **4n**, respectively.

10) Private communication from Dr. Kazuo Tori, Research Laboratory, Shionogi and Co., Ltd.: for *anti*-7-chlorobicyclo-[2.2.1]heptene; C_2, 135.4; C_7, 68.2 ppm; $J_{^{13}C-H}$ of C_7, 165.5 Hz: for the *syn*-7 isomer; C_2, 132.0; C_7, 73.6 ppm; $J_{^{13}C-H}$ of C_7, 157.0 Hz.