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Carbon-13 Nuclear Magnetic Resonance Spectra of Chlorinated Pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decanes

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The ¹³C NMR spectra of dodecachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane and four of its hydrogen-substituted derivatives have been obtained. The assignment of the ¹³C resonances was based on chemical shifts, coupling constants, and Overhauser enhancements of the signals. Good correlation was found between the observed chemical shifts and those predicted from substituent parameters and between ¹H chemical shifts and ¹³C chemical shifts. Some unusual variations in the two- and three-bond coupling constants were observed.

Proton-coupled ¹³C NMR studies have generally been limited to simple molecules because of the complexity of the spectra and the low sensitivity associated with this technique. The availability of dodecachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane (compound **1**) and some of its hydrogen derivatives provided an excellent opportunity to investigate the ¹H-¹³C coupling and the inductive effects in a set of closely related and relatively large molecules. These compounds have a rigid carbon skeleton, and on account of its symmetry, **1** contains only three sets of magnetically different carbons. Four hydrogen derivatives of **1** were available from photochemical reactions²⁻⁴ and other synthetic routes.⁵

Compound **1** was first synthesized in 1945 by Prins.⁶ Its structure was deduced from infrared,⁷ x-ray,⁸ and mass

spectral⁹ data. This compound has been used commercially as a pesticide (Mirex)[®] and a fire retardant (Dechlorane)[®] and has been the subject of pyrolysis,¹⁰ chemical,^{5,8} and photochemical²⁻⁴ investigations. The structures of compounds **2**, **3**, and **5** were assigned from NMR, infrared, and mass spectral data.²⁻⁴ The geometry of compound **4** was deduced in this study.

Experimental Section

The ¹³C NMR spectra were obtained at 22.6 MHz with a Bruker HX-90 spectrometer, operated in the single coil configuration with a heteronuclear ¹⁹F lock and equipped for fast Fourier transformation with a Nicolet 1083 data system. ¹H NMR spectra were obtained at 90 MHz in the continuous wave mode with a homonuclear lock.

Chemical shifts were measured while employing noise-modulated ¹H decoupling¹¹ at ambient probe temperature (approximately 25°C). Saturated solutions in carbon disulfide containing 5% (v/v) hexafluorobenzene and 10% (v/v) tetramethylsilane were used for the lock and chemical shift reference, respectively. Approximately 1.3 ml of sample solution was contained in 10-mm o.d. sample tubes fitted with vortex plugs. Chemical shift data encompassing a 5000-Hz spectral region were collected into 8K data points, yielding a computer resolution of 1.2 Hz (0.04 ppm). Typically, 20 000 scans with a delay time of 2 sec between scans were necessary to obtain a good spectrum.

Gated, noise-modulated ¹H decoupling was applied in order to observe long-range ¹³C-¹H coupling.^{12,13} The BSV-2 decoupler was on for 1.8 sec and off 0.2 sec prior to the data acquisition, using circuitry similar to that of Dorn et al.¹⁴

Compound **1** (98%), obtained from Allied Chemical Corp., was recrystallized from benzene. Two hydrogen-substituted derivatives of compound **1** were prepared by the methods of Dilling.⁵ Two other derivatives were prepared by the photolysis of compound **1** as described elsewhere.^{2,3}

Discussion

The ¹³C spectrum for compound **1** (Table I) consisted of three singlets at 91.6, 82.4, and 76.5 ppm downfield from Me₄Si with relative areas of 1:3:2. The peak at the lowest field and with the smallest intensity was assigned to the di-

