(10 mL) was added, and the reaction mixture was stirred for 24 h. The solution was washed with water, and the solvent was removed. The product was redissolved in methylene chloride, and 2 g of bromine was added. Crystals slowly formed and after 4 days 4.8 g (67% yield) of 1,1,3,3,5,5-hexakis(3-fluoro-3,3-dinitropropyl)cyclotrisiloxane was isolated by filtration. The product was recrystallized from ethyl acetate and Skelly F to give white crystals: mp 207–209 °C; proton NMR (acetone-d_6) δ 3.14 (m, 4 H, CH_2CF), 1.20 (m, 4 H, CH_2Si); fluorine NMR (acetone-d_6) ϕ 106.0; IR (KBr) 1590, 1320, 1270, 1210, 1090 cm^{-1}. Anal. Calcd for $C_6H_8N_4O_9F_2Si$: C, 20.83; H, 2.33; N, 16.19. Found: C, 21.00; H, 2.36; N, 16.17; mol wt (vapor phase osmometer/EtOAc), 1010 ± 5% (trimer = 1038).

Registry No.—Sodium nitrite, 7632-00-0; (3-bromopropyl)trimethylsilane, 10545-34-3; (3-nitropropyl)trimethylsilane, 64035-55-8; (3-hydroxypropyl)trimethylsilane, 2917-47-7; (4-bromobutyl)trimethylsilane, 18379-55-0; (4-nitrobutyl)trimethylsilane, 64035-56-9; (3-bromobutyl)trimethylsilane, 18379-54-9; (3-nitrobutyl)trimethylsilane, 64035-57-0; (3-hydroxybutyl)trimethylsilane, 18387-24-1; (3-nitrotobutyl)trimethylsilane, 64035-58-1; (3,3-dinitropropyl)trimethylsilane, 64035-59-2; (4,4-dinitrobutyl)trimethylsilane, 64035-60-5; (3,3-dinitrobutyl)trimethylsilane, 64035-61-6; (3-fluoro-3,3-dinitropropyl)trimethylsilane, 64035-62-7; (4-fluoro-4,4-dinitrobutyl)trimethylsilane, 64035-63-8; (hydroxymethyl)trimethylsilane, 3219-63-4; trimethylsilylmethyltriflate, 64035-64-9; 2-fluoro-2,2-dinitroethanol, 17003-75-7; trimethylsilylmethyl 2-fluoro-2,2-dinitroethyl ether, 64035-65-0; allyl bromide, 106-95-6; chloromethyldiphenylsilane, 144-79-6; allylmethyldiphenylsilane, 17922-43-9; (3-bromopropyl)methyldiphenylsilane, 64035-66-1; allyloxytrimethylsilane, 18146-00-4; (3-hydroxypropyl)methyldiphenylsilane, 64035-67-2; toluenesulfonyl chloride, 98-59-9; (3-p-toluenesulfonatopropyl)methyldiphenylsilane, 64035-68-3; (3-nitropropyl)methyldiphenylsilane, 64035-69-4; (3,3-dinitropropyl)methyldiphenylsilane, 64035-70-7; (3-fluoro-3,3-dinitropropyl)methyldiphenylsilane, 64035-71-8; (3-fluoro-3,3-dinitropropyl)methyldibromosilane, 64035-72-9; (3-fluoro-3,3-dinitropropyl)methyldifluorosilane, 64035-73-0; (3-fluoro-3,3-dinitropropyl)methylmethoxyfluorosilane, 64035-74-1; 1,3-bis(3-fluoro-3,3-dinitropropyl)-1,3-dimethyl-1,3-difluorodisiloxane, 64035-75-2; dichlorodiphenylsilane, 80-10-4; 3-chloropropanol, 627-30-5; bis(3-chloropropoxy)diphenylsilane, 63802-06-2; bis(3-hydroxypropyl)diphenylsilane, 34564-72-2; diallyldiphenylsilane, 10519-88-7; diphenylsilane, 775-12-2; bis(3-bromopropyl)diphenylsilane, 64035-76-3; bis(3-p-toluenesulfonatopropyl)diphenylsilane, 64035-77-4; bis(3-nitropropyl)diphenylsilane, 64035-78-5; bis(3,3-dinitropropyl)diphenylsilane, 64035-79-6; bis(3-fluoro-3,3-dinitropropyl)diphenylsilane, 64035-80-9; 1,1,3,3,5,5-hexakis(3-fluoro-3,3-dinitropropyl)cyclotrisiloxane, 64035-81-0; $(CF_3SO_2)_2O$, 358-23-6.

