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Effect of Carbon–Halogen Bonds on Nuclear Magnetic Resonance Chemical Shifts. 2. Proton and Carbon Nuclear Magnetic Resonance Spectra of Cyclobutyl Halides[1,2]

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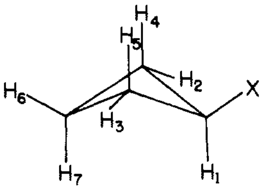
Abstract: As part of a study of the effect of carbon–halogen bonds on NMR chemical shifts, the proton and carbon NMR spectra of the cyclobutyl halides have been determined. The proton spectra have been completely analyzed. The coupling constants were found to be essentially invariant on going from one halide to the next, indicating that all had the same geometry. In several cases, for both the proton and ^{13}C spectra, the replacement of a hydrogen by a halogen led to an upfield shift rather than the more usual downfield shift. The changes in proton chemical shift from one halide to the next are linearly related to the changes in carbon chemical shifts, suggesting that similar mechanisms are operative for both.

Although proton and carbon chemical shifts have been studied for many years, origins of the shifts are still not well understood.[4] Simple formulations which include the magnetic anisotropy and field effect of a substituent in a classical fashion are not adequate to explain the magnitude of the effects.[5] In order to clarify the problem, it appears necessary to have data for a large number of protons and carbons having different geometrical relationships to the bond causing the chemical shift. This would map the geometrical component of the shifts and would permit one to analyze the factors involved in creating them. We are examining the NMR spectra of a series of halides which have well-defined geometries. Halides were chosen since the carbon–halogen bond is cylindrically symmetrical, thus simplifying the analysis of the problem. Also, since the dipole moments of the several C–X bonds are similar,[6] the contribution of the field effect to the difference in chemical shift from one halide to the next should be minimal.

The proton NMR spectra of the cyclopropyl halides[2,7] as well as the ^{13}C NMR spectra have been reported.[8] We have presented a complete analysis of the seven-spin system, cyclobutanol.[9] We now report the proton NMR spectra of the cyclobutyl halides, along with the ^{13}C NMR spectra. Subsequently, we shall present the spectra of some bicyclo[2.1.1]hexyl halides and norbornyl halides.

Whereas cyclobutane is conformationally mobile with a very low barrier to inversion,[10] the cyclobutyl halides exist predominantly in one conformation. The structures of cyclobutyl chloride[11] and bromide[12] have been determined by microwave spectroscopy, and both were found to be puckered in the same fashion as cyclobutane itself. Unlike the cyclohexyl halides

Table I. Coupling Constants (ppm) and Chemical Shifts (Hz) for Cyclobutyl Halides