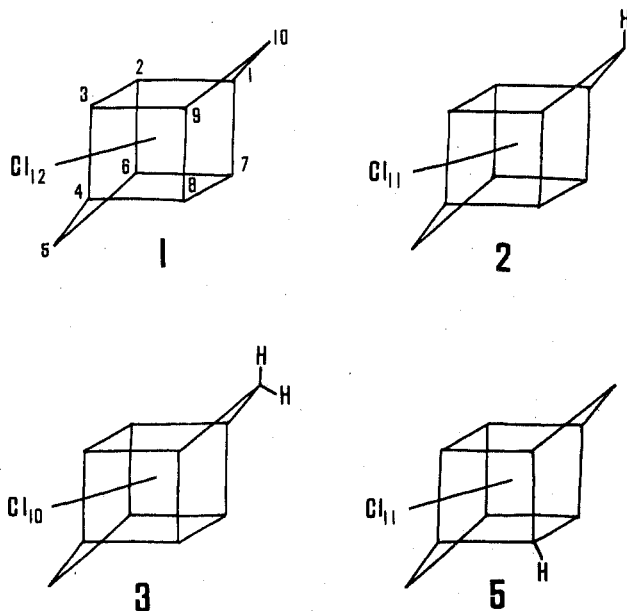


Table I

Compd	Decoupled spectra			Coupled spectra		
	Chemical shifts, ppm from Me ₄ Si	Relative area	Multiplicity	Coupling constant, Hz	Relative area	Assignment
1	91.6		1	0	1.0	5 and 10
	82.4		1	0	3.0	1, 4, 6, and 9
	76.5		1	0	2.0	2, 3, 7, and 8
2	92.0	1.0	1	0	1.0	5
	83.1	2.9	1	0	2.6	4 and 6
	78.2	9.3	2	3.9 ± 1	5.1	2 and 3
	77.1	2.3	2	8.7 ± 1	1.7	7 and 8
	75.4	3.7	1	0	2.4	1 and 9
	67.4	30	2	164 ± 1	25	10
3	92.7		1	0	1.0	5
	83.2		1	0	3.1	4 and 6
	77.0		3	5.4 ± 1	10	2, 3, 7, and 8
	75.1		3	5.4 ± 1	24	1 and 9
	45.9		3	141 ± 1	120	10
4	93.5	1.0	1	0	1.0	5 and 10
	76.8	3.0	1	0	1.8	1, 4, 6, and 9
	71.8	1.1	2	17 ± 1	1.0	3 and 7
	61.0	9.6	2	176 ± 1	4.8	2 and 8
5	92.6	2.2	1		2.2	5 and 10
	82.8	1.8	1		1.8	1 and 6
	78.6	1.0	2	12.2 ± 1	1.0	2 or 3
	76.2	4.5	1	0	3.8	3 or 2
	76.2	...	1	0	...	4 and 9
	69.6	1.6	2	4.9 ± 1	1.6	7
	60.9	9.4	2	176 ± 1	5.2	8

chloromethylene bridge carbons (C-5 and C-10). The bridgehead carbons (C-1, C-4, C-6, and C-9) are bonded to one dichloro carbon and two monochloro carbon atoms. Thus, they have one more β -chlorine substituent than carbons C-2, C-3, C-7, and C-8 and would be expected to appear at approximately 6 ppm lower field strength.¹⁵ Therefore, the resonance at 82.4 ppm was assigned to C-1, C-4, C-6, and C-9, and the one at 76.5 ppm was assigned to C-2, C-3, C-7, and C-8. The discrepancy in the relative intensity of the resonance lines was attributed, in part, to the experimental conditions employed.¹⁶

For the hydrogen derivatives, the resonances for carbon atoms bonded to hydrogen were differentiated from those for carbons not bonded to a hydrogen by the higher field chemical shift values, the larger coupling constants and, in the proton-decoupled spectra, the nuclear Overhauser effect. The chemical shifts of other resonances were compared to predicted values¹⁵ for carbons in various positions. In a study of perchlorinated compounds, it was observed that replacement of a chlorine substituent by a hydrogen produced a high-field shift of 25 and 6 ppm at the α and β carbons, respectively, and a low-field shift of 1 ppm at the γ carbons.¹⁵ Except for the β parameters, these substituent increments are in good agreement with those reported for one group of aliphatic compounds¹⁷ but are somewhat smaller than those reported for polychloromethanes¹⁸, 1-chloroalkanes,¹⁹ chlorocyclohexane, and chloroadamantane.²⁰

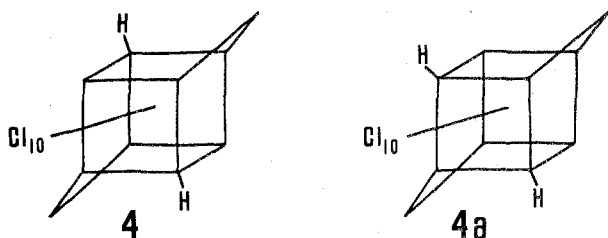
Compound 2 (1,2,3,4,5,5,6,7,8,9,10-undecachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane) has fewer symmetry planes than compound 1 and thus has six magnetically different carbon atoms. The spectrum of 2 (Table I) consisted of six resonances at 92.0 (s), 83.1 (s), 78.2 (d, $J = 3.9$ Hz), 77.1 (d, $J = 8.7$ Hz), 75.4 (s), and 67.4 ppm (d, $J = 164$ Hz). The large, one-bond ¹³C-¹H coupling and the high-field shift readily identified the 67.4-ppm absorption as that due to the monochloromethylene bridge carbon, C-10. The resonances at 83.1 and 92.0 ppm were assigned to carbons C-4 and C-6 and carbon C-5, respectively, using arguments analogous to those made for the assignments of the resonances in 1. The resonance at 75.4 ppm was assigned to car-