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^{13}C–^{13}C Spin Coupling Constants within the Bicyclo[2.2.2]octane and Bicyclo[3.2.1]octane Systems

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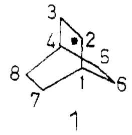
A series of eight derivatives of the bicyclo[2.2.2]octane and the bicyclo[3.2.1]octane system with a ^{13}C label have been synthesized. The ^{13}C–^{13}C spin coupling constants have been measured and interpreted in terms of substituent and conformational dependence.

The early work on carbon–carbon spin coupling constants mainly centered on directly bonded carbon atoms. The substituent dependence, the effect of orbital hybridization, and the sign of these coupling constants were investigated by the research groups of Roberts,[1] Grant,[2] and Maciel.[3] Early theoretical work by Pople[4] again focussed on the interpretation of $^1J_{C,C}$. More recently the interest shifted to two- and three-bond coupling constants,[5] both in experimental[6] and in theoretical[7] work. The current interest in ^{13}C–^{13}C couplings apparently seems to be threefold: (i) in a series of papers[8] the usefulness of both direct and long-range coupling constants in determining biosynthetic pathways is demonstrated; (ii) the conformational dependence of carbon coupling constants is investigated;[9] and (iii) the mechanism of carbon coupling constant transmission in π systems is open to question.[10]

Very recent theoretical predictions on the angular dependence of ^{13}C–^{13}C spin couplings[11] led us to continue our studies of compounds[9] in which the labeled carbon atom is directly part of a rigid bi- or tricyclic system, whereby the carbon–carbon long-range coupling constants are not subject



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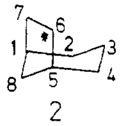

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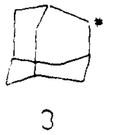

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Table I. ^{13}C Chemical Shifts of the Derivatives of 1, 2, and 5[a]

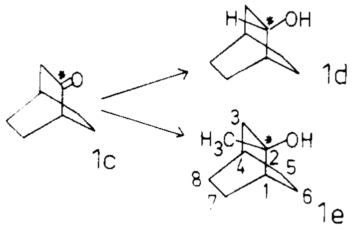
Compd	Registry no.	Carbon atom 1	2	3	4	5	6	7	8
1a	64162-90-9	50.9	212.9	43.3	27.9	38.0	54.4	17.3	24.2
b	64200-02-8	50.5	211.4	43.9	28.4	37.7	55.2	22.7	23.3
c	64162-91-0	41.6	217.3	44.6	27.9	24.7	23.3	23.3	24.7
d	64162-92-1	31.6	69.5	37.5	24.9	25.7	18.7	23.8	24.6
e[b]	64162-93-2	36.6	71.7	44.1	26.2	24.4[c]	21.1	23.3	24.6[c]
2a	64162-94-3	32.0	26.0	28.3	58.5	53.5	216.2	42.9	31.5
b	64162-95-4	32.0	30.5	18.7	30.3	45.9	221.2	43.3	37.0
c	64162-96-5	34.3	32.6	19.5	26.8	39.3	75.0	38.0	37.9
5a	64162-97-6	30.5	31.3	125.7	126.9	24.7	28.4	40.9	179.8
b	64162-98-7	30.5	30.2	124.4	126.4	24.0	27.4	52.8	172.0

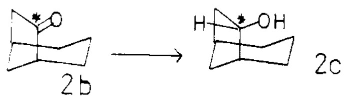
[a] ppm vs. internal Me_4Si. [b] CH_3, 30.3 ppm. [c] Relative assignment is tentative.