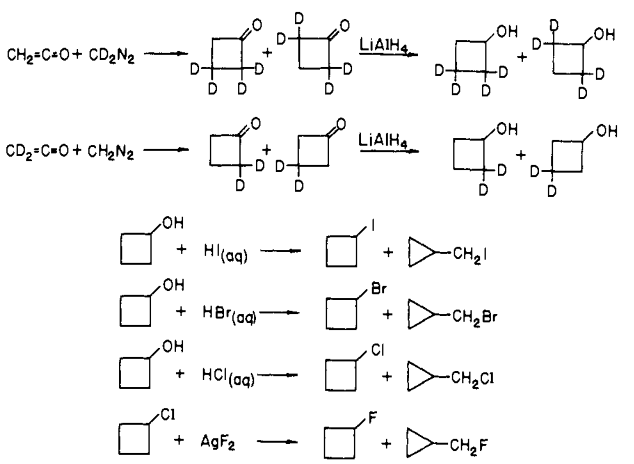


Parameter	F^a	Cl	Br	I	HO
ω_1	4.843	4.325	4.441	4.513	4.123
$\omega_2 = \omega_3$	2.272	2.495	2.597	2.669	2.196
$\omega_4 = \omega_5$	2.144	2.279	2.465	2.596	1.877
ω_6	1.748	1.993	2.094	2.080	1.629
ω_7	1.420	1.766	1.873	2.047	1.407
$J_{12} = J_{13}$	6.77	7.31	7.36	7.50	6.96
$J_{14} = J_{15}$	7.28	8.24	8.32	8.58	8.09
J_{16}	−1.03	−0.90	−0.78	−0.64	−1.07
J_{17}	−0.01	0.11	0.21	0.26	−0.01
J_{23}	5.06	4.70	4.61	4.48	5.16
$J_{24} = J_{35}$	−11.42	−11.55	−11.72	−11.75	−10.91
$J_{25} = J_{34}$	−0.94	−1.02	−1.12	−1.26	−0.93
$J_{26} = J_{36}$	2.59	2.98	3.18	3.35	2.25
$J_{27} = J_{37}$	7.91	8.04	8.05	8.01	7.90
J_{45}	0.17	0.17	0.17	0.16	0.01
$J_{46} = J_{56}$	10.32	9.85	9.83	9.64	9.65
$J_{47} = J_{57}$	10.20	9.87	9.67	9.41	10.37
J_{67}	−11.06	−10.99	−10.89	−10.75	−10.95
No. lines assigned	469	300	300	243	299
Rms error	0.079^b	0.055^c	0.053^c	0.055^c	0.065^c

[a] $J_{F3} = 55.32$; $J_{F2} = J_{F3} = 6.14$; $J_{F4} = J_{F5} = 20.63$; $J_{F6} = 8.54$; $J_{F7} = -0.03$. [b] In hertz at 270 MHz. [c] In hertz at 100 MHz.

where the rotational lines of both the axial and equatorial conformers may be seen in the microwave spectrum,[13] the cyclobutyl halides gave lines corresponding only to the equatorial halogens.[11,12] Infrared studies of the low-frequency ring puckering modes led to a difference in energy between the equatorial and axial (or planar) conformations of about 700 cm^{-1} (1.7 kcal/mol)[14] which corresponds to 95% equatorial at 25 °C.

The proton NMR spectra were first determined for a mixture of the cyclobutyl-*2,2,3,3-d*$_4$ and cyclobutyl-*2,2,4,4-d*$_4$ halides. They were prepared as shown in Scheme I, and were separated and purified by gas chromatography. The relative order of the hydrogen resonance was found to be the same as for cyclobutanol,[9] i.e., α-hydrogen, equatorial β-hydrogens, axial β-hydrogens, equatorial γ-hydrogens, and axial γ-hydrogens. The analysis of the NMR spectra of the tetradeuterated cyclobutyl halides also provided values for the coupling constants between the α hydrogen and the methylene hydrogens.



The spectra were then determined for a mixture of cyclobutyl-*2,2-d*$_2$ and cyclobutyl-*3,3-d*$_2$ halides. The spectrum of each cyclobutyl-*2,2,-d*$_2$ halide was initially calculated with the coupling constants between β and γ hydrogens being assumed to be the same as those found for cyclobutanol. The expected peaks were then located in the spectrum of the mixture. After adjustment of the coupling constants and chemical shifts, the peaks of the calculated spectrum were subtracted from the spectrum of the mixture to give that of the cyclobutyl-*3,3-d*$_2$ halide. The spectrum of the latter was calculated with the cross-ring coupling constants between β- and β′-hydrogens being assumed to be the same as those found for cyclobutanol. Fitting of the calculated spectra to the experimental spectrum provided the final coupling constants necessary for the initial calculation of the undeuterated cyclobutyl halide.

In the cases of cyclobutyl chloride, bromide, and iodide, the spectrum of the undeuterated halide could be fit, since the coupling constants were now known. An excellent fit was obtained with a root mean square error on the order of 0.06 Hz. Plots were made based on the "best fit" parameters and the intensities were found to be in excellent agreement with the observed spectra.[15] The parameters are given in Table I.

The spectrum of cyclobutyl fluoride presented an additional difficulty, since the fluorine also couples with the protons. The α-hydrogen pattern and the high-field half of the axial β-hydrogen pattern in the spectrum of cyclobutyl-*2,2,3,3-d*$_4$ fluoride appeared to be first order. The geminal fluorine–hydrogen coupling constant was found to be 55 Hz and was taken to be positive, since Bernheim and Lavery have shown this to be true for methyl fluoride.[16] The same conclusion was reached by Mackor and MacLean for dichlorofluoromethane.[17] The equatorial β-hydrogen pattern and the low-field half of the axial β-hydrogen pattern appeared in the spectrum as eight lines. The vicinal fluorine–hydrogen coupling constants could not be obtained directly, since a first-order analysis would have predicted 12 lines. Several trial spectra were calculated. It was assumed that geminal and vicinal fluorine–hydrogen coupling constants have identical signs as has been found by Evans, Manatt, and Elleman for a series of fluoroethanes and fluoropropanes.[18] The observed spectrum could be matched with either of the sets of parameters given in Table II. Spectra calculated from the two sets at a second frequency, 60 MHz, were quite different. The experimental spectrum at 60 MHz clearly matched only the spectrum calculated from the first set of parameters.