Table II

Compd	Carbon atom	δ observed	δ predicted	Δ
1	5, 10	91.6		
	1, 4, 6, 9	82.4		
	2, 3, 7, 8	76.5		
2	5	92.0	91.6	+0.4
	4, 6	83.1	82.4	+0.7
	2, 3	78.2	77.5	+0.7
	7, 8	77.1	77.5	-0.4
	1, 9	75.4	76.4	-0.1
	10	67.4	66.6	+0.8
3	5	92.7	91.6	+1.1
	4, 6	83.2	82.4	+0.8
	2, 3, 7, 8	77.0	78.0	-1.0
	1, 9	75.1	71.4	+3.7
	10	45.9	45.6	+0.3
4	5, 10	93.5	93.6	-0.1
	1, 4, 6, 9	76.8	77.4	-0.6
	3, 7	71.8	71.5	+0.3
	2, 8	61.0	51.5	+9.5
5	5, 10	92.6	92.6	0.0
	1, 6	82.8	83.4	-0.6
	2	78.6 or 76.2	76.5	+2.1 or -0.3
	3	76.2 or 78.6	77.5	-1.3 or +1.1
	4, 9	76.2	76.5	-0.3
	7	69.6	70.5	-0.9
	8	60.9	51.5	+9.4

bons C-1 and C-9 which is in good agreement with the predicted value¹⁵ (Table II) for these carbon atoms. The inductive effect associated with the replacement of a chlorine on C-10 with a hydrogen will be transmitted through bonds equally to carbons C-2 and C-3 and to carbons C-7 and C-8. However, the interaction exerted on carbons C-7 and C-8 by the chlorine atom on C-10 will be absent for carbons C-2 and C-3, which have a hydrogen situated syn to them. This leads to the expectation that C-7 and C-8 will resonate at a higher field (77.1 ppm) than carbons C-2 and C-3 (78.2 ppm).^{17,21-24} Similar 1,4-nonbonded interactions in aliphatic hydrocarbons produce approximately a 2.5-ppm high-field shift,²¹ while the steric compression exerted on C-6 of *endo*-2-chloro and *endo*-2-hydroxy derivatives of bornane causes approximately a 9-ppm high-field shift.¹⁷

The ^{13}C NMR spectrum for 1,2,3,4,5,6,7,8,9-decachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane (compound 3, Table I) consisted of five resonances at 92.7 (s), 83.2 (s), 77.0 (t, $J = 5.4$ Hz), 75.1 (t, $J = 5.4$ Hz), and 45.9 ppm (t, $J = 141$ Hz). The high-field shift and the large coupling constant of the resonance at 45.9 ppm dictated that it be assigned to the methylene bridge, C-10. The assignment of the triplets at 75.1 and 77.0 ppm was made to carbons C-1 and C-9 and to carbons C-2, C-3, C-7, and C-8, respectively. This assignment minimized the deviations between the observed and the predicted chemical shifts. The enhancement of the 75.1-ppm resonance supported its assignment to C-1 and C-9. By analogy with the resonances of compound 1, the peaks at 83.2 and 92.7 ppm were assigned to carbons C-4 and C-6 and carbon C-5, respectively.