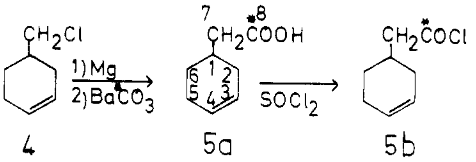
to conformational or rotational averaging. In this work, we report the ^{13}C–^{13}C spin couplings in the bicyclo[2.2.2]octane system (**1**) labeled at C-2 and the bicyclo[3.2.1]octane system (**2**) labeled at C-6 and compare these with the results of the adamantane system (**3**) previously reported.[9]

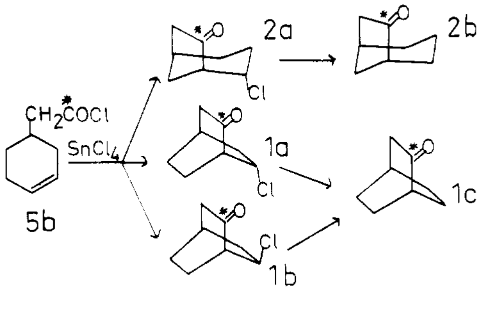
Results and Discussion

Synthesis of the Labeled Compounds. Monti and White[12] recently reported a new synthesis for bicyclo[2.2.2]octan-2-one (**1c**) which seemed feasible for labeling purposes. Thus, we prepared from 3-cyclohexene-1-methylene chloride (**4**) the carboxyl-^{13}C-labeled 3-cyclohexene-1-acetic acid (**5a**) and its acid chloride (**5b**). On intramolecular Friedel–Crafts reaction, **5b** yields three keto chloride isomers, separable by preparative GLC. Monti and White[12] assigned the structures **1a** and **2a** to two of the isomers. Contrary to their work, we were able to reduce all three isomers by tri-*n*-butyltin hydride. Since the third isomer yields, like **1a**, bicyclo[2.2.2]octan-2-one (**1c**) on reduction, we assign the *endo*-chloro ketone structure **1b** to it according to the spectroscopic results outlined below. **1c** was further reduced to the alcohol **1d** and to the methyl alcohol **1e**. **2b** was reduced to the alcohol **2c**. The limited amount of labeled material did not allow further transformations.







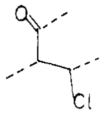


^{13}C Chemical-Shift Assignments. The ^{13}C chemical shifts of the derivatives of **1**, **2**, and **5** are given in Table I. The chemical-shift assignment of **1c** follows the assignment of Stothers,[13] who investigated in detail the bicyclo[2.2.2], -[2.2.1], and -[3.2.1] systems. From these results and the incremental shift values for chlorine in the bicyclo[2.2.1] system,[14] it was possible to assign the exo and endo structures of the two bicyclo[2.2.2]keto chlorides **1a** and **1b**. Stothers has shown that substituents cause similar incremental shifts in both the bicyclo[2.2.2] and the bicyclo[2.2.1] systems. For **1a** there is a typical γ shielding effect for C-7 of 6 ppm if one compares its shift position with the chemical shift of C-7 in **1c**. Compound **1d** has already been reported, and our values are in agreement with the literature.[13] The closely resonating carbon atoms C-5, C-7, and C-8 were distinguished using the incremental shifts of the OH group.[14] The addition of a methyl group to the same C-2 already bearing a hydroxyl group in **1e** deshields the resonance of C-2 only by 2.2 ppm. Its effect on the chemical shift of C-3 and C-1, however, is in the predicted range. C-6, being in a γ anti position with respect to the methyl group, is deshielded by 2.4 ppm, and C-7 moves only slightly upfield to 23.2 ppm, a value quite comparable with that of the corresponding carbon atom of 2,2-dimethylbicyclo[2.2.2]octane.[13] The relative assignment of C-5 and C-8 is tentative.