Similarly, it was found that the cyclobutyl-*2,2,4,4-d*$_4$ fluoride spectrum could be matched using two sets of parameters which differed only in the coupling of the fluorine with the axial γ-hydrogen. Spectra obtained at 60 MHz again served to distinguish between the two sets. The positive value was used.

Table II. NMR Parameters for Cyclobutyl-*2,2,3,3*-d_4 Fluoride

Parameter	Set 1	Set 2
ω_1	4.829 ppm	4.829 ppm
ω_2	2.253	2.225
ω_4	2.125	2.153
J_{F1}	55.34 Hz	55.34 Hz
J_{F2}	6.17	0.45
J_{F4}	20.67	26.23
J_{12}	6.79	6.93
J_{14}	7.35	7.26
J_{24}	−11.55	−11.50

Table III. ^{13}C NMR Spectra for Cyclobutyl Halides (ppm)

Parameter	F[a]	Cl	Br	I
$\omega_{C(1)}$	86.49	52.32	42.34	15.78
$\omega_{C(2)} = \omega_{C(4)}$	31.10	34.75	35.46	36.87
$\omega_{C(3)}$	10.54	16.33	18.84	22.94

[a] $J_{F-^{13}C(1)} = 214.55$; $J_{F-^{13}C(2)} = 18.49$; $J_{F-^{13}C(3)} = 20.35$ Hz.

Both positive and negative values of the coupling constants between the fluorine and the equatorial γ-hydrogen were used for the calculation of trial spectra of cyclobutyl-*2,2*-d_2 fluoride. The γ-hydrogen region could be reproduced only when the positive values was used. The NMR spectrum of undeuterated cyclobutyl fluoride was not analyzed, since the coupling with the fluorine led to an eight-spin system which could not be calculated using LAOCN3[19] and the available computer.

More recently, it was possible to obtain 270-MHz NMR spectra for these compounds. The high-field spectrum of cyclobutyl fluoride was analyzed using the program LACX,[20] giving the parameters listed in Table I. They are in good agreement with the 100-MHz data. The spectra of the other halides were calculated using the parameters given in Table I, and were compared with the observed spectra. Except for small shifts (<0.005 ppm) of entire patterns along the frequency axis, excellent fits were obtained with the chloride and bromide. In the case of the iodide the small change in chemical shift (expressed in parts per million) at 270 MHz was especially noticeable in the pattern for the protons at C(3). At 100 MHz, the difference in chemical shift for the equatorial and axial protons was 0.033 ppm. In order to fit the 270-MHz spectrum, the difference in chemical shift had to be decreased to 0.021 ppm, although none of the coupling constants required adjustment.

One possible reason for the change in chemical shift was the difference in probe temperature between the two instruments. The 100-MHz spectra were obtained at an average temperature of 33 °C, whereas the 270-Mhz spectrometer normally operates at 22 °C. When the temperature was raised to 33 °C, the observed spectrum agreed very well with the calculated using the parameters given in Table I. The same is true with the chloride and bromide. The changes in chemical shifts were in all cases very small.

The similarity of the coupling constants between the 2, 4 and 6, 7 protons (Table I) from one halide to the next indicates that the conformations are essentially the same. If the ring were to approach planarity (or if the conformer with an axial halogen dropped in energy so that the observed spectrum became an average of the equatorial and axial species) J_{26} would increase while J_{47} would decrease. The smallest conformational preference would be expected with fluorine, but here, the equatorial-equatorial coupling has the smallest values and the axial-axial coupling has the largest value. The almost identical values for cyclobutyl chloride and bromide strongly suggests almost identical ring puckering. The microwave spectra for the two compounds indicated dihedral angles of 20 and 29°, respectively.[11,12] The latter value could be obtained only by making some structural assumptions. Therefore, it appears that a dihedral angle of 20° should be used with both compounds.