The structure of a second dihydro derivative of compound 1 is either 4 or 4a.² Compound 4 has four magnetically different carbons, and 4a has five because the molecules have different symmetry properties. The observed four-peak spectrum is consistent with structure 4 (1,3,4,5,5,6,7,9,10,10-decachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane). The observed resonances were at 93.5 (s), 76.8 (s), 71.8 (d, $J = 17$ Hz), and 61.0 ppm (d, $J = 176$ Hz). The absence of a signal near 82 ppm excluded from consideration structure 4a (the 3,8-dihydro isomer). The resonance at 61.0 ppm can be assigned unequivocally to the carbons bonded directly to the hydrogens (C-2 and C-8) by reason of the large splitting of this peak (176 Hz). The peak at 93.5 ppm was assigned to the dichloromethylene bridges (C-5 and C-10), utilizing arguments analogous to those employed for compounds 1, 2, and 3. The methylene bridgeheads (C-1, C-4, C-6, and C-9) are each bonded to a dichloro carbon atom and a monochloro carbon atom, whereas carbons C-3 and C-7 have only two chlorines in the β positions. The predicted values¹⁵ for the methylene bridgeheads (C-1, C-4, C-6, and C-9) and carbons C-3 and C-7 are 77.4 and 71.5 ppm, respectively. The predicted values deviated from the observed ones by an average of only 0.5 ppm if the 76.8-ppm resonance was assigned to carbons C-1, C-4, C-6, and C-9, and the 71.8-ppm resonance was assigned to carbons C-3 and C-7. The normalized intensity ratios revealed a slight Overhauser enhancement for the 76.8-ppm resonance, supporting its assignment to C-1, C-4, C-6, and C-9.

The ^{13}C NMR spectrum of 1,2,3,4,5,5,6,7,9,10,10-undecachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane (compound 5, Table I) consisted of six resonances at 92.6 (s), 82.8 (s), 78.6 (d, $J = 12.2$ Hz), 76.2 (s), 69.6 (d, $J = 4.9$ Hz), and 60.9 ppm (d, $J = 176$ Hz) from Me_4Si . The line width and relative integrated intensity of the 76.2-ppm resonance indicated that it was a pair of overlapping resonances. The resonances at 92.6 and 82.8 ppm were assigned to the dichloromethylene bridges (C-5 and C-10) and their bridgeheads (C-1 and C-6), respectively. The large splitting of the resonance at 60.9 ppm (176 Hz) dictated that it be assigned to carbon C-8. The doublet at 69.6 ppm was assigned to carbon C-7, since it is bonded to the most shielded carbon (C-8) and to only two monochloro carbon atoms (C-4 and C-9). The chemical shift of this resonance compared favor-

ably with a value of 70.5 ppm predicted from literature parameters.¹⁵ The resonance at 76.2 ppm was assigned to carbons C-4 and C-9 because the closely related carbons (C-1, C-4, C-6, and C-9) in 4 resonate at 76.8 ppm. The two remaining resonances at 76.2 and 78.6 ppm could not be assigned unequivocally. The predicted chemical shift¹⁵ for carbon C-3 is 77.5 ppm, and the 12-Hz coupling constant is not unreasonable for a three-bond coupling. However, all the carbon atoms which are three bonds from the hydrogen atom were not coupled with it; and in compound 4, C-3 and C-7 were coupled to only one hydrogen atom. In both the coupled and decoupled spectra, the 78.6-ppm resonance had the smallest signal intensity. Therefore, these couplings and the nuclear Overhauser enhancement indicated that the resonances at 76.2 and 78.6 ppm were from C-3 and C-2, respectively. This assignment requires that carbon C-2 be coupled to the hydrogen through four bonds (12 Hz). Although the assignment of the 78.6-ppm resonance to C-2 was not certain, the unusually large four-bond coupling could find its basis in the overlapping back lobes^{25,26} of bonding orbitals of the two carbon atoms (C-2 and C-8).

Table II contains the observed resonances, a set of predicted chemical shifts, and the deviations between the predicted and observed values. The predicted shifts were obtained by adding the appropriate substituent parameters^{15,17} to the resonances of compound 1. The influence of a substituent on a given carbon was counted once for each equivalent path.²⁷ The range of observed chemical shifts was 48 ppm. Agreement of predicted and observed values was good except for the hydrogen-substituted carbons of compounds 4 and 5, for which the largest deviations were 20% of the range. The next largest deviation is 8% for C-1 and C-9 of compound 3. The range of the deviations for the remaining nineteen shifts was only 0–4.4%.

A comparison of the chemical shift of each carbon atom bonded to a hydrogen and the chemical shift of that hydrogen^{2,5} revealed that the two shifts were related linearly. These data yielded the empirical equation

$$\delta_c = 12.5 \delta_H + 13.8$$

The correlation coefficient for the regression analysis of the data was 0.999. Spiess and Schneider^{28,29} also have observed linear relationships between chemical shifts of hydrogen and carbons for groups of similar compounds but found that these relationships broke down where steric hindrance was important.