The ^{13}C chemical shifts of bicyclo[3.2.1]octan-6-one (**2b**) have been reported.[15] For bicyclo[3.2.1]keto chloride **2a**, where only one isomer was isolated, the exo structure was determined from the chemical-shift values of C-8 and C-2, both of which again show the typical γ upfield effect. All the other chemical-shift values in this isomer are in reasonably good agreement with shift values calculated by the incremental shifts for chlorine.[14] The chemical shifts of **2c** were very recently discussed by Stothers.[16]

The chemical shifts for the cyclohexene compounds **5a** and **5b** were assigned with the help of the data from Lippmaa,[17] who studied a variety of substituted cyclohexenes. All the assignments given in Table I have been checked by off-reasonance spectra.

^{13}C–^{13}C Spin Coupling Constants. The ^{13}C–^{13}C spin coupling constants of the derivatives of **1**, **2**, and **5** are given in Table II. The one-bond coupling constants do not vary much; their relative insensitivity to structural changes has already been pointed out.[2] However, it might be noted that starting from the unsubstituted ketone **1c**, $^1J_{C\text{-}2,C\text{-}1}$ decreases for the chloro ketone **1a** and increases for the endo isomer **1b**. This might further support the correctness of the structural assignment of **2a** since the lowering of $^1J_{C\text{-}6,C\text{-}5}$ compared to that in **2b** would emphasize a structure in which the carbonyl



group and the chlorine atom are in a transoid arrangement. The open chain compounds (**5**) show $^1J_{C,C}$ values in the known range for acetic acid derivatives.[3]

The geminal coupling constants in the bicyclo[2.2.2] system (**1**) tend to be smaller than the vicinal ones. This confirms our findings from the adamantane system.[9] As in the adamantane system, the carbon atom syn to the polarizing substituent (C-6 in **1d** and **1e**) shows the higher geminal coupling constant. Thus, we can possibly conclude that this is a general feature of geminal $^{13}C-^{13}C$ coupling constants in aliphatic compounds.

The vicinal coupling constants in butane were calculated by Barfield et al.[7] to be 1.94 Hz for a dihedral angle of 60°. In a later paper,[11] the authors gave values ranging from 0.86 to 2.54 Hz using different refinements of their INDO FPT approach. In the bicyclo[2.2.2] series (**1**), a dihedral angle of 60° between the labeled C-2 atom and the vicinal coupling partners C-5 and C-8 applies. Our experimental values range from 1.4 to 2.4 Hz, as in the adamantane series where the same dihedral angle applies.

In the bicyclo[3.2.1] system (**2**) the geminal coupling constants show a remarkable change. C-1 shows in all three compounds measured the normal magnitude already found in the bicyclo[2.2.2]octane series. The geminal coupling constant of C-4 can not be resolved in **2a**; the other two compounds again show normal values. Unexpectedly high, however, are the values for C-8 in all three compounds (**2a–c**). The value of 6.1 Hz in **2c** is probably the highest reported geminal coupling constant in aliphatic compounds. Currently we have no reasonable explanation for this circumstance. The vicinal coupling constants for C-2 are not resolvable; in **2b** and **2c** the vicinal coupling constants to C-3 are very small. Theoretically[11] one expects no resolvable coupling constant for C-2 in these systems since the dihedral angle between the bonds C-6, C-7, and C-1, C-2 can be estimated to be about 90°. If one assumes a flattening of the six-membered ring in the bicyclo[3.2.1]octane derivatives,[18] the dihedral angle between the bonds C-6, C-5 and C-4, C-3 can get close to 90° as well. Thus, if the theoretical predictions are valid, the very small vicinal $^{13}C-^{13}C$ coupling constant in these compounds would indicate a flattening of the six-membered ring. Finally, the open-chain compounds (**5**) show the largest vicinal coupling constants of the series reported here, a result which probably supports the idea of impinging back lobes[11] reducing the coupling constants for stereochemically rigid compounds.