The chemical shift of the protons in cyclobutane is 1.96 ppm.[21] This is the average of the shifts for equatorial and axial hydrogens. As in the case of cyclohexane, the axial hydrogens would be expected to have an upfield shift in comparison to the equatorial hydrogens.[22] If the difference in shift were on the order of 0.3 ppm (half that for cyclohexane), the shifts for the axial and equatorial protons would be on the order of 2.1 and 1.8 ppm, respectively. A comparison of these values with the shifts given in Table I indicates a substantial upfield shift for the protons at C(3) for both cyclobutyl chloride and fluoride.

The ^{13}C NMR spectra of the four halides were obtained, and the results are summarized in Table III. The signal derived from C(2) and C(4) was easily identified because of its higher intensity. Gated decoupling was used to differentiate between the signals from C(1) and C(3), the latter becoming a triplet, whereas the former becomes a doublet. In the case of cyclobutane, the ^{13}C chemical shift is 22.4 ppm.[23] It can be seen that the band for C(3) appears upfield from that of cyclobutane for the fluoride, chloride, and bromide.

The upfield shifts observed at C(3) are not unique, and analogous carbon shifts have been found in other systems. Eliel et al.[24] have observed such shifts in cases having an antiperiplanar arrangement for an XCCC[13] system, where X is N, O, or F, and Poindexter and Kropp[25] have found an upfield shift at C(4) of 1-halonorbornanes. It is important to note that in the present case the upfield shift is found for both C(3) and the protons attached to this carbon.

There is an obvious similarity in the proton and carbon chemical shifts for these halides. The similarity is strikingly shown in Figure 1 where the two shifts are plotted against each other for the β and γ positions. The α-position was not included because the inductive effect of the halogens appears to lead to a different effect at this position. Rather good correlations were found for all except the axial C(3) proton of cyclobutyl iodide. This correlation of proton and carbon chemical shifts is not unique to cyclobutane. As shown in Figure 2, the same is true for the methyl protons of the ethyl halides,[26] and it may be noted that the slopes are essentially the same.

It is clear from these results that the difference in the proton and carbon chemcial shift from one halide to the next have similar origins.[27] Both plots include the point for the parent compound. Since the lines do not pass through this point, other factors are involved in determining the change in chemical shifts between the substituted and unsubstituted compounds.

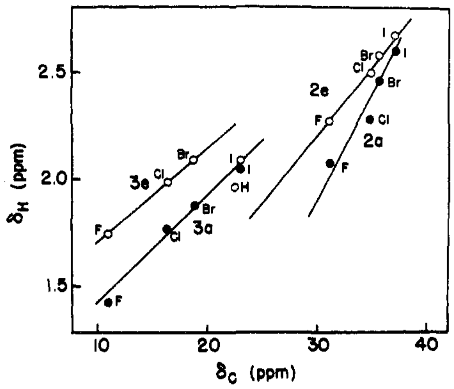


Figure 1. Relation between proton and carbon chemical shifts for cyclobutyl halides.

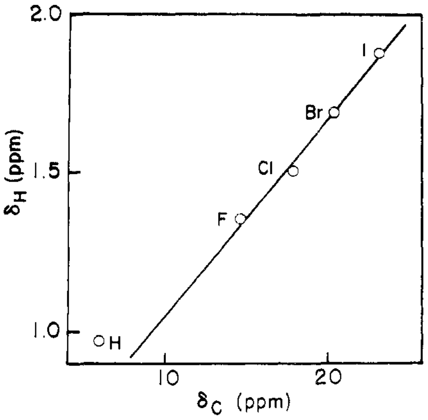


Figure 2. Relation between proton and carbon chemical shifts for methyl group of ethyl halides.

In view of the similarity in the bond dipoles for the several carbon–halogen bonds,[6] one might accept as a zeroth order approximation that the difference in chemical shift from one halide to the next is not due to the charge distribution in the carbon–halogen bond. The field effect caused by the carbon–halogen bonds would presumably be one component of the chemical shift difference between the unsubstituted compound and the halides.

There are several possible mechanisms for producing the differential chemical shift between halides. One of the few methods available for distinguishing between these mechanisms is to study the geometrical dependence of this chemical shift. This will be reported for a number of rigid systems, and the problem will be discussed in greater detail at that time.