There were some anomalies in the ^1H - ^{13}C coupling of these molecules. For compounds with a hydrogen on the 2 or 8 position (compounds 4 and 5), the hydrogen coupled with only one of the three β carbons. Variations in the two- and three-bond coupling constants were assumed to be related to the hybridization of the carbons,^{30–33} the dihedral angles,^{34,35} and the substituent effects.^{30,33} The magnitude of the two- and three-bond coupling constants for compound 3 were identical, and for compound 2 the hydrogen was coupled with the γ carbons but not with the β carbons. Although this seemed unusual, similar results have been obtained for other compounds.^{31,32} In compound 2, the three-bond, ^1H - ^{13}C coupling constant for carbons C-7 and C-8 was different than the one for carbons C-2 and C-3. These differences could be the result of a sensitive dependence on the dihedral angle³⁴ or of coupling by a back lobe overlap mechanism.^{24,25,36} These results indicate that caution should be employed when long-range ^1H - ^{13}C coupling constants are used as criteria for structure assignments. Preparation of additional compounds related to those in this study has been initiated. These compounds will be used to investigate variations in the ^1H - ^{13}C coupling constants.

Registry No.—1, 2385-85-5; 2, 845-66-9; 3, 15443-23-9; 4, 57096-48-7; 5, 39801-14-4.

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Carbon-13 Chemical Shifts in Bicyclo[2.2.2]octanes

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The ^{13}C chemical shifts for a number of bicyclo[2.2.2]octanes substituted in the 2 and 2,5 positions have been obtained in natural abundance. Substitution parameters have been derived from the 2-substituted compounds and these parameters can be used to determine the relative stereochemistry of groups at C-2 and C-5. A comparison of the presently derived parameters with the known parameters for the norbornyl system has been made.

The value of ^{13}C NMR spectroscopy for the study of the stereochemistry of relative rigid molecules, such as norbornyl derivatives, has been demonstrated by Grutzner et al.¹ and Schneider and Bremser.² In the course of synthetic studies we have had occasion to prepare a number of bicyclo[2.2.2]octane derivatives, largely with substituent at positions 2 and 5,³ and we have examined the ^{13}C NMR spectra of these compounds as an aid to the assignment of the relative stereochemistry of these substituents. Following the earlier studies,^{1,2,4} we have classified the substituent perturbations in terms of α , β , γ , and δ effects, the substituent being introduced at the α -carbon atom. The special γ effect which is operative in the norbornyl series¹ is operative in the bicyclo[2.2.2]octanes. The parameters obtained in the present work have been compared with those obtained for the norbornyl system, and substantial agreement both in the size and magnitude of the shifts is observed. Differences can probably be accounted for in the greater flexibility of the bicyclo[2.2.2]octane framework.

Assignments. Our initial studies were carried out on bicyclo[2.2.2]octane (1), bicyclo[2.2.2]octan-2-ol (2), and the three epimeric bicyclo[2.2.2]octan-2,5-diols (3a-c). The structure and assignment are shown in Table I. The epimeric diols 3b and 3c were extremely valuable in establishing these assignments, since each contain only four carbon

atoms with different chemical environments due to the symmetry of the system. In 3b, C-2 and C-5, the carbons substituted by the hydroxyl groups, were shown to be doublets by an off-resonance experiment, and show the largest downfield shift compared to the corresponding carbons in bicyclo[2.2.2]octane, and this is readily correlated with a similar α shift in alcohols. The tertiary carbons C-1 and C-4 are also doublets in the off-resonance experiment, and are shifted downfield, mainly due to the β effect. The remaining carbons to be assigned are the equivalent pairs C-3, C-6 and C-7, C-8. Based on the shielding and deshielding effect of the γ effect in norbornanes, we assign the carbons shifted downfield as C-3, C-6 and those upfield as C-7, C-8. In 3c, C-2 and C-5 were again doublets in the off-resonance experiment, and are again shifted downfield, and the tertiary atoms C-1 and C-4 are also doublets and show a downfield shift. With the remaining two pairs of carbon atoms, C-3, C-6 and C-7, C-8, the assignments are again based on the expected direction of shift from the norbornanes. Further, the gross magnitude of the shifts are as expected, C-7, C-8 less affected in 3c than in 3b because of the smaller interaction, and the C-3, C-6 shift in 3c smaller than in 3b because of the opposed direction of the two effects. The assignments receive further strong support from the spectrum of the unsymmetrical isomer, 3a. Here C-1,