Conclusions

In this work, we have shown that the principal results found earlier in the adamantane series regarding the directional substituent dependence for geminal and vicinal coupling constants between carbon atoms are also valid in the bicyclo[2.2.2] system. The values for the bicyclo[3.2.1] system possibly indicate a flattened six-membered ring; however, there are only limited examples. It is evident that further studies of labeled and geometrically fixed systems are needed to check the theoretical results.

Experimental Section

Materials. 3-Cyclohexene-1-methylene chloride (**4**) was prepared[19] from 1-hydroxymethylene-3-cyclohexene (EGA Chemie). 3-Cyclohexene-1-[^{13}C]acetic acid (**5a**) was prepared[20] by reacting a Grignard solution of **4** (300 mmol in 100 mL of dry ether) on a high-vacuum line as described by Murray and Williams[21] with $^{13}CO_2$ developed from 90% enriched $BaCO_3$ and concentrated H_2SO_4; yield 80%. Acid chloride **5b** was prepared by stirring **5a** with an equimolar amount of $SOCl_2$. *exo*-6-Chlorobicyclo[2.2.2]octan-2-one (**1a**), *endo*-6-chlorobicyclo[2.2.2]octan-2-one (**1b**), and *endo*-4-chlorobicyclo[3.2.1]-octan-6-one (**2a**) were prepared according to Monti and White.[12] They were separated by preparative GLC (Aerograph A 90 P, Carbowax 20 M on Chromosorb G, 60–80 mesh, 1.8 m, ¼ in, 180 °C, 70–80 mL of He).

Tri-*n*-butyltin hydride reduction of these compounds was achieved according to the procedure given by Monti and White[12] with the exception that a spatula tip of azoisobutyric acid dinitrile was added. Under these conditions, all three isomers could be reduced.

Compounds **1d**, **1e**, and **2c** were obtained by $LiAlH_4$ reduction of **1c** and **2b** and by methyllithium addition to **1c** via standard procedures. The physical constants of all compounds reported here are already in the literature.[12,13,22,23]

NMR Measurements. The ^{13}C spectra were obtained on a Varian XL-100-15 spectrometer equipped with a 16K 620 L computer and a Varian disc system. Thus, 32K FT spectra were obtained with no exponential filtering and with a digital resolution of less than 0.2 Hz/point. Where no coupling constants are given in Table II, the value is lower than 0.35 Hz. Spectra were mostly taken three times in rather diluted solutions of $CDCl_3$ due to the limited amount of material. Agreement between the different runs was excellent.

Table II. $^{13}C-^{13}C$ Spin Coupling Constants (Hz) in the Derivatives of 1, 2, and 5

	Carbon atom							
Compd	1	2	3	4	5	6	7	8
1a	36.5		35.5	1.2	1.4	1.1	2.0	2.4
b	39.4		35.6	1.6	1.8	2.7	1.8	2.7
c	38.6		34.6	1.5	2.2	1.7	1.7	2.2
d	36.0		34.7	1.0	2.4	1.9	0.7	2.4
e[a]	36.7		35.4	1.2	1.7	1.7		1.8
2a	2.2				35.0		36.7	3.9
b	2.3		0.7	2.0	37.4		35.6	4.4
c	1.7		0.4	2.2	35.6		36.3	6.1
5a		3.4	0.4			2.6	55.1	
b	1.9	3.9	0.3			4.0	52.9	

[a] $^1J_{C-2,CH_3}$ = 40.2 Hz.

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Para-Substituted Toluenes. Evaluation of Long-Range Carbon–Hydrogen Coupling Constants

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Carbon-13 NMR spectra for a series of para-substituted toluenes were obtained and the proton-coupled spectra were analyzed. It is shown that the coupling patterns observed are characteristic for each type of carbon signal and can be used as "fingerprints". One-bond carbon–hydrogen coupling constants J_{77} and J_{22} were found to vary systematically and were analyzed using the Swain–Lupton $\mathcal{F}$ and $\mathcal{R}$ treatment. Chemical-shift substituent effects were found to be similar in direction and magnitude to those obtained for monosubstituted benzenes.