Experimental Section

Cyclobutyl Halides. The preparation of the deuterium-labeled alcohols has been given previously.[9] Cyclobutyl chloride was prepared by mixing 10 g of cyclobutanol with 60 g of concentrated hydrochloric acid and heating to 90–100 °C. The product was distilled from the reaction mixture, washed with water, and dried over sodium sulfate (11 g). A GC analysis indicated 15% allylcarbinyl chloride, 25% cyclopropylcarbinyl chloride, and 60% cyclobutyl chloride. Preparative GC separation gave 4 g of pure cyclobutyl chloride. Cyclobutyl bromide was prepared by the reaction of the alcohol with phosphorus tribromide.[28] The crude product contained 10% allylcarbinyl bromide, 30% cyclobutyl bromide, and 60% cyclopropylcarbinyl bromide. Preparative GC separation gave pure cyclobutyl bromide. Cyclobutyl iodide was prepared by the reaction of 5 g of cyclobutanol with 30 g of concentrated hydriodic acid for 5 min at 100 °C. The iodide was separated, washed with water, and dried (8 g). A GC analysis indicated 30% allylcarbinyl iodide, 30% cyclopropylcarbinyl iodide, and 40% cyclobutyl iodide. Preparative GC separation gave pure cyclobutyl iodide. Cyclobutyl fluoride was prepared by the reaction of cyclobutyl chloride with silver difluoride.[11] A GC analysis indicated 75% cyclobutyl fluoride, 10% cyclopropylcarbinyl fluoride, and minor amounts of several other compounds. Preparative GC separation gave pure cyclobutyl fluoride.

Spectra. The 100-MHz proton spectra were obtained using an HA100 spectrometer. The spectra were determined using 2.0 M solutions in carbon tetrachloride containing 4% tetramethylsilane at 33 °C. The peak widths (fwhm) were generally 0.1 Hz, and the peak positions were measured by stopping the sweep at the peak maximum and counting the frequency shift with respect to the lock frequency. In this way the positions could be determined to ±0.1 Hz. Approximately 250–300 peaks were located in the spectra of each of the parent compounds.

The 270-MHz proton spectra were obtained using a Brucker spectrometer using the CW mode. Each section of the spectra (corresponding to different protons) was plotted at 2 Hz/cm, and the beginning and end of each spectrum was determined to ±0.1 Hz by direct counting. No attempt was made to fit the spectra of the chloride, bromide, and iodide. The calculated spectra based on the parameters derived from the 100-MHz spectra gave excellent correspondences with the observed spectra. The 270-MHz spectrum of cyclobutyl fluoride was analyzed in the same fashion as the other halides at 100 MHz and also gave an excellent fit to the observed spectrum.

The 20-MHz carbon spectra were obtained using a Varian CFT-20 spectrometer. The spectra were obtained using 2.0 M solutions in chloroform-*d*. Proton decoupling was normally used, and peak positions were obtained with an uncertainty of 0.05 ppm or less. The 2- and 4-carbon signals were easily identified because of their greater intensity. The 1- and 3-carbon signals were identified by gated decoupling. Here, the 1-carbon signal became a doublet and the 3-carbon signal became a triplet. The carbon shifts were measured relative to the solvent and were converted to the Me_4Si scale by $\delta_{Me_4Si} = \delta_{CDCl_3} + 76.9$ ppm.

Calculations. The NMR spectra were calculated, and the "best fit" parameters were obtained using LAOCN3.[19] Using the available computer, this allowed systems up to seven spins to be studied. Subsequently LACX[20] became available and was used for the calculation of the spectrum of cyclobutyl fluoride, and eight-spin system.

References and Notes

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(2) Part 1: K. B. Wiberg, D. E. Barth, and P. H. Schertler, *J. Org. Chem.*, **38**, 378 (1973).

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(6) The dipole moments of the methyl halides (F, Cl, Br, I) are 1.81, 1.87, 1.80, and 1.64 D, respectively, and those of the ethyl halides are 1.92, 2.05, 2.01, and 1.87 D (C. P. Smyth, "Dielectric Behavior and Structure", McGraw-Hill, New York, N.Y., 1955, p 269). In addition, the dipole moment derivatives for the antisymmetric H–C–X bending mode of the methyl halides are the same (J. W. Russell, C. D. Needham, and J. Overend, *J. Chem. Phys.*, **45**, 3383 (1966)), suggesting that the C–H bond dipoles are the same.

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