A great number of studies concerning the carbon-13 NMR spectral properties of aromatic compounds, particularly benzenoid systems, have been reported over the last few years.[1b–e] While considerable attention has been devoted to chemical-shift data and substituent effects, natural-abundance carbon-13–hydrogen coupling constant data have been generally neglected.[2] (In favorable instances, one-bond carbon–hydrogen coupling constants have been obtained from the carbon-13 satellites appearing in proton NMR spectra.[3]) Natural-abundance long-range carbon-13–hydrogen coupling-constant investigations of benzene derivatives are indeed rare, limited only to benzene,[4] halobenzenes,[5] toluene[6] and some substituted phenols.[7] The major problem associated with obtaining proton-coupled carbon-13 spectra is inherent in the nature of the carbon-13 nucleus.[8] However, recent advances in instrumentation, especially the introduction of "gated-decoupling,"[9] have facilitated the measurement of proton-coupled spectra. Additionally, a spectrometer system equipped with a crystal filter[10a] or quadrature detection[10b] can reduce the total time necessary to obtain a spectrum by ca. one-half.

The information contained in the proton-coupled spectrum can be perceived in a study of ortho-disubstituted benzenes, whereby carbon-13 shift assignments were made by simple inspection of the coupling "fingerprint."[11] (The use of "fingerprints" in proton NMR aromatic shift assignments is exemplified in an investigation by Zanger.[12]) While the above example represents the ideal situation, careful inspection of the more complex proton-coupled spectrum of monosubstituted benzenes can often lead to the carbon-shift assignments.[7,13] The purpose of the present report is to evaluate the proton-coupled carbon-13 spectra for a series of para-substituted toluenes.

Experimental Section

All compounds used in this study were commercially available materials requiring no further purification as indicated by the lack of significant additional signals in both the proton and carbon-13 NMR spectra. Sample concentrations, in deuteriochloroform, were ca. 20% w/v for chemical-shift determinations, and ca. 60% w/v for coupling-constant data. Sample tubes with an o.d. of 10 mm were used. The carbon-13 magnetic resonance spectra were obtained in the Fourier transform mode on a JEOL FX-60 spectrometer system operating at 15.03 MHz, and equipped with a Texas Instruments computer with 24K memory.

General NMR spectral and instrumental parameters used were: internal deuterium lock to solvent, spectral width of 2500 Hz for decoupled spectra and 500 Hz for proton-coupled spectra, a pulse width of 4 μs, corresponding to a 36° pulse angle, and a pulse repetition time of 1.8 s. All proton-coupled spectra were obtained in the "gated" mode, and the free induction decay signal was worked up without a window function. For all decoupled spectra 8K data points were used, while for proton-coupled spectra 16K data points were employed.

All chemical shifts are referenced to internal Me_4Si and are esti-

Table I. Carbon-13 Chemical Shift Values (δ_c) for a Series of Para-Substituted Toluenes[a]

X	Registry no.	C_1	C_2	C_3	C_4	C_7
H	108-88-3	137.8	129.3	128.5	125.6	21.3
F	352-32-9	133.4	130.4	115.0	161.3	20.5
Cl	106-43-4	136.2	130.4	128.3	131.2	20.7
Br	106-38-7	136.5	130.7	131.1	119.0	20.8
I	624-31-7	136.9	130.9	136.9	90.2	20.9
OH	106-44-5	130.2	130.2	115.4	152.8	20.3
OMe	104-93-8	129.7	129.9	113.8	157.7	20.4
SH	106-45-6	126.7	129.7	129.7	135.2	20.8
NH_2	106-49-0	127.5	129.7	115.2	144.0	20.5
CN	104-85-8	143.8	130.0	131.9	109.3	21.7 (119.1)
NO_2	99-99-0	146.2	129.9	123.4	146.2	21.5
CH_3	106-42-3	134.6	129.0	129.0	134.6	20.9

[a] In parts per million from internal Me_4Si.